

BIOPOLYMERS: REUSE, RECYCLING, AND DISPOSAL

Michael Niaounakis



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More will I tell thee too: there is no birth
Of all things mortal, nor end in ruinous death;
But mingling only and interchange of mixed
There is, and birth is but its name with men.

Empedocles

From William Ellery Leonard's *The Fragments of Empedocles* (Chicago: The Open Court Publishing Company, 1908).

An outline of certain chapters of this book was presented at the Annual Symposium of Biopolymers, held in Denver, 8-10 October 2010, under the title: Disposal, Recycling and Reuse of Biopolymers - The patent perspective.

The expression biopolymer or bioplastic is used to describe two different terms at the same time, which often leads to confusion. It can mean that the polymer or plastic is biodegradable or that the raw material used is renewable or bio-based. According to the first definition a biodegradable polymer derived from fossil fuel resources is considered as biopolymer. The same applies for a non degradable bio-based polymer; for more details see Chapter 2.

The scope of this book is to present and investigate a novel phenomenon related to the recycling and/or disposal of biopolymers. At first, the idea of recycling these polymers is contradicting with the nature and scope of biodegradable biopolymers. As the current interest of biopolymers is largely based on their biodegradability, to consider recycling these polymers is to ignore one of its most important properties. However, there are good reasons for the recycling of biopolymers. Most commercial biopolymers, such as polylactide (PLA), are not degraded under ordinary conditions even in presence of microorganisms. Furthermore, the disposal of biopolymer articles has the disadvantage of discarding valuable raw materials, which could be efficiently reutilized.

Currently, biopolymers lack economies of scale, representing still a small niche within the overall plastics industry, making up less than 1% of the global plastic market, while their waste streams are small and scattered. Surprisingly enough, there is much activity in patenting on the waste treatment of biopolymers, especially from Japanese universities, institutions and companies. All these patent applicants are poised to benefit from the continuous growth of biopolymers when these materials mature and reach a critical mass, which is necessary for recycling to become profitable.

Not much attention has been paid to the waste management of these materials so far. Meanwhile,

biodegradable biopolymers such as polylactide (PLA) are a serious problem when and where they enter either conventional plastics recycling (e.g. of PET) or green-waste composting streams. This problem is expected to grow as biodegradable biopolymers proliferate in residential areas. With the current rate of growth, it is expected that waste issues concerning biopolymers will emerge in the future similarly to the situation of conventional polymers that are currently used.

The book consists of 10 chapters.

Chapter 1 starts with a presentation of the main motivations for using biopolymers. A large section gives an extensive introduction to most of the existing and newly developed biopolymers and provides updated lists of their commercial products and current applications. The following section investigates the possible sources of biopolymers, including first, second and third generation feedstocks. A separate section is dedicated to the sources of scrap and waste biopolymers, which are intended for recycling.

Chapter 2 clarifies and explains the various terms used to describe biopolymers. A separate section presents the positions of the advocates of bioplastics and oxodegradable polymers and the arguments of each group against the other. In the following section are described the main types and mechanisms of (bio) degradation. The last section reviews the tests methods which have been developed for biodegradable including field tests, simulation tests and laboratory tests.

Chapter 3 describes all the possible ways of reusing discarded biopolymers. A distinction is made between reuse and physical recycling (see Chapter 5).

Chapter 4 examines all the known techniques for the disposal of biopolymers, including landfilling, disposal in soil or water and composting (industrial or home). A separated section summarizes the various microbes (aerobic and anaerobic) and enzymes used for the biodegradation of biopolymers. The following section examines alternative waste disposal systems. The last section describes the

destructive thermal methods such as incineration (combustion) and pyrolysis.

Chapter 5 examines the various methods for the physical or mechanical recycling of biopolymers including techniques for identifying and sorting materials by polymer type. A separate section reviews the various marker systems including the Resin Identification Codes (RIC) and fluorescent additives.

Chapter 6 examines the various methods for the chemical recycling of biopolymers including hydrolysis/alcoholysis, dry heat depolymerization, hydrothermal depolymerization, and the relatively new enzymatic depolymerization technique.

Chapter 7 examines the various techniques of modifying and/or controlling the degradation rate of biopolymers, by suppressing or accelerating the degradation speed at will.

Chapter 8 analyzes and correlates trends in patenting related to the waste management of biopolymers. The methodology includes the collection of statistical data all over the world for the period from 01.01.1990 to 31.08.2012. A separate section presents the prospects and limitations of the main waste treatment options for biopolymers. The next section summarizes the current state of patents in the prior art. The last section reviews the developments of new waste treatment processes and biopolymers.

Chapter 9 presents the regulatory framework of biopolymers by grouping all the international standards related to recycling, disposal, biodegradation (aerobic and anaerobic), composting, and ecotoxicity. A separate group of standards refers to the determination of bio-based content. Other groups of standards refer to Life-Cycle-Assessment (LCA) and eco-labeling. A separate section describes the process of certification.

Chapter 10 constitutes of three parts. The first part reviews the few available economic analyses on the disposal and recycling of waste biopolymers. The second part presents life cycle assessment (LCA) analyses of the main biopolymers, i.e., starch, PLA and polyhydroxyalkanoates (PHAs). The third part examines the possible environmental and health effects resulting from the production, use and waste treatment of biopolymers.

The Appendix contains three tables: Table 1 is a collection of the bibliographic data of all patents related to recycling, reuse or disposal of biopolymers. Table 2 is a collection of the bibliographic data of the patents related to biodegradation on demand.

Table 3 is a collection of the bibliographic data of the supplementary patents, which do not refer necessarily to biopolymers, and are used as references to processes and/or materials mentioned in the text.

This book is unique in its coverage encompassing scientific publications as well as patents. Emphasis has been given to patents, since patents refer predominantly to industrial applications and have a potential economic value. Patents, although they represent a substantial part of literature, till recently they were underrepresented in the cited bibliography. Patents are innovative, have an industrial applicability and they are not self-repeated. Although they are not peer reviewed, they have been searched and examined. Most of them come from major industries and international laboratories and the reason for this is possibly the high costs in obtaining and maintaining a patent.

It has to be clarified that the book is not a mere “list” of patents, but rather a critical review of all the available technologies on the issue of the waste management of biopolymers. A patent application is drafted on the so-called “problem-solution” approach; this means that a would-be inventor drafts its patent application by outlining the shortcomings of the prior art and proposing solutions to the stated problem. By summarizing and analyzing all the critical comments of several inventors/applicants on every prior art of each technology, the author was able to build up a clear opinion on the benefits and weaknesses of each technology. Although all this information is indeed available online, it is the author’s opinion that is almost impossible for a would-be researcher to retrieve all the available patent literature by simple searching techniques, without prior expertise. At least for the issue of disposal and recycling of biopolymers most of the available patent literature is in Japanese with only a short abstract in English. On the basis of the abstract, an English speaker may consult online a machine translation of the text, which is a very tedious and not always reliable procedure. Furthermore, the relevant literature is scattered in many technical fields making the retrieval and/or combination of all available information difficult.

The book tries to be neutral on several issues surrounding the use of biopolymers and their recycling, reuse or disposal and to present all different arguments (pros and cons). In this context ground is given to both fighting “camps” in the field of degradable polymers, bioplastics and oxodegradable

polymers, to present their position. Furthermore, the book keeps a critical eye on unjustified claims of properties which cannot and have not yet been validated or the false use of the term bioplastic or biopolymer for marketing purposes. In the same context, it is noted that there are not enough full scale assessments (LCAs) of biopolymers so far. Therefore, biopolymers have still a long way to go to convince the scientific community and the public that they can form a reliable alternative of polymers or plastics derived from fossil fuel resources.

Several of the commercial products mentioned in the manuscript and the accompanying tables are not anymore available in the market (obsolete). However, since these products are used to exemplify certain aspects of the cited patents, they were kept in the text.

The recycling of natural rubber, the most well known biopolymer, has already been analyzed and reviewed extensively in the past, and will not form part of this book.

One of the most striking results of this survey is the excessively large number of Japanese patent applications related to the waste treatment of biodegradable biopolymers. Actually, Japan has the highest number of patent applications worldwide relating to the waste treatment of biopolymers (66% of all patents). In spite of the large number of patents owned by Japanese companies, only two non-Japanese companies are actively involved on a large scale with the recycling of biopolymers or bioplastics; namely NatureWorks in the USA and

Galactic S.A in Europe. However, in view of the large number of patent applications on the recycling of biopolymers future commercial implementation would be expected.

To the best of the author's knowledge there are no books with a similar subject in the market. Useful books, but with a different scope and partial coverage, are the following:

-Handbook of Biodegradable Polymers Handbook of Biodegradable Polymers, 2005, Bastioli, C. (Ed), Smithers Rapra Technology, ISBN: 1859573894.

-Engineering Biopolymers - Markets, Manufacturing, Properties and Applications, 2011, Endres H. J., Siebert-Raths A., Hanser Publications, ISBN: 9781569904619.

-Biodegradable Plastics and Polymers, NIIR board, ISBN: 8178330350.

-Bioplastics In The Waste Stream (CD, online), 2012, iSmithers Rapra Publishing, 2012, ISBN: 9781847359452.

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For Supporting materials and web links to patents, please visit the companion website: <http://booksite.elsevier.com/9781455731459>

Rijswijk
Dr Michael Niaounakis

Abbreviations of Biopolymers

β -PPL	poly(β -propiolactone)	PBT	poly(butylene carbonate)
β -PBL	poly(β -butyrolactone)	PBP	poly(butylene pimelate)
γ -PGA	poly(γ -glutamic acid)	PBS	poly(butylene succinate); see also poly(tetramethylene succinate) (PTeMS); (different CAS)
ϵ -PL	poly(ϵ -lysine)		
CA	cellulose acetate		
CAB	cellulose acetate butyrate	PBSA	poly(butylene succinate-co-adipate)
CAP	cellulose acetate propionate		
CN	cellulose nitrate	PBSC	poly(butylene succinate-co-carbonate)
P2HB	poly(2-hydroxybutyrate)	PBSE	poly(butylene sebacate)
P3HB	poly(3-hydroxybutyrate) (or PHB)	PBSL	poly(butylene succinate-co-lactide)
P3HB4HB	poly(3-hydroxybutyrate-co-4-hydroxybutyrate)	PBST	poly(butylene succinate-co-terephthalate)
P3HD	poly(3-hydroxydecanoate) (or PHD)	PCHC	poly(cyclohexene carbonate)
P3HN	poly(3-hydroxynonanoate) (or PHN)	PCL	poly(ϵ -caprolactone)
P3HP	poly(3-hydroxypropionate)	PDLA	poly(D-lactide)
P4HB	poly(4-hydroxybutyrate)	PDLLA	poly(D,L-lactide)
P4HB2HB	poly(4-hydroxybutyrate-co-2-hydroxybutyrate)	PDLGA	poly(D,L-lactide-co-glycolide)
P4HP	poly(4-hydroxypropionate)	PDO	polydioxanone (or PDS)
P4HV	poly(4-hydroxyvalerate)	PE	polyethylene (biobased)
P5HV	poly(5-hydroxyvalerate)	PEA	poly(ethylene adipate)
P6HH	poly(6-hydroxyhexanoate)	PEAM	poly(ester amide)
PA 1010	polyamide 1010	PEAz	poly(ethylene azelate)
PA 1012	polyamide 1012	PEC	poly(ethylene carbonate)
PA 11	polyamide 11	PEDe	poly(ethylene decamethylate)
PA 410	polyamide 410	PEF	poly(ethylene furanoate)
PA 610	polyamide 610	PEOx	poly(ethylene oxalate)
PBA	poly(butylene adipate)	PES	poly(ethylene succinate)
PBAT	poly(butylene adipate-co-terephthalate)	PESA	poly(ethylene succinate-co-adipate)
		PESE	poly(ethylene sebacate)

PEST	poly(ethylene succinate-terephthalate)	PLLGA	poly(L-lactide- <i>co</i> -glycolide)
PESu	poly(ethylene suberate)	α -PMA	α -type polymalic acid, polymalate
PET	poly(ethylene terephthalate) (biobased)	POE I	poly(ortho ester) I
PEUU	poly(ester urethane urea) (biodegradable)	POE II	poly(ortho ester) II
PGA	polyglycolide, poly(glycolic acid)	POE III	poly(ortho ester) III
PGCL	poly(glycolide- <i>co</i> -caprolactone)	POE IV	poly(ortho ester) IV
PHA	polyhydroxyalkanoate	PPA	polyphthalamide
PHB	polyhydroxybutyrate (or P3HB)	PPHOS	polyphosphazene
PHBHD	poly(3-hydroxybutyrate- <i>co</i> -3-hydroxydecanoate)	PPF	poly(propylene fumarate)
PHBHP	poly(3-hydroxybutyrate- <i>co</i> -3-hydroxypropionate)	PPL	poly(β -propiolactone)
PHBHx	poly(3-hydroxybutyrate- <i>co</i> -3-hydroxyhexanoate) or poly(hydroxybutyrate- <i>co</i> -hydroxyhexanoate)	PPS	poly(propylene succinate)
PHBO	poly(3-hydroxybutyrate- <i>co</i> -3-hydroxyoctanoate) (or P3HB/3HO)	PPT	poly(propylene terephthalate) (biobased); see also PTT
PHBHV	poly(3-hydroxybutyrate- <i>co</i> -3-hydroxyvalerate)	PTeMAT	poly(tetramethylene adipate- <i>co</i> -terephthalate); see also poly(butylene adipate- <i>co</i> -terephthalate (PBST).
PHD	polyhydroxydecanoate (or P3HD)	PTeMC	poly(tetramethylene carbonate)
PHHp	poly(3-hydroxyheptanoate)	PTMC	poly(trimethylene carbonate)
PHHx	poly(3-hydroxyhexanoate)	PTeMS/ PTeMC	poly[(tetramethylene succinate)- <i>co</i> -(tetramethylene carbonate)]
PHN	polyhydroxynonanoate (or P3HN)	PTMA	poly(trimethylene adipate)
PHO	poly(3-hydroxyoctanoate)	PTMAT	poly(methylene adipate- <i>co</i> -terephthalate)
PHP	poly(3-hydroxypropionate) (or P3HP)	PTeMA	poly(tetramethylene adipate)
PHSE	poly(hexamethylene sebacate)	PTMG	poly(tetramethyl glycolide)
PHV	poly(3-hydroxyvalerate)	PTeMS	poly(tetramethylene succinate); see also poly(butylene succinate) (PBS) (different CAS)
PLA	polylactide, poly(lactic acid)	PTT	poly(trimethylene terephthalate) (biobased); see also PPT
PLCL	poly(lactide- <i>co</i> -caprolactone)	PU	polyurethane (biobased)
PLGA	poly(lactide- <i>co</i> -glycolide)	PVOH	poly(vinyl alcohol)
PLLA	poly(L-lactide)	TPS	thermoplastic starch

1 Introduction to Biopolymers

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1.1 Rationale for Use of Biopolymers

One of the fastest-growing materials sectors in the last several years has been the production of polymers from renewable resources. Their development is fueled by the potential these polymers hold to replace fossil fuel-based polymers. The main reasons for this

drive can be summarized as follows: (1) limited fossil fuel resources; (2) pricing volatility of fossil fuel; (3) contribution of fossil fuel as a feedstock to climate change; (4) its occasional role as a political weapon; and (5) its association with the waste disposal problem created by the fossil fuel-derived polymers.

Polymers derived from renewable resources draw attention as environment-friendly resins because they

are produced without relying on fossil fuel resources. In addition, the plants which provide the raw materials for these polymers absorb carbon dioxide as they grow, while the polymers themselves emit smaller quantities of CO₂ when they are disposed of with an incinerator. The polymers that are based on renewable raw materials, as well as the polymers that are produced by biological routes, are generally biodegradable. The bio-based polymers, however, do not necessarily need to be biodegradable. This means that polymers that contribute to the protection of the environment include not only the bio-based polymers that are not biodegradable, but also biodegradable polymers. For this reason, the terms “environmental polymer,” “enviropolymer,” and “biopolymer” were coined for the sake of convenience in order to give a generic name to the bio-based polymers that are not biodegradable, and to the biodegradable polymers (including fossil fuel-based and bio-based polymers; see Chapter 2: Definitions and Assessment of (Bio)degradation; Section 2.1: Define the Terms).

The main property that distinguishes biopolymers from fossil fuel-derived polymers is their sustainability, especially when combined with biodegradability. Biodegradable biopolymers from renewable resources have been synthesized to provide alternatives to fossil fuel-based polymers. They are often synthesized from starch, sugar, natural fibers, or other organic biodegradable components in varying compositions. The biopolymers are degraded by exposure to bacteria in soil, compost, or marine sediment. When the biodegradable biopolymers are subjected to waste disposal by utilizing their characteristic of being degradable by the bacteria in the ground, it significantly reduces emission of CO₂ compared with conventional incineration. Therefore, attention is drawn to the use of biodegradable biopolymers from the viewpoint of global warming prevention. In recent years, with the critical situation of the global environment worsening due to global warming, the construction of systems with sustainable use of materials has been accelerated from the viewpoint of effectively using limited carbon resources and conserving limited energy resources. The Kyoto protocol, together with the desire to reduce society's dependence on imported crude oil, has directed researchers' efforts toward the use of biomass as a source of energy and of commodity chemicals. Furthermore, the cost of petroleum feedstocks has risen dramatically and there is a rising consumer interest in using “green” (or renewable resources) as the basis for consumer products.

Biodegradable biopolymers offer promise in solving the problem of conventional polymer disposal. In principle, it is not necessary to collect articles made of biodegradable biopolymers after the end of their useful life because they can be left to biodegrade in the environment. They offer a lot of advantages, such as increased soil fertility, low accumulation of bulky plastic materials in the environment, and reduction in the cost of waste management. But there have been several obstacles so far. Depending on the type and ratios of the components in biodegradable biopolymers, and depending on the environment where biodegradable biopolymers are disposed of, the rate of biodegradation may be less than desired. Another obstacle is that as the thickness of the product containing biodegradable biopolymer increases, its biodegradability property is diminished. A greater problem still is that many biopolymers have inferior properties, and it is often necessary to either blend them with other polymers or to compound them with various additives. As a result, many biopolymer blends or composites do not have uniform mechanical properties. Also, most known biodegradable polymers are aliphatic polyesters that have low softening temperatures (T_m), which prevents their use in a variety of fields.

In spite of several setbacks, biodegradable polymers are moving into the mainstream because conventional polymers are nondegradable and they exhaust fossil fuel sources. However, biopolymers still face a number of challenges, including cost reduction, wider availability, the need to improve their thermomechanical and barrier properties, speed of biodegradability, and availability and optimization of composting processes. As the demand for biopolymers increases, it is expected that their production capacity will expand and their prices will fall, and eventually, a denser network of industrial composting facilities will be created. But the ultimate issue is whether the performance properties and processability of biopolymers will ever be able to compete with the nonrenewable polymers.

1.2 Types of Biopolymers

Biopolymers are classified in several different ways at different scales. As explained in Chapter 2: Definitions and Assessment of (Bio)degradation; Section 2.1: Define the Terms, biopolymers can be divided into two broad groups, namely biodegradable

and non-biodegradable, and alternatively, into bio-based and non-bio-based biopolymers.

On the basis of their polymer backbone, biopolymers can be classified roughly into the following groups, each of which is subdivided into several subgroups (this list is not exhaustive):

Polyesters

Poly(hydroxy acid)s top the list, and they include biopolymers such as the following:

- Poly(α -hydroxyalkanoic acid)s
 - Polylactide (PLA, PLLA, PDLA)
 - Polyglycolide (PGA)
 - Poly(lactide-*co*-glycolide) (PLGA)
 - Poly(tetramethyl glycolide) (PTMG)
 - Poly(glycolide-*co*-trimethylene carbonate) (PGA/PTMC)
 - Poly(2-hydroxybutyrate) (P2HB)
 - α -type polymalic acid (α -PMA)
- Poly(β -, γ -, δ -hydroxyalkanoate)s (PHAs)
 - Poly(3-hydroxypropionate (P3HP or PHP)
 - Poly(3-hydroxybutyrate (P3HB or PHB)
 - Poly(3-hydroxyvalerate) (P3HV or PHV)
 - Poly(3-hydroxyhexanoate) (P3HH or PHH)
 - Poly(3-hydroxyheptanoate) (P3HHp or PHHp)
 - Poly(3-hydroxyoctanoate) (P3HO or PHO)
 - Poly(3-hydroxynonanoate) (P3HN or PHN)
 - Poly(3-hydroxydecanoate) (P3HD or PHD)
 - Poly(4-hydroxypropionate (P4HP)
 - Poly(4-hydroxybutyrate) (P4HB)
 - Poly(4-hydroxyvalerate) (P4HV)
 - Poly(3-hydroxybutyrate-*co*-hydroxypropionate) (PHBHP)
 - Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (P3HB/P3HV or PHB/PHV or PHBH_x)
 - Poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate) (P3HB/3HO or PHBO)
 - Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P3HB/P3HV or PHBHV)
 - Poly(3-hydroxyoctanoate-*co*-3-hydroxyhexanoate) (P3HO/3HH or PHO/HH)
- Poly(3-hydroxybutyrate-*co*-3-hydroxydecanoate) (PHBHD)
- Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB/P4HB)
- β -type polymalic acid (β -PMA)
- Poly(5-hydroxyvalerate) (P5HV)
- Poly(ω -hydroxyalkanoate)s
 - Poly(β -propiolactone) (β -PPL)
 - Poly(β -butyrolactone) (β -PBL)
 - Poly(ϵ -caprolactone) (PCL)
- Poly(alkylene dicarboxylate)s
 - Poly(ethylene succinate) (PES)
 - Poly(propylene succinate) (PPS)
 - Poly(butylene succinate) (PBS)
 - Poly(tetramethylene succinate) (PTeMS)
 - Poly(ethylene adipate) (PEA)
 - Poly(butylene adipate) (PBA)
 - Poly(tetramethylene adipate) (PTA)
 - Poly(hexamethylene adipate)
 - Poly(ethylene succinate-*co*-adipate) (PESA)
 - Poly(butylene succinate-*co*-adipate) (PBSA)
 - Poly(butylene pimelate) (PBP)
 - Poly(hexamethylene malonate)
 - Poly(ethylene diethyl glutarate)
 - Poly(tetramethylene glutarate)
 - Poly(hexamethylene glutarate)
 - Poly(hexamethylene diethyl glutarate)
 - Poly(ethylene azelate) (PEAz)
 - Poly(ethylene sebacate) (PESE)
 - Poly(butylene sebacate) (PBSE)
 - Poly(tetramethylene sebacate) (PTSE)
 - Poly(hexamethylene sebacate) (PHSE)
 - Poly(ethylene decamethylate) (PEDe)
 - Poly(ethylene suberate) (PESu)
 - Polyoxalate [poly(ethylene oxalate) (PEOx)]
 - Poly(propylene fumarate) (PPF)
- Aliphatic-aromatic copolyesters
 - Poly(butylene adipate-*co*-terephthalate) (PBAT)

- Poly(butylene succinate-*co*-terephthalate) (PBST)
- Poly(tetramethylene glutarate-*co*-terephthalate-*co*-diglycolate)
- Poly(tetramethylene glutarate-*co*-terephthalate)
- Poly(ethylene glutarate-*co*-terephthalate)
- Poly(tetramethylene adipate-*co*-terephthalate) (PTeMAT)
- Poly(tetramethylene succinate-*co*-terephthalate)
- Poly(tetramethylene-*co*-ethylene glutarate-*co*-terephthalate)
- Aromatic (co)polyesters
 - Poly(ethylene terephthalate) (bio-based PET)
 - Poly(ethylene furanoate) (PEF)
 - Poly(trimethylene terephthalate) (bio-based PTT)

Poly(ether-ester)s

- Polydioxanone (PDO or PDS)

Polycarbonates, aliphatic

- Poly(ethylene carbonate) (PEC)
- Poly(propylene carbonate) (PPC)
- Poly(trimethylene carbonate) (PTMC)
- Poly(butylene carbonate) (PBC)
- Poly(tetramethylene carbonate) (PTeMC)
- Poly(cyclohexene carbonate) (PCHC)
- Poly(propylene carbonate)/poly(cyclohexene carbonate) (PPC/PCHC)
- Poly[(tetramethylene succinate)-*co*-(tetramethylene carbonate)] (PTMS/PTeMC)
- Poly(glycolide-*co*-trimethylene carbonate) (PGA/PTMC)

Polyamides

- By polycondensation of diamines and dicarboxylic acids:
 - Polyamide 1010 (PA 1010)
 - Polyamide 1012 (PA 1012)
 - Polyamide 410 (PA 410)
 - Polyamide 610 (PA 610)
 - Polyphthalamides (PPA)

- By polycondensation of ω -amino carboxylic acids or lactams:

- Polyamide 11 (PA 11)
- Poly(α -amino acid)s
 - Poly(γ -glutamic acid) (γ -PGA)
 - Poly(α -aspartic acid)
 - ϵ -Poly(L-lysine) (ϵ -PL)
 - Polypeptides (collagen, casein, fibrin, gelatin)
 - Proteins

Poly(ester amide)s

- Poly(butylene adipate-*co*-caproamide)
- Hyperbranched poly(ester amide)s

Polyurethanes (bio-based PU)

- Poly(ester urethane)s
- Poly(ether urethane)s

Polysaccharides

- Cellulose derivatives
 - Methyl cellulose
 - Ethyl cellulose
 - Propyl cellulose
 - Hydroxyethyl cellulose
 - Carboxymethyl cellulose
 - Hydroxypropyl cellulose
 - Cellulose acetate (CA)
 - Cellulose acetate butyrate (CAB)
 - Cellulose acetate propionate (CAP)
 - Cellulose nitrate (CN)
 - Cellulose-chitosan
- Starch
- Lignin
- Chitin, chitosan

Vinyl Polymers

- Polyolefins (bio-based polyethylene, PE, LDPE, HDPE; bio-based polypropylene, PP)
- Poly(vinyl chloride) (bio-based PVC)
- Poly(vinyl alcohol) (PVOH)

Other Biodegradable Polymers

- Polyorthoesters I, II, III, IV (POE)
- Polyanhydrides
 - Poly(carboxyphenoxy hexane-sebacic acid)
 - Poly(fumaric acid-sebacic acid)
 - Poly(imide-sebacic acid)
 - Poly(imide-carboxyphenoxy hexane)
- Polyphosphazenes (PPHOSs)

1.3 Polyesters

Polyesters, especially the aliphatic ones, are the most extensively studied class of biopolymers [1]. They can be classified into two groups according to the bonding of the constituent monomers [2]. The first group consists of the poly(hydroxy acid)s. These are polyesters synthesized from hydroxy acids (hydroxy-carboxylic acids), HO-R-COOH, or by ring-opening polymerization of cyclic monomers, $-R-COO-$. The second group consists of the poly(alkylene dicarboxylate)s. These are polyesters prepared by polycondensation of diols and dicarboxylic acids.

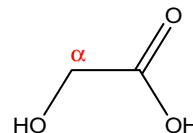
1.3.1 Poly(hydroxy acid)s

A series of hydroxy acids are the hydroxyalkanoic acids, and the corresponding polymers are subdivided into three categories: poly(α -hydroxyalkanoic acid)s, poly(β -hydroxyalkanoic acid)s and poly(ω -hydroxyalkanoate)s. The term polyhydroxyalkanoate is normally used for poly(hydroxyalkanoic acid)s derived from β -hydroxyalkanoic acids, and in certain cases, even γ -, δ -, and ϵ -hydroxyalkanoic acids.

1.3.1.1 Poly(α -hydroxyalkanoic acid)s

Poly(α -hydroxyalkanoic acid)s are poly(α -ester)s derived from α -hydroxyalkanoic acids (see Scheme 1.1). A list of common α -hydroxyalkanoic acids is shown in Table 1.1.

Common α -hydroxyalkanoic acids include lactic acid, glycolic acid, tartaric acid, malic acid, mandelic acid, benzylic acid, valeric acid, α -hydroxybutyric acid, α -hydroxyoctanoic acid, α -hydroxystearic acid, and mixtures thereof. The most used α -hydroxyalkanoic acids are lactic acid, glycolic acid, and mixtures thereof; the corresponding polymers,



Scheme 1.1 α -Hydroxyalkanoic acid.

polylactide (PLA) and polyglycolide (PGA), and copolymers thereof, have been known for years.

Polylactide (PLA)

Polylactide or polylactic acid (PLA) is a linear aliphatic poly(α -ester) or α -hydroxyalkanoic acid-derived polyester (see Scheme 1.2).

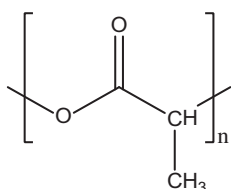
PLA is obtainable primarily by the ionic polymerization of lactide, a ring closure of two lactic acid molecules. At temperatures between 140° and 180°C and under the action of catalytic tin compounds (such as tin oxide), a ring-opening polymerization takes place. Lactide itself can be made through lactic acid fermentation from renewable resources such as starch by means of various bacteria. PLA can also be produced directly from lactic acid by polycondensation. However, this process yields low molecular weight polymers, and the disposal of the solvent is a problem in the industrial production. Various procedures for synthesizing, purifying, and polymerizing lactide are disclosed in **US4057537 A** (1977, GULF OIL CORP), **EP0261572 A1** (1988, BOEHRINGER INGELHEIM KG; BOEHRINGER INGELHEIM INT) and described in the literature [3–5].

There are two optically active forms of lactic acid: L-lactic acid and D-lactic acid. Consequently, the lactide, the cyclic dimer of lactic acid, may occur in three isomeric forms depending on whether it consists of: (1) two L-lactic acid molecules, L-lactide; (2) two D-lactic acid molecules, D-lactide; or (3) one L-lactic acid molecule and one D-lactic acid molecule, meso-lactide. The meso-lactide is characterized by a melting point (T_m) of around 50°C, whereas the melting point of the L- and D-lactide isomers is 97°C. An equimolar mixture of the L- and D-lactides results in LD-lactide (*rac*-lactide) (see Scheme 1.3).

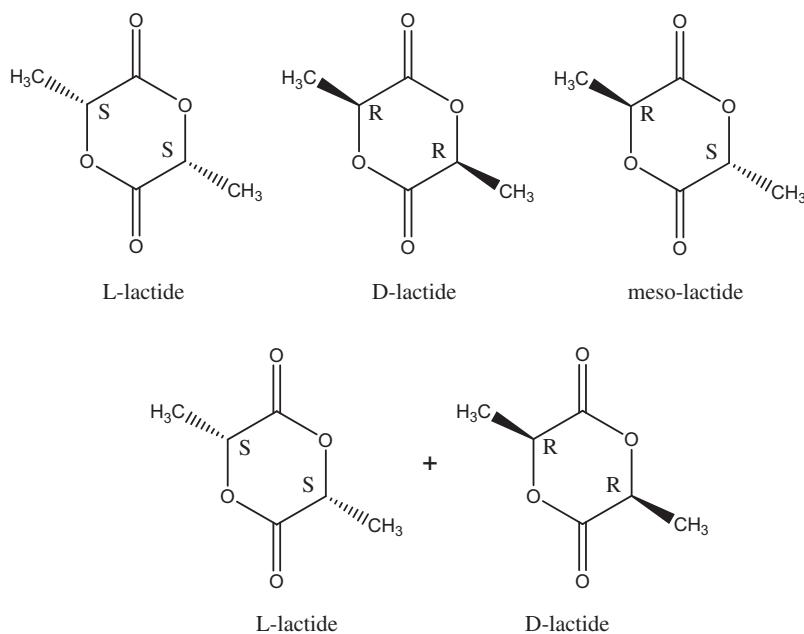
Polylactide resins are classified into poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), syndiotactic poly(D,L-lactide) (syndiotactic PDLLA), atactic poly(D,L-lactide) (atactic PDLLA), and copolymers with other polymers, depending on the type of constitutive monomer (see Scheme 1.4). There is also another form of PLA known as isotactic

Table 1.1 List of α -hydroxyalkanoic acids

α -Hydroxyethanoic acid (glycolic acid)	α -Hydroxydecanoic acid (α -hydroxycapric acid)
α -Hydroxypropanoic acid (α -lactic acid)	α -Hydroxyundecanoic acid (α -hydroxyhendecanoic acid)
2,3-Dihydroxybutanedioic acid (tartaric acid)	α -Hydroxydodecanoic acid (α -hydroxylauric acid)
Hydroxybutanedioic acid (malic acid)	α -Hydroxytridecanoic acid
2-Hydroxy-2-phenylacetic acid (mandelic acid)	α -Hydroxytetradecanoic acid (α -hydroxymyristic acid)
2-Hydroxy-2,2-di(phenyl)acetic acid (benzylic acid)	α -Hydroxypentadecanoic acid
α -Hydroxypentanoic acid (2-hydroxyvaleric acid)	α -Hydroxyhexadecanoic acid (α -hydroxypalmitic acid)
1-Hydroxy-1-cyclohexane carboxylic acid	α -Hydroxyheptadecanoic acid
2-Hydroxy-2-(2-tetrahydrofuryl) ethanoic acid	α -Hydroxynonadecanoic acid
2-Hydroxy-2-(2-furyl) ethanoic acid	α -Hydroxystearic acid
2-Hydroxy-2-phenylpropanoic acid	α -Hydroxyarachidic acid
2-Hydroxy-2-methylpropanoic acid	α -Hydroxybehenic acid
2-Hydroxy-2-methylbutanoic acid	α -Hydroxylignoceric acid
2-Hydroxy-2-ethylhexylcarboxylic acid	α -Hydroxycerotic acid
α -Hydroxybutanoic acid (α -hydroxybutyric acid)	α -Hydroxyoleic acid
α -Hydroxypentanoic acid (α -hydroxyenanthoic acid)	α -Hydroxylinoleic acid
	α -Hydroxylinolenic acid
α -Hydroxyheptanoic acid (α -hydroxyenanthoic acid)	α -Hydroxyarachidonic acid
α -Hydroxyoctanoic acid (α -hydroxycaprylic acid)	
α -Hydroxynonanoic acid (α -hydroxypelargonic acid)	

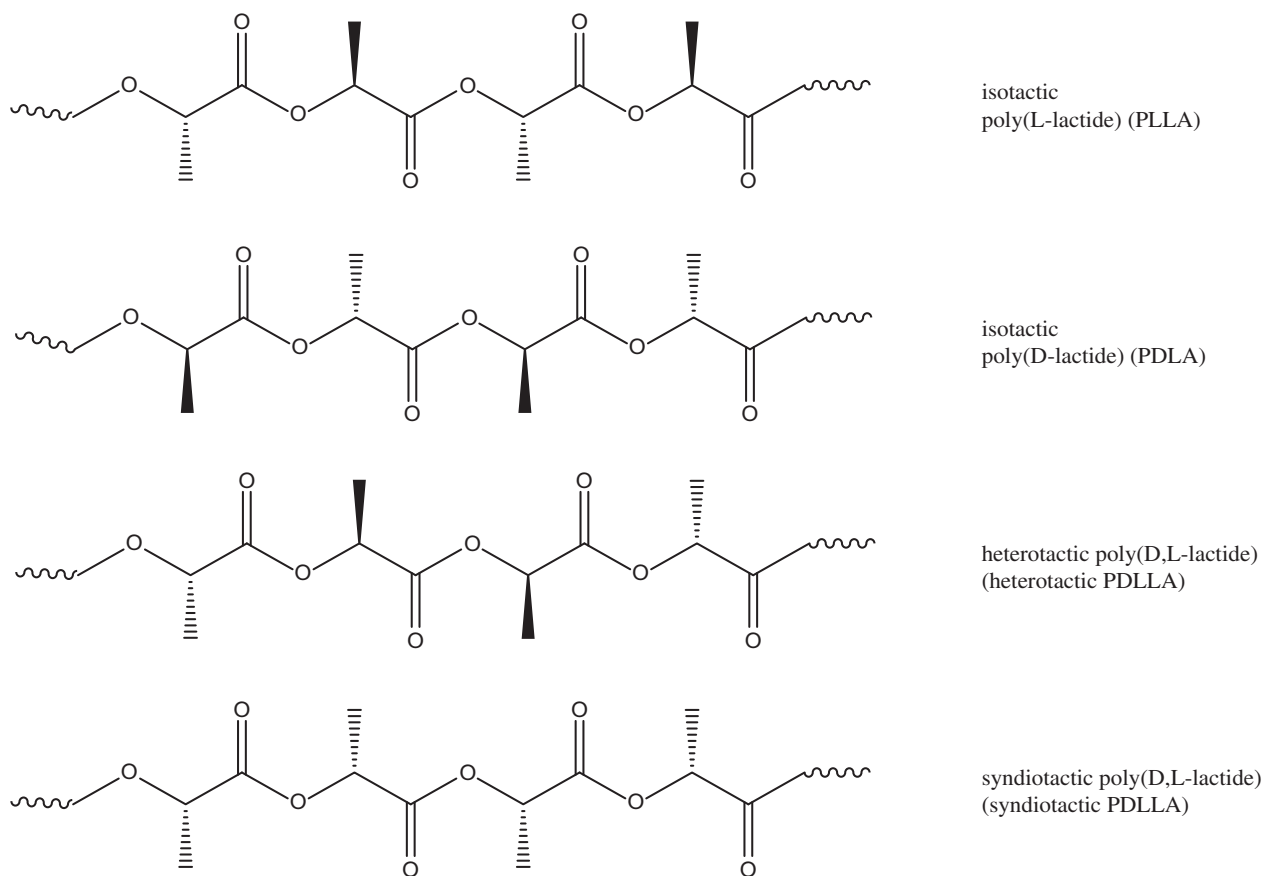
**Scheme 1.2** Polylactide (PLA).

stereocomplex, prepared from *rac*-lactide using a racemic catalyst (isopropoxide), which has the added advantage of possessing a melting point approximately 50°C higher than the homochiral polymers [6]. The mechanical properties of all these types of PLA are as different as their degradation times [7]. Thus, a regular PLLA is a hard, transparent polymer; it has a T_m of 165–185°C, a glass transition temperature (T_g) of 53–63°C, and a crystallization



LD-lactide (rac-lactide): equimolar mixture of L-lactide and D-lactide

Scheme 1.3 Stereoisomeric forms of lactide.



Scheme 1.4 Stereoisomeric forms of polylactide (PLA).

temperature (T_c) of 100–120°C. On the other hand, atactic PDLA has no melting point, a T_g around 55°C, and it shows much lower tensile strength [8].

The properties of PLA depend primarily on the molecular mass, the degree of crystallinity, and possibly the proportion of co-monomers. A higher molecular mass raises T_g , as well as T_m , tensile strength, elastic modulus, and lowers the strain after fracture. Due to the CH_3 side group (see Scheme 1.2), the material has water-repellent or hydrophobic behavior. PLA is soluble in many organic solvents, such as dichloromethane or the like. PLA has higher transparency than other biodegradable polymers, and is superior in weather resistance and workability.

PLA has low melt viscosity, which is required for the shaping of a molding. PLA is, however, slow in the crystallization rate with long molding cycles and has poor gas properties; furthermore, it has inferior thermal resistance and mechanical characteristics (toughness, impact resistance, and the like) compared with those of existing synthetic resin molded articles. To solve these problems, many countermeasures are used in forming PLA, including blending PLA with other polymers, and compounding various kinds of substances as filler; thus, PLA products have been entering practical applications.

PLA is gaining a lot of interest due to its biodegradability, biocompatibility, and renewable resource-based origin. It can be said that PLA is a low environment load polymer that does not cause a direct increase in the total amount of carbon dioxide gas, even if the polymer is finally biodegraded or burned up. The biodegradability of PLA, however, has both positive and negative aspects. The positive aspects of PLA are its ability to form non-hazardous products when PLA polymers or articles are discarded or composted after completing their useful life, and its slow degradation period (several weeks up to about one year), which is advantageous for some applications as it leads to a relatively good shelf life. The negative aspects are that the thermal degradation of PLA during processing causes deterioration of properties, and that the degradation rate of PLA is still low as compared to the waste accumulation rate, which means that a large amount of PLA left untreated outdoors may cause a new environmental problem. Thus, the same properties that make PLA polymers desirable as replacements for nondegradable fossil fuel-based polymers also create undesirable effects which must be overcome. PLA has a considerably lower biodegradability than poly(ϵ -caprolactone)

(PCL) or poly(3-hydroxybutyrate) (PHB). PLA is the most common biopolymer currently on the market. As such, it has a variety of brand names associated with it (see Table 1.2).

Polyglycolide (PGA)

Polyglycolide (PGA) is the simplest linear aliphatic polyester (see Scheme 1.5). Glycolide monomer is synthesized from the dimerization of glycolic acid. Ring-opening polymerization yields high molecular weight materials, with approximately 1–3% residual monomer present. PGA is highly crystalline (45–55%), with a high T_m (220–225°C) and a T_g of 35–40°C [9]. Because of its high degree of crystallinity, it is not soluble in most organic solvents, the exceptions being highly fluorinated organics such as hexafluoroisopropanol.

PGA has an extremely high gas-barrier property, as high as ca. 3 times or higher (i.e., ca. 1/3 or lower in terms of an oxygen transmission coefficient) than that of ethylene-vinyl alcohol copolymer (PEVOH), which is a representative gas-barrier resin used heretofore. This means that a bottle (especially one made of PET) with a remarkably improved gas-barrier property can be obtained by including a thin layer of PGA in addition to the principal resin layer. Accordingly, it becomes possible to effectively prevent the degradation of contents due to oxidation or poorer quality due to dissipation of carbon dioxide gas. Furthermore, PGA has a substantial hydrolyzability with alkaline washing liquid, water (particularly warmed water), or acidic water. In contrast, PLA does not exhibit gas-barrier properties like that of PGA, and can only show a slower hydrolyzation speed with alkaline water, water, or acidic water (WO03097468 A1, 2003, KUREHA CHEM IND CO LTD). Fibers from PGA exhibit high strength and modulus and are too stiff to be used as sutures except in the form of braided material. Sutures of PGA lose about 50% of their strength after two weeks and 100% at four weeks, and are completely absorbed in 4–6 months. Glycolide has been copolymerized with other monomers to reduce the stiffness of the resulting fibers. PGA can be utilized as a packaging material (e.g., lightweight PET bottles) as well as for oil recovery and other industrial and medical applications.

Poly(lactide-co-glycolide) (PLGA)

Poly(lactide-co-glycolide) (PLGA) is a copolymer of hydrophobic PLA and hydrophilic PGA (see Scheme 1.6). L-lactide and D,L-lactide have been used for copolymerization with glycolide. Amorphous

Table 1.2 Commercial α -hydroxycarboxylic acid-derived polyesters

Biopolymer	Commercial name	Manufacturer	Application
PLA	Ingeo™ grades NatureWorks® 2000 series: 2003D TDS NatureWorks® 3000 series: 3001D SDS, 3052D SDS, 3251D SDS, 3801X SDS NatureWorks® 4000 series: 4032D TDS, 4043D TDS, 4060D TDS NatureWorks® 6000 series: 6060D TDS, 6201D TDS, 6202D TDS, 6204D TDS, 6400D TDS, 6251D TDS, 6252D TDS, 6302D TDS, 6751D TDS, 6752D TDS NatureWorks® 7000 series: 7001D TDS, 7032D TDS	NatureWorks LLC (USA)	2003D TDS: food packaging; 2003D TDS, 3001D TDS, 3052D TDS, 3251D TDS: service ware; 3001D SDS, 3052D SDS, 3251D SDS, 3801X SDS: durable goods; 4032D TDS, 4043D TDS, 4060D TDS: films, cards, folded cartons; 6201D TDS, 6204D TDS: apparel; 6201D TDS, 6202D TDS, 6204D TDS, 6400D TDS: home textiles (woven and knitted); 6060D TDS, 6202D TDS, 6251D TDS, 6252D TDS, 6302D TDS, 6751D TDS, 6752D TDS: nonwovens; 7001D TDS, 7032D TDS: bottles
PLA	Econstrong®	Far Eastern Textiles (TW)	Catering products (cups, trays, cutlery)
PLA	Eco plastic®	Toyota (JP)	Floor mats in cars
PLA	Heplon	Chronopol (USA)	Bags
PLA	Lacea® H-100 Lacea® H-280 Lacea® H-400 Lacea® H-440	Mitsui Chemicals (JP)	Bags, containers, films, nonwovens, packaging (stationery, cosmetic containers, pots for seedlings)
PLA	Lacty® 5000 series Lacty® 9000 series Lacty® 9800 series	Shimadzu Corp. (JP)	Injection molding, fibers, films, sheets
PLA	Terramac®	Unitika Ltd. (JP)	
	TE-2000 TE-1030 TE-1070		Injection: smaller goods, containers, various plastic parts, etc.
	TE-7000 TE-7307		Injection: containers, table wear, chassis, etc.

(Continued)

Table 1.2 Commercial α -hydroxycarboxylic acid-derived polyesters (*Continued*)

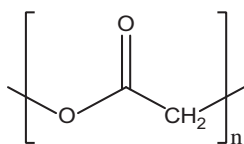
Biopolymer	Commercial name	Manufacturer	Application
	TE-7300 TE-8210 TE-8300		
	TP-4000 TP-4030 HV-6250H		Extrusion, blown, and foam: containers, bottles, pipes, foam sheet, etc.
PLA	Ecolaju [®] S series	Mitsubishi Plastics, Inc. (JP)	Films, sheets
PLA, recycled	LOOPLA [®] Galacid [®]	Galactic (BE) Futero Total/Galactic (BE)	Recycled PLA grades are not suitable for food-grade applications
PLA	Palgreen [®]	Mitsui Chemicals Tohcello	Films
PLA	L-PLA D-PLA PDLA [®] PURALACT [®]	Purac (NL) & Sulzer Chemtech	Molded plastic parts, fibers, films, foam, heat-stable applications
PDLLA	BIOFRONT [®]	Teijin (JP)	Fibers, injection molding, eyeglass frames; films and sheets
PLA	RECODE 100 series RECODE 200 series	Daishin Pharma-Chem Co., Ltd./ Zhejiang Hisun Biomaterials Co., Ltd. (CN)	Fixed installations such as bone plates, bone screws, surgical sutures, spinning
PLA, PCL blend	VYLOECOL BE-400 [†] VYLOECOL BE-600 VYLOECOL BE-910 VYLOECOL HYD-306 VYLOECOL BE-450 VYLOECOL BE-410 VYLOECOL HYD-006	Toyobo (JP)	Printing ink, adhesive, paint, master batch resin, etc; BE-400 (pellet): general purpose grade, agent for various coating; BE-600 (sheet): anchor coating for vapor deposition film, anchor coating for printing ink; BE-910 (sheet): adhesive for dry lamination
PLA (co) polymers	Ecodear [®] series: Ecodear [®] L4E6 Ecodear [®] V351X51 (glass fiber reinforcement, 30%) Ecodear [®] V554R10 (glass fiber reinforcement, 30%) Ecodear [®] V554X51 Ecodear [®] V751X52 (glass fiber reinforcement, 30%) Ecodear [®] V911X51 (glass fiber reinforcement, 30%)	Toray Industries (JP)	Electric, commodity appliances; film, bags, fibers; food packaging applications (frozen foods, snacks, cookies, cereal and nutrition bars, and confectionery items); packaging for nonfood items (personal care items, fashion accessories, promotional items, toys, office supplies, and other retail goods)
PGA	Kuredux [®] Kuresurge [®]	Kureha (JP)	Kuredux [®] : used in multilayer PET bottles for carbonated drinks; Kuresurge [®] : used for surgical sutures

Table 1.2 Commercial α -hydroxycarboxylic acid-derived polyesters (*Continued*)

Biopolymer	Commercial name	Manufacturer	Application
PGA	PURASORB PG 20	Purac (NL)	Medical device and pharmaceutical industry
PLGA	PURASORB PLG 8531 PURASORB PLG 8523 PURASORB PLG 8560 PURASORB PLG 8218 PURASORB PLG 8055 PURASORB PLG 1017	Purac (NL)	Medical device and pharmaceutical industry
PLGA	Coated VICRYL TM RAPIDE (polyglactin 910)	Ethicon, Inc. (USA)	Coated absorbable sutures
PGCL	MONOCRYL TM Plus Antibacterial (poliglecaprone 25) Suture	Ethicon, Inc. (USA)	Monofilament absorbable sutures

Abbreviations: PGA, Polyglycolide; PGCL, Poly(glycolide-co-caprolactone); PLA, Polylactide; PLCL, Poly(lactide-co-caprolactone); PLGA, Poly(lactide-co-glycolide).

[†]VYLOECOL[®] is made from lactides supplied by Purac. They are marketed under the brand name PURALACTTM.

**Scheme 1.5** Polyglycolide (PGA).

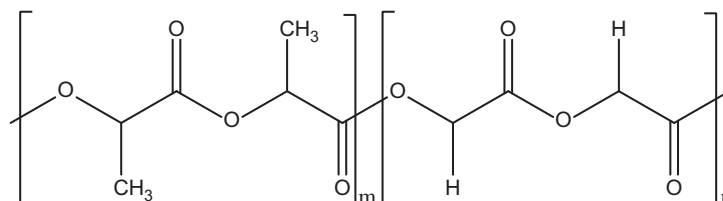
polymers are obtained for a 25 lactide/75 glycolide monomer ratio. A copolymer with a monomer ratio of 80 lactide/20 glycolide is semicrystalline. When the ratio of monomer lactide/glycolide increases, the degradation rate of the copolymer decreases [1].

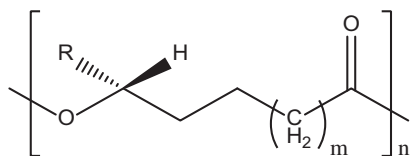
PLGA is useful in drug delivery and tissue regeneration applications since it degrades into harmless substances. Since polymers of lactic acid and glycolic acid and their copolymers (PLGA) degrade quickly in the body into nontoxic products, PLGA is used for biodegradable sutures and can potentially be used in implantable screws, intravascular stents, pins, drug delivery devices, and as a temporary scaffold for tissue and bone repair. Additionally, PLGA has good

mechanical properties that improve the structural integrity of such devices. However, since PLGA degrades completely by bulk erosion, it loses more than 50% of its mechanical strength in less than two months, which can lead to uncontrollable drug release rates and biocompatibility problems; this is probably due to an accumulation of lactic and glycolic acids during degradation (US6077916 A, 2000, PENN STATE RES FOUND).

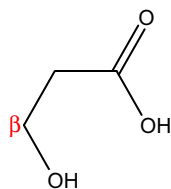
1.3.1.2 Poly(β -, γ -, δ -hydroxyalkanoate)s (PHAs)

Polyhydroxyalkanoates (PHAs) are polyesters in which the hydroxyl group and the carboxyl group of hydroxyalkanoic acids are linked via oxoester bonds. The general formula of polyhydroxyalkanoates is given in Scheme 1.7. The hydroxyalkanoic acids are distinguished mainly by the position of the hydroxyl group in relation to the carboxyl group (see Scheme 1.8a and b), by the length of the side-alkyl chain, by a large variety of substituents in the

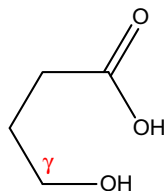
**Scheme 1.6** Poly(lactide-co-glycolide) (PLGA).



Scheme 1.7 General formula of polyhydroxyalkanoates; wherein $m \geq 1$, $R = H$, (un)substituted alkyl.



Scheme 1.8a β -Hydroxyalkanoic acid.



Scheme 1.8b γ -Hydroxyalkanoic acid.

side chains, and by one additional methyl group at carbon atoms between the hydroxyl and the carboxyl groups [10]. Unlike polymers derived from α -hydroxyalkanoic acids, like PLA and PGA, the polyhydroxyalkanoates are normally comprised of β -hydroxyalkanoic acids, and in certain cases, even γ - and δ -hydroxyalkanoic acids.

To date, more than 150 hydroxyalkanoic acids have been detected as constituents in bacterial PHAs; these constituents are produced by microorganisms grown on carbon substrates containing different types of chemical structures [10–12]. Beside linear and branched β -, γ -, δ -, and ϵ -hydroxyalkanoates, various constituents such as PHAs containing halogenated or aromatic side chains have been described [13,14]. A list of β -, γ -, and δ -hydroxyalkanoic acids is given in Table 1.3.

PHAs are commercially produced by several bacteria as intercellular carbon and energy storage materials [15]. PHAs may constitute up to 90% of the dry cell weight of bacteria, and are found as discrete granules inside the bacterial cells. Produced naturally by soil bacteria, PHAs are degraded upon subsequent exposure to these same bacteria in soil, compost,

or marine sediment. Biodegradation begins when microorganisms start growing on the surface of PHA and secrete enzymes that break down the biopolymer into hydroxy acid monomeric units. The hydroxy acids are then taken up by the microorganisms and used as carbon sources for growth. The monomers and polymers can also be produced chemically.

In addition to commercial use as a biodegradable replacement for synthetic commodity resins, PHAs have been extensively studied for use in biomedical applications. These studies range from potential applications in controlled release, to use in formulation of tablets, surgical sutures, wound dressings, lubricating powders, blood vessels, tissue scaffolds, surgical implants to join tubular body parts, bone fracture fixation plates, and other orthopedic uses (WO9932536 A1, 1999, METABOLIX INC).

Because of their great compositional diversity, PHAs with a range of physical properties can be produced [16]. There are currently several commercially available PHAs, including poly-3-hydroxybutyrate (PHB), poly-(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB), and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx), which are derived from bacterial fermentations (Table 1.4).

This class of polyesters is attractive as a potential alternative to conventional fossil fuel-based polymers. PHAs can be processed by traditional polymer techniques for use in an enormous variety of applications, including consumer packaging, disposable diaper linings, garbage bags, and food and medical products [15,17].

Polyhydroxybutyrate (PHB or P3HB)

Polyhydroxybutyrate (PHB or P3HB) is synthesized and stored within cells as an energy source for various microorganisms [18,19]. PHB can be extracted from the microorganisms. Example techniques are disclosed in AU5560680 A (1980, ICI PLC) and EP0046335 A2 (1982, ICI PLC) (Scheme 1.9).

PHB is a homopolymer having stereoregular structure with high crystallinity. The high crystallinity leads to a rather stiff and brittle material. PHB has low melt viscosity and a narrow processing window. Its inherent brittleness and thermal instability during melt processing impedes its commercial applications [20]. Plasticization of PHB or addition of processing additives (e.g., nucleants) is often practiced in order to overcome its brittleness (see Section 1.14.2: Additives and Modifiers). The commercial products of PHB are outlined in Table 1.4.

Table 1.3 List of β -, γ - and δ -hydroxycarboxylic acids

β-Hydroxycarboxylic acids	γ-Hydroxycarboxylic acids	δ-Hydroxycarboxylic acids
β -Hydroxypropanoic acid (hydracrylic acid)	γ -Hydroxypropanoic acid	
β -Hydroxybutanoic acid (β -hydroxybutyric acid)	γ -Hydroxybutanoic acid (γ -hydroxybutyric acid)	
3-Hydroxy-2-methylpropanoic acid (3-hydroxyisobutyric acid)		
β -Hydroxypentanoic acid (β -hydroxyvaleric acid)	γ -Hydroxypentanoic acid (γ -hydroxyvaleric acid)	δ -Hydroxypentanoic acid (δ -hydroxyvaleric acid)
3-Hydroxy-3-methylpentanoic acid (3-hydroxy-3-methylvaleric acid)		
β -Hydroxyhexanoic acid (β -hydroxycaproic acid)	γ -Hydroxyhexanoic acid (γ -hydroxycaproic acid)	δ -Hydroxyhexanoic acid (δ -hydroxycaproic acid)
β -Hydroxyheptanoic acid (β -hydroxyenanthoic acid)	γ -Hydroxyheptanoic acid (γ -hydroxyenanthoic acid)	δ -Hydroxyheptanoic acid (δ -hydroxyenanthoic acid)
β -Hydroxyoctanoic acid (β -hydroxycaprylic acid)		
β -Hydroxynonanoic acid	γ -Hydroxynonanoic acid	
	γ -Hydroxydecanoic acid (γ -hydroxycapric acid)	δ -Hydroxydecanoic acid (δ -hydroxycapric acid)
β -Hydroxydodecanoic acid (β -hydroxy lauric acid)	γ -Hydroxydodecanoic acid (γ -hydroxy lauric acid)	
	γ -Hydroxytridecanoic acid	
	γ -Hydroxyhexadecanoic acid (α -hydroxypalmitic acid)	

PHB is used in the manufacture of body-waste bags, whether alone or as a coating on a water-soluble polymer, because of its good impermeability to water and vapor (US4372311 A, 1983, UNION CARBIDE CORP). Films or coatings of PHB may be made by solution-coating techniques or by melt extrusion. Upon degradation of PHB, the water-soluble polymer can dissolve, thus avoiding obstruction of sewage pipes and sewage treatment plants. However, it is claimed that the degradation rate of PHB is often too slow to avoid the formation of the aforementioned obstructions (AU3521984 A, 1985, ICI PLC). The rate of degradation can be markedly increased by modification of the pH of the bag contents (see Chapter 7: Degradability on Demand; Section 7.3.4: Compounds Which Can Initiate and/or Propagate Depolymerization).

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a copolymer in which 3-hydroxyvalerate

(HV) units are incorporated in the PHB backbone during the fermentation process (see Scheme 1.10). Microbiologically produced PHBV can be made by the techniques described in EP0052459 A1 (1982) and EP0069497 A2 (1983, ICI PLC). The use of copolymers (e.g., containing 10 to 25, and particularly 15 to 20 mol% of HV units) may in some cases be advantageous for lowering the modulus of the PHB since bags made from a film of such copolymers would be less likely to make rustling noises upon movement by the wearer.

PHBV has improved flexibility and toughness and a lower processing temperature than PHB. Presently, PHBV with an HV content below 15 mol% is commercially available, while large-scale production of PHBV with higher HV content is presently not commercially viable due to the surprisingly high production cost [21]. The available PHBV (with an HV content of less than 15 mol%) has a low toughness and elongation at break. PHBV has achieved a certain

Table 1.4 Commercial polyhydroxyalkanoates (PHAs)

Biopolymer	Commercial name	Manufacturer	Applications
PHB	Biogreen®	Mitsubishi Gas Chemical Company Inc (JP)	As component material for biodegradable polymers; (cast) films, in natural latex gloves
PHB	Mirel™ 3000 series ("P" and "F" versions) ¹ Mirel 400 series ("P" and "F" versions)	Telles (ADM/Metabolix) (USA) ²	Mirel™ 3000: thermoforming Mirel 400: sheet applications
PHB	Biocycle™ -B1000 -B18BC-1 -B189C-1 -B189D-1	PHB Industrial S/A (BR)	Films, disposables, medical applications
PHBV and PHB	Biomer® 300 -P300E -P300F -P300EF	Biomer Inc (DE)	P300E: for extrusion, but not for film blowing; P300F: for food contact (EU only); P300EF: for extrusion and food contact, not for film blowing
PHBV, PHBV/PLA	ENMAT™ Y1000 ENMAT™ Y1010 (with nucleating and stabilizing agent) ENMAT™ Y1000P ENMAT™ Y3000 ENMAT™ Y3000P ENMAT™ F9000P	Tianan Biologic, Ningbo (CH)	Thermoplastics: injection molding, extrusion, thermoforming, blown films; fiber & nonwovens; denitrification: water treatment
PHBHx	Nodax ³	Meredian (USA)	Packaging, laminates, coatings, nonwoven fibers
PHBHx	Kaneka PHBH	Kaneka Co. (JP)	Film, sheets, foam, injection moldings, fibers, etc.; expected to be used in agricultural and construction interior materials, automotive interior materials, electrical devices, packaging, etc.
P3HB4HB	GreenBio®	Tianjin Green Bio-Science Co. (CN)/DSM (NL)	Fresh film, mulch film, laminating film, wrapping film, heat shrinkable film, etc.; food packaging, shopping bags, garbage bags, gift bags, produce bags, etc.
PHBHx	AONILEX®	Kaneka Co. (JP)	High-durability molded products: bottles and containers, auto interiors, electrical equipment
PHBV	BIOPOL® ⁴	Metabolix, Inc. (USA)	Disposable products used in the food industry (utensils, cups and plates); plastic wrap for packaging, coatings for paper and cardboard, moisture barrier films for hygienic

Table 1.4 Commercial polyhydroxyalkanoates (PHAs) (*Continued*)

Biopolymer	Commercial name	Manufacturer	Applications
			products, disposable containers for shampoo and cosmetics, and disposable items (razors, garbage bags and disposable nappies); agricultural uses include a carrier for slow release of pesticides, herbicides or fertilizers; medical and pharmaceutical uses (gauzes, sutures, filaments, implants, drug carriers, and coatings for drugs); bicycle helmet with BIOPOL [®] fibers and cellulose high performance fibers
P4HB	TephaFLEX [®]	Tepha, Inc.	Monofilament suture; absorbable surgical film

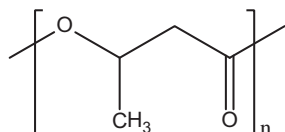
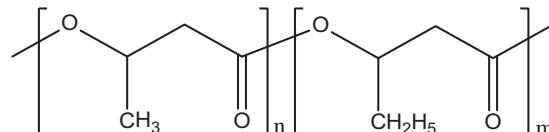
Abbreviations: PHB, Polyhydroxybutyrate; PHBV, Poly(3-hydroxybutyrate-co-3-hydroxy valerate); P3HB4HB, Poly(3-hydroxybutyrate-co-4-hydroxybutyrate); PHBHx, Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).

¹The “P” and “F” versions refer to general purpose and food contact applications, respectively.

²On 12 January 2012 Metabolix announced that Archer Daniels Midland Company (ADM) had given notice of termination of the Telles, LLC joint venture for PHA bioplastics. Telles was established as a joint venture between Metabolix and ADM in July 2006. The joint venture sold PHA-based bioplastics, including Mirel and Mvera, in the US, Europe and other countries.

³Meredian, Inc. bought Nodax PHA technology from Procter & Gamble Co.

⁴Monsanto's rights to BIOPOL[®] were sold to the American company Metabolix in 2001.

**Scheme 1.9** Poly(3-hydroxybutyrate) (PHB or P3HB).**Scheme 1.10** Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV).

economic importance because of its polypropylene-like properties. Its commercial products are outlined in Table 1.4. They have the potential to replace polypropylene (PP) and other conventional fossil-based polymers if the PHB and PHBV-based materials can be developed with a balance of properties such as stiffness and toughness. PHB and PHBV often have unsatisfactory properties. PHB tends to be thermally unstable, while PHB and PHBV often have slow crystallization rates and flow properties that make processing difficult. For example, PHBV remains tacky for long periods of time, and may stick to itself when being processed into films.

Commercially available PHB and PHBV represent only a small component of the property sets available

to PHAs. For example, the elongation at break of PHB and PHBV ranges from around 4 to 42%, whereas the same property for poly-4-hydroxybutyrate (P4HB) is about 1000%. Similarly, the values of Young's modulus and tensile strength for PHB and PHBV are 3.5 to 0.5 GPa and 40 to 16 MPa (for increasing HV content to 25 mol%), respectively, compared to 149 MPa and 104 MPa, respectively, for P4HB [22].

In addition to finding commercial use as a biodegradable replacement for synthetic commodity resins, PHB and PHBV have been extensively studied for use in biomedical applications. These studies range from potential uses in controlled drug delivery [23,24], to use in formulation of tablets, surgical sutures, wound dressings, lubricating powders, blood vessels, tissue

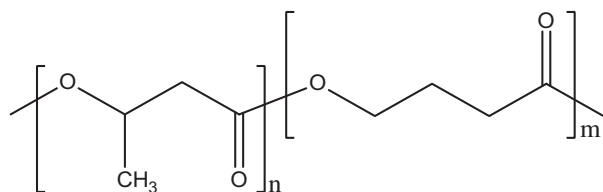
scaffolds, surgical implants to join tubular body parts, bone fracture fixation plates, and other orthopedic uses, as described in **WO9851812 A2** (1998, METABOLIX INC). PHB and PHBV are also used for preparation of a porous, bioresorbable flexible sheet for tissue separation and stimulation of tissue regeneration in injured soft tissue as disclosed in **EP0349505 A2** (1990, ASTRA MEDITEC AB).

Poly(3-hydroxybutyrate-co-4-hydroxybutyrate)
(P3HB4HB)

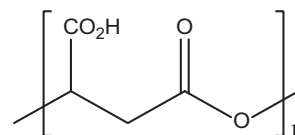
Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB) was first found in 1988 from *Ralstonia eutropha* cultivated with 4-hydroxybutyric or 4-chlorobutyric acid as carbon sources. The incorporation of 4-hydroxybutyrate (4HB) units into PHB (or P3HB) improves the material application potential, and the copolymer shows a wide range of physical properties ranging from highly crystalline polymer to elastic rubber, depending on the polymer composition (see [Scheme 1.11](#)). Generally, carbon sources structurally related to 4HB are required to generate 4HB-containing PHA, such as 4-hydroxybutyric acid, γ -butyrolactone, and 1,4-butanediol. However, these carbon sources are much more expensive than glucose or other 3HB-generating carbon sources. The high cost of raw material for the copolymer production has become an obstacle for the wide production and application of P3HB4HB. **US2012214213 A1** (2012, TIANJIN GREENBIO MATERIAL CO LTD) discloses methods of producing P3HB4HB with high 4HB monomer content using carbon sources which are structurally unrelated to 4-hydroxybutyrate.

Poly(β -malic acid) (PMLA)

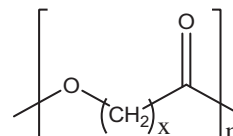
Poly(β -malic acid) (PMLA) is a biodegradable and bioabsorbable water-soluble aliphatic polyester with modifiable pendant carboxyl groups (see [Scheme 1.12](#)). PMLA has been reported to be produced by *Penicillium cyclopium*, *Physarum polycephalum*, and *Aureobasidium* [25]. Various representative industrial methods for producing PMLA are described in **CN102002148 A** (2011, ZHANGJIAGANG CHAINENG BIOLOG SCIENCE CO LTD),



Scheme 1.11 Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB).



Scheme 1.12 Poly(β -malic acid) (PMLA).



Scheme 1.13 Poly(ω -hydroxyalkanoate)s.

JP2004175999 A (2004) and **JP2005320426 A** (2005, NAT INST FOR MATERIALS SCIENCE). PMLA has various important applications in the biomedical field.

1.3.1.3 Poly(ω -hydroxyalkanoate)s

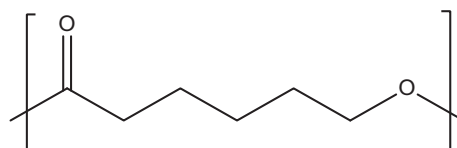
The general formula of poly(ω -hydroxyalkanoate)s is given in [Scheme 1.13](#). A representative example of poly(ω -hydroxyalkanoate)s is poly(ϵ -caprolactone) (PCL).

Poly(ϵ -caprolactone) (PCL)

PCL is the most thoroughly investigated poly(ω -hydroxyalkanoate) owing to the possibility of blending this aliphatic polyester with a number of miscible commercial polymers such as PVC, chlorinated polyethylene, styrene-co-acrylonitrile copolymers, and bisphenol-A polycarbonate [26].

PCL is a fossil fuel-based aliphatic polyester, manufactured by ring-opening polymerization of ϵ -caprolactone in the presence of a tin octoate catalyst (see [Scheme 1.14](#)). PCL is a semicrystalline polymer with a degree of crystallinity of about 50%. It has a rather low T_g (-60°C) and T_m (60°C). Examples of commercially available products of PCL are shown in [Table 1.5](#).

A block copolymer of ϵ -caprolactone with glycolide, which offers reduced stiffness compared to pure



Scheme 1.14 Poly(ϵ -caprolactone) (PCL).

Table 1.5 Commercial polylactones

Biopolymer	Commercial name	Manufacturer	Applications
PCL	Tone [®] series ¹ Tone [®] P-300 Tone [®] P-700 Tone [®] P-767 Tone [®] P-787 Tone [®] UC-261	Dow Chemicals Co. (ex Union Carbide) (USA)	Coatings, elastomers, agricultural films, drug delivery systems, matrices for the controlled release of pesticides, herbicides and fertilizers
PCL	Capa [™] 6000 series Capa [™] 6200 Capa [™] 6250 Capa [™] 6400 Capa [™] 6430 Capa [™] 6500 Capa [™] 6500C Capa [™] 6506 Capa [™] 6800 Capa [™] FB100 Capa [™] 7000 series (copolymers)	Perstorp (UK)	Medical applications: alternative to traditional plaster, orthopedic splints, dental impressions, and oncology immobilization systems; Films and laminates: blown films, laminates and packaging (e.g., foamed packaging or wrapping for both direct and indirect food contact Other applications: universal master batches
PCL	Celgreen PH	Daicel Corporation (JP)	Mulch films, loose fill packaging, developing foam products, etc.
PCL, PCL derivatives	Placel [®] 200 series Placel [®] 300 series Placel [®] F Series (macro-monomers) Placel [®] H1P (M _w 10,000)	Daicel Corporation (JP)	Chemical compounds for use in or as coating materials or polyurethanes; modifiers for plastics; electric insulating materials; ink binders; additives for adhesives
PGCL	MONOCRYL [™] Plus Antibacterial (poliglecaprone 25)	Ethicon, Inc. (USA)	Monofilament absorbable suture

Abbreviations: PCL, Poly(ϵ -caprolactone); PGCL, Poly(glycolide-co-caprolactone).

¹The production of Tone[®] has been stopped or sold.

PGA, is being sold as a monofilament suture by Ethicon, Inc. under the trade name MONOCRYL[™].

1.3.2 Poly(alkylene dicarboxylate)s

Poly(alkylene dicarboxylate)s are polyesters derived from dicarboxylic acids and dihydroxy compounds. These biodegradable polyesters can be characterized as belonging to three general classes: (1) aliphatic polyesters (derived solely from aliphatic dicarboxylic acids); (2) aliphatic-aromatic polyesters (derived from a mixture of aliphatic dicarboxylic acids and aromatic dicarboxylic acids); and (3) aromatic polyesters. Commercially available industrial poly(alkylene dicarboxylate)s are shown in Table 1.6.

1.3.2.1 Aliphatic (co)polyesters

The polyesters derived solely from aliphatic dicarboxylic acids, also called poly(alkylene alkanate)s, are polyesters prepared from a dicarboxylic acid containing four to ten carbon atoms and a diol containing two to six carbon atoms; two or more kinds of each dicarboxylic acid and diol may be employed. Examples include poly(ethylene adipate) (PEA), poly(ethylene succinate) (PES), and poly(butylene succinate) (PBS).

Poly(ethylene succinate) (PES)

Polyethylene succinate (PES) is chemically synthesized either by polycondensation of ethylene glycol and succinic acid or by ring-opening polymerization of succinic anhydride with ethylene

Table 1.6 Poly(alkylene alkanoate)s

Biopolymer	Commercial name	Manufacturer	Applications
PBS	Skygreen® SG100	SK Chemicals (KR)	Injection molding, disposable goods, fibers
PBS	EnPol® G4000 series EnPol® G4560 EnPol® G4560J (> MFI)	IRE Chemical Ltd. (KR)	Enpol® G4560: disposable goods (forks, spoons, knives, golf tees), horticulture equipment (plant pot, clip), fishing gear
PBS	Bionolle™ 1000 series Bionolle™ 1001MD ¹ Bionolle™ 1020MD Bionolle™ 1903MD	Showa Highpolymer Co., Ltd. (JP)	Bionolle™ 1001MD: blown film (mulch films, compost bags), monofilament, blow molding, sheets, flat yarns; Bionolle™ 1020MD: injection molding, staple fiber; Bionolle™ 1903MD: foamed sheet, extrusion coating, uses for additive
PBSA	Bionolle™ 3000 series Bionolle™ 3001 Bionolle™ 3003 Bionolle™ 3020 Bionolle™ 3900 Bionolle™ 5000	Showa Highpolymer Co., Ltd. (JP)	Bionolle™ 3001MD: blown film (mulch films, compost bags), monofilament, blow molding, sheets, flat yarns; Bionolle™ 3020MD: injection molding, staple fiber
PBSA	Skygreen™ SG200	SK Chemicals (KR)	Extrusion films, sheets, extrusion coating
PBSL	GS Pla® AD92W GS Pla® AZ91T GS Pla® GZ95T	Mitsubishi Chemical (JP)	Biodegradable multi-films for agriculture; disposable table utensils

Abbreviations: PBA, Poly(butylene adipate); PBS, Poly(butylene-co-succinate); PBSA, Poly(butylene succinate-co-adipate); PBSL, Poly(butylene succinate-co-lactide); PES, Poly(ethylene succinate); PESA, Poly(ethylene succinate-co-adipate).

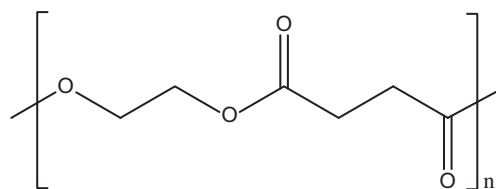
¹Bionolle™ 1001 is synthesized from succinic acid and 1,4-butanediol using 1,6-hexamethylene diisocyanate as a chain-extending agent.

oxide [27,28] (**JPH0931174 A**, 1997, UNITIKA LTD; **CN101628972 A**, 2010, QINGDAO INST OF BIOMASS ENERGY) (see [Scheme 1.15](#)). PES has a T_m of 103–106°C and good mechanical properties, especially elongation [29,30]. It has a high oxygen gas barrier property, which is an advantageous property when taking film utility into consideration, and it has excellent biodegradability (**EP1564235 A1**, 2005; **JP2005264155 A**, 2005, NIPPON CATALYTIC CHEM IND).

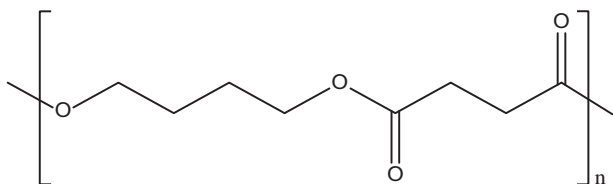
Poly(butylene succinate) (PBS)

Poly(butylene succinate) (PBS)¹ is chemically synthesized by polycondensation of 1,4-butanediol

and succinic acid or its anhydride in the presence of a catalyst [27] (**JPH083302 A**, 1996, UNITIKA LTD; **JPH0931176 A**, 1997, SHOWA HIGHPOLYMER; SHOWA DENKO KK; **JP2001098065 A**, 2001, MITSUBISHI CHEM CORP; **WO2010123095 A1**, 2010, HITACHI PLANT TECHNOLOGIES LTD) ([Scheme 1.16](#)).

**Scheme 1.15** Poly(ethylene succinate) (PES).

¹ Poly(tetramethylene succinate) (PTeMS) has the same structure as PBS, but a different CAS number.



Scheme 1.16 Poly(butylene succinate) (PBS).

The succinic acid can be manufactured by fermentation of a saccharide such as sugarcane or corn (maize) (**JP2005211041 A**, 2005, NIPPON CATALYTIC CHEM IND). Showa Denko K.K. (SDK) announced that it has succeeded in producing its PBS under the trademark Bionolle™ using bio-based succinic acid. Another company already producing bio-based PBS (containing bio-succinic acid) is Mitsubishi Chemical Company [31].

PBS has a relatively high melting temperature ($T_m = 113^\circ\text{C}$) and favorable mechanical properties, which are comparable to those of such widely used polymers as polyethylene and polypropylene [32]. PBS has a relatively low biodegradation rate because of its high crystallization rate and high crystallinity. The enzymatic degradability of PBS was reported to be lower than that of PCL, a low-melting-point (62°C) aliphatic polyester [33]. Examples of commercially available products of PBS are shown in Table 1.6.

Another form of poly(butylene succinate) is poly(2,3-butylene succinate), which is an amorphous PBS with a relatively low softening point (45 to 50°C) that is used in pharmaceutical applications. It has relatively “fast” *in vivo* bioresorption rates,

with samples becoming completely metabolized in four to six weeks without any observable untoward effects (**US5439688 A**, 1995, DEBIO RECH PHARMA SA).

Poly(butylene adipate) (PBA)

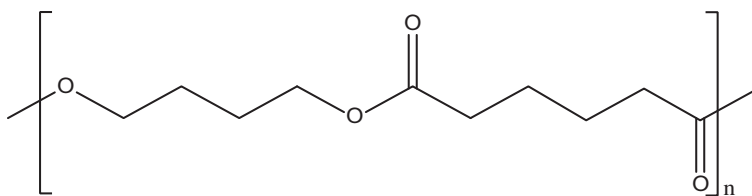
PBA is chemically synthesized through polycondensation of adipic acid or its lower alkyl ester with 1,4-butanediol in the presence of a polymerization catalyst such as a titanium compound (**JPS63251424 A**, 1988, UNITIKA LTD; **JPH08301996 A**, 1996, KANEBO LTD; **JP2001098065 A**, 2001, MITSUBISHI CHEM CORP) (see Scheme 1.17).

Poly(butylene succinate adipate) (PBSA)

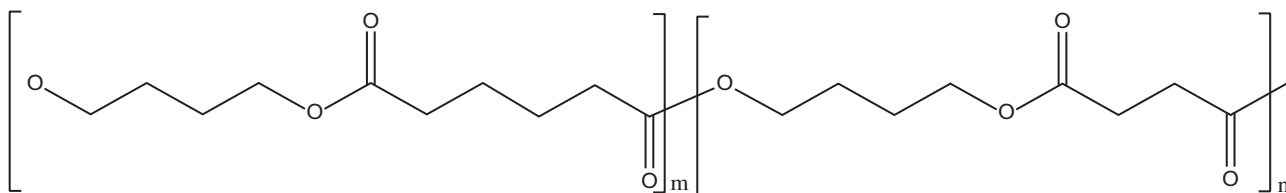
Poly(butylene succinate-co-butylene adipate) (PBSA) is a combination of 1,4-butanediol, succinic acid, and adipic acid [27] (see Scheme 1.18). PBSA is prepared by adding adipic acid to source materials during PBS synthesis. Although usually synthesized from fossil fuel, it is also possible for the monomers that make up PBSA to be produced from bio-based feedstock. PBSA degrades faster than PBS. Furthermore, PBS and PBSA are known to biodegrade more slowly than PHAs. Of the two, PBS has higher crystallinity and is better suited for molding, while PBSA has lower crystallinity and is better suited to film applications. Both polymers have a low (sub-zero) T_g , and their processing temperatures overlap with PHAs.

Polyoxalates

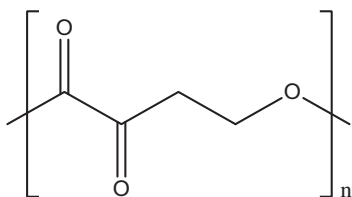
The synthesis of polyoxalate polymers was first reported by Carothers et al. [34]. They described the ester interchange reaction of diols, such as ethylene glycol, 1,3-propanediol, or 1,4-butanediol, with



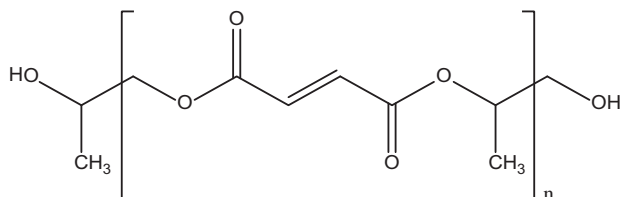
Scheme 1.17 Poly(butylene adipate) (PBA).



Scheme 1.18 Poly(butylene succinate adipate) (PBSA).



Scheme 1.19 Poly(ethylene oxalate) (PEOx).



Scheme 1.20 Poly(propylene fumarate) (PPF).

diethyl oxalate to yield a mixture of monomer, soluble polymer, and insoluble polymer. The reaction of oxalic acid and an alkylene glycol to form polyester resins is described in **US2111762 A** (1938, ELLIS FOSTER CO), while methods for the preparation of polyoxalates of fiber-forming quality, and the formation of sutures from filaments made of polyoxalates are described in **US4141087 A** (1979) and **GB1590261 A** (1981, ETHIKON INC).

The synthesis of a poly(ethylene oxalate) (PEOx) (see [Scheme 1.19](#)) is also described in **WO 2008038648 A1** (2008, TOYO SEIKAN KAISHA LTD) (see Chapter 7: Degradability on Demand; Section 7.3.7: Blending with other Polymers).

Poly(propylene fumarate) (PPF)

Poly(propylene fumarate) (PPF) is a biodegradable unsaturated linear polyester that is typically synthesized via transesterification (see [Scheme 1.20](#)). The fumarate double bonds in PPF can be cross-linked at low temperatures to form polymer networks. The high mechanical strength of cross-linked PPF matrices and their ability to be cross-linked *in situ* make them especially suitable for orthopedic applications. PPF degrades in the presence of water into propylene glycol and fumaric acid, degradation products that are easily cleared from the human body by normal metabolic processes.

Representative synthetic methods and applications for PPF are described in **WO0062630 A1** (2000, UNIV WM MARSH RICE) and **WO9529710 A1** (1995, RICE UNIVERSITY) and **US2004023028 A1** (2004, MAYO FOUNDATION).

1.3.2.2 Aliphatic-aromatic copolyesters

Aliphatic-aromatic polyesters are obtained by condensing aliphatic diols, aliphatic dicarboxylic acids, and aromatic dicarboxylic acids/esters. The aliphatic-aromatic copolyesters are synthetically polymerized and therefore are not generally renewable. Some well known biodegradable aliphatic-aromatic copolyesters are poly(butylene succinate-*co*-terephthalate) (PBST) and, poly(butylene adipate-*co*-terephthalate) (PBAT). Various representative industrial methods for producing aliphatic-aromatic copolyesters are described in **US5171308 A** (1992, DU PONT), **WO9514740 A1** (1995, DU PONT), **WO9625446 A1** (1996, BASF AG), **EP1108737 A2** (2001, IRE CHEMICAL LTD), and **EP1106640 A2** (2001, IRE CHEMICAL LTD). Examples of commercially available aliphatic-aromatic polyesters are shown in [Table 1.7](#).

1.3.2.3 Aromatic polyesters (bio-based)

Bio-based aromatic polyesters are capable of reducing the use of fossil fuel resources and the accompanying increase in carbon dioxide, but they are not biodegradable. Examples of commercially available bio-based aromatic polyester are shown in [Table 1.8](#).

Poly(ethylene terephthalate) (PET) (bio-based)

Bio-based poly(ethylene terephthalate) (PET) is made from ethylene glycol and terephthalic acid or its ester-forming derivative, wherein at least one of the diol component or terephthalate component is derived from at least one bio-based material (see [Scheme 1.21](#)).

WO2009120457 A2 (2009, COCA COLA CO) and **US2010028512 A1** (2010, COCA COLA CO) disclose such a bio-based PET. This bio-based PET is comprised of about 25 to about 75 wt.% of a terephthalate component and about 20 to about 50 wt.% of a diol component, wherein at least 1 wt.% (preferably 10 wt.%) of the diol component and/or terephthalate component are derived from at least one bio-based material (e.g., corn and potato). The bio-based PET is useful for making bio-based containers for packaging food products, soft drinks, alcoholic beverages, detergents, cosmetics, pharmaceutical products, and edible oils.

Coca-Cola's current renewable bottle, named PlantBottle™, is made by converting sugarcane into ethylene glycol, which represents 30 wt.% of the total

Table 1.7 Aliphatic-aromatic (co)polyesters

Biopolymer	Commercial name	Manufacturer	Applications
PBAT	EnPol [®] G8000 Series: EnPol [®] G8002; EnPol [®] G8060; EnPol [®] G8060F (G8060 & biomass)	IRE Chemical Ltd. (KR)	Enpol [®] G8060: packaging films, plastic bags, PLA modifier; EnPol [®] G8060F: high quality films
PBAT	Skygreen [™] SG300	SK Chemicals (KR)	Extrusion, film, sheet
PBAT	FEPOL [®] 1000 series FEPOL [®] 2000 series: FEPOL [®] 2024	Far Eastern New Century Co. (TW)	Packaging films, agricultural films and compost bags
PBAT	Ecoflex [®] series: Ecoflex [®] F 1200; Ecoflex [®] F BX 7011	BASF (DE)	Packaging films, agricultural films, compost bags, coated applications
PBAT	Origo-Bi [®] (ex Eastar Bio ^{™1})	Novamont (IT)	Plastic bags, plastic sacks, plastic envelopes
PBST	Biomax [®] (modified PET)	DuPont (USA)	Fast food disposable packaging, yard-waste bags, diaper backing, agricultural films, flowerpots, bottles
PEST	Green Ecopet (recycled PET fiber/resin)	Teijin (JP)	Fibers

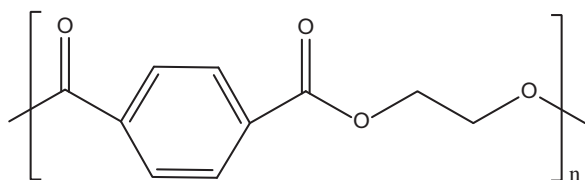
Abbreviations: PBAT, Poly(butylene adipate-co-terephthalate); PBST, Poly(butylene succinate-co-terephthalate); PEST, Poly(ethylene succinate-co-terephthalate).

¹The Eastman Chemical's Eastar Bio technology was bought in 2004 by Novamont.

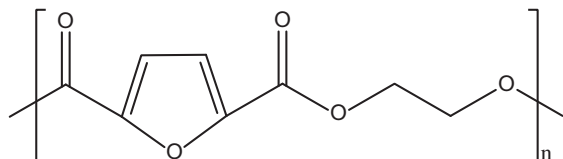
Table 1.8 Aromatic polyesters

Biopolymer	Commercial name	Manufacturer	Applications
PET bio-based	Up to 30% bio-based PET (PlantBottle [™])	Coca-Cola Co. (USA)	Containers for packaging food products, soft drinks, alcoholic beverages, detergents, cosmetics, pharmaceutical products and edible oils
PTT	Sorona [®]	DuPont (USA)	Fibers, multifilament surgical devices (suture, mesh, sternal closure device, cable and tape)
PTT	Biomax [®] PTT 1100 Biomax [®] PTT 1002	DuPont (USA)	Biomax [®] PTT 1002: packaging and industrial applications; Biomax [®] PTT 1100: injection-molded containers, cosmetic packaging and other parts where polyesters are used

Abbreviations: PET (bio-based), Poly(ethylene terephthalate); PTT, Poly(trimethylene terephthalate).

**Scheme 1.21** Poly(ethylene terephthalate) (PET).

composition of PET [35]. Deriving terephthalic acid from nature has been much more difficult. In November 2011, Japanese industrial group Toray announced that it had produced the world's first "fully renewable" bio-based PET fiber with terephthalic acid made from *p*-xylene derived from biomass via isobutanol from Gevo (USA) [36]. Gevo's yeast-based fermentation



Scheme 1.22 Poly(ethylene furanoate) (PEF).

process converts cornstarch-derived sugar into isobutanol, which after subsequent chemical reactions is transformed into a stream of aromatics containing more than 90% *p*-xylene. Its technology is easily retrofitted into existing ethanol plants.

JP2011219736 A (2011, TORAY IND INC) discloses a bio-based poly(alkylene terephthalate) obtained by using as raw materials biomass resource-derived glycol and biomass resource-derived terephthalic acid and/or its ester-forming derivative. A phosphorus compound was also included.

Poly(ethylene furanoate) (PEF)

Poly(ethylene furanoate) (PEF) is made from ethylene glycol and 2,5-furan dicarboxylic acid (FDCA) (see [Scheme 1.22](#)). Avantium (NL) developed a process using catalytic reactions to create FDCA, which reacts with ethylene glycol to make PEF. PEF is a bio-based alternative to PET; the main component of PET is terephthalic acid, which could be replaced by bio-based FDCA. According to Avantium, PEF exceeds PET in terms of oxygen barrier and temperature performance.

Even though the PEF production process is still under development, it has been estimated that the complete substitution of PET by PEF is likely to offer savings of between 43 and 51% of fossil fuel, and a reduction of between 46 and 54% of CO₂ emissions for the system cradle-to-grave [37].

Poly(trimethylene terephthalate) (PTT) (bio-based)

Poly(trimethylene terephthalate) or poly(propylene terephthalate) (PPT) belongs to the group of linear aromatic polyesters next to poly(ethylene terephthalate) and poly(butylene terephthalate) (PBT) with three methylene groups in the glycol repeating units (see [Scheme 1.23](#)). The odd number of methylene units affects the physical and chemical structure of PTT,

which results in several excellent properties such as high elastic recovery and dyeing ability [38]. Initially PTT was intended for the carpeting market, but due to its processability, like spinning and dyeing properties, it turned out to be more suitable for the fiber market in the fields of sportswear and active wear [38,39].

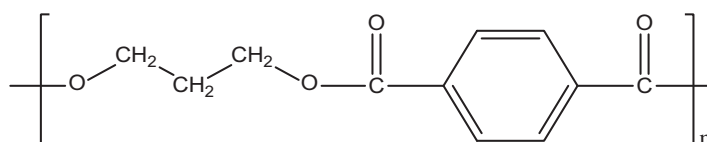
PTT is made by polycondensation of 1,3-propanediol and either terephthalic acid or dimethyl terephthalate. This polymer has attracted attention in recent years after the development of production of 1,3-propanediol from starch-derived glucose, a renewable resource (**WO0112833 A2**, 2001, DU PONT). As disclosed in **WO0111070 A2** (2001, DU PONT) and **US6428767 B1** (2002, DU PONT; GENENCOR INT), bio-based 1,3-propanediol and polymers derived therefrom can be distinguished from their petrochemical-derived counterparts on the basis of ¹⁴C and dual carbon-isotopic fingerprinting.

Bio-based PTT is marketed by DuPont Company as Sorona[®] fibers, and the polymer is additionally used in many other end-use applications for films, filaments, and engineering plastics. DuPont's Sorona[®] EP thermoplastic polymers contain between 20 and 37% renewably sourced material (by weight) derived from corn sugar 1,3-propanediol. The new material exhibits performance and molding characteristics similar to high-performance PBT.

DuPont Packaging & Industrial Polymers introduced Biomax[®] PTT, which contains up to 35% renewably sourced content for packaging applications, where chemical resistance and durability are essential features. Biomax[®] PTT 1100 is an unfilled resin especially suitable for use in injection-molded containers, cosmetic packaging, and other parts where polyesters are used.

1.4 Poly(ether-ester)s

Poly(ether-ester)s are generally prepared by a two-stage melt transesterification process from readily available starting materials such as dimethyl terephthalate, an alkane diol, and a poly(alkylene glycol)



Scheme 1.23 Poly(trimethylene terephthalate) (PTT).

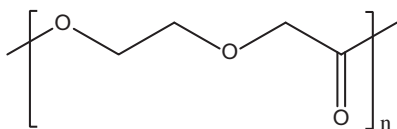
ether). The resulting poly(ether-ester)s consist of sequences of crystallizable alkylene terephthalate sequences (hard segments) and elastomeric poly(alkylene oxide) sequences (soft segments). These materials show a wide range of properties depending upon the content of alkylene terephthalate segments and the length of poly(alkylene oxide) [40–42]. Several commercially available block poly(ether-ester)s based on PBT and poly(tetramethylene oxide) are known, such as Hytrel[®] RS (DuPont) and Arnitel[®] Eco (DSM). These materials combine many interesting properties, including a high temperature T_m , a low T_g , high yield stress, elongation at break, and elasticity. They are also easy to process [42]. According to DuPont, Hytrel[®] RS thermoplastic elastomers have many applications, including hoses and tubing for automotive and industrial uses, boots for CV joints, air bag doors, and energy dampers. According to DSM, Arnitel[®] Eco is suitable for applications in consumer electronics, sports and leisure, automotive interiors and exteriors, furniture, alternative energy, and specialty packaging. The material is designed for a long service lifetime under extreme conditions.

Polydioxanone (PDO or PDS)

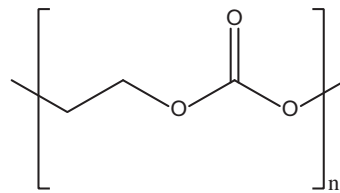
Referred to as poly(oxyethylene glycoate) and poly(ether-ester), the ring-opening polymerization of *p*-dioxanone results in a synthetic suture known as PDS or polydioxanone (US4490326 A, 1984, ETHICON INC) (see Scheme 1.24). The polymer is processed at the lowest possible temperature to prevent depolymerization back to monomer. The monofilament loses 50% of its initial breaking strength after three weeks and is absorbed within six months, providing an advantage over other products for slow-healing wounds. A commercial product of poly(*p*-dioxanone) is PDS[™] Plus Antibacterial Suture from Ethicon, Inc., which is a monofilament synthetic absorbable suture.

1.5 Aliphatic Polycarbonates

The synthesis of high molecular weight poly(alkylene carbonate)s was first reported by Inoue



Scheme 1.24 Polydioxanone (PDO).



Scheme 1.25 Poly(ethylene carbonate) (PEC).

et al. in the late 1960s [43]. These rather new polymers are derived from carbon dioxide and are produced through the copolymerization of CO₂ with one or more epoxy compounds (ethylene oxide or propylene oxide). They can contain up to 50% CO₂ or CO by mass and sequester this harmful greenhouse gas permanently from the environment.

Poly(ethylene carbonate) (PEC)

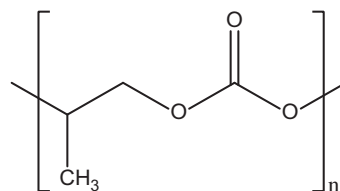
Poly(ethylene carbonate) (PEC) is the product of alternating copolymerization of ethylene oxide and carbon dioxide (see Scheme 1.25). PEC is a biodegradable amorphous polymer with a T_g of 15–25°C, and it exhibits elastomeric characteristics at ambient temperature. Extruded films of PEC have high oxygen barrier properties that make it useful as a barrier layer for food packaging applications. PEC has also been found to decompose cleanly at lower temperatures, both in nitrogen and in air, than most other commercial polymers.

Empower Materials Inc. commercializes QPAC[®] 25, a PEC, which is used as binder or sacrificial material.

Novomer also commercializes PEC in two application markets: as a traditional polymer for packaging, and as a clean-burning sacrificial material for high-end processing, including ceramic and electronic processing.

Poly(propylene carbonate) (PPC)

Poly(propylene carbonate) (PPC) is the product of alternating copolymerization of ethylene oxide and carbon dioxide (see Scheme 1.26). Until recently, high molecular weight PPC has been predominantly synthesized using zinc carboxylate catalysts to copolymerize propylene oxide and carbon dioxide.



Scheme 1.26 Poly(propylene carbonate) (PPC).

The resulting material was the focus of intense investigation, and several companies have explored applications for the material as a commodity thermoplastic. To date, PPC has been commercialized only as a sacrificial polymer in applications where the clean thermal decomposition of PPC is advantageous. Commercialization of the material for thermoplastic applications has been complicated by poor thermal and processing properties. Recently, transition metal complexes have been developed for the copolymerization of carbon dioxide and epoxides, but such complexes have not been fully exploited and/or optimized in the preparation of improved PPC materials. PPC has good properties such as compatibility and impact resistance. Its thermal stability and biodegradation need to be improved. A classical way to do this is to blend it with other polymers [44].

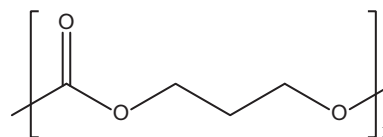
Empower Materials Inc. commercializes QPAC[®]40, a PPC, which like QPAC[®]25 is used in binder and sacrificial structure applications.

In addition to PEC and PPC, Empower Materials Inc. synthesized multiple other QPAC[®] polymers on a pilot scale including: QPAC[®]60 (polybutylene carbonate, PBC), QPAC[®]100 (polypropylene carbonate/polycyclohexene carbonate, PBC/PCHC), and QPAC[®]130 (polycyclohexene carbonate, PCHC).

Novomer (USA) and SK Energy Co., Ltd. (SK) are also commercializing PPC. SK is creating its 44% CO₂-based Greenpol[™] PPC using a proprietary catalyst and a continuous polymerization process. PPC has potential uses for packaging materials, competing with commodity polymers such as polyolefins.

Novomer is working with Eastman Kodak to develop PPC for packaging applications. Novomer plans on making enough PPC resins and films that potential customers can test them in packaging applications. Novomer targets its first PPC product, NB-180, as a temporary binder for electronics. Because it breaks down into carbon dioxide and water when exposed to high temperatures, it can be burned off without a trace. Both NB-180 and the new PPC polymer are made by polymerizing propylene oxide with carbon dioxide using a proprietary catalyst. As a packaging polymer, PPC is touted as offering unique impact resistance, stiffness, and oxygen barrier properties.

WO2011005664 A2 (2011, NOVOMER INC) discloses PPC films as parts of a multilayer film. In certain embodiments, PPC acts as a tie layer in a laminate film. In some embodiments, a PPC composition provides a structural layer in a multilayer



Scheme 1.27 Poly(trimethylene carbonate) (PTMC).

film. In certain other embodiments, the films comprise a PPC composition in combination with one or more other degradable polymers such as PLA, PHB, poly(3-hydroxypropionate (P3HP or PHP), starch, or modified cellulose. In still other embodiments, the layer containing the PPC composition acts as a barrier layer to retard the transmission of oxygen, water vapor, carbon dioxide, or organic molecules.

Poly(trimethylene carbonate) (PTMC)

Poly(trimethylene carbonate) (PTMC) is a biodegradable polycarbonate with rubber-like properties. PTMC is obtained by ring-opening polymerization of trimethylene carbonate (TMC) and catalyzed with diethyl zinc [1] (see Scheme 1.27). A high molecular weight flexible polymer was prepared, but displays poor mechanical performance [45]. Due to this property, its applications are limited and copolymers are more often used. Copolymers with glycolide and dioxanone have also been prepared [9].

Mitsubishi Gas Chemical Co. has marketed a copolyester carbonate, namely poly[oligo(tetramethylene succinate)-*co*-(tetramethylene carbonate)] (PTeMS/PTeMC). The copolyester carbonate is composed of a polyester part and a polycarbonate part. The carbonate content inside the copolymer is variable. The melting point of the copolymer is about 100–110°C. Introducing poly(tetramethylene carbonate) (PTeMC) into poly(tetramethylene succinate) (PTMS) probably causes disorder in the crystal structure, thus lowering its melting point and increasing its susceptibility to enzymatic and microbial attacks [1]. The microbial degradability of the copolyester carbonate was confirmed to be higher than that of both of its constituents [46].

1.6 Polyamides

Polyamides are polymers with amide groups (R-CO-NH-R') as integral parts of the main polymer chain. Bio-polyamides are basically formed from polycondensation of the following: (1) diamines and dicarboxylic acids; (2) ω -amino carboxylic acids as bi-functional monomers; and (3) α -amino carboxylic acids as bi-functional monomers [47]. Bio-polyamides

include both bio-based polyamides and biodegradable fossil fuel-based polyamides. The commercially available bio-polyamides are shown in Table 1.9.

1.6.1 Polycondensation of Diamines and Dicarboxylic Acids

Dicarboxylic acids can be derived from renewable resources such as castor oil. Diamines are mainly derived from fossil fuel [47]. Commercial bio-polyamides produced by the polycondensation of diamines and dicarboxylic acids include polyamide 1010 (PA 1010), polyamide 410 (PA 410), polyamide 610 (PA 610), and polyphthalamides (PPA).

1.6.2 Polycondensation of ω -Amino Carboxylic Acids or Lactams

An example of a bio-polyamide produced by the ring-opening polymerization of ϵ -caprolactam is polyamide 11 (PA 11).

1.6.3 Poly(α -amino acid)s

Synthetic polymers of α -amino acids contain peptide bonds in the main chain and can be composed of the same structural units (α -amino acids) as poly(amino acids) of natural origin, such as polypeptides and proteins. In this regard they may be considered as being protein analogues. Two amino acid homopolymers comprising a single type of amino acid are known in nature [48]: poly(γ -glutamic acid) (γ -PGA) and ϵ -poly(L-lysine) (ϵ -PL).

Poly(α -amino acids) are mainly used to create high-purity materials needed for biomedical applications. To date, commercial applications of protein polymers, such as poly(D-lysine) and poly(L-lysine), are limited to use as adhesives/substrates for cell culture. Copolymers of α -amino acids (such as serine) with other biodegradable polymers (such as PLA) are synthesized as drug delivery systems (WO9828357 A1, 1998, CONNAUGHT LAB). In addition to drug delivery and targeting, poly(amino acids) are being investigated for applications such as biodegradable sutures and artificial skins.

Three kinds of poly(amino acids) — poly(γ -glutamic acid), poly(α -aspartic acid) and ϵ -poly(L-lysine) — have attracted more attention because of their unique properties and various applications.

Poly(γ -glutamic acid) (γ -PGA)

Poly(γ -glutamic acid) (also known as polyglutamate and γ -PGA) is a water-soluble, anionic, biodegradable polyamide consisting of D- and L-glutamic acid monomers connected by amide linkages between α -amino and γ -carboxyl groups (see Scheme 1.28). γ -PGA is synthesized by several bacteria and its molecular weight can vary anywhere from 20,000 to over 2 million Da depending on the method of production. A major advantage of using γ -PGA is its low cost and relative abundance [49,50]. γ -PGA has several environmental/industrial, agricultural, food, and pharmaceutical applications. One environmental application of γ -PGA is its use as a flocculent. Another newer environmental application of γ -PGA is in removing heavy metal contaminants, such as those used by the plating industry. γ -PGA has a very large anionic charge density. Contaminants such as copper, lead, mercury and other positively charged metal ions associate very strongly with γ -PGA, and can then be concentrated and removed from the waste stream.

Since γ -PGA is comprised of an amino acid, it is an excellent source of nitrogen. This suggests an application in agriculture as a fertilizer. For analogous reasons it is good for drug delivery. A polymer mixture can be packed with nutrients for a particular crop. Once the fertilizer is applied, it has a longer residence time in the soil since the fertilizer nutrients are protected from the natural environment by the γ -PGA.

In the food industry, work has been done that shows PGA functions as a cryoprotectant. γ -PGA has been shown to have antifreeze activity significantly higher than glucose, a common cryoprotectant. In the medical field, PGA is being studied as a biological adhesive and a drug delivery system (US2005095679 A1, 2005, CRESCENT INNOVATIONS INC).

PGA is degraded by a class of extracellular enzymes called γ -glutamyl hydrolases, and as a polyamide is more resistant than synthetic polyesters to random chain hydrolysis. In biological systems γ -PGA undergoes enzymatic degradation from the surface, rather than bulk hydrolysis. Thus, γ -PGA provides benefits for use as a scaffold material because it prevents rapid deterioration in scaffold strength. In addition, due to the presence of the carboxyl group ($-\text{COOH}$) on the side chain, γ -PGA exhibits unique advantages over other materials in terms of scaffold applications (WO2012004402 A1, 2012, IMP INNOVATIONS LTD).

Table 1.9 Commercially available bio-polyamides

Biopolymer	Commercial name	Manufacturer	Applications
PA 11	Rilsan®	Arkema (FR)	Electrical cables, automotive, pneumatic and hydraulic hose
PA	Rilsan® Clear G830 Rnew	Arkema (FR)	Molding applications, ideally suited for optics as high end eyewear frames
Co-PA	Platamid® Rnew	Arkema (FR)	Hot melt adhesive
PA 1010	Grilamid 1S	EMS-GRIVORY (DE)	Reinforced Grilamid 1S: manufacture of stiff covers; Non-reinforced, amorphous grades: injection-molding processes for overmolding metal sheets
PA 1010	VESTAMID® Terra DS	Evonik (DE)	Injection molding, fibers, powder, extrusion, and films
PA 1010	Zytel® RS LC1000 BK385 Zytel® RS LC1200 BK385 Zytel® RS LC1600 BK385	DuPont (USA)	Multiple extrusion applications
PA 1010	Hiprolon® 200 series	Suzhou Hipro Polymers (CN)	Gear, electronics housing parts, rigid technical tubing, technical film, powder coating
PA 1012	VESTAMID® Terra DD	Evonik (DE)	Injection molding, fibers, powder, extrusion, and films
PA 1012	Hiprolon® 400 series	Suzhou Hipro Polymers (CN)	Automotive tubing systems, oil and gas pipe, technical decorative films
PA 410	EcoPaXX™	DSM (NL)	Automotive and electrical applications: engine cover, cooling circuit components, sensors
PA 610	VESTAMID® Terra HS	Evonik (DE)	Injection molding, fibers, powder, extrusion, and films
PA 610	Grilamid® 2S	EMS-GRIVORY (DE)	Injection molding, extrusion (tubes for automotive industry)
PA (amorphous)	Grilamid® BTR	EMS-GRIVORY (DE)	Used to make windows
PA 610	Ultramid® S Balance	BASF (DE)	Overmolding metal and electronic components, plug-in connectors, pipes and reservoirs in cooling circuits
PA 610	Zytel® RS LS3030 NC010 Zytel® RS LC3060 NC010 Zytel® RS LC3090 NC010	DuPont (USA)	Zytel® RS LS3030 NC010: injection applications; Zytel® RS LC3060 NC010: injection and extrusion applications; Zytel® RS LC3090 NC010: extrusion applications

Table 1.9 Commercially available bio-polyamides (*Continued*)

Biopolymer	Commercial name	Manufacturer	Applications
PA 610	Hiprolon® 70 series	Suzhou Hipro Polymers (CN)	Monofilament, industrial parts with high heat resistance and extrusion tubing product
PA 612	Hiprolon® 90 series	Suzhou Hipro Polymers (CN)	Monofilament and other industrial parts with different compounding process
Longchain PA	Hiprolon® 11	Suzhou Hipro Polymers (CN)	Auto fuel lines, air brake tubing, cable sheathing
Long-chain PA	Hiprolon® 211	Suzhou Hipro Polymers (CN)	Auto fuel lines, air brake tubing, cable sheathing
PPA	Rilsan® HT	Arkema (FR)	Flexible tubing, injection molding
PPA	Grivory HT3	EMS-GRIVORY (DE)	Electronic connector applications
PPA	VESTAMID® HT plus	Evonik (DE)	Material for housings of pumps and filter systems or for use in vehicles in the vicinity of the engine, as in the charge air duct

PA 1010: Polyamide 1010; produced from 1,10-decamethylene diamine (castor oil derivative) and sebacic acid (both derived from castor oil).

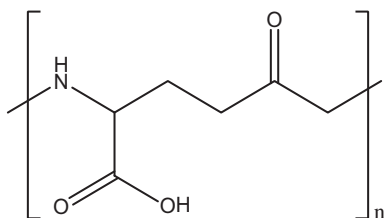
PA 11: Polyamide 11; produced from 11-aminodecanoic acid (derived from castor oil).

PA 1012: Polyamide 1012; produced from 1,10-decamethylene diamine and 1,12-dodecanedioic acid (both derived from plant oil, e.g., palm kernel oil).

PA 410: Polyamide 410; produced from tetramethylene diamine and sebacic acid (derived from castor oil).

PA 610: Polyamide 610; produced from hexamethylene diamine and sebacic acid (derived from castor oil).

PPA: Polyphthalamide; produced from decamethylene diamine, terephthalic acid and amino acid.

**Scheme 1.28** Poly(γ-glutamic acid).

US2005095679 A1 (2005, CRESCENT INNOVATIONS INC) discloses a method for producing high molecular weight γ-PGA via the fermentation of a nonpathogenic organism, which may include *Bacillus subtilis*, or recombinant *E. coli*, though *Bacillus licheniformis* ATCC 9945a is preferred. This PGA may be isolated and purified via a series of membrane filtration steps and/or pH adjustment and centrifugation. Inclusion of all steps results in a medical grade product capable of being used *in vivo* without any immune response from the body. If lower levels of purity are required, they may be achieved by selectively eliminating various purification steps. Purification is accomplished by buffer exchange via

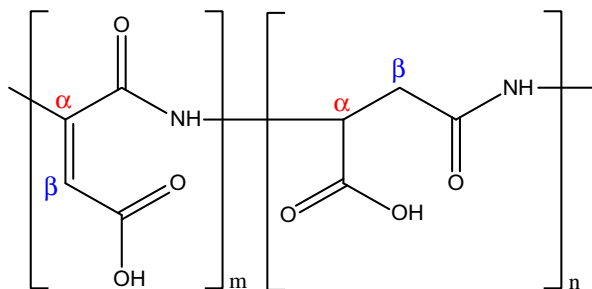
diafiltration using a filter with a molecular weight cutoff of less than about 100 kDa, and preferably at least about 30 kDa. Typically, in order to produce agricultural-grade PGA, viable cells are removed by filtration at about 0.22 μm. For a food-grade product, this would be followed by filtration at about 0.1 μm, which clarifies the product. Any medical use requires the diafiltration steps.

US4450150 A (1984, LITTLE INC A) and **FR2786098 A1** (2000, FLAMEL TECH SA) disclose copolymers of polyglutamic acid and polyglutamate that are pharmaceutically acceptable matrices for drugs or other active substances wherein the copolymer controls the rate of drug release.

Poly(α-aspartic acid)

Poly(α-aspartic acid) (also called polyaspartate) is a biodegradable polyamide synthesized from L-aspartic acid, a natural amino acid (see [Scheme 1.29](#)). Poly(α-aspartic acid) has similar properties to the polyacrylate, and so it is used as an antifouling agent, dispersant, antiscalant, or superabsorber.

US5315010 A (1994, DONLAR CORP) discloses a method for producing poly(α-aspartic acid) by



Scheme 1.29 Thermal poly(α,β -D,L-aspartate).

hydrolysis of polysuccinimide (anhydropolyaspartic acid). The polysuccinimide is produced by thermal condensation polymerization of L-aspartic acid comprising the following steps:

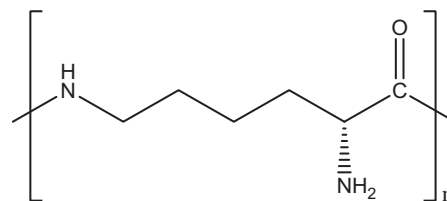
- (1) Heat powdered L-aspartic acid to at least 188°C (350°F) to initiate the condensation reaction and produce a reaction mixture.
- (2) Raise the reaction mixture temperature to at least 232°C (450°F).
- (3) Maintain at least the 232°C (450°F) temperature for the reaction mixture until at least 80% conversion has occurred.

NanoChem, which bought the Donlar assets, produces polyaspartates for industrial and consumer applications. NanoChem polyaspartates have a wide range of molecular weights:

Low molecular weight polyaspartates A-2C, A-3C, and A-5D have applications as general-purpose antiscalants in hard water environments, corrosion inhibitors, dispersants for mineral slurries, and for control of redeposition of soil in laundry and hard surface cleaners.

High molecular weight polyaspartates C-5D and C-10D have applications as general-purpose dispersants, for clay-soil removal, for inorganic scale removal, as antiscalants in hard water environments, as mineral slurry dispersants, and for control of redeposition of soil in laundry and hard surface cleaner applications.

Low color polyaspartates C-LC, C-LC/SD and C-LC/GC have applications as general-purpose antiscalants in hard water environments, dispersants for mineral slurries, and for control of redeposition of soil in laundry and hard surface cleaners. Because of their low color, these polymers are specifically designed for applications where color affects the end use.



Scheme 1.30 ϵ -Poly(L-lysine) (ϵ -PL).

ϵ -Poly(L-lysine) (ϵ -PL)

ϵ -Poly(L-lysine) (ϵ -PL) is a biodegradable, water-soluble, natural homopolymer of the essential amino acid L-lysine that is produced by bacterial fermentation (see [Scheme 1.30](#)). ϵ -PL consists of 25 to 35 L-lysine residues with linkages between α -carboxyl groups and ϵ -amino groups produced by *Streptomyces albulus*; they have highly selective antimicrobial activity. This biopolymer is widely used as a food additive. It has also been used for preparation of biodegradable hydrogels by γ -irradiation of microbial ϵ -poly(L-lysine) aqueous solutions [51].

Ajinomoto and Toray have entered into an agreement to begin joint research for manufacturing the nylon raw material 1,5-pentanediamine (1,5-PD) from the amino acid lysine produced from plant materials by Ajinomoto using fermentation technology. The goal is to commercialize a bio-based nylon made from this substance. The bio-based nylon that Ajinomoto and Toray will research and develop is produced from plant materials by decarbonating the amino acid lysine through an enzyme reaction to make 1,5-PD, which Toray then polymerizes with dicarboxylic acid. This bio-based nylon fiber made from 1,5-PD is not only sustainable because it is plant-based, but also shows promise for development into highly comfortable clothing. For example, PA 56 (nylon 56) fiber manufactured using 1,5-PD is pleasing to the touch, yet has the same strength and heat resistance as conventional nylon fiber made from the petrochemical derivative hexamethylenediamine. It also absorbs and desorbs moisture nearly as well as cotton [52].

1.7 Poly(ester amide)s

Poly(ester amide)s constitute a promising family of biodegradable materials since they combine a degradable character, afforded by the easily hydrolyzable ester groups ($-\text{COO}-$), with relatively good thermal and mechanical properties given by the

strong intermolecular hydrogen bonding interactions that can be established between their amide groups ($-\text{NHCO}-$) [53].

Poly(ester amide)s which can be easily produced and are also completely biodegradable are known from **DE4327024 A1** (1995, BAYER AG). In 1995 Bayer AG introduced a series of biodegradable poly(ester amide)s for film and molding applications under the name BAK[®]. In 2001 Bayer stopped the production of BAK[®]. Bayer's poly(ester amide)s are based on the following combinations of monomers: (a) adipic acid, 1,4-butanediol, and ϵ -caprolactam; and (b) adipic acid, 1,4-butanediol, diethylene glycol, and hexamethylene diamine. The various commercial products which result from the combination of monomers (a) are based on polyamide 6 and named BAK[®] 404, BAK[®] 401, and BAK[®] 1095. The products which result from the combination of monomers (b) are based on polyamide 6,6 and named BAK[®] 402 and BAK 2195[®] [54] (DE19754418 A1, 1999, BAYER AG).

Hyperbranched poly(ester amide)s are produced on an industrial scale and commercialized by DSM (Hybrane[®]). These poly(ester amide)s are intrinsically biodegradable and synthesized from cyclic anhydride (e.g., succinic anhydride) and a diisopropanol amine. Hyperbranched poly(ester amide)s are used as performance additives in many applications, such as oil field chemicals, demulsifiers, drug carriers, paper coatings, etc.

1.8 Poly(ether amide)s

Poly(ether amide)s are thermoplastic elastomers (TPEs) that can be processed by injection molding and profile or film extrusion. A commercially available product from poly(ether amide)s is the Pebax[®] series (Arkema). Pebax[®] is a range of plasticizer-free poly(ether-*b*-amide)s. Pebax[®] Rnew is a thermoplastic elastomer from renewable sources (up to 90% derived from castor), made up of block copolymers consisting of a sequence of polyamide 11 (PA 11) and polyether segments.

1.9 Polyurethanes (Bio-Based PUs)

The term “polyurethane” includes all polymers incorporating more than one urethane group

($-\text{NH-CO-O}-$) in the polymer backbone. Polyurethanes are commonly formed by the polyaddition reaction of a polyisocyanate such as a diisocyanate with a polyol such as a diol; this results in the formation of linear, branched, or cross-linked polymers. Other low molecular weight reagents such as chain extenders or cross-linking agents may be added during the polyaddition process.

Two popular polyol components used as raw materials for bio-based polyurethanes (PUs) are polyether and polyester polyols derived from natural resources. Polyether polyols are produced from sucrose, glucose, fructose, and glycerol. Polyester polyols are made from diacids and di- or tri-functional polyols. Suitable diacids include adipic acid, succinic acid, azelaic acid, and glutaric acid, etc. Suitable polyols include ethylene glycol, glycerol, 1,4-butanediol, 1,2-propanediol, 1,6-hexanediol, and 1,10-dodecanediol, etc. Most bio-based polyols used for bio-based PUs are synthesized from vegetable oils. Vegetable oils include castor, soy, sunflower, rapeseed, and linseed oils. Chain extenders that break down to compounds such as amino acids have been used for formulating biodegradable PUs. The commercially available polyols derived from renewable resources are summarized in Table 1.10.

The isocyanate component is not produced from renewable resources. Aliphatic polyisocyanates such as hexamethylene diisocyanate (HDI), butane diisocyanate (BDI), lysine diisocyanate ethyl ester, and lysine diisocyanate methyl ester are used for the production of bio-based PUs.

The poly(ester-urethane)s are more liable to biodegrade than the poly(ether-urethane)s. Polyester polyols such as polycaprolactone, polylactide, and polyglycolide are the most widely used polyols in biodegradable polyurethanes. In a thermoplastic elastomer polyurethane (TPS), the polyester polyol forms the “soft” segment of the polymer while the diisocyanate and the chain extender form the hard segment. The hard segment forms ordered domains due to hydrogen bonding and imparts high mechanical strength to the material. The soft domains are formed largely by the polyester polyol and provide elastic properties to the polymer. The biodegradation of these polymers occurs largely due to the hydrolytic degradation of the ester, urethane, and urea linkages of the polymer. The urethane or urea linkages in the hard segment degrade by hydrolysis at a significantly slower rate than ester linkages. Because of the relatively slow degradation rates of these linkages, compared with

Table 1.10 Commercially available polyols derived from natural resources for the production of bio-based polyurethanes (as reviewed by Desroches et al. [57])

Bio-based polyols	Commercial name	Manufacturer	Applications
Sorbitol	NEOSORB®	Roquette	Polyether PUs
Maltitol, sorbitol, isosorbide	POLYSORB®	Roquette	Polyether PUs
Polytrimethylene ether glycol	Cerenol™	DuPont	PU elastomers and fibers
Epoxidized soybean oil	JEFFADD™ B650	Huntsman	PU rigid foams, sprays, coatings, adhesives, mastics, elastomers
Epoxidized soybean oil	Agrol® Agrol® DIAMOND	BioBased Technologies	PUs
Epoxidized soybean oil	BiOH®	Cargill	PU flexible foams
Epoxidized vegetable oils	Sovermol®	Cognis, BASF	PU adhesives, binders, floor coatings, castings
Epoxidized vegetable oils (castor oil, linseed oil, soybean oil)	MERGINOL	HOBUM Oleochemicals	PU foams, coatings, dispersions
Epoxidized vegetable oils (sunflower, rapeseed, soybean)	RADIA® ¹ RADIA® 7291 RADIA® 7292 RADIA® 7293	Oleon (Sofiproteol)	RADIA® 7291 & 7292: flexible poly(ester urethane) foams; RADIA® 7293: rigid poly(ether urethane) foams
Epoxidized vegetable oils (soybean)	BAYDUR PUL 2500	Bayer	PU flexible and rigid foams
Functionalized of vegetable oils (soybean)	Renuva™ ²	Dow Chemicals Co.	PU flexible foams, coatings, adhesives, mastics, elastomers
Castor oil	Lupranol® BALANCE 50	BASF	Poly(ether urethane) rigid foams, mattress
Soybean oil	Soyol	Urethane Soy Systems	PU foams, sealing, coatings
Fatty acid dimers	Pripol™	Croda	
Castor oil		Mitsui Chemicals	

¹Ex Novenol of Novance.²Production of this polyol has stopped.

ester linkages, the polymer degradation may lead to oligomers containing mainly hard segments. The soft segment of the polyurethane degrades significantly faster than the hard segment as a result of the presence of relatively easily hydrolyzable ester linkages and the amorphous nature of the soft segment (WO2007033418 A1, 2007, POLYNOVO BIOMATERIALS PTY LTD; GUNATILLAKE P).

Numerous industrial methods for the production of polyols derived from renewable sources and the bio-based PUs prepared thereof are known from the

patent literature; see for example, **CA2541366 A** (2006) and **CA2568765 A1** (2007, BAYER MATERIALSCIENCE AG), **WO2007020904 A1** (2007, MITSUI CHEMICALS POLYURETHANES), **WO2009095363 A1** (2009, BASF SE), **JPH05148352 A** (1998, SHOWA HIGHPOLYMER CO LTD), **JPH0413710 A** (1992, REGURUSU KK) and **SU1016314 A1** (1983, INST FIZIOL IM I S BERITASHVIL).

PUs have a broad spectrum of types and properties (soft and flexible foams, coatings, elastomers, and

fibers) and are used in a wide range of applications. The market for bio-based PUs is small, and premium applications are being targeted. As one example, Metzeler Schaum currently produces bio-based PU flexible foam from a sunflower oil and/or rapeseed oil polyol, the Rubex[®] Nawaro flexible foam for the furniture and auto industry [55]. Biodegradable PUs are used as “shock absorber” materials in shoe soles and heels, and as a carpet backing (soy-derived PU). Biodegradable polyurethane applications can also be found in regenerative medicine. One example is the fabrication of porous scaffolds for use in soft-tissue engineering and cartilage repair [56]. Other medical applications include bone graft substitutes and wound dressings.

Merquinsa markets a range of bio-based poly(ester urethane)s and poly(ether urethane)s under the trade name PEARLTHANE[®] ECO polyurethanes. These have a bio-content between 20 and 90%, including special extrusion polyether TPU grades and non-yellowing aliphatic TPU resins.

A commercial product of a bio-based PU is DegraPol[®] (ab medica), which is a block poly(ester-urethane) consisting of a polyhydroxybutyrate-diol (hard segment) and a polycaprolactone-diol (soft segment) linked with trimethylhexamethylene diisocyanate (TMDI) units (7 wt.%). Using various ratios of hard and soft segments it is possible to modulate the mechanical properties of the final product. DegraPol[®] shows a broad range of elastic moduli, making it a potential new material for the regeneration of many types of biological tissues.

1.10 Polysaccharides

Cellulose

Cellulose is a complex polysaccharide which differs from starch in the glucosidic bond between the groups (steric configuration). Compared to starch it is more resistant to hydrolysis because of the stronger hydrogen bonds. See Table 1.11 for examples of commercially available cellulose and its derivatives.

Cellulose derivatives

Cellulosic derivatives are produced by chemical modification of cellulose. Cellulose derivatives of starch and proteins (e.g., gelatin or casein), however, display some disadvantages. For example, their considerable sensitivity to moisture, stemming from their propensity to strongly absorb water (hygroscopicity), increases with the addition of plasticizers.

Cellulose acetate (CA)

Cellulose acetate (CA) is the acetate ester of cellulose, and is made by reacting cellulose with acetic acid. CA is not itself a thermoplastic since the decomposition temperature is below the melt temperature, but it is possible to induce melt-processible properties through the addition of a plasticizer. It is used for a variety of products which include, among other things, textiles (e.g., linings, blouses, dresses, wedding and party attire, home furnishings, draperies, upholstery and slip covers), industrial products (e.g., cigarette and other filters for tobacco products, and ink reservoirs for fiber tip pens), high absorbency products (e.g., diapers and surgical products), photography film, and computer tape. As with many processes, the manufacturing results in some waste product which is not utilized in the final product, as well as considerable waste postconsumer (**US2010175691 A1**, 2010, CELANESE ACETATE LLC).

Cellulose acetate butyrate (CAB)

Cellulose acetate butyrate (CAB) is made by treating fibrous cellulose with butyric acid, butyric anhydride, acetic acid, and acetic anhydride in the presence of sulfuric acid. Typically it contains about 15% combined acetic and about 40% combined butyric acid.

Cellulose acetate propionate (CAP)

Cellulose acetate propionate (CAP) is made by treating fibrous cellulose with propionic acid (propionic acid), and acetic acid and anhydrides in the presence of sulfuric acid.

Cellulose nitrate (CN)

Cellulose nitrate (CN) is made by treating fibrous cellulosic materials with a mixture of nitric and sulfuric acids. Celluloid was a major cellulose nitrate, plasticized with camphor, but it is of little use today.

Starch

Starch is a low cost naturally occurring biopolymer. Since natural starch generally has a granular structure, it needs to be destructured before it can be melt processed. Commonly, starch is destructured by applying mechanical work under elevated temperatures in the presence of (added) water and other possible processing agents (e.g., plasticizers). Converting native starch to thermoplastic starch (TPS) is typically achieved through extrusion processes. **US4673438 A** (1987, WARNER LAMBERT CO) describes such methods for the conversion of native starch to TPS and subsequent

Table 1.11 Commercially available cellulose and its derivatives

Biopolymer	Commercial name	Manufacturer	Applications
CA CAB CAP	Tenite™ Acetate (7 grades) Tenite™ Butyrate (3 grades) Tenite™ Propionate (46 grades)	Eastman (USA)	CA: ophthalmic sheet, tool handles; CAB: automotive and furniture trims, displays and profiles, pen barrels, tool handles, toys and sporting goods; CAP: appliance parts, cosmetic and personal care containers, film and tubing for packaging, health care supplies, ophthalmic and optical care safety frames, toothbrush handles, sunglasses
CA	CA-320S NF/EP CA-320S CA-394-60S CA-398-10 CA-398-3 CA-398-30 CA-398-30L CA-398-6 CA-436-80S	Eastman (USA)	Osmotic drug delivery and taste- masking; coatings; molded and extruded articles; films, packaging, and paper and paperboard food contact applications; LCD displays, and photographic films
CAB	CAB-171-15 CAB-321-0.1 CAB-381-0.1 CAB-381-0.5 CAB-381-2 CAB-381-20 CAB-381-20B CAB-500-5 CAB-531-1	Eastman (USA)	Films, coatings, inks, nail care
CAP	CAP-482-0.5 CAP-482-20 CAP-504-0.2	Eastman (USA)	Printing inks and clear overprint varnishes, nail lacquer topcoats
CA (blends)	Biograde® Biograde® C 7500 C Biograde® C 7500 W Biograde® C 9550 Biograde® C 9555	FKuR (DE)	Injection molded parts such as writing utensils, disposable cutlery, cups, bottles
CAB	Cellidor® B 500-05 Cellidor® B 500-10 Cellidor® B 500-13 Cellidor® B 500-15 Cellidor® B 500-20 Cellidor® B 531-07 Cellidor® B 531-10 Cellidor® B 631-10 Cellidor® B 631-12	Albis Plastic (DE)	Optical goods, tools, writing materials, automotive construction

Table 1.11 Commercially available cellulose and its derivatives (*Continued*)

Biopolymer	Commercial name	Manufacturer	Applications
CAP	Cellidor® CP 2810-11 Cellidor® CP 300-10 Cellidor® CP 300-13 Cellidor® CP 300-15 Cellidor® CP 300-17 Cellidor® CP 300-20 Cellidor® CP 310-10	Albis Plastic (DE)	Optical goods, tools, writing materials, automotive construction
CA	Acetyloid® Acety®	Daicel Corporation (JP)	Optical films for LCDs, cigarette filters, acetate fiber, and photographic film; Acetyloid®: plastic sheet for glass frames; Acety®: pellet for tools (screwdriver), oil tanks etc.
CMC	CMC (23 grades)	Daicel Corporation (JP)	Thickener, dispersion stabilizer
HEC	HEC (13 grades)	Daicel Corporation (JP)	Dispersion stabilizer; general use and cosmetic applications
Cationic cellulose	JELLNER (2 grades)	Daicel Corporation (JP)	Haircare conditioner
Microfibrillated cellulose)	CELISH (11 grades)	Daicel Corporation (JP)	Binder of fibers and powders, paper strength enhancer in paper making, texture improver in foods, filtration agent for liquors, etc.
Ethylcellulose	Ethocel™	Dow Chemicals Co. (USA)	Protective coatings, as binders, flavor fixative
Sawdust & binder	Fasal® BIO 322 Fasal® BIO 337 Fasal® BIO 465	IFA (AT)	Injection molding applications
Sawdust starch & binder	Ecoplast	Groen Granulat (NL)	

Abbreviations: CA, Cellulose acetate; CAB, Cellulose acetate butyrate; CAP, Cellulose acetate propionate; CMC, Sodium (carboxymethyl cellulose); HEC, Hydroxyethyl cellulose.

injection molding processing. Suitable naturally occurring starches include cornstarch, potato starch, sweet potato starch, wheat starch, sago palm starch, tapioca starch, rice starch, soybean starch, arrow root starch, bracken starch, lotus starch, cassava starch, waxy maize starch, high amylose cornstarch, and commercial amylose powder. Blends of starch may also be used. Though all starches are useful herein, the most commonly used are natural starches derived from agricultural sources, which offer the advantages of being in abundant supply, easily replenishable, and inexpensive. Naturally occurring starches, particularly cornstarch, wheat starch, and waxy maize starch, are the starch polymers of choice due to their

economics and availability. Starch is frequently used in short use applications such as packaging, containers, and cultivation articles. Exemplary, commercially available starches are shown in [Table 1.12](#).

Lignin

Lignin is a complex polymer of phenylpropane units which are cross-linked to each other by a variety of chemical bonds (see [Scheme 1.31](#)). Lignin fills the spaces between the cell membranes of ligneous plants and turns them into wood, thereby producing a mixed body of pressure-resistant lignin and cellulose having good tensile strength. Depending on the type of wood, the phenyl groups of the lignin can be substituted by up to two methoxy groups and the

Table 1.12 Commercially available starch-based products

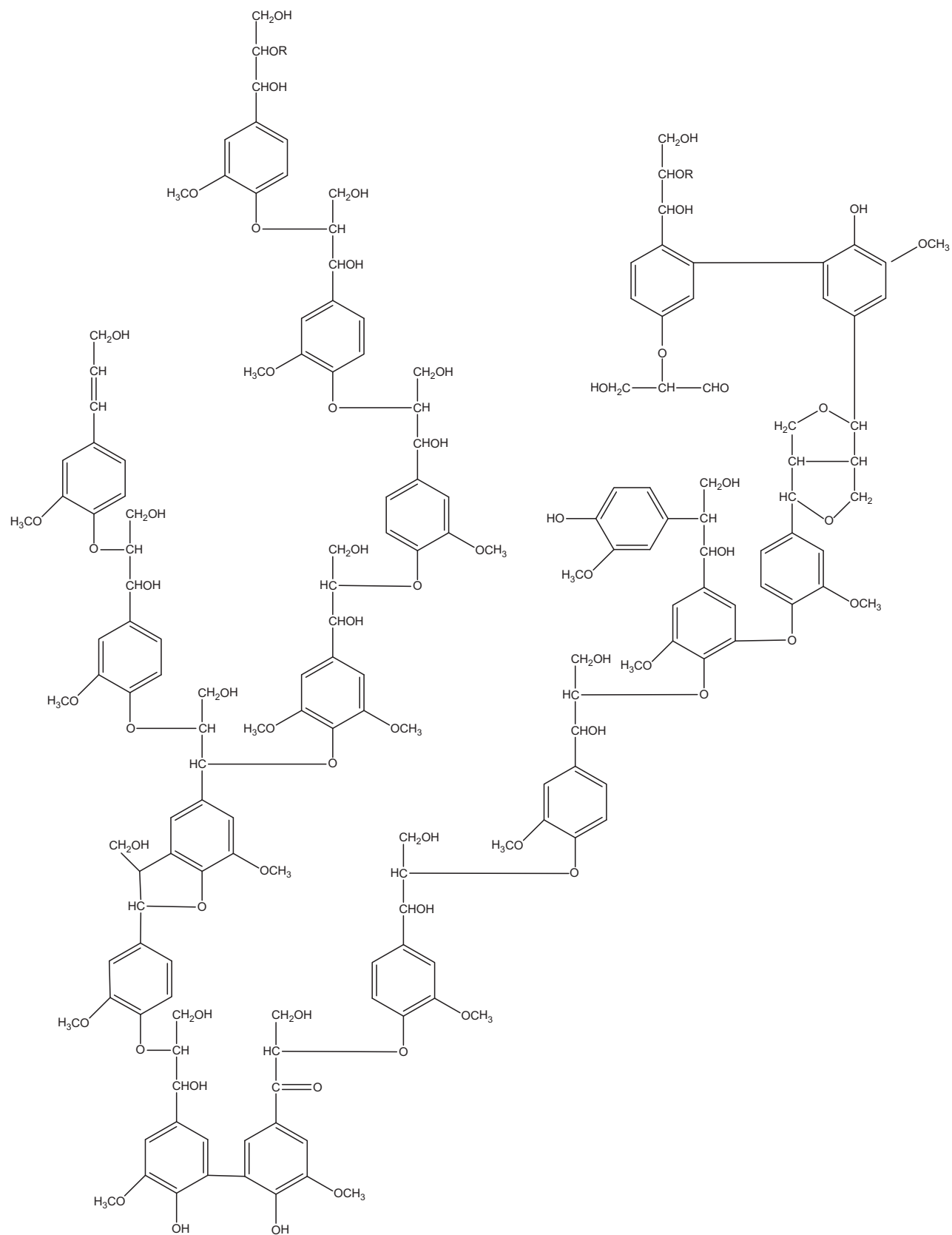
Biopolymer	Commercial name	Manufacturer	Applications
Cornstarch	Mater-Bi®	Novamont (IT) ¹	Bags, mulch films, disposable tableware, accessories, packaging, biofiller for the automotive sector
Cornstarch	Plantic® HP Plantic® R1	Plantic (AU)	Packing foods and goods
Starch	BIOPLAST GF 106/02 BIOPLAST GS 2189 BIOPLAST WRAP 100 BIOPLAST TPS	Biotec (DE)	Food packaging, cosmetics packaging, bags, waste bags, foamed products, thermoformed trays, visit cards, etc.
Cereal grains and specific Limagrain maize varieties	Biolice®	Limagrain (FR)	Fast food cutlery, packaging, mulch films, bags (garbage, garden waste and dog litter), clamshells, lining material for jute bags, canvas bags and paper bags
Plants, cereals	VEGEMAT®	VEGEPLAST (FR)	Vineyard fasteners, coffee machine capsules, disposable cutlery, dog treats, parachute links, golf tees, candle wicks
Reclaimed potato starch	Solanyl® BP Solanyl C1xxx grades (injection molding): C1001 C1201 C1203 Solanyl C2xxx grades (thermoform grade) C2201 Solanyl C8xxx grades (blown film): C8101 C8201	Rodenburg Biopolymers (NL)	Packaging, plant pots, disposable cutlery, cup holders, golf tees, toys, CD and DVD trays, plant stakes
Grafted starch ²	Gaialene®	Roquette (FR)	Packaging, bottles, foams, hangers, soles, thermoplastic specialities

¹C. Bastioli and her team at Novamont S.p.a in Novara, Italy won the European Inventor Award in 2007 for inventing biodegradable plastics made from starch (category: SMEs/research).

²Non-biodegradable copolymer; based on a 50/50 thermoplastic starch/fossil fuel-based polymer.

propyl groups by up to two hydroxyl groups (WO0027923 A1, 2000, FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG). Besides cellulose, lignin is the second most common organic material on earth,

about 20 billion tons of lignin being formed each year by photosynthesis. This ensures an almost infinite supply of lignin as a raw material without competing with food products. Approximately 60 million tons of lignin are produced annually as a byproduct within

**Scheme 1.31** Possible structure of lignin.

Adapted from Adler [58].

the cellulose industry, mainly in the production of paper. Lignin may even be extracted from tree bark, sawdust, or straw. Lignin is particularly recalcitrant to biodegradation, and also reduces the bioavailability of the other cell wall constituents.

Lignin has considerably improved material properties compared to other natural polymers, and is characterized by a relatively high strength, rigidity, impact strength, and high resistance with respect to ultraviolet light. Lignin is also a suitable material for heat and sound insulation.

One of the main sources of lignin is spent pulping liquors, known as black liquor, where lignocellulosic materials, such as wood, straw, corn stalks, bagasse and the like, are processed to separate the cellulose fibers or pulp from the lignin. Lignin includes both alkali lignin from the sulfate pulping process and lignin derived from other alkaline processes, such as the soda or modified soda processes, and sulfonated lignin, such as sulfite lignins from acid and neutral processes, or sulfonated alkali lignin. Alkali lignin is usually recovered from black liquor as water-insoluble products by acidification and precipitation procedures. Lignin obtained from the kraft, soda, or other alkaline processes is not recovered as a sulfonated product, but may easily be sulfonated, if desired, by reacting the product with a bisulfite or sulfite. The lignin sulfonate of commerce is usually sold as salts of sulfonic acid, such as calcium lignosulfonate. Alkali lignin from the cellulose industry is used as a binding agent for hardboard made from wood and cellulose, as a dispersing agent, and as a stabilizer in asphalt emulsions.

Other known natural starting materials for obtaining corresponding natural substance plastics are some lignin derivatives. In **US3619222 A** (1971, DARLING & CO) a modified protein base adhesive composition comprising a protein, a polyhydric compound, and a lignin extract (lignosulfonate) is disclosed. The compositions are useful as natural adhesives, glues (e.g., hot-melts) that display thermosetting and water-insoluble properties.

The lignin extract used is preferably a lignin sulfonate extract material which has been recovered from spent sulfite liquors produced by treatment of wood pulp, and comprises, in addition to lignin sulfonate, sugars and minor amounts of inorganic salts.

In **CH250077 A** (1947, HOLZER TIBOR) a method for the production of molded articles is disclosed whereby sulfite waste liquor (a sulfonated lignin product from the lignin extraction) is treated

with proteins, thus providing an elastomeric, tacky mass which is dried and hardened by means of suitable hardeners.

Although both documents, **US3619222** and **CH250077**, disclose compositions based on natural starting materials, the starting materials themselves, as well as the final products, do not have the requisite thermoplastic properties, and require suitable hardeners and other chemical compounds in order to obtain a material suitable for molding (**WO0107166 A1**, 2001, FRAUNHOFER GES FORSCHUNG).

DE19700902 A1, **DE19700903 A1**, and **DE19700905 A1** (1998, HUETTERMANN A), **DE19700907 A1** (1998, NESTE OY), and **DE19701015 A1** (1998, WIBMER GMBH U. CO. KG PAPIER-FORMTECHNIK) disclose intermediate products for the production of polymer products from lignin derivatives which are produced in the cellulose industry, wherein lignin derivatives are reacted with phenol-oxidizing enzymes in the presence of oxidizing agents such as oxygen. These intermediate products are used as a coating agent for the production of waterproof papers and cartons, as a coating agent or binding agent for the production of particle board, as a binding agent for starch for the production of waterproof starch derivatives, as an insulating material, and as a component of a composite material enriched with plant fibers.

DE4331747 A1 (1995, WUENNING P) discloses a natural granulated material produced from alkali lignin and proteins or protein derivatives. It can be decayed and composted, and is produced through stereochemical modification via treatment with organic acids, acetic acid in particular. This material can be processed thermoplastically into structural parts.

WO9806785 A1 (1998, SILBINGER J) describes a similar composition wherein lignin and a protein are heated and melted. This material is not suitable for most purposes since proteins are odorous and frequently hygroscopic, even when processed.

WO0027923 A1 (2000, FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG) discloses a bioplastic made from a polymer blend containing at least one lignin-based natural polymer. In particular, it is based on alkali lignin produced during the extraction of cellulose and at least one other synthetic and/or natural polymer which increases the impact resistance, with the exception of proteins. In a preferred embodiment, the lignin portion of the inventive plastic material is

between 2 and 90 mass%, in particular between 5 and 65 mass%. The material is suitable as a substitute for wood or wooden materials due to its various properties, color, and consistency. Due to its good heat and sound insulating properties, the bioplastic is particularly suitable for the production of structural components such as profiles for windows or door frames, and for door inner linings, etc. The material can also be used for producing housings for electric or electronic devices such as TV and radio sets or the like.

DE19852034 C1 (2000, FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG) discloses a composition for the production of shaped bodies containing up to 80% lignin, up to 80% natural fibers, and up to 70% shellac. Materials that are reinforced with fibers (e.g., cellulose fibers) to stabilize their shapes require the addition of a natural processing aid. Shellac functions as a processing aid. Shellac is produced by the louse “*kerria lacca*” to protect their eggs from external weather effects, and can be melted at temperatures of around 80°C. The good film-forming properties of shellac contribute to favorable processing properties of the natural fiber mixture using extruders, injection molding machines, or presses.

DE10151386 A1 (2003, TECNARO GES ZUR IND ANWENDUNG) discloses a composition containing natural fibers, lignin, and/or lignin derivatives, and optionally, small amounts of additives for forming thermoplastic reprocessing into profiled bodies; it contains 1–20 wt.% (preferably 8–12 wt.%) water on the mixture dry weight.

A commercially available lignin product is Arboform® (TECNARO²), a bioplastic composed of three natural components: lignin, various cellulose fibers such as hemp and flax, and some natural additives. As a thermoplastic, it can be molded and is therefore also called liquid wood. The mixture of renewable resources is processed further through special procedures to form granules that can be used for various products manufactured by conventional plastic fabrication techniques.

Chitosan

Chitin and chitosan are highly basic polysaccharides. Chitosan is the common name for

poly-[1-4]- β -D-glucosamine. Chitosan is chemically derived from chitin, which is a poly-[1-4]- β -N-acetyl-D-glucosamine, and is included in the cell walls of fungi and the exoskeletons of insects and (most commonly) crustaceans. Chitin is inexpensively derived from widely available materials. It is available as an article of commerce from such companies as Primex Corporation (IS), Biopolymer Engineering, Inc. (USA), Biopolymer Technologies, Inc. (USA), and CarboMer, Inc. (USA).

Chitin is treated with strong alkalis to remove acetyl groups producing chitosan. Depending on the specific treatment of chitin, chitosan may vary in the degree of deacetylation. Chitosan is generally insoluble in water, but dissolves in dilute solutions of organic acids, such as acetic, formic, tartaric, valeric, lactic, glycolic, and citric acids, and also dissolves in dilute mineral acids such as hydrochloric and sulfuric acids.

1.11 Vinyl Polymers

Polyolefins (bio-based)

WO2008067627 A2 (2008, BRASKEM SA) describes a method for the production of one or more olefins, namely propylene, and optionally ethylene and butylene, mainly from the residues of the processed renewable natural agricultural raw material (second-generation feedstock). The propylene is obtained from the gasification reaction of the lignocellulosic materials and other organic products contained in the raw material residues. This is followed by the formation of methanol and its subsequent transformation into propylene; this route may further generate ethylene and/or butylene as byproducts. The propylene, ethylene, and butylene generated by the methods according to the invention in this patent can be used to obtain their known derivatives, preferably for the production of polypropylene and its copolymers, and polyethylene and its copolymers. This results in polymers whose composition includes, when using only raw materials and residues from renewable natural sources, 100% carbon from renewable natural sources, as determined by the test method according to the ASTM D 6866-06 standard.

One other complementary alternative consists of the use of other raw materials of non-natural (fossil) origin for the production of synthesis gas, such as naphtha, natural gas, coal, recycled plastics, and

² The company TECNARO GmbH, a Fraunhofer spin off, was winner of the European Inventor Award 2010 (in the SMEs research category).

Table 1.13 Commercially available biopolyolefins

Biopolyolefins	Trade name	Manufacturer	Applications
PE (LDPE, HDPE), PP	Green PE Green PP	Braskem (BR)	Personal care, cleaning, cosmetics, food and automotive industries
PE (based on Braskem's Green PE)	Terralene®	FKuR (DE)	

combustion gas from thermoelectrical power generation plants. This is based on the provision that the end products (olefins and their known derivatives), as well as polymers such as polyethylene and its copolymers, polypropylene and its copolymers, and PVC, include at least 50% (preferably at least 80%) carbon from a renewable natural source as determined by the test method according to the ASTM D 6866-06 standard.

WO2011066634 A2 (2011, BRASKEM SA; UNIV ESTADUAL CAMPINAS-UNICAMP) describes a method for the production of olefins (e.g., ethylene used for preparing polyolefins such as polypropylene) that comprises the production of carboxylic acids from the fermentation of at least one organic substrate from a renewable and natural raw material, followed by the subsequent anodic decarboxylation of the carboxylic acids thus obtained for formation of the olefins. The carboxylic acids obtained by fermentation are propionic acid, butyric acid, valeric acid, or caproic acid, which generate ethylene, propylene, butylene, or pentene, respectively, through the anodic decarboxylation thereof. The organic substrates from renewable and natural raw materials are selected from starch, cellulose, hemicellulose, glycerol, sorbitol, lactose, lactates, and sugars. The fermentation process is performed in the presence of bacteria such as those of the genera *Propionibacterium*, *Clostridium*, *Butyrivibrio* and *Butyrivibrio*; preferred bacteria are *Propionibacterium acidipropionici*, *Clostridium tyrobutyricum*, *C. butyricum*, *C. thermobutyricum*, *C. ciditolerans*, *C. acetobutylicum*, or *C. thermoamylolyticum*.

WO2009070858 A1 (2009, BRASKEM SA) describes an integrated process for the production of ethylene-butylene copolymers from at least one renewable natural raw material. The ethylene monomer is obtained by the ethanol dehydration reaction, where ethanol is produced by the fermentation of sugars, and the 1-butylene co-monomer is obtained according to at least one of the following

reactions: (1) dehydration reaction of 1-butanol directly produced by the fermentation of sugars; (2) dehydration reaction of 1-butanol obtained from ethanol via a chemical route, where ethanol is produced by the fermentation of sugars; and/or (3) dimerization reaction of ethylene produced by the dehydration of ethanol obtained from the fermentation of sugars, followed by isomerization of the 2-butylene isomers then formed.

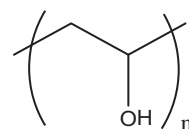
Bio-based polyethylenes (PE) have the same properties as PEs derived from fossil-based resources. Bio-based PEs are not biodegradable, and they are resistant to hydrolysis and oxidation as are their fossil-based counterparts. Due to their thermoplastic properties, bio-based PEs are suitable for physical recycling (also called mechanical recycling). Alternatively, they can be rendered oxodegradable by use of pro-oxidant additives (see Chapter 2: Define the Terms; Section 2.3: Biopolymers versus Oxodegradable Polymers). The commercially available biopolyolefins are shown in Table 1.13.

Poly(vinyl chloride) (bio-based PVC)

Ethylene derived from bioethanol can serve as raw material for the production not only of polyethylene, but also of PVC. Solvay announced that it is going to invest \$135 million in a factory in Brazil for the production of 60,000 tons/year of bioethanol as the basis for the production of bio-based PVC.

Poly(vinyl alcohol) (PVOH)

Poly(vinyl alcohol) (PVOH) is a water-soluble polymer prepared via the hydrolysis of poly(vinyl acetate) (see Scheme 1.32). PVOH is a synthetic polymer that is used extensively in fibers, films,

**Scheme 1.32** Poly(vinyl alcohol) (PVOH).

papers, and adhesives. PVOH is a thermoplastic material commonly used in laminates for food containers due to its excellent film-forming and oxygen barrier properties. Commercially available PVOHs are shown in Table 1.14.

1.12 Diene Polymers

cis-1,4-Polyisoprene

cis-1,4-Polyisoprene is a hydrophobic and biodegradable polymer naturally occurring as latex in the laticiferous vessels or parenchymal (single) cells of rubber-producing plants such as *Hevea brasiliensis* [59]. Natural rubber contains 97 wt.% *cis*-1,4-polyisoprene and about 3 wt.% proteins. The protein moieties can be considered to be natural compatibilizers between the polyisoprene and other hydrophobic compounds such as starch. Natural rubber was one of the first commercialized polymers and its structure and properties, and processing and recycling has been studied extensively.

1.13 Other Biodegradable Polymers

Poly(Ortho Ester)s (POE I, II, III, IV)

Poly(ortho ester)s (POEs) are hydrophobic, biocompatible, and bioerodible polymers potentially useful as sustained drug delivery systems. The development of POEs dates back to the early 1970s. POEs have evolved through four families, designated as POE I, POE II, POE III, and POE IV (see Scheme 1.33). Of these, only POE IV has been shown to have all the necessary attributes to allow commercialization [60].

The synthesis and characterization of the four distinct families of POEs have been described by Heller [61]. POE I is prepared by the transesterification of diethoxytetrahydrofuran with diols. POE II is prepared by the condensation of 3,9-bis(ethylidene-2,4,8,10-tetraoxaspiro[5,5]undecane) with diols to produce a linear polymer, or with a triol to produce a cross-linked polymer. POE III is prepared by the condensation of a flexible triol with alkyl orthoacetate to produce ointment-like materials. POE IV is prepared by the condensation of a rigid triol with alkylorthoacetate to produce solid materials. **US4079038 A** (1978, ALZA CORP), **BE837935 A1** (1976, ALZA CORP), **US4131648 A**

(1978, ALZA CORP), and **US4180646 A** (1979, ALZA CORP) disclose biodegradable or bioerodible POEs. These polymers are formed by a reaction between an orthoester (or orthocarbonate) such as 2,2-diethoxytetrahydrofuran and a diol such as 1,4-cyclohexanedimethanol. The reaction requires elevated temperature and reduced pressure and a relatively long reaction time. Drugs or other active agents are retained in the polymer matrix and are released as the polymer biodegrades due to hydrolysis of the labile linkages. **WO8103278 A1** (1981, STANFORD RES INST INT) discloses polymers prepared by reacting a polyol with a polyfunctional ketene acetal. These polymers represent a significant improvement over the aforementioned patents of ALZA Corporation since synthesis proceeds readily at room temperature and atmospheric pressure, and the resulting polymers have superior properties. Because of the backbone stability of POEs, excipients must be added to the matrix to promote degradation. These excipients, usually inorganic water-soluble salts, tend to swell in aqueous media and thus promote diffusional release.

Polyanhydrides

Polyanhydrides are biodegradable polymers characterized by anhydride bonds that connect repeat units of the polymer backbone chain (see Scheme 1.34). Synthesis of aromatic polyanhydrides was first reported in 1909. In the 1930s, Hill and Carothers prepared a series of aliphatic polyanhydrides intended as substitutes for polyester textile applications [62,63]. However, they were discarded because of their hydrolytic instability.

Traditionally, polyanhydrides have been prepared by melt condensation polymerization by reacting dicarboxylic acid monomers with excess acetic anhydride at a high temperature and under a vacuum to form the polymers. Catalysts may be used to achieve higher molecular weights and shorter reaction times. Generally, a one-step synthesis is used, which does not require purification.

Aliphatic homo-polyanhydrides have limited applications because of their high crystallinity and fast degradation. This is the case of poly(sebacic anhydride) [1]. To improve mechanical properties of polyanhydrides for specific medical applications, copolymers of anhydrides are used [64]. The degradation rate of polyanhydrides can be managed by adjusting the hydrophobic and hydrophilic components in the copolymer. Typical polyanhydrides include poly(carboxyphenoxy hexane-sebacic acid),

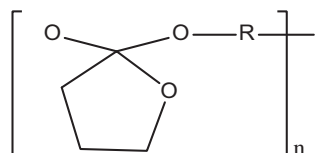
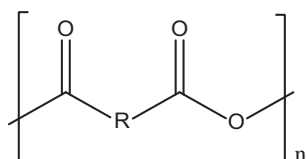
Table 1.14 Commercially available poly(vinyl alcohol)s

Biopolymer	Commercial name	Manufacturer	Applications
High purity PVOH	GOHSENOL™ EG series: EG-05, EG-05P, EG-40, EG-40P, NH-17Q	Nippon Synthetic Chemical Industry Co., Ltd. (JP)	Pharmaceuticals: binder, suspending agent, cataplasm; cosmetics: base resin for face-pack, lotion, cream; electronics: fluorescent material binder, illuminant binder materials; ceramics: fine ceramic binder
Anionic PVOH	GOHSENAL™ series: T330H, T-300, T-350	Nippon Synthetic Chemical Industry Co., Ltd. (JP)	Printing stock, coat paper, NCR paper, release paper, emulsifying stabilizer, adhesive, film, drilling fluid control agents
Hydrophilic group- modified PVOH	ECOMATY™ series: WO-320R, WO-320N	Nippon Synthetic Chemical Industry Co., Ltd. (JP)	Ink jet printing
Modified PVOH with a sulfonic group (–SO ₃ X group) on its side chain	GOHSERAN™ series: L-3266, CKS-50, L-0302, L-0301	Nippon Synthetic Chemical Industry Co., Ltd. (JP)	Emulsifier, dispersant, adhesive, coating agent, and binder
Low saponification hydrophilic PVOH	GOHSEFIMER™ series: LW-100, LW-200	Nippon Synthetic Chemical Industry Co., Ltd. (JP)	Hot melt resins, dispersing auxiliaries for suspension polymerization of vinyl chloride, adhesives, coating agents, binders and pressure-sensitive adhesives
PVOH	Mowiol®/Kuraray Poval® Mowiflex TC® Exceval™ Kuraray Poval® K Kuraray Poval® L Kuraray Poval® LM Kuraray Poval® R	Kuraray (JP)	Adhesives, papers, building materials (additive for mortar, cement, oil well cementing, etc.), polymerization (emulsion/suspension), temporary binders for ceramics, gas barrier coating, films/foil, textiles sizing
PVOH	J-POVAL Fully Hydrolyzed Type (8 grades) Medium Hydrolyzed J-POVAL Type (11 grades) J-POVAL Partially Hydrolyzed Type (17 grades)	JAPAN VAM & POVAL Co., LTD (JP)	Textiles, paper processing, adhesives, dispersant, film formation, caking agents, construction

Table 1.14 Commercially available poly(vinyl alcohol)s (*Continued*)

Biopolymer	Commercial name	Manufacturer	Applications
PVOH-co-plasticizer (polyalkyleneoxy acrylate)	Vinex [®]	Air Products & Chemicals	Blown and cast films, extrusion coating, fibers, tubing and profile, injection molding
Modified PVOH	Aqua-Novon [®]	Novon (USA)	Sanitary applications
PVOH, amorphous	Nichigo G-Polymer Powder type: AZF8035W OKS-6026 OKS-1011 OKS-8041 OKS-8049 OKS-1028 OKS-1027 OKS-1109 Pellet type: OKS-8049P OKS-8084P OKS-8042P	Nippon Synthetic Chemical Industry Co., Ltd. (JP)	Powder type: used primarily for aqueous solution applications; pellet type: used primarily for melt-casting applications

Abbreviation: PVOH, Poly(vinyl alcohol).

**Scheme 1.33** Poly(ortho ester) (POE I).**Scheme 1.34** Polyanhydride.

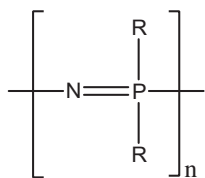
poly(fumaric acid-sebacic acid), poly(imide-sebacic acid), and poly(imide-carboxyphenoxy hexane).

The main application of polyanhydrides is in the medical device and pharmaceutical industries. Polyanhydrides degrade *in vivo* into nontoxic diacid monomers that can be metabolized and eliminated from the body. Since their degradation products are safe, polyanhydrides are considered to be biocompatible. These polymers display superior physical and mechanical properties with respect to erodible carriers for controlled release drug delivery systems.

The erosion rates of polyanhydrides can be changed several thousand fold only by changing the monomers or the composition of the copolymers (CA2202676 A1, 1998, UNIV MONTREAL). In contrast to POEs, polyanhydrides may be sufficiently labile in hydrolysis to produce heterogeneous erosion without the addition of any excipient. Polyanhydrides and POEs offer a number of advantages over the more commonly used lactide/glycolide copolymers since they offer better control over polymer properties and erosional behavior. Synthesis methods, structures, and characterization of polyanhydrides have been reviewed by Kumar et al. [65]; see also Domb et al. [66], EP0260415 A2 and EP0266603 A1 (1988, MASSACHUSETTS INST TECHNOLOGY).

Polyphosphazenes (PPHOSs)

Polyphosphazenes (PPHOSs) are polymers with an inorganic backbone consisting of alternating phosphorus and nitrogen atoms separated by alternating single and double bonds, and organic substituents (R) covalently bonded to the phosphorus atoms as side groups (see Scheme 1.35). Polymers with a wide range of properties can be synthesized from this polymer backbone by incorporating different side groups, by varying the side group in single-substituent PPHOSs, and/or by using two or more



Scheme 1.35 Polyphosphazene (PPHOS).
R can be an alkoxy, aryloxy, or amino group.

co-substituents. An individual PPHOS may be hydrophobic, amphiphilic, or hydrophilic; water-stable or water-erodible; crystalline or amorphous; bio-inert or bioactive. The hydrophobicity of the PPHOS can be increased by adding hydrophobic side groups, such as aromatic groups, to the backbone. Such polymers can be particularly useful as drug delivery carriers, plasma expanders, and biocompatible coatings for medical devices.

PPHOSs were first synthesized by Allcock and Kugel [67]. Even though PPHOSs have good physical properties, they have not been widely used due to their cost, and have only been used for limited purposes.

Methods for the synthesis of various types of PPHOS have been described by Allcock [68–71]; Laurencin et al. [72,73]; Gunatillake and Adhikari [74]; **US4440921 A** (1984), **US4495174 A** (1985) and **US4880622 A** (1989, RES CORP TECHNOLOGIES INC); **US4946938 A** (1990, UNIV PITTSBURGH); **US6077916 A** (2000, PENN STATE RES FOUND).

1.14 Biopolymer Compositions

1.14.1 Blends

Biopolymers are seen as promising sustainable alternatives to conventional petrochemical products. Until now, however, their widespread use has been hampered by sometimes unsatisfactory material properties. The processability of nearly all pure biodegradable biopolymers is not comparable with those of standard thermoplastics. Polymer blends offer a solution to this problem by combining biodegradable biopolymers with another polymer, not necessarily a biodegradable one. The blending of biodegradable biopolymers reduces the overall cost of the material and modifies the desired properties and degradation rates. Compared to copolymerization methods, blending may be a much easier and faster way to achieve the desired properties. More

importantly, through blending, other less expensive polymers could be incorporated with one another. Miscibility of the blends is one of the most important factors affecting the final polymer properties. Some of the advantages of producing miscible blends include single-phase morphology and reproducibility of the mechanical properties. However, formation of miscible blends, especially with non-biodegradable polymers, can slow down or even inhibit the degradation of the biodegradable components [30].

There is a broad range of biopolymer blends in the market nowadays. Representative commercially available biopolymer blends are shown in [Table 1.15](#).

Starch, in particular deconstructed starch, is generally hard and brittle in the dried state or even at water contents below 10%, and cannot be molded at the high temperatures typically employed in thermoforming or molding shaped articles, sheets, or films. The moldability of starch can be increased by adding thermoplastic polymers (synthetic fossil fuel-based or renewable-based, as well as non-biodegradable or biodegradable polymers) in order to obtain an extrudable or injection moldable material. Various thermoplastic polymers for admixing or blending are proposed in the prior art. Good results in terms of processability and overall biodegradability — however, not always at competitive price levels — are obtained with biodegradable (vinyl)ester (co)polymers. This combination of starch and thermoplastic polymers is disclosed in various patents, such as **EP327505 A2** (1989, WARNER LAMBERT CO), **WO2004085533 A1** (2004, WACKER POLYMER SYSTEMS GMBH), **WO9929733 A1** (1999, RODENBURG VEEVOEDERS BV), and **WO9925756 A1** (1999, BIOPOLYMER GMBH).

FR2782999 A1 (2000, ULICE SA) discloses a biodegradable material based on a dispersive blend (e.g., a homogeneous mixture of polymer and cereal flour). The polymer is selected for its mechanical properties and its ability to be extruded.

PLA has been blended with *cis*-1,4-isoprene, which is the major ingredient in natural rubber, to improve its toughness [76]. But the incompatibility between two polymer phases is a major drawback. PLA has been also blended with other high impact biodegradable polymers such as PCL [77]. However, incompatibility between two polymer phases is again a major problem.

PHB has also been blended with rubber to improve its toughness [78], but these blends have drastically lower modulus and strength. PHB has also been

Table 1.15 Blends of biopolymers

Blends	Trade name	Manufacturer	Applications
Starch blends	Mater-Bi® Z class Mater-Bi® Y class Mater-Bi® V class	Novamont (IT)	Mater-Bi® Z class: films and sheets (bags, nets, paper lamination, mulching films, twines, wrapping films); Mater-Bi® Y class: rigid and dimensionally stable injection molded items (cutlery, boxes, flowerpots, seedling and plant trays, golf tees, vending cups, pens); Mater-Bi® V class: rigid and expanded items (loose fillers and packaging foams as a replacement for polystyrene); injection molded items: soluble cotton swabs, soluble items [75]
Co-PBS/PLA (NatureWorks)	Bio-Flex® series Bio-Flex® F 1130 Bio-Flex® F 1110 Bio-Flex® F 2110 Bio-Flex® F 6510 Bio-Flex® A 4100 CL Bio-Flex® S 1100 Bio-Flex® S 6540	FKuR (DE)	Bio-Flex® F 1130, F 1110 and F 2110: carrier or shopping bags, waste bags, flexible packaging film and air pillows/bubble wrap; agricultural and mulch films; Bio-Flex® F 2110 and F 1130: fruit and vegetable nets; Bio-Flex® F 6510: injection molded products, such as writing utensils and other promotional articles
PLA/PBAT (Ecoflex®)	Ecovio® L BX 8145 Ecovio® FS Shrink Film C 2100 (63% bio-based) Ecovio® FS Paper C1500 (75% bio-based)	BASF (DE)	Mulch films, carrier bags, waste bags, foam packaging (plates, trays), shrink films, paper coating
Starch or flour/Vinex®		Wacker Chemie (DE)	Packaging, catering products, gardening, landscaping
Blend of PHB (Mirel™)	Mvera™	Telles (ADM/ Metabolix) (USA)	Can liners, retail bags, yard-waste bags, and stretch wrap
Reactive blends of starch/ PCL, cellulose esters, zein	Envar™	Bioplastics Inc. (USA)	Compost bags, mulch films, paper coatings, etc.
Styrene copolymer/30% PLA (Ecodear®)		Toray (JP)	Similar to ABS
PBS (Bionolle™)/starch, PBS (Bionolle™)/starch/ PLA	Starcla™ series	Showa (JP)	Mulch films
PLA/PBAT (Ecoflex®)	Cereplast Compostables® 3000 film grade	Cereplast (USA)	Films

(Continued)

Table 1.15 Blends of biopolymers (*Continued*)

Blends	Trade name	Manufacturer	Applications
Aliphatic and aromatic polyesters	EcoWorks®	Cortec Corporation (USA)	Film extrusion applications: food packaging, grocery bags, community composting programs, garbage, mulch bags, etc.
Starch/LLDPE Starch/PP Starch/PBAT Starch/HIPS Starch/LLDPE Starch/PP Starch/PBAT Starch/HIPS	Terraloy™ BP-10001A (≤ 30% TPS) Terraloy™ BP-13001A (≤30% TPS) Terraloy™ BP-20001A (≤ 40% TPS) Terraloy™ BP-18003A (≤ 30% TPS) Terraloy™ MB-10000A (≤ 50% TPS) Terraloy™ MB-13000A masterbatch (≤ 50% TPS) Terraloy™ MB-20001A masterbatch (≤ 50% TPS) Terraloy™ MB-18003A masterbatch (≤ 50% TPS)	Teknor Apex (USA)	Blown and cast film, sheet; extrusion sheet and coating; thermoformed and injection molded parts

Abbreviations: ABS, Acrylonitrile butadiene-styrene; EVA, Ethylene vinyl acetate; HIPS, High impact polystyrene; LDPE, Low density polyethylene; LLDPE, Linear low density polyethylene; PBAT, Poly(butylene adipate-co-terephthalate); PBS, Poly(butylene succinate); PCL, Poly(ϵ -caprolactone); PHB, Polyhydroxybutyrate; PLA, Polylactide; TPS, Thermoplastic starch.

blended with other high-impact biodegradable polymers such as PCL [79] and PBS [80]. A thorough review of the blends of PHB or PHBV with other polymers is provided by Ha and Cho [81]; incompatibility between two different polymers remains a major problem. Furthermore, the addition of a fossil fuel-based biodegradable polymer (such as PCL) in large quantity reduces the weight fraction of the renewable PHB in the overall blend composition.

PHB blends with random ethylene-propylene rubber (EPR) and ethylene-vinyl acetate (EVA) copolymers were found to be immiscible, presenting distinct and unaltered T_m and T_g [82]. PHB and poly(vinyl acetate) (PVA) blends were found to be miscible, with T_m and T_g values intermediate between those of PHB and PVA. PVA reduced the crystallinity and crystallization rate of PHB, which constituted the most marked phenomenon at higher concentrations of PVA [83,84]. PHB blends with poly(ethylene oxide) (PEO) were found to be miscible, but there was a decrease in the values of T_m and T_g of PHB proportional to the amount of PEO

in the blend [85–87]. The T_g and depression of the T_m provide miscibility criteria for PHB/PEO blends [88].

Blends of lignin with biodegradable biopolymers, with or without fiber reinforcement, are a promising option for the manufacture of low-cost biodegradable materials. Films containing up to 30% commercial pine kraft lignin mixed with wheat starch were found to improve the mechanical properties of starch films, with the low molecular weight fraction of the pine kraft lignin acting mainly as a starch plasticizer [89,90]. Lignin, wood flour-based PCL composites have also been reported [91]. Maleic anhydride-grafted PCL was used as a compatibilizer for improving tensile properties [92]. Lignin also acted as a new type of nucleating agent in improving the thermal properties of lignin-polyhydroxy butyrate (PHB) composites [93]. Lignin is also used as an adhesion promoter in cotton fiber reinforced PLA composites [94]. A lignin/PLLA blend has been reported to retain its thermomechanical properties when the content of lignin is less than about 20%.

The lignin would accelerate the thermal degradation of PLLA when the content of lignin was more than 20% [95].

WO2010139056 A1 (2010, UNIV GUELPH) discloses a biodegradable biopolymer composite comprising lignin, grass fibers, and PBS. The grass fiber is switchgrass, miscanthus, hemp, jute, and/or kenaf. The PBS is provided preferably as a blend of PBS and PHBV. The biocomposite comprises less than 65%. The thermomechanical properties of the material can be controlled by increasing or decreasing the lignin content.

The following are recent products based on biopolymer blends [96]:

Cereplast Compostable[®] 3000 film grade for food packaging based on PLA/PBAT (Ecoflex[®]) blend; the film has enhanced balance puncture strength, toughness, and can be processed on existing blown film extrusion machines.

EcoWorks[®] of Cortec Corporation, a partially bio-based blend of aliphatic and aromatic polyesters for biodegradable film extrusion applications. In addition to the biodegradability, EcoWorks[®] also contains PLA (Ingeo[™]). Films produced from EcoWorks[®] are shelf-stable and will not degrade prematurely; they will degrade when placed in a proper composting environment.

Terraloy[™] 20000 series of Teknor Apex, a blend of thermoplastic starch (TPS) and PBAT, with TPS content ranging up to 40%. The Terraloy 20000 series is designed for blown and cast film, sheet, and thermoformed and injection molded parts intended for composting. Teknor Apex recommends using the compounds for replacing polyolefins and polystyrene in applications such as shrink wrap, produce wraps and trays, cosmetics jars and containers, carrier bags, can liners, trays and plates, cutlery, and flowerpots.

BIOLLOY[™] of JSR, a blend produced by combining a fossil-based thermoplastic with PLA. The product line includes BIOLLOY[™] products, which contain blends of polyolefin-based polymers such as polypropylene, polyethylene, and ABS. Depending on the application, the combination ratio of PLA can range from 5 to 80%, which allows users to achieve a flowability suitable to their processing method, such as injection molding (for molding complex shapes), blow molding, extrusion, and film.

Updating Ecovio[®] grades of BASF: blends of PLA and PBAT (Ecoflex[®]) for paper coating and manufacturing shrink films comprising Ecovio[®] FS Paper, which is 75% bio-based, and Ecovio[®] FS Shrink Film, which is 63% bio-based, respectively. Paper and paperboard coated with Ecovio[®] FS Paper C1500 have excellent sealability, a temperature stability up to 100°C, and they can be re-pulped. Shrink films made from Ecovio[®] FS Shrink Film C2100 are not only compostable, they are also easy to open with high puncture.

1.14.2 Additives and Modifiers

Biodegradable biopolymers are rarely used on their own to make biodegradable plastics. A range of additives and modifiers are generally added to obtain useful performance properties that approach those of conventional plastics. Such additives include, for example, plasticizers, impact modifiers, colorants including dyes and pigments, antioxidants, light and UV stabilizers, antistatic agents, releasing agents, de-nesting agents, matting agents, anti-aging agents, fluorescent brighteners, melt strength enhancers, lubricants, thickeners, chain extenders, coupling agents, cross-linking agents, nucleating agents, heat stabilizers, viscosity stabilizers, anti-blooming agents, foaming agents, mildew proof agents, antibacterial agents, drying agents (desiccants), etc. [97] With the purpose of functional improvement or addition of a new function, additives may be incorporated into a biodegradable biopolymer in any proportions during any stage of polymerization or processing. A favorable way of incorporating various additives into a biopolymer is by using masterbatches. A masterbatch provides a convenient way of handling small amounts of critical ingredients, like specialized additives in higher concentrations than those occurring in a normal mixture for subsequent dilution with the remainder of the ingredients.

Additives are used to enhance thermal stability, tensile strength, and melt lubricity of a biopolymer during processing. Other additives are used to improve the performance of the biopolymers, especially impact strength, heat resistance, and gas-barrier properties. Additives for biopolymers must not have any adverse environmental or health effect and not compromise the biodegradability of the material.

Processability boosters

Processing aids are used in extrusion or injection molding to reduce friction between the biopolymer melt and the metal, which facilitates processing.

Melt strength enhancers are added to improve the processing of biopolymers. Paraloid™ BPMS 250 of Rohm and Haas is a melt strength enhancer that improves the processing of PLA and its blends. Biostrength® 700 of Arkema is a melt strength improver/rheology modifier. CESA-extend chain extender of Clariant is an epoxy-functional styrene/acrylic oligomer masterbatch that can be used to relink polymer chains that have broken due to thermal, oxidative, and hydrolytic degradation; it has shown encouraging results with PLA. Processing Aide of DaniMer is a renewable-based additive that enables improved processing efficiencies such as higher operating speeds, increased throughput, and reduced defects. The DaniMer processing aide also provides “de-nesting” characteristics and reduces the material’s adherence to metal during processing. Terraloy™ MB-90001A1 masterbatch of Teknor Apex is a melt strength enhancer that broadens the processing window of PLA in cast film and sheet for packaging and other applications.

Slip/antiblocking, antistatic, de-nesting, and mold-release agents are added to biopolymers during processing to control or stop biopolymers from sticking to themselves and metal surfaces. OnCap™ BIO additives of PolyOne are an additive concentrate range designed to provide optimal properties to current biodegradable biopolymers, including slip, antiblock, antistatic, and de-nesting properties.

Heat stabilizers are antioxidants that are used to protect biopolymers from the degrading effects of heat during processing or use. Typical antioxidants include hindered phenol-type compounds, phosphite-type compounds, thioether-type compounds and the like. CESA-compostable additive masterbatches of Clariant include UV-stabilizer and antioxidant packages. Biomax® Thermal 300 of DuPont is a renewable heat stabilizer that allows PLA thermoformed packaging to withstand elevated temperatures during transport, storage, and use.

Compatibilizers are used to improve the mixing of incompatible polymers. CESA-mix of Clariant is a compatibilizer that enables different polymers to form a homogeneous structure.

Drying/desiccant agents eliminate the need for pre-drying resin before processing, and also help to protect metal tools from oxidation. They are

particularly recommended in applications where high moisture levels negatively influence processability. CESA-dry MB 1 of Clariant is a masterbatch of specific active substances in a polyethylene carrier that can be used to facilitate processing of recycled resins, resins containing biodegradable starch, and other high-moisture-level polymers.

Performance boosters

Plasticizers are added to increase the flexibility of biodegradable biopolymers. Plasticizers are often used to overcome the brittleness of PLA. A number of plasticizers have been tried with appreciable success. Plasticizers reported in the literature [98–101] are citrate esters, 1,2-propylene glycol, glycerol, poly(ethylene glycol), glucose monoesters, and fatty acids. In order to get a film grade PLA, sometimes 20 to 30 wt.% of plasticizers may be needed to achieve the desired flexibility. The major drawback of these plasticizers is their low thermal stability. In long-term use, these plasticizers have the problem of leaching out, which results in embrittlement of PLA. As techniques of application to the field of soft and semi-hard products, various methods that involve adding plasticizers have been proposed. **JP2000302956 A** and **EP1029890 A2** (2000, MITSUI CHEMICALS INC) disclose the addition of glycerin diacetyl monofatty acid esters to a biodegradable biopolymer such as PLA; **EP1728818 A1** (2006, KAO CORP) discloses the addition to biodegradable resins (e.g., PLA, PBS, PBST) of plasticizers such as hardened castor oil-acetylated monoglyceride (GRINDSTED SOFT-N-SAFE), glycerin diacetomonoacaproate, and diacetyl monofatty acid (C₁₂ to C₁₈) glyceride (GRINDSTED ACETEM95CO).

PHB is also brittle. One way to amend its brittleness is through addition of a plasticizer. The common plasticizers reported in the literature [102] are dioctyl phthalate, dioctyl adipate, triacetyl glycerol, and polyadipate. However, these plasticizers do not improve the flexibility of PHB remarkably. They also lower properties of the polymer such as modulus, strength, and gas barrier.

Moldability of starch can be enhanced by additives such as plasticizers, for example glycerol being able to reduce the melting temperature of starch below its decomposition temperature as described in **US5362777 A** (1994, TOMKA I). However, resulting products will be unstable and properties will diminish in time due to migration or even loss of plasticizers during storage and use. Furthermore, products will remain highly water and humidity sensitive.

Nucleating agents promote crystallization during the thermoforming process and improve the heat resistance and mechanical strength of the molding. Typical nucleating agents include talc, boron nitride, calcium carbonate, magnesium carbonate, or titanium oxide.

Impact modifiers improve toughness and reduce brittleness of end products. Biomax[®] Strong 120 of DuPont Packaging is an ethylene copolymer designed to modify PLA for improved toughness properties in packaging and industrial applications without sacrificing product clarity. Similarly, PLAMATE[®] PD-150 of DIC is a modifying agent that improves the flexibility and impact resistance of PLA while at the same time preserving PLA's characteristic transparency. OnCap[™] BIO Impact T of PolyOne is a transparent impact modifier for PLA and is available as a compound, solid, or liquid concentrate. Paraloid[™] BPM-500 of Rohm and Haas is an acrylic PLA impact modifier. Biostrength[®] additives of Arkema include impact modifiers such as Biostrength[®] 280 and Biostrength[®] 150. These are targeted for transparent and opaque applications of PLA. In addition, Terraloy[™] 90000 series masterbatches of Teknor Apex, for use with PLA, increase impact strength 10 to 20 times while providing excellent clarity for flexible and thermoformed packaging, extrusion coating, and food service disposables. The masterbatches are formulated with Biostrength[®] impact modifier from Arkema and carrier polymers consisting of Ingeo[™] PLA from NatureWorks LLC. Teknor Apex recommends adding the masterbatch to PLA resins at 5 to 10% levels.

Colorants, including pigments or dyes, are used to alter the color or improve the aesthetics of the biopolymer. Like other additives, colorants must not be toxic or harmful to the environment. In addition to the traditional colorants, bio-based colorants are now industrially available. The RENOL-compostable product line of Clariant includes masterbatches based on over 80 different pigments that can be incorporated into several biopolymers. The OnColor[™] BIO Colorants of PolyOne are a range of masterbatches based on sustainable materials and can be used with commercially available biodegradable biopolymers including starch, PLA, PHA, PHBV, PBS, PBAT, and their blends. Teknor Color Company has three series of color concentrates for use in PLA and its blends that are suitable for injection molding, extrusion, and blow-molding processes. The three series of colorants differ in terms of their carrier

resins, which are either PLA or polyesters compatible with PLA, and thus are readily blended into it. Ampacet markets a series of color masterbatches, including organic-based pigments from renewable resources, for a broad range of biopolymers. DaniMer also offers a wide range of colorants compounded with PLA.

Light and UV stabilizers are used to protect biopolymers from discoloration and premature degradation by inhibiting initiation of the degradation process via preferentially absorbing incident UV radiation. Typical light and UV absorber stabilizers include benzophenone-type compounds, benzotriazole-type compounds, aromatic benzoate-type compounds, oxalic acid anilide-type compounds, cyanoacrylate-type compounds, hindered amine-type compounds, and the like. PolyOne and Clariant have developed bio-based UV stabilizer masterbatches that protect the contents of transparent biopolymer packaging. The CESA-light UV stabilizers of Clariant include three major classes of UV stabilizers: UV absorbers, nickel quenchers, and hindered amine light stabilizers (HALS).

Heat distortion temperature (HDT) modifiers improve heat deflection of a biopolymer. DaniMer provides a renewable additive that improves the heat deflection of PLA to 88°C (190°F), enabling PLA to provide the performance characteristics for many thermoformed and injection molded articles. This material is not transparent, and will produce some increased opacity, depending upon the percent of additive used. DuPont Biomax[®] Thermal 300 is a heat-stabilizing modifier that allows PLA thermoformed packaging to withstand elevated temperatures. PLA thermoformed packages can be stored shelf-stable, shipped normally, and even reheated in the microwave without deformation.

Coupling agents improve the interaction and compatibility of mixed polymers. Starch and PLA do not have readily reactive functional groups, so their mutual compatibility is poor. To overcome this shortcoming a chemical with isocyanate functional groups, such as methylenediisocyanate (MDI), is reactively blended with the starch and PLA.

Fillers are often added to biodegradable biopolymers to reduce cost. Typical fillers include calcium carbonate (most common), magnesium carbonate, titanium dioxide, talc, and silicon dioxide. Since fillers are generally inorganic, they have the potential to accumulate over time in soil or other disposal environments.

Flame retardants increase fire resistance, typically by reducing the ease with which a polymer burns. However, certain flame retardants, such as halogen compounds, may generate harmful gases during combustion. The environmental hazards and toxicity associated with many of these additives make them less viable candidates in biodegradable biopolymer compositions. Non-halogenated flame retardants are preferable as they do not suffer from these issues. Non-halogenated flame retardant additive materials include inorganic compounds (e.g., metal hydroxides, metal sulfates, metal nitrates, carbonate compounds, tin compounds, titanium compounds, zirconium compounds, and molybdenum compounds), silica compounds, phosphorus compounds, boric acid-containing compounds, organic compounds, and nitrogen compounds.

Anti-fog agents are used to control moisture fogging of the interior surfaces of transparent bio-based packaging. OnCap™ BIO of PolyOne is an additive concentrate range that also includes anti-fog agents.

Anti-slip agents are used to improve stackability by roughening the surface of a biopolymer film, thus reducing its slip properties.

Corrosion inhibitors are added to packaging film to protect the appearance and extend the service life of metal parts and components.

Antimicrobials protect films, fibers, and molded products against bacterial growth, fungi, mold, and mildew.

Several more additives are used by manufacturers and product designers to handle the inherent weaknesses of biopolymers. While most of these additives stabilize biopolymers under various conditions so that they can be used in many applications, they also compromise the biodegradability of a biopolymer.

1.15 Biodegradable Biopolymer Additives

Bio-Tec Environmental developed a different approach towards the use of biopolymers. Instead of forming completely new and different polymer types, Bio-Tec tries to render traditional polymers biodegradable by mixing them with biopolymer additives without adding much cost. The additive is used the same way as a colorant, and is meant to speed up the degradation process. The additive is not supposed to weaken the properties of the polymer in any way, and the degradation process only begins and occurs in an

environment like a landfill or compost. Bio-Tec Environmental's previous product was sold under the trade name Bio-Batch®, which was purchased from ECM Biofilms. With further improvements and refinements, Bio-Batch® has evolved into today's EcoPure®, which is a non-starch-based additive and non-destructive to the environment. EcoPure® is compatible with various types of polymers, including the following: high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), PP, PET, PETG, general purpose polystyrene (GPPS), high impact polystyrene (HIPS), Nylon, PVC, ethylene vinyl alcohol (EVOH), and polycarbonate (PC). The newest formulation, EcoPure® G2, is designed for use with clear PET in applications such as films and bottles. In most applications, EcoPure® can be added to polymers at a ratio of 1 wt.%. EcoPure® requires the action of certain enzymes for the biodegradation process to begin, so polymers containing EcoPure® will never begin to biodegrade during normal use. EcoPure® performs best in anaerobic environments.

US2008103232 A1 (2008, BIO TEC ENVIRONMENTAL LLC) discloses an additive material including a biopolymer that is physically blended with polymeric material to increase the biodegradation of polymers such as LDPE and LLDPE, PP, polystyrene (PS), and other nondegradable polymers. Combining granular starch mixed with polyethylene, together with an unsaturated polymer, a thermal stabilizer, and a transition metal, produces a material with increased susceptibility to photooxidation, thermolysis, and biodegradation. This particular material has an induction time before degradation can be initiated. The use of starch alone in polyethylene, for example, requires large amounts in order to really create an increase in the biodegradation rate.

Addition of starch to polyethylene or polypropylene can render these compositions biodegradable without seriously compromising their effectiveness as a moisture barrier, but such additives do not enable films produced from these compositions to be classified as compostable in accordance with the definition of compostability in such international standards as EN 13432:2000 or ASTM D6400-12.

1.16 Sources of Biopolymers

The source materials for biopolymers include both bio-based materials and fossil fuel-based raw

materials. Biopolymers derived from bio-based materials (bio-based biopolymers) can be produced by biological systems (microorganisms, plants, and animals), or chemically synthesized from biological starting materials (e.g., sugar, starch, etc.). Biopolymers derived from fossil fuel-based raw materials include biodegradable polymers (e.g., PCL, PBS, etc.).

Currently, most bio-based biopolymers are derived from the so-called first-generation feedstock, which includes edible biomass such as sugar, starch, and plant oils, and non-edible sources such as natural rubber, one of the first used biopolymers. The fermentation of sugars derived from crops such as sugarcane and beets, or the hydrolysis of starch derived from crops such as corn, produces ethanol, which can be used as raw material for the production of a wide variety of biopolymers. Other products commercially produced by fermentation are, for example, lactic acid, *n*-butanol, acetone, and even polymers such as polyhydroxyalkanoates. However, there has been concern that biopolymers obtained from edible materials are in direct competition with food and animal feed production. In particular, the production of biopolymers is claimed to have the same disadvantages/side effects associated with

biofuels — increased food costs and deforestation for the creation of extra cultivation fields (see Chapter 10: Economic Evaluation and Environmental Impacts; Section 10.3: Environmental Impacts). This led the biopolymers industry to seek alternative feedstocks that do not compete with food markets in the future. Two categories of feedstock dominate research, namely non-edible biomass, the so-called second-generation feedstock, and alternative sources (see Table 1.16).

Second-generation feedstocks include food waste products and lignocellulose. Food waste products include non-edible, nonfood supplies such as waste cooking oil or fat and waste potato skins. Lignocellulose feedstocks include: (1) short rotation coppice such as willow, poplar, or miscanthus and (2) lignocellulose byproducts such as forestry and agricultural residues (e.g., sugarcane bagasse, sugarcane straw, corn straw, wheat straw and rice straw, corn cobs, and wood kindling). The main components of these materials are cellulose, hemicellulose, and lignin. The hydrolysis of cellulose and hemicellulose by either an acidic or enzymatic route produces various sugars, which are fermented in the presence of various microorganisms, the most important of them being the yeast *Saccharomyces cerevisiae* (WO2008067627 A2,

Table 1.16 Feedstocks for the production of biopolymers

1 st generation (edible and non-edible biomass)			2 nd generation (non-edible biomass)			Other sources
Starch-rich plants	Sugar-rich plants	Oily plants	Lignocellulose (short rotation coppice)	Lignocellulose byproducts	Food byproducts	Natural rubber
Corn	Sugarcane	Sunflower seeds	Willow	Forestry waste (e.g., wood chips)	Waste vegetable oil (e.g., cooking oil)	Microalgae
Potato	Sugar beet	Soybean seeds	Poplar	Agricultural waste (e.g., straw, corn stover, bagasse)	Animal fat (lard tallow, waste grease)	Perennial grasses
Grain	Sweet sorghum		Miscanthus	Paper waste	Potato skins	Jatropha
Rice	Molasses	Rapeseed seeds	Switchgrass	Municipal waste	Spirulina dregs	Greenhouse gas (CO ₂)
		Castor seeds				

2008, BRASKEM SA). The conversion of lignocellulose byproducts into a usable output is more difficult than other types of biomass; the main reason for this is that the protective shield of hemicellulose and lignin that surrounds cellulose has to be broken down, which is a highly energy-intensive process [103]. Second-generation biomass does not provide a higher yield than sugarcane, and is still linked to “food” crop market dynamics. In Brazil, second-generation technologies making optimal use of the biomass generated in sugar farming (conversion of the bagasse into ethanol instead of burning it) are seeing strong growth despite the wide availability of sugarcane. To date, the industry is still in a nascent state, with most second-generation biorefinery plants (using cellulose material) only expected to be ready for large-scale commercial production in a few years [103]. Although the same feedstocks are used for the production of biofuels and biopolymers, there are, however, significant differences between the use of agricultural feedstocks for production of biofuels and biopolymers (see Chapter 10: Economic Evaluation and Environmental Impacts).

Another not widely used technology for reutilization of lignocellulosic materials is the gasification of lignocellulose and its transformation into synthesis gas (a mixture of CO and H₂). Using that process, practically all the carbon content of any form of organic matter can be transformed into carbon monoxide. The synthesis gas is used for the production of methanol, which in turn is used for the formation of olefins such as propylene (see Section 1.2). However, in spite of the numerous developments achieved to date, there is still no commercial unit in operation for the production of synthesis gas from biomass or from reutilization of carbon dioxide, the main reason for this being the high cost of the process as a whole (WO2008067627 A2, 2008, BRASKEM SA).

Galactic has already carried out research on second-generation biomass (lignocellulosic biomass) which consists of redeploying the residual non-edible parts of crops [96].

Nowadays, raw materials employed in the production of lactic acid require the use of “food” crops. First-generation biomass consists of beet and sugarcane, or corn and wheat starch-based glucose. For this reason, third-generation biomass, which is based on microalgae, appears to be the most interesting option.

Alternative sources include the use of third-generation biomass, which is based on microalgae,

for the production of biopolymers. This type of biomass, which is produced in an aquatic environment, has no need for fertile land and provides a high yield per hectare. Nevertheless, it does require the addition of nutrients and a CO₂ source, as well as sunlight. Algae biopolymers were mainly evolved as byproducts of algae biofuel production, where companies were exploring alternative sources of revenue to those from biofuels. Companies active in the field of algae biopolymer research are Cereplast, Dow, and Petro Sun. Cereplast developed a new process, RezInnovationTM, for the production of algae-based biopolymers [104]. Dow partnered with Algenol Biofuels to build a pilot plant that will use algae to convert carbon dioxide emissions into ethanol. The obtained ethanol could replace fossil fuels in the production of ethylene, a feedstock for many polymers [105]. Petro Sun investigated the possibility of using the algae oil produced in its open-pond algae farm as feedstock for the production of biopolymers [106]. While algae-based biopolymers are in their infancy, once commercialized, they are likely to find applications in a wide range of industries. Soley Biotechnology Institute produces biopolymer from *Spirulina dregs*. The company utilizes this dreg, which is left as a byproduct when extracting useful products from *Spirulina* [107]. Representative patents on algae-based biopolymers are the following: **US4078331 A** (1978) and **US4236349 A** (1980, MOBIL OIL CORP), and **US2010272940 A1** (2010, KIMBERLY-CLARK WORLDWIDE INC).

Biopolymers are also being produced from a greenhouse gas itself, namely CO₂. Novomer, Inc. (USA) and SK Energy Co., Ltd. (SK) are commercializing polymers made from carbon dioxide, namely polypropylene carbonate (see Section 1.2).

1.17 Applications and Parts

The fields of application for biopolymers are increasing steadily. Biopolymer applications are characterized either by biodegradability or by sustainability or both. Today, biopolymers can be found mainly within the following market segments:

- Service packaging (e.g., films, bags, containers, etc.).
- Food services (e.g., cups, trays, cutlery, bottles, etc.).

- Agriculture/forestry/horticulture (e.g., mulch films, temporary replanting pots, delivery systems for fertilizers and pesticides, etc.).
- Fishery (fishing lines and nets, fishing hooks, fishing gear, etc.).
- Consumer electronics (mobile phone casings, laptops, etc.).
- Automotive industry (e.g., interior trim, spare tire covers, etc.).
- Textiles/fibers (carpets, clothing, upholstery, etc.).
- Medical/pharmaceutical sector (e.g., medicines, sutures, implants, etc.).
- Cosmetics.
- Outdoors sports.
- Building/construction industry.

More markets are starting to use biopolymers, such as the building and construction industry, while existing ones continue to expand the range of products made from biopolymers. Products that show high growth rates are, among others, bags, catering products, mulch films, and food/beverage packaging. Biopolymers are mostly available in the form of flexible films (packaging films, waste bags, mulch films) and rigid hollow moldings (bottles and containers). Both categories can have a single- or multilayered structure. Most of the applications of biopolymers have already been mentioned in the tables accompanying the analysis of each biopolymer family.

1.17.1 Service Packaging

Biopolymers have been used broadly in packaging. Starch-based biopolymers are the most commonly used biopolymers for biodegradable packaging. Starch accounts for a 50% share of biodegradable packaging globally in 2007. Starch-based polymers are commonly used in biodegradable packaging such as compostable bags, consumer goods packaging, and fresh food packaging for fruits, vegetables, and bakery products. They are also used in disposable packaging for the food service industry. Starch is followed by PLA, which accounts for a 40% share by volume [108]. PLA dominates the fresh food packaging sector. The rapid capacity expansion of this polymer is set to boost the growth of its biodegradable packaging applications. Other polymers,

such as PHA and polyesters, account for the remaining 10% share.

The last few years have witnessed several breakthroughs in bio-packaging. New biopolymers are now available, such as bio-polyethylene (bio-PET). Several bio-packaging products exhibit properties such as high sealability, “soft-touch,” good breathability, good thermal stability, good puncture resistance, great clarity, toughness, high tear resistance, and also water, oil, and fat protection; these products can be bio-based and/or biodegradable [109].

Here is an overview of some recent products in service bio-packaging [110]:

- Aldi bags made from Ecovio® (Aldi /BASF).
- Compostable BIOSHRINK® film for beverages; made from renewable resources (Alesco).
- Compostable films for fruits and vegetables (Alesco).
- Compostable bag made from Mater-Bi® (Unicoop Florence/Novamont).
- Kitchen tidy bag (Cardia Bioplastics).
- Flower wrapping made from Bio-Flex® A 4100 CL (FKuR).
- Sugarcane bag (Lidl GmbH, Austria).
- Baby diapers made from PLA (W.I.P.).

1.17.2 Food Services

Food-related applications include beverage bottles, containers, cups, disposable tableware, and packaging. In 2007, 65% of bio-based biopolymers were used in packaging and food-related applications. In 2025 it is estimated that this share will shrink to just 40% because automotive and electronics applications, which have a higher profit potential than the packaging and food industries, are expected to profit and gain a higher market share, potentially reaching over 25% [108].

Here is an overview of some recent biopolymer-based products in food packaging [111]:

- Coca-Cola PlantBottle™ with 30% renewable content.
- Coca-Cola PlantBottle™ by DASANI® and Odwalla® with 100% renewable content.

- Compostable NatureFlex™ bread bags (Innovia Films).
- Twinings teabags wrapped in compostable NatureFlex™ film (Innovia Films).
- Innovative cereal bag uses compostable NatureFlex™ film as part of the packaging (Innovia Films).
- Boulder Canyon™'s potato chip package incorporates metallized NatureFlex™ NKM (Innovia Films).
- Sonnentor herbs and spices packed in high-barrier NatureFlex™ film (Innovia Films).
- Quality Street® wrappers go compostable with NatureFlex™ colored film (Innovia Films).
- Mister Nut Bio products from New Factor wrapped in high-barrier NatureFlex™ (Innovia Films).
- Confectionery manufacturer Thorntons Melts brand wrapped in metallized NatureFlex™ film (Innovia Films).
- 90% of Sainsbury's organic fresh produce is available in compostable, recycled, or recyclable packaging using Amcor's NaturePlus compostable film (Amcor/Sainsbury).
- Belgian Delhaize supermarkets use NatureWorks® PLA packaging (NatureWorks LLC).
- Compostable deep-freeze packaging from McCain (McCain).
- Swiss chocolate range features cornstarch-based Plantic® tray (Marks&Spencer).
- Leclerc uses cookie trays made from Ingeo™.
- PLA trays with lids (Natura).
- Organic pasta packaged in biopolymers based on cellulose (Birkel).
- Noble Orange Tangerine Juice bottle made from Ingeo™ (Blue Lake Citrus Products).
- Sant'Anna mineral water uses bottles made from Ingeo™ (Sant'Anna — Fonti di Vinadio).
- Heinz® PlantBottle™ ketchup (NatureWorks LLC).
- BioWare single-use cold drink cups made from NatureWorks® PLA (Huhtamaki).
- BioNet compostable net tubing made from a starch-based material for produce and seafood packaging (BioPak).
- Starch-based forks (Novamont).

1.17.3 Agriculture/Forestry/Horticulture

Biodegradable biopolymers are making rapid advances in the agriculture and horticulture sectors. Mulch films and flowerpots made of decomposable biopolymers are the most successful products because of their adjustable lifespan and the fact that these materials do not leave residues in the soil. This helps reduce work and cost as these products can simply be left to decompose, after which they are plowed into the soil. Plant pots used for flowering and vegetable plants can be composted along with gardening and kitchen litter.

Other applications of biopolymers in agriculture and horticulture include: yarns, tapes, and clips made of biodegradable biopolymers that are used to secure high-growing plantations. Compostable seed belts and active component capsules made out of biopolymers have also proven to be beneficial. Additionally, biodegradable foils and nets are used for farming/growing mushrooms and the coating of tree and bush-roots. Foils, yarns, and nets made out of biopolymers help to secure freshly created slopes and mounds and protect them from erosion until the roots of the plants have developed sufficiently [112,113].

Here is an overview of some recent biopolymer-based products in agriculture and horticulture:

- BioFoam® molded trays for horticultural applications (Synbra).
- Biodegradable mulch films (BASF).
- Biodegradable plant pot (Limagrain).

1.17.4 Consumer Electronics

Nowadays components and accessories of a large proportion of consumer electrical appliances are made of biopolymers or biocomposites. Biocomposites include materials containing a biopolymer in conjunction with structural reinforcement materials such as carbon, plant, or wood fiber.

Here is an overview of some recent biopolymer-based products in consumer electronics [114]:

- NEC has developed PLA/carbon fiber and PLA/Kenaf biocomposites with enhanced heat conductivity and strength for use in mobile phone and computer casings.
- Samsung's mobile phone Samsung Reclaim™; 40% of the casing is made from biopolymers.

- Fujitsu's new computer keyboard is made from FKUR's Biograde[®], and the palm rest is made from Tecnaro's Arboform[®].
- Fujitsu's biodegradable mouse uses FKUR's Biograde[®].
- Michael Young (UK) and EOps have developed the EOps Noisezero i+ Eco edition. It uses corn-starch biopolymer for the earbuds and the microphone housing.
- Ventev[™] Element Case is made from 100% Naturacell[™], a natural, renewable, wood pulp-based material.
- Bioserie bioplastic iPhone 3G/3GS BioCover, the world's first fully bio-based bioplastic iPhone accessory. Product consists of a unique blend of biodegradable and environmentally friendly components (100%), all derived from plants and annually renewable natural resources.
- Biodegradable iPhone case cover, iNature, is made from APINAT[®] (Biomood and Med Computer); composition of APINAT[®] is proprietary, but is believed to be based on TPU and aliphatic copolyester.
- Drum cover of Fuji Xerox Copy Machine.
- Biomass plastic with plant-based content of more than 50 wt. %.
- Bio-based parts of printers and MFPs (Oki Data Corporation, using PLA).
- Bio-based polyamide (PA 11) for the terminal cover on the back of an ultra-slim OLED TV (Sony Corporation).

1.17.5 Automotive Industry

The automotive industry is a sector of bulk plastics users that has high-performance specifications. Automotive components that incorporate bio-based materials have been used by many automobile manufacturers around the world, including Audi, BMW, Chrysler, Fiat, Ford, General Motors, Honda, Mazda, Mercedes Benz, Opel, Peugeot, Renault, Toyota, Volkswagen, and Volvo [115].

In the 1930s, Henry Ford used bio-based materials (soybeans, hemp, wood pulp, cotton, flax, and ramie) in the production of vehicle parts and components, and in 1941 Ford unveiled a prototype car that had plastic body panels made of 70% hemp fibers, 30% phenolic resins, and were extended with soybean

meal. The use of bio-based materials in car components again gained traction in the 1990s. Toyota was the first to develop biopolymers in 1999, and four years later it started selling car accessories made from these materials. It employed biopolymers in the cover for the spare tire in the Raum, a car model that was launched in 2003. In 2008 Toyota announced plans to replace 20% of the polymers used in automobiles with bio-based biopolymers.

Here is an overview of some recent biopolymer-based products in the automotive industry:

- Toyota designed a floor mat made from 100% PLA, and a spare tire cover made from PLA and kenaf fibers. Toyota has adopted DuPont's Sorona[®] EP partially renewably sourced polymer as material for the ceiling surface skin, sun visor, and pillar garnish of its new SAI model. DuPont's Sorona[®] fibers also were selected as materials for optional Toyota floor mats. In addition, Toyota's new hybrid vehicle, Prius Alpha, also has parts (instrument panel air-conditioning system outlet) made of Sorona[®].
- Biocomposites can be found in the radiator end tank of the 2010 Toyota Camry sedan. The part was jointly developed in collaboration between Toyota, DENSO, and DuPont Automotive. This part is injection molded from a 30% short glass-reinforced blend of DuPont's Zytel[®] RS polyamide 1010 matrix. About 40% of the resin bio-based monomers are derived from castor beans. The Camry's radiator end tanks have to withstand the extreme environment in the engine compartment, and they are a compelling illustration of the fact that biopolymers can meet demanding mechanical, thermal, and chemical requirements. Several Lexus models (e.g., CT200H and ES 300) use bio-based biopolymers with kenaf and bamboo fiber reinforcements for interior components such as the luggage compartment, package shelves, floor mats, etc.
- Ford uses soy-based seating foam in all of its North American vehicles; the Ford Escape has a soy-based headliner. The European Ford Fiesta was the first vehicle to use corn-based Goodyear tires [115].
- Fiat has used castor oil-derived polyamides and soya-derived polyurethanes to replace their

fossil fuel-derived equivalents in several vehicle models. Fiat cars designed for Brazil contain polyurethane seat foams with about 5% soy-polyol. In 2011, its use of DuPont's Zytel® RS polyamide 1010 in some diesel fuel lines won the Automotive Innovation Award in the environmental category from the United States and Europe-based Society of Plastics Engineers.

- Mazda's Premacy Hydrogen RE Hybrid vehicle uses bio-based car seat fabrics made from BIOFRONT® fibers, a heat-resistant stereo-complex PLA (50/50 L- and D-lactide blend) (Teijin and Mazda) [109].
- Fiat's Phylla™ solar car has parts that integrate bio-based polymers. It integrates an aluminum-based structure, while exterior components are made from bio-based materials supplied by Novamont. Furthermore, the Phylla™'s tires are made from vegetable-based renewable resources that are used to replace silica and carbon black of conventional tires.
- Motive announced the development of Canada's first biocomposite-bodied electric vehicle, the Kestrel.

1.17.6 Textiles/Fibers

In the sectors of fabrics and furnishings, the biopolymer products that are being heavily promoted are Ingeo™ (NatureWorks LLC) and Sorona® (DuPont), both PLA-based fibers with a growing share of the fabric market; and soy-based foam for upholstery.

Here is an overview of some recent biopolymer-based products in textiles/fibers [116]:

- UNITIKA travel luggage made from Rilsan® fiber, Arkema's new grade of 100% renewably sourced PA 11.
- Calvin Klein Golf Jacket made from Sorona® polymer (DuPont).
- MobileEdge has incorporated Sorona® into their ScanFast™ 2.0 Collection of laptop bags; Sorona® contains 37 wt.% annually renewable plant-based material.
- SmartStrand Carpet made from Sorona® polymer (DuPont).
- Gattinoni Wedding Dress made from Ingeo™ (NatureWorks® PLA).

- Sofa fabric made from 100% BIOFRONT® PDLLA (Teijin and Tango Chirimen).
- Eco2Punch® carpets made from fiber based on NatureWorks® PLA (75/25 blend) (Sommer Needlepunch).

1.17.7 Medical and Pharmaceutical Sectors

Biopolymers have found very relevant and practical uses in the medical and pharmaceutical sectors, beginning with the biodegradable sutures first approved in the 1960s. Since that time, diverse products based on PLA and PGA and other materials, including PDS, PTT, and PCL, have been used as medical devices. Nowadays, the list of biopolymers used for medical and pharmaceutical purposes has been enriched with more "exotic" biopolymers, such as polyanhydrides, POEs, PPHOSs, and the like.

The very instability of these polymers, which leads to biodegradation, has proven to be important in medical applications. An orthopedic fixation device made from a biodegradable biopolymer that can be used as an implant will not require a second surgical intervention for removal. Besides eliminating the need for a second surgery, the biodegradation may offer other advantages. A fractured bone that has been fixated with a rigid implant prepared from a biodegradable biopolymer can be engineered to degrade at a rate that will slowly transfer load to the healing bone. On the other hand, a fractured bone that has been fixated with a stainless steel implant has a tendency for refracture upon removal of the implant. Because the stress is borne by the rigid stainless steel, the bone has not been able to carry sufficient load during the healing process.

Sutures are the major area of application for biodegradable biopolymers in the medical devices market. Other applications include staples, biodegradable screws, rods for pinning and repairing ligaments, orthopedic moldings, cardiovascular applications, and intestinal supports [117]. Biodegradable biopolymers also form the basis for drug delivery, either as a drug delivery system alone, or in dual function as a medical device.

Biodegradable biopolymers also have use in dental applications. Porous biopolymer particles are packed into the cavity of an extracted tooth to assist in quicker healing. A guided tissue regeneration barrier membrane formed from a biodegradable biopolymer

keeps unwanted gum tissue away from the tooth and underlying bone, which permits undisturbed regrowth of new bone, and thus additional tooth stability [117].

1.17.8 Cosmetics

The continuing growth of biopolymers is driven by a variety of industries, including the cosmetics and health care sectors, which use a lot of fast-moving goods. The cosmetics industry is testing and perfecting packaging made from biopolymers. Cosmetics place very high demands on packaging materials, but there is still a call for more sustainability and an increased use of biopolymers.

Here is an overview of some recent biopolymer-based products used in cosmetics:

- Body care packaging made from EarthFirst® PLA (Sidaplast).
- Haircare packaging film made from EarthFirst® PLA (Sidaplast).
- NatureWorks Cargo lipstick made from 100% Ingeo™ (Cargo Cosmetics).
- Cosmetic Bag made from Bio-Flex® (FKuR).
- Cosmetic pen made from Biograde® C 7500 CL (FKuR).
- Laundry olive oil soap “Ecolive” wrapped in fully compostable Bio-Flex® (FKuR and Umbria Olii International).
- Impact Zero face & body lotion in PLA Bottle (Eudermic and NatureWorks).
- Pantene V shampoo and conditioner bottles primarily made from bio-based PET (Procter & Gamble and Braskem).

1.17.9 Outdoor Sports

Outdoor sports and the environment are naturally intertwined, and the use of bio-based biopolymers in sporting goods has gotten a positive reception by the general public. In combination with the prerequisites of the sports market, such as high growth rates, high willingness to pay, and high material cost-insensitivity, the applications of bio-based biopolymers in sporting equipment and apparel are increasing [118].

Here is an overview of some recent biopolymer-based sports products [118]:

- The Hurricane ski boot from Scarpa and the Renu ski boot from Atomic use Arkema’s bio-based thermoplastic elastomer (TPE) Pebax® Rnew, cotton, and bamboo.
- Wave® Technology plates in four models of Mizuno’s running shoes, and the FIFA soccer ball from Sony, contain Arkema’s Pebax® Rnew.
- Evolve snow goggles from Smith Optics use Merquinsa’s Pearlthane® ECO, a bio-based TPU that contains 20–90% Cerenol™ bio-polyol from DuPont.
- Ghost ski boots made from Hytrel® RS (Salamon and DuPont).
- Trekking poles made from APINAT® (API Spa and FIZAN).
- Green Silence running shoes and BioMoGo midsoles from Brooks Sports use DuPont’s Hytrel® RS.

1.17.10 Building/Construction Industry

The building and construction industry is among the new markets that have started to use biopolymers.

Here are some recent biopolymer-based building and construction products:

- Fischer wall plugs made of renewably sourced DuPont’s Zytel® RS polyamide 1010 (PA 1010) have consistently shown the same retaining values as the conventional UX universal plugs (Fischerwerke GmbH & Co. KG).
- Tricoya® technology for wood/plastic composites (INEOS and Accsys).

1.17.11 Other Applications of Biopolymers

Here is an overview of some as yet unclassified applications of biopolymers [109]:

- Bioplastic-based contactless IC card (e-money or security card) from Sony Corporation (FeliCA™, based on PLA).
- Bio-sourced smart cards (Gemalto Unveils).
- Wire and cable using bio-based Zytel® polyamides and bio-based Hytrel® RS poly(ether ester) thermoplastic elastomer (DuPont).

- High-performance cables using VESTAMID Terra DS bio-based polyamide 1010 (PA 1010) (Evonik).
- Eyeglass frames made from BIOFRONT® PDLLA grades (Teijin and Tanaka Foresight Inc.).
- 3D glasses for movie theaters (Oculus3D using Cereplast PLA based on Ingeo™ grades).
- Tectubes' biodegradable toothpaste tube made from FKUR's bioresins.
- Components for Nordic walking stick based on renewably sourced DuPont's Zytel® RS Polyamide 610 (PA 610). Parts include the hand grip, tip, cap, and interlocking elements of the new "Exel NW Trainer" Nordic walking stick designed by the Austrian plastic converter Metall und Plastikwaren Putz GmbH and commercialized by the German company Exel Sports Brands GmbH (ESB).
- Bioverse's innovative biodegradable system for water treatment. The product consists of a submersible, plastic-enclosed water treatment system for stagnant pools and golf course ponds. The material is a Mirel™ grade supplied by Metabolix, Inc. (i.e., a polyhydroxyalkanoate, PHA).
- Bio-based solar panel backsheet for Si-based photovoltaic solar cells (BioSolar).
- Biodegradable key fob and trolley tokens made from APINAT® (Publsearch S.r.l.).
- Soy-based foam for quilted top layer mattresses (Denver Mattress) using BioFlex™ hybrid foam produced by Flexible Foam Products, Inc. This product is molded using a patented process called EnviroFlex™ technology and Cargill BiOH® soy-based polyol.

1.18 Sources of Scrap and Waste Biopolymers

Most disposed biodegradable items come from the food service and health care sectors. Food service items include products such as bottles, utensils, plates, cups, trays, cup holders, napkins, tablecloths, towels, toothpicks, straws, and sticks. They also include infant food service items such as nipples, baby bottles, bottle liners, teething rings, and pacifiers.

Health care items include products used in providing medical, dental, or veterinarian care, such as gloves, medical tubing (intravenous tubing, airways, catheters, shunts, drains, dialysis tubing, and parenteral feeding tubing), blood pressure cuffs, clothing elastic, face masks, sutures, anesthesia mouthpieces, toothbrushes, toothpicks, dental floss, dental bite blocks, dental cofferdams, dental retainers, mouth guards, respirator bellows, adhesive tape, bandages, sheets, pads, bed items (sheets, pillowcases, towels, washcloths, and foam mattress pads), waste bags, enema bags and tips, intravenous fluid bags, syringes, bedding items, and mixtures thereof. Hospital or other medical waste is hazardous to public health and requires special treatment before disposal. Incineration is the method of choice for most hazardous health care wastes and is still widely used. If a municipality or medical authority genuinely lacks the means to treat wastes before disposal, the use of a landfill is regarded as an acceptable disposal route.

Waste material also originates from agricultural, forestry, fishery, civil engineering, construction, and automotive articles made from biopolymers.

Another important source of waste biopolymers are postindustrial residues, including: (1) sprues, runners, and selvages left behind during molding and production processes; (2) off-grades formed by polymerization reactions and not meeting the standard requirements; and (3) rejected articles (see Chapter 3: Reuse).

Waste biopolymers can be collected from producers and end-users. The option of collecting waste biopolymers from industries is preferred since they generate large amounts of them. These represent a particularly advantageous source of "clean" waste biopolymers available in large quantities. The option of collecting from end-users is practiced by some companies that specialize in collecting waste biopolymers from large events such as football matches and festivals. Large streams of biopolymer waste are produced during these events from cups, bottles, and fast food boxes. Currently, most of these wastes either end up in the waste bins and find their way to landfill or, at best, are delivered to a composting waste processing company. The process for postconsumer wastes is the most complex since it involves collecting and separating the targeted biopolymer(s) from other visually similar polymers (see Chapter 5: Physical Recycling).

In Europe, the Belgian company Galactic (www.lactic.com) developed the LOOPLA® concept to

provide an end-of-life option for PLA wastes. LOOPLA® also offers the possibility of going directly back to the original monomer lactic acid by PLA hydrolysis. Galactic collects discarded items from a variety of postconsumer and postindustrial PLA residue sources and transports them to its facilities to start the LOOPLA® recycling process. PLA is separated from PET (with which it is often mixed). This minimizes the effects on PET recycling yield and quality, and also helps in recovering a single stream of PLA for recycling. There are technical solutions, including near-infrared (NIR) installations, that are able to effectively separate PLA and PET from mixed waste. According to the InnovativeIndustry.net blog, it has not been reported whether this sorting method is already installed, or if the LOOPLA® concept still depends on the end-user's awareness of the importance of sorting waste to recover PLA [119].

In the United States, BioCor LLC (<http://biocor.org>) buys postconsumer PLA, and in cooperation with Plarco, Inc., converts it back into its original lactic acid feedstock for subsequent use in a variety of existing end markets. BioCor LLC has created an optical sorting machine able to detect and sort PLA from PET or HDPE at high speeds. The company intends to buy all postindustrial and postconsumer products made of PLA, such as water bottles, juice bottles, clamshells, cups, cutlery, and several other products. To date, BioCor LLC, in cooperation with Plarco, Inc., has converted over 20 million pounds of postindustrial PLA back into its lactic acid feedstock. NatureWorks LLC is a minority stakeholder in BioCor LLC, and has agreed to purchase all the lactic acid made by Plarco, Inc. and use it to produce PLA resin.

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2 Definitions and Assessment of (Bio)degradation

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2.1 Define the Terms

In the literature and patents there is no consensus over the exact definition of the generic terms “degradable,” “biodegradable,” “bio-based,” “compostable,” and “biopolymer,” which appear to have multiple and overlapping meanings.

“Degradable” is a broad term applied to polymers or plastics that disintegrate by a number of processes, including physical disintegration, chemical degradation, and biodegradation by biological mechanisms. As a result of this definition, a polymer may be degradable but not biodegradable.

“Biodegradable” is a term focused on the functionality of a polymer, “biodegradability,” and is applied to polymers that will degrade under the action of microorganisms within a specific period of time and environment. On its own, the term “biodegradable” has no clear meaning and can create confusion. According to the withdrawn American Society for Testing and Materials (ASTM) standard ASTM D5488-94de1, biodegradable polymers refer to polymers that are

“capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms that can be measured by standard tests, over a specific period of time, reflecting available disposal conditions.”

The Japan Bioplastics Association (JBPA) defines the term “biodegradability” as the characteristics of a material that can be microbiologically degraded to the final products of carbon dioxide and water, which in turn are recycled in nature. Biodegradation should be distinguished from disintegration, which simply means the material is broken into small, separate pieces. Biodegradability of plastics is determined by ISO methods and evaluated based upon pre-established criteria. Only biodegradable plastics that meet these rigorous criteria, such as contents of heavy metals and safe intermediate reaction products, may be classified as GreenPla[®] [1].

Biodegradable polymers are certified according to any of the following legally binding international

standards (see Chapter 9: Regulatory Aspects Framework; Section 9.2: Certification):

ISO 17088:2012

EN 13432:2000, EN 14995:2006

ASTM D6400-12

“Bio-based” is a term focused on raw materials, and it is applied to polymers derived from renewable resources. Raw materials are defined as renewable if they are replenished by natural procedures at rates comparable or faster than their rate of consumption [2].

Bio-based products as defined by the Farm Security and Rural Investment Act of 2002 (FSRIA) [3] are products determined by the US Secretary of Agriculture to be “commercial or industrial goods (other than food or feed) composed in whole or in significant part of biological products, forestry materials or renewable domestic agricultural materials, including plant, animal or marine materials.” [4] ASTM defines a bio-based material as “an organic material in which carbon is derived from a renewable resource via biological processes. Bio-based materials include all plant and animal mass derived from CO₂ recently fixed via photosynthesis, per definition of a renewable resource.” In practical terms a bio-based polymer is not *per se* a sustainable polymer. This depends on a variety of issues, including the source material, production process, and how the material is managed at the end of its useful life. Not every bio-based polymer is biodegradable (e.g., bio-based polyethylene or polyamide 11) and not every biodegradable polymer is bio-based (e.g., poly(ε-caprolactone) or polyglycolide), although some fall into both categories, such as polyhydroxyalkanoates (PHAs).

Currently there are no standards on what can be called a “bio-based product.” However, there are objective ways to quantify the bio-based content of a product. ASTM and ISO have developed standards for measuring the bio-based content of materials via carbon isotope analysis. Relevant standards include: ASTM D6866-12 and ASTM D7026-04.

The bio-based content of a biopolymer can be determined by calculating the number of carbon atoms that come from the short CO₂ cycle, that is, from biomass as raw material. It is known in the art that carbon-14 (¹⁴C), which has a half-life of about

5700 years, is found in bio-based materials but not in fossil fuels. Thus, “bio-based materials” refer to organic materials in which the carbon comes from non-fossil biological sources. The detection of ¹⁴C is indicative of a bio-based material. ¹⁴C levels can be determined by measuring its decay process (disintegrations per minute per gram carbon, dpm/gC) through liquid scintillation counting. A bio-based PET comprises at least about 0.1 dpm/gC of ¹⁴C (see also Section 2.5: (Bio)degradation Testing).

“Compostable” polymer was defined by ASTM D6002 as “a plastic which is capable of undergoing biological decomposition in a compost site as part of an available program, such that the plastic is not visually distinguishable and breaks down to carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with known compostable materials (e.g., cellulose) and leave no toxic residue.” However, this definition drew much criticism, and in January 2011, ASTM withdrew standard ASTM D6002 (see Chapter 9: Regulatory Aspects Framework; Section 9.1: Standards).

In order for a polymer to be called compostable, it should meet any of the following international standards:

ASTM Standard D6400 (for compostable plastics) or D6868 (for compostable packaging).

CEN standard EN 14995:2006 (for compostable plastics) or EN 13432:2000 (for compostable packaging).

ISO 17088:2012.

The standards ISO 17088:2012 and ASTM D6400 describe the same check scheme as EN 13432:2000. The ISO Standard not only refers to plastic packaging but to plastics in general.

A polymer that meets the requirements of any of these standards also has the following characteristics: (1) disintegrates rapidly during the composting; (2) biodegrades quickly under the composting conditions; (3) does not reduce the value or utility of the finished compost and the compost can support plant life; and (4) does not contain high amounts of regulated metals or any toxic materials.

The difference between biodegradable polymers and compostable polymers is determined by the rate of biodegradation, disintegration, and toxicity. All compostable polymers are by default biodegradable, but not vice versa.

Two different criteria underline the definition of a “biopolymer” (or “bioplastic”): (1) the source of the raw materials; and (2) the biodegradability of the polymer. A differentiation can be made between three types of biopolymers:

- (a) Biopolymers that are made from renewable raw materials (bio-based) and are biodegradable.
- (b) Biopolymers that are made from renewable raw materials (bio-based) and are not biodegradable.
- (c) Biopolymers that are made from fossil fuels and are biodegradable.

The biopolymers of (a) can be produced by biological systems (microorganisms, plants, and animals), or chemically synthesized from biological starting materials (e.g., corn, sugar, starch, etc.). Biodegradable bio-based biopolymers include: synthetic polymers from renewable resources, such as polylactide (PLA); biopolymers produced by microorganisms, such as PHAs; and naturally occurring biopolymers, such as starch or proteins. Natural polymers are by definition those which are biosynthesized by various routes in the biosphere. The most used bio-based biodegradable polymers are starch and PHAs.

The biopolymers of (b) can be produced from biomass or renewable resources and are non-biodegradable. Non-biodegradable bio-based biopolymers include: (1) synthetic polymers from renewable resources such as specific polyamides from castor oil (polyamide 11), specific polyesters based on bio-propanediol, biopolyethylene (bio-LDPE, bio-HDPE), biopolypropylene (bio-PP) or biopolyvinylchloride (bio-PVC) based on bio-ethanol (e.g., from sugarcane), etc.; and (2) naturally occurring biopolymers such as naturally rubber or amber.

The biopolymers of (c) are produced from fossil fuel, such as synthetic aliphatic polyesters made from crude oil or natural gas, and are certified biodegradable and compostable. Poly(ϵ -caprolactone) (PCL), poly(butylene succinate) (PBS), and certain “aliphatic-aromatic” copolyesters are at least partly fossil fuel-based polymers, but they can be degraded by microorganisms.

According to European Bioplastics, a plastic material is defined as a bioplastic if it is either bio-based, biodegradable, or features both properties [5]. On the basis of this definition biopolymers or bioplastics consist of either biodegradable polymers (e.g., polymers of type (a) or (c)) or bio-based polymers (e.g., polymers of type (a) or (b)).

Table 2.1 Biodegradable vs. bio-based polymers

	Biodegradable	Non-biodegradable
Bio-based	CA, CAB, CAP, CN, PHB, PHBV, PLA, starch, chitosan	PE (LDPE), PA 11, PA 12, PET, PTT
Partially bio-based	PBS, PBAT, PLA blends, starch blends	PBT, PET, PTT, PVC, SBR, ABS, PU, epoxy resin
Fossil fuel-based	PBS, PBSA, PBSL, PBST, PCL, PGA, PTMAT, PVOH	PE (LDPE, HDPE), PP, PS, PVC, ABS, PBT, PET, PS, PA 6, PA 6.6, PU, epoxy resin, synthetic rubber

Abbreviations: ABS, Acrylonitrile butadiene-styrene; CA, Cellulose acetate; CAB, Cellulose acetate butyrate; CAP, Cellulose acetate propionate; CN, Cellulose nitrate; HDPE, High density polyethylene; LDPE, Low density polyethylene; PA 6, Polyamide 6; PA 6.6, Polyamide 6.6; PA 11, Amino-undecanoic acid-derived polyamide; PA 12, Laurolactam-derived polyamide; PBAT, Poly(butylene adipate-co-terephthalate); PBS, Poly(butylene succinate); PBSA, Poly(butylene succinate-adipate); PBSL, Poly(butylene succinate-co-lactide); PBST, Poly(butylene succinate-co-terephthalate); PBT, Poly(butylene terephthalate); PCL, Poly(ϵ -caprolactone); PE, Polyethylene; PET, Poly(ethylene terephthalate); PGA, Polyglycolide; PHB, Polyhydroxybutyrate; PHBV, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PLA, Polylactide; PP, Polypropylene; PS, Polystyrene; PTMAT, Poly(methylene adipate-co-terephthalate); PTT, Poly(trimethylene terephthalate); PVOH, Poly(vinyl alcohol); PVC, Poly(vinyl chloride); PU, Polyurethane; SBR, Styrene-butadiene rubber.

Therefore, a biopolyethylene derived from sugarcane, nicknamed “green polyethylene,” is non-biodegradable, but emits fewer greenhouse gases when compared to fossil-based polyethylene. It is classified as a biopolymer. The interrelationship between biodegradable polymers and bio-based polymers is shown in Table 2.1. To summarize: “Biopolymers are defined as polymers that are derived from renewable resources, as well as biological and fossil-based biodegradable polymers.”

2.2 Classification of Biopolymers

In Chapter 1: Introduction to Biopolymers; Section 1.2: Types of Biopolymers, biopolymers were classified according to the chemical nature of their backbone. Biopolymers can also be divided into

Table 2.2 Classification of biopolymers

Biodegradable				Non-biodegradable
Bio-based			Fossil-based	Bio-based
Plant	Microorganisms	Animal		
Cellulose and its derivatives [†] (polysaccharide)	PHAs (e.g., P4HB, PHB, PHBH, PHBHx, PHBV)	Chitin (polysaccharide)	Poly(alkylene dicarboxylate)s (e.g., PBA, PBS, PBSA, PBSE, PEA, PES, PESE, PESA, PPF, PPS, PTA, PTMS, PTSE, PTT)	PE (LDPE, HDPE), PP, PVC
Lignin	PHF	Chitosan (polysaccharide)	PGA	PET, PPT
Starch and its derivatives (monosaccharide)	Bacterial cellulose	Hyaluronan (polysaccharide)	PCL	PU
Alginate (polysaccharide)	Hyaluronan (polysaccharide)	Casein (protein)	PVOH	PC
Lipids (triglycerides)	Xanthan (polysaccharide)	Whey (protein)	POE	Poly(ether-ester)s
Wheat, corn, pea, potato, soy, potato (protein)	Curdlan (polysaccharide)	Collagen (protein)	Polyanhydrides	Polyamides (PA 11, PA 410, PA 610, PA 1010, PA 1012)
Gums (e.g., <i>cis</i> -1,4-polyisoprene)	Pullulan (polysaccharide)	Albumin (protein)	PPHOS	Polyester amides
Carrageenan	Silk (protein)	Keratin, PFF (protein)		Unsaturated polyesters
PLA (from starch or sugarcane)		Leather (protein)		Epoxy
				Phenolic resins

Abbreviations: HDPE, High density polyethylene; LDPE, Low density polyethylene; P4HB, Poly-4-hydroxybutyrate; PBA, Poly(butylene adipate); PBS, Poly(butylene succinate); PBSA, Poly(butylene succinate-adipate); PBSE, Poly(butylene sebacate); PC, Polycarbonate; PCL, Poly(ϵ -caprolactone); PE, Polyethylene; PEA, Poly(ethylene adipate); PES, Poly(ethylene succinate); PESA, Poly(ethylene succinate-co-adipate); PESE, Poly(ethylene sebacate); PET, Poly(ethylene terephthalate); PFF, Poultry feather fiber; PGA, Polyglycolide; PHA, Polyhydroxy alkanoate; PHB, Polyhydroxybutyrate; PHBHx, Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); PHBV, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PHF, Polyhydroxy fatty acid; PHH, Poly(3-hydroxyhexanoate); PLA, Polylactide; POE, Poly(ortho ester); PP, Polypropylene; PPF, Poly(propylene fumarate); PPHOS, Polyphosphazenes; PPS, Poly(propylene succinate); PTA: Poly(tetramethylene adipate); PTMS, Poly(tetramethylene succinate); PTSE, Poly(tetramethylene sebacate); PTT, Poly(trimethylene terephthalate); PVC, Poly(vinyl chloride); PVOH; Poly(vinyl alcohol); PU, Polyurethane.

[†]Acetyl cellulose (AcC) is either biodegradable or non-biodegradable, depending on the degree of acetylation. AcCs with low acetylation can be degraded, while those with high substitution ratios are non-biodegradable.

two broad groups, namely biodegradable and non-biodegradable biopolymers. Alternatively, biopolymers can be classified according to their origin as being either bio-based or fossil fuel-based. The bio-based biopolymers can be produced from plants, animals, or microorganisms. There are many more

non-degradable bio-based biopolymers than there are biodegradable bio-based biopolymers [2].

Table 2.2 presents the main categories for distinguishing between the different types of biopolymers. This is not meant to be a comprehensive or all-inclusive list. Several of these biopolymers can be

derived from both bio-based and fuel-based resources, such as PLA, PBS, PTT, etc. Although PLA is largely produced by fermentation from renewable resources such as starch and sugarcane, it can also be synthesized from fossil fuel.

Biopolymers can also be classified based on the ways in which they respond to heat as thermoplastics, thermosets [6], or elastomers. Nowadays, the volume of bio-based thermoset biopolymers exceeds the volume of bio-based thermoplastic biopolymers [2].

Biopolymers can also be classified based on their composition as blends, composites, or laminates. Biopolymer blends are mixtures of polymers from different origins, such as the commercial product Ecovio®, which is a blend of PLA and poly(butylene adipate-co-terephthalate) (PBAT) (Ecoflex®). Another group is the biocomposites, which are biopolymers or synthetic polymers reinforced with natural fibers, such as sisal, flax, hemp, jute, banana, wood, and various grasses, and/or fillers and additives. Novel biocomposites are based on a biodegradable matrix resin reinforced with natural fibers.

2.3 Biopolymers versus Oxodegradable Polymers

Historically, there have been two camps of research and development in the field of degradable polymers. One group of companies has focused on the biodegradable biopolymers, while another group of companies has focused on the so-called oxodegradable polymers. The two groups have functioned independently and in competition with each other, and because their technologies are different, there has been little collaboration between the two (GB2464285 A, 2010, WELLS PLASTICS LTD).

Oxodegradable polymers are based on commodity polyolefins, particularly polyethylene and polypropylene, that contain metal-containing additives (prodegradants or prooxidants) to degrade the otherwise inherently more stable polymers. Typical prodegradants use salts of transition metals such as iron (Fe), nickel (Ni), cobalt (Co), or manganese (Mn). Since oxodegradable polymers are compounded with metal-containing additives, they should be referred to as polymer systems or mixtures. Their performance during manufacture and use is indistinguishable from that of regular polyolefins, and their degradation is initiated by the prodegradants that promote the oxidation process. The

time over which the degradation process takes place depends on the concentration of additive in the polymer and the amount of sunlight and/or heat to which it is exposed.

The length of useful life of an oxodegradable polymer product is determined by antioxidants (processing stabilizers and UV stabilizers) contained within the formulation, which can be modified so that the polymer product degrades according to whatever timescale is required. If any oxodegradable polymer is going to be recycled, it will have to be collected and recycled before it has become embrittled. The presence and proportion of any prodegradant in an oxodegradable polymer can be checked by an X-ray fluorescence test [7]. Oxodegradable products such as shopping bags will normally have a useful life before embrittlement of about 18 months, and if they have not been collected and recycled by then, they probably never will be [8].

According to the advocates of oxodegradable polymers (called by them oxobiodegradable) these polymers are a solution to the littering problem caused by plastic waste, which gets accidentally or deliberately into the open environment [7]. Oxodegradable polymers are designed to degrade because oxodegradable packaging will eventually degrade and then (bio)degrade. Oxodegradation of polymers is defined by TC249/WG9 of CEN (the European Standards Organization) as “degradation identified as resulting from oxidative cleavage of macromolecules”; and oxobiodegradation as “degradation identified as resulting from oxidative and cell-mediated phenomena, either simultaneously or successively.”

Oxodegradable polymers are tested according to the following standards [9]:

- ASTM D6954-04: “Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation.”
- BS 8472:2011: “Methods for the assessment of the oxo-biodegradation of plastics and of the phyto-toxicity of the residues in controlled laboratory conditions.”
- Swedish Standard SPCR 141: “Certification rules for classification for treatment of polymeric waste.”
- UAE.S 5009:2009: “Standard & Specification For Oxo-Biodegradation Of Plastic Bags And Other Disposable Plastic Objects.”

- Jordanian Standard 2004/2012: “Packaging — Specifications for Oxo-biodegradable plastics and packaging.”

The French standards organization AFNOR has also published an Accord no. T51-808 for testing oxo-biodegradable plastics.

Following are the arguments presented by each camp in favor of either biopolymers or oxodegradable polymers.

Support from European Bioplastics [10] for biopolymers can be summarized as follows:

Oxodegradable polymers are not suitable for organic recovery. While these polymers are sometimes advertised as being “biodegradable” or even “compostable,” such claims are misleading if they are not substantiated by showing compliance with the relevant European standards EN 14995:2006 or EN 13432:2000 13432. These define the requirements for materials which can be called “compostable.” In the case of packaging, such claims are bound by legal definition under EN 13432:2000. There are no known oxodegradable materials in the market that fulfill either of these standards. Claims of compostability for such products are therefore wrong and untrustworthy. In Italy and Australia, lawsuits result in fines for using misleading claims in the marketing of such products [11].

Companies providing truly compostable plastic products will make use of the established, producer independent, certification schemes proving compostability on the basis of tests according to EN 13432:2000 or EN 14995:2006. These certification schemes provide the so-called “seedling” label (see Chapter 9: Regulatory Aspects Framework; Section 9.2: Certification) as a sign of compliance. This label is currently in use in several European countries and is expanding to represent a European label for compostable plastic items [11].

Oxodegradable polymers may cause negative environmental impact for the following reasons: (1) they are not based on renewable resources; (2) they have the potential to disperse catalytic metals in to the environment; (3) they convert carbon from a carbon sink (oil) to atmospheric carbon and thus contribute to net greenhouse gas inventories; and (4) they disintegrate into

tiny particles, do not truly biodegrade, and the small fragments that remain still have too high a molecular weight to break down to low molecular weight materials [12].

Standard ASTM D6954-04 is not an acknowledged standard. The validity of citing the standard is questionable because it has no pass/fail criteria. It simply describes how to perform tests in the laboratory.

The counterarguments by advocates of oxodegradable polymers, as expressed by the Oxo-Biodegradable Plastics Association (OPA) [7] and Professor G S Scott [13], can be summarized as follows:

Standard ASTM D6954-04, which is used to verify the biodegradability of oxodegradable polymer products, is legitimate, and claims made by the sector are sound. Tests on oxodegradable polymer products are usually conducted by independent laboratories such as Smithers Rapra (USA/UK), Pyxis (UK), Applus (ES), etc., according to the test methods prescribed by ASTM D6954-04.

There is no requirement in ASTM D6954-04 for the polymer to be converted to carbon dioxide in 180 days because, while timescale is critical for a commercial composting process, it is not critical for biodegradation in the environment. Time in the natural environment depends on the amount of heat, light, and stress to which the material is subjected.

The requirement in EN 13432, ASTM D6400, and similar standards for 90% conversion to carbon dioxide within 180 days is not useful even for composting because it contributes to climate change instead of contributing to the fertility of the soil. A compostable polymer, 90% of which has been converted to carbon dioxide, is actually useless in compost.

Oxodegradable polymers can be recycled in the same way as commodity polymers. By contrast biodegradable biopolymers or bioplastics (often referred to as hydro-biodegradable plastics) are physically incompatible with the most abundant components of plastic waste (PE, PP, ABS, and PET), and aliphatic polyesters or starch cannot be readily reprocessed with commercial aromatic polyesters due to their thermal incompatibility.

Therefore, they have to be segregated from the waste stream and treated separately, which results in a considerable increase in cost. Also, it is difficult for the manufacturers of recyclate to physically distinguish between biodegradable polymers (hydro-biodegradable) and normal polymers.

Biodegradable polymers have been called into question by recyclers [14]. PLA and starch-based plastics could have a negative impact on plastics recycling as a whole. The fear is that biopolymers will increasingly find their way into the plastics recycling stream, which would impact quality and undo the work already done on raising public awareness of plastics recycling.

Biodegradable biopolymers often do not break down under reasonable conditions when they are used in certain products, such as thick films or medium-to-large-gauge packaging or containers. In such cases, even though the polymers may be comprised of chemical structures that render them biodegradable, such as ester linkages, the bulk nature of the product means that they do not hydrolyze easily. This presents considerable disposal, environmental, and cost issues, as well as other practical disadvantages.

An independent study, carried out by Loughborough University and commissioned by the Department for Environment, Food, and Rural Affairs (DEFRA), UK, assessed the environmental impact of oxodegradable polymers across their life cycle and drew the following conclusions [15]:

- The incorporation of additives into fossil fuel-based polymers can cause those polymers to undergo accelerated degradation. This does not improve their environmental impact, and can potentially give rise to certain negative effects.
- No evidence was found that oxodegradable fragments have a harmful bio-accumulative effect, but neither was there evidence that they do not.
- No evidence was found of a toxicological impact of oxodegradable additives. It is concluded that the transition metals used are present in such small amounts that they will not significantly increase the concentrations naturally present in the soil at expected levels of usage.

- The degradability of oxodegradable bags limits their reusability: they are unsuitable for storing items for an extended length of time.
- Oxodegradable polymers are not suitable for recycling with mainstream plastics. Oxodegradable additives in the recyclate will render the product more susceptible to degradation. Although additive producers suggest that stabilizers can be added to protect against the oxodegradable additives, it would be problematic for recyclers to determine how much stabilizer needs to be added and to what extent the oxodegradable polymer has already degraded. On this basis it seems unreasonable to claim recyclability of oxodegradable polymers in existing recycling streams.
- To avoid potential problems caused by the incorrect disposal of oxodegradable polymers, packaging should be clearly labeled with the appropriate means of disposal. Life cycle analysis suggests that the best means of disposal for oxodegradable polymers is incineration. If incineration is not available, then landfill is the next best option.
- There is a lack of evidence about what actually happens to oxodegradable plastics in landfill. It is possible that they will degrade in landfill sites if sufficient oxygen is present, but the most likely scenario is that they will not degrade.
- Oxodegradable polymers do not degrade for approximately 2–5 years, and they still remain visible as litter before they start to degrade [15].

Symphony Environmental Technologies, developer and supplier of oxodegradable plastic products under its d2w trademark, disputed the key findings and recommendations of the Loughborough report as being controversial for the following reasons [8]:

- Inaccurate descriptions of oxobiodegradable (OBD) plastic technology and mechanisms.
- Conclusions drawn for OBD plastics in relation to recycling, biodegradation, and other issues are not supported by the evidence.
- Considerable weight is placed on European standard EN13432 and ASTM standard D6400 as standards for specifying biodegradability of plastics. This is a fundamental error. According to a timescale required by industrial

composters these standards are for biodegradation in the special conditions found in industrial composting.

According to Symphony Environmental Technologies the report confirmed that OBD plastics degrade abiotically in a normal environment, degrade abiotically under elevated temperatures found in landfill, biodegrade, do not emit methane even deep in landfill, are safe for food contact, and contain no heavy metals [8].

2.4 Types and Mechanisms of (Bio)degradation

Changes in polymer properties due to physical, chemical, or biological reactions resulting in bond scissions and subsequent chemical transformations are categorized as polymer degradation. The various types of degradation may be classified either by the inducing mechanisms or by the nature of the agents causing degradation. The main degradation mechanisms are:

- (1) Depolymerization.
- (2) Random scission.
- (3) Elimination.

The main agents that initiate degradation and the corresponding types of degradation are:

- (1) Heat (thermal degradation).
- (2) Heat plus oxygen (thermooxidative degradation).
- (3) Visible light and ultraviolet (UV) light (photodegradation).
- (4) High-energy radiation (e.g., X-rays, γ -rays).
- (5) Mechanical stress (mechanochemical degradation).
- (6) Chemical attack (e.g., solvolysis/hydrolysis, ozonolysis, catalytic degradation).
- (7) Biological organisms (biodegradation aerobic, anaerobic).

2.4.1 Thermal Degradation

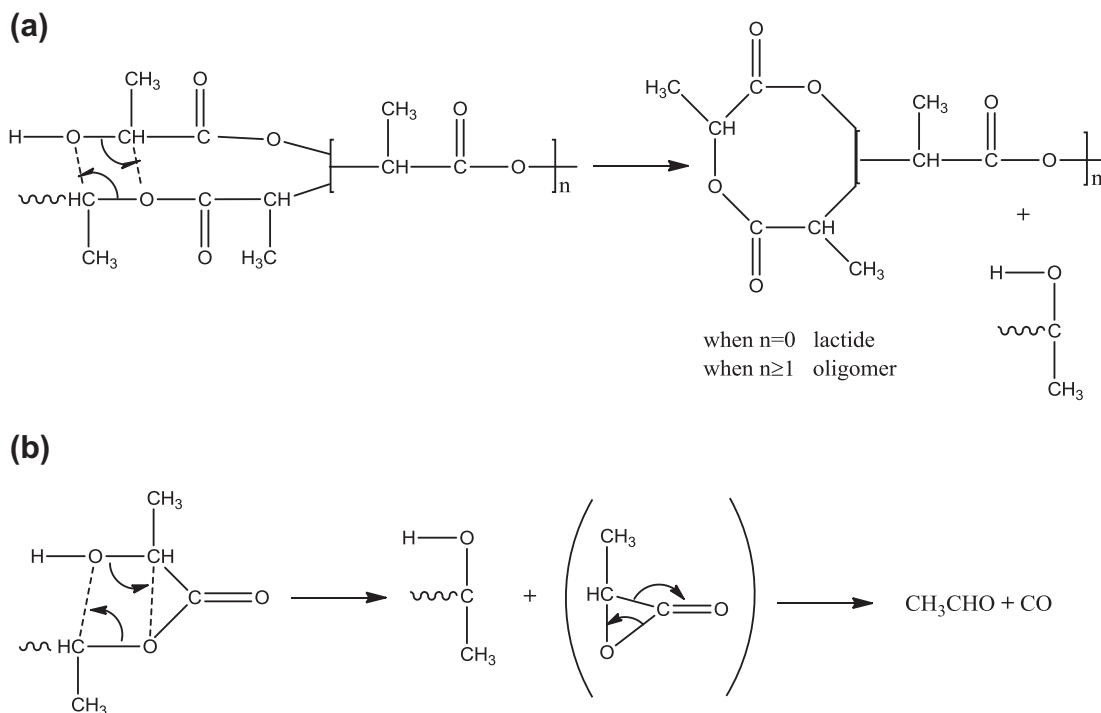
Thermal degradation of thermoplastic polymers occurs during processing at increased temperatures ($T \geq T_m$), when the polymer is transformed from

solid to melt. The thermal degradation of PLA is attributed mainly to random main-chain scission and unzipping depolymerization reactions. The random degradation reaction involves hydrolysis by trace amounts of water, oxidative degradation, *cis*-elimination, and inter- and intramolecular transesterification reactions [16]. Above 200°C, PLA can degrade through inter- and intramolecular ester exchange, *cis*-elimination, and radical and concerted non-radical reactions, which result in the formation of CO, CO₂, acetaldehyde and methylketene [17]. There are suggestions that the thermal degradation of PLA is a non-radical, “backbiting” ester interchange reaction involving the —OH chain ends [18,19]. Depending on the point in the backbone at which the reaction occurs, the product can be a lactide molecule, an oligomeric ring, or acetaldehyde plus carbon monoxide (see Scheme 2.1). At temperatures in excess of 270°C, homolysis of PLA occurs [20]. The formation of acetaldehyde is expected to increase with increasing process temperature due to the increased rate of the degradation reactions [21].

Almost all the active chain end-groups, residual catalysts, residual monomers, and other impurities enhance the thermal degradation of PLA. As a consequence of these reactions, when PLA is melt-processed during the manufacture of industrial products at high temperatures, undesired molecular weight reduction and weight loss occur [22].

The thermal instability of PHAs during melt processing has triggered interest in the thermal degradation of PHAs, especially polyhydroxybutyrate (PHB).

The thermal degradation behavior of PHB has been discussed in many reports. Random chain scission by β -elimination has been considered the dominant mechanism based on the presence of crotonic acid and oligomers with a crotonate end-group at almost all chain ends of the pyrolysis products [23–26]. Kawalec et al. [27] proposed an E1cB mechanism proceeding via α -deprotonation by a carboxylate anion to produce the same products. There were suggestions that other reactions out of the random scission occur during the PHB thermal characterization. Ariffin et al. [28] detected the presence of crotonic anhydride and its oligomers as minor products from condensation reactions between carboxyl groups. The anhydride production must be one reaction out of the process of conforming to the random degradation statistics, and contributes to the complexity of PHB pyrolysis. Based on the above



Scheme 2.1 Thermal degradation of PLA [19]. Non-radical backbiting ester interchange reactions; (a) $n = 0$ lactide, $n \geq 1$ oligomeric ring; (b) acetaldehyde plus carbon monoxide.

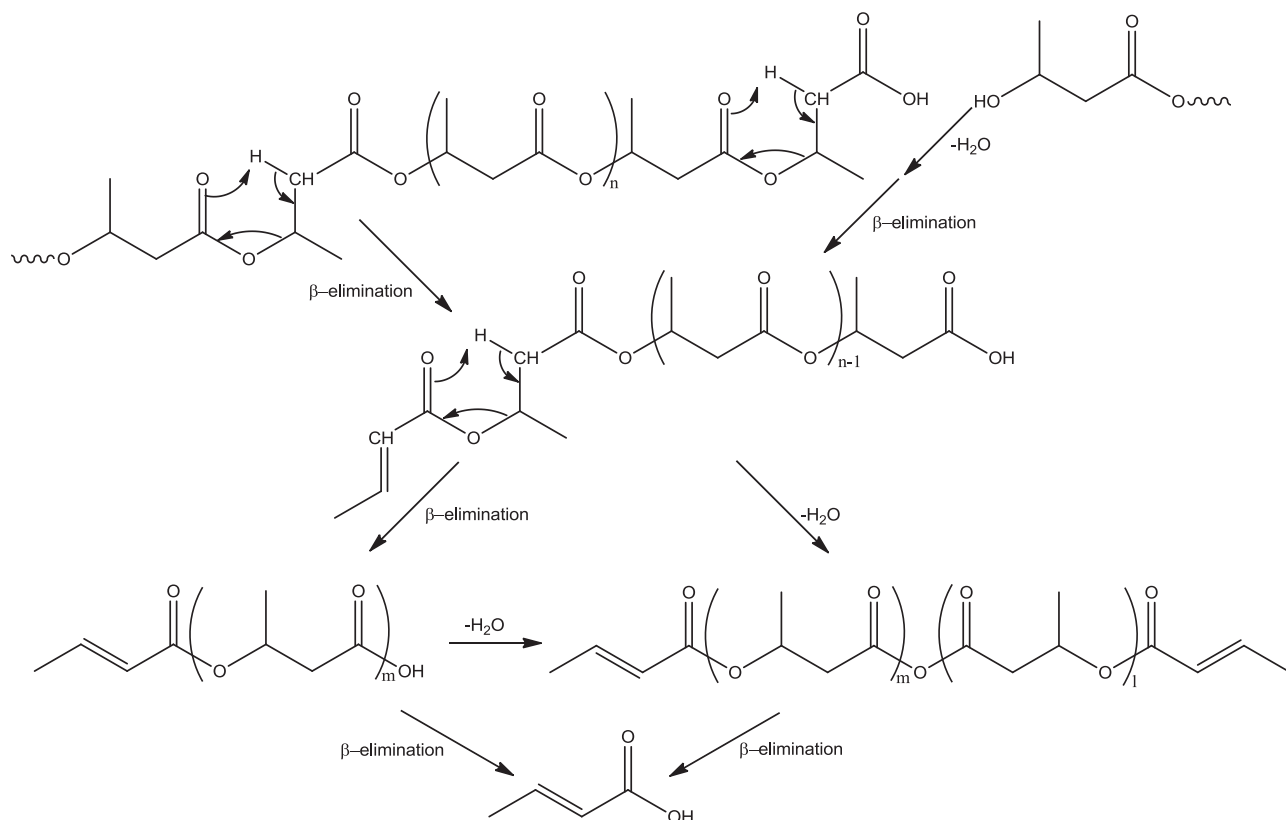
results, Ariffin et al. [28] proposed that an anhydride formation process (i.e., dehydration as a minor reaction) should be included in the thermal degradation pathways of PHB in which the random β -elimination is predominant. Expected thermal degradation pathways of PHB are illustrated in Scheme 2.2. The anhydride formation is one mechanism out of the processes conforming to the random scission statistics. The β -elimination leads to oligomeric acids and finally crotonic acid with monotonous decrease in the molecular weight. The dehydration may get in the way of the decrease. Moreover, the production of anhydrides may influence the reactions caused by carboxyl groups, such as the E1cB mechanism [27] and inter-/intra-trans-esterifications, which contributes to the complexity of PHB pyrolysis.

2.4.2 Photodegradation

Photodegradation of polymers is induced by the action of light and is attributed to photochemical reactions arising from the absorption of UV radiation by carbonyl groups present on the polymer backbone. Photodegradation mechanisms are mainly expressed by the Norrish reactions that transform the polymers by photoionization (Norrish I) and chain scission

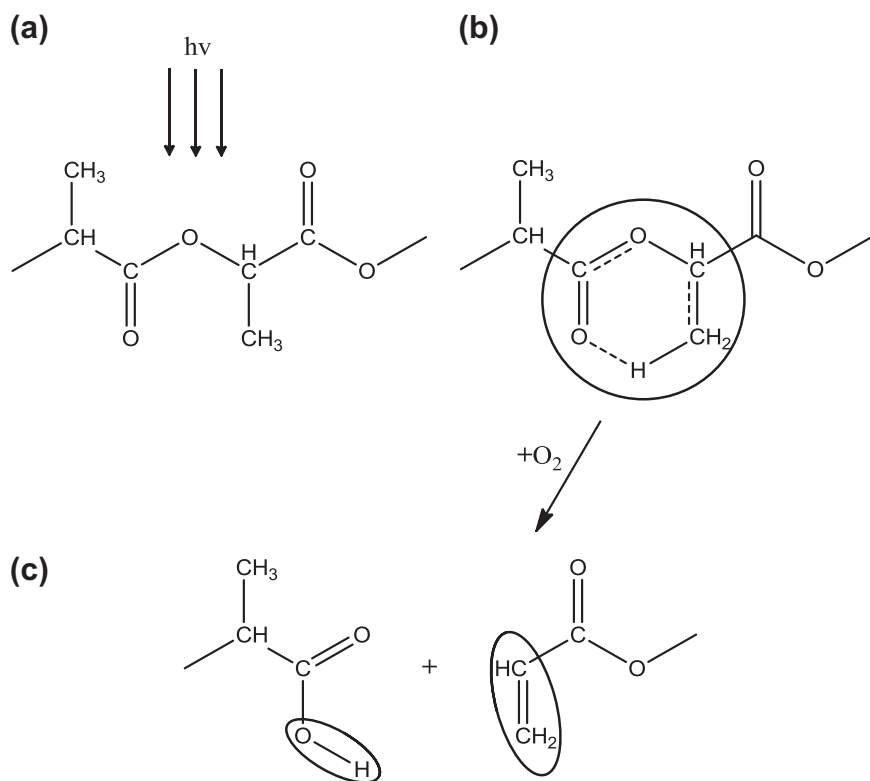
(Norrish II). Photodegradation can conduce to Norrish reactions and/or cross-linking reactions, or oxidative processes [29]. The photodegradation mechanism of PLA and PCL has been suggested to proceed via the Norrish-type photo-cleavage, especially the Norrish II type reaction, which explains the chain scission (decrease of molecular weight), formation of C=C double bonds, and hydroperoxide O—H at newly formed chain terminals [30–33] as is shown in Scheme 2.3.

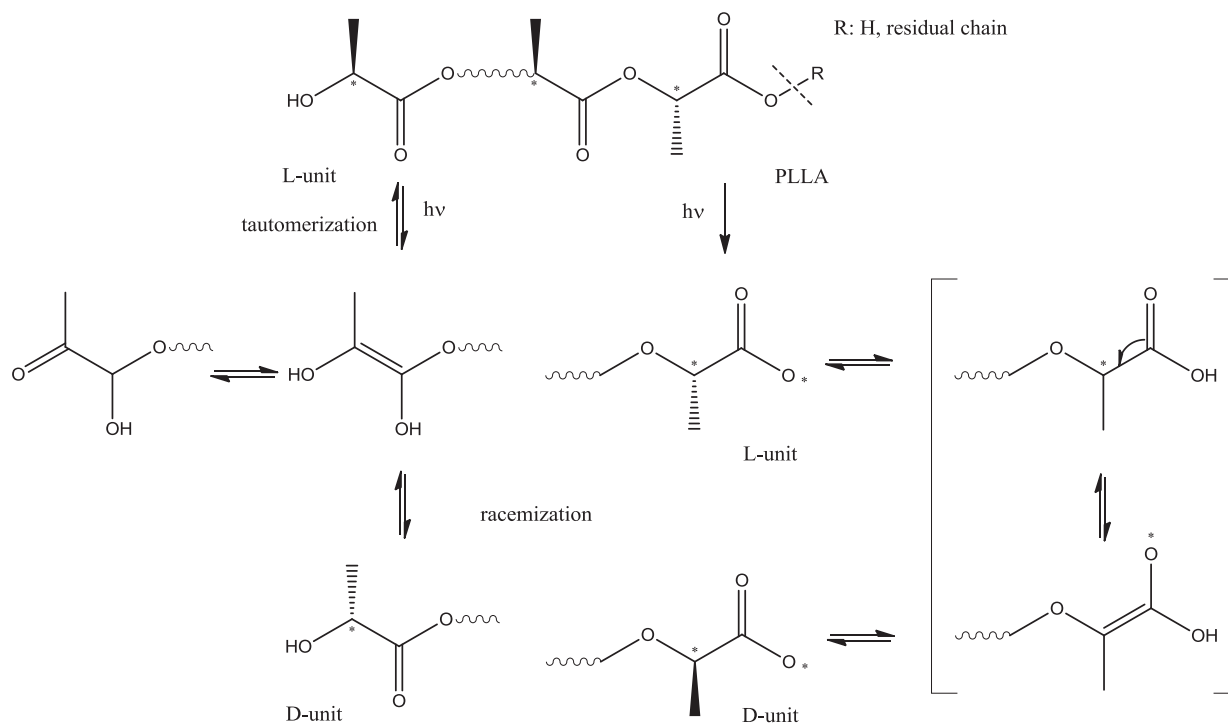
Sakai et al. [35] proposed other photodegradation mechanisms in which the UV degradation of PLA is comprised of a dissociation reaction at the RCOO—R' bond followed by the dehydrogenation of α -hydrogen on an asymmetric carbon. Taking into account the reported mechanism, Yasuda et al. [36] proposed the possible photodegradation mechanism shown in Scheme 2.4. This mechanism ignores the Norrish II type reaction because of the non-detection of acrylic acid. Instead, it assumes that an RCOO—R' bond is cleaved to produce carbonyl and alkyl radicals, which abstracts a tertiary proton on the chiral carbon and results in a racemization equilibrium at the carbonyl chain end unit. At another chain end, the hydroxyl group must be predominant because of hydrolysis accelerated by the irradiation. The hydroxyl chain end unit is highly mobile and



Scheme 2.2 Thermal degradation pathways of PHB, where l , m , and n indicate repetition numbers for the 3-hydroxybutyrate unit and l and m are less than n [28].

Scheme 2.3 Norrish II photodegradation mechanism of PLA [34]. (a) UV irradiation; (b) photophysical excitation; (c) oxidation and scission reactions.





Scheme 2.4 Possible photodegradation mechanisms of poly(L-lactide) (PLLA) under UV [36].

therefore reactive, like L-lactic acid, which results in the shift into racemization equilibrium under irradiation. The racemization equilibrium converts the original L-lactate units into D,L-lactate units at both chain ends, and thus the D-unit formation becomes statistically close to the chain scission ratio [36].

Cross-linking and chain scission reactions were found to be the main degradation mechanisms of poly(butylene adipate-*co*-terephthalate) (PBAT) or Ecoflex® biodegradable mulch films when exposed to solar radiation [37,38].

2.4.3 Mechanical Degradation

Biopolymer articles can undergo several mechanical degradations during processing, storage, and use. Mechanical degradation can take place due to shear forces, tension, and/or compression [39,40]. Agitation, grinding, and extrusion are the main causes of mechanical degradation during processing. The basic phenomenon involved when subjecting the polymer to very powerful shearing forces is the breakage of the molecule. Mechanical degradation reduces the average molecular weight of the polymer.

Although mechanical factors are not predominant during biodegradation, they can activate or accelerate it. In field conditions, mechanical stresses act in

synergy with other environmental parameters, such as temperature, UV, humidity, etc. [29].

2.4.4 Hydrolysis

The most prevalent type of biodegradable biopolymer degradation is hydrolysis of ester linkages, other labile bonds, or the hydrolytically unstable backbone. In general, hydrolytic degradation is thought to proceed through a series of somewhat overlapping steps, including:

- Initial hydrolysis that yields polymers with reduced molecular weight (i.e., conversion of polymers to oligomers).
- Continued loss of molecular weight (i.e., formation of smaller oligomers) and gradual loss of plasticizers incorporated into the material.
- Initial loss of physical properties (e.g., pliability).
- Loss of further properties, resulting in an opaque and hazy material.
- Major loss of physical properties, such as tensile strength and form-stability, that correlates to a reduction in the molecular weight of the polymer ($M_n < 50,000$ daltons).

- Weight loss and volume loss until the material is essentially degraded to monomers or small oligomers.

The hydrolysis of PLA is a good example for demonstrating the mechanism of abiotic hydrolysis. As is illustrated in [Scheme 2.5](#), cleavage of the ester bonds by absorption of water produces a successive reduction in molecular weight.

The hydrolysis of semicrystalline biodegradable biopolymers initially occurs in the amorphous phase and forms low molecular weight, water-soluble fragments. This reduction in molecular weight in the amorphous phase does not result in reduction of the mechanical properties because the crystalline regions provide the required strength to the structure. Then hydrolysis of the crystalline phase occurs, which results in loss of molecular weight and mechanical properties.

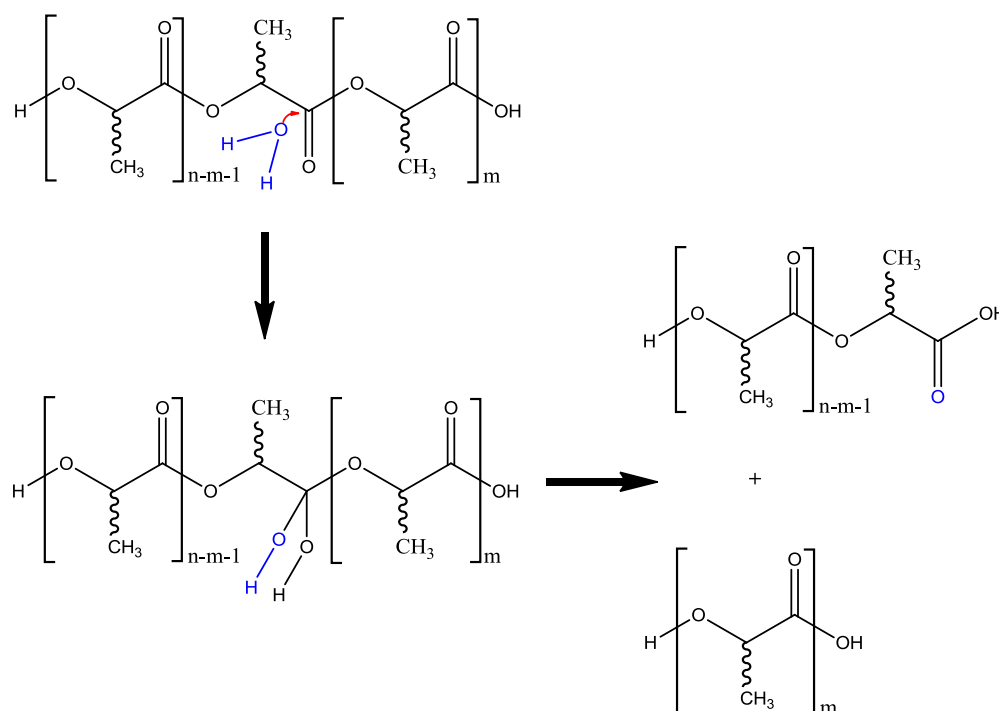
There are two main ways by which biopolymers can be hydrolyzed, passively by chemical hydrolysis, or actively by enzymatic reaction. The latter method is most important for naturally occurring polymers such as polysaccharides and PHAs. PLA and PGA degrade by simple hydrolysis of the ester bond and do not require the presence of enzymes to catalyze hydrolysis.

2.4.5 Biodegradation

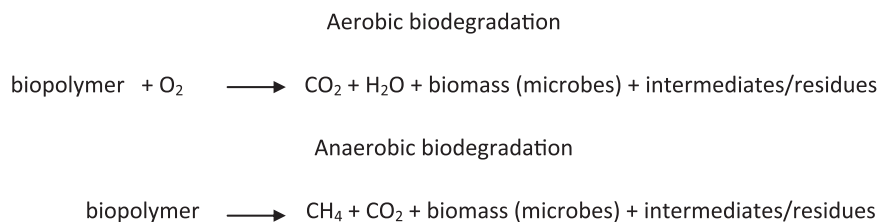
Biodegradation starts when microorganisms begin growing on the surface of the biopolymer and secrete enzymes that break down the biopolymer into oligo- or monomeric units such as hydroxy acids. In the case of aliphatic polyesters, the hydroxy acids are then taken up by the microorganism and used as carbon sources for growth. In aerobic environments the biopolymers are degraded into carbon dioxide and water, whereas in anaerobic environments the degradation products are carbon dioxide and methane (biogas) [43] (see [Scheme 2.6](#)).

As can be seen in [Scheme 2.6](#), a minor part of the organic compound of the biopolymer is converted to biomass. The biomass yield is in the 10–40% range depending on the biopolymer. The intermediates/residues are comprised of non-degraded carbon compounds and/or in-between degradation products [44]. The whole biodegradation process can vary from days to months to years, and depends on the type of polymer. Over a long period of time cell biomass and other intermediates will eventually be mineralized to CO₂.

Biodegradation is a composite effect of different mechanisms that proceed simultaneously or consecutively on the polymer. Exemplary mechanisms of biodegradation include disintegration, dispersion,



Scheme 2.5 Hydrolysis of PLA [41,42].



Scheme 2.6 Schematic representation of aerobic and anaerobic biodegradation reactions [44].

dissolution, erosion, hydrolysis, and enzymatic degradation. Most of the microbial reactions are sequential so that the end product of metabolism of a given substrate by one organism becomes the substrate for another organism (WO9928366 A1, 1999, UNIV NEBRASKA).

Biodegradation processes can affect polymers in a number of ways. Microbial processes that can affect polymers include mechanical damage caused by growing cells, direct enzymatic effects leading to breakdown of the polymer structure, and secondary biochemical effects caused by excretion of substances other than enzymes that may directly affect the polymer or change environmental conditions, such as pH or redox conditions.

PHB and PCL are primarily attacked by enzymes at the surface. PLA is initially degraded by a non-enzyme-catalyzed hydrolysis mechanism that is temperature dependent. Enzymes are large molecules and are unable to diffuse through the crystalline regions of PLA. As a result, little enzymatic degradation occurs at the beginning of the degradation process. Enzymatic involvement can produce pores and fragmentation, making more polymer regions accessible to the enzymes. Hydrolysis is also the principal mechanism by which enzymes degrade cellulose-based polymers. The first step in depolymerization occurs outside of microbial cells through the action of extraordinary enzymes. After cleavage, the resulting small oligomers can be transported into cells for final mineralization [45].

2.5 (Bio)degradation Testing

The test methods which have been developed for biodegradable polymers can be classified into three categories: field tests, simulation tests, and laboratory tests [46]. The rate at which the biopolymers are degraded can be monitored by a variety of methods.

2.5.1 Visual Examination

Visual examination involves the evaluation of macroscopic changes on the surface structure of the biodegraded polymer: roughening of the surface, creation of holes and cracks, changes in color, formation of microbial colonies over the surface, etc. The visual changes can be used for an initial estimation of biodegradation [46]. Several microscopic techniques can be used to investigate the biodegradation-induced changes on the surface of the polymer, such as photonic microscopy, polarization microscopy, electronic microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and scanning force microscopy (SFM). Microbial colonies can be seen by the naked eye. The colonization of microorganisms on Petri dishes can be estimated by several normalized tests [29]. This is a simple, cheap, and quick method, but its results are qualitative because the microbial colonies may be utilizing additives within the polymer and not the polymer itself. Furthermore, some structural differences may be due to chemical degradation rather than biodegradation [47].

2.5.2 Changes in Thermo-mechanical and Physical Properties

Stress—strain tests (tensile strength, elongation at break, modulus, and yield stress) are used to measure mechanical changes during degradation. The same standardized mechanical tests that are used for conventional polymers can be applied to biopolymers. A disadvantage of using the mechanical properties, or any other property that relies on the macromolecular nature of the substrate for the estimation of biodegradability, is that these properties can only address the early stages of the biodegradation process. Mechanical properties are usually used to support the results of other tests.

The thermal properties such as glass transition temperature (T_g), melting point (T_m), enthalpy, crystallinity, and cold crystallization, are usually estimated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The crystallinity content can also be measured by X-ray diffraction. Dynamic mechanical analysis (DMA) is often used to measure T_g , storage modulus (E'), and loss (or viscous) modulus (E'').

2.5.3 Molecular Weight

A decrease in the average molecular weight, and the broadening of the molecular weight distribution, provide initial evidence of the degradation of a polymer. A change in molecular weight is a measure of bulk deterioration, whereas biodegradation occurs initially on the surface of the polymer. Therefore, no degradation may be observed from molecular weight measurements even when there has been a significant amount of weight loss. However, the method can be used to indicate where cleavage occurs in the polymer chain during biodegradation. Change in molecular weight is an easy measurement of biodegradation, and when used with other methods, it can be a useful indicator of the degree of biodegradability [47]. The molecular weight of a biodegradable polymer can be measured by gel permeation chromatography (GPC).

2.5.4 Chemical Changes

Spectroscopic analysis, such as Fourier transform infrared (FTIR), UV, fluorescence, nuclear magnetic resonance (NMR), and mass spectroscopy (MS), are regularly used to detect chemical changes in the polymer structure.

2.5.5 Hydrolysis

Hydrolysis is a type of chemical degradation. The analysis of the residual monomers and released fragments is realized by a series of techniques such as GPC, weight loss, DSC, TGA, FTIR, and NMR.

2.5.6 Thermal Degradation

Thermal degradation is usually followed by TGA.

2.5.7 Weight Loss

Another frequently used method for the estimation of biodegradation is measurement of weight loss when the polymer is exposed to a mixture of selected microbes in culture media with the polymer as the

sole source of carbon. This method is standardized for in-field and simulation biodegradability tests (ASTM D7473-12). Problems can arise with the correct cleaning of the sample or if the material disintegrates excessively [46]. Measurement of the weight loss of samples is not really representative of a material biodegradability, since this loss of weight can be due to the vanishing of volatile and soluble impurities [29]. Furthermore, the method addresses only the early stages of the biodegradation process, but gives no information on the extent of mineralization [48].

2.5.8 Gas (CO_2/CH_4) Evolution

Well-established biodegradation tests use evolved carbon dioxide (CO_2) or methane (CH_4) as analytical parameters to determine the ultimate biodegradability of polymers.

Under aerobic conditions, microbes use oxygen to oxidize carbon and form carbon dioxide as one of the major metabolic end products. The amount of carbon dioxide evolved, expressed as a percentage of the theoretically expected value for total conversion to carbon dioxide, is a measure for the extent of biodegradation achieved. A value of 60% carbon conversion to CO_2 achieved within 28 days for resins made from a single polymer is generally taken to indicate ready degradability. A respirometer is used to measure carbon dioxide production. Carbon dioxide evolution is the method most often used to measure biodegradation [48].

A number of well-known tests have been standardized for aerobic biodegradation, such as the modified Sturm test and the laboratory controlled composting test (ISO 14852:1999, ISO 14855-1:2005, ISO 14855-2:2007, ISO 17556:2012, EN 14047:2002, EN 14048:2002, JIS K 6951:2000).

Anaerobic tests generally follow biodegradation by measuring the increase in pressure and/or volume due to methane evolution, usually in combination with gas chromatographic analysis of the gas phase.

A number of well-known tests have been standardized for anaerobic biodegradation of biopolymers, such as the anaerobic sludge test and the anaerobic digestion test (ISO 13975:2012, ISO 15985:2004, ISO 14853:2005, ASTM D5526-12).

2.5.9 Oxygen Consumption

The amount of oxygen consumed during biodegradation is also an indicator of biodegradation. It can

be measured by comparing the biological oxygen demand (BOD) to the chemical oxygen demand (COD). A respirometer is used to measure the oxygen consumption [47]. The method for the determination of oxygen consumption is based on the so-called MITI test and is standardized (ISO 14851:1999, ISO 17556:2012, EN 14048:2002, JIS K 6950:2000, ISO 17556:2012) [44].

2.5.10 Radiolabeling

Radiolabeling is a simple, non-destructive technique for measuring biodegradation. With radiolabeling, the carbon of the polymer is radiolabeled with carbon isotope ^{14}C and exposed to a microbial environment. By comparing the amount of radioactive $^{14}\text{CO}_2$ or $^{14}\text{CH}_4$ to the original radioactivity of the labeled product, it is possible to determine the duration of exposure. The amount of $^{14}\text{CO}_2$ evolved is measured by absorption and a liquid scintillation counter. This method is not subject to interference by biodegradable impurities or additives in the polymer. Among the disadvantages of this method are the difficulty and cost in preparing radiolabeled polymers, licensing, and waste disposal of the radioactive samples [48,49].

The method is standardized for the determination of aerobic biodegradation of radiolabeled polymer materials in an aqueous or compost environment (ASTM D6340-98(2007)).

2.5.11 Clear-Zone Formation

This is an agar plate test in which the polymer is dispersed as very fine particles within the synthetic medium agar. This results in the agar having an opaque appearance. After inoculation with microorganisms, the formation of a clear halo around the colony indicates that the microorganisms are at least able to depolymerize the polymer, which is the first step of biodegradation. The method is usually applied to screen microorganisms that can degrade a certain polymer, but it can also be used to obtain semi-quantitative results by analyzing the growth of clear zones [29].

2.5.12 Ecotoxicity

Ecotoxicity is measured by having concentrations of heavy metals below the limits set by the standards, and testing plant growth by mixing the compost with soil in different concentrations and comparing it with controlled compost. The ecotoxicity of composted

biodegradable polymer on the plant growth can be assessed with EN 13432, Annex E, which is based on the OECD Guidelines for Testing for Chemicals 208 [50], and ISO 11269-1:2012 and ISO 11269-2:2012.

The ecotoxicity tests that have been most used to test the effect of biodegradable polymers on solid substrates, including compost and soil, are the ISO 11268-1:2012 (Effects of pollutants on earthworms), or its similar OECD 207 (Earthworm Acute Toxicity Test), and OECD 202 (*Daphnia* sp. Acute Immobilization Test [51]).

Other types of ecotoxicity tests are the microbial toxicity tests. They are based on the reaction of a single species or a mixture of microbes to molecules. Among these tests, the bioluminescence tests are based on the change in light emission by luminescent microorganisms [51].

An extensive review of the ecotoxicity of biodegradable polymers is provided by Fritz [52].

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Supplementary patents (not necessarily relating to biopolymers)

Patent	Pub. date	Family members	Applicant	Title
GB2464285 A	20100414	US2011200771 A1 20110818; MX2011003798 A 20110729; WO2010041063 A2 20100415; WO2010041063 A3 20100916; EP2334723 A2 20110622; CN102177196 A 20110907	WELLS PLASTICS LTD	Transition metal additives for enhancing polymer degradation
WO9928366 A1	19990610	AU1709099 A 19990616; US5990266 A 19991123; US6121033 A 20000919	UNIV NEBRASKA	Novel degradable polyesters useful in packaging, agricultural, and biomedical applications

OUTLINE

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Reuse is a common practice applied to discarded or used polymer products. Rejected preforms or moldings and used articles are reprocessed as they are, without changing the chemical nature of the polymer; an example of this is the conversion of PET bottles to fibrous material. As a result, most of the applied techniques are similar to those of physical (or mechanical) recycling described in Chapter 5: Physical Recycling. However, there are certain differences. The methods of physical recycling, such as grinding, sorting, compacting, etc., are usually pretreatment processes preceding the reprocessing or recycling of the waste material. Recycling in particular is expensive because the separation of the different polymers is difficult. Reusing polymers is preferable to recycling as it uses less energy and fewer resources. Reuse involves one or more of the following: (1) direct recuperation of scrap material during molding (e.g., feedback of used material); (2) blending of the polymer to be used with other polymers, often in combination with compatibilizers to make new products; (3) mixing with various additives such as antioxidants and/or reinforcing agents; and/or (4) modification of the polymer structure (e.g., by reactive extrusion) to recover its original properties.

3.1 Recuperation

This practice is widely employed for the recycling of industrial scrap, in which these industrial residues

are ground and mixed with virgin material, and directly introduced into the processing machinery. Sources of industrial scrap can be melt lumps, sprues, and defective parts in injection molding, parison waste in blow-molding or, for example, edge trim, cutoffs, and off-spec startup material in film and fiber production processes. The reutilization of these plastics wastes — which exist in considerable quantities in the production or processing of biopolymer products — by direct processing in an extruder is possible only to a very limited extent because of their voluminous nature and poor flow property. Such plastics wastes must first be pretreated appropriately by comminution. The plastics particles which have thereby become flake-like or fleece-like are then agglomerated into highly compacted, free-flowing, and abrasion-resistant granules. During the heat treatment required for the agglomeration, the biopolymers must not be thermally damaged (i.e., they must not be heated above their melting temperature, T_m) since they decompose chemically and release gases that are harmful in most cases, and cause the wastes to become useless for technological reutilization. The granules obtained in this way must have the same quality as the granules of virgin material so that they can be proportionately admixed with the latter. The adjustment of the composition of recycled material in the blend, and the optimization of the processing procedure, are the main technological considerations required to achieve material properties similar to those of the virgin one [1].

Scrap biopolymers generated during molding operations can be viewed as potential resources for the manufacture of new products through recycling processes, with a similar status given to virgin biopolymers. The prospect of reusing scrap polylactide (PLA) as is appears appealing from the aspect of recycling when taking into account the average cost of PLA compared to conventional plastic products. The following are sources of waste PLA: (1) sprues, runners, and selvages left behind during molding and production processes; (2) off-grades of PLA formed by polymerization reaction and not meeting the standard requirements; and (3) used PLA. However, the reprocessing of biopolymer waste is not an easy task. PLA is highly susceptible to thermal deterioration, and reuse of waste PLA is liable to cause coloration, degeneration, and decrease in molecular weight. Other problems such as hygroscopicity, stickiness at high temperatures, and thermal instability of several biopolymers, must also be taken into consideration. Thus, for example, in the reprocessing of PLA, it is important that the material being recycled be as dry as possible in order to prevent a hydrolytic breakdown of the molecular chains during plasticization. However, PLA is hygroscopic, which makes an efficient drying difficult. Furthermore, the low T_g at which the PLA material becomes sticky at higher temperatures, along with a relatively long crystallization time, make it hard to crystallize and/or dry amorphous production wastes (especially residues of deep-drawn films) with conventional crystallization systems and drying systems (WO2008058303 A1, 2008, EREMA). Therefore, unlike general use polymers, it is difficult to reuse PLA. Similarly, plasticized starch is sensitive to hydrolysis during use, and cannot normally be reprocessed for use in the same application. Like PLA, it is not compatible with mainstream plastics used in packaging and cannot be co-recycled into useful secondary products. Additional problems with reprocessing industrial scrap and virgin biopolymers include: (1) inconsistent feeding performance of the production extruder; (2) air inclusions in the melt that lead to defects in the finished products; and (3) difficulty in removing process materials like printing inks and similar materials.

CN101230129 A (2008, SHANGHAI NEW SHANGHUA POLYMER) discloses a recrystallization method for waste PLA that comprises the following steps: recovered PLA with 30 to 400 ppm water content is heat treated and recrystallized

for 5–100 min, preferably 30 min at 20–140°C (30–110°C is preferred), by adopting different temperatures, according to two to eight ascending temperature gradients (preferably two to four), to obtain recrystallized PLA. Waste PLA refers to PLA rim leftovers and discarded products after first processing. The melting enthalpy of the melting peak of PLA crystallization (ΔH_m) is 10 to 30 J/g, the T_m is 140 to 180°C, and the T_g of PLA is 40 to 70°C. Recrystallization of PLA is a simple operation, does not need additional post-processing, requires a relatively short time, and yields recrystallized PLA with satisfactory properties. In addition, the recrystallized PLA can be easily reprocessed.

WO2008058303 A1 (2008, EREMA) discloses a method for the pretreatment, reprocessing, or recycling of thermoplastic material, especially PLA (Figure 3.1). The thermoplastic material is heated in a receiving tank or reactor (1) under constant mixing or movement and/or comminution at a temperature below T_m (preferably over T_g of the thermoplastic, 90 to 110°C). At the same time it is crystallized, dried, and/or purified, especially in a single step. For mixing and heating of the thermoplastic material, at least one comminuting or mixing tool (12) is used. It must be able to turn about a vertical axis (8) and is typically arranged on several levels, one above the other, with working edges that act on the material with a comminuting and/or mixing effect. Heating occurs by applying mechanical energy. The method is best carried out either in a one-stage EREMA PC reactor or in a one- or two-stage VACUREMA reactor.

The mild, constant movement of the polymer material prevents clumping or sticking of the material in the critical temperature range until adequate crystallization of the surface of the particles can prevent individual particles from sticking together. In the treatment tank, the mild and constant movement ensures not only an abeyance of sticking, but at the same time also ensures that the temperature in the tank remains high enough and that each particle remains heated gently to the proper temperature. At the same time, the movement supports a detachment of the migrating molecules from the surface of the particles.

WO2009100473 A1 (2009, EREMA) is a modification of patent WO2008058303. Pretreated thermoplastic material is transferred into a screw injection molding machine (10) having a screw (16) rotating in a housing (17) and being axially

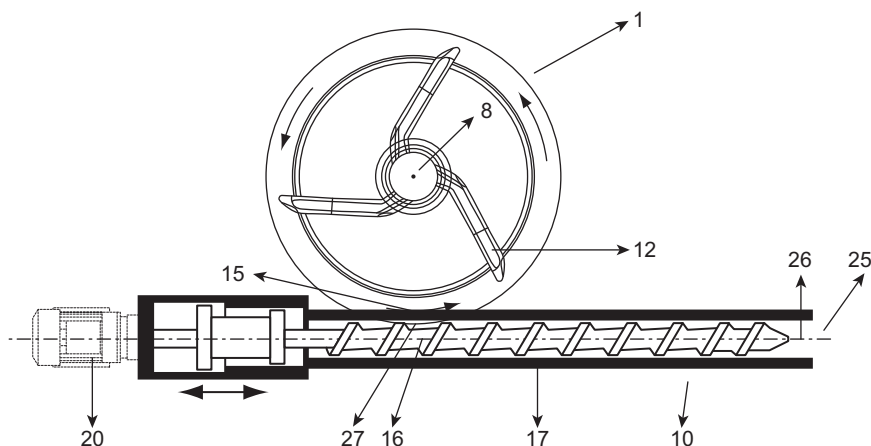


Figure 3.1 Device comprising a reactor or cutter-compactor (1) and a worm-gear injection molding device (10).

1: Reactor or cutter-compactor;
2: Worm-gear injection molding device; 8: Vertical axis; 10: Injection molding machine; 12: Mixing tool; 15: Removal opening; 16: Screw; 17: Housing; 20: Motor; 25: Nozzle; 26: Worm antechamber; 27: Catchment opening
(WO2009100473 A1, 2009, EREMA).

displaceable therein and/or acting as a piston, is plasticized in said screw, and molded into a molded part, for example a preform (Figure 3.1).

At the NPE 2009 tradeshow in Chicago, plastics recycling systems provider EREMA demonstrated a recycling system of turning scrap PLA film into near margin quality pellets, using a non-vented Model 906T reclaim extruder for PE film. With a normal non-barrier screw for PE, it processed oriented PLA scrap provided by Biax International, Inc., a large producer of oriented PLA film (OPLA) sheet. Frictional heat generated in the standard cutter/compactor acts like a dryer, removing and venting moisture that makes this material difficult for some systems to reprocess. The use of a short extruder L/D ratio also helps to avoid thermal degradation. EREMA says about 9 million kilograms per year of bioplastic scrap (mostly PLA) is reprocessed on EREMA reclaim extruders in the USA, and about the same amount in Europe (PLA and starch based films for compost bags) [2,3].

At the NPE 2012 tradeshow in Milan, recycling equipment maker Tecnova demonstrated the Refil/1 in-line system for reclaiming film scrap. Production rates of the system, which can handle a wide range of materials, including biopolymers, are claimed to be 40–45 kg/hr. The company also showed the Mini 60 line, which is able to process bioplastic, in addition to LDPE/HDPE/PP film. The line is equipped with a special grinder, a die-face cutter, and a cooling system, all specifically designed to be able to handle biopolymers as well as conventional plastics. The regenerated granules can be directly reintroduced into the extrusion process for the production of (biodegradable) film [3].

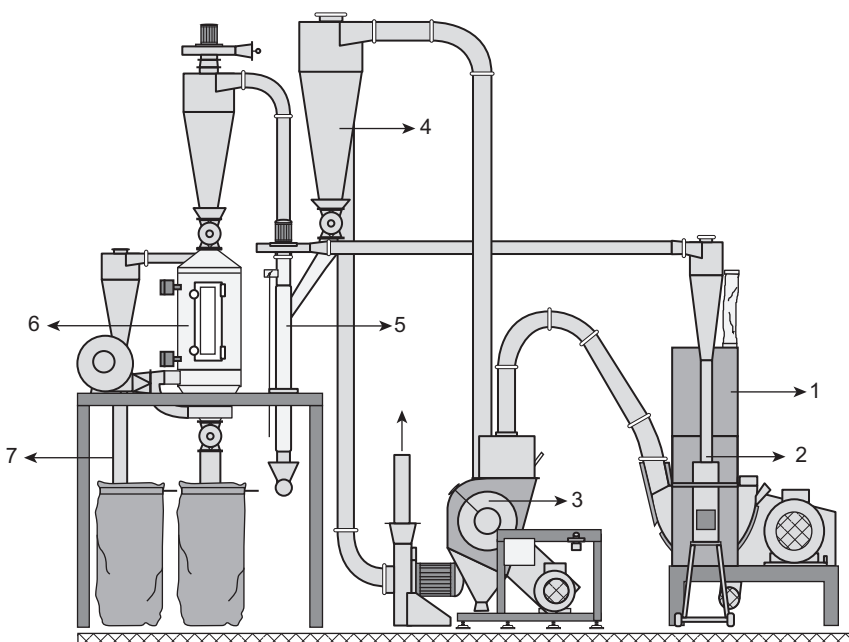
Next Generation Recyclingmaschinen GmbH (NGR) has developed a new technology for bioplastics recycling. NGR's solution uses recycling machines that feed the material to the extruder with an integrated cutter-feeder, which consists of a slow rotating cutter shaft with knives that cut against fixed knives like scissors, and a feeding zone that conveys the material to the extruder without pre-heating it. The NGR cutter-feeder-extruder can reportedly recycle most of the commonly used biopolymers, such as starch or PLA-based products. The screws, vacuum vent and melt filter can all be tailored to the special requirements of biopolymers, such as low heating of the material or the removal of printing inks. This method is also sensitive towards monitoring slight changes in the molecular mass distribution resulting from the inevitable heat stress in any polymer processing step [4].

Pallmann Maschinenfabrik GmbH & Co. has developed a special process for recycling waste generated during the production and processing of PLA foam and film. As shown in Figure 3.2, PLA waste pre-cut into a size smaller than ½" is conveyed into the storage bin of the Plast-Agglomerator with a pneumatic conveyor system. From the hopper the feed material is continuously dosed into the agglomeration chamber by a feeding screw. Through mechanical pressure and only frictional heat, the material is evenly sintered through the die holes within fractions of a second. The frictional heat and mechanical pressure can be adjusted in such a way that the sintering is performed below the T_m of each type of plastic to ensure minimal thermal degradation of the product. Waste is generated during the production and processing of PLA foam and film.

Figure 3.2 Plast-Agglomerator, Type PFV

1: Hopper; 2: Plast-Agglomerator;
3: Hot-melt granulator; 4: Cyclone;
5: Sifter; 6: Granules cooler;
7: Sacking station

Pallmann Maschinenfabrik GmbH & Co. KG [5].



Valuable virgin material can be saved by recycling this waste, and recycled production waste can be reintroduced into the process for the production of new material.

Suitable apparatus for the continuous regranulation of thermoplastics wastes — in particular, films, fibers, filaments, foam materials and the like — are described in **DE3842072 C1** (1989) and **US2006283340 A1** (2006, **PALLMANN MASCHINENFABRIK GMBH & CO. KG**). These apparatus are mainly used to transform wastes such as polyethylene, polyvinyl chloride, polypropylene, polystyrene, polyamide, mixtures of these wastes, similar thermoplastics, and other organic or inorganic materials, into uniform, free-flowing, and abrasion-resistant granules. This can all be done without thermal damage to the material, as is required for further technological processing in extruders, pressers, or injection-molding machines.

3.2 Restabilization

The reprocessing of waste polymers leads to materials with generally worse properties than those of the original materials. This is due to changes in the chemical structure caused by previous degradation processes. Restabilization is a well-known practice for protecting recycled materials from thermo-mechanical degradation during reprocessing, and for

enhancing long-term stability throughout reuse. Restabilization does not effectively recover the degraded material, but it does prevent further degradation processes that may be catalyzed by the oxidative moieties present in its structure or by moisture. Several processing and light stabilizers, including combinations of hindered phenols and hindered amine stabilizers, have been employed for the restabilization of recycled biopolymers. Without restabilization, these biopolymers can interfere in the auto-oxidation cycle by neutralizing peroxide radicals and decomposing hydroperoxides [1]. Some additives, such as catalyst deactivators, have been reported to stabilize PLAs in the melt. Such additives include benzoyl peroxide [6,7], 1,4-diaminoanthraquinone [8,9], 2-hydroxy-2,4,6-cycloheptatrienone (tropolone) [10], natural, and biodegradable acid [11]. Additives such as carbodiimide compounds are used to retard the hydrolysis of biopolymers. Compatibilizers are also added to improve the performance of waste biopolymers (see also Chapter 7: Degradation on Demand; Section 7.2: Suppression of (Bio)degradability).

3.3 Blending Recycled Biopolymers with other Polymers

Blending recycled polymers with virgin materials is one of the most common and well-established

procedures for upgrading the properties of single-stream waste polymeric materials.

Sharp has developed recycling technology for repeatedly recovering plastic from used consumer electronics and reusing it in parts in new consumer electronics. In 2010, the volume of plastic that was derived from this closed-loop recycling technology and reused in new products increased to 1300 tons. Sharp has disclosed a number of patents for related methods and apparatus for recovering and reusing biodegradable aliphatic polyesters such as PLA and PHB. The methods are used for the recovery and recycling of bio-based thermoplastics from discarded domestic electrical appliances such as air conditioners, televisions, refrigerators, and washing machines, as well as from electronic office equipment and electrical-electronic components.

JP2007284495 A (2007, SHARP KK) discloses a method for the separation, recovery, and reuse of thermoplastic resin (A) from waste material comprised of a thermoplastic resin derived from renewable resources, and a thermoplastic resin derived from fossil resources. Thermoplastic resin (B) is then added to thermoplastic resin (A), and mixed and molded. The method further involves a resin collection process and a gravity-separation process. In the resin collection process, thermoplastic resin is separated and recovered from a waste material using water that has a specific gravity difference. Similarly, the thermoplastic resin (B) is recovered from the waste material. The gravity-separation process involves separating and recovering other thermoplastic resin from crushed material containing plastic. The thermoplastic resin composition derived from renewable resources contained in thermoplastic resin (A) is PLA consisting of L-lactic acid and/or D-lactic acid units. The thermoplastic resin composition derived from fossil fuel resources contained in thermoplastic resin (A) is polyolefin composition or polystyrene composition. While mixing thermoplastic resin (A) with thermoplastic resin (B), additive (which assigns hydrolysis resistance), a compatibilizing agent and/or antioxidant, and a compatibilizing agent having reactive functional group(s) on a side chain, are added. The quantity of additive, compatibilizing agent, and antioxidant with respect to 100 parts by weight of thermoplastic resin (A) and thermoplastic resin (B) are 0.01–10, 0.01–30 and 0.01–5 parts by weight, respectively. The preferred additive is carbodiimide compound, the thermoplastic resin

component is a polyolefin-type resin composition, and the compatibilizing agent is a block copolymer containing PLA as a main component. The compatibilizing agent with reactive functional group(s) in its side chain is a copolymer (a) containing an olefin-type thermoplastic resin component and a styrene-type thermoplastic resin component, or is a modified polymer (b) with a structural unit containing a carboxylic acid group or its derivative(s) group in the principal chain or side chain of the olefin-type thermoplastic resin. The content of copolymer (a) and modified polymer (b) are 0.1–20 and 0.1–10 parts by weight, respectively. The preferred antioxidant is a phenolic antioxidant and/or a phosphorus-type antioxidant.

JP2009161655 A (2009, SHARP KK) discloses a method for recycling a bio-based thermoplastic resin waste by mixing the bio-based thermoplastic resin waste with at least one polymer selected from a styrene-based resin (A), an aliphatic polyester resin (B), and a vinyl-based polymer (C), and heating and melting the mixture. The bio-based thermoplastic resin waste material contains acrylonitrile butadiene-styrene copolymer (ABS), and PLA having L-lactic acid and/or D-lactic acid. The styrene resin (A) is acrylonitrile butadiene-styrene copolymer (ABS). The aliphatic polyester resin (B) is PLA that consists of L-lactic acid and/or D-lactic acid units. The vinyl polymer (C) contains polymer of (meth)acrylic ester, and has hydroxyl and/or functional groups that have carboxyl group reactivity. The thermoplastic resin composition further contains (in weight parts) rubber-containing copolymer (D) (0.1–50), phenolic antioxidant and/or phosphorus-type antioxidant (E) (0.01–5), and hydrolysis-proof stabilizer (F) (0.01–10). The rubber-containing copolymer (D) is silicone acrylic-type and/or core shell-type acrylic-type copolymer.

JP2010005948 A (2010, SHARP CORP) discloses a method for reusing a biodegradable polymer waste. It is comprised of the following two processes: (1) mixing the biodegradable polymer waste, which is composed mainly of an acrylic resin (e.g., PMMA), and at least one biopolymer selected from the group consisting of L-lactic acid and D-lactic acid units, with polymers containing a styrene-based resin (e.g., ABS), preferably in combination with at least one antioxidant and a hydrolysis-proof stabilizer. This mixture is then thermally melted to obtain a raw material as resource; and (2) manufacturing a biodegradable molded article from the recycled

material. The biodegradable polymer waste is selected from domestic electrical appliances, electronic office equipment, electrical and electronic components, and the like.

JP2008100413 A (2008, SHARP CORP) discloses a method for recycling waste plastic material having a paint film formed from a bio-based coating. It includes the following steps: (1) crushing the waste plastic material having the paint film; (2) heating/melting the crushed waste plastic material; (3) producing a plastic raw material using it; and (4) producing a plastic molding. The recycling method does not adversely affect the environment, while preventing the lowering of the physical properties of a regenerated plastic material even when the waste plastic material having a paint film, without removing the paint film, is mixed with a plastic material to be coated to be recycled.

JP2002226623 A (2002, KANEBO LTD) discloses a method of reclaiming a foam molding from a biodegradable aliphatic polyester (e.g., PLA or PBS) by grinding and molding the foam again. Furthermore, a reclaimed molded article is obtained by mixing the ground foam with unused PLA-based foam beads (primary foam) of 70% or more and then molding the mixture. The reclaimed foam is used for shock-absorbing materials and for packing.

EP1241231 A1 (2002, CANON KK) discloses in one of its embodiments the recycling of molded articles obtained from a biodegradable polymer composition, comprising a biodegradable biopolymer (A) and a biodegradable liquid crystalline biopolymer (B). The source material for the biodegradable biopolymer or liquid crystalline biopolymer can be waste paper. Molded articles include ink tanks of ink-jet printers, toner containers of electrophotography apparatus, packing materials, casings of printers and cameras, transparency sheets, and so forth. In one example, a transparent sheet prepared from butyl ester of hydroxyethylcellulose (B) and PLA (A) was melted and pressed again to mold a transparency sheet. This sheet was found to be usable as a transparency sheet without causing problems in light transmissivity and other properties. In another example, the transparency sheet was melted, pelletized, and then molded into a casing of an ink-jet printer casing by an injection machine. The casing was formed with no problem in molding (see also Chapter 6: Chemical Recycling; Section 6.3: Hydrothermal Depoly-merization).

WO2011146562 A2 (2011, DU PONT) discloses a method for making a fiber containing from 0.1 to 99.9 wt.% (preferably 5 to 10 wt.%) with recycled poly(trimethylene terephthalate) (PTT). It is comprised from the following steps: (1) providing carpet yarns containing recycled PTT (Sorona®); (2) melt-pelletizing the yarns; (3) combining the recycled PTT with virgin PTT to form a blend; and (4) spinning the blend to form a fiber. In some preferred embodiments, the PTT being reclaimed and recycled and/or virgin PTT with which the PTT is combined are bio-derived; i.e., the PTT can be prepared from 1,3-propanediol that has been produced using a biological method such as fermentation (see also Chapter 1: Introduction to Biopolymers; Section 1.3.2.3: Aromatic Polyesters (Bio-Based)). The use of bio-derived starting materials in virgin PTT, and preferably also in the PTT in the carpet being used for the recycled polymer, provides a sustainable and more environmentally friendly consumer product than processes using only fossil fuel-based raw materials.

CN101275009 A, US2008237910 A1 (2008, FUJI XEROX CO LTD; FUJIFILM CORP), and **CN101130627 A** (2008, FUJI XEROX CO LTD) disclose methods of recycling biodegradable polymer compacts used mainly as exterior parts of a printer, a copying machine, a facsimile and the like. In CN101275009 A and US2008237910 A1 (2008, FUJI XEROX CO LTD; FUJIFILM CORP) the biodegradable polymer composition comprises 21 to 70% of an aliphatic polyester (e.g., PLA), 35–65% of a second polymer having a glass transition temperature (T_g) higher than the T_g of the aliphatic polyester (e.g., polycarbonate) and 1–20 mass percent of an aluminum phosphate as flame retardant. In CN101130627 A (2008, FUJI XEROX CO LTD) the composition comprises an aliphatic polyester and a lignophenol. The general recycling method comprises freeze-grinding, heating the obtained ground product at a temperature lower than the T_m of the aliphatic polyester, and injection molding the ground product to obtain a biodegradable polymer compact (see also Chapter 5: Physical Recycling; Section 5.2: Grinding). Examples of the aliphatic polyesters include PLA, poly(3-hydroxybutyrate) (PHB), poly(butylene succinate) (PBS), and poly(butylene adipate) (PBA). Of those, the commercially available PLA and PHB are preferred, with PLA being particularly preferred. The use of lignophenol endows the polyester with oxidation resistance, heat resistance, surface hardness, abrasion resistance,

weather resistance, and recycling efficiency (see also Chapter 7: Degradability on Demand; Section 7.2.3: Functional Group-Capping Agents and Catalyst-Deactivation Agents).

3.4 Modification of the Chemical Structure

Chemical modification of the structure of the recyclates is another way to upgrade effectively the properties of recycled products. The use of certain compounds such as radical generators, compounds with reactive functional groups, or chain extenders can be effective in inducing branching and/or cross-linking reactions, or increasing the molecular weight of the degraded polymeric chains from waste materials during melt reprocessing (reactive extrusion). This procedure increases the molecular weight of the polymer chains and improves rheological and mechanical properties [1]. Chemical modification has been successfully applied to upgrade degraded bio-based aromatic polyesters.

US2011071235 A1 (2011, SABIC INNOVATIVE PLASTICS US LLC) discloses a method of making an *in situ* biodegradable composition containing an aliphatic-aromatic copolyester from used aromatic polyesters. In one of its embodiments the aromatic polyester is recycled polyethylene terephthalate (PET) or poly(trimethylene terephthalate) (PTT) derived from renewable resources. The biodegradable copolyester can be prepared by two methods. The first entails reacting the recycled aromatic polyester with a dihydric alcohol selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, 1,4-butanediol tetramethyl cyclobutanediol, isosorbide, cyclohexanedimethanol, bio-derived alcohols, hexylene glycol, and an aliphatic dicarboxylic acid of the formula $(CH_2)_m(COOH)_2$, where m is 4–10, at a temperature from 160°C to 250°C in the presence of a transition metal catalyst (e.g., a titanium alkoxide catalyst to form a first mixture). The second method requires subjecting the first mixture to vacuum distillation at a pressure of less than 2 Torr and a temperature of 220°C to 260°C to form a molten aliphatic-aromatic copolyester.

Chain extenders are reactive additives that, when added during melt processing, enhance the mechanical properties of polyesters, such as PET, and polyesters derived from renewable resources

such as PLA and polyhydroxybutyrate (PHB). Chain extenders can be classified according to the polyester functional groups with which they react: carboxyl-end or hydroxyl-end chain extenders. Common chain extenders are dianhydrides, bis(oxazolines), bis-(hydrooxazine), carbodiimides, diepoxides, and diisocyanates. The chain extension process depends fundamentally on the chain extender concentration and the processing parameters; it is critical to adjust the concentration of the chain extender to successfully achieve chain extension and avoid undesired extensive branching and cross-linking reactions.

BASF's Joncryl® ADR chain extenders are reactive polymers that can be used to upgrade the mechanical properties of degraded aliphatic polyesters such as PLA and PHB. The usage of Joncryl® functional additives typically requires good compounding and feeding techniques to ensure that the additive is evenly dispersed into the polymer matrix and performs its function, be it chain extension or flow enhancement [12].

3.5 Multiple Processing

When polymer materials are subjected to the elevated temperatures and pressures typically applied in the referenced molding processes, the polymers can be prone to molecular degradation, unwanted polymerization, and unwanted reaction with other materials that may be present in the polymer material. This is particularly true in polymer materials that have been processed once and are processed a second time at elevated temperature. This means they are subjected to a second melting and processing cycle as is typical in reuse of scrap or recycled polymer preforms or bottles as the raw polymer material for new preforms and bottles. Such polymer reaction processes can cause the polymer material to acquire undesirable coloring, yellowing, blackening, haze, or other degradation of transparency. These processes may also cause a reduction in melt strength or intrinsic viscosity, or may otherwise deleteriously affect their processability or layer compatibility during subsequent molding into a shaped article, or the physical or aesthetic properties of such article during use.

Multiple processing is used to assess the recyclability of polymeric materials and to study the thermo-mechanical degradation during processing and mechanical recycling. The analysis of structural and morphological changes induced by consecutive

processing steps offers useful information for the optimization of processing conditions during mechanical recycling in order to avoid further degradation. One example is the choice of processing conditions and the further addition of stabilizers and other additives. Vilaplana and Karlsson [1] reviewed the factors that affect the final properties of reprocessed polymers: condition of incoming waste material (degradation state, presence of impurities, degree of branching, residual presence of additives, constituent copolymers), and reprocessing conditions (temperature profiles, screw type, presence of residual oxygen in the extruder). The structural and macroscopic properties of polymers are therefore modified during multiple processing. Chain scission is responsible for a decrease in the molecular weight of the polymeric chains, which leads to an increase in the degree of crystallinity in semicrystalline polymers, a decrease in viscosity, and a modification of the mechanical properties. This results in a progressive embrittlement of the reprocessed material [1].

Several research papers have analyzed the effects of multiple processing on the structural, rheological, and mechanical properties of the most common biopolymer, PLA.

The effect of seven injection cycles on the rheological and mechanical properties of PLA on a pilot scale was studied by Pillin et al. [13]. The viscosity of PLA decreased strongly (from 3960 to 713 Pa s) after only one injection cycle, and after four cycles PLA's viscosity became nearly 150 Pa s. Most of the mechanical performances of PLA also rapidly became rapidly too weak for an industrial application of the polymer. This decrease could be explained by the strong degradation of PLA during processing, which yields large chain scission as evidenced by rheological experiments and molecular weight measurements. Reprocessing of PLA induced an increase of crystallization during cooling with the thermo-mechanical cycles. This can be explained by higher chain mobility due to chain scission during injection. The addition of stabilizers suppressed this crystallization during cooling. Quinone was found to be an efficient stabilizer for trapping free radicals and maintaining PLA chain length with time at the processing temperatures. On the basis of these results, it was concluded that the main phenomenon of the degradation of PLA is driven by free radicals and not by hydrolysis due to moisture. These results indicate that PLA industrial waste can support moderate recycling, which is

a significant improvement on the environmental impact of this polymer.

The effect of multiple (up to 10 times) extrusions of PLA on its physical and mechanical properties was also studied by Żenkiewicz [14]. By raising the number of extrusion cycles, the tensile strength diminished slightly and the impact strength clearly decreased. The melt flow rate (MFI) and water vapor and oxygen transmission rates steadily increased. Variation of the number of extrusion cycles did not affect T_g , whereas it did cause a lowering of the cold crystallization temperature and slightly diminished the T_m . The results indicate that PLA industrial waste is suitable for reuse as an additive to a virgin polymer.

The effect of multiple extrusions and injections on the rheological and mechanical properties of a 50/50 polylactide/polystyrene blend (PLA/PS) was studied by Hamad et al. [15]. The viscosity of the blend decreased when increasing the processing cycle number, which was attributed to the reduction of the molecular weights with the processing cycle. The mechanical properties of the blend worsened with an increasing processing cycle number, and the tensile strength and elongation at break of the blend decreased sharply after two processing cycles. The least change was observed for Young's modulus (reduction by a factor of 0.26 after four processing cycles). The results indicate that PLA/PS waste is suitable for reuse as an additive during compounding of PLA/PS blends or as the raw polymers, PLA and PS.

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CN101230129 A	20080730		SHANGHAI NEW SHANGHUA POLYMER
CN101275009 A	20081001	JP2008274222 A 20081113; CN101275009 B 20120222	FUJI XEROX CO LTD; FUJIFILM CORP
DE3842072 C1	19891228	EP0373372 A2 19900620; JPH02202403 A 19900810; US5009586 A 19910423; EP0373372 A3 19910502; EP0373372 B1 19930908; JP6013176 B 19940223	PALLMANN MASCHINENFABRIK GMBH & CO KG
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(Continued)

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JP2009161655 A	20090723		SHARP CORP
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US2006283340 A1	20061221	DE102005027861 A1 20061228; DE102005027861 B4 20120802; US7467585 B2 20081223	PALLMANN MASCHINENFABRIK GMBH & CO KG
US2008237910 A1	20081002	US7767744 B2 20100803	FUJI XEROX CO LTD; FUJIFILM CORP
US2011071235 A1	20110324	WO2011038071 A1 20110331; CN102498151 A 20120613; EP2480589 A1 20120801; KR20120099384 A 20120910	SABIC INNOVATIVE PLASTICS US LLC
WO2008058303 A1	20080522	CA2668902 A1 20080522; AU2007321746 A1 20080522; MX2009004892 A 20090521; KR20090092806 A 20090901; EP2101974 A1 20090923; CN101535018 A 20090916; AT505462 A1 20090115; JP2010509413 A 20100325; US2010216902 A1 20100826; KR20110007259 A 20110121; RU2009122359 A 20101220; RU2412804 C1 20110227; EP2295218 A1 20110316; AU2007321746B B2 20110818; CN102357943 A 20120222; JP2012066588 A 20120405; AT552958 T 20120415; ES2385105 T3 20120718; DK2101974 T3 20120723	EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT MBH
WO2009100473 A1	20090820	AU2009214810 A1 20090820; CA2715048 A1 20090820; AT506489 A1 20090915; CN101945743 A 20110112; EP2252440 A1 20101124; KR20100120212 A 20101112; MX2010008248 A 20100823; AT506489 B1 20101215;	EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT MBH

(Continued)

Patents (*Continued*)

Patent	Pub. date	Family members	Applicant
		US2011049763 A1 20110303; JP2011514850 A 20110512; RU2010137909 A 20120320	
WO2011146562 A2	20111124	WO2011146562 A3 20120518; US2012128924 A1 20120524	DU PONT

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4.1 General

Biopolymer products that have reached the end of their useful life often find their way into a wide variety of terrestrial and aquatic environments. These environments differ physically (temperature, mineral structure), chemically (pH, oxygen, moisture content, nutrients), and biologically (microorganisms, enzymes) [1].

Waste biopolymers are disposed of in either a controlled or uncontrolled way in the environment. The various options available for the disposal of biopolymers are depicted in Figure 4.1.

4.2 Landfilling

Landfilling, also known as solid waste treatment (see Figure 4.1), involves dumping materials that are either non-biodegradable or relatively difficult to degrade into a specially designed structure built into the ground (a pit) or on top of the ground. This structure is usually lined with plastic film and/or clay, and covered with dirt when full. In landfills, solid waste is isolated from groundwater and rain. Humidity is low,

the temperature is that of the surrounding soil or ambient air, and the conditions are typically anaerobic, which prevents degradation by microbial action and results in a relatively slow breakdown. In comparison, a bioreactor landfill more rapidly transforms and degrades solid waste by the addition of liquid and air, which enhances microbial processes of degradation similar to those in composting.

Polymer films, and especially packaging materials, often take up a disproportionate volume in waste disposal facilities. Molded polymers have the extra disadvantage that they are difficult to compact. When polymer wastes are contaminated with hazardous materials such as putrefied organic materials or pathogenic microorganisms, special countermeasures for protection from bad smells or infection are required for the transfer of these wastes to disposal facilities. Particularly when wastes are contaminated with pathogenic microorganisms, common landfill disposal leads to a danger of spreading infectious disease, and incineration becomes a requisite treatment. In spite of all these disadvantages, the majority of discarded polymer articles end up in landfills without any pretreatment.

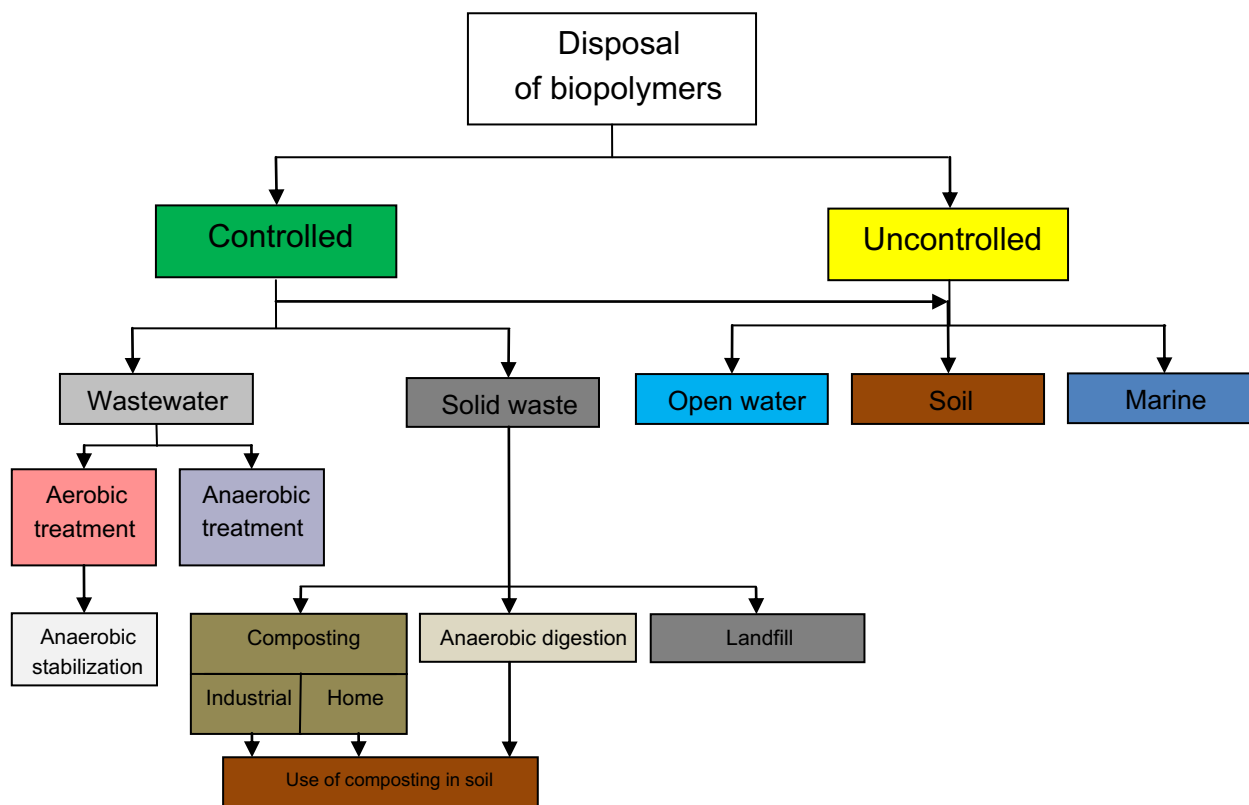


Figure 4.1 Options of disposing biopolymers.
Adapted from De Wilde [2].

A growing environmental problem is the excessive number of disposable products that make up an increasing volume of materials in landfills. Disposable products of large volume include disposable diapers, shrink-wrapping (food wraps, consumer product wraps, pallet and/or crate wraps, and the like), and bags (grocery bags, food storage bags, sandwich bags, garbage bags, and the like). A conventional disposable absorbent product is to a large extent already compostable. A typical disposable diaper, for example, consists of about 80% compostable materials (e.g., wood pulp fibers and the like). However, the backsheet, which is one of the largest noncompostable components of a conventional disposable absorbent article, is made of polyethylene. Several manufacturers have come up with solutions for producing disposable products that are either 100% compostable or have an accelerated biodegradation rate after the end-of-service life (WO03035753 A1, 2003, PROCTER & GAMBLE CO; MEREDIAN INC).

WO03035753 A1 (2003, PROCTER & GAMBLE CO; MEREDIAN INC) and **MXPA04003665 A** (2004, PROCTER & GAMBLE CO) developed a biodegradable film and/or laminate from a composition

comprised of destructured starch and a polyhydroxyalkanoate copolymer such as poly(hydroxybutyrate-*co*-hydroxyhexanoate) (PHBH). The film can be used to replace polyethylene backsheets in absorbent articles with liquid-impervious films of compostable material. It can also be used for making a variety of disposable products such as bags or wraps. In an anaerobic solid waste treatment facility or sanitary landfill, disposable articles of this composition biodegrade more rapidly than articles not of this composition.

Biodegradable biopolymers such as aliphatic polyesters may be degraded spontaneously in a landfill, but the time required for degradation is too long to provide a noticeable lessening of the burden on the landfill. Under most moisture and temperature conditions in landfills, adequate depolymerization for the pulverization of film and similar products — predominantly made of polylactide (PLA) and polyglycolide (PGA) — occurs in 6 months to 2 years. The acceleration of the biodegradation rate requires significant energy input in terms of high temperatures and potential cleanup of the surrounding soil and groundwater owing to the harsh acid needed to break down the polymers (US2005261465 A1, 2005 and WO2005118693 A1,

2005, DU PONT). Ultimately, landfill use is not a sustainable long-term solution given its ever-increasing economic and environmental costs.

Theoretically, biodegradable biopolymers should relatively quickly close the loop on the carbon cycle, thus making the carbon again available in the atmosphere for use in biological growth (note that this does not apply to fossil fuel-based biodegradable polymers). Because carbon dioxide is captured from the air as their raw materials grow, one could say that their atmospheric carbon is “temporarily sequestered” in a sealed landfill for some months or years [3]. According to Tolinski [3], by closing the loop in landfill disposal, biodegradable biopolymers may have an advantage in terms of long-term, life-cycle impact. They may, however, present a distinct disadvantage in the short term in that methane, a very potent global warming gas from initial anaerobic degradation, escapes before it can be captured [3]. Unfortunately, most landfills are not equipped with biogas collection systems. Therefore, any methane produced from quick biopolymer degradation could escape into the atmosphere [4].

4.2.1 Pretreatment Before Disposal

A number of patents disclose various techniques for pretreating biodegradable biopolymers before discarding them in waste disposal sites; these techniques are intended to increase biodegradation rates (see Section 4.4.1.1: Size reduction via hydrolysis; and Chapter 7: Degradability on Demand; Section 7.3: Promotion of (Bio)degradability).

JP2002355819 A (2002, TOYOTA MOTOR CORP) discloses a method for the pretreatment of a biodegradable biopolymer — such as PLA, poly(ϵ -caprolactone) (PCL), poly(butylene succinate) (PBS), or poly(vinyl alcohol) (PVOH) — where the biopolymer is ground up in its frozen state into small particles that can be discarded in a waste disposal site. In a preferred process the ground biopolymer is discarded after absorbing water-containing microorganisms. The proposed method permits the grinding of bulky biodegradable items such as foams, which are incapable of being ground into small particles by usual methods, and promotes the biodegradation process (see also Chapter 5: Physical Recycling; Section 5.2: Grinding).

US5278256 A (1994, DU PONT) discloses a way to increase the hydrolysis rate of discarded articles made of PLA or PGA by compounding the polymers with a depolymerization-enhancing agent such as a quaternary ammonium compound. After

use, depolymerization-enhanced articles made of PLA and PGA, when discarded in landfills, are quickly hydrolyzed to environmentally benign low molecular weight products such as a hydroxycarboxylic acid monomer that poses no danger to groundwater and is rapidly degraded to water and carbon dioxide. Normally, a molar ratio of medium to hydroxycarboxylic acid moieties of 1:1 to 100:1 will effect optimum depolymerization. Of course, in a landfill, lower water to hydroxycarboxylic acid ratios are frequently encountered. Nevertheless, adequate depolymerization will occur in a few months (preferably 3–6 months) by introducing a quaternary ammonium compound into PLA or PGA (see also Chapter 7: Degradability on Demand; Section 7.3: Promotion of (Bio)degradability).

4.3 Biological Processes

The various biological waste treatment options for biopolymers are presented in Figure 4.2. These options provide differing conditions in terms of temperature, oxygen, and microorganisms for the breakdown of biopolymers. Biopolymer biodegradation can take place either aerobically or anaerobically. An example of aerobic biodegradation is composting, of which there are two types, home and industrial. Similarly, depending on the temperature, one can distinguish between thermophilic (50–60°C) and mesophilic (35°C) anaerobic digestion (or biogasification).

4.3.1 Aerobic Biodegradation

4.3.1.1 Biodegradation in soil (soil burial)

The natural degradation of biopolymers in soil can be a slow process. The degradation of PLA in soil is slow and can take several years. Thus, there is the fear that a large amount of PLA left outdoors may cause new environmental problems.

A biodegradable polymer is decomposed in soil or water by microbes living therein, and is converted into an inorganic substance such as oxygen, nitrogen, hydrogen, and carbon (or gas thereof) if the polymer is completely decomposed. More specifically, various microbes (such as bacteria and fungi) are living in soil. The microbe emits an exoenzyme into soil either by secretion or through cell dissociation. An organic substance (e.g., a biodegradable polymer) is decomposed by the action of the exoenzyme and becomes

	Anaerobic Bacteria, no fungi	Aerobic Bacteria & fungi
50–60°C	Chemical pulp Starch PLA Starch/PCL PHA	Chemical pulp Mechanical pulp Starch PLA starch/PCL PHA PBAT
≤35°C	Chemical pulp Starch Starch/PCL PHA	Chemical pulp Mechanical pulp Starch starch/PCL PHA PBAT

Figure 4.2 The four types of biological waste treatment for biopolymers [5]:

aerobic: (1) home and ii) industrial composting; (2) anaerobic; (3) thermophilic (50–60°C); and (4) mesophilic digestion (35°C).

Abbreviations: PBAT, poly(butylene adipate-co-terephthalate); PCL, poly(ϵ -caprolactone); PHA, polyhydroxyalkanoate; PLA, polylactide.

(from Hermann *et al.* [5]).

lower molecular weight substances. On the other hand, saccharides (such as fructose and glucose) or amino acids produced by decomposition of the organic substance into lower molecular weight substances can provide food (substrate) for the microbe to grow and proliferate. As the number of microbes increases through proliferation, the secreted or emitted exoenzyme increases and activates decomposition (i.e., biodegradation) of the organic substance. However, since the amount of food (substrate) is generally small in soil, and there are both food-rich and food-poor soils (depending on locale), it is not definite that there will be a large number of microbes living in the soil where the molded resin object is disposed of (US2007082202 A1, 2007, FUJITSU LTD; see also Chapter 7: Degradability on Demand; Section 7.3.3: Enzymes and Microbial Nutrients).

Biopolymers have several applications in agriculture. Biodegradable films such as mulch films can be buried in soil and left to degrade naturally. These materials can be tilled into the soil, which results in reduced labor input, landfill charges, and solid waste. These films do not need to be removed from the fields and do not have any environmental impact.

JP2002348406 A (2002) and **JP2003041047 A** (2003, MITSUBISHI CHEM CORP) provide

a disposal method for the efficient decomposition of an agricultural mulch film made from a biopolymer. It entails contacting the film with enzymes and/or microorganisms, plowing the film into the soil, and reclaiming the soil for agriculture. The biopolymer is an aliphatic or alicyclic polyester polymer such as PLA, poly(butylene succinate-co-lactate) (PBSL), or poly(ethylene succinate) (PES). The enzyme, which decomposes the biopolymer in a short period of time, is a hydrolase or an oxidative degradation enzyme; the microorganisms belong to the genera *Pseudomonas*, *Bacteroides*, *Mucor*, and *Humicola*.

JP2002226624 A (2002, UNITIKA LTD) discloses a degradation method for aliphatic polyester-based molded articles in which the molded articles are put into soil or culture medium under an atmosphere humidity of at least 60% and a temperature of at least 60°C and decomposed. Large-size waste biopolymers, especially those made of PLA (such as mulch films), are also decomposed within a short period of time without using any special compost.

JP2004339420 A (2004, KANEBO LTD; KANEBO SYNTHETIC FIBERS LTD) discloses a method for decomposing in a relatively short time a mixture of plant and molding comprised of a biodegradable polymer used as manure. This is

accomplished by adding urea to the mixture. Preferably, the urea is dissolved in water and then the water solution is added to the mixture. This method is suitable for moldings comprised of PLA.

4.3.1.2 Composting

Biopolymers are generally considered unsuitable for conventional polymer recycling once biodegradation has been triggered during service life or in the waste stream. Rather, they are more suitable for composting [6]. Composting is an environmentally attractive waste disposal process that involves the biodegradation of materials by microbial action; this results in the formation of gases (such as CO₂), water, and compost. As shown in Figure 4.2, home composting occurs when bacteria and fungi degrade biopolymers under aerobic conditions at ambient temperatures (35°C). Industrial composting occurs when bacteria and fungi degrade biopolymers under aerobic conditions, typically at temperatures not higher than 70°C (and averaging 55–60°C) at 100% relative humidity, and during an exposure period that lasts from several weeks to several months. Biodegradation of an aliphatic polyester in compost involves two steps. The first step occurs via hydrolysis of the ester bonds by extracellular hydrolytic enzymes. These are normally secreted by a mixture of microbial flora, and cleave the polyester backbone into smaller fragments and/or respective monomers. Eventually, cleavage results in fragments and/or monomers capable of being taken up by one or more of the microbial flora, which may or may not be the same as those that secreted the enzymes. The second step is biological: microbes take up the fragments and/or monomers and metabolize them into biomass, biogas (which includes CO₂), and liquid leachate (US2005261465 A1, 2005 and WO2005118693 A1, 2005, DU PONT).

Composting can serve as an auxiliary to landfilling to reduce the amount of non-recyclable solid landfill waste and produce cheap, beneficial fertilizer. Composting is more expensive because of the need for initial waste sorting and/or separation.

Conventional composting of waste biopolymers in a composting facility is a slow process. PLA is not degraded during garden or municipal composting because the temperatures in small-scale compost heaps are not sufficiently high enough for PLA degradation [6]. Biopolymers, when presented in larger sections or in arid composting conditions, can fail to hydrolyze (and subsequently biodegrade) at a rate acceptable to industrial composting facilities.

The environmental benefits of degrading biopolymers are marginal. They release CO₂ when composted, the same as if they are burned. In contrast polyethylene (PE) sitting inert in a landfill sequesters carbon for a long time.

One limitation to marketing compost as fertilizer is its visible contamination by non-degraded polymers such as polymer film, fiber fragments, tableware, etc.

Currently, composting is the most preferred end-of-life disposal method for waste biopolymers. Domestic and municipal composting is favored over landfill disposal. Industrial composting is a promising disposal alternative for biopolymers [7], especially for soft packaging (e.g., films), but it requires an infrastructure that includes collection systems and composting facilities. It does not, however, represent a practical solution for most cases of agricultural polymer wastes as compared to biodegradation in soil [8].

Disposed of biopolymers are commonly found in admixture with food refuse, yard trims, etc. The discarded biopolymers are usually in the form of bags or tableware (utensils, plates, and cups).

A number of patents describe various methods and apparatus for improving and optimizing the composting of biopolymers.

DE102008025758 A1 (2009, BERNDT & PARTNER GMBH) describes a device for composting biodegradable packaging and easily compostable leftovers. The device comprises many chambers arranged one above the other, where the first chamber is a feeding chamber equipped with a cutter, and the other chambers are real composting areas. These are kept at a constant temperature by heating modules and are equipped with filter fans for a filtered air supply and air removal. The final chamber is open so that the end product can be removed.

JPH09249474 A and **JPH09249475 A** (1997, JAPAN STEEL WORKS LTD) disclose the composting treatment of an organic waste containing discarded biopolymer(s) and an accompanying apparatus. The biopolymer is crushed and mixed with an easily decomposable organic waste and the obtained mixture is subjected to fermentation treatment to obtain compost. As necessary, the fermented compost, or a biodegradable polymer separated from the compost, is added to a mixture of the crushed biodegradable polymer, and the easily decomposable organic waste and the obtained mixture is fermented. The treatment apparatus is provided with (a) an apparatus capable of crushing the biodegradable plastic before fermentation treatment, (b) a mixing apparatus capable of mixing

the crushed polymer with the easily decomposable waste, and (c) a fermentation tank. A device capable of mixing fermented compost or a biodegradable polymer separated from the compost is used as the mixing apparatus. The organic waste is kitchen waste (crude refuse), processing residue generated from a food-processing factory, and agricultural waste, etc. Biopolymers (e.g., starches, PHAs, or aliphatic polyesters) are crushed to pieces of 5–50 mm (preferably 5–20) for a smooth fermentation and decomposition treatment; a biopolymer of this size can decompose after about 20 days. The content of the biopolymer in the waste mixture is 2–20 wt.% (preferably 5–10).

JPH09201579 A (1997, JAPAN STEEL WORKS LTD) discloses a process for separating and recovering paper from biodegradable polymer-coated paper, which is a used food package comprised of paper and a biodegradable polymer containing an aliphatic polyester as its main component; the paper often has food refuse attached to it. The package (optionally crushed) is supplied to a fermentation tank, and the polymer and the food refuse are preferentially aerobically fermented and decomposed by microorganisms to provide compost; then the paper that is left after fermentation is separated from the compost and recovered. Preferably, the aerobic fermentation decomposition is carried out at 40–80°C. The obtained compost is added to the used food packages so that the resulting water content is 30–75 wt.%. The conventionally required washing process that removes the food refuse from the packages can be omitted. The coating material can be degraded alone in a short time and easily separated from paper, and the conventionally required process of separating the coating material from the paper can be omitted. This is considered to be an economical and environmentally friendly process. The proposed method obviates the need for washing off residual food and facilitates the peeling of plastics from paper.

A food packaging material in which paper is coated with biodegradable polymer containing an aliphatic polyester as a main component, and to which residual food adheres, is supplied to a fermentation tank; the polymer and the residual food are decomposed by aerobic fermentation into compost. After that, residual paper that is not decomposed is separated from the compost to be recovered.

To enable the quick and complete decomposition of a biodegradable polymer, it is crushed, mixed with an easily decomposable organic waste, and the mixture is fermented. Waste biodegradable plastic is

crushed and mixed with an easily decomposable organic waste, and the obtained mixture is subjected to fermentation to obtain compost. As necessary, the fermented compost, or a biodegradable plastic separated from the compost, is added to a mixture of the crushed biodegradable plastic, and the easily decomposable organic waste and the obtained mixture are fermented. The treatment device is provided with (a) an apparatus capable of crushing the biodegradable polymer before fermentation treatment, (b) an apparatus capable of mixing the crushed polymer with the easily decomposable waste, and (c) a fermentation tank. An apparatus capable of mixing a fermented compost or a biopolymer separated from the compost is used as the mixing apparatus (b).

JP2001205233 A (2001, EBARA CORP) provides a method and an apparatus for treating a biodegradable biopolymer bag in which garbage is collected; it can produce good compost and can reduce the amount of residues to be discharged outside a composting facility (Figure 4.3). The filled biodegradable bag (12) is shredded and sorted by a selective shredding sorting device (1), and a material (13), primarily comprised of the biodegradable bag after garbage (14), has been sorted, is decomposed by fermentation treatments (4, 5). The fermentation treatments of the biodegradable bag can be performed with addition of compost. The material (14), primarily comprised of the garbage that has been shredded and sorted, is subjected to fermentation treatments (9, 10) separately from the material primarily comprising the biodegradable plastic bag.

JP2005131480 A (2005, NAKAMURA K; HIRANO K; YOKOYAMA S; INOUE K; TAIRA T) discloses a method for recycling biodegradable waste (1) by successively performing a hydrolytic treatment (2) and a drying treatment (3) (Figure 4.4). In the hydrolytic treatment (2), foodstuff residues (1b) put in a bag made of a biodegradable biopolymer such as PLA (1a) are heated by steam (along with the bag) while being stirred and mixed; the biodegradable biopolymer is hydrolyzed to low molecular weight matter. In the drying treatment (3), the biodegradable waste (1) is dehydrated, not only for a reduction in volume, but also for recycling as a biodegradable waste resource. The foodstuff residues (1b) containing the biodegradable biopolymer are recycled as compost and feed (4a), and if the material to be treated is composed only of a biodegradable biopolymer (1a) such as PLA, it is recycled as lactic acid, being the raw material (4b) of the

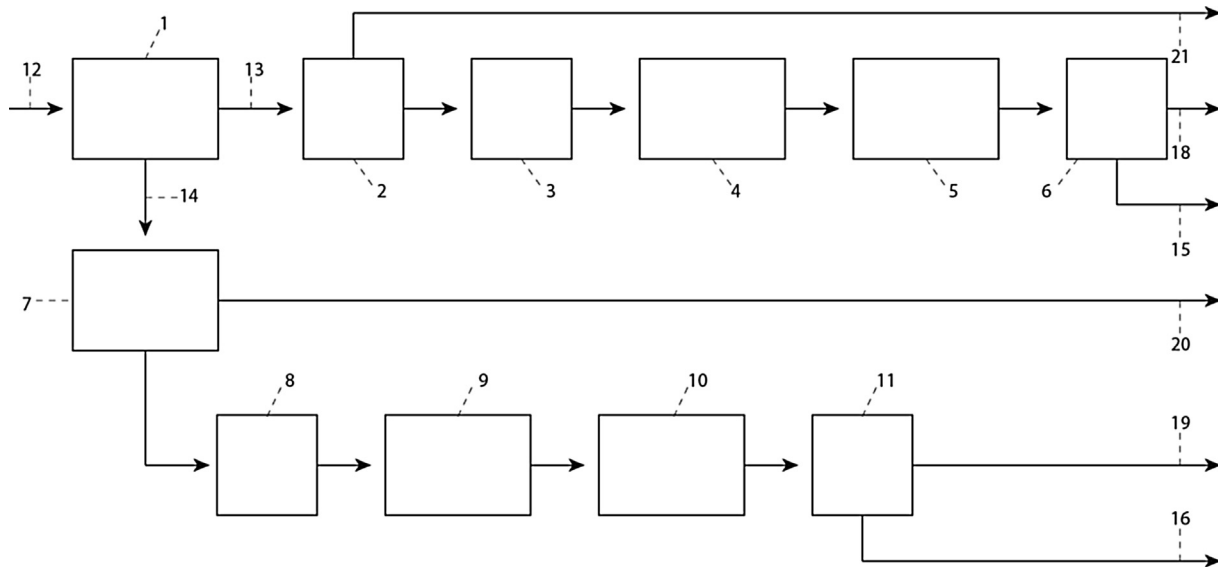


Figure 4.3 Outline diagram of the biodegradable polymer bag processing apparatus according to JP2001205233 A (2001, EBARA CORP).

1: Sorting crushing apparatus; 2: Magnetic separator; 3: Crusher; 4, 9: Primary fermentation tank; 5, 10: Secondary fermentation tank; 6: Sieve; 7: Magnetic separator; 8: Chaff addition and water content adjustment; 11: Sieve; 12: Biodegradable polymer bag (13) filled with organic refuse (14); 13: Biodegradable polymer bag; 14: Organic refuse; 15, 16: Compost; 18, 19: Residue ; 20, 21: Magnetic separation (empty cans, dry cells, etc.).

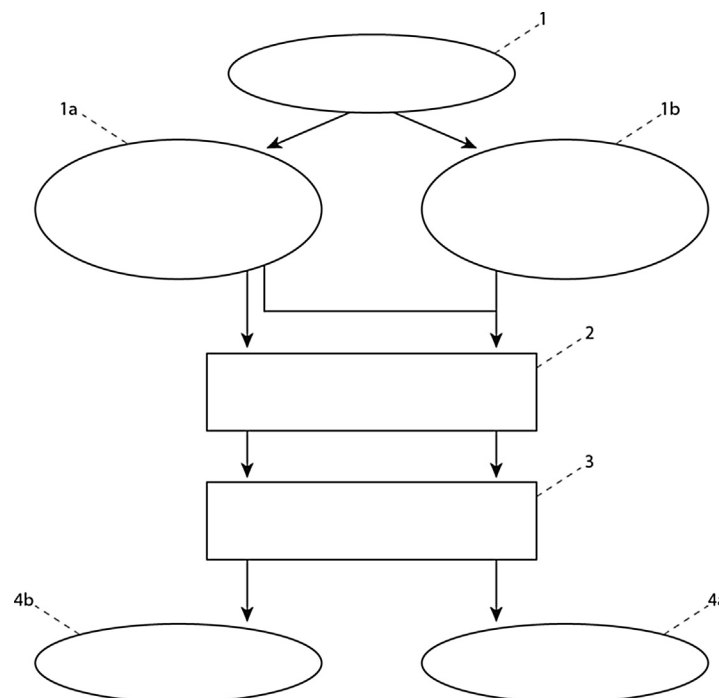


Figure 4.4 Outline diagram of the organic waste recycling method according to JP2005131480 A (2005, NAKAMURA K; HIRANO K; YOKOYAMA S; INOUE K; TAIRA T).

1: Filled bag; 1a: Biodegradable polymer (e.g., PLA); 1b: Foodstuff residues; 2: Hydrolytic treatment; 3: Drying treatment; 4a: Fertilizer; 4b: Biopolymer's degradation product (e.g., lactic acid).

biodegradable biopolymer. The method allows foodstuff residues and a dust bag to be recycled as resources without fractionating them.

JP2002255675 A (2002, NEZU KIYOMI; SHIMIZU K) describes a composting circulation method for garbage from food and disposable tableware (made of biopolymers) generated at a restaurant. The garbage is enclosed by a biodegradable bag and is conveyed into a fertilizer plant. A normal mark is printed on the biodegradable bag, which enables the worker to confirm the contents of the bag. The obtained compost is transported to a farmhouse through a direct or circulation mechanism for the cultivation of vegetables and fruits.

JP2002293982 A (2002, KANEBO KASEI KK) provides a method for decomposing discarded biodegradable biopolymer by contacting an aliphatic polyester composition (such as PLA) with a heated decomposition promoter solution selected from water, water-containing nonvolatile solute, and water-containing acid. This results in an intermediate degradation product that is then treated with a microorganism method compost-forming device. In one example a plate comprised of PLA was immersed in aqueous NaCl solution (20 wt.%) at a temperature of 105°C for 15 min. The volume reduction and compost processing of organic refuse and discarded biodegradable polymer are performed simultaneously.

JP2003012858 A (2003, UNITIKA LTD) discloses a method for decomposing discarded biopolymer products made of an aliphatic polyester such as PLA by pretreating the polymer with an alkaline material (dissociation constant $pK_a \geq 7.0$) and passing the treated product into a compost apparatus. The alkaline material is an amine compound, which promotes the degradation of the biopolymer by lowering its molecular weight.

JP2005298565 A (2005, NIPPON ESTER CO LTD) discloses a method for accelerating the decomposition of biodegradable molded products subjected to composting (which is traditionally slow). A discarded molded product containing a biopolymer, such as PLA, PBS, or an aromatic-aliphatic polyester, is contacted with steam ($\geq 100^\circ\text{C}$) for more than 5 min; the molded product is then treated in a compost-forming installation of a microorganism system.

4.3.2 Anaerobic Biodegradation

Anaerobic decomposition occurs naturally in swamps, waterlogged soils and rice fields, deep bodies

of water, and in the digestive systems of termites and large animals. Anaerobic processes can also be managed in a “digester” (airtight tank) or covered lagoon (pond) for waste treatment. Depending on the temperature, one can distinguish between thermophilic (50–60°C) and mesophilic ($\leq 35^\circ\text{C}$) digestion. PLA will only degrade in a thermophilic environment [5]. Anaerobic digestion results in the formation of gases (e.g., CO_2 , CH_4 , and N_2O), water, and digestate.

Most research on biodegradation processes of biopolymers is focused on aerobic environments such as soil, compost, or surface water. In contrast, not much is known about anaerobic biodegradation of biopolymers, although anaerobic digestion of bio-waste is becoming more and more established because of the additional energetic benefit of biogas recovery.

JP2005095729 A (2005, KOBE STEEL LTD; AICELLO CHEMICAL CO) discloses a method and an apparatus for treating an organic-type waste containing intermingled biodegradable polyesters. The system uses methane fermentation technology to decompose and ferment the organic waste and recover methane gas efficiently in a short period. The method outlined in Figure 4.5 is comprised of the following steps: (i) hydrolysis of organic waste intermingled with biodegradable polymer (1) by diluting with water (25) in a hydrolysis tank (21); (ii) fermentation of the hydrolyzed decomposed product under anaerobic conditions (23) using a methane

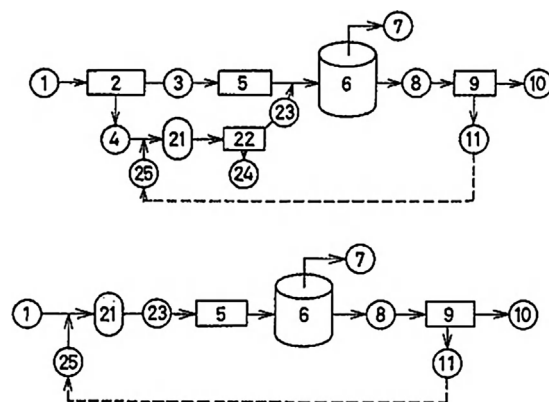


Figure 4.5 Process profile of organic waste recycling according to JP2005095729 A (2005, KOBE STEEL LTD; AICELLO CHEMICAL CO).

1: Organic refuse intermingled with biodegradable polymers; 3: Fermentable organic waste; 4: Non-fermentable organic waste; 5: Adjustment tank; 6: Methane fermentation tank; 7: Methane gas; 21: Hydrolysis tank; 25: Water.

fermentation tank (6); and (iii) recovery of the methane gas (7) generated by the fermentation process.

Alternatively, the method is comprised of the following steps: (i) classifying the organic waste containing biodegradable polymers as fermentable (3) and non-fermentable (4); (ii) hydrolyzing non-fermentable organic waste (4) by diluting with water; (iii) carrying out methane fermentation of hydrolyzed decomposed product under anaerobic conditions (23); and (iv) recovering methane gas (7) generated during the fermentation process.

A preferred method involves separating non-fermentable organic waste after the hydrolysis process. It involves adjusting the input of the concentration of hydrolyzed decomposition product and/or fermentable organic waste prior to methane fermentation. The hydrolysis step is carried out at 120–250°C for 5–60 min. Hydrolysis of non-fermentable organic waste is carried out by adding water until the solid content of non-fermentable organic waste becomes 50% or less. The method uses the dehydrated supernatant liquid of the digest that is emitted from the methane fermentation step as a dilution agent (water) for the hydrolysis step. The biodegradable polymer comes from discarded containers for organic wastes and from food-stuff packaging containers made of aliphatic polyesters.

JP2009154125 A (2011, OSAKA GAS CO LTD) discloses a solubilization method for the conversion of waste PLA into a raw material by methane fermentation. The efficiency of PLA solubilization is remarkably improved by heating the PLA in an anaerobic atmosphere with methane-fermentation sludge at $T \geq 65.5^\circ\text{C}$.

JP2004223470 A (2004, FUJI ELECTRIC CO LTD) provides a method and apparatus for processing a mixture of biodegradable polymers and organic waste comprised of the following steps: (i) grinding the waste mixture; (ii) slurring the ground mixture; (iii) decomposing the biodegradable polymers under anaerobic conditions at 40–60°C; and (iv) methane fermentation of the slurry. The methane fermentation processing apparatus outlined in Figure 4.6 contains a crusher (11), a grinder (12) for grinding the mixture of biodegradable polymers and organic waste, a polymer degradation tank (13) for decomposing biodegradable polymers, a methane fermentation tank (15), and a temperature control unit for maintaining the temperature of the polymer degradation tank at 40–60°C. The method and apparatus are used for

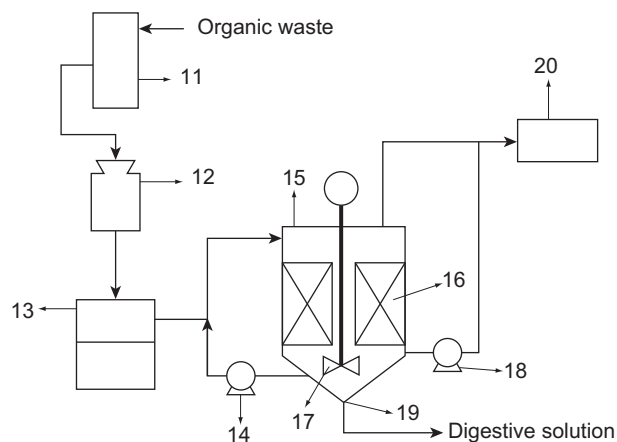


Figure 4.6 Outline diagram of the methane fermentation processing apparatus according to JP2004223470 A (2004, FUJI ELECTRIC CO LTD). 11: Crusher; 12: Grinder; 13: Polymer biodegradation tank; 14: Pump; 15: Methane fermentation tank; 16: Fixing filter bed; 17: Stirring blade; 18: Gas cylinder; 19: Extraction opening; 20: Gasholder.

processing organic waste such as surplus sludge emitted from activated sludge treatment; human waste; organic refuse emitted from restaurants, homes, etc.; and food processing residue emitted from food-stuffs factories, etc.

Methane fermentation of the organic waste can be promoted by irradiating the mixture with ultraviolet radiation (UV) or by contacting the mixture with ozone gas. The methane fermentation processing apparatus has a secondary grinding unit, a UV irradiation unit, and an ozone gas supply unit within the polymer degradation tank; a pressure regulation unit maintains the high pressure inside the polymer degradation tank. The proposed method and apparatus claim to efficiently pulverize and decompose a mixture containing organic wastes and biodegradable polymers. It is also supposed to generate less residue after methane fermentation.

JP2004292705 A (2004, KAJIMA CORP) discloses a processing method and system for efficiently decomposing biodegradable biopolymers with decreased energy consumption. Processing of a biodegradable polymer involves pulverizing and mixing the polymer with a slurry of organic refuse waste material, and carrying out methane fermentation by contacting with methane-fermentation microorganisms. The processing system, outlined in Figure 4.7, is provided with a bioreactor (9) having a reaction chamber (10) containing a carrier (12) to which methane-fermentation microorganisms are adhered; a grinding apparatus (3)

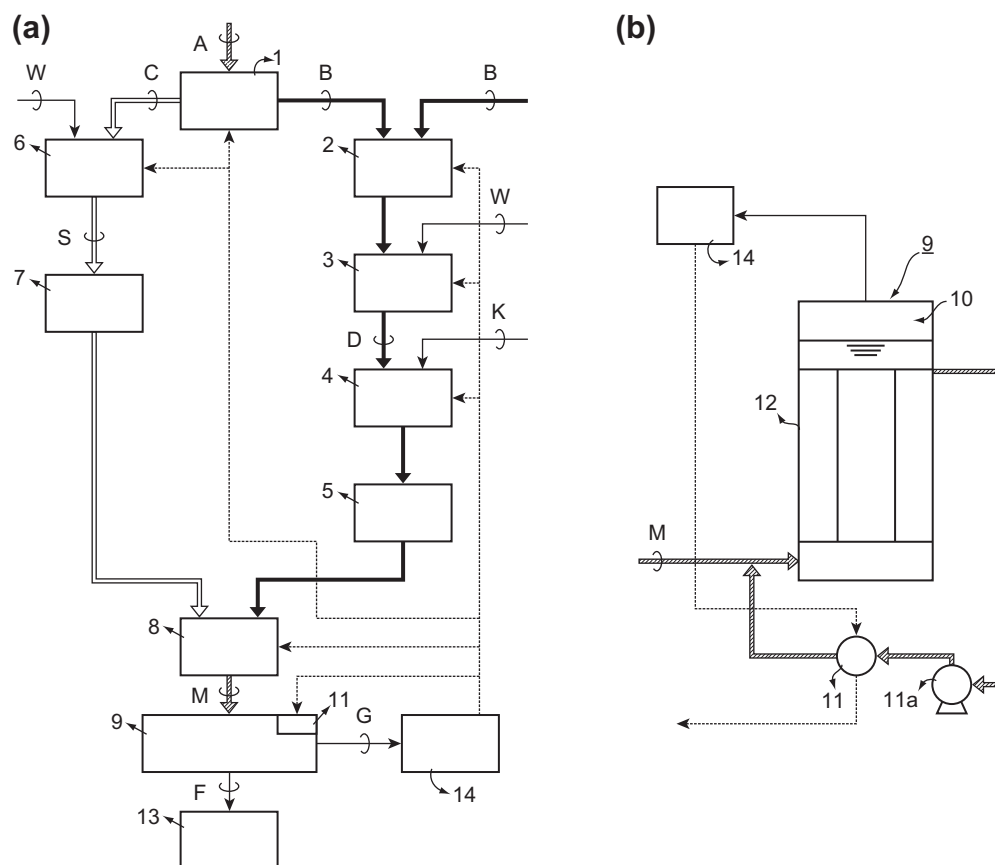


Figure 4.7a and 4.7b Outline diagram of the methane fermentation processing apparatus according to JP2004292705 A (2004, KAJIMA CORP).

1: Sorting apparatus; 2: Coarse crusher; 3: Grinding apparatus; 4: Decomposition tank; 5: Neutralization tank; 6: Pulverizer; 7: Slurry tank; 8: Mixing unit; 9: Bioreactor; 10: Reaction chamber; 11: Heat retention unit; 11a: Circulation pump; 12: Microorganisms carrier; 13: Secondary-treatment facility; 14: Energy recovery equipment. A: Organic-refuse waste material; B: Waste biodegradable biopolymer; C: Organic matter; D: Polymer granules; K: Alkali; M: Mixture of the polymer grains (D) and organic matter slurry (S); S: Organic matter slurry; W: Dilution water.

for pulverizing the biodegradable biopolymer (B) to grains (D) and inducing the pulverized polymer into the reaction chamber (10); a slurry tank (7) for storing a garbage-like organic material slurry (S), which is connected to the reaction chamber (10); and a mixing unit (8) for mixing the polymer grains (D) and the organic material slurry (S) to a composition (M) suitable for methane fermentation. Preferably, a decomposition tank (4) for decomposing the polymer grains (D) with an alkali (K) is placed between the grinding apparatus (3) and the mixing unit (8). The alkali K is preferably ammonia. Optionally, a neutralization tank (5) is provided between the decomposition tank (4) and the mixing unit (8). The processing system further has energy recovery equipment (14) for collecting and converting biogas generated in the bioreactor into

energy, and supplying the energy to the coarse crusher and/or grinding apparatus.

4.3.3 Microbes and Enzymes

4.3.3.1 Aerobic

The distribution of PLA-degrading microorganisms is limited in the natural environment when compared with microorganisms that are able to degrade other polyesters, such as PCL and polyhydroxybutyrate (PHB). Most of the PLA-degrading microorganisms phylogenetically belong to the family of *Pseudonocardaceae* and related genera such as *Actinomadura*, *Amycolatopsis*, *Streptomyces*, *Lentzea*, *Kibdelosporangium*, *Streptoalloteichus*, and *Saccharothrix*. Microorganisms for directly biodegrading waste PLA are

actinomycetes *Actinomadura viridis* (FERM P-16247)¹, *Amycolatopsis mediterranei* (FERM P-14921), and the *Streptomyces* spp. (FERM P-15869, FERM P-15870); and the bacteria *Staphylococcus hominis* (FERM P-115867), *S. epidermidis* (FERM P-15868), *Bacillus subtilis* (FERM P-16181), *B. circulans* (FERM P-16182) and *B. stearothermophilus* (FERM P-16183) (**JP3128577 B1**, 2001, NAT INST ADV IND SCI TECHN).

The National Institute of Industrial Science and Technology (Japan), in cooperation with various industries, isolated and cultured a number of actinomycetes capable of degrading PLA and other PHAs under aerobic conditions to convert the polymer to a useful substance such as an organic acid or compost.

JPH1146755 A (1990, NAT INST IND SCI TECHN; SHIMADZU CORP) uses an actinomycete belonging to the genus *Actinomadura*. In particular, *A. viridis* (FERM P-16247) and PLA are added to a medium containing an inorganic acid salt to degrade the biopolymer under the following culturing conditions: pH 4.0–6.0, 10–75°C, and aerobic atmosphere.

JP2008167701 A (2008, UNIV SHIZUOKA NAT UNIV CORP) uses the actinomycete *Actinomadura atraherbacea* T16 having PLA-decomposing ability; especially *A. atraherbacea* T16-4 sp. nov. (FERM P-21063) is used for the decomposition of PLA.

JPH11127850 A (1990, NAT INST SCI TECHN; SHIMADZU CORP) uses an actinomycete with the ability to degrade silk, such as the silk-utilizing *Amycolatopsis* sp. strain KT-s-9 (FERM P-16463), for the degradation treatment of a composition containing PLA (e.g., paper diapers).

JP2000060540 A (2000, RIKAGAKU KEN-KYUSHO) isolated the actinomycete *Amycolatopsis* sp. No. 3118 strain (FERM P-16947), which has the ability to strongly degrade PLA. The bacterium was

obtained from samples collected from the soil and river water of Wakoh City, Saitama Prefecture, Japan, and places along the railway tracks of the Tobu and Tojo line and the Ogose line. Then, a PLA film obtained by dissolving PLA into chloroform and drying the solution is bonded thereon and bacteria therein are cultured at 30°C for 8–16 weeks. Furthermore, strains grown through the film are subjected to stationary culture at 30°C for 8 weeks in a liquid medium to which film pieces are added; strains judged as effective by measurement of residual amounts of film are subjected to stationary culture at 37°C for 4 weeks, and strains with a high weight-reducing ratio of film are selected.

Microbial degradation of PLA using *Amycolatopsis* sp. was first reported in the literature by Pranamuda et al. [9].

JPH0937776 A (1997, NAT INST IND SCI TECHN; SHIMADZU CORP) uses the actinomycete *A. mediterranei* for the waste treatment of PLA. *A. mediterranei* (FERM P-14921) is an actinomycete belonging to the genus *Amycolatopsis*; it has a PLA-hydrolyzing ability. The bacterium was obtained from samples collected from water in soil, river, lake, or marsh at Tsukuba City in Ibaraki Prefecture, Japan, and cultured in a medium containing PLA, picking up a strain forming a transparent region in the periphery of a colony, and carrying out isolation operations.

JPH10108669 A (1998) and **US6066492 A** (2000, NAT INST IND SCI TECHN; SHIMADZU CORP) use actinomycetes belonging to the genus *Streptomyces* for the degradation of PLA. Two actinomycetes, *S. violaceusniger* (FERM BP-6110) (FERM P-15869) and *S. cyaneus* (FERM P-15870) (FERM BP-6111), were separated from the soil, river water, or lake water collected in Tsukuba City, Ibaraki Prefecture, Japan, and cultured in a medium containing PLA under aerobic conditions. The culturing temperature is usually 10 to 47°C, preferably 10 to 40°C.

JP3128577 B1 (2001) and **US2005032181 A1** (2005, NAT INST ADV IND SCI TECHN; TOKIWA Y) disclose a method for decomposing PLA waste with an actinomycete belonging to the genera *Saccharothrix*, *Streptoalloteichus*, *Kibdelosporangium*, *Lentzea*, *Actinokineospora*, *Saccharomonospora*, *Saccharopolyspora*, or *Actinopolyspora*. Among actinomycetes belonging to the above genera, the following are preferred: *Saccharothrix flava*, *S. coerulescens*, *S. longispora*, *S. australiensis*, *S. mutabilis* subsp. *mutabilis*, *S. aerocolonigenes* subsp. *aerocolonigenes*,

¹ FERM: Acronym derived from the former name of Fermentation Research Institute (FRI) in Japan, which later became the Patent Microorganism Depository of the National Institute of Bioscience and Human Technology (NIBH).

Holdings of International Patent Organism Depository (IPOD) preserves around 14,000 samples being deposited for patent application, which include microorganisms (fungi, yeasts, bacteria, actinomycetes) and plasmids, animal cell cultures and embryos, plant cell cultures, algae, protozoa, and seeds. All of these samples are managed via their FERM BP accession numbers.

S. syringae, *S. coeruleoviolacea*, *S. cryophilis*, *S. espanaensis*, *S. texasensis*; *Lentzea waywayandensis* (formerly *Saccharothrix waywayandensis*), *L. albidocapillata*; *Streptoalloteichus hindustanus*; *Kibdelosporangium aridum*; *Actinokineospora riparia*; *Saccharomonospora azurea*; *Saccharopolyspora erythraea*, *S. hordei*; and *Actinopolyspora halophila*, and *A. mortivallis*. Furthermore, the use of the disposal technique at composting facilities enables conversion of PLA into useful materials such as organic acids or compost.

JP2001128671 A (2001, NAT INST ADV IND SCIEN; TOKIWA Y) discloses a method for decomposing PLA with the actinomycete *Streptoalloteichus hindustanus*.

JP2001128668 A (2001, NAT INST ADV IND SCIEN; TOKIWA Y) discloses a method for decomposing PLA with the actinomycete *Saccharomonospora azurea*.

JP2001128667 A (2001, NAT INST OF ADV IND TECHN; TOKIWA Y) discloses a method for decomposing PLA with an actinomycete *Saccharopolyspora erythrae* or *S. hordei*.

JP2001128669 A (2001, NAT INST ADV IND SCIEN; TOKIWA Y) discloses a method for decomposing PLA with the actinomycete *Lentzea albidocapillata*.

JP2001128670 A (2001, NAT INST ADV IND SCIEN; TOKIWA Y) discloses a method for decomposing PLA with the actinomycete *Kibdelosporangium aridum*.

US5925556 A (1990) and **JPH10108670 A** (1998, NAT INST IND SCI TECHN; SHIMADZU CORP) use bacteria belonging to the genus *Staphylococcus* for the degradation of PLA. Two bacteria, *S. hominis* (FERM BP-6108) (FERM BP-15867) and *S. epidermidis* (FERM BP-6109) (FERM BP-15868) were separated from the soil collected in Tsukuba City, Ibaraki Prefecture, Japan, and cultured in a medium containing PLA under aerobic conditions. The culturing temperature is between 10 and 60°C, preferably between 30 and 50°C. The medium used for cultivation contains a nitrogen source such as ammonium sulfate, ammonium phosphate, or ammonium carbonate, and commonly used mineral salt nutrients such as potassium primary phosphate, potassium secondary phosphate, magnesium sulfate, sodium chloride, ferrous sulfate, sodium molybdate, sodium tungstate, and manganese sulfate; its pH ranges from 4.0 to 10.0 (preferably from 5.0 to 8.0). The desired amount of PLA added to the medium is 0.01 to 10% by

weight. The degrading method in compost-making facilities enables the conversion of PLA to manure and useful substances such as organic acids.

Several thermophilic bacteria such as *B. brevis*, *B. stearothermophilus*, and *Geobacillus thermocatenulatus* have been reported to possess PLA-degrading activity [10,11,12].

JPH114680 A (1990, NAT INST IND SCI TECHN; SHIMADZU CORP) uses bacteria belonging to the heat-resistant genus *Bacillus* for the decomposition of PLA: *Bacillus subtilis* (FERM P-16181), *B. circulans* (FERM P-16182), and *B. stearothermophilus* (FERM P-16183).

JP2007319078 (2007, NATIONAL UNIV CORP SHIZUOKA UNIV) discloses a method for degrading PLA using the bacterium *Bacillus licheniformis*; in particular *B. licheniformis* T7-2 (FERM AP-20920) or a pulverized material thereof.

The most effective enzyme for the degradation of PLA is Proteinase-K (also called protease-K), a serine protease produced by *Tritirachium album*, a fungus that grows on native keratin as its sole carbohydrate and nitrogen source [13] (see also WO2004013217 A1 2004, UNIV KEIO; Chapter 6: Chemical Recycling; Section 6.4: Enzymatic Depolymerization). In addition to Proteinase-K from *T. album*, subtilisin, a microbial serine protease, and some mammalian serine proteases such as α -chymotrypsin, trypsin, and elastase, could also degrade PLA [14].

JP2003009846 A (2003, NAT INST ADV IND SCI TECHNOL; ALMIGHTY KK) and **JP2003009855 A** (2003, NAT INST ADV IND SCI TECHNOL; ALMIGHTY KK) disclose a method for decomposing PLA by composting PLA in the coexistence of at least one inducer of a PLA-decomposing enzyme producing bacterium or Proteinase-K-like protease-producing bacterium. This inducer of the PLA-decomposing enzyme-producing microbe comprises at least one selected from the group consisting of a glycine residue-containing oligopeptide, an alanine residue-containing oligopeptide, a valine residue-containing oligopeptide, valine, alanine, glycine, gelatin, soybeans, collagen, elastin, keratin, silk fibroin, a silk fibroin hydrolysate, and the like. The bacteria are preferably selected from the following genera: *Tritirachium*, *Amycolatopsis*, *Saccharothrix*, *Streptomyces*, *Bacillus*, *Streptoalloteichus*, *Kibdelosporangium*, *Lentzea*, *Saccharomonospora*, *Staphylococcus*, and *Saccharopolyspora*.

JP2004075905 A (2004, NAT RES INST OF BREWING) discloses an agent for decomposing an aliphatic polyester comprising lipase CS2 as the active

component. The lipase CS2 is derived from microbes belonging to the genus *Cryptococcus* or is produced by a recombinant DNA technology, has a newly clarified amino acid sequence with high similarity to cutinase, and, accordingly, exhibits decomposing action on the aliphatic polyester. The method involves culturing yeast *Cryptococcus* sp. strain S-2 (FERM P-15155) and contacting the obtained culture or its treated substance with the biopolymer. The decomposing agent is useful for decomposing aliphatic polyesters such as PLA, PES, PBS, poly(ester amide)s (PEAMs), PCL, and PHB.

JP2005162832 A (2005, ALMIGHTY KK; NAT INST ADV IND SCI TECHN) discloses a method for decomposing PLA with subtilisin, a microbial serine protease derived from *Bacillus subtilis*.

JP2006036899 A (2006, NAT INST ADV IND SCI TECHNOL) discloses a method for decomposing PLA with at least one enzyme selected from Proteinase-K, subtilisin, α -chymotrypsin, pronase, chymopapain, papain, plasmin, elastase, trypsin, and the powder or extract of *Hypsizygus ulmarium* (*Lycophyllum ulmarium*), figs, or passion fruit.

JP2010248516 A (2010, NAT INST ADV IND SCI TECHN) discloses a method for decomposing PLA with at least one enzyme, powder, or extract selected from chymopapain, plasmin, elastase, trypsin, and powder or extracts of *Hypsizygus marmoreus*, figs, or passion fruit.

JP2003252966 A (2003, NAT INST ADV IND SCI TECHN; KONAN CHEMICAL MFG) discloses a method for decomposing poly(D-lactide-co-glycolide) copolymer (PDLGA) — which is used for clothing, biocompatible material, tableware, mulch films, and garbage bags — with a splitting enzyme such as protease, lipase, or α -chymotrypsin (a mammalian serine protease).

JP2007177247 A (2007, NAT INST ADV IND SCI TECHN; KONAN CHEMICAL MFG) discloses a similar method for decomposing PDLGA limited to α -chymotrypsin.

WO2005045017 A1 (2005, NAT INST ADV IND SCI; TOKIWA Y) and **US2007259413 A1** (2007, TOKIWA Y) disclose a method for decomposing PHA by bringing PHA into contact with an actinomycete belonging to the genus *Streptomyces*. Examples of preferred actinomycetes of the genus *Streptomyces* include *S. thermovulgaris*, *S. thermoolivaceus*, *S. thermohygroscopicus*, and *S. thermocarboxydovorans*. A more preferred actinomycete of the genus *Streptomyces* is a bacterial strain discovered

by the present inventor and named MG2 (FERM P-19578) (FERM ABP-10158). The method comprises incubating PHA, preferably PHB (e.g., Biogreen®), with the actinomycete or enzymes derived from the actinomycete in a medium containing inorganic salts at a temperature between 40 and 55°C.

JPH09252791 A (1997, NAT INST IND SCI TECHN; SHOWA DENKO KK) uses the actinomycete *A. mediterranei* HT-6 (FERM P-15,023) for the decomposition of PBS and the production of 4-hydroxybutyric acid, which can be used again in the synthesis of a polymer.

JPH11225755 A (1998, MITSUBISHI CHEM CORP) discloses an enzyme for decomposing PBS that consists of esterase obtained from a microorganism of the genus *Acidovorax*. The manufacture of esterase involves cultivating *A. delafieldi* in a culture medium and extracting esterase from the culture. Decomposition of PBS involves using the culture or processed material of *A. delafieldi*, or a crude purified fraction of esterase extracted from the microbial cell or culture. The purified enzyme is brought in contact with PBS in an aqueous solution to enable hydrolysis of PBS.

JP2003310248 A (2002, OKURA INDUSTRIAL CO LTD) discloses a method for decomposing biodegradable polymers such as PBS, polybutylene succinate-adipate (PBSA), PES, and PCL using a microorganism belonging to the genus *Burkholderia*, or a cultured product thereof. The microorganism is of strain FERM P-18822, FERM P-18823 or FERM P-18824.

JP2001226518 A (2001, NAT INST ADV IND SCI TECHN) discloses a method for decomposing PBS with actinomycetes belonging to the genus *Microbispora*, preferably *Microbispora rosea aerata*. *M. rosea aerata* strains IFO 14046 and IFO 14047 degraded PBS more effectively when compared with other various actinomycetes. The method degrades PBS within a short period, does not produce any harmful exhaust gas, and converts PBS into useful substances and composts, such as organic acids.

JP2007319092 (2007, TOYO SEIKAN KAISHA LTD) discloses a method of decomposing a biopolymer, such as PLA, PBS, PCL, PHB, poly(ethylene adipate) (PEA), PGA, and poly(tetramethylene adipate) (PTeMA), involving culturing *Streptomyces coelicolor* and contacting it with the biopolymer.

JP2004166542 A (2004, JAPAN SCIENCE & TECH AGENCY) discloses a method for decomposing a biopolymer using a bacterium belonging to the genus *Paenibacillus*, preferably *P. amylolyticus*

TB-13 strain (FERM P-1910). The bacterium is useful for decomposing biopolymers with ester bonds such as PLA, PBS, PBSA, PES, and poly(ester urethane), and is also used in biological waste treatment.

EP0679412 A1 (1995, BOEHRINGER MANNHEIM GMBH) discloses a method for the disposal of waste material in which the solid components consist mainly of PLA, PHB, PHV, PHBV, PCL, and/or PC; the waste material is also contaminated with potentially infectious biological substances. The method comprises incubating the waste in aqueous medium in the presence of microorganisms and/or heating in aqueous alkaline medium until the biopolymers are at least partially dissolved. Preferred microorganisms are *Pseudomonas lemoignei*, in particular Isolat SK 404² and Isolat SK 37³. The method allows for the inexpensive disposal of large amounts of waste plastic material from laboratories, industrial units, and hospitals in a reasonable time without using aggressive chemicals and without adverse environmental effects.

JPH05344897 A (1993, AMANO PHARM KK) discloses a method of decomposing an aliphatic polyester using immobilized lipase bound with a water-soluble polymer carrier; the lipase is derived from the genus *Pseudomonas*. The immobilized lipase with a water-soluble polymer carrier can be used for the improvement of the texture of fibers made of aliphatic polyesters, particularly PCL, without losing fiber strength. Lipase derived from *P. cepacia*, *P. fluorescens*, and *Rhizopus oryzae* decomposed PCL well, while lipase derived from *R. niveus* did not show any activity.

JPH06319532 A (1994, SUMITOMO METAL IND) discloses the decomposition of wastes containing PCL using *Pseudomonas* sp. 2665 (registered as FERM P-13407) or an enzyme obtained from it. The microorganism was collected from the yard of the Hasaki Research Center, Sumitomo Metal Industries, Ltd., Kashima County, Ibaraki Prefecture, Japan. The microorganism rapidly biodegrades waste polymers containing a high proportion of PCL.

JPH06319533 A (1994, SUMITOMO METAL IND) discloses the decomposition of wastes

containing poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) using *Pseudomonas testosteroni* 2601 strain (registered as FERM P-13408). The microorganism was collected from the same area as described above in JPH06319532.

JPH10117768 A (1998, SHOWA DENKO KK) discloses the decomposition of an aliphatic polyester using microorganisms selected from the genera *Mucor*, *Humicola*, *Thermomyces*, *Talaromyces*, *Chaetomium*, *Torula*, *Sporotrichum*, and *Malbranchea*. Preferably, a mold having polyester decomposing activity and an optimum growth temperature of $\geq 40^\circ\text{C}$, such as *Mal. sulfureum* SD71 strain (FERM P-15895), is used. The method enables quick disposal treatment with a domestic garbage disposal machine, etc., by bringing the aliphatic polyester such as PCL at $40\text{--}80^\circ\text{C}$ into contact with a specific microorganism.

JP2006008780 A (2006, MITSUBISHI CHEM CORP) discloses a method for the decomposition of aliphatic or alicyclic polyesters (such as PBS) by bringing the biodegradable polyester to be disposed of into contact (at $T < 20^\circ\text{C}$) with an aqueous solution containing an enzyme produced from a microorganism that has the capability of decomposing the polyester at an optimum growth temperature of $T \leq 35^\circ\text{C}$. The method promotes biodegradation of aliphatic or alicyclic polyesters at low temperature and enables decomposition in a short period of time without producing environmental pollution. Suitable microorganisms are selected from one of the following strains: *Mucor*, *Aspergillus*, *Achromobacter*, *Bacillus*, *Thermomyces*, *Candida*, *Talaromyces*, *Chaetomium*, *Torula*, *Sporotrichum*, *Malbranchea*, *Chromobacter*, *Fusarium*, *Humicola*, *Hyphozyma*, *Pseudomonas*, *Penicillium*, *Rizomucor*, *Rhizopus*, *Geotrichum*, *Flavobacterium*, *Acinetobacter*, *Burkholderia*, *Alcaligenes*, *Aeromonas*, *Xanthomonas*, *Arthrobacter*, or *Psychrobacter*. Preferred microorganisms are strains from the genus *Pseudomonas*, preferably *P. fragi*. Enzymes produced from these microorganisms include hydrolases such as lipase, esterase, cutinase, phospholipase, lysophospholipase, protease, amylase, glucoamylase, peptidase, serine hydrolase, cellulase, chitinase, xylanase, and pectinase; peroxidase, monooxygenase, dioxygenase, and laccase are also mentioned. Lipase and cutinase are especially preferred.

Aerobic degradation of PHB by members of the genus *Pseudomonas* was reported by Delafield et al. [15] and Chowdhury [16]. The immediate hydrolysis product is D-3-hydroxybutyric acid [16].

² Lusty CJ, Doudoroff M. Poly- β -hydroxybutyrate depolymerases of *Pseudomonas lemoignei*. Proceedings of the National Academy of Sciences USA 1966;56:960–5.

³ DSM: Deutsche Sammlung von Mikroorganismen und Zellkulturen, DSM 8962.

PEAMs can also be degraded with enzymes. In this case the molecular weight of the polymer is reduced to such an extent that products made from it are completely decomposed. The enzymatic degradation takes place without any expensive buffering of the enzyme-containing solution. If, however, pure polyester is incubated with the enzymes that degrade it, the liberation of acid groups causes significant acidification. If the pH value is not maintained constant by buffering or adding lye, degradation soon stops, as most esterases and lipases cease to be active at low pH values (WO9743014 A1, BAYER AG, 1997).

WO9743014 A1 (1997, BAYER AG) discloses a method for the enzymatic degradation of PEAMs, wherein the PEAMs are mixed with enzymes selected from esterase, lipase, and protease groups in an aqueous solution, which may be buffered. The proteases preferably come from bacteria of the genus *Bacillus*, with proteases of *B. alcalophilus* and *B. licheniformis* being particularly suitable. These proteases are generally accessible and commercially available. The aqueous enzyme-containing solution is either mixed with PEAM or is sprayed onto the coating or the molded body that is to be degraded. As shown in Table 4.1, practically complete degradation (determined through weight loss %) of a thin blown film made of PEAM in admixture with various quantities of the claimed enzymes was achieved.

DE19706023 A1 (1998, BAYER AG; NOVO-ZYMES AS) discloses a method for the enzymatic decomposition of biodegradable polymers, particularly

PEAMs and polyester urethanes that contain urea groups (e.g., Bionolle® 1010 and 1030 of Showa Highpolymer Co., Ltd., and Degranil® DLN of Bayer). The biodegradable polymers are treated with an aqueous solution that can be buffered and that contains one or more lipases or cutinases selected from the following group: the lipase from *Candida antarctica* (particularly component B), the lipase from *Mucor miehei* (e.g., Lipozyme 20,000 L), the lipase from *Aspergillus niger*, and the cutinase from *Humicola insolens*. The lipases and cutinases may be used in combination with other enzymes.

DE19706023 A1 also states that fine particles of PLA are degraded in the presence of a specific lipase in a potassium phosphate buffer solution. However, it is a well known fact that PLA is not degraded under ordinary conditions even if microorganisms are present therein and PLA is not degraded by microorganisms without conditions (for example) of high temperature and high humidity. It is thought that this is because PLA is first hydrolyzed at high temperature and high humidity so that a fall in the molecular weight occurs, and it is not until the stage at which the hydrolysis advances that PLA starts to be degraded by the participation of microorganisms (a two-stage reaction) [17]. It appears that lipase degradation of PLA in a potassium phosphate buffer solution, described in the aforementioned publication, is based on the following: PLA is first hydrolyzed so that a fall in the molecular weight thereof occurs since PLA is made into very fine powder; lipase acts on the low molecular weight PLA.

Table 4.1 Biodegradation of poly(ester amide) (PEAM) films by means of enzymes

Preparation	Microorganism	Enzyme quantity (v/v)	pH after incub.	wt. loss (%)
Film + buffer without enzyme		0	7.93	2
Film + buffer + Opticlean	<i>Bacillus alcalophilus</i> ¹	1%	7.64	53
Film + buffer + Opticlean	<i>B. alcalophilus</i> ¹	5%	7.59	55
Film + buffer + protease	<i>B. licheniformis</i> ¹	1%	7.51	71
Film + buffer + protease	<i>B. licheniformis</i> ¹	5%	7.35	91
Film + buffer + esterase	<i>B. spec.</i> ²	1%	7.66	47
Film + buffer + esterase	<i>B. spec.</i> ²	5%	7.65	34
Film + buffer + alcalase	<i>B. licheniformis</i> ²	1%	7.53	75
Film + buffer + alcalase	<i>B. licheniformis</i> ²	5%	7.35	89

¹Commercial product of the firm Solvay, Germany.

²Commercial product of the firm Novo Nordisk, Denmark.
(WO9743014 A1, 1997, BAYER AG)

DE19754063 A (1999, BAYER AG) discloses a method for degrading biopolymers that comprises introducing the polymer into an aqueous nutrient solution and inoculating the solution with a pure or mixed culture containing at least one bacterium selected from the following: *Paenibacillus lautus* (DSM 11870), *Bacillus pumilus* (DSM 11871), *Aeromicrobium* sp. (DSM 11872), *Thermobispora bispora* (DSM11873), *Bacillus* sp. RNA-Group V, and *Brevibacillus* sp. Also included are the enzymes produced by these microorganisms, such as esterases, lipases, and oligo-amidases. The method applies especially to aliphatic or partially aromatic PEAMs, polyester urethanes containing urea groups (PEUUs), and poly(ester carbonate)s.

The method can be used, among other things, to delaminate polymer-laminated composite materials; to disassemble polymer-bonded wooden shuttering; to remove polymers from paper and packaging for recycling; to degrade polymer articles or textiles for disposal; to remove polymer coatings; to remove polymer film from materials after sterilization; for de-inking; to remove polymers from electronic components; to increase the biodegradability of polymers in composting or anaerobic digestion processes; and especially for degrading biodegradable PEAMs and PEUUs.

JPS5282773 A (1977) and **JPS5282774 A** (1977, KOGYO GIJUTSUIN) disclose a method for decomposing a polyester by treatment with a lipolytic enzyme. Specifically disclosed polyesters in the working examples include PEA and PCL. Suitable lipolytic enzymes include lipase, esterase, and (lyso) phospholipase, which can be prepared, for example, by *Pseudomonas mephitica lipolytica* (FERM P-520), *Achromobacter iophagus*, and *Candida paralipolytica*. Preferably, a buffer agent is combined in the reaction mixture to maintain an optimum pH range, and a surfactant is added to enlarge the contacting surface of lipase and polyester. Prior to decomposition, the polyesters are cut into fine fibers or powders to increase surface area. The decomposition is preferably effected at 20–60°C at a pH of 5–8 in liquid or solid phase, and with a suitable amount of water.

JP2009207424 A (2009, KANEKA CORP) discloses a method for decomposing PHA that includes a hybrid-type copolyester, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx) at a high temperature, a microbial preparation that is fed to a compost and used, and an enzyme preparation. The method includes decomposing PHA at 55–80°C in the

presence of bacteria of the genus *Thermobifida*, an enzyme composed of a specific amino acid sequence isolated from the bacteria, its variant, or a transformant producing them.

JP2006271367 A (2006, UNIV TSUKUBA) discloses a method for obtaining a gene encoding a thermophilic enzyme for degrading a biopolymer and a method for degrading the biodegradable polymer by utilizing the enzyme or a microorganism expressing the enzyme. The biopolymer-degrading enzyme has degradation activity at high temperature and is used for the degradation of aliphatic polyesters such as PLA, PBS, or PBSA. The enzyme is produced by culturing a host cell containing a vector which consists of the gene encoding the protein having biodegradable biopolymer degrading activity under conditions suitable for the growth of cells, and isolating and purifying the enzyme from the host cell. According to the embodiment the biodegradable biopolymer is contacted with the enzyme or with the host cell containing the enzyme for a definite period in compost under high-temperature conditions. The gene can be acquired by directly extracting DNA from the surface of the biodegradable biopolymer. Host cells suitable for the expression of the enzyme include *Escherichia coli*, *Bacillus subtilis*, yeast, etc.

JP2005304388 A (2005, TOHOKU TECHNO ARCH CO LTD) discloses an esterase protein useful for degrading non-degradable polymers such as polyester, polyurethane, polypropylene, polyvinyl chloride, and polystyrene, and also for biodegradable biopolymers including PLA, PBS, PBSA, PCL, and PHB. The enzyme consists of (a) a protein having a fully defined 269 amino acid sequence, or (b) a protein having an amino acid sequence where one or several amino acids are deleted, substituted, or added in the specific amino acid sequence and have substantially equivalent esterase activity to that of the protein (a). A DNA encoding the protein is provided. The esterase is produced by cultivating prokaryotic microorganisms such as those of genera *Escherichia*, *Bacillus*, or *Streptomyces*, or eukaryotic microorganisms such as filament-forming fungi including yeast of genera *Aspergillus*, *Penicillium*, *Trichoderma*, *Rhizopus*, *Monascus*, *Acremonium*, or *Mucor*; *A. oryzae* or *A. sojae* are preferred.

PHB and other PHAs are known to be hydrolyzed by microbial extracellular PHB depolymerases. Extracellular PHB depolymerases are produced by various bacteria in natural environments such as soil [15,18–20], activated sludge [21], and freshwater [22].

The degradation of PHBs, which are water-insoluble and partially crystalline polymers, is known to occur also in a marine environment [23–25]. Kita et al. [25] isolated a marine bacterium, *Alcaligenes faecalis* AE122, from a seawater sample and characterized its PHB-degrading ability. The strain required seawater for growth on PHB. *A. faecalis* AE122 also grew on other PHAs, i.e., poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate-co-4-hydroxyvalerate) (P3HB4HB) [26]. Growth was fastest on P3HB4HB followed by PHB, and then PHBV [25].

Six hundred PHA depolymerases from various microorganisms have been identified so far [27]; comparison of their amino acid sequences provided a basis for uniting them in eight superfamilies including 38 families [27,28].

JPH09191887 A (1997, KYOTO DAIICHI KAGAKU CORP) obtained a new enzyme from *Alcaligenes faecalis* having a specific amino acid or a sequence in which part of the amino acid sequence is mutated. This new depolymerase has an amino acid sequence of 635 or a sequence in which more than one amino acid is deleted, substituted, or added in the amino acid sequence. The enzyme is suitable for the catalytic hydrolysis of a PHA, such as PHB, and is useful for treating a biopolymer waste as an immobilized enzyme. The enzyme is obtained by inoculating *A. faecalis* AE122 in a medium, shake culturing at 30°C for 48 h, recovering supernatant by subjecting to ultracentrifuge to obtain a crude enzyme solution, passing the resultant solution into a diethylaminoethyl cellulose (DEAE-C) column, eluting with a linear gradient of NaCl, and gel-filtrating an active fraction.

JP2010168595 A (2010, NAT INST ADV IND SCI TECHN) discloses a method for decomposing PHB by means of at least one lipase selected from an alkali lipase derived from genus *Achromobacter*, a lipoprotein lipase derived from genus *Alcaligenes*, a lipase derived from genus *Pseudomonas*, a lipase derived from genus *Candida*, a lipase derived from genus *Mucor*, a lipase derived from genus *Rhizopus*, a lipase derived from genus *Penicillium*, a lipase derived from genus *Phycomyces*, and a porcine pancreas lipase and a human pancreas lipase. The method is useful for biodegradation of PHB in labeling and packaging materials (e.g., soft drink bottles); horticulture materials (e.g., coating materials of pots for seedlings); civil engineering materials; waterproof materials (e.g., fishing nets and seaweed nets); laminated containers (e.g., garbage bags and water draining nets); medical

materials (e.g., medical devices); and sundry materials (e.g., cosmetic bottles and pens).

JP2006124678 A and **JP2006124677 A** (2006, MITSUBISHI CHEM CORP; NOVOZYME AS) disclose a method for decomposing waste aliphatic or alicyclic polyesters in a short period by accelerating biodegradation. The decomposition method entails bringing the polyester to be disposed of into contact with an aqueous liquid comprised of a microbe and/or an enzyme with the capability of decomposing the biodegradable polyester, a microbe proliferation agent, and a water retention agent. The enzyme is hydrolase or oxidoreductase. The microbe proliferation agent is selected from culture medium components of microbes, food additives, saccharide for foodstuffs, food processing waste material, and chemical fertilizer. The liquid further contains surfactant and/or water retention agent. The water retention agent is preferably glycerol. The decomposition treatment liquid further contains a surface-active agent having hydrophilic lipophilic balance (HLB) of 4–20. The amount of water retention agent and surface-active agent in aqueous decompose-treatment liquid is 1–50 wt.% and 0.001–10 wt.%, respectively.

JP2006104262 A (2006, MITSUBISHI CHEM CORP; NOVOZYME AS) discloses a method for decomposing a biodegradable polyester resin molding in a short time by accelerating its biodegradation after its service life; it is influenced less by the weather, soil quality, season, etc., of the environment where it is decomposed. The method comprises bringing a hydrolase derived from *Humicola insolens* with an amino acid sequence modified so as to increase the decomposition rate of ester linkages into contact with the surface of the molding at the time of its decomposition under temperature conditions of 15 to 65°C.

While many aliphatic polyesters are biodegradable by several microorganisms and/or enzymes, the aliphatic-aromatic copolyesters can be biodegraded only in a certain range of composition [29]. It has been found that the biodegradability of aliphatic-aromatic copolyesters decreases with the content of aromatic constituents [30]. For poly(butylene adipate-co-terephthalate) (PBAT), a maximum content of about 50–60% terephthalic acid in the diacid component was reported to be the limit for biodegradability [31,32]. Thermophilic actinomycetes proved to be the group of microorganisms that is very active in degrading aliphatic-aromatic copolyesters [29].

JP2009039095 A (2009, KURABO IND LTD; UNIV OKAYAMA) discloses a microorganism with

the ability to decompose aliphatic-aromatic copolyesters, and a method for decomposition treatment of the copolyesters using the microorganism. The microorganism is selected from bacterial strain BHK25, actinomycetes strain AHK109 (FERM BP-10828), actinomycetes strain AHK119 (FERM BP-10829), and fungal strain AKH190 (FERM BP-21507). The strain exhibits thermophilic properties that decompose aliphatic-aromatic polyesters and aliphatic polyesters. The strains are isolated from a compost containing polyester. The strains were useful for degradation of poly(butylene succinate-co-terephthalate) (PBST), especially thermostable DuPont Biomax[®] products (specifically Biomax[®] 4024, Biomax[®] 4025, Biomax[®] 4026, and Biomax[®] 4027), or PBAT (specifically Ecoflex[®] F and S grade). The method for the decomposition treatment of the copolyester comprises the following process: either one of the strains is applied to the surface of the copolyester and/or compost to embed the copolyester therein to conduct an accelerated biodegradation reaction of the copolyester by the strain.

JP2002348405 A (2004, SUMITOMO CHEM CO LTD) discloses a method to dispose of hard-to-degrade polymer wastes in which *Agaricales* fungus fruit body-culture medium acts on the polymer wastes. The culture medium is prepared using the extract of the fruiting body of *Agaricales* fungi. A nutrient such as urea can be added to the culture medium, and the polymer is embedded in the culture medium. The polymer is PLA, rayon, polyester, or polyurethane. The *Agaricales* fungi culture medium contains *Schizophyllum commune*, shiitake mushroom (*Lentinula edodes*), *Lyophyllum shimeji* (*Lyophyllum aggregatum*), bunashimeji mushroom (*Hypsizygus marmoreus*), oyster mushroom (*Pleurotus ostreatus*), maitake mushroom (*Grifola frondosa*), *Celtis sinensis* var. japonica (*Collybia velutipes*), *Agaricus* (*Agaricus brazilie*), nameko mushroom (*Pholiota glutinosa*), and button mushroom (*Agaricus bisporus*).

US2005261465 A and **WO2005118693 A1** (2005, DU PONT) disclose a method to increase the biodegradation rate in typical composting conditions of throwaway copolyesters, which were previously regarded as very slow to biodegrade, by contacting at least one hydrolytic enzyme in an aqueous solution to the copolyester. The treatment applies to aliphatic-aromatic copolyesters with a high aromatic content having more than 60 mol% aromatic acid content based on total acid content. The aqueous solution comprises between about 0.1 and about 10 wt.% of at

least one hydrolytic enzyme, which may be selected from the group consisting of proteases, lipases, cutinases, esterases, and a combination of these. Lipases are the preferred enzymes, specifically Novozyme[®] 871, a lipase from *Thermomyces lanuginosus*; Palatase 20,000 L, a lipase from *Rhizomucor miehei*; and Lipolase 100 L, a lipase from *Thermomyces lanuginosus*. In one embodiment, contacting of at least one hydrolytic enzyme to the copolyester occurs before degradation of the copolyester by the microorganisms. In another embodiment, the contacting occurs when the copolyester is situated in a waste context, which may be solid waste or compost or a wastewater treatment system. Contacting at least one hydrolytic enzyme to the copolyester of interest may be done by spraying, painting, coating, applying, or mixing.

In aliphatic-aromatic copolyesters the tendency towards biodegradability decreases with the aromatic content [30].

Some studies have also shown that aliphatic polycarbonates have some degree of biodegradability [33].

JPH08187090 A (1996, NAT INST ADV IND SCI TECHN; JSP CORP) discloses the microbial decomposition of waste aliphatic polycarbonate by bringing it into contact with microorganisms belonging to the genus *Pseudomonas*. In particular, *P. paucimobilis* PC61 strain (FERM-P-14657) is added to a jar fermenter filled with a culturing solution containing inorganic salts and cultured at 30°C for two days; a film made of an aliphatic polycarbonate resin (poly(ethylene carbonate), for example) by hot pressing at 100°C is projected, brought into contact with the strain, and cultured in conditions of 5–37°C and pH 5–9. The aliphatic polycarbonate resin is efficiently decomposed, which makes possible its conversion into a valuable substance or compost. The decomposition products can be used as organic intermediates for fertilizers.

JPH08151476 A (1997, NAT INST ADV IND SCI TECHN) discloses a method for enzymatically decomposing an aliphatic polycarbonate resin such as a poly(tetramethylene carbonate) (PTeMC) by contacting it with at least one enzyme selected from porcine pancreas lipase, *Pseudomonas* sp. lipase, and *Pseudomonas* sp. lipoprotein lipase in the presence of water.

JP2003250527 A (2003, KAO CORP) discloses a method for degrading poly(vinyl alcohol) (PVOH) by bringing PVOH into contact with *Sphingomonas*

bacterium or its cell component. A preferred bacterial strain is *Sphingomonas capsulate* UP-3 strain (FERM-P18699). The method is useful for degrading and assimilating PVOH present in wastewater, drainage fluid, or soil. The method is also useful in compost processing.

WO9928366 A1 (2001, UNIV NEBRASKA) discloses a method for degrading aliphatic polyesters that comprises treating a polyester with a mixed culture of microorganisms made up of *Rhizopus chinensis*, *R. delemar*, *Penicillium pinophilum*, *Aspergillus niger*, and *Pseudomonas aeruginosa*, wherein said polyesters are degraded into respiratory gases and biomass. The polyesters include thermoplastic aliphatic polyesters made by reacting a diol with blocked glutamic acid; thermoset heterochain polyesters and thermoset heterochain aromatic polyesters made by reacting an epoxy compound with blocked glutamic acid; PLA, PCL, and PGA.

Each of the thermoplastic aliphatic polyesters, the thermoset heterochain polyesters, and the thermoset heterochain aromatic polyesters, can be hydrolyzed into their monomeric units by many biological catalysts. An esterase enzyme, such as lipase, which is extracted from the microorganism *R. delemar* or other microorganisms, is one example of a biological catalyst that may be used to hydrolyze the polyesters. Another biological catalyst that can be used is hog liver esterase.

The thermoset heterochain aromatic polyester described in the patent resisted biological degradation when contacted by the mixed culture of microorganisms discussed above. It further resisted degradation when *P. cruciviae*, *P. putida*, and *Corynebacterium restricta*, all three of which are capable of metabolizing aromatic structures, were added to the mixed culture. The thermoset heterochain aromatic polyester is a hard and brittle material due to the stiffness associated with the aromatic structure of the main chain. It appears that the chemical structure of the thermoset heterochain aromatic polyester does not allow fungus adhesion followed by extracellular enzyme secretion, both of which are necessary for microbial degradation.

4.3.3.2 Anaerobic

Most studies published on anaerobic biodegradation of biopolymers focus on mixed and unspecified microbial communities such as diverse anaerobic sludges and/or sediments evaluating the anaerobic biodegradation of PHAs, PCL, PLA [34–44], starch,

or cellulosesters [45–47]. Nishida and Tokiwa characterized the distribution of PCL degrading aerobic and anaerobic microorganisms in different environments [48]. Investigations using individual cultures were restricted to PHB degradation by an organism described as *Ilyobacter delafildii*, which was isolated and identified by Janssen and coworkers [49,50]. Abou-Zeid et al. published systematic investigations on the anaerobic degradation of PHB, PHBV, and PCL using mixed microbial consortia, especially individually isolated anaerobic strains of the genus *Clostridium* or *Propionispora* [51–53]. In contrast to aerobic conditions, PHB degrades faster than PHBV; however, the degradation rate of PCL is significantly lower than for PHB and PHBV. Other synthetic polyesters such as poly(trimethylene adipate) (PTMA), poly(tetramethylene adipate) (PTeMA), and PBAT exhibit only very low anaerobic microbial susceptibility. In contrast to aerobic conditions, the aliphatic-aromatic copolyesters (PBAT) were anaerobically only attacked when contents of aromatic component were low (up to 20 mol% terephthalic acid of the acid component). An aliphatic-aromatic copolyester such as PBAT with a higher amount of terephthalic acid resisted anaerobic breakdown even under thermophilic conditions and/or when blended with starch [53].

JPH06253865 A (1994, NAT INST ADV IND SCI TECHN; MITSUI SHIPBUILDING ENG) discloses a method for decomposing an aliphatic polyester based on nonrenewable (fossil) resources using anaerobic bacteria. Preferably the aliphatic polyester is PCL or PEA. Cultivation media for anaerobic bacteria are, for example, ammonium chloride, ammonium sulfate, ammonium phosphate, and ammonium carbonate. *Bacteroides* sp. IT-802 (FERMP-13479) is a preferred anaerobic bacterium. This method eliminates the need to bury discarded biodegradable polyesters made from fossil fuels.

JPH07132272 A (1995, NAT INST ADV IND SCI TECHN; MITSUI SHIPBUILDING ENG) discloses a method for decomposing an aliphatic polyester based on nonrenewable (fossil) resources such as PCL under anaerobic conditions. An anaerobe belonging to the genus *Clostridium* (e.g., *C. sporogenes* JCM No. 1416T) capable of decomposing the aliphatic polyester is used.

JPH09263653 A (1997, NAT INST ADV IND SCI TECHN; CHIKYU KANKYO SANGYO GIJUTSU; TOYOBO CO LTD) discloses a method for decomposing a poly(hydroxy alkanoate) (PHA) such as

PHB by degrading the aliphatic polyester with an anaerobic bacterium belonging to the genus *Clostridium* and/or with a degradation enzyme separated from the culture product of the anaerobic bacterium under anaerobic conditions.

The anaerobic degradation of PHB, PHBHV, and PCL using isolated anaerobic individual strains of the genus *Clostridium* has been reported in the literature [51,52].

JP2004058010 A (2004, TOYOBO CO LTD) discloses a method of efficiently performing anaerobic biodegradation treatment of an organic waste containing molded articles made of biopolymers by adding an enzyme, such as lipase, esterase, cellulase, or a micro-organism producing the enzyme, to the organic waste. The method is useful for processing organic waste containing discarded moldings made of biopolymers such as PCL, PHB, or cellulose; such items include paper diapers, sanitary products, disposable chopsticks, water-draining nets, cups, trays, food containers, lunch boxes, clothes, cushioning materials, films, fishing lines, fishing nets, and seedling pots.

JP2005206735 A (2005, TAKUMA KK; HITACHI SHIPBUILDING ENG CO) discloses a method for recovering energy from PLA. The method involves a step of anaerobic fermentation at 50–60°C by bringing PLA into contact with a methanogen in the presence of water, and a step for recovering a biological gas containing methane generated from the fermentation. In a suitable embodiment, PLA is mixed with an organic waste in the anaerobic fermentation tank. The methanogen is anaerobic and of sludge origin. The anaerobic fermentation is performed for 10 days. The residue is separated after methane fermentation.

The methane fermentation of PLA has the disadvantage of requiring a long period of time. **JP2005232336 A** (2005, TAKUMA KK) proposes a method of accelerating the fermentation process by solubilizing PLA before initiating the methane fermentation. The method comprises the following steps: (1) waste containing PLA is mixed with wastewater obtained after methane fermentation; (2) the insoluble plastics are separated from the PLA solution; (3) the PLA solution is subjected to methane fermentation at 50–60°C under anaerobic conditions; and (4) the generated biogas is recovered. The PLA solution of step (3) may be mixed with organic wastes (carbohydrate, protein, and lipid) and subjected to methane fermentation. The wastewater after methane fermentation of step (1) is preferably wastewater obtained after anaerobic methane fermentation of PLA. The residue

after methane fermentation is subjected to solid-liquid separation, and the resulting wastewater is used either in step (1) for solubilizing the waste PLA, or in step (3) for adjusting water content in the mixture of PLA solution and organic waste. However, PLA cannot be solubilized efficiently, and the quantity of generated lactic acid is low (WO2012001784 A1, 2012, OSAKA GAS CO LTD; TSUBOTA J).

WO2012001784 A1 (2012, OSAKA GAS CO LTD; TSUBOTA J) attempts to overcome the aforementioned problems by impregnating an organic material containing PLA and organic refuse with a treatment solution containing an organic acid salt and/or an inorganic acid salt of an amine compound at a temperature $\geq 40^\circ\text{C}$ and a pH of 8–9. The organic acid salt and/or inorganic acid salt of the amine compound are chosen from ammonium carbonate, ammonium hydrogen carbonate, triammonium phosphate ammonium borate, and triammonium citrate; they have buffer capacity. The concentration of molecular ammonia is 500 mg/l or more. The proposed decomposition method is claimed to decompose PLA with high efficiency so that the PLA can readily undergo the decomposition by a biological treatment such as methane fermentation.

JP2009091463 A (2009, SHIMIZU CONSTR CO LTD) discloses a volume reduction method for decomposing PLA by ammonia generated through fermentation. In the volume reducing method molded matter composed of PLA and urea is added to a composition including urease-producing microorganisms, which generate ammonia by urease reaction, or a urease-containing composition. The urease-producing microorganisms are *Helicobacter pylori*.

Wang et al. evaluated the promotion effect of ammonia on the biodegradation of PLA under hyperthermophilic (80°C) and thermophilic (55°C) anaerobic conditions [54,55]. The results showed that PLA was transformed into lactic acid under hyperthermophilic conditions, but that the transformation ratio was negligible under thermophilic conditions. The hydrolysis process can be markedly increased with ammonia addition and microorganism activity.

The various microorganisms and enzymes described in Section 4.3.3 are summarized in Table 4.2.

4.4 (Bio)degradation in Water

Hydrolytic degradation is the process by which moisture penetrates a disposable material and hydrolyzes, for example, ester bonds, thereby breaking down polymers in the material.

Table 4.2 Microorganisms and enzymes used for biodegradation of biopolymers

Biopolymers	Microorganisms	Enzymes	Patent applications
PLA	<i>Bacillus circulans</i> (FERM P-16182) <i>B. stearothermophilus</i> (FERM P-16183) <i>B. subtilis</i> (FERM P-16181)		JPH114680 A (1990, NAT INST ADV IND SCI TECHN; SHIMADZU CORP)
PLA	<i>B. subtilis</i>	Subtilisin	JP2005162832 A (2005, ALMIGHTY KK; NAT INST ADV IND SCI TECHN)
PLA	<i>B. licheniformis</i> T7-2 (FERM AP-20920)		JP2007319078 (2007, NATIONAL UNIV CORP SHIZUOKA UNIV)
PLA	<i>Actinomadura viridis</i> (FERM P-16247)		JPH1146755 A (1990, NAT INST ADV IND SCI TECHN; SHIMADZU CORP)
PLA	<i>A. atraherbacea</i> T16-4 sp. nov. (FERM P-21063)		JP2008167701 A (2008, UNIV SHIZUOKA NAT UNIV CORP)
PLA	<i>Amycolatopsis mediterranei</i> (FERM P-14921)		JPH0937776 A (1997, NAT INST ADV IND SCI TECHN; SHIMADZU CORP)
PLA	<i>Am. sp.</i> KT-s-9 (FERM P-16463)		JPH11127850 A (1990, NAT INST ADV IND SCI TECHN; SHIMADZU CORP)
PLA	<i>Am. sp.</i> No. 3118 strain (FERM P-16947)		JP2000060540 A (2000, RIKAGAKU KENKYUSHO)
PLA	<i>Streptomyces cyaneus</i> (FERM P-15870) (FERM BP-6111)		JPH10108669 A (1998, NAT INST ADV IND SCI TECHN; SHIMADZU CORP); US6066492 A (2000, NAT INST ADV IND SCI TECHN; SHIMADZU CORP)
PLA	<i>St. violaceusniger</i> (FERM BP-6110) (FERM P-15869)		JPH10108669 A (1998, NAT INST ADV IND SCI TECHN; SHIMADZU CORP); US6066492 A (2000, NAT INST ADV IND SCI TECHN; SHIMADZU CORP)

(Continued)

Table 4.2 Microorganisms and enzymes used for biodegradation of biopolymers (*Continued*)

Biopolymers	Microorganisms	Enzymes	Patent applications
PLA	<i>Saccharothrix flava</i> , <i>S. coeruleofusca</i> , <i>S. longispora</i> , <i>S. australiensis</i> , <i>S. mutabilis</i> subsp. <i>mutabilis</i> , <i>S. aerocolonigenes</i> subsp. <i>aerocolonigenes</i> , <i>S. syringae</i> , <i>S. coeruleoviolacea</i> , <i>S. cryophilis</i> , <i>S. espanaensis</i> , <i>S. texasensis</i> <i>Streptoalloteichus</i> <i>Kibdelosporangium</i> <i>Lentzea waywayandensis</i> (formerly <i>S. waywayandensis</i>) <i>Actinokineospora</i> <i>Saccharomonospora</i> <i>Saccharopolyspora</i> <i>Actinopolyspora</i>		JP3128577 B1 (2001, NAT INST ADV IND SCI TECHN)
PLA	<i>Streptoalloteichus hindustanus</i>		JP2001128671 A (2001, NAT INST ADV IND SCI; TOKIWA Y)
PLA, PES, PBS, PEAMs, PCL, PHB	<i>Cryptococcus</i> sp. strain S-2 (FERM P-15155)	Lipase CS2	JP2004075905 A (2004, NAT RES INST OF BREWING)
PLA	<i>Kibdelosporangium aridum</i>		JP2001128670 A (2001, NAT INST ADV IND SCI TECHN; TOKIWA Y)
PLA	<i>Lentzea albidocapillata</i>		JP2001128669 A (2001, NAT INST ADV IND SCI TECHN; TOKIWA Y)
PLA	<i>Saccharomonospora azurea</i>		JP2001128668 A (2001, NAT INST ADV IND SCI TECHN; TOKIWA Y)
PLA	<i>Saccharopolyspora erythrae</i> , <i>Sa. hordei</i>		JP2001128667 A (2001, NAT INST ADV IND SCI TECHN)
PLA	<i>Staphylococcus hominis</i> (FERM BP-6108) (FERM BP-15867) <i>St. epidermidis</i>		US5925556 A (1990, NAT INST ADV IND SCI TECHN; SHIMADZU CORP); JPH10108670 A (1998, NAT INST ADV IND SCI TECHN; SHIMADZU CORP)

PLA	<i>Tritirachium</i> <i>Amycolatopsis</i> <i>Saccharothrix</i> <i>Streptomyces</i> <i>Bacillus</i> <i>Streptoalloteichus</i> <i>Kibdelosporangium</i> <i>Lentzea</i> <i>Saccharomonospora</i> <i>Staphylococcus</i> <i>Saccharopolyspora</i>	Proteinase-K	JP2003009846 A (2003, NAT INST ADV IND SCI TECHN; ALMIGHTY KK); JP2003009855 A (2003, NAT INST ADV IND SCI TECHN; ALMIGHTY KK)
PLA		Proteinase-K Subtilisin α -Chymotrypsin Pronase Chymopapain Papain Plasmin Elastase Trypsin Powder or extract of <i>Hypsizygus ulmarium</i> (<i>Lyophyllum ulmarium</i>) Figs or passion fruit	JP2006036899 A (2006, NAT INST ADV IND SCI TECHN)
PLA		Chymopapain Plasmin Elastase Trypsin Powder or extract of <i>Hypsizygus marmoreus</i> Figs or passion fruit	JP2010248516 A (2010, NAT INST ADV IND SCI TECHN)
PLA	<i>Helicobacter pylori</i>	Urease	JP2009091463 A (2009, SHIMIZU CONSTR CO LTD)
PLA, PBS, PBSA	<i>Escherichia coli</i> <i>Bacillus subtilis</i> Yeast	Gene encoding a thermophilic enzyme	JP2006271367 A (2006, UNIV TSUKUBA)
PLA, PBS, PBSA, PCL, PHB	<i>Escherichia</i> <i>Bacillus</i> <i>Streptomyces</i>	Esterase	JP2005304388 A (2005, TOHOKU TECHNO ARCH CO LTD)

(Continued)

Table 4.2 Microorganisms and enzymes used for biodegradation of biopolymers (*Continued*)

Biopolymers	Microorganisms	Enzymes	Patent applications
	<i>Aspergillus oryzae</i> and <i>A. sojae</i> <i>Penicillium</i> <i>Trichoderma</i> <i>Rhizopus</i> <i>Monascus</i> <i>Acremonium</i> <i>Mucor</i>		
PLA, PGA, PCL, PBS, PES, PHB, PEA, PTeMA	<i>Streptomyces coelicolor</i>		JP2007319092 (2007, TOYO SEIKAN KAISHA LTD)
PLA, PBS, PBSA, PES, poly(ester urethane)	<i>Paenibacillus amylolyticus</i> TB-13 strain (FERM P-1910)		JP2004166542 A (2004, JAPAN SCIENCE & TECH AGENCY)
PBS	<i>Am. mediterranei</i> HT-6 (FERM P-15,023)		JPH09252791 A (1997, NAT INST IND SCI TECHN; SHOWA DENKO KK)
PBS	<i>Microbispora rosea aerata</i>		JP2001226518 A (2001, NAT INST ADV IND SCI)
PBS	<i>Pseudomonas fragi</i>	Lipase Cutinase	JP2006008780 A (2006, MITSUBISHI CHEM CORP)
PBS	<i>Acidovorax delafieldi</i>	Esterase	JPH11225755 A (1998, MITSUBISHI CHEM CORP)
PBS, PBSA, PES, PCL	<i>Burkholderia</i> strain FERM P-18822, FERM P-18823 or FERM P-18824		JP2003310248 A (2002, OKURA INDUSTRIAL CO LTD)
PDLGA		Protease Lipase α -Chymotrypsin	JP2003252966 A (2003, NAT INST ADV IND SCI TECHN; KONAN CHEMICAL MFG)
PDLGA		α -Chymotrypsin	JP2007177247 A (2007, NAT INST ADV IND SCI TECHN; KONAN CHEMICAL MFG)
PHA, PHB (Biogreen®)	<i>Streptomyces thermovulgaris</i> , <i>Str. thermoolivaceus</i> ,		WO2005045017 A1 (2005, NAT INST ADV IND SCI TECHN; TOKIWA Y);

	<i>Str. thermohygroscopicus</i> , <i>Str. thermocarboxydovorans</i>		US2007259413 A1 (2007, TOKIWA Y)
PHB	<i>Achromobacter</i> <i>Alcaligenes</i> <i>Pseudomonas</i> <i>Candida</i> <i>Mucor</i> <i>Rhizopus</i> <i>Penicillium</i> <i>Phycomyces</i>	Alkali lipase Lipoprotein lipase Porcine pancreas lipase Human pancreas lipase	JP2010168595 A (2010, NAT INST ADV IND SCI TECHN)
PHB	<i>Alcaligenes faecalis</i>	Depolymerase with specific amino acid sequence	JPH09191887 A (1997, KYOTO DAIICHI KAGAKU CORP)
PHA, PHBHx	<i>Thermobifida</i>		JP2009207424 A (2009, KANEKA CORP)
PHB	<i>Clostridium</i>		JPH09263653 A (1997, NAT INST ADV IND SCI TECHN; CHIKYU KANKYO SANGYO GIJUTSU; TOYOBO CO LTD)
PHB, PHV, PHBHV	<i>Pseudomonas lemoignei</i> : Isolat SK 404, Isolat SK 37 (DSM 8962)		EP0679412 A1 (1995, BOEHRINGER MANNHEIM GMBH)
PHBHV	<i>Pseudomonas testosteroni</i> 2601 strain (FERM P-13408)		JPH06319533 A (1994, SUMITOMO METAL IND)
PCL	<i>Pseudomonas cepacia</i> , <i>P. fluorescens</i> <i>Rhizopus oryzae</i>	Lipase	JPH05344897 A (1993, AMANO PHARM KK)
PCL	<i>Pseudomonas</i> sp. 2665 strain (FERM P-13407)		JPH06319532 A (1994, SUMITOMO METAL IND)
PCL	<i>Clostridium sporogenes</i> JCM No. 1416T		JPH07132272 A (1995, NAT INST ADV IND SCI TECHN; MITSUI SHIPBUILDING ENG)
PCL	<i>Mucor</i> <i>Humicola</i> <i>Thermomyces</i> <i>Talaromyces</i>		JPH10117768 A (1998, SHOWA DENKO KK)

(Continued)

Table 4.2 Microorganisms and enzymes used for biodegradation of biopolymers (*Continued*)

Biopolymers	Microorganisms	Enzymes	Patent applications
	<i>Chaetomium</i> <i>Torula</i> <i>Sporotrichum</i> <i>Malbranchea sulfureum</i> SD71 strain (FERM P-15895)		
PCL, PEA	<i>Bacteroides</i> sp. IT-802 (FERMP-13479)		JPH06253865 A (1994, NAT INST ADV IND SCI TECHN; MITSUI SHIPBUILDING ENG)
PCL, PHB, cellulose	<i>Acinetobacter</i> <i>Amycolatopsis</i> <i>Arthrobacter</i> <i>Comamonas</i> <i>Trichosporon</i> <i>Bacillus</i> <i>Microbispora</i> <i>Pseudomonas</i> <i>Saccharopolyspora</i>	Lipase Esterase Cellulase	JP2004058010 A (2004, TOYOBO CO LTD)
PCL, PEA	<i>Pseudomonas mephitica lipolytica</i> (FERM P-520) <i>Achromobacter iophagus</i> <i>Candida paralyolitica</i> .	Lipase Esterase (Lyso)phospholipase	JPS5282773 A (1977, KOGYO GIJUTSUIN); JPS5282774 A (1977, KOGYO GIJUTSUIN)
PLA, PBSL, PES	<i>Pseudomonas</i> <i>Bacteroides</i> , <i>Mucor</i> <i>Humicola</i> <i>Talaromyces</i> <i>Thermomyces</i> <i>Chaetomium</i> <i>Torula</i> <i>Sporotrichum</i> <i>Malbranchea</i> <i>Acidovorax</i> <i>Rhizopus</i>	Oxidoreductase Hydrolase	JP2002348406 A (2002, MITSUBISHI CHEM CORP); JP2003041047 A (2003, MITSUBISHI CHEM CORP)
PBSL & PBAT (Ecoflex®)	<i>Mucor</i> <i>Aspergillus</i> <i>Bacillus</i>	Oxidoreductase Hydrolase Lipase	JP2006124678 A (2006, MITSUBISHI CHEM CORP; NOVOZYME AS);

	<i>Thermomyces</i> <i>Candida</i> <i>Talaromyces</i> <i>Chaetomium</i> <i>Torula</i> <i>Sporotrichum</i> <i>Malbranchea</i> <i>Chromobacter</i> <i>Fusarium</i> <i>Humicola</i> <i>Hyphozyma</i> <i>Pseudomonas</i> <i>Penicillium</i> <i>Rhizomucor</i> <i>Rhizopus</i> <i>Geotrichum</i> <i>Flavobacterium</i> <i>Psychrobacter</i>	Cutinase Esterase Protease	JP2006124677 A (2006, MITSUBISHI CHEM CORP; NOVOZYME AS)
Aliphatic or alicyclic polyesters	<i>Humicola insolens</i>	Hydrolase	JP2006104262 A (2006, MITSUBISHI CHEM CORP; NOVOZYME AS)
PBST (Biomax [®] 4024, Biomax [®] 4025, Biomax [®] 4026, Biomax [®] 4027), PBAT (Ecoflex [®] F or S grade)	Bacterial strain BHK25 Actinomyces strains: AHK109 (FERM BP-10828), AHK119 (FERM BP-10829) Fungal strain: AKH190 (FERM BP-21507)		JP2009039095 A (2009, KURABO IND LTD; UNIV OKAYAMA)
PLA, rayon, polyester, polyurethane	Agaricales fungi: <i>Schizophyllum commune</i> , shiitake mushroom (<i>Lentinula edodes</i>), <i>Lyophyllum shimeji</i> (<i>Lyophyllum aggregatum</i>), bunashimeji mushroom (<i>Hypsizigus marmoreus</i>), oyster mushroom (<i>Pleurotus ostreatus</i>), maitake mushroom (<i>Grifola frondosa</i>), <i>Celtis sinensis</i> var. japonica (<i>Collybia velutipes</i>), <i>Agaricus</i> (<i>Agaricus brazillie</i>), nameko mushroom (<i>Pholiota glutinosa</i>), button mushroom (<i>Agaricus bisporus</i>)		JP2002348405 A (2004, SUMITOMO CHEM CO LTD)
Aliphatic (co)polyesters, PEAM, aliphatic polyester urethanes (Degranil [®] DLN), aliphatic-aromatic polyester carbonates	<i>Candida antarctica</i> <i>Mucor miehei</i> <i>Aspergillus niger</i> <i>Humicola insolens</i>	Lipases: Component B Lipozyme 20,000 L Lipase (<i>Aspergillus niger</i>) Cutinase (<i>Humicola insolens</i>)	DE19706023 A1 (1998, BAYER AG; NOVOZYMES AS)

(Continued)

Table 4.2 Microorganisms and enzymes used for biodegradation of biopolymers (*Continued*)

Biopolymers	Microorganisms	Enzymes	Patent applications
Aliphatic-aromatic copolyesters: PET/ dimethyl glutarate/ dimethyl 5-sulfoisophthalate	<i>Thermomyces lanuginosus</i> <i>Rhizomucor miehei</i>	Lipases: Novozyme® 871 Palatase 20,000L Lipolase 100 L	US2005261465 A (2005, DU PONT); WO2005118693 A1 (2005, DU PONT)
PEC	<i>Pseudomonas paucimobilis</i> -PC61 strain (FERM-P-14657)		JPH08187090 A (1996, NAT INST ADV IND SCI TECHN; JSP CORP)
PTeMC	<i>Pseudomonas</i> sp.	Porcine pancreas lipase <i>Pseudomonas</i> sp. lipase <i>Pseudomonas</i> sp. lipoprotein lipase	JPH08151476 A (1997, NAT INST ADV IND SCI TECHN)
PEAM	<i>Bacillus alcalophilus</i> , <i>B. licheniformis</i>	Esterases Lipases Proteases	WO9743014 A1 (1997, BAYER AG)
PEAM, PEUU	<i>Paenibacillus lautus</i> (DSM 11870) <i>Bacillus pumilus</i> (DSM 11871) <i>Aeromicrobium</i> sp. (DSM 11872) <i>Thermobispora bisporea</i> (DSM11873) <i>B. sp.</i> RNA-Group V <i>Brevibacillus</i> sp.	Esterases Lipases Oligo-amidases	DE19754063 A (1999, BAYER AG)
PVOH	<i>Sphingomonas capsulate</i> UP-3 strain (FERM-P18699)		JP2003250527 A (2003, KAO CORP)
Amine-protected glutamic acid-based thermoplastic, thermosetting & thermosetting heterochain polyesters	<i>Rhizopus chinesis</i> , <i>Rhizopus delemar</i> , <i>Penicillium</i> <i>pinophilum</i> , <i>Aspergillus niger</i> , <i>Pseudomonas aeruginosa</i>	Lipase	WO9928366 A1 (2001, UNIV NEBRASKA)

Abbreviations: PBAT, Poly(butylene adipate-co-terephthalate); PBS, Poly(butylene succinate); PBSA, Poly(butylene succinate-co-adipate); PBSL, Poly(butylene succinate-co-lactate); PBST, Poly(butylene succinate-co-terephthalate); PCL, Poly(ϵ -caprolactone); PDLGA, Poly(D,L-lactide-co-glycolide); PEA, Poly(ethylene adipate); PEAM, Poly(ester amide); PEC, Poly(ethylene carbonate); PES, Poly(ethylene succinate); PET, Poly(ethylene terephthalate); PEUU, Poly(ester urethane urea) (biodegradable); PGA, Polyglycolide; PHA, Polyhydroxyalkanoate; PHB, Polyhydroxybutyrate; PHBHx, Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); PHBHV, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PHV, Poly(3-hydroxyvalerate); PLA, Polylactide; PTeMA, Poly(tetramethylene adipate); PVOH: Poly(vinyl alcohol); PTeMC, Poly(tetramethylene carbonate).

The hydrolysis rate of high molecular weight hydroxycarboxylic acid-derived polyesters is too slow to offer a significantly reduced burden when disposed of in landfills or in the environment.

Furthermore, many biodegradable polymers, which may be dissolved in hot water (such as poly(vinyl alcohol), PVOH) will form highly viscous and sticky solutions; these are difficult to handle and dispose of.

4.4.1 Hydrolysis

JPH09111036 A (1997, SHINETSU CHEM IND CO LTD) discloses a method of decomposing molded products that comprises a resin composition that consists mainly of a biodegradable polyester (generally a copolyester of lactic acid and another hydroxycarboxylic acid) with a disposal treatment solution that mainly contains an alkali. The content of the biodegradable polyester in the molded product is preferably ≥ 75 wt.%. The molded product is preferably a printed sheet for an overhead projector transparency (OHP) at the point that the sheet can immediately be subjected to the disposal treatment to prevent the leakage of the printed contents. The main component of the disposal treatment solution is preferably NaOH, KOH, etc. The concentration of the disposal treatment solution is preferably 1–15 wt.%, and the solvent is preferably water for safety and profitability reasons. The used disposal treatment solution generated after the contact decomposition of the molded product is preferably neutralized with a neutralizing agent consisting mainly of an acid, and is subsequently released into the sewerage system, etc.

JPH11349729 A (1999, SEIKO SANGYO) describes a device capable of rapidly treating a biopolymer such as PLA with an alkali solution, an organic solvent, and heat treatment until recovery and drainage of the decomposed product is made possible; it is useful for the waste treatment of biodegradable articles such as disposable medical treatment items. This device is used for dissolving or degrading (A) an alkali soluble biodegradable polymer (preferably PLA) in (B) an alkali solution (preferably a solution of NaOH or KOH) and subsequently recovering the original substance or draining the degradation product. The device comprises a pressure vessel capable of being sterilized with high-pressure steam, has a volume and a function which make it possible to stir and mix the

alkali-soluble biodegradable polymer A and the alkali solution B.

WO0236675 A2 (2002, PROCTER & GAMBLE CO) discloses a method of disposing of PHA articles originating from the health care and food service sectors by exposing the articles to an aqueous hot alkaline solution, preferably in the temperature range 120–170°C and at a pH of at least 8.5. A convenient method of decomposing, which also serves to decontaminate pathogenic organisms, is steam autoclave, as commonly used in hospitals. It is suggested that the hot alkaline treatment hydrolyzes the biopolymer to a mixture of monomers and possibly low molecular weight oligomers and/or small particulates. The resulting liquid, which may be in the form of a solution, slurry, or suspension, is biodegradable, and thus disposable in a sewerage system. As one advantage, the liquid tends to have low viscosity, and any particulates tend to stay suspended rather than precipitating. The resulting liquid is easily handled and disposed of. The articles to be digested may be in the forms of films, sheets, fibers, foams, and molded or thermoformed articles. Representative examples are soft films made of poly(3-hydroxybutyrate-co-3-hydroxyoctanoate) (PHBO), and flexible cups made of either PHBO or poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx).

WO03097468 A1 (2003, KUREHA CHEM IND CO LTD) discloses a method for recycling a bottle, which has a laminate structure including a main resin material layer of polyethylene terephthalate (PET) and at least one layer of PGA. The method comprises the steps of crushing the bottle and washing the resulting crushed product with an alkaline water, water, or an acidic water to remove the PGA layer and recover the main resin material. The alkaline water washing may be performed by using 0.01–5 normal of alkaline water-washing liquid at 20–100°C (preferably 40–98°C) for 5 min up to 10 h, and can efficiently hydrolyze PGA in a short time into glycolic acid. The water washing may be performed by using water at an elevated temperature of at least 40°C (and optionally under pressure) so as to accelerate the hydrolysis. It is also possible to use steam as a portion of the water and as a heat source. Acidic water also has the effect of accelerating the hydrolysis of PGA (similar to alkaline water) and is used at 20–100°C (preferably 40–98°C). Glycolic acid is the preferred acid. The washing may be performed once or many times. Incidentally, the adhesion strength between a PGA layer and a PET layer is not strong, and partial peeling may frequently occur during the bottle-breaking step.

This is also a factor in accelerating the removal by dissolution of PGA during washing with alkaline water, water, or acidic water. The glycolic acid formed by hydrolyzation of PGA in the washing waste liquid can be biologically decomposed into carbon dioxide gas and water by subjecting it to neutralization and treatment with activated sludge; this reduces its load on the environment.

WO2005049710 A1 (2005, KUREHA CHEM IND CO LTD) relates to an improvement in the previously proposed bottle recycling method. It has been found that the step of removing the PGA layer by washing with alkaline water involves an induction period; it becomes possible to remarkably shorten the step of removing the PGA layer (including the induction period) if the PGA layer is caused to contain a certain amount of water in advance. This phenomenon is found not only for PGA, but also for other aliphatic polyester resins, such as PLA. More specifically, the method of recycling a laminate-shaped product, such as a three-layer PET/PGA/PET bottle, is based on these findings, and comprises the following steps: (1) crushing the bottle to small pieces of approximately 2 cm² in size; (2) storing the broken pieces at 80°C and 95% relative humidity atmosphere for 18 h so that the moisture content of the aliphatic polyester layer is adjusted to at least 0.5 (preferably 1.0) wt.% or higher; (3) washing the broken pieces with alkaline water, preferably 1.5% caustic soda at 85°C for 15 min; and (4) removing the aliphatic polyester layer from the main resin. The humidification step shortens the induction period of the alkaline water-washing step, which results in streamlining the overall recovery operation. The waste liquid formed by washing with alkaline water, etc., contains aliphatic acid resulting from hydrolysis of the aliphatic polyester resin. This can be discharged as is after neutralization (since aliphatic acid is an organic acid occurring in nature), but is preferably subjected to an activated sludge treatment to biologically decompose the aliphatic acid into H₂O and CO₂, thereby alleviating the load to the ecological system.

4.4.1.1 Size reduction via hydrolysis

There are occasions when it is convenient to combine the hydrolysis of biodegradable biopolymers with a volume reduction of the disposed of articles. The volume reduction (1) lightens the burden necessary for daily garbage disposal in an ordinary household and the like; (2) contributes to prolonging the life of the reclaimed ground and the incinerator; (3) reduces

transportation costs of wastes and the like; and (4) reduces the load to the environment by allowing wastes that are even found in the natural environment as the scattered wastes to be incorporated into the natural cycle.

JP2004123810 A (2004, KANEBO LTD) discloses a volume-reduction method that involves exposing a biodegradable foam to 100–130°C water vapor to reduce its volume by 50% or more. The biodegradable foam is preferably composed of PLA. Alternatively, the foam volume is reduced by heating the foam for 2 min or more in a microwave oven with water. In one example, a biodegradable foam-molded product containing 80 wt.% of PLA and 20 wt.% of PCL was heated for 2 min in a microwave oven with 10 ml of water. The reduction in volume when evaluated after processing was 91.4%.

JP2005075865 A (2005, SHIMIZU CONSTRUCTION CO LTD) discloses a method and a disposal system for the volume reduction of discarded biodegradable plastic materials. The volume-reduction apparatus (1), depicted in [Figure 4.8](#), has a steam boiler (2) for generating steam (14) from water (13); the steam is supplied to a jetting mechanism (8) through a connection pipe (7). The steam (14) is jetted from nozzles disposed on the inside of the frame of the jetting mechanism (8) toward the discarded biodegradable plastic materials (12) that are in contact with the opening. The discarded articles, such as curing sheets (12) made of PBS and accommodated in a garbage bag (16), are exposed to steam (14) and are therefore shrunk to reduce the volume. A conveyor sends the volume-reduced curing sheet to a waste material disposal site. A decomposition unit in the disposal site decomposes the curing sheet. The disposal system can be used for the treatment of discarded biodegradable articles such as agricultural mulch sheets, packaging materials, curing sheets used in the construction field, and auxiliary industrial materials. The method reduces transport costs and the time of conveying the biodegradable plastic material to the disposal site. It also reduces the industrial disposal costs and enables efficient disposal of the biodegradable plastic material and industrial waste adhering to the biodegradable plastic material.

4.4.2 Enzymatic Hydrolysis

The enzymatic degradation of aliphatic polyesters by hydrolysis is a two-step process. The first step involves adsorption of the enzyme on the surface of the substrate through the surface-binding domain,

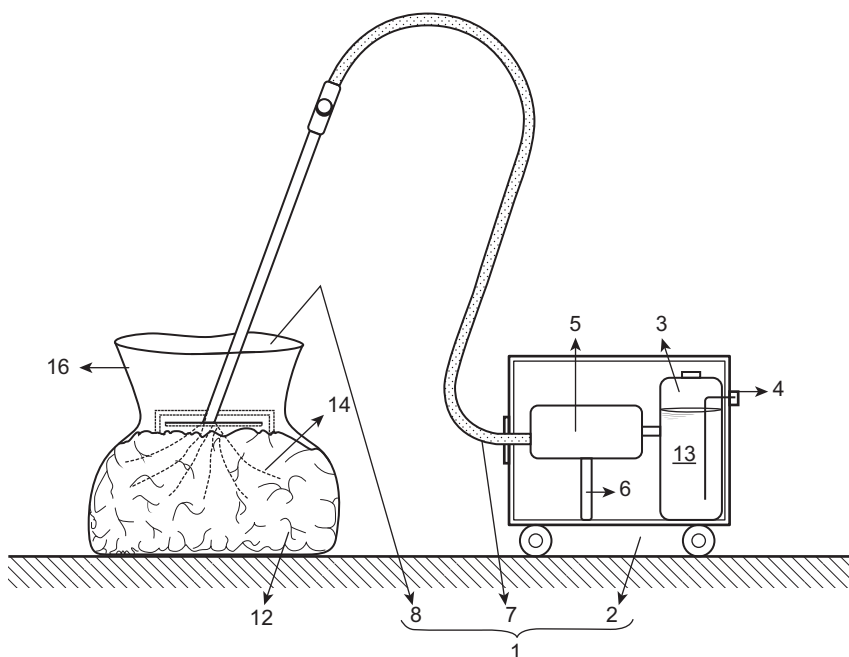


Figure 4.8 Schematic view of the volume reduction apparatus of biodegradable plastic material (JP2005075865 A, 2005, SHIMIZU CONSTRUCTION CO LTD).

1: Volume reduction apparatus;
2: Steam boiler apparatus; 3: Flush tank; 4: Drainage prevention sensor; 5: Steam boiler; 6: Safety valves; 7: Connection pipe; 8: Jetting mechanism; 12: Curing sheet; 13: Water; 14: Steam; 16: Garbage bag

and the second step involves hydrolysis of the ester bond [14].

JP2003221461 A (2003, TOYOTA CENTRAL RES & DEV) discloses a method of efficiently lowering the molecular weight of an aliphatic polyester, particularly PLA, and improving its biodegradability. The aliphatic polyester resin is heated and hydrolyzed in the presence of one or more kinds of compounds containing a nucleophilic nitrogen atom in order to lower its molecular weight, thereby preventing the increase of crystallinity that takes place upon lowering the molecular weight by a simple heating hydrolysis. The easily biodegradable aliphatic polyester thus obtained is further subjected to enzymatic monomer decomposition by microorganisms. The monomer decomposition may be an artificial enzymatic or chemical decomposition. The compound containing nitrogen is an ammonium salt, an amine compound, or urea. The compound containing a nucleophilic nitrogen atom is harmless to organisms, and is used as a plant nutrient. Microorganisms perform enzymatic decomposition in the environment.

JP2010131528 A (2010, TOYO SEIKAN KAISHA LTD) discloses a method of treating an organic waste containing a biodegradable biopolymer by solubilizing the organic waste. It entails adding microorganisms that generate enzymes and/or enzymes that decompose the biopolymer fermenting with solubilized decomposition product, and then collecting the fermented products. The preferred organic solvent is ethanol and

the preferred biopolymer is PLA. The enzyme used for solubilization decomposition is protease, lipase, cutinase, cellulase, or esterase.

JP2010116481 A (2010, TOYO SEIKAN KAISHA LTD) discloses a method for the degradation of a resin composition containing two different aliphatic polyesters (A) and (B) by subjecting the resin composition to a hydrothermal treatment and/or a heat treatment and then to an enzymatic decomposition. Aliphatic polyester (A) has a crystallinity of less than 20%. Aliphatic polyester (B) has a higher degradation rate than polyester (A) and polyester (B) releases an acid having a pH of 2.0 or less when it is hydrolyzed in water at a concentration of 0.005 g/ml. Polyester (B) hydrolysis releases oxalic acid or maleic acid. The enzymatic decomposition takes place in an enzyme liquid containing hydrolase. Examples of easily degradable aliphatic polyester (B) include poly(ethylene oxalate), poly(neopentyl oxalate) (PNOx), poly(ethylene malate), etc.

An exemplary resin composition is obtained by dispersing polyoxalate (B) in PLA (A). The hydrothermal treatment and heat process are carried out at 250°C or more for less than 5 min, and 200°C or more for less than 5 min, respectively. The method is used to break down the compositions found in items such as containers, cover materials for tray cups, pouches, stickers, and pillow packing bags.

While disposal by hydrolysis is a significant step in minimizing litter and long-term landfill, it has the

disadvantage of discarding the valuable polyhydroxycarboxylic acid.

4.4.3 Wastewater Treatment

Any biopolymer that meets the compostability criteria can in principle degrade in a sewage environment. Sewage is a favorable medium for biodegradation of biopolymers as there is a preponderance of microbes and high levels of nitrogen and phosphorus. As with landfilling and composting, wastewater treatment is practiced at the community level and involves the treatment of sewage and the renovation of wastewater before the water is reused or reenters a body of water. Preliminary sewage treatment screens out solid materials — such as diapers and other copolyester goods, sand, gravel, and large food particles from garbage disposals, etc. — from untreated human waste and grey water. The collected debris is subsequently disposed of in a landfill and/or composting system. Other kinds of sedimented organic waste collected from wastewater systems include sludge and scum. These may contain biodegradable polymers. Once sedimented from wastewater, sludge and scum are pumped into digesting tanks where microorganisms break down the waste for about a month, at which point it is sent to a landfill. Activated sewage sludge will convert approximately 60% of a biodegradable polymer to carbon dioxide while the remaining 40% will enter the sludge stream where it will be converted to methane by anaerobic digestion [56].

Biodegradable biopolymers have potential uses in various flushable sanitary products such as sanitary towels, colostomy bags, and other absorbent products. Flushable biodegradable biopolymers can have an adverse impact on wastewater treatment plants due to the very fast throughputs (typically 4 to 8 h) from the drain to the plant. This length of time is insufficient for many biodegradable biopolymers to lose their structure. Such polymers can foul the wastewater treatment plant primary screens.

US4372311 A (1983, UNION CARBIDE) (see supplementary list of patents) proposes making disposable articles, such as body-waste bags, from a water-soluble polymer coated with a degradable polymer. PHB is one such degradable polymer. The specification suggests that upon degradation of the degradable polymer, the water-soluble polymer can dissolve and thus prevent obstruction of sewage pipes and sewage treatment plants. According to **AU3521984 A** (1985, ICI PLC), PHB is well-suited to

the manufacture of body-waste bags, whether alone or as a coating on a water-soluble polymer, by virtue of its good water and vapor impermeability characteristics; but their rate of degradation is often too slow to avoid the formation of the aforementioned obstructions. The inventors of **AU3521984 A** (1985, ICI PLC) have found that the degradation rate can be markedly increased by modification of the pH of the bag contents. They disclose a disposal method for body-waste bags (made with PHB) that contain human feces and/or urine. The method consists of adjusting the bag contents to a pH of 12 and then introducing the bag and its contents into the sewage system. The pH is conveniently modified by addition of a base, preferably as a solid (see also Chapter 7: Degradability on Demand; Section 7.3: Promotion of (Bio)degradability).

4.4.4 Marine and Freshwater

The rate of biopolymer biodegradation in marine environments is affected by water temperature. PLA-based polymers degrade slowly over a period from several weeks up to about one year. Compared to water-soluble or water-swelled polymers, which fall apart quickly in water, PLA-based polymers can only be classified as moisture-sensitive because they degrade slowly. For instance, after a month's immersion in water, PLA and certain copolymers thereof show no reduction in molecular weight; but after six months, physical properties drop significantly (see also Chapter 7: Degradability on Demand; Section 7.3.6: Plasticizers, [Table 7.2](#)).

PHB and PHBHV films disposed of in seawater disappeared within 8 weeks [57]. Brandl and Puchner calculated that PHBHV shampoo bottles have a life span of 10 years in a Swiss lake [58].

O'Brine and Thompson investigated the degradation of oxodegradable, compostable, and conventional plastic carrier bags in the marine environment [59]. Four types of polymers that are used as carrier bags were compared. The first two bags were made from two oxodegradable polyethylenes (PE). The first PE used the d2w[®] Self-destruct oxodegradable plastic additive manufactured by Symphony Plastics (UK), and the second PE used the Totally Degradable Plastics Additives (TDPA[™]) manufactured by EPI Environmental Products, Inc. (CA). The third bag was made from Mater-Bi[®] produced by Novamont, which consists of cornstarch, vegetable oils, and compostable polyesters. The fourth bag was made from standard PE containing 33% recycled material.

Tensile strength of all materials decreased during exposure, but at different rates. The compostable polyester degraded more than all the other polymers with 100% surface area loss between 16 and 24 weeks, while the other polymers lost only approximately 2% after 40 weeks. Some polymers required UV light to degrade. Transmittance of UV light through oxodegradable and standard PE decreased as a consequence of fouling such that these materials received approximately 90% less UV light after 40 weeks. The data indicate that compostable biopolymers may degrade relatively quickly compared to oxodegradable and conventional polymers. While biodegradable polymers offer waste management solutions, there are limitations to their effectiveness in reducing hazards associated with plastic debris. Some biodegradable biopolymers may not degrade quickly in natural habitats, with the added concern that some formulations could merely disintegrate into small pieces that are not in themselves any more degradable than conventional polymers.

Several microorganisms have been identified that can degrade PHAs in freshwater [27,60] and marine environments [27,61–64]. Amongst them are the bacteria *Pseudoalteromonas* sp. NRRL B-30083, *Marinobacter* sp. NK-1, *Alcaligenes faecalis* AE122, and the actinomycetes *Nocardiopsis aegyptia* and *Streptomyces* sp. SNG9.

4.5 Other Waste Disposal Systems

Septic systems and garbage disposal systems are used at the individual residence level and are typically not implicated in the disposal of goods made of biodegradable polymers, like soft drink bottles or diapers. Disposal of such goods in these systems generally causes costly damage (US2005261465 A1, 2005 and WO2005118693 A1, 2005, DU PONT).

Another common practice is the uncontrolled disposal of items into the environment. The visual pollution problem of littering is unlikely to decrease with the use of biopolymers since most of them will not be exposed to proper biodegradation conditions in a short period of time. Biopolymers can potentially add to the litter problem as the consumer may erroneously believe that they just “break down and disappear” after disposal.

US2005286398 A1 (2005, SANYO MAVIC MEDIA CO LTD) discloses a method for discarding an optical disc, such as a CD, DVD, Blu-ray Disc, or advanced optical storage disk (AOD or HD DVD), in

which a substrate of the optical disc is formed of a transparent polymer made from PLA as a main raw material; steps include discarding said optical disc after erasure of the data (pits) by leaving the optical disc at a temperature equal to or more than a heat deflection temperature of PLA for a predetermined time period. In one embodiment, the optical disc is soaked in hot water at a temperature between the glass transition temperature (T_g) of the material and up to 100°C. Examples of PLA include Lacty® (Toyota Motor Corporation), Lacea® (Mitsui Chemicals), and TERRAMAC® (Unitika Ltd). According to the invention described in the patent, by applying heat to the optical disc, the data (pits) of the optical disc are easily erased and made unreadable before the optical disc is discarded and biodegraded. Thus, the data is never compromised, in accordance with the disposal of the optical disc.

JP2000290428 A (2000, CANON KK) discloses a device for decomposing biodegradable polymer waste generated from industries (Figure 4.9). It comprises a decomposition treatment tank (101) equipped with a power supply (109) for creating specific redox potentials between electrodes, a supply unit for introducing aqueous electrolyte solution into the tank, and a supply unit for providing biodegradable polymer to the anode side of the electrode. It is preferable to configure the electrolytic solution supply unit near the anode. The treatment tank also includes a stirring unit.

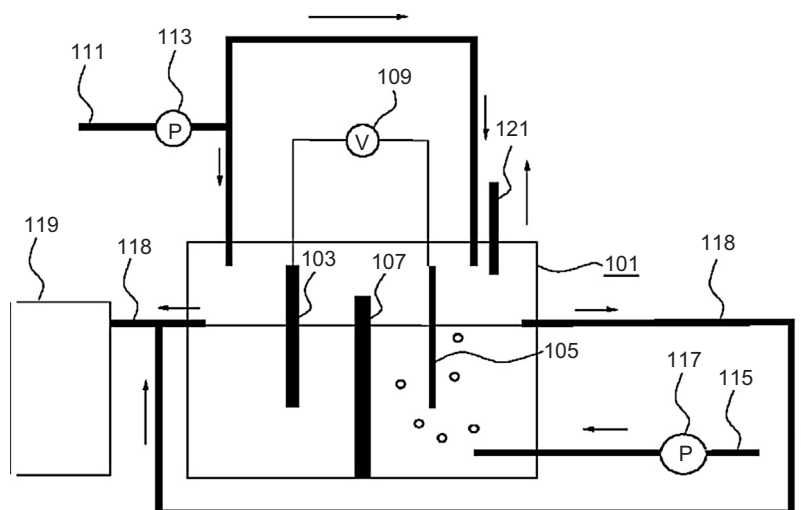
A redox potential of 800–1500 mV is created between the platinum (working) electrode (105) and the silver-silver chloride (reference) electrode (103) immersed in acidic functional water with a pH of 1–4 and a chloride concentration of 5–150 mg/l. A biodegradable polymer is then contacted with the water and decomposed (Figure 4.9).

The preferred biodegradable biopolymer is one or more of the following: aliphatic polyesters, starch, and sugar-inorganic composite. Preferred aliphatic polyesters are chemosynthesized aliphatic polyesters, microorganism-synthesized polyesters, natural polymer group aliphatic polyesters, and/or sugar-chain polyesters. Preferably, the aqueous electrolyte solution contains inorganic acid, sodium hypochlorite, sodium chloride, and potassium chloride. Preferred inorganic acids are hydrochloric, hydrofluoric, hydrobromic, sulfuric, phosphoric, and/or boric acids.

Example: Acidic functional water with pH of 2.6 and chloride concentration of 75 mg/l at redox

Figure 4.9 Biodegradable polymer decomposition device (JP2000290428 A, 2000, CANON KK).

101: Decomposition treatment tank;
103: Cathode; 105: Anode;
109: Power supply



potential of 1000 mV, and pH of 2.1 and chloride concentration of 54 mg/l at redox potential of 1150 mV, was prepared. A sodium chloride electrolyte solution containing the functional water was prepared. Functional water (10 ml) was added into a glass vial container. A (3×3) cm² sheet of sugar-silica composite containing 70/30 of acetyl cellulose and tetramethoxy silane was immersed in the electrolyte solution. The solution was then left undisturbed at 25°C for a month. The composite decomposed efficiently and quickly. The control method using pure water as electrolyte was not found to decompose the composite.

The device is claimed to decompose large quantities of biodegradable polymer waste efficiently, safely, and economically under normal temperature and pressure. Different kinds of biodegradable polymers can be simultaneously decomposed.

JP2006193357 A (2006, NISSAN MOTOR) discloses a method of producing hydrogen by decomposing a biodegradable polymer under the activation of a photocatalyst and reducing water. Microorganisms capable of degrading the biopolymer are incorporated into the water. The photocatalyst that reacts only with UV is arranged on the surface, and the photocatalyst that reacts with visible light is used inside. The hydrogen-producing system is provided with a means for bringing the photocatalyst, the biopolymer material, and the water into contact with each other, and also a means for irradiating with light, for separating hydrogen from carbon dioxide gas, for recovering hydrogen, and for recovering carbon dioxide gas. The photocatalyst is chosen from titanium oxide, zinc oxide, niobium oxide, tantalum oxide, and gallium oxide group photocatalysts. The biopolymer waste is

obtained from motor vehicles and domestic electrical appliances, and is effectively utilized for hydrogen production.

4.6 Destructive Thermal Processes

4.6.1 Incineration (Combustion)

Incineration is not a preferred method of disposal because it can result in the emission of dioxins and other atmospheric pollutants, and it contributes to global warming. The potential contaminants could also decrease the lifetime of the incinerator. Furthermore, the high moisture content of some solid wastes impedes the incinerators from running at maximum efficiency because the incinerators must expend extra energy in order to evaporate off the moisture in the waste. In combination with enforced clean air regulations, which led to the shutdown of several waste incinerators, the cost for the disposal of plastics by incineration is expected to increase. Additionally, incineration (combustion) cannot recover monomers that constitute the wasted polymer, and are therefore unfavorable to the economy.

Upon incineration, both PLA and PGA burn with a clean blue flame; they do not generate poisonous or corrosive gases and release the same quantity of carbon dioxide as that generated during production. Plants absorb carbon dioxide generated by incineration of PLA. Photosynthesis converts the carbon dioxide to carbohydrates for plant growth. This forms a carbon dioxide generation-consumption cycle. Because of this cycle, the incineration of PLA does not increase the overall quantity of carbon dioxide in the air, which makes PLA an environmentally friendly

material. In this regard, it is better than fossil-based polymers, which generate only carbon dioxide by incineration. Furthermore, the incineration of PLA produces no nitrogen gases and only one-third of the combustible heat generated by polyolefin. Also, it does not damage the incinerator, and therefore provides significant energy savings [65].

Incineration is recommended for the disposal of biodegradable items originating from the health care sector (like hospitals) or other medical wastes that are hazardous to public health and require special treatment before disposal. Transfer of these materials to an incineration facility is required, so a specially designed incinerator must often be installed in the neighborhood where the waste is generated. When these wastes are contaminated with hazardous materials such as putrefied organic materials or pathogenic microorganisms, special countermeasures for protection against bad smell or infection are required during transfer to a disposal facility.

Although biodegradable resins are satisfactory from the perspective of environmental safety, their compositions could be damaging to the environment (see also Chapter 10: Economic Evaluation and Environmental Impacts; Section 10.4: Health and Safety Impacts). Biodegradable resins containing halogen-based flame retardant additives yield halogen gases on incineration, so complex processing is required in order to make the halogen gases innocuous to humans (WO2005054373 A1, 2005, SONY CORP).

4.6.2 Pyrolysis

WO2009081362 A1 (2008, TORINO POLITECNICO) discloses a process for the disposal and recycling (see Chapter 6: Chemical Recycling; Section 6.5: Miscellaneous Processes) of waste polymers. In this method, waste materials are subjected to pyrolysis, and the gaseous products are converted into carbon nanotubes via vapor-phase chemical deposition in an inert gas; this is done with the help of an unsupported organometallic catalyst. The process makes it possible to convert pyrolysis products into a raw material of high value (nanotubes). The waste polymers are derived from electronics wastes. The process applies mainly to non-biodegradable polymers, but it also includes aliphatic polyesters.

A new technology uses waste biopolymers in the flash pyrolysis of biomass. The flash pyrolysis of biomass waste streams is a promising method to obtain energy and raw materials (bio-char, biogas,

bio-oil) without endangering the basic food supply. A major drawback of flash pyrolysis of biomass is the inherent production of pyrolytic water, which results in a bio-oil with a relatively high water content. Studies have shown that the flash co-pyrolysis of biomass and biopolymer waste synergistically improves the characteristics of the pyrolysis process, for example, reduction of the water content of the bio-oil, greater bio-oil production and less char production, and an increase of the higher heating value (HHV) of the oil [66–69]. Of all the biopolymers under investigation, PHB is the most promising, followed by (in order of decreasing profits) Eastar® (aliphatic-aromatic copolyester), Biopearls™ (PLA-based biopolymer), potato starch, PLA, cornstarch, and Solanyl® (starch-based biopolymer). Taking into account uncertainties, flash co-pyrolysis is expected to be cheaper than composting biopolymer waste streams (except for cornstarch). Under the condition that biopolymers make their full entry into the plastics industry, flash co-pyrolysis of willow and PHB is the only option to be commercialized in the short term.

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WO9928366 A1	19990610	AU1709099 A 19990616; US5990266 A 19991123; US6121033 A 20000919	UNIV NEBRASKA

Supplementary patents (not necessarily relating to biopolymers)

Patent number	Pub. date	Family members	Applicant
US4372311 A	19830208		UNION CARBIDE CORP

5 Physical Recycling

OUTLINE

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5.1 General

At first, the idea of recycling biopolymers seems odd as most biopolymers are biodegradable themselves. However, there are some good reasons for recycling.

The arguments in favor of recycling can be summarized as follows:

- Disposal of biopolymer articles has the disadvantage of discarding valuable raw materials (e.g., polyhydroxy acids).
- Recycling of biopolymers is crucial in reducing the consumption of renewable resources needed for the synthesis of the corresponding monomers. Waste biopolymer articles may become alternative feedstocks for monomers and synthetic intermediates.
- The production and processing of biopolymers require a considerable amount of energy.
- Most commercial biopolymers (e.g., polylactide PLA) are not degraded under ordinary conditions even in the presence of microorganisms. Large amounts of disposed of PLA may create new environmental problems in the future.

The arguments against recycling can be summarized as follows:

- Biodegradable biopolymers pose a serious problem when they enter either conventional plastics recycling or green-waste composting streams.
- A growing number of polyethylene terephthalate (PET) recyclers, recycling associations, and officials have expressed concerns over the potential contamination of the PET recycling stream by PLA bottles, yield loss, increased cost for sorting, and the impact on recycled PET (RPET) quality and processing.
- A critical mass of biopolymers (at least 200 million kg produced annually) is necessary for independent rigid packaging recycling to be profitable [1].

Meanwhile, biopolymer recycling remains a controversial issue. The debate on recycling biopolymers, specifically PLA with mainstream PET, continues to rage on, and studies on the subject seem to contradict each other. At present, physical (or mechanical) recycling of rigid biopolymers could be handled as a sideline in existing recycling facilities provided the value of the recycled product exceeds incurred costs [1].

Physical recycling involves reducing the size and/or separating the different polymers from a waste mixture without significantly altering the chemical

structure of the recovered polymer(s). The physical methods work with much lower temperatures than the chemical, thermal, or enzymatic methods. This means that the structure, and especially the molecular chain length of the recycled plastic, remains essentially intact. The physical recycling techniques are usually followed by chemical, thermal, or enzymatic depolymerization of the recovered biopolymer.

Within this category, the processing methods applied so far to the physical recycling of biopolymers are as follows.

5.2 Grinding

One of the techniques of recycle sorting of various plastic materials, such as bottles and other similar containers, is to grind the materials into particulates or flakes of about $\frac{1}{8}$ " to perhaps as much as a $\frac{1}{2}$ " in width or diameter. Grinding a biodegradable polymer can be carried out according to techniques known to those skilled in the art, for example shearing, impact, dry, or water grinding. Grinding a waste molding formed by a biodegradable polymer composition and remolding the ground polymer gives products with inferior properties. Most grinding apparatus have inherent disadvantages that limit their usability.

For instance, large shaped articles cannot be fed as such into a grinding apparatus. They must be reduced in size before entering the grinding apparatus or they must be made brittle to facilitate the grinding. A suitable way to overcome this problem is to use freeze-grinding, a technique that minimizes the damage incurred by the biodegradable biopolymers. By cooling the shaped article with liquid nitrogen, the material can be made brittle. This does, however, necessitate the use of special equipment that can withstand such low temperatures. Also, the materials easily attract water under these conditions. Further, these grinding methods invariably lead to the formation of substantial amounts of fines (< 1 mm), which are difficult to feed into polymer processing equipment such as extruders or injection molding machines. These fines should therefore be removed, which necessitates the use of a separate sieving step, and leads to loss of material. The latter particularly counts when the material is expensive, such as is the case with biopolymers used in medical applications. Another disadvantage of a conventional grinding apparatus, such as a knife mill, is the heat

generated when large lumps or parts of polymeric materials are ground. This heat can melt or soften materials that have a melting temperature (T_m) or glass transition temperature (T_g) that is relatively low. When grinding such low T_m or low T_g products, the molten or tacky material may impair the functioning of the grinding apparatus. Such heat is further detrimental for those polymers that are heat labile and which can degrade upon heating. Furthermore, it is regularly observed that many knife grinding apparatus release small metal particles from their knives when grinding large lumps, particularly when such apparatus are not specifically designed for grinding polymers (EP1741536 A1, 2007, PURAC BIOCHEM BV).

In order to overcome the aforementioned problems, **EP1741536 A1** (2007, PURAC BIOCHEM BV) proposes a method for comminuting a polymeric shaped article into particles having an average particle size smaller than 6 mm by using a grinding apparatus. Prior to grinding, the shaped article is subjected to a milling step in a milling apparatus to convert the shaped article into chips. The chips are then fed into a grinding apparatus such as a knife mill for further comminuting, which yields at least 25 wt.% fewer particles having a size less than 1 mm than obtained by the grinding step only. The addition of small, well-defined particles to grinding apparatus substantially prevents the formation of fines, the production of excessive heat, the occurrence of metal particles, and usually leads to narrow particle distributions. The shaped articles are preferably aliphatic polyesters including PLA (co)polymers, polyglycolide (PGA) (co)polymers, poly(lactide-co-glycolide) (PLGA) copolymers, and poly(ϵ -caprolactone) (PCL) (co)polymers.

CN101275009 A (2008, FUJI XEROX CO LTD; FUJIFILM CORP) discloses in one of its embodiments a method of recycling a resin compact used mainly as exterior parts of a printer, a copying machine, a facsimile and the like. The resin composition comprises 21–70 mass% of aliphatic polyester (e.g., PLA), 35–65 mass% of a second polymer having a T_g higher than the T_g of the aliphatic polyester (e.g., polycarbonate), and 1–20 mass% of an aluminum phosphate as flame retardant. The recycling method comprises freeze-grinding, heating the obtained ground product at a temperature lower than the melting point of the aliphatic polyester, and injection-molding the ground product to obtain a resin compact.

Grinding alone or in combination with other physical techniques such as dissolution is used in several methods as a preliminary step in order to facilitate the subsequent depolymerization of the recovered material. For this purpose **WO2010118954 A1**, **AU2010237249 A1**, and **WO2010118955 A1** (2010, GALACTIC SA) use one or more steps for grinding PLA or a polymer blend containing PLA, the number depending on the starting product, but also on the cost of these operations and the targeted final granulation. The objective of this step is to increase the specific surface area of the biodegradable material so as to obtain a weight/volume ratio between 0.05 and 1.4 t/m³. This makes the handling steps easier and speeds up the subsequent dissolving step, which makes the process more easily industrially applicable. Similarly, in **JP2003128900 A** (2003), **JP2004216378 A** (2004), and **US2005250931 A1** (2005, MITSUBISHI PLASTICS INC), the use of PLA shredder dust for the recovery of lactide provides the advantage that the larger surface area of the shredder dust improves the efficiency of recovery (see also Chapter 6: Chemical Recycling; Section 6.1: Dry-Heat Depolymerization).

5.3 Sorting

There are various techniques for identifying and sorting materials by polymer type. Some of these techniques include manual sorting, density separation, electrostatic processes, and various optical systems including optical inspection using photodiodes or CCD machine vision, near infrared (NIR), ultraviolet (UV), X-ray analysis, and fluorescent light or laser radiation.

As can be seen from the aforementioned techniques, manual sorting is tedious, expensive, prone to error, and can be unsafe. X-ray analysis is effective only for separating polyvinyl chloride (PVC) plastics from PET and has not been tested for biopolymers. Optical scanning of postconsumer plastics is useful for sorting plastics according to transparency and color, but is unable to provide chemical identification of polymers. Furthermore, optical techniques require the use of costly apparatus, such as video cameras, electronic devices, infrared detectors, and organic “markers,” to provide effective segregation of like plastics. However, even sorted plastic waste can present problems in processing as a result of density and chemical differences among polymers

that fall into the same general class but are made by different plastics manufacturers. Further, sorted plastic scrap must be subjected to batch grinding to produce flake scrap material that then must be pelletized and ground again to provide powder feedstock for blow molding, rotational molding, some extruding, spray coating, and other melt processing techniques that require powder feedstock. The high cost of sorting has greatly limited widespread use of recycling approaches that require a sorting step. In particular, collected and sorted postconsumer plastic materials are usually more expensive than the corresponding virgin plastic materials. Thus, users of plastic materials are discouraged from using sorted, recycled plastic materials.

The only area of successful physical recycling involves the sorting of rigid plastic packaging materials, in particular PET and high density polyethylene (HDPE) bottles. The business of bottle recycling is sufficiently profitable since the supply of bottles is large enough and growing steadily, the technology is available to convert used bottles into a number of value-added products, and the products can be sold at a profit [1]. However, although the processes for recycling PET are very effective, they are relatively complex and sensitive. It has been demonstrated that the presence of PLA, even at low levels in the region of 1%, completely disrupts the process, the residue rate is higher (and the yield is therefore not as good), and the quality of the final PET is lower (**WO2011015433 A1**, 2011, GALACTIC SA).

In the case of biopolymers the situation is presently unfavorable since these polymers have not yet reached a critical mass, the minimum amount of available material which is necessary to support freestanding recycling facilities.

5.3.1 Density Separation Systems

The density (also called specific gravity or float-sink) separation systems are usually used to separate components heavier than water from those lighter than water. Density separation of granulated plastics by sink/float in a water bath yields only a float product and a sink product and is not useful for a primary sort of mixed plastics. Density separation technology has been shown to be efficient for sorting polyolefins from a waste plastics stream of rigid packaging comprised of PET, HDPE, and biopolymers. HDPE separates by floating in water while

the biopolymers sink together with the PET¹. The further separation of the biopolymers from the PET is not an easy and economically profitable task as both polymers have a density greater than 1 g/cm³. The use of water presents some issues in that the biopolymers have to be extensively dried prior to recycling in order to prevent a hydrolytic decomposition of the molecular chains during the plasticization or upon melting (see Section 5.4: Drying).

The invention concerns a method for selectively separating predetermined materials contained in mixtures of materials, in particular mixtures formed by waste and containing other materials with characteristics similar to the predetermined materials. The method is characterized by the fact that the mixtures of materials are subjected, according to a known operation, to a process of automatic separation by density, where the materials of mass density within a first range of values are separated from those within a second range of values. Before or while they are being treated, the predetermined materials are enriched with an additive that provides them with a mass density within the first range of values. This method enables simple and economical separation — for example, high value or biodegradable synthetic materials contained in waste mixtures — such that they can be subsequently treated in accordance with prescribed rules or upgraded during removal.

WO0107166 A1 (2001, FRAUNHOFER GES FORSCHUNG) provides a method for the selective separation of thermoplastic polymers from material mixtures, especially mixtures formed from waste materials, by adding additives to a specific polymer to vary its specific gravity from that of the other materials. Materials in the mixture initially have similar specific gravities, and to enable specific materials to be separated from the others by an automatic density difference process, additives are added during the processing which alter the specific gravity range of the specified materials from that of the other materials. The density of the materials is increased by not less than 10% compared to the other

materials. The additive is a mineral filler, especially a metal, metallic oxide, or salt (preferably dolomite, calcium carbonate, barium sulfate, or barium ferrite). The preferred thermoplastic polymers to be separated are biodegradable biopolymers (see Table 5.1). The method is used for separating thermoplastics from material mixtures, especially scrap materials from the packaging industry, automobile recycling, or electronic equipment, where the materials have similar specific gravities.

With the density separation system, there is no capability to sort the segregated polymer types into colors since different colors do not change the density of the polymer. Therefore, an end market for the mixed-color polymer would have to be used, or subsequent equipment would be required to color segregate each polymer type [3].

5.3.2 Electrostatic Separation Systems

Electrostatic separation systems are used to separate a mixture of plastics that can acquire different sign charges through triboelectrification. For this to be possible the materials must not be aggregated; they must be separate discrete particles, and they must be distinct from one another in their triboelectric charging behaviour (or contact charging due to friction of the particles with one another). Using triboelectric charging capacity as the separation criterion, it is even possible to separate materials whose conductivities are virtually identical. Triboelectric charging can be carried out in mixers, fluidized bed dryers, or pneumatic conveying systems. The selectivity and intensity of the charge can be increased considerably by adjusting climatic conditions, such as temperature and moisture content, and by adding conditioning agents. Such particles can be so highly positively or negatively charged that in free fall through a high-voltage electrical field, they can be deflected towards the appropriate counter electrode and thus separated from one another. Since triboelectric charging depends not only on the chemical constitution of the particles to be separated, but also on their surface condition, the particles must be clean and dry. Different plastics additives such as pigments, flame retardants, plasticizers, etc., influence the charging characteristics. It is therefore necessary to adjust conditions to achieve the selective

¹ Most of the commercial biopolymers have densities greater than 1.0 g/cm³. The density of solid amorphous PLA is about 1.25 g/cm³. The density of purely crystalline poly-L-lactide acid (PLLA) is estimated to be 1.37–1.49 g/cm³ [2]. The densities of PS (1.05 g/cm³) and PP (0.91 g/cm³) are well below that of PLA. The density of PET is approximately 1.30–1.38 g/cm³.

Table 5.1 Selective separation of biodegradable biopolymers from material mixtures

Biodegradable biopolymer	Density range, unfilled (g/cm ³)	Density (g/cm ³) with dolomite		
		10%	20%	30%
PHBV (BIOPOL [®] , Monsanto)	1.25	1.32	1.41	1.50
PCL (Tone [™] , Union Carbide)	1.15	1.22	1.31	1.40
Poly(ester amide) (PEAM) (BAK [®] , Bayer)	1.07	1.14	1.22	1.32
PBAT(Ecoflex [®] , BASF)	1.25–1.27	1.32–1.34	1.41–1.43	1.50–1.52
PLA (Lacea [®] , Mitsui Chemicals)	1.26	1.33	1.42	1.51
PBST (Biomax [®] , DuPont)	1.35	1.43	1.51	1.60
PES (Bionolle [®] , Showa Highpolymer)	1.23–1.32	1.30–1.39	1.39–1.48	1.48–1.57
Starch/PCL blend (Mater-Bi [®] , Novamont)	1.12	1.19	1.27	1.37
CA (BIOCETA [®] , Rhone Poulenc)	1.27–1.32	1.34–1.39	1.43–1.48	1.52–1.57
Non-biodegradable polymers				
PE	0.91–0.97	0.98–1.04	1.05–1.12	1.14–1.21
PP	0.90–0.94	0.97–1.01	1.04–1.09	1.13–1.18
PS	1.05–1.08	1.12–1.15	1.20–1.23	1.30–1.33
PA	1.05–1.20	1.12–1.27	1.20–1.36	1.30–1.45
PC	1.20–1.23	1.27–1.30	1.36–1.39	1.45–1.48
PET	1.35–1.40	1.43–1.48	1.51–1.56	1.60–1.65
PVC	1.34–1.43	1.41–1.50	1.50–1.59	1.59–1.68

Abbreviations: CA, Cellulose acetate; PBAT, Poly(butylene adipate-co-terephthalate); PBST, Poly(butylene succinate-co-terephthalate); PCL, Poly(ϵ -caprolactone); PE, Polyethylene; PES, Poly(ethylene succinate); PA, Polyamide; PC, Polycarbonate; PEAM, Poly(ester amide); PET, Poly(ethylene terephthalate); PHBV, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PLA, Polylactide; PP, Polypropylene; PS, Polystyrene; PVC, Poly(vinyl chloride).

According to WO0107166 A1 (2001, FRAUNHOFER GES FORSCHUNG).

charging that is desired by adjusting climatic conditions, or by choosing a specific conditioning agent.

Hamos GmbH Recycling und Separationstechnik, a manufacturer of electrostatic separation equipment, owns a series of patent applications for the dry electrostatic separation of metal/non-metal and plastic/plastic-mixtures (DE19522147 A1, 1997; WO9828080 A1, 1998; DE19740027 A1, 1999; DE19739992 A1, 1999; DE19829200 A1, 2000; DE19901743 A1, 2000).

The most common plastics (PVC; PET; polyethylene, PE; polystyrene, PS; polyamide, PA; polycarbonate, PC; poly(methyl methacrylate), PMMA) can be electrostatically sorted from each other. As the material separation takes place in absolutely dry conditions, auxiliary equipment to handle separation

liquids or conditioners are not necessary. Hamos dry plastic/plastic separators are supplied as single- or double-stage with throughput capacities ranging from 200 to 750 kg/h depending on the materials to be separated.

The Hamos electrostatic separation technology was tested by the Waste & Resources Action Program (WRAP) to separate mixed polymer flake. This was tested for PVC removal from PET, and also polypropylene (PP) from HDPE flake. The level of separation was not acceptable for either of the trials. This technology is primarily used as a clean-up function for removing PVC from PET flake, and the level of contamination within the trial material provided was deemed too high to be considered successful [3].

The electrostatic separation has been adapted to effectively identify and sort PLA before forwarding it to material recycling [4]. However, no reports or published experimental results are available.

The material mixture or pre-separated components of the mixture of the method described by **WO0107166 A1** (Section 5.4: Drying) may additionally be subjected to a magnetic separation method by adding ferromagnetic additives (e.g., iron powder) before or during the processing stage.

5.3.3 Optical Systems

The optical sorting of plastics is conventionally done in a conveyor operation wherein the materials to be sorted, whether bottles or flake material, are moved along via the conveyor or similar moving carrier to be irradiated by an electromagnetic energy source, such as at near infrared radiation (NIR), and the electromagnetic energy passing through the various irradiated articles is detected by one or more detectors. According to a preselected scheme of determination and evaluation of relative levels of transmitted or reflected electromagnetic energy, various of the passing articles or material are ejected from the stream (US2001045518 A1, 2001, SOMMER E J; NATIONAL RECOVERY TECHNOLOGIES INC).

5.3.3.1 Near infrared (NIR)

A popular technology for sorting whole rigid plastics is based on cameras operating in the near infrared (NIR) or visible parts of the electromagnetic spectrum to achieve polymer or color sorting. This type of unit is widely used in the UK for plastic bottle separation, and in Europe for sorting both bottles and other packaging plastics. NIR systems can effectively remove PLA and carton board from a mixed packaging stream.

NIR has many advantages. The most significant is the speed of identification. Because of the great scanning speed of the spectroscopic instrument, many readings of one sample can be taken in short periods of time. This allows multiple checks to ensure proper identification. The speed also provides for increased volume of plastics sorted in smaller amounts of time. A second advantage is the lack of specimen preparation. Labels, or other obstructions like dirt, do not interfere with readings. Another advantage of this system is that color does not interfere with proper resin identification. Except for black, the readings are independent of the color of the resin [5]. Black is

a strong absorber in the NIR region, and scanning of black plastics results in a featureless spectrum.

An apparatus which uses infrared spectroscopy and Fourier transform infrared (FTIR) to take an infrared reflection spectrum of the surface of a plastic component in the mid-IR (MIR) region in a wave length region between 400–4000 cm^{-1} and correlate it to set of plastic materials is claimed to be able to identify black-colored plastics (GB2284477, 1995, BRUKER ANALYTISCHE MESSTECHNIK GMBH).

A key weakness of the NIR sorting technology is when an item contains more than one material or plastic type (e.g., label), the identification sensor may not recognize the item, or may identify it based on the minority material. Further misidentification can occur when homeowners have placed one item inside another or when two items get stuck together, usually through compaction or baling.

NIR spectroscopy (700–2500 nm) has been applied for the identification and separation of PLA from a mixed-waste plastic stream composed mainly of PET and a minor amount of PLA. NatureWorks surveyed equipment manufacturers that had the potential to sort biopolymers from other polymers like PET, HDPE and PVC using infrared, ultraviolet, X-ray, color identification, and laser sorting. NatureWorks identified a dozen companies and then worked closely with three of them to determine the accuracy of the sorting systems [6]. Titech's NIR sorting systems removed PLA (IngeoTM) from a PET sorting stream at an accuracy of 97.5%, which is about as effective as removing contaminants and other items unwanted in the PET stream [7]. MSS also used an NIR system on IngeoTM and found that the PLA emits a unique polymeric signature that the system can be programmed to identify and remove [8]. According to NatureWorks, NIR has the most promise for automated sorting of PLA from a PET recycling stream. A report published by WRAP confirmed the above findings, stating that "NIR systems can effectively remove PLA and carton board from a mixed packaging stream" [9]. NatureWorks also attempted to establish the level of PLA contamination that PET and HDPE could handle. The results of these studies indicated that PLA affects the haze and color of PET above 0.1% concentration, thus limiting its end-use markets. PLA has no effect on the color or melt index of HDPE flake at up to 2% concentration.

NatureWorks' assertions were contested by various recycling associations, such as the National

Association for PET Container Resources (NAPCOR) [10], the Association of Postconsumer Plastic Recyclers (APR) [11], and the Industry Council for Packaging and the Environment (INCPEN) [12]. These groups expressed concerns that the accuracy level of the NIR systems was not high enough to remove PLA and prevent contamination problems, while too much PET could be falsely rejected along with the PLA. In addition, the cost of a NIR system could be prohibitive.

Other key issues to be addressed by the NIR specialists are identification of PLA in blends, coated articles, multilayers, black moldings, containers placed inside each other, and in situations where two items are stuck together.

No patents dedicated to NIR sorting of biopolymers have been retrieved so far.

5.3.3.2 Laser

This technique offers fast (less than a microsecond) identification of plastics based on atomic emission spectroscopy (AES). A laser is used to release excited ions and atoms from the material surface, and these can then be identified through spectral analysis to provide the elemental composition of the material (including polymer type and additives present). Laser-sorting systems are commercially available from companies such as Unisensor GmbH and Visys NV. Unisensor

uses laser Raman fluorescence spectroscopy and Visys NV systems utilize the reflection of laser light to perform detection.

Unisensor GmbH developed a flake-sorting technology called Powersort 200[®] that uses ultra-high-speed laser spectroscopy. **DE19816881 A1** (1999, KRIEG G) and **WO0070331 A1** (2000, KRIEG G) describe a process wherein powerful lasers expose granulate or plastics crushed into flakes to ultraviolet, visible, and infrared light (Figure 5.1). The light excites molecules in the plastic that disperse the light. The wavelengths in the scattered light are a characteristic physical fingerprint of the material. Sensors that capture the light and analyze it instantaneously are able to differentiate PET reliably from other polymers, color residues, and impurities, such as paper or glue residues. The process even works on minute particles. Supersonic air jets remove the unwanted substances.

A laser (4) beam is guided over the measuring material (3) in a linear manner using an optical system (2). The laser beam (4) scans the entire angular range (5) for detection across the entire width of the conveyor belt (6), which is supplied with granulate material (3) via a silo (7) or with tablets or other test material via a feed device (not shown in detail). Illumination of test samples (3) is effected point-by-point (9) through cycling of the laser light. Linear scanning is also feasible through use of

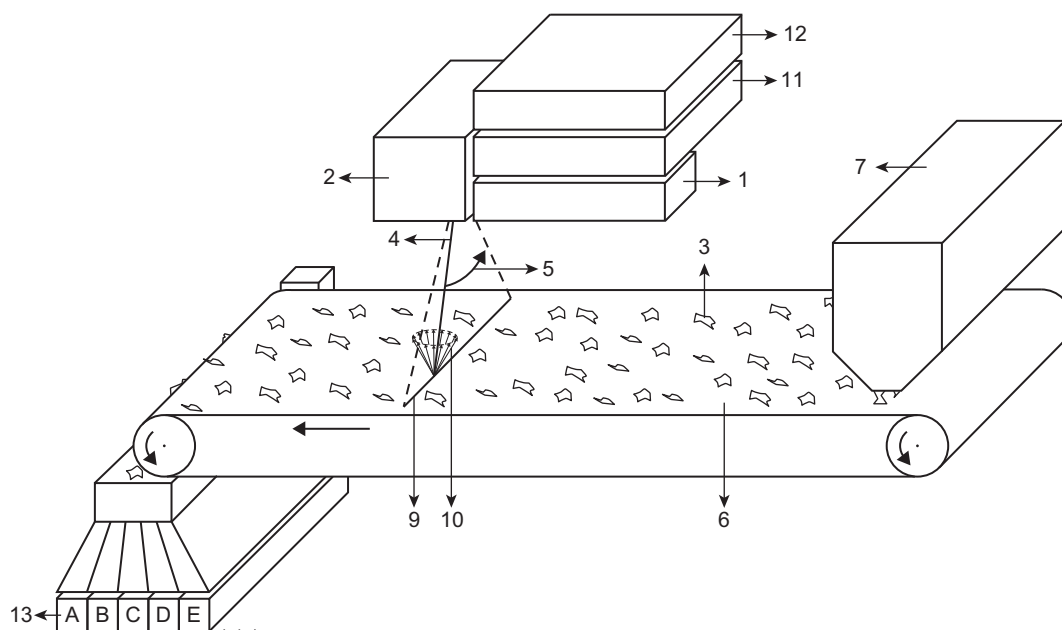


Figure 5.1 Basic construction of the overall system for on-line detection and sorting of contaminated granulates or tablets of different colors and different base materials.

a continuously radiating laser (1). The secondary light (10) generated through scattering, fluorescence, Raman laser radiation, reflection, and other optical re-emission effects is detected by the optical system (2) in a wide angular region and supplied to a spectrometer (11), whose signals are processed by an evaluation unit (12). Following classification of the test samples (3) into individual color classes, separate material classes, and contaminants, they are sorted via a conventional separation system (e.g., cycled nozzles) into different separate portions (13) which can be transported in this form to another production process or, if contaminated, to a disposal system (DE19816881 A1, 1999; WO0070331 A1, 2000, KRIEG G).

According to NatureWorks, Unisensor's laser technology is capable of sorting PLA (Ingeo™) flakes from desired PET flakes at efficiencies as high as 96–99%. This is consistent with other plastics considered contaminants in the PET flake-sorting technology. This technology allows for sensitivity to be adjusted for specific materials, depending on the incoming stream composition changes. According to WRAP, the system can sort black flakes but is not designed to handle whole packaging items such as black pots, tubs, or trays [3].

5.3.3.3 Marker systems

5.3.3.3.1 Resin Identification Codes (RIC)

Most of the current plastic sorting is done by hand. Manual sorting is a simple process that needs very little technology, but it leaves much room for improvement. Manual sorting is a very labor intensive, costly, and inefficient method for sorting plastics. One problem with efficiency is that the labor force involved in manual sorting has a high turnover rate. This high turnover rate creates an improperly trained or inexperienced workforce. Also, it is difficult to differentiate between the resin types used in packages through the visual means employed by manual sorting [13]. For this reason, the Society of the Plastics Industry (SPI) introduced the Resin Identification Code (RIC) system in 1988, a voluntary labeling system that allows consumers and recyclers to differentiate types of plastics while providing manufacturers with a consistent and uniform coding system [14]. The overwhelming majority of plastic packaging is made with one of six resins: PET (or PETE), HDPE, PVC (or V),

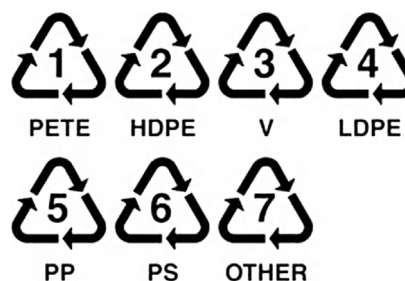


Figure 5.2 Resin Identification Codes (RICs).



Figure 5.3 Resin Identification Code (RIC) of biopolymers.

low density polyethylene (LDPE), PP, and PS. The RIC assigns each of these resins a number from 1 to 6, which is encircled by the recycle logo, a triangle of arrows (Figure 5.2). The RICs are used solely to identify the plastic resin used in a manufactured article, mainly containers and bottles, and are located on the bottom of plastic moldings.

The RIC system also includes a seventh code, identified as “7-OTHER” (Figures 5.2 and 5.3), which applies to a number of new plastics, including biopolymers. It has limited practical value².

The recycling industry has established a recycling code numbering system that runs from 1 to 7 for plastic materials. The higher the number, the more difficult the material is to profitably deploy into useful postconsumer applications, i.e., it must be burned for energy recovery or disposed of in landfills, which can create environmental problems. Polyesters, specifically PET, are afforded the No. 1 recycling code characterization as the most readily recycled plastic manufactured as a commodity. PET is the primary material used in the beverage bottle industry. PET bottles are relatively easily collected, separated, and recycled into a multitude of postconsumer applications such as fiber, carpeting, bottles, and strapping applications. The No. 2 recycling plastic is HDPE, which is used for manufacturing milk containers

² In 2007, a State Senate bill in California (SB 898) proposed the marking of PLA with a new “0” code. However, this part of the bill was removed before passage.

as well as various other packaging applications. Currently, only 20–25% of all plastics manufactured are recycled into useful postconsumer products. The major part is landfilled, which aggravates environmental problems.

The code is molded, formed, or imprinted on all containers that are large enough to accept the $\frac{1}{2}$ " minimum-sized symbol. It is placed in an inconspicuous location on the manufactured article, such as the bottom or back, and is usually accompanied by the abbreviation symbol of the plastic.

Coding enables individuals to perform sorting before recycling, which ensures that the recycled plastic is as homogeneous as possible to meet the needs of the end markets. Another potential benefit of coding is that it may facilitate the recovery of plastics not currently collected for recycling.

In 2008, SPI began work with ASTM International, a globally recognized leader in the development and delivery of international voluntary consensus standards, to develop a new standard that would expand the current RIC system. In 2010, ASTM International issued ASTM D7611 — Standard Practice for Coding Plastic Manufactured Articles for Resin Identification. Other modifications to the RIC are currently being discussed and developed by ASTM's D20.95 subcommittee on recycled plastics.

5.3.3.3.2 Fluorescent additives

Alternative methods entail marking either the plastic article or the resin itself with a dye that is readily detectable. In particular, fluorescent dyes have been used for the identification and separation of plastic waste. The dye in the plastic to be sorted is excited by an irradiation source that produces scattered emitted light, which is intercepted by a detector and recorded. This signal is used for triggering the classifying operation. In the case of small, granulated particles, this can involve electrostatic charging and deflection in an electric field, or in the case of larger particles, a simple process of mechanical separation. The fluorescent dyes must have high detection sensitivity, wide-ranging use fastness properties, be used in minute quantities, and be non-toxic.

DE4029167 A1 (1992, BAYER AG) and **DE19530449 A1** (1997, BAYER AG) disclose a method for the identification of plastics in which a small amount of a fluorescent dye is added to the plastic during or after its manufacture. In principle, a plastic treated in this way can be irradiated with UV

light and can be identified again by examining the fluorescent radiation. Suitable fluorescent dyes for a broad range of plastics, including biopolymers, are coumarins, perylene dyes, benzantrones, anthrapyrimidines, and anthrapyridones. Of particular preference are polymeric complexes of rare earth metals, such as europium (Eu) or terbium (Tb), which can be distinguished by sharply defined red and green fluorescence emission bands, respectively, and can be identified by irradiation with a normal lamp. A further advantage of these substances is that they display considerably longer-lasting fluorescence than customary organic fluorescent dyes and therefore produce a signal that can easily be differentiated from the fluorescent emissions of other substances that might be present. One difficulty with this type of identification is that the amount of suitable fluorescent dyes is limited. Moreover, in order to be able to separate different plastics labeled with different fluorescent dyes, it must be ensured that the fluorescence spectra are sufficiently different from each other.

EP566948 A1 (1993, BAYER AG) details a method for the identification of different plastics. Each plastic is provided with a plurality of fluorescent dyes that differ in terms of their emission frequencies and/or the duration of their fluorescence, so that a fluorescence pattern, which is distinguished by the duration of the fluorescence and/or by the frequencies occurring, can be unambiguously assigned to each plastic. For example, if two materials with a green fluorescence and two materials with a red fluorescence are available, as described above, 15 different combinations can be formed. In other words, 15 different plastics can be labeled using only these four marker materials so that they can be unambiguously re-identified.

DE4231477 A1 (1994, HAN KYUNG TAE; KOELLNER M; SAUER M; SEEGER S; WOLFRUM J; SCHMITT C; SCHULZ A) discloses a method for the sorting and separation of plastic waste into its different types by marking the plastics with multiplex³ fluorescence dyes (added during the course of their production) and measuring their fluorescence wavelength and specific fluorescence lifetime. The multiplex fluorescence dyes have the

³ Multiplex detection refers to the process of simultaneously labeling a specimen with two or more fluorescent probes to allow correlation of multiple structural or functional features.

same absorption and emission wavelengths with differing quantum yields and fluorescence lifetimes. Furthermore, the addition of small quantities makes necessary the use of fluorescent dyes with a high extinction coefficient at the excitation wavelength, good photostability, and reasonable quantum yields. Suitable multiplex fluorescence dyes are selected from coumarin, flavine, fluorescein, carbocyanine, phenoxazine, carbazine, oxazine and rhodamine, and are formed from dyes that absorb and fluoresce in the far UV visible and/or the near IR regions (600–1000 nm). The process is rapid, requires small quantities of dye additive, and by a combined measurement of fluorescence wavelength and lifetime, allows differentiation of a greater number of marked plastic types than prior art.

WO9309172 A1 (1995, EASTMAN KODAK CO) discloses the use of near infrared (NIR) fluorescing compounds or copolymerized residues for the identification, sorting, and recycling of thermoplastic containers made when exposed to electromagnetic radiation having a wavelength of about 670 to 2500 nm. The preferred NIR fluorescent compounds are selected from phthalocyanines, naphthalocyanines and squaraines (derivatives of squaric acid).

These plastic fluorescence identification methods do not refer necessarily to biodegradable biopolymers.

The following patents propose the use of fluorescent dyes for the identification and separation of biodegradable polymers from non-biodegradable polymers in a recycling process.

JPH06297458 A (1994, MITSUI TOATSU CHEMICALS) discloses a method for separating biodegradable polymers from non-biodegradable polymers by printing optically readable barcode patterns using fluorescent ink on biodegradable polymer moldings. The fluorescent substance is preferably a fluorescent whitening dye having a maximum absorption wavelength of 300–400 nm. In **JPH06240045 A** (1994, MITSUI TOATSU CHEM INC) the same fluorescent whitening dye is added to a biodegradable polymer composition to enable differentiation of the composition from a non-degradable polymer composition.

JPH06315935 A (1994, MITSUI TOATSU CHEMICALS) discloses a method for separating packaging materials (films, bottles, and housings of electrical appliances) made of biodegradable polymers such as PLA from non-biodegradable polymer articles. The method uses visual discriminative marks printed on the molded products made of

biodegradable polymers. The mark is printed with a green biodegradable polymeric ink. The marked biodegradable polymer can be separated from the plastics waste at the time of recovery.

JPH06240004 A (1994, MITSUI TOATSU CHEM INC) discloses a method for separating a biodegradable polymer composition from a plastic waste by coloring the biodegradable polymer such as PLA during processing with an edible dye (e.g., C.I. disperse blue) to distinguish it from non-degradable polymers in appearance. The edible dye is used for food wrapping purposes.

DE19848873 A1 (2000, BASF AG) discloses a method for labeling a biodegradable polymer (e.g., an aliphatic polyester) by mixing the polymer with at least one fluorescent dye in an amount such that the prepared composition shows a strong fluorescence that can be detected when the composition is subjected to electromagnetic radiation. The fluorescence labeling facilitates sorting in a compost mill; the biodegradable polymer is separated from the unlabeled non-biodegradable polymer, which is removed from the compost mill. Fluorescent dyes which absorb in the NIR, visible, or UV range of the electromagnetic spectrum can be used. Particularly preferred fluorescent dyes are optical brighteners (e.g., cyanostyryl compounds), which absorb in the range of 400–470 nm, are free of ionic groups, and can be obtained from the class of bis-styrylbenzene, stilbene, benzoxazole, coumarin or pyrene compounds.

5.3.4 Dissolution

Dissolution combined with separation techniques such as filtration, precipitation, etc., is used to dissolve the biopolymer and simultaneously separate solid polymers and undissolved impurities from the polymer mixture. The dissolution uses either a single solvent at multiple temperatures or combinations of solvents. The use of organic solvents is discouraged since the need to control emissions and to recover the solvents increase the costs of such systems. There is also concern about residual solvent in the recovered polymer, as well as its tendency to leach into products. For instance, various solvents are known to dissolve PLA, such as benzene, toluene, isopropyl ether, dichloromethane, chloroform, chlorobenzene, and the like. Even though these solvents are well able to dissolve PLA, they are nevertheless not recommended in view of environmental concerns.

JP2004308077 A (2004), **JP2005132901 A** (2005), **JP2005131856 A** (2005) and **JP2007031538 A** (2007, TEIJIN FIBERS LTD) disclose related methods for removing different material(s) contained in a recovered aliphatic polyester such as PLA without reducing the recovery yield of the aliphatic polyester. The recovered aliphatic polyester containing PE, PP, and/or PVC, or PET, is dissolved in a solvent to obtain an aliphatic polyester solution with viscosity of 0.0001–0.1 Pa s (0.1–100 cP). The different material, whose specific gravity is lower than that of the solution, floats to the surface of the aliphatic polyester solution and is separated (see also Chapter 6: Chemical Recycling; Section 6.2: Hydrolysis/Solvolysis (Alcoholysis)).

WO2010118954 A1, **AU2010237249 A1**, **WO2010118955 A1**, **WO2011029648 A1** (2010, GALACTIC SA) and **WO2011015433 A1** (2011, GALACTIC SA) use a dissolution step for separating PLA from a polymer blend by dissolving PLA in a lactic acid ester. Suitable lactic acid esters include methyl lactate, ethyl lactate, isopropyl lactate, butyl lactate, hexyl lactate, and more generally, a lactic acid alkyl ester, the alkyl radical of which has from 1 to 12 carbon atoms. The dissolution of PLA in lactic ester can be carried out at higher temperatures (up to the melting point of PLA) than those reached during solubilization in the alcohol from which this ester is derived. Indeed, the boiling temperature of the ester is generally higher than that of the alcohol, which enables dissolution of more PLA. With regard to the boiling point of the recommended lactic acid esters, it is possible to eliminate water present in PLA by carrying out the dissolution at a temperature of more than 100°C and at atmospheric pressure. In the case of contamination of a PLA flow by another polymer (PET, PE, PVC, PP, or any other common polymer), it is possible to remove the latter through filtration while hot, or by any other means known to those skilled in the art. Moreover, the dissolution process is fast enough and carried out quite rapidly.

WO2010118954 A1, **AU2010237249 A1**, **WO2010118955 A1** (2010, GALACTIC SA) and **WO2011015433 A1** (2011, GALACTIC SA) disclose methods for purifying a conventional polymer stream (PE, PP, PET, PVC, etc.) contaminated with a maximum of 50% PLA by suspending the

polymer blend in lactic ester able to dissolve PLA. The method includes the following steps:

- (1) Grinding the polymer blend until a weight/volume ratio between about 0.05 and about 1.4 t/m³ is obtained.
- (2) Suspending the polymer blend in lactic ester in a weight ratio of polymer to lactic ester of 0.1–1 to dissolve PLA.
- (3) Recovering undissolved polymers for separate and subsequent processing by filtration or any other means enabling solid/liquid separation.
- (4) Recovering the PLA solution with a weight ratio of PLA to solvent of between 0.5 and about 3.

The dissolution can be carried out without prior grinding if the form of PLA (weight/volume ratio) permits it. Indeed, one of the problems of processing this type of flow is the difference in specific weight between the different reprocessed materials even after the grinding step. The suspension step (2) is preferably carried out at 50°C and the melting temperature of the polymer mixture, or at 50°C and the boiling temperature of the lactic ester; the pressure is between 0.05 and 20 bars, preferably 1 to 5 bars.

The PLA solution from step (4) may be subjected to catalytic hydrolysis or alcoholysis so as to produce a lactic ester from PLA (see Chapter 6: Chemical Recycling; Section 6.2: Hydrolysis/Solvolysis (Alcoholysis)). The alcohol used for this transesterification depolymerization method will preferentially be that corresponding to the lactic ester used for purifying the polymer stream. The lactic ester does not block its depolymerization, and in addition does not impose further purification steps.

The proposed methods are useful for purifying the polymer, which is of petrochemical origin, and are useful in the packaging field (e.g., rigid trays for fresh produce, packaging films for salads, bottles, and disposable utensils, plates, cups, and cutlery).

An alternative to organic solvents is the use of supercritical fluids. A supercritical fluid is a dense gas that is maintained above its critical temperature (the temperature above which it cannot be liquefied by any pressure). Such fluids are less viscous and diffuse more readily than liquids. Examples of supercritical fluids are carbon dioxide, and certain alkanes such as methane, ethane, and propane. Carbon dioxide is especially useful because it is non-toxic, non-flammable, chemically inert, completely recoverable,

abundant, and inexpensive. At room temperature and above its vapor pressure, carbon dioxide exists as a liquid with a density comparable to organic solvents, but with excellent wetting properties and a very low viscosity. Above its critical temperature and pressure (31°C and 7.4 MPa), carbon dioxide is in the supercritical state (scCO₂) and has gas-like viscosities and liquid-like densities. Small changes in temperature or pressure cause dramatic changes in the density, viscosity, and dielectric properties of scCO₂, making it an unusually tunable, versatile, and selective solvent.

WO2008045516 A1 (2008, QLT USA INC) provides methods of extracting a biodegradable polyester with a supercritical fluid to effectively obtain a purified biodegradable polyester, such as a purified biodegradable poly(lactide-glycolide) (PLGA). The supercritical fluid can be carbon dioxide at an elevated pressure, or can be carbon dioxide with one or more cosolvents. Methods for carrying out stepwise purification of the biodegradable polyester at multiple pressures or multiple temperatures, or both, are also provided. When the polyester is PLGA, a purified PLGA copolymer is obtained having a narrow molecular weight distribution with respect to the unpurified polyester. The purified PLGA copolymer can have a polydispersity index of less than about 1.7, less than about 2% monomers, and less than about 10% oligomers. The purified PLGA copolymer can exhibit a reduced initial burst effect when incorporated into a controlled release formulation such as a flowable implant adapted for injection into body tissues.

5.4 Drying

In the recycling of aliphatic polyesters, it is important that the material being recycled is as dry as possible in order to prevent hydrolytic decomposition of the molecular chains during the plasticization or upon melting. However, PLA is hygroscopic, which makes an efficient drying difficult. Furthermore, the presence of water during melt recycling creates bubbling in the recycle due to the generation of steam.

Another issue encountered during drying is the stickiness of many biopolymers at high temperatures. The low T_g ⁴ at which the PLA material becomes

sticky, coupled with a relatively long crystallization time, make it hard to crystallize and/or dry amorphous production wastes with conventional crystallization and drying systems. This is especially true for residues of deep-drawn films. Such conventional drying systems, known from the prior art, are dry air dryers, which operate at an air flow of around 1.85 m³/h and kg of granulate. For example, noncrystalline PLA is dried at 45°C for ca. 4 h at a dew point of 40°C; crystallized PLA at 90°C for ca. 2 h at a dew point of -40°C.

Due to the rather low drying temperatures, especially when processing noncrystallized material, the drying time is relatively long, and precise temperature management is necessary. This is extremely difficult, if not impossible, for granulates, and especially for all other forms, such as flakes, films, fleece, etc. For this reason, one can try to achieve a crystallization of the plastic prior to drying. Such crystallization can be achieved by moving or mechanically manipulating the particles uniformly at a temperature lower than the drying temperature, or at least at a temperature lower than the melting or plasticization temperature. The movement is advantageous for preventing the individual particles from sticking together (WO2008058303 A1, 2003, EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT MBH).

WO2008058303 A1 (2003, EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT MBH) provides a method in which biopolymers being recycled, especially PLA, can be dried, and possibly crystallized, in one step at the same time, regardless of type, form, and composition. The biopolymer material to be treated is heated in at least one receptacle or reactor while undergoing constant mixing or movement and/or comminuting at a temperature below the melting temperature of the plastic material. As a result, it is crystallized, dried, and/or purified at the same time. At least one rotatable comminuting or mixing tool, with working edges that act on the material with a comminuting and/or mixing effect, is used for the mixing and/or heating of the plastic material, with heating taking place by application of mechanical energy.

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⁴ The glass transition temperature (T_g) of PLA lies between 55°C and 58°C, the crystallization temperature between 100°C and 120°C, and the melting temperature between 165°C and 183°C.

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6 Chemical Recycling

OUTLINE

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From the point of view of the effective use of carbon resources, it is ideal that discarded products be restored to raw materials by chemical recycling processes. The chemical recycling of biopolymers involves the recovery of monomers and/or oligomers by depolymerization reactions, and includes thermal, chemical, and enzymatic processes. Chemical recycling of biopolymers is aimed mainly at saving the material resources and reusing the recovered monomers for producing new polymers, and less at reducing the amount of wastes generated by slowly degrading biopolymers.

6.1 Dry-Heat Depolymerization (in the Melt)

Dry-heat depolymerization involves depolymerization of an aliphatic polyester, such as polylactide (PLA), to its cyclic dimer or lactide at elevated temperatures (e.g., higher than the melting temperature).

The depolymerization of PLA to its dimer by heating and reduced pressure is an old and much studied process [1,2]. The depolymerization processes of the prior art, wherein an oligomeric or higher polymeric PLA is heated at elevated temperatures in the presence or absence of a catalyst, suffer in that depolymerization to the cyclic ester tends to be slow; this is attributable to the difficulty

of getting heat (thermal energy) rapidly and uniformly distributed throughout the polymeric mass (see Chapter 2: Definitions and Assessment of (Bio)-degradation; Section 2.4: Types and Mechanisms of (Bio)degradation). Side reactions occur, attributable at least in part to the formation of localized hot spots within the depolymerization mass, including decomposition of the polymer to charred and tarry products that result in difficult-to-handle reactor heels. The heat distribution problem is more severe with solid/higher molecular weight polymers than with liquid/lower molecular weight polymers as they tend to form more viscous melts (US5342969 A, 1994, DU PONT). The dry-heat depolymerization of PLA causes the racemization of the lactic acid ester structural unit above the melting temperature of PLA regardless of the molecular weight. In particular, when the temperature exceeds 320°C, racemization of the lactic acid ester structural unit in PLA or the derivative thereof proceeds readily. As a result, formation of meso-lactide is promoted, and the optical purity of the lactide is degraded. On the other hand, hardly any thermal decomposition of PLA or derivative thereof takes place at a temperature that is equal to or less than the melting temperature of PLA or derivative thereof.

One way to accelerate the depolymerization speed of high molecular weight PLA is by increasing the concentration of oligomers in PLA. One such process for the depolymerization of waste PLA or

polyglycolide (PGA) to its corresponding dimeric cyclic ester is disclosed in **US5342969 A** (1994, DU PONT). The process comprises the following steps: (a) depolymerizing PLA to its corresponding dimeric cyclic ester by heating PLA in a reaction zone at a temperature and pressure at which PLA is molten; (b) forming a vapor product stream containing the dimeric cyclic ester; (c) removing the vapor product stream from the reaction zone; and (d) recovering the dimeric cyclic ester from the product stream. The improvement comprises adding dimeric cyclic ester to step (a) in a ratio of 0.01 to 0.5 parts by weight of dimeric cyclic ester per part by weight of PLA. The liquid cyclic ester added in step (a) reduces the melting point and the viscosity of PLA (preferably 10–30% of the initial value) and aids distribution of catalyst and thermal energy rapidly and uniformly through the mass. Unrecovered oligomer can be recycled. The process is claimed to provide smoother and faster melting of the polymer and more rapid depolymerization than previous methods. The cyclic esters are produced in high yield and side reactions are minimized.

Another way to accelerate the depolymerization speed of high molecular weight PLA is by adding a catalyst in combination with high temperature. Suitable catalysts for promoting the thermolysis of the polymer to cyclic esters are generally metals or compounds of metals of group IV, group V, and group VIII of the periodic table. Preferred are metals of group IV, notably Sn, as the metal (powdered), oxide, halogenide, or carboxylate, or group V, notably Sb, usually as the oxide Sb_2O_3 . Preferred are Sn(II) carboxylates, especially those that are soluble in the molten polymer exemplified by stannous bis(2-ethylhexanoate), commonly referred to as stannous octoate. The catalyst is employed in catalytically effective amounts, which can vary widely depending upon the particular feed material employed and the reaction conditions. For example, with stannous octoate as the catalyst, the quantity of catalyst will generally be such that the reaction mass contains from about 0.01 to about 5% by weight (usually from about 0.3 to 3%), and for best results, at least about 1%. High catalyst loadings are desirable because polymer residence time decreases with an increase in the initial catalyst concentration, thereby improving the cyclic ester production rate.

DE19637404 A1 (1997, SHIMADZU CORP; TOYOTA MOTOR CO LTD) discloses a method for

the recovery of lactide from PLA comprised of these steps: (a) heat-treating a high molecular weight PLA to a temperature equal to or higher than its melting point (170–300°C) in the presence of a catalyst comprising one or more metals selected from elements of group IA, group IVA, group IVB, and group VA of the periodic table, or compounds thereof; and (b) reducing the pressure to equal to or less than the vapor pressure of lactide (< 200 mmHg) at said temperature to thereby distill and recover the produced lactide.

All the above catalysts are conventionally used in the polymerization to give PLA. Among them, catalysts of group IVA, especially catalysts comprising tin or a compound thereof, are preferably used in terms of catalyst activity. The catalyst is preferably used in an amount of 0.05–15% (preferably 3–7%) by weight of PLA to be treated. A disadvantage of this method is the high amount of catalyst used and the high temperature (up to 300°C). The method uses trimmings that remain after the molding is cut to a fixed length as a starting material.

The thermal decomposition temperature of PLA depends greatly on the level of trace amounts remaining of a polymerization initiator (e.g., tin compounds) [1]. When the tin content is 169 ppm or greater, the decomposition temperature of PLA is very low, and lactide that has high optical purity is selectively formed as a decomposition product. On the other hand, when the tin content is 60 ppm or less, the decomposition temperature of the lactic acid polymer increases, the optical purity of the decomposition product is degraded, and contamination with oligomer becomes noticeable. Such a function of tin is effective in chemical recycling, but since decomposition easily occurs during melt-molding of PLA, in general, as much residual tin compound as possible is extracted prior to melt-molding. This is one cause of the high cost of PLA (**WO2005105775 A1**, 2007, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI).

WO03091238 A1 (2003, NISHIDA H; FAN Y; SHIRAI Y) discloses a catalyst and depolymerization conditions for efficiently converting waste poly(L-lactide) (PLLA) into a lactide with a high optical purity. The method is characterized by adding an alkaline earth metal compound to PLLA and heating the mixture to a temperature of 320°C or lower.

WO2005105775 A1 and its family member **EP1741707 A1** (2007, KYUSHU INST OF

TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI) disclose a method for efficiently recovering lactide of high optical purity by thermally decomposing a mixture of PLLA or derivative thereof and aluminum hydroxide at a temperature in the range from at least the melting temperature of PLLA or derivative thereof to no greater than 320°C (and preferably 200 to 300°C). In general, the lower the molecular weight of a polymer, the lower the temperature range in which decomposition proceeds. In addition to the above components, the mixture may contain a resin such as polystyrene, a reinforcing fiber, a filler, or an additive, etc. The appropriate amount of this resin to add may be selected according to physical properties required for the product, but in general it is 200 parts by weight or less relative to 100 parts by weight of PLLA or derivative thereof, preferably 100 parts by weight or less, and even more preferably 50 parts by weight or less. The resin is normally melted during the chemical recycling of PLLA or derivative thereof and subjected to material recycling by repelletizing.

When aluminum hydroxide is added to PLLA, in the case where the PLLA contains a large amount of residual tin compound, the thermal decomposition temperature tends to increase in response to an increase in the amount of aluminum hydroxide added (which contributes to stability during melt-molding). On the other hand, in the case of a purified PLLA from which most of the residual tin compound has been extracted, the thermal decomposition temperature tends to decrease in response to an increase in the amount of aluminum hydroxide added. That is, the addition of aluminum hydroxide has the effect of making thermal decomposition of the PLLA polymer converge to a specific temperature range, and also an effect in counteracting the outstanding decomposition promotion effect of the tin compound and contributing to stabilization of PLLA containing residual tin. Therefore, PLLA containing a tin compound can easily be melt-molded as a mixture with aluminum hydroxide even without specially removing the tin compound.

As is demonstrated in Figure 6.1 and Table 6.1, in tin-containing PLLA on its own, which did not contain aluminum hydroxide, weight reduction due to decomposition of PLLA started beyond 180°C and the decomposition was almost complete at about 250°C. In contrast, compositions containing 10 to 30 parts by weight of aluminum hydroxide start to thermally decompose at around 200°C, with

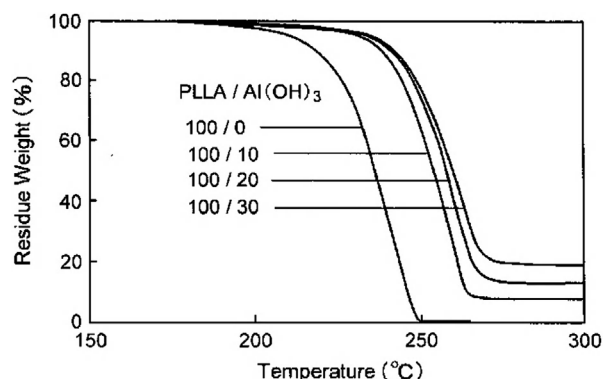


Figure 6.1 Thermogravimetric/differential thermal analysis (TG/DTA) curves of tin-containing poly-(L-lactide) (PLLA)/aluminum hydroxide $\text{Al}(\text{OH})_3$ compositions obtained using a TGA/DTA6200 under a nitrogen atmosphere at a heating rate of 5°C/min (EP1741707 A1, 2007, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI).

Table 6.1 Thermal decomposition products of tin-containing PLLA/ $\text{Al}(\text{OH})_3$ compositions

PLLA/ $\text{Al}(\text{OH})_3$		Final residue (wt.%)	$\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3$ conversion factor (%)
Ratio by weight	$\text{Al}(\text{OH})_3$ (wt.%)		
100/0	~0		
100/10	9.1	8.1	32
100/20	16.7	13.3	59
100/30	23.1	19.0	51

Thermal decomposition products of tin-containing poly(L-lactide) (PLLA)/aluminum hydroxide $\text{Al}(\text{OH})_3$ compositions using a TGA/DTA6200 under a nitrogen atmosphere at a heating rate of 5°C/min (EP1741707 A1, 2007, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI).

decomposition almost complete at about 270°C, and an amount of residue remaining that corresponds to the amount of aluminum hydroxide added. The aluminum hydroxide used undergoes a dehydration reaction at a temperature of 200°C or higher, releases 34.6 wt.% of water (in theory), and changes into alumina. The amount of aluminum hydroxide converted into alumina in this temperature range is 32–59%. From these results, it is clear that the tin-containing PLLA/aluminum hydroxide composition gives an increase in the thermal depolymerization temperature of about 20°C compared with the

tin-containing PLLA alone. It's also clear that the PLLA is almost completely depolymerized and vaporized, and that the aluminum hydroxide partly changes into stable alumina (WO2005105775 A1, 2007, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; KINKI UNI).

JP2008231048 A (2008, KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION) discloses a method for efficiently recovering a highly pure lactide from PLA in a manner capable of enhancing the catalytic function of magnesium oxide as a catalyst for depolymerizing the polymer. The method for the lactide recovery involves adding 0.1–10 parts by weight, per 100 parts by weight PLA, of magnesium oxide having a specific surface area of 5 m²/g or larger to the polymer and heating the mixture to 200–300°C. A high optical purity lactide can be more efficiently recovered when the magnesium oxide is heat-treated in the temperature range of 300–600°C or when the surface hydroxyl groups of the magnesium oxide are replaced by carbonate groups.

JP2011162480 A (2011, KITAKYUSHU FOUNDATION) discloses a method of efficiently recovering L-lactide as a raw material from a resin composition comprising PLLA and aromatic polycarbonate by selectively decomposing PLA. The method of recovering lactide comprises adding an ester exchange catalyst such as tin oxide and/or an organoaluminum compound into the resin composition, heating the mixture preferably to 200 to 330°C to selectively decompose PLLA, and recovering the resulting L-lactide as a raw material.

JP2008201679 A and **JP2008201680 A** (2008, TEIJIN FIBERS LTD) provide a method for thermally degrading PLA, wherein the thermal decomposition temperature of PLA is lowered to produce a lactide of good quality. The method is characterized in that PLA is degraded in the coexistence of an acid compound, preferably a lactic acid oligomer, and a catalyst at a temperature of 170 to 240°C, at a pressure equal to or lower than the vapor pressure of the lactide (< 200 mmHg), while distilling away the produced lactide. The lactic acid oligomer compound is a mixture of a dimer and/or polymer compound. The catalyst is a tin compound.

JP2003128900 A (2003), **JP2004216378 A** (2004) and **US2005250931 A1** (2005, MITSUBISHI PLASTICS INC) provide a method for recycling shredder dust that includes pulverisates of automobile parts and home electric appliances that consist

mainly of PLA. The PLA-based resin composition includes 30 to 100% by weight of PLA, and 0 to 50% by weight of an aliphatic polyester, such as poly(butylene succinate) (PBS), and/or an aromatic-aliphatic polyester, such as poly(tetramethylene adipate-*co*-terephthalate) (PTeMAT). In the basic procedure, shredder dust that could contain metals and/or glass as contaminants is put into a sealed vessel and heated, with purging by an inert gas such as dehumidified air or air, to decompose PLA and recover the formed vapor. Reducing the pressure in the heating vessel and recovery passages to 13.3 kPa (100 Torr) or less, preferably 2.6 kPa (20 Torr) or less, facilitates recovery of the lactide vapor. The heating temperature is desirably within the range of 150 to 280°C, preferably 170 to 250°C. Addition of 0.1 to 3 wt.% of tin, titanium, and zirconium compounds to the shredder dust upon heating accelerates the decomposition rate of PLA. However, this is not always necessary. It is considered that shredder dust contains more or less catalyst component such as metals that exhibit a similar effect of acceleration. The recovered lactide can be polymerized again by a known method, such as described in US4057537 A (1977, GULF OIL CORPORATION). Recovering lactide by using the shredder dust provides the advantage that the larger surface area of the shredder dust improves the efficiency of recovery (Figure 6.2).

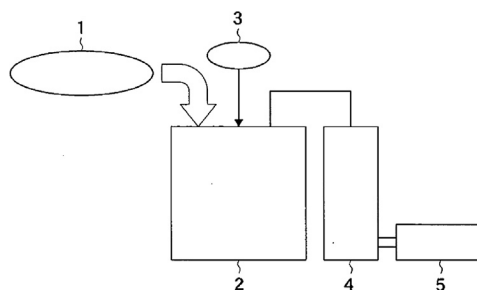


Figure 6.2 Schematic diagram depicting the method for recovering lactide. Shredder dust (1) for recycling is charged in a heating vessel (2), which is heated by a heating means (not shown) while purging by an inert gas (3) to generate a vapor component. The generated vapor component is cooled in a cooling vessel for recovering lactide (4). The cooling is preferably performed under conditions where reduced pressure is established by removing inert gas and the like by a pressure reduction unit (5) (US2005250931 A1, 2005, MITSUBISHI PLASTICS INC).

The shredder dust has a particle size of preferably 20 mm or less, more preferably 10 mm or less. Besides parts related to automobiles, automobile parts include parts casings, etc. that constitute an automobile. In addition to the ordinary parts of home electric appliances such as lampshades, these appliances also include parts casings, etc.

6.2 Hydrolysis/Solvolysis (Alcoholysis)

6.2.1 Hydrolysis

The hydrolysis rates of aliphatic polyesters appear to be too slow to permit recovery from other insoluble ingredients and reuse of the valuable hydroxycarboxylic acid moieties within a time frame. For monomer recovery, hydrolytic degradation of aliphatic biodegradable polyesters in the solid state is not recommended because highly hydrolysis-resistant crystalline residues (or extended chain crystallites) are formed, and their very slow degradation give a low monomer yield in a limited short period or take a long time to give a high yield.

Another disadvantage of hydrolysis involves the partial racemization of PLA. This means that the hydrolysis of a PLA, consisting for example of 98% L-lactic acid and 2% D-lactic acid, results in a lactic acid mixture with a D-content larger than 2%. Other biodegradable polymers, such as polycaprolactone (PCL), depolymerize slowly or to a limited degree when treated with alkaline solutions. Some of these biodegradable polymers undergo alkaline depolymerization at a convenient rate only at temperatures greater than about 170°C. Such high temperatures may not be reached by some simple steam systems, such as steam autoclaves (WO0236675 A2, 2002, PROCTER & GAMBLE CO).

US5268507 A (1993, DU PONT) discloses a method for depolymerizing waste aliphatic hydroxycarboxylic acid-derived polyesters by reacting the polyester with an amine to form monomeric amide. The amine is ammonia, methylamine, or dimethylamine. The molar ratio of amine to polyester is in the range 1:1 to 2:1.

US5229528 A (1993, DU PONT) discloses a process for depolymerizing waste aliphatic hydroxycarboxylic acid-derived polyester, preferably PLA, to monomeric hydroxyl acid monomer and low molecular weight oligomers. The polyester is mixed in water at

sufficient temperature (100–200°C), pressure (0.35–1.40 MPa), and time to significantly depolymerize the polymer, with the temperature and pressure being insufficient to form undesirable degradation products. The amount of water used affects the time required to carry out the depolymerization and the percent conversion. Normally a molar ratio of water to PHA (on an acid unit basis) in the range of 1:1 to 5:1, preferably 1.5:1 to 2:1, is used. An important economical aspect of the process is the speed of the depolymerization. By selecting optimal reaction conditions, particularly pressure and temperature, significant quantities of PHA can be batch-depolymerized, often in one hour, and even in as little as 15 minutes. Reactor design (i.e., agitation, etc.) also plays an important role in reaction rate. Where speed is less a factor, batch times as long as 16 hours may be appropriate. Continuous process depolymerization is also possible, such as with the feed materials being continuously introduced into the first depolymerization stage of a multistage system, and the monomer and oligomer product being recovered from the last stage.

US5264626 A (1993, DU PONT) is a modified version of the process described in US5229528 A that involves depolymerization of the waste aliphatic polyester in acidic water, and subjecting the resulting mixture to a temperature and pressure sufficient to at least partially depolymerize the aliphatic hydroxycarboxylic acid-derived polyester. In general, strong organic or inorganic acids that do not react with the polyester to form depolymerization products or form undesirable byproducts can be used. Liquid or water-soluble solid catalysts are preferable for ease of use and concentration. Sulfuric acid and *p*-toluene sulfonic acid (solid) are suitable, inexpensive acid catalysts. Methane sulfonic acid is also acceptable. Hydrochloric acid, although effective, is generally undesirable because of its excessive corrosiveness to equipment. Very small quantities of acid are required, preferably in the weight range of 0.1 to 1.0% by weight of said polyester, to be catalytically effective. The depolymerization proceeds even if large quantities of water are introduced along with the acid (dilute acid). The depolymerization product is a low molecular weight oligomer, the average molecular weight depending on the depolymerization conditions of time, temperature, and pressure of heating, and the water/acid content of the dissolving liquid. Depolymerization is continued long enough to yield a depolymerization product at a concentration of at least 10%, preferably greater

than 70%, in the acidic water so that it can be handled as a liquid.

EP0573042 A1 (1993) and **JPH0649266 A** (1994, MITSUI TOATSU CHEM INC) disclose a method for decomposing an aliphatic hydroxycarboxylic acid-derived polyester homopolymer or copolymer in an alkaline solution, such as calcium hydroxide of pH 10 or more, while maintaining the configuration intact. The alkaline solution used for the decomposition of the biopolymer can be prepared by adding an inorganic base, such as sodium and potassium hydroxide, to an aqueous solvent. The hydroxycarboxylic acid is recovered by electrodialysis or acid precipitation and can be used as the raw material for a polymer. Suitable aliphatic polyesters are PLA and poly (D,L-lactide) (PDLA). Suitable copolyesters include poly(D,L-lactide-*co*-glycolide) (PDLGA) and poly(L-lactide-*co*- ϵ -caprolactone). Other co-monomers that can be used include, for example, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 4-hydroxyvaleric acid, 5-hydroxyvaleric acid, and 6-hydroxycaproic acid (6-hydroxyhexanoate).

JPH1036553 A (1998, SHIMADZU CORP) provides a method for treating an aliphatic polyester waste that involves hydrolysis of the aliphatic polyester, such as PLA, in a tank equipped with a rotating moving body using a motor (**Figure 6.3**). Waste PLA

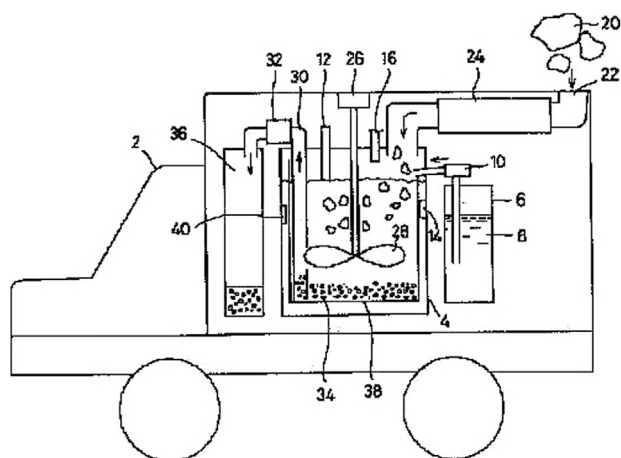


Figure 6.3 Outline cross-sectional view showing an example of the recovery vehicle that was adapted in the invention described in JPH1036553 (1998, SHIMADZU CORP).

2: Recovery vehicle; 4: Decomposition tank; 6: Tank of calcium hydroxide aqueous solution; 20: Waste PLA; 22: Charging port; 24: Crusher; 26: Motor; 28: Stirrer; 30: Recovery tube; 32: Pump; 34: Precipitates; 36: Recovery tank; 38: Heater.

(20) is charged from a charging port (22), finely crushed with a crusher (24), and subsequently charged into a tank (4). The tank (4) is equipped with a stirrer (28) driven with a motor (26) to always stir and mix the crushed waste resin with an alkali aqueous solution. The rotation of the moving body causes alkali hydrolysis of the aliphatic polyester waste. When the PLA is hydrolyzed, precipitates are generated and accumulated on the bottom of the tank (4). Then a recovery tube (30) reaching the bottom of the tank (4) is disposed, and the precipitates (34) accumulated on the bottom of the tank (4) are recovered into a recovery tank (36) with a pump (32).

JP2006274231 A (2006, CHIBA PREFECTURE) provides a method and an apparatus suitable for depolymerizing and solubilizing PLA and recovering the treated PLA as a monomer lactic acid in order to carry out recycle treatment of PLA. A monomer lactic acid can be obtained by treating one part L-type or D-type PLA, or PLA containing L-type and D-type in an arbitrary ratio, at a temperature of less than 200°C in the presence of at least 0.2–20 parts water in the solution state. The monomer lactic acid, having an arbitrary ratio of L-type to D-type in which the ratio of L-type to D-type retains the ratio of L-type and D-type of PLA or the ratio of L-type to D-type is 1:1, can be obtained by controlling mutual transfer of L-type and D-type of PLA. The treatment of PLA at a temperature of less than 200°C inhibits reactions other than lactic acid formation.

JP2007224113 A (2007, TEIJIN FIBERS LTD) discloses a method for recovering the effective components from waste biodegradable polyester by depolymerizing the polyester with water at a temperature of about 80 to about 300°C, and then recovering a monomer/oligomer mixture as the depolymerization product. The preferred biodegradable polyester is PLA, the monomer depolymerization product is lactic acid, and other depolymerization products are lactide and lactic acid oligomer. The waste material originates from agricultural, forestry, fishery, civil engineering and construction articles, and food packaging containers made from biodegradable polyesters.

JP2005132901 A (2005), **JP2005131856 A** (2005) and **JP2007031538 A** (2007, TEIJIN FIBERS LTD) disclose related methods for removing different material(s) contained in a recovered aliphatic polyester such as PLA without reducing the recovery yield of the aliphatic polyester. The recovered aliphatic polyester containing polyethylene (PE) and polypropylene (PP) and/or polyvinyl chloride (PVC) is

depolymerized in aqueous ammonia at 80°C to obtain a depolymerized reaction liquid with a viscosity of 0.0001–0.1 Pa s (0.1–100 cP); the different material(s), of which the specific gravity is lower than that of the solution, floats to the surface of the depolymerized reaction liquid and is separated. Alternatively, the recovered aliphatic polyester is dissolved in solvent (see also Chapter 5: Physical Recycling; Section: 5.3.4 Dissolution).

JP2007277389 A (2007, AKAMATSU K; KONISHI N; NAKAMURA K) discloses a method for separation and recovery of plastic wastes comprising a mixture of biodegradable biopolymers derived from renewable (plant-based) and fossil fuel-based resources, respectively, and non-biodegradable polymers. The method allows the recovery of groups of polymers by batch processing of plastic wastes without classification beforehand. The recovery process by types comprises the following steps: (1) crushing the plastic wastes into a controlled size; (2) hydrolyzing the crushed plastics; (3) extracting a crude acid aqueous solution of a monomer (e.g., lactic acid) formed from the plant-based biodegradable polymer (e.g., PLA); (4) sorting the biodegradable fossil-based polymer in powder form from the remaining solid component; and (5) sorting the non-biodegradable fossil-based polymer by removing the impurities from the residual solid component. The plastic wastes are generated from industries that handle perishable foodstuffs, preservation processed products, and cooked products, and also from restaurants, supermarkets, and convenience stores.

JP2008050351 A (2008, VICROR COMPANY OF JAPAN) discloses a method for hydrolyzing waste PLA by mixing PLA with water and a depolymerization catalyst slightly soluble or insoluble in water, heating the resultant mixture, degrading PLA and thereby recovering lactic acid. PLA can be degraded at a relatively low temperature in a short time, and the produced lactic acid can be recovered and used as raw material for PLA. The depolymerization catalyst is an oxide, a carbonate, or a hydroxide of at least one kind of element selected from group 2A, group 4A, group 5A, group 6A, group 7A, group 8, group 1B, group 2B, group 3B, and group 4B of the periodic table; preferably an oxide of beryllium, magnesium, titanium, zirconium, vanadium, chromium, manganese, rhenium, iron, ruthenium, cobalt, nickel, copper, silver, zinc, cadmium, aluminum, indium, tin, lead, and/or silicon; and more preferably, magnesium carbonate, calcium carbonate, barium carbonate,

manganese carbonate, cobalt carbonate, nickel carbonate, copper carbonate, silver carbonate, zinc carbonate, cadmium carbonate, lead carbonate, magnesium hydroxide, calcium hydroxide, chromium hydroxide, iron hydroxide, nickel hydroxide, gold hydroxide, zinc hydroxide, aluminum hydroxide, and/or lead hydroxide.

WO2010118954 A1, **AU2010237249 A1**, and **WO2010118955 A1** (2010, GALACTIC SA) and **WO2011015433 A1** (2011, GALACTIC SA) disclose methods for the catalytic hydrolysis or alcoholysis of PLA, which has been dissolved in a lactic ester solvent (see Chapter 5: Physical Recycling; Section 5.3.4: Dissolution). The PLA solution is subjected to a catalytic hydrolysis or alcoholysis reaction at a temperature between about 80 and about 180°C and a pressure between about 0.05 and about 10 bars in order to transform PLA into lactic ester or a derivative thereof.

The PLA hydrolysis or alcoholysis step enables the recovery of a lactic acid ester by breaking down a PLA ester linkage followed by protonation of the carbonyl group and a nucleophilic attack. The protonation of the carbonyl group is carried out through the use of a transesterification catalyst, which may be solid or liquid and of Lewis acid type — such as tin octoate, tin lactate, antimony octoate, zinc octoate, APTS (*p*-toluene sulfonic acid), etc. — or preferably basic type, a member of the guanidine family, such as triazabicyclodecene (TBD) and derivatives thereof. Since the amount of water or alcohol influences reaction kinetics, it is important to compromise to avoid removing too much alcohol during the following purification steps. In **WO2010118954 A1** the nucleophilic attack is carried out using water or an alkaline solution such as NaOH, KOH, and the like. In **WO2010118955 A1** the nucleophilic attack is carried out using an alcohol. Suitable alcohols contain from 1 to 12 carbons, ideally corresponding to the ester used for dissolving, such as methanol, ethanol, *n*-butanol, isobutanol, *sec*-butanol, *tert*-butanol, *n*-propanol, *iso*-propanol, 2-ethylhexanol, 2-ethylbutanol, hexanol, and the like.

A problem common to all these methods is that they do not make it possible to eliminate the D-enantiomers that may be generated first by the whole of the PLA production process and second by the various chemical recycling processes (see Chapter 1: Introduction to Biopolymers; Section 1.3: Polyesters). This means that D-enantiomers are formed when working with an L-type PLA (the form mainly present on the market).

Similarly, there will be the formation of L-enantiomers when working with D-type PLA. This progressive enrichment in undesired enantiomer with regard to the lactic acid or derivatives thereof will have a significant impact on the yield and the costs of production of a new PLA.

WO2011029648 A1 (2010, GALACTIC SA) addresses this problem by disclosing a method for chemical stereospecific recycling of a mixture of polymers containing PLA, characterized in that the method comprises the following steps:

- (1) Combining the mixture of polymers and a lactic ester into a solution, wherein the lactic ester is capable of dissolving in the PLA fraction.
- (2) Depolymerizing the PLA fraction of step (1) by transesterification, wherein the depolymerization is stopped subsequent to forming an oligoester mixture with an average molecular weight between about 400 and about 5000 Da, preferably between 400 and 3000 Da.

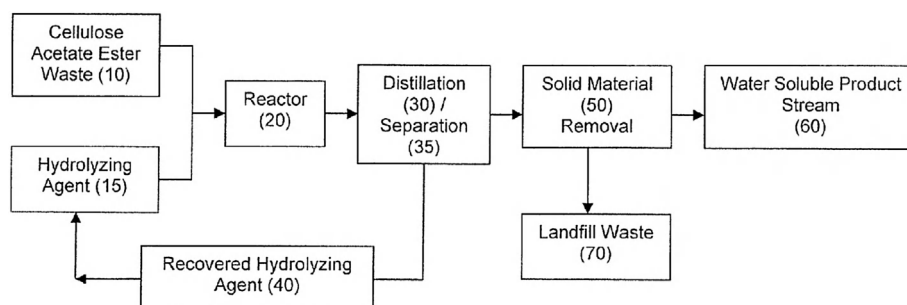
The reaction can be stopped by elimination of the alcohol function from the lactic ester or the alcohol, which makes it possible to keep control of the molecular weight of the oligoester. In this context, any technology that allows rapid extraction of the alcohol or lactic ester will be favored, such as thin film technology. Once formed, the oligoester mixture may be subjected to a catalytic cyclization step, wherein a vapor phase rich in lactide and a liquid phase rich in oligoesters are produced. The use of a catalyst is essential in order to reduce the thermocracking temperature and thus to prevent chemical and optical deterioration of the synthesized lactide. The catalysts are the same as those used in the depolymerization by transesterification step (see also WO2010118955 A1). The vapor phase rich in lactide is condensed to raw lactide, wherein volatile components are removed. The raw lactide is subjected to stereospecific purification into a purified lactide fraction, wherein the

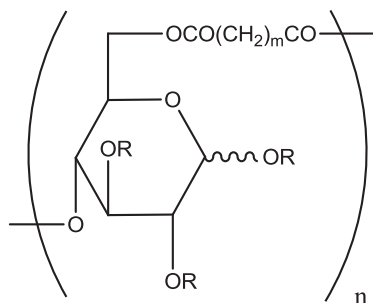
purified lactide fraction has a meso-lactide content between about 0.1 and about 40% by weight, preferably between 0.1 and 20%, which makes it possible to control, and therefore prevent, the enrichment in D-enantiomer in the whole process.

As with many processes, the manufacture of cellulose acetate results in some waste products that are not utilized in the final, desired products, as well as considerable waste postconsumer. In the past, many of these waste products from the manufacture of products or postconsumer used materials that incorporate cellulose acetate were simply shipped off to the landfill. **US2010175691 A1** (2010, CELANESE ACETATE LLC) discloses a process for recycling cellulose acetate ester waste resulting from the production of materials (e.g., tobacco products) through the use of carboxylic acids. The process for recycling cellulose acetate ester waste (10), outlined in [Figure 6.4](#), is comprised of the following steps:

- Providing a reactor (20).
- Adding cellulose acetate ester waste to the reactor.
- Adding a hydrolyzing agent (15) to the reactor to create an agent/waste mixture.
- Hydrolyzing the cellulose acetate ester waste by agitating and heating the agent/waste mixture for a period of time to create a hydrolyzed mixture.
- Distilling (30) and/or separating out (35) the hydrolyzing agent from the hydrolyzed mixture.
- Separating and removing solid material (50) that may end up as landfill waste (70) from the hydrolyzed mixture to create a water-soluble product stream (60), which includes monosaccharides, polysaccharides, partially hydrolyzed cellulose, acetic acid, or combinations thereof.
- Collecting the water-soluble product stream.

Figure 6.4 Recycling of cellulose acetate ester waste by hydrolysis (US2010175691 A1, 2010, CELANESE ACETATE LLC).





Scheme 6.1 D-Glucopyranose.

R: Hydrogen atom, acetyl, propionyl, butyryl, methyl, ethyl, or benzyl; m: Integer between 2 and 16; n: Integer between 1 and 35,000 representing the degree of polymerization.

The hydrolyzing agent is a carboxylic acid selected from the group consisting of acetic acid, formic acid, or combinations thereof.

In one of its embodiments, **JP2001040078 A** (2001, CANON KK) discloses a process for recycling a thermoformed product produced from a sugar chain polymer compound in which the thermoformed body is ground and hydrolyzed to produce D-glucopyranose (Scheme 6.1) and an aliphatic dicarboxylic acid, which are used again to produce the sugar chain polymer compound.

The sugar chain polymer compound is useful for the production of thermoformed articles, such as packaging containers, toys, and sheets, by alternately ester-copolymerizing a specific D-glucopyranose derivative and an aliphatic dicarboxylic acid. The hydroxyl group bonded to the 4- and 6-carbon atoms of the D-glucopyranose is alternately ester-copolymerized with an aliphatic dicarboxylic acid.

6.2.2 Alcoholysis

US5264614 A (1993, DU PONT) discloses a method for the recovery of waste aliphatic hydroxycarboxylic acid-derived polyester by (a) heating the waste under pressure in the presence of a lower alkyl alcohol (C_1 – C_6 alcohol), and optionally also water so as to solubilize the polyester, the heating being such that significant degradation of the polyester is avoided; and (b) cooling the solution and recovering the polymer.

US5264617 A (1993, DU PONT) discloses a method for depolymerizing waste aliphatic hydroxycarboxylic acid-derived polyester through alcoholysis by (a) heating the waste in the presence

of a lower alcohol (C_1 – C_6 alcohol) so as to solubilize the polymer; (b) removing the undissolved trash material optionally by filtering; and (c) adding acid catalyst and heating to produce an alkyl ester.

CA2098220 A1 (1994, DU PONT) discloses a method for the recovery and recycling of hydroxycarboxylic acid from waste aliphatic hydroxycarboxylic acid-derived polyester such as fast food containers by (a) contacting the waste with a solubilizing fluid selected from the group consisting of water, lower alkyl alcohol (C_1 – C_6 alcohols), mixtures of water and said alcohols, amines, diamines, and mixtures of said amines and/or diamines with water and/or said alcohols; (b) maintaining the resultant mixture at a temperature and time sufficient to at least solubilize the polymer and form a liquid phase of increased monomer and oligomer hydroxyl acid value; and (c) isolating the liquid phase. Regardless of the nature of the solubilizing fluid, it is important to use temperatures and pressures adequate to cause rapid solubilization of the PHAs, but not severe enough to form undesirable degradation products. Higher temperature increases the rate of depolymerization and solubilization. By selecting optimal reaction conditions, particularly pressure and temperature, significant quantities of the aliphatic polyester can be adequately solubilized by a batch method, often in 1 h and even in as little as 0.25 h. In many cases, overall economics and reaction kinetics dictate running the method at atmospheric pressure, although elevated pressure sometimes is needed to reach the necessary temperatures for rapid and complete solubilization. Normally autogenous pressure is adequate. The method can be used for the depolymerization of PLA and the recovery of lactic acid. Once the PLA is depolymerized back to lactic acid, the resulting lactic acid must be synthesized into lactide before carrying out polymerization to form PLA. This method is considered to be complicated and not economically advantageous.

All three DU PONT patents use waste originating mainly from discarded food containers made from hydroxycarboxylic acid-derived polyesters; the hydroxycarboxylic acid-derived polyesters are selected from PLA, PGA, or a copolymer containing a major portion of PLA and PGA copolymerized with up to 30% ϵ -caprolactone, δ -valerolactone, 1,5-dioxepan-2-one, 1,4-dioxan-2-one, β -butyrolactone or β -propiolactone, and/or 6-methyl-2,5-morpholinedione and mixtures thereof. Typically the temperature of the process is in the range from 100

to 200°C and the time is in the range of 15 min to 16 h. The alcohol is preferably *n*-butanol.

JPH09241417 A (1997, DAINIPPON INK & CHEM INC) discloses a method for recovering lactide from lactic acid-based polymer wastes by adding specific alcohols and a heat-decomposing catalyst to the lactic acid-based polymer and carrying out alcoholysis. The method involves adding alcohols, which have a boiling point of 170°C or higher at 1 kPa (7.5 Torr), and a heat-decomposing catalyst to a lactic acid-based polymer, such as PLA or a copolymer of a polyester comprised of a diol, a dicarboxylic acid, and a lactide. This mixture is then heated under reduced pressure or in an inert gas atmosphere to carry out the alcoholysis. A back-bite reaction is then conducted to recover the produced lactide. Preferred alcohols are monohydric alcohols with ≥ 6 carbons, diols with ≥ 5 carbons, triols, or tetrols. The preferred catalyst is a compound containing tin.

JPH08253619 A (1997, MATSUSHITA DENKI SANGYO KK) discloses a method for decomposing molded products containing biodegradable polyester(s) by contacting the molded products (A) with a solution (B) containing at least an alkali metal compound or an alkaline-earth metal compound, and an alcohol (C) such as methanol. Among the aliphatic polyesters are poly(3-hydroxyvalerate) (PHV) and its copolymers, poly(3-hydroxybutyrate) (PHB), polycaprolactone (PCL), poly(ethylene succinate) (PES), poly(ethylene glutarate), poly(ethylene adipate) (PEA), poly(butylene adipate) (PBA), and poly(butylene succinate) (PBS). The addition of an alcohol to the treating solution accelerates the decomposition of the polyester to monomers by promoting the solvolysis of ester bonds without the application of heat or pressure. It is preferable that the component (A) to be treated is immersed in a solution containing both the components (B) and (C) and then inorganic compound particles (D) be added (e.g., alumina particles with a size of 10 μm to several mm), followed by agitation. The method is claimed to be effective for recovery of the monomers of the decomposed polymer.

The outline of the method of adding, stirring, and processing inorganic compound particles in a solution is shown in Figure 6.5. A polymer sample (1) of size 10 mm x 20 mm x 1 mm, and made of polyethylene adipate (PEA), was used. As the inorganic compound particle (3) 2.5 g calcium carbonate particles (with a diameter of 350–500 μm) were added in a solution (2) comprised of 1.1 g sodium

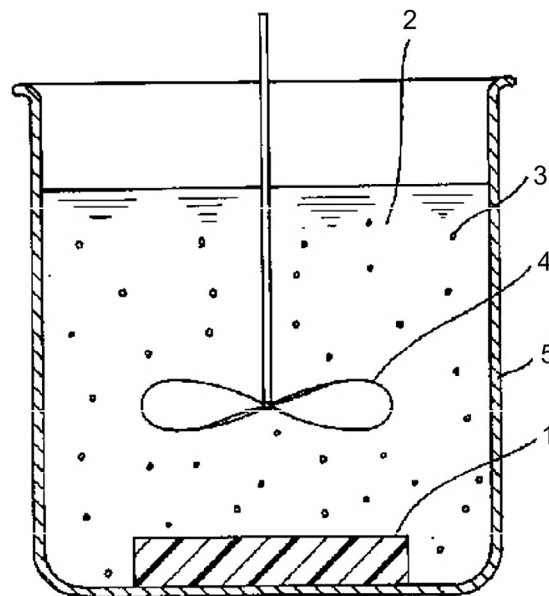


Figure 6.5 Schematic diagram showing the disposal method of the biodegradable polymer molding in one working example (JPH08253619 A, 1997, MATSUSHITA DENKI SANGYO KK).

1: Biodegradable polymer sample; 2: Treating solution; 3: Inorganic compound particle; 4: Agitating blades; 5: Container

hydroxide, 21.0 g ethanol, and 6.0 g water. The aforementioned polymer sample (1) was immersed in this solution at room temperature (20°C), and the agitating blades (4) stirred the mixture at a revolving speed of 100 rpm. The weight of the sample was measured at a fixed time interval and the degradation rate was 260 mg/h. When the same experiment was conducted using the treating solution without adding the calcium carbonate particles, the degradation rate was 180 mg/h (i.e., the degradation rate was promoted by the addition of the inorganic compound particles).

WO2005105908 A1 (2005 UNIV KEIO) discloses a method for the depolymerization of an aliphatic polyester by reacting the polyester with a solid acid catalyst, thereby obtaining a repolymerizable monomer and/or oligomer as a depolymerization product; also disclosed is a method for producing an aliphatic polyester by polymerizing the repolymerizable monomer and/or oligomer obtained by the depolymerization. The aliphatic polyesters are PLA, PCL, poly(alkylene alkanoate), or PHA. The depolymerization reaction is generally carried out by dispersing the solid acid catalyst in a solvent (toluene or ethanol) in which the polymer is dissolved, and

then regulating it to an appropriate temperature for a predetermined time. Known representative solid acid catalysts include Nafion[®]-H, sulfated zirconia(VI), and montmorillonite K10. Other options for the solid acid catalyst are Dowex[®] 50W-X8 or 50W-X2 or Duolite[®] C20. It is also possible to use vermiculite or heteropolyacid, or even a zeolite catalyst such as MCM-22.

Among the solid acids above, both montmorillonite K10 and Nafion[®]-H have a high activity, but montmorillonite K10 is preferable as the solid acid catalyst as it is a clay mineral which is safe, easy to handle, and is a substance with a low environmental load. It is also inexpensive and available in large quantities (at a cost of from 0.5 to 2 times that of 95% sulfuric acid). Nafion[®]-H is a cation exchange resin (perfluorosulfonic acid ion-exchange powder) developed by Du Pont, has a side chain with a terminal sulfonic group on a linear chain of a fluorinated resin, and exhibits an acidity stronger than that of 100% sulfuric acid.

JP2009072759 A (2009, UNIV KEIO; KUROSAKI H; KOGYO KK; MIZUSAWA IND CHEM LTD) discloses a method for the depolymerization of PLA by heating PLA in the presence of a solid catalyst consisting of acid-treated dioctahedral smectite clay. The acid-treated dioctahedral smectite clay has 0.28–0.63 mmol/g solid acid content when measured in an absolutely dried state, 0.25–0.40 cm³/g pore volume of pores having a 17–3000 Å pore size when measured by a nitrogen adsorption method, and 150–400 m²/g BET specific surface area. The solid acid catalyst allows oligomers with predetermined polymerization degrees to be obtained in a short time by depolymerization, and it is separated easily from oligomers to be obtained by depolymerization so that oligomers of PLA can be recovered at a high rate.

The proposed solid acid catalysts described in the last two patents are insoluble in a solvent, and have the following advantages in comparison with soluble catalysts (WO2005105908 A1, 2005, UNIV KEIO):

(1) Conventional alkali processes are usually incapable of yielding an oligomer mixture with re-polymerization properties and reactivity. For example, alkali depolymerization of PLA decomposes it to a lactic acid monomer. When the decomposition product is intended for re-polymerization, it is preferable that the depolymerization product is in the form of an

oligomer, which is also a polymerization intermediate, rather than a monomer. In this respect the depolymerization by a solid acid makes it easier to obtain an oligomer mixture with repolymerization properties and reactivity.

- (2) An oligomer mixture, having repolymerization properties and reactivity, can be obtained directly, at a relatively low temperature. In prior technologies, for example, decomposition with an alkali, the product is an alkali salt, which requires a neutralizing operation with an acid in order to be used as a polymerization raw material or a chemical raw material. This operation requires a strong acid in addition to the alkali as the catalyst, and generates a salt. Also, a purifying operation is required in order to remove salts, excessive acid, or unreacted salts. In addition, the alkali decomposition requires a considerably higher temperature, is accompanied by generation of byproducts and decomposition products other than the desired ones, and is accompanied by a color deterioration associated therewith. The chemical recycling utilizing the solid acid is expected to achieve energy savings and have a low environmental load.
- (3) The use of solid acid catalyst enables separation of the product by filtration alone. On the other hand, in decomposition of polymer (such as a PLA) with an alkali (such as ammonia), the generated lactic acid forms a salt that has to be neutralized, thus generating an unnecessary salt; also, a dehydration process and purification of hydrated lactic acid become necessary. With a solid acid catalyst, lactic acid is obtained as a free carboxylic acid, and therefore does not require neutralization, providing free lactic acid oligomers which are directly repolymerizable as they are.
- (4) The solid acid catalyst is reusable repeatedly by simple post-processing, such as rinsing with water and drying.
- (5) The solid acid catalyst is not deactivated even at a high temperature, and is applicable to decomposition of a broad range of polymers.
- (6) The solid acid catalyst is easy to handle as it lacks an irritant odor or corrosive properties, and is not very hazardous.

JP2009029757 A (2009, TEIJIN FIBERS LTD) discloses a depolymerization method for PLA that

uses an easily handleable catalyst. The depolymerization method comprises alcoholizing PLA (e.g., Lacty[®] 9010) using methanol at 60–100°C in the presence of a zinc compound catalyst composed of zinc carboxylate (e.g., zinc acetate) and/or zinc carbonate. Methyl lactate is obtained in adequate quantity. PLA originates from agricultural material, fishery material, food packaging containers, and civil engineering and construction material.

6.2.3 Foam Hydrolysis

JP2009242545 A (2009, KANEKA CORP) discloses a pretreatment method that can precede the chemical recycling of a PLA-based foam that is difficult to reduce in volume by crushing. The PLA-based foam is treated at 80–100°C in a relative humidity of 80% or more and then crushed and injected into a reaction extruder without using a large-size crusher.

6.3 Hydrothermal Depolymerization

Hydrothermal depolymerization involves hydrolysis of biodegradable polymers at high temperature and often with high-pressure water. The reaction can be performed under subcritical and supercritical conditions either in the presence or absence of oxidants.

The hydrothermal depolymerization of hydroxycarboxylic acid-derived polyesters, and especially of PLLA, has been studied by Saeki et al. [4]. PLLA was readily depolymerized by hydrolysis under hydrothermal conditions in the absence of catalysts. The optimum conditions for depolymerization of PLLA were found to be 220°C for 20 min. Under these conditions, more than 95% L-lactic acid was recovered without loss of optical purity. At a higher temperature (260–300°C), the optical purity decreased with increasing temperature, and a racemic mixture was formed at 300°C.

High-temperature hydrolysis is effective for rapidly hydrolyzing PLLA to L-lactic acid without the use of catalysts [5]. When the hydrolysis is carried out at a temperature lower than the melting point of PLLA, crystalline residues are formed as a result of selective hydrolysis of the chains in the amorphous regions. The crystalline residues prolong the time required for the complete hydrolysis of PLLA, or decrease the yield of L-lactic acid when the hydrolysis is short [6]. The reported yield of water-soluble monomers and oligomers from PLLA was as

low as 56% even when the hydrolysis temperature was increased to 97°C and the hydrolysis was continued as long as 40 h [6]. Hydrolysis carried out at a temperature above the melting point of PLLA causes racemization and decomposition of the formed lactic acids due to high temperature [7].

The hydrolytic degradation of biodegradable aliphatic polyesters in the melt with high-temperature and high-pressure water overcomes the problem of slow degradation encountered during the hydrolysis in the solid state. On the other hand, hydrothermal depolymerization and dry-heat depolymerization require high temperatures, normally above 200°C.

JPH05178977 A (1993, TOYO INK MFG CO) discloses a hydrolysis method where moldings mainly comprised of PLA are subjected to high-temperature steam (> 100°C) and high pressure (> 1 atm). Preferably, the hydrolysis takes place in tight closed vessels that prevent oxidation with air. The hydrolyzed polymers become powdery or pasty. The method permits simple and easy recovery and reuse of PLA.

JPH07309863 A (1995, JAPAN STEEL WORKS LTD) discloses a method for recovering lactide from a PLA product in a short time, in high yield, and at low cost by heating and blending the PLA product in a screw-type extruder in the presence of water and a catalyst at a specific temperature. A PLA product (A), such as a film sheet or hollow article, is heated and blended by a screw-type extruder in the presence of water (B) and a catalyst (C), such as an alkyl-aluminum, zinc oxide, or manganese acetate, at 200–400°C and hydrolyzed and depolymerized to recover the objective lactide from component A. The amounts of components B and C used are preferably 0.1–5.0 wt.% of component B and 0.1–1.0 wt.% of component C based on the amount of component A.

JP2007002160 A (2007, TEIJIN FIBERS LTD) and **JP2007023176 A** (2007, TEIJIN FIBERS LTD) provide related methods for the depolymerization of a biodegradable polyester such as PLA by mixing the polyester (at least part of which is in a molten state) with water at a reaction temperature of 150–300°C and pressure of 0.1 up to 1 MPa (1–10 atm) and removing the depolymerized product from the gaseous phase portion with water vapor. In one example, 100 parts of PLA is put in a reaction tank heated to 220°C and stirred at 100 rpm for 4 h at atmospheric pressure. Water vapor is extracted by superheating. The depolymerization product is a mixture containing lactic acid, lactide, and/or lactic

acid oligomers. The ratio converted into lactic acid is 28% (optical purity: 98% L-forms) with respect to the PLA. The process enables the recovery of the depolymerized product of a biodegradable polyester that does not contain foreign materials or unreacted products in the biodegradable polyester polymer reaction product.

EP1241231 A1 (2002, CANON KK) discloses the recycling of molded articles obtained from a biodegradable resin composition comprised of a biodegradable polymer (A) and a biodegradable liquid crystalline polymer (B). Molded articles include ink tanks of ink-jet printers, toner containers of electrophotography apparatus, packing materials, casings of printers and cameras, transparency sheets, and so forth. In one example, a transparent sheet prepared from the butyl ester of hydroxyethyl-cellulose with PLA was shredded into chips by a shredder. The sheet chips were decomposed by the action of high-temperature and high-pressure water (400°C and 35 MPa), or fuming hydrochloric acid (25°C). The glucose chemically separated from the decomposition product was used as a source-material for synthesis of glucose-sebacic acid copolymer.

JP2007210889 A (2007, TEIJIN FIBER KK; UNIV TOYOHASHI) provides a method for monomerizing a stereocomplex-type PLA by processing the biodegradable polymer at 170–330°C for 5–240 min at a pressure of 0.8–16 MPa (8–160 atm) in an atmosphere of inert gas in the presence of water. The preferred composition of the stereocomplex-type PLA is one that contains PLLA and PDLA mixed in the weight ratio of 4:6 to 6:4. A lactic acid mixture of L-lactic acid and D-lactic acid is obtained.

JP2007051202 A (2007, NAKAMURA K; AKATSU S; NAGAHAMA M; YOKOSUKA M) discloses a method for the regeneration of PLA used for containers and bags that comprises hydrolysis treatment and supercritical extraction treatment. PLA and water in an amount of 20% with respect to the total amount of material to be processed are reacted at 140°C under saturated water vapor pressure to hydrolyze PLA and to produce an aqueous lactic acid solution. The aqueous lactic acid solution is introduced in to a supercritical environment of carbon dioxide (scCO₂) at a temperature of 60°C and pressure of 8 MPa (80 atm) and made to dissolve in scCO₂. The generated refined lactic acid is separated from carbon dioxide at normal temperature and pressure. The method enables efficient regeneration

of lactic acid of high purity from PLA without impairing the quality.

In actual recycling of PLA products, however, there are many kinds of mixing substances such as ink and paint attached to the products of substances mixed in the products, and also fillers. Therefore, practical application of this technology has the problem of separation, and also how to extract solely lactic acid (WO2007102488 A1, 2007, NAKAMURA K).

WO2007102488 A1 (2007), **JP2007238691 A** (2007) and **JP4118313 B1** (2008, NAKAMURA K) and **JP2008179713 A** (2008, REAL PLASTIC KK) disclose related methods for the decomposition and reclamation of discarded PLA articles by conducting hydrolysis and separate recovery successively. The discarded PLA articles are exposed to a water vapor atmosphere in a treatment chamber filled at or below the saturated water vapor pressure and heated at a temperature at or below the melting point of the polymer, preferably in the range from about 130 to about 150°C (Figure 6.6). It was found that the hydrolysis completion time is between about 1.5 and 4.5 h from the start of the treatment for PLA samples of Terramac[®] (molding, pellet); in particular, the 1.5 h lower limit was reached at a hydrolysis temperature of 150°C. The waste biodegradable polyester can be hydrolyzed without establishing the supercritical state, and the reaction products are separated into gas or liquid component and solid component and collected separately.

In one of its embodiments, the decomposition method includes a pretreatment step, preceding the hydrolysis treatment, to crystallize PLA by heating the PLA articles to a temperature in a range from the crystallization point to the melting point of PLA for at least 30 min. As a result of the pretreatment, the hydrolysis of the crystallized PLA can be shortened. In addition, the pretreatment considerably increases the brittleness of PLA so that the polymer can be easily pulverized.

The collected components of the decomposition can be used as raw materials for the regeneration of PLA. A practical application of the proposed technology is the problem of separating substances, such as ink and paint attached to PLA products, filler, and the sole extraction of lactic acid. The invention is not limited to the hydrolysis of PLA and can be applied in a quite similar manner to the hydrolysis of other polyesters including biodegradable polymers such as PBS, PCL, polyhydroxyalkanoate (PHA), and non-biodegradable polymers such as poly(ethylene

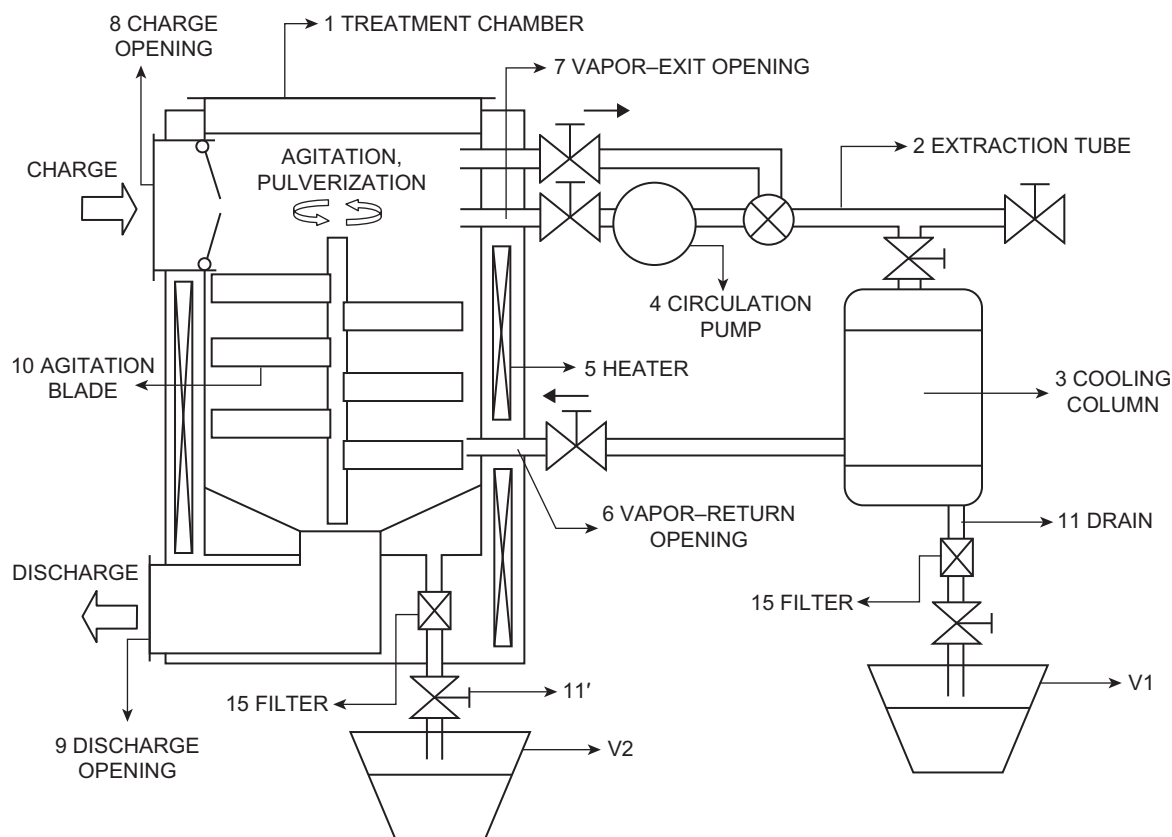


Figure 6.6 Schematic diagram of the hydrolysis apparatus (WO2007102488 A1, 2007, NAKAMURA K).

terephthalate) (PET) and polyamide 6 (PA 6 or Nylon 6).

JP2007001940 A (2007, MITSUBISHI HEAVY IND LTD) provides a method for the recycling of a poly(alkylene succinate) and monomer recovery. The method involves adding water (1–20 parts weight) to poly(alkylene succinate) (1 part weight), decomposing and monomerizing by heating at 200–400°C under 1–30 MPa (10–300 atm) pressure, and purifying the monomer. The poly(alkylene succinate) is PES, PBS, poly(butylene succinate-*co*-adipate) (PBSA), poly(butylene succinate-*co*-carbonate), and/or poly(ethylene succinate-*co*-terephthalate) (PEST).

Tsuji et al. studied the hydrolytic degradation of aliphatic dicarboxylic acid/aliphatic diol-derived biodegradable polyesters such as PBS and PBSA in the melt [3].

JP2009249508 A (2009, KYUSHU INSTITUTE OF TECHNOLOGY; MUSASHINO KAGAKU KENKYUSHO KK) discloses a method for the recycling of PLA and/or its derivative(s) which combines partial hydrolysis of PLA with depolymerization of the obtained oligomers to lactide. The method comprises the following steps: (1) putting

a PLA having 50,000–2,000,000 weight-average molecular weight and/or its derivative in a reactor and introducing steam into the reactor by decompressing the reactor and/or replacing a gas phase of the reactor with steam; (2) hydrolyzing the PLA and/or its derivative in a heated steam atmosphere; (3) discharging the steam by decompressing the reactor and introducing dry air and/or an inert gas; and (4) recovering the lactic acid oligomer having 1000–50,000 weight-average molecular weight and/or its derivative which are obtained in step (3).

The hydrolysis of PLA and/or its derivative(s) is performed under coexistence of heat steam atmosphere and basic atmosphere by using alkali. The alkali is chosen from $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, CaO , MgO , and/or NaOH . The water vapor is introduced under reduced pressure of 0.02 MPa (0.2 atm) or less. The heating process is performed at 100–150°C under pressure of 0.05–0.56 MPa (0.5–5.6 atm). The water vapor is discharged under reduced pressure of 0.02 MPa (0.2 atm) or less. The method is claimed to recover lactide without loss of its optical purity. A disadvantage of the recycling method is that the hydrolysis occurs batch-wise by adding steam to

solid PLA. This adds further cost to the process of recycling PLA, making it economically less viable at a large scale.

JP2003300927 A (2003, INST NAGOYA IND SCIENCE RES), **JP2005330211 A** (2005, UNIV TOYOHASHI; TEIJIN FIBERS LTD), **JP2005298401 A** (2005, UNIV TOYOHASHI TECHNOLOGY), **JP2006137892 A** (2006, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD), and **JP2007099663 A** (2007, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD) provide a series of related methods and apparatus for decomposing biodegradable polyesters, such as PLA, PHB, and PCL, and recovering the generated monomers. A representative example of these patents is **JP2003300927 A** (2003, INST NAGOYA IND SCIENCE RES), which discloses a method and an apparatus (**Figure 6.7**) for depolymerizing PLLA and recovering L-lactic acid for recycling the PLLA. The monomerization of PLLA is performed by treating 1 part PLLA in approximately 20 parts water at a high temperature of 200–350°C (preferably 200–300°C) for approximately 5–60 min (preferably 5–30 min). As an especially favorable condition, the L-lactic acid is recovered in at least 90% yield at 250°C reaction temperature for approximately 10 min reaction time. The depolymerization maintains the optical activity of PLLA.

JP2005330211 A (2005, UNIV TOYOHASHI; TEIJIN FIBERS LTD) discloses a method and an apparatus (**Figure 6.7**) for separating and recovering PLA from a polymer waste mixture by hydrolysis. The method comprises treating a mixture of PLA and a general-purpose polymer (e.g., PET or PS) with water at a high temperature of about 160°C to about 200°C for about 30 min or more and then separating and recovering the lactic acid. According to the method, the lactic acid can be separated and recovered in a high yield and the optical activity of the lactic acid is held in the original optical activity state. The mixture of PLA, general-purpose polymer, and water in a liquid state are reacted in a continuous-type or a batch-type high-temperature processing machine, the pressure of which is kept higher than 1 MPa.

JP2005298401 A (2005, UNIV TOYOHASHI TECHNOLOGY) provides a method with which a biodegradable polyester such as PHB or PCL is reacted with high-temperature and high-pressure water and thereby converted into a monomer. In particular, PHB is reacted with water at a temperature of 250–300°C for 5–20 minutes, preferably

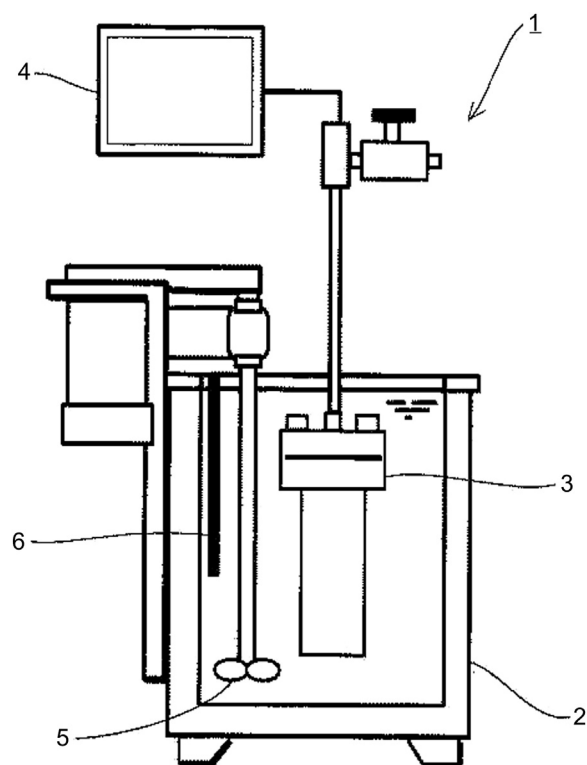


Figure 6.7 Schematic diagram of a high-temperature, high-pressure, water-processing apparatus for a biodegradable polyester (**JP2003300927 A**, 2003, INST NAGOYA IND SCIENCE RES; **JP2005330211 A**, 2005, UNIV TOYOHASHI; TEIJIN FIBERS LTD; **JP2005298401 A**, 2005, UNIV TOYOHASHI TECHNOLOGY; **JP2005298401 A**, 2005, UNIV TOYOHASHI TECHNOLOGY; **JP2006137892 A**, 2006, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD; and **JP2007099663 A**, 2007, UNIV TOYOHASHI TECHNOLOGY, TEIJIN FIBERS LTD).

1: Processing apparatus; 2: Thermostat; 3: Reaction container; 4: Pressure indicator; 5: Rotary blade; 6: Heater

100–240°C for 120–360 min; PLC is reacted with water under a temperature of 350–400°C for 5–30 minutes. The monomers 3-hydroxybutanoic acid and 6-hydroxycaproic acid can be obtained from R-PHB and PCL, respectively, in a short time in high yield. The processing apparatus (**Figure 6.7**) is a continuous-type or batch-type. The processing apparatus is set at a high pressure of more than 0.1 MPa (1 atm) such that water and biodegradable polyester in a liquid state are mixed by the high-temperature processing machine.

JP2006137892 A (2006, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD) discloses a method and apparatus for recovering lactic acid

from waste PLA in high yield and purifying the lactic acid to a prescribed optical purity. The method for the regeneration of waste PLA comprises three steps: (1) monomerize PLA by heating a composition containing PLA in the presence of water at a high reaction temperature (i.e., about 110°C to about 300°C) for about 5 min to about 96 h; (2) determine the optical purity of the lactic acid obtained by the monomerization step; and (3) purity adjustment to heat the lactic acid having determined optical purity in the presence of water at a high reaction temperature (i.e., about 180°C to about 300°C for about 5 min to about 96 h to adjust the optical purity to a prescribed level). When the optical purity of the lactic acid is lower than the prescribed level, the acid is subjected to a mixing step to mix the recovered lactic acid with a lactic acid having an optical purity of $\geq 90\%$; this prepares the lactic acid with the prescribed optical purity.

An apparatus (20) for separating and recovering lactic acid is described in Figure 6.8. It has a high-temperature processing machine (21) for performing initial stage processing of waste material, and a reaction liquid extraction hole (29) for removing reaction liquid in the processing machine. The lactic acid is efficiently recovered with high optical purity from the waste material.

JP2007099663 A (2007, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD) discloses a method for recovering lactic acid from a mixed waste material (16) containing two or more PLAs having different melting points. The mixed waste material is heated at 110–200°C with water (W) for

1 h or more in a high-temperature treatment apparatus (see Figure 6.7). The reaction liquid is recovered at predetermined time intervals of 10 min to 24 h. Lactic acid is separated and recovered and its optical purity is checked. The optical purity is adjusted to a prescribed level (90% or more) by heating the lactic acid in the presence of water at a high reaction temperature (i.e., about 180°C to about 300°C for about 5 min to about 96 h). When the optical purity of the lactic acid is lower than the prescribed level, the acid is subjected to a mixing step to mix the lactic acid with a lactic acid having an optical purity of $\geq 90\%$; this prepares the lactic acid with the prescribed optical purity. PLA recycling can be effectively performed by this method.

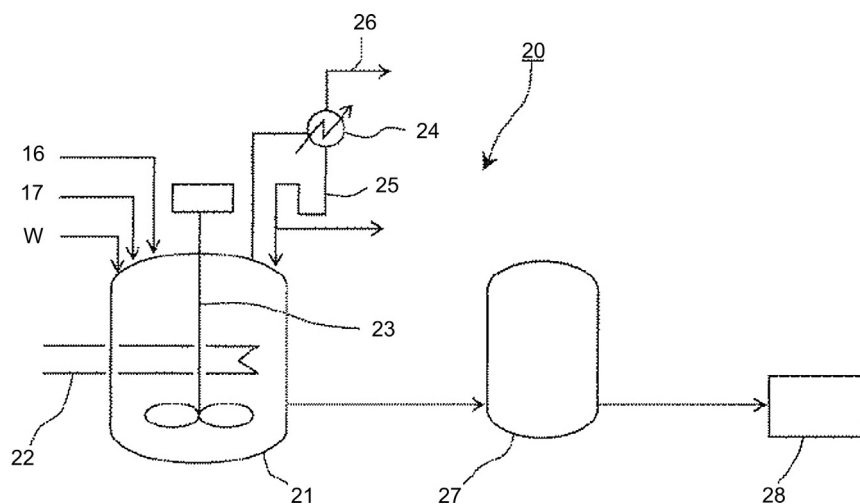
JP2008007611 A (2008, KUMAMOTO TECH & IND FOUND) discloses a method for recovering lactic acid and/or water-soluble oligomer by decomposing PLA for food packaging film without impairing the optical specificity of lactic acid. The method involves soaking the PLA in an aqueous solution of lactic acid, which contains 10% or more lactic acid, and then heating at 120–135°C under pressurization to recover lactic acid and/or water-soluble oligomer from PLA. The preferred weight ratio of PLA and lactic acid is 1:1 to 1:100. The water-soluble oligomer of lactic acid is a dimer or trimer of lactic acid.

6.4 Enzymatic Depolymerization

Most of the aforementioned thermal and chemical recycling processes consume significant energy, have

Figure 6.8 Outline diagram of a processing apparatus for recovering and separating lactic acid (JP2006137892 A, 2006;

JP2007099663 A, 2007, UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD).
16: PLA waste material; 17: Circulation liquid; 20: Separation recovery apparatus; 21: Reaction tank; 22: Thermal treatment equipment; 23: Agitator; 24: Cooler; 25: Return path; 26: Vent path; 27: Hold tank; 28: Purification; 29: Reaction liquid extraction hole; W: Water.



a low yield of monomers in a short period, and require the removal of catalysts and additives used for depolymerization, hydrolysis, or solvolysis [7]. Furthermore, if the depolymerization of PLA is conducted by thermal degradation or chemical degradation, both ends of a generated low molecular weight compound are irregular and such a compound cannot be repolymerized into a polymer.

Enzymatic depolymerization is a rather new recycling technique. This technique is distinguished from the techniques described in Chapter 4: Disposal (for example, see Sections 4.3.3: Microbes and Enzymes; and 4.4.2: Enzymatic Hydrolysis) by the fact that the main aim is to reuse the products generated after the enzymatic degradation.

One of the advantages of using an enzyme (especially hydrolase) is the reversible reaction between polymerization and depolymerization. Biodegradable biopolymers containing enzymatically hydrolyzable moieties such as esters are first cleaved by the action of a hydrolase enzyme. The degradation products containing low molecular weight fragments are repolymerized by the enzyme under water-limited conditions.

The enzymatic depolymerization and repolymerization were carried out with the objectives of developing the enzymatic recycling of aliphatic polyesters, such as PCL, PHB, PBA, PBS, poly(butylene adipate-co-succinate) (PBAS), and PLA, which are typical biodegradable biopolymers. They were degraded by lipase in an organic solvent solution containing a small amount of water to produce cyclic oligomers. The produced (cyclic) oligomers were readily repolymerized in bulk by the same catalyst to produce a polyester having an equal or higher molecular weight compared to the parent polymer [8–12].

Most of the research so far on the enzymatic recycling of biopolymers has been carried out at Keio University in Japan (<http://www.keio.ac.jp>), and all patent applications have been filed by the same university.

JP2002017384 A (2002, UNIV KEIO) discloses a method for producing trimethylene carbonate (TMC) by selectively converting a poly(trimethylene carbonate) (PTMC) to a repolymerizable monomer in the presence of a hydrolase. The hydrolase used for depolymerizing was recovered and used repeatedly without reducing its activity. The preferred hydrolase is lipase derived from *Candida antarctica* (Novozym® 435). The lipase was added to chloroform and separated by filtration using citrite. Solvent was concentrated from a filtrate using an evaporator. Trimethylene

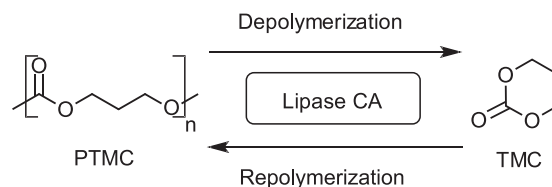
carbonate was obtained at 75% yield by silica gel column chromatography. PTMC transformed into monomer can be repolymerized selectively.

Matsumura et al. [12–15] reported the recycling of PTMC using an enzyme. The enzymatic transformation of PTMC with an M_n of about 3000 to about 48,000 using lipase from *Candida antarctica* in acetonitrile at 70°C afforded the corresponding cyclic monomer, TMC, in a yield of up to 80% [15]. The obtained TMC readily polymerized again using lipase (see Scheme 6.2).

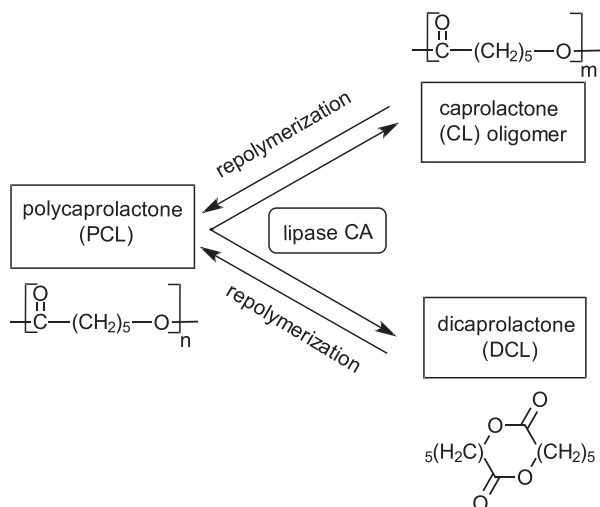
JP2002017385 A (2002, UNIV KEIO) discloses a depolymerizing method for producing dicaprolactone by selectively converting PCL to a repolymerizable monomer using a hydrolase. Using this depolymerization method, dicaprolactone is produced in a high yield, and the dicaprolactone can be repolymerized in the presence of a hydrolase such as lipase derived from *Candida antarctica*. The hydrolase used for depolymerization can be recovered and used repeatedly since enzyme activity is seldom reduced. The recovered dicaprolactone can be used as a monomer for the same polymer, and also as a co-monomer for improving the polymer properties [16].

The enzymatic depolymerization of PCL into dicaprolactone generally requires large amounts of organic solvent, such as 0.2% toluene solution, in order to facilitate intramolecular cyclization [17]. Organic solvents, such as toluene and volatile chloroform, may cause pollution and harm when released into the environment.

Besides the selective ring-closing depolymerization of PCL into the cyclic dimer, dicaprolactone, there is another route for the enzymatic recycling of PCL [17] (see Scheme 6.3). This second method involves the enzymatic conversion of PCL into repolymerizable 6-hydroxyhexanoate oligomers [8,14]. This oligomer can be used for the reproduction of PCL. In one example PCL with an M_n of 110,000 was degraded into the corresponding oligomer using immobilized lipase CA in toluene and water. The obtained viscous caprolactone (CL)



Scheme 6.2 Enzymatic recycling of poly(trimethylene carbonate) (PTMC) [12].



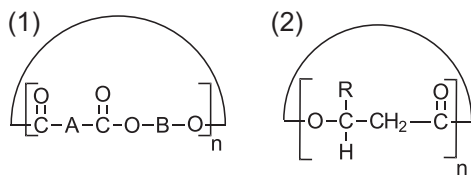
Scheme. 6.3 Lipase-catalyzed chemical recycling of poly(ϵ -caprolactone) (PCL) [12].

Adapted from Matsumura [12].

oligomer with a molecular weight of about 500 could be repolymerized by lipase for 6 h at 70°C under a slightly reduced pressure to yield a high molecular weight PCL having an M_n of greater than 80,000.

JP2002320499 A (2002, UNIV KEIO) discloses a depolymerizing method for converting poly(alkylene alkanoate) or poly(3-hydroxyalkanoate) (PHA or P3HA) to cyclic oligomers mainly composed of cyclic compounds of formula (1), and particularly formula (2) (Scheme 6.4), using a hydrolase, lipase in particular. The original polymers can be produced by repolymerizing the cyclic oligomers in the presence of a hydrolase or a polymerization catalyst.

There are two routes for the enzymatic recycling of PHAs. One is enzymatic degradation using the specific hydrolase enzyme related to PHB, which is secreted by the PHB-degrading microbes as



Scheme. 6.4 Oligomer consisting essentially of the ring compound represented by chemical formulas (1) and (2) (JP2002320499 A, 2002, UNIV KEIO).

In (1): A is a 2–8 C alkylene group; B is a 2–6 C alkylene group; and m is an integer of 1–6. In (2) R is a hydrogen atom or a 1–12 C alkyl group; and n is an integer of 2–10.

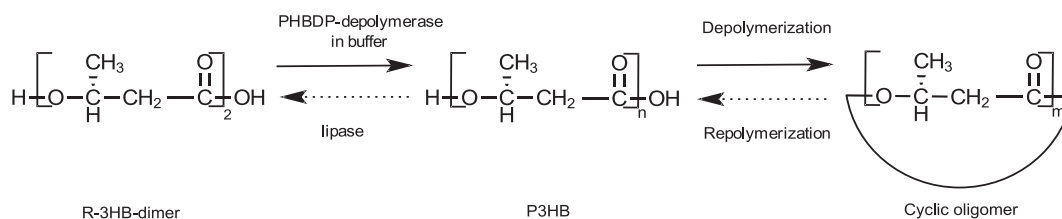
extracellular PHB-depolymerase (PHBDP). The other is enzymatic degradation using conventional lipase, which shows a broad substrate specificity in an organic solvent. Scheme 6.5 depicts the two routes for the enzymatic recycling of PHB (or P3HB).

Takahashi et al. reported the transformation of PLA into a cyclic oligomer by lipase in an organic solvent [11]. Kobayashi et al. used Proteinase K in a buffer solution for the enzymatic degradation of PLA [8–10].

The depolymerization methods in the aforementioned patent applications consume low energy because of the use of an enzyme, and the products obtained by the depolymerization can be again polymerized into polymers by an enzyme; these methods can effectively utilize the carbon resources without waste and can be considered a complete recycling type polymer reutilization. Therefore, from the viewpoint of sustainable material utilization, the aforementioned methods are practical chemical recycling methods. Also the enzyme catalyst methods are optimal for obtaining cyclic monomer or oligomer that is repolymerizable.

On the other hand, one detriment resulting from the substrate specificity of enzymes is that these methods are limited to polymers susceptible to an enzyme reaction. Also, the enzyme catalyst, being a protein catalyst, has inherent limitations, such as the fact that the reaction temperature cannot be made very high and that it requires a long time to complete the reaction for a polymer with high crystallinity and a high intermolecular force.

In order to be able to make an enzyme act on a solid polymer as it is, and also to dissolve the polymer, organic solvents, such as acetonitrile, tetrahydrofuran, toluene, or benzene, are necessary. To obtain the cyclic oligomer, which is especially excellent in repolymerizability, a lot of organic solvents are necessary. However, many organic solvents cause pollution when discharged into the environment with a volatile compound. On the other hand, the use of supercritical fluids instead of organic solvents is capturing the spotlight recently (see Chapter 5: Physical Recycling; Section 5.3.4: Dissolution). The supercritical fluids used are carbon dioxide and fluoroform (CHF_3). Carbon dioxide and fluoroform are suitable for handling relatively hydrophobic and hydrophilic molecules, respectively. Carbon dioxide is harmless, inexpensive, and nonflammable, with a critical point of about 31°C at 7.4 MPa. The carbon



Scheme. 6.5 The two routes for enzymatic recycling of polyhydroxybutyrate (PHB or P3HB) [18].

Adapted from Kaihara et al. [18].

dioxide easily reaches its critical point and is suitable as the medium for the depolymerization and repolymerization of aliphatic polyesters or polycarbonates.

JP2003079388 A (2003, UNIV KEIO) describes a process of depolymerizing an aliphatic polyester or polycarbonate in a supercritical fluid (scCO₂ or scCHF₃) in the presence of a hydrolase. The recovered cyclic oligomer(s) can be repolymerized in a supercritical fluid in the presence of an enzyme or polymerization catalyst. Polyesters that can be used for depolymerization include PCL, PBS, PBA, and PBSA. The preferred hydrolase is lipase. Novozym® 435 from Novozymes Japan Ltd which is an immobilized enzyme derived from *Candida antarctica*, is a suitable lipase, for example.

Takamoto et al. [9] reported that the lipase-catalyzed degradation of PCL in scCO₂ in the presence of acetone produced an oligomer of lower molecular weight (less than 500), which can be polymerized by the same catalyst. Similar results were obtained such that PCL beads were transformed in scCO₂ in the presence of a small amount of water and lipase to produce repolymerizable oligomers having an M_n of about 500 [13]. The produced caprolactone oligomer was again polymerized with *Candida antarctica* lipase by a dehydration process to yield a PCL having an M_n greater than 80,000. scCO₂ was also an adequate reaction medium for the lipase-catalyzed depolymerization of a PCL of $M_n=110,000$ into a cyclic dicalpactone (DCL) using immobilized lipase CA in scCO₂ fluid containing a small amount of water within 6 h at 40°C and 18 MPa scCO₂ and with a yield of 91%. The DCL was readily polymerized by lipase CA in scCO₂ to yield PCL with $M_n = 33,000$ after 6 h [17].

Osanai et al. [19] used lipase in both an organic solvent and scCO₂ for the selective degradative transformation into polymerizable oligomers and repolymerization of PCL, PHB, and PBA.

WO2004013217 A (2004, UNIV KEIO) discloses a method for the enzymatic depolymerization of PLA

which comprises depolymerizing PLA in an organic solvent or supercritical fluid in the presence of a hydrolase to yield a repolymerizable oligomer. Also disclosed is a process for producing PLA in which the repolymerizable oligomer obtained by the depolymerization method is polymerized in the presence of a hydrolase or polymerization catalyst. The hydrolase used to conduct the depolymerization or the polymerization can be collected and used repeatedly.

Any solvent in which PLA can be dissolved at least partly, and furthermore, one in which the enzyme is not inactivated, such as *o*-xylene, toluene, acetonitrile, 1,4-dioxane, tetrahydrofuran, hexane, or the like, may be used without any limitation. It has been confirmed that xylene and toluene are particularly useful for the depolymerization step. Combinations of various solvents at specific composition ratios make it possible to push the conversion ratio higher than by the use of any one of the organic solvents alone. For example, although it is not preferable to use chloroform alone (because this inactivates the enzyme), the conversion ratio is made better in the case of mixing a small amount of chloroform with hexane than in the case of 100% hexane. The addition of hexane to *o*-xylene or toluene makes the conversion ratio better than the use of *o*-xylene or toluene only.

In the invention, a supercritical fluid can be used as the depolymerizing solvent. PLA depolymerization is conducted by putting the PLA acid and a hydrolase into a pressure-resistant reaction tube and pouring liquefied carbon dioxide into it while pressuring the carbon dioxide with a liquid-feeding pump. This pushes the carbon dioxide into a supercritical state, which causes the PLA to undergo a depolymerization reaction for a suitable time while keeping the supercritical carbon dioxide (scCO₂) at a suitable temperature, all while stirring the solution. The temperature of scCO₂ at the time of depolymerization is preferably about 40 to 90°C, and the pressure

is preferably about 7.2 to 30 MPa. The most desirable reaction time for the depolymerization is at least 3 h. The upper limit of the reaction time is not particularly limited.

The PLA is a poly(L-lactic acid), poly(D,L-lactic acid), or PLA copolymer. The preferred hydrolase is lipase. An example of the immobilized enzyme derived from *Candida antarctica* is Novozym[®] 435 from Novozymes Japan Ltd. An example of lipase derived from *Rhizomucor miehei* is Lipozyme RM IM[™], also from Novozymes Japan Ltd. Besides this, Biopraxe[™] from Nagase ChemteX Corporation, which is a protease derived from *Bacillus subtilis*, may also be used as the hydrolase in the same manner.

WO2005026245 A1 (2005, UNIV KEIO) discloses a method for the continuous depolymerization of an aliphatic polyester such as PLA or polycarbonate. The method entails continuously passing both a supercritical fluid (preferably scCO₂) and an organic solvent solution of the polymer through a column packed with a hydrolase (e.g., Novozym[®] 435) to depolymerize the aliphatic polyester or polycarbonate by the action of the hydrolase, and then separating the depolymerization product from the reaction. It also discloses an apparatus for use in the continuous depolymerization method which is comprised of a device for producing a supercritical fluid, a column packed with a hydrolase, a back-pressure regulator, a means for separating a depolymerization product from a reaction mixture containing the depolymerization product, a means for sending the supercritical fluid produced by the device to the column, and a means for sending an organic solvent solution of a polyester, polycarbonate, or PLA to the column (Figure 6.9). Since the enzyme in the column used in this invention is stable for a long period of time (several months) and does not deteriorate, the same column can be used continuously for a long period of time, which makes for high-volume, high-efficiency processing.

Compared with degradation results using pure organic solvents (e.g., toluene), by the addition of scCO₂ as a mobile phase, the polymer transformation into cyclic oligomers through the enzyme column was significantly promoted with respect to the reaction time, temperature, and polymer concentration [19].

The continuous enzymatic degradation of aliphatic polyesters into cyclic oligomers was carried out using an immobilized lipase column with an organic solvent and scCO₂. Poly(D,L-3-hydroxybutanoate), PCL, and PBA were readily depolymerized into the corresponding cyclic oligomers by passage through the

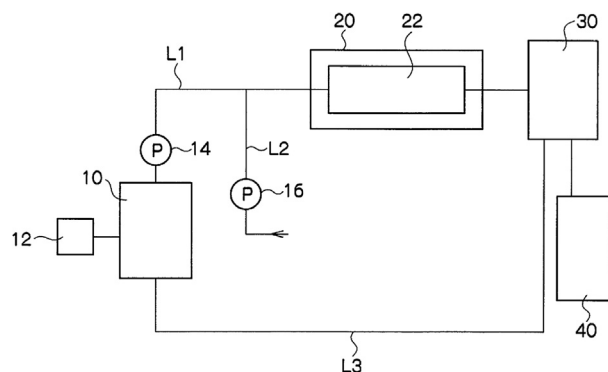


Figure 6.9 Description of the symbols (WO2005026245 A1, 2005, UNIV KEIO).

10: Supercritical carbon dioxide generation apparatus; 12: Supply for carbon dioxide; 20: Equipped with the heating apparatus and temperature control apparatus (that are not illustrated) so that column temperature may be kept constant by the thermostat; 22: Hydrolase-packed column; 30: Back-pressure regulator; 40: Means to isolate/separate the organic-solvent solution of a depolymerization product to an organic solvent and a depolymerization product.

L1: Pipe that sends the supercritical fluid generated by the supercritical fluid production generation apparatus with the pump 14 to the packed column; L2: Pipe that sends the polymer dissolved in an organic solvent to the packed column with the pump 16; L3: Pipe that collects the carbon dioxide gas released from a back-pressure regulator, and is returned to a supercritical fluid generation apparatus.

enzyme column packed with immobilized lipase CA using a toluene solution or scCO₂ at 40°C. The enzyme column packed with immobilized lipase CA using toluene was active for at least three months at 40°C.

WO2010050482 A (2010, TOYO SEIKAN KAI-SHA LTD) discloses a method for producing an oligomer and/or a monomer by biodegrading an aliphatic polyester (e.g., PLA or PBS) in a degradation liquid containing an enzyme (e.g., hydrolase), a buffer agent, an organic solvent (e.g., ethanol), and water. The SP value (Hildebrand solubility parameter) of the organic solvent is less than 8.5 or more than 11.5, and the percentage content of the organic solvent (by volume) in the degradation liquid is higher than 1% and lower than 15%. The biodegradable resin also contains a decomposition promotion agent such as poly(ethylene oxalate) (PEOx). The decomposition promotion agent discharges an acid by hydrolysis and

has a higher degradation rate than that of the aliphatic polyester. The hydrolase is protease, lipase, cellulase, or cutinase. In the method for producing an oligomer or a monomer, the degradation percentage of the biodegradable polymer is low, and deposits of aggregates of the oligomer and/or the monomer are few, so the recovery percentage is high (see also Chapter 7: Degradability on Demand; Section 7.3.7: Blending with other Polymers).

The advantages and disadvantages of enzymatic depolymerization can be summarized as follows:

- The products obtained by depolymerization can be repolymerized into polymers by an enzyme so that the carbon resources can be effectively utilized without waste and can be considered as a polymer reutilization of complete recycling type. The enzymatic depolymerization is of low energy consumption.
- Enzymatic depolymerization is an optimum method for obtaining cyclic monomers or oligomers that are repolymerizable.
- Enzymatic depolymerization is limited to polymers susceptible to an enzyme reaction.
- The enzyme catalyst, being a protein catalyst, has limitations such as the fact that the reaction temperature cannot be made very high.
- Enzymatic depolymerization requires a long time for reaction completion for a polymer with high crystallinity and a high intermolecular force.

JP2004290130 A (2004, MITSUBISHI CHEM CORP) discloses a method for recovering monomers that constitute a polyester. It comprises carrying out a contact reaction of the polyester with an esterase in a solution to hydrolyze the polyester and recovering the monomers constituting the polyester or their salts from the resultant solubilized hydrolyzate. The invention claims to depolymerize aromatic and aliphatic polyesters. The aliphatic polyesters are selected from the group which consists of PES, PBS, PBSA, poly(butylene succinate-co-lactide) (PBSL), PLA, PCL, and a copolymer that has these as a main component. The esterase is one with thermal stability, preferably carboxylate-ester hydratase, and more preferably cutinase or lipase.

The enzymatic recycling of biopolymers is a promising method of establishing a sustainable polymer recycling system of biodegradable polymers, such as aliphatic polyesters, polycarbonates, and polyamino

acids [11,12]. The biopolymer can be depolymerized into low molecular weight compounds without using high energy such as fossil fuel; the low molecular weight compounds can be effectively utilized, and if desired, the original polymer can be obtained from the low molecular weight compounds without similarly consuming any high energy (WO2004013217 A, 2004, UNIV KEIO). In spite of its obvious benefits, there are no reports so far for the practical application of this method to the recycling of biopolymers. More research is needed in terms of a more efficient use of enzymes, improved polymerizability of the cyclic oligomers, etc. The repetitive production and chemical recycling of polymeric materials using an enzyme may become an effective method.

During tobacco manufacturing substantial amounts of waste filter material and cigarette paper are generated. Such waste materials generally have no utility in cigarette manufacturing, and are typically disposed of by burning after separation from the tobacco components. Disposal of these waste products, and the associated economic losses, could be avoided by converting the waste materials to a product useful in the manufacture of tobacco products.

US4298013 A (1981) and **GB2107320 A** (1983, PHILIP MORRIS INC) disclose a process for recycling cellulose waste material generated during tobacco manufacturing by (a) subjecting the waste to enzymatic saccharification to hydrolyze cellulose to simple sugars, especially glucose, (b) recovering the sugars, and (c) using the recovered sugar in a tobacco treatment process. The cellulose waste material is preferably first comminuted and dispersed in water. Cellulose acetate is then de-esterified by treatment with an alkali (e.g., NaOH or KOH). The material is then washed free of excess alkali. A *Trichoderma viride* cellulase is employed to effect enzymatic saccharification.

6.5 Miscellaneous Processes

Ariffin et al. [20] investigated the chemical recycling of PHAs by thermal degradation from the viewpoint of biorefinery (see also Chapter 2: Define the Terms; Section 2.4: Types and Mechanisms of (Bio)degradation). The thermal degradation resulted in successful transformation of PHAs into vinyl monomers using alkali earth compound catalysts. Poly-(3-hydroxybutyrate-co-3-hydroxyvalerate)s (PHBVs) were smoothly and selectively depolymerized into crotonic acid (CA) and 2-pentenoic (2-PA) acid at

lower degradation temperatures in the presence of CaO and $\text{Mg}(\text{OH})_2$ as catalysts. The CA obtained from 3-hydroxybutyrate sequences in PHBV was copolymerized with acrylic acid to produce useful water-soluble copolymers (e.g., poly(crotonic acid-co-acrylic acid)) that have high glass transition temperatures. The copolymerization of CA derived from PHA pyrolysis is an example of cascade utilization of PHAs, which meets the idea of sustainable development [20].

A special case of chemical recycling is disclosed by **WO2009081362 A1** (2008, TORINO POLITECNICO) for the recycling of waste polymers, including aliphatic polyesters described in Chapter 4: Disposal; Section 4.6.2: Pyrolysis. Although this patent does not conform strictly to the definition and aim of chemical recycling – which is the recovery of raw materials such as monomers and/or oligomers with the purpose of making new polymers – it was found expedient to also classify it under the general heading of chemical recycling.

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JPH07309863 A	19951128	JP2821986 B2 19981105	JAPAN STEEL WORKS LTD
JPH08253619 A	19961001		MATSUSHITA DENKI SANGYO KK
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WO2005026245 A1	20050324	JP2005082710 A 20050331	univ keio
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WO2007102488 A1	20070913	KR20080109010 A 20081216; EP2022818 A1 20090211; US2009099270 A1 20090416; US7985778 A1 20090416	NAKAMURA K
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WO2011029648 A1	20110317	BE1018882 A3 20111004; MX2012002137 A 20120314; CN102482369 A 20120530; US2012165554 A1 20120628	GALACTIC SA

Supplementary patents (not relating necessarily to biopolymers)

Patent number	Pub. date	Family members	Applicant
US4057537 A	19771108		GULF OIL CORP

7 Degradability on Demand

OUTLINE

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7.1 Control of Degradation Rate

A distinction should be made between environmentally biodegradable disposable biopolymers and biodegradable biopolymers, which are used in the medical sector (e.g., sutures, implants, and drug delivery systems). The first category of materials begins accelerated degradation during its disposal stage, having exhibited only a minor amount of

degradation during its operative stage; the second category of materials is designed to undergo substantial, and often controlled, degradation during use in the body (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD).

An ideal environmentally biodegradable article would (1) retain its structural integrity, independent of the environmental conditions, for a specified

period of time with minimal or no degradation; and (2) undergo accelerated degradation after the product has achieved its desired functional effect or achieved the end of its functional purpose or useful life. Such an article shall be triggered to degrade at the desired time. Often the tuning of these contradictory requirements is difficult to achieve as it depends on the variability of environmental conditions (temperature, humidity, light, etc.) over time and place.

The balance between durability and biodegradability is an ever-present consideration in achieving cost-effective waste disposal. Aliphatic polyesters are environmentally attractive, yet lack acceptable durability; on the other hand, aromatic polyesters have the preferred sturdiness, but their disposal is much more ecologically burdensome.

Presently, all biodegradable biopolymers suffer from the same basic problem: environmental conditions have a substantial influence on the degradation rate. The weather may cause a material to decompose either too quickly or too slowly. For example, a biodegradable agricultural film may degrade too quickly if the crop season is either wet or unusually sunny, and may degrade slowly if the crop season is either dry or cloudy. These complications have allowed biomulch films to gain only minor acceptance by the agricultural community (WO0075259 A1, 2000, EASTMAN CHEM CO). Since weather conditions are highly variable over time and locality, it is a major problem to develop a biodegradable material that will be stable during use and decompose quickly when discarded.

The rate at which an environmentally degradable disposable material degrades depends on a variety of factors, including, but not limited to, the following:

- Chemical modification of the polymer backbone.
- Changes to the morphology/structure.
- Alterations to the polymer composition.
- Selection of processing conditions.
- Form of the polymeric article.
- After-treatment of the article.
- Environmental conditions (moisture, pH, temperature, radiation).

The polymer backbone of biopolymers can be modified through selection of the monomers that are incorporated or grafted into the polymer chain; by alteration of the linkages, pendant, or end-groups; and by manipulation of the molecular weight.

The morphology/structure can be controlled in a variety of ways including the stereoisomerism content, overall crystallinity, free volume, and molecular weight.

The composition can be altered by the presence of impurities or by the addition of various additives.

The processing conditions (e.g., shear rate, temperature, pressure) can have an impact on the structure/morphology of the material.

The form of the article can be modified by altering its surface area, porosity, and density.

The article can be after-treated by coating, surface cross-linking, or adsorption of various additives.

The environmental conditions include temperature, moisture, pH, radiation and time of exposure, and biological activity of the environment into which the material is placed.

The degradation rates can be measured using a variety of short- or long-term tests, including, but not limited to (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD):

- (1) Environmental chamber tests in which the temperature and humidity of the environment can be manipulated.
- (2) Boiling water tests.
- (3) Seawater tests.
- (4) Microbiologically active sewage sludge tests.
- (5) Composting tests that simulate soil degradation.

An advantage of the environmental chamber tests is that the conditions are controlled and that the degradation rates of disposable materials can be evaluated by accelerated short-term testing under which the materials are exposed to harsh conditions. For example, when certain of the disposable materials are subjected to conditions in which the temperature is about 35°C and the relative humidity is about 95%, the disposable materials typically degrade at about the same rate as the materials degrade in seawater in the summer, about 16 times as rapidly as the materials degrade in seawater in winter, about 2 to about 8 times as rapidly as materials degrade on a landfill, about 10 times as rapidly as the material degrades in a compost bed, and about 4 to about 100 times as rapidly as materials degrade when buried in a landfill, depending on the moisture content and microbial activity in the landfill (US2002123546 A1, 2002, ECOPOL LLC;

CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD).

The rate at which the biopolymers are degraded can be monitored by a variety of methods, including changes in molecular weight, moisture penetration, stiffness, strength, hardness, weight, volume, shape, transparency, crystallinity, and glass transition temperature (T_g) of the disposable material (US6323307 B1, 2001, CARGILL DOW POLYMERS LLC).

7.2 Suppression of (Bio)-degradability

An environmentally disposable article produced by only a biodegradable biopolymer has insufficient long-term storage stability and moisture and heat resistance, which causes problems such as reduction in strength and molecular weight and deteriorated appearance. Such an article cannot endure applications where it is subjected to either repeated or prolonged use.

When biodegradable biopolymers are used in water for marine materials such as a fisherman's net, service life thereof is limited to a very short period. Furthermore, dyeing a fabric made of biodegradable fibers at high temperature in an aqueous solution dispersed with dye abruptly decreases the tear strength of the fabric. Thus, only dyeing under comparatively low-temperature conditions is tolerated, which in turn makes deep color dyeing impossible (EP1564316 A1, 2005, NISSHIN SPINNING).

Therefore, there are good reasons to suppress the degradability of environmentally disposable biopolymers during their service life, or if desired, to prolong their lifetime. The following are ways of suppressing the biodegradation of biopolymers (see also Table 7.1):

1. Control of the physical features of the biopolymer:
 - (a) Structure (chemical structure, higher molecular weight).
 - (b) Morphology (stereoisomerism, increased crystallinity, orientation).
 - (c) Composition (reduced number of impurities or residues).
 - (d) Form (less porosity, smaller surface area, higher density).

- (e) Condition of the article (physical aging, processing conditions).
2. Modification of the polymer backbone (hydrophobic bonds, grafts with hydrophobic groups).
3. Functional group-capping agents and catalyst-deactivating agents.
4. Desiccants (blotting compounds).
5. Antibacterial (antibiotic) compounds.
6. Antioxidants, UV and light stabilizers.
7. Cross-linking.
8. Plasticizers.
9. Blending with other polymers.
10. Physical separation of degradation additives (e.g., by encapsulation or coating).
11. Coatings.
12. Surface modification.

7.2.1 Control of the Physical Features of the Biopolymer

7.2.1.1 Structure (chemical structure, higher molecular weight)

Poly(lactide) (PLA) has a bulky methyl group that resists the attack of water molecules; hence it is hydrophobic and has a slower degradation rate compared to polyglycolide (PGA), which is easily attacked by water. PGA has no bulky methyl group in its chemical structure and hence it is hydrophilic and undergoes faster degradation.

Increasing the molecular weight (i.e., chain length) of a biopolymer decreases its degradability. Poly(ϵ -caprolactone) (PCL) with higher molecular weight ($M_n > 4000$) was degraded more slowly by *Rhizopus delemar* lipase than that with low M_n [1].

7.2.1.2 Morphology (stereoisomerism, increased crystallinity, orientation)

The morphology of polymers also greatly affects their rates of biodegradation. The crystalline part of a biopolymer is more resistant to degradation than the amorphous region. The rate of degradation of PLA decreases with an increase in crystallinity of the polymer [2,3]. As shown in Figure 7.1, the melting temperature (T_m) of aliphatic polyesters has a strong effect on the enzymatic degradation of polymers [4].

Table 7.1 Suppression of biodegradability

Biopolymers	Ways of suppressing biodegradability	Conditions/compounds	Patents
PGA	Increasing molecular orientation	Stretching	WO2007060981 A1 (2007, KUREHA CORP)
PLA	Reduced number of impurities or residues	≤ 2 wt.% low molecular weight compounds of $M_n \leq 1000$ (lactic acid, lactide, and lactyl lactate)	JPH07316272 A (1995, TOYOBO CO LTD)
PLA (fibers)	Reduced number of impurities or residues	≤ 1 wt.% low molecular weight (lactic acid, lactide, and lactyl lactate); preferably ≤ 0.3 wt. %	JPH0921018 A (1997, TOYOBO CO LTD)
PLA	Reduced number of impurities or residues	Low molecular weight compounds (linear or cyclic oligomers)	JPH0912688 A (1997, TOYOBO CO LTD); JP2005023218 A (2005, TOYOBO CO LTD)
Aliphatic polyester	Polymerization reaction system in the molten state under reduced pressure	Substantially free from low molecular weight compounds	JPH0912690 A (1997, TOYOBO CO LTD)
PGA	Treat PGA particles with high-temperature dry gas	~ 0.2 wt.% residual monomer	US3565869 A (1971, AMERICAN CYANAMID CO)
PGA	Treat molten PGA under reduced pressure	≤ 2 wt.% residual monomer	EP0368571 A2 (1990, MITSUI TOATSU CHEMICALS)
Aliphatic polyesters (PHB), cellulose derivative, polypeptide, PVOH, natural polymers	Grafting hydrophilic monomers	(Meth)acrylic acid, hydroxyethyl (meth)acrylate, acrylamide, vinyl acetate, vinyl propionate, vinyl butyral	JP2006225427 A (2006, JAPAN ATOMIC ENERGY AGENCY; UNIV GUNMA)
PLA (medical device)	Neutralization of carboxyl end-groups	Inorganic coral, caffeine	CA2605791 A1 (2008, CORDIS CORP)
PLA	Functional group-capping agent	Aliphatic alcohol	JPH07316273 A (1995, TOYOBO CO LTD)
PLLA (fibers)	Functional group-capping agent	Aromatic monocarbodiimide (<i>N,N'</i> -di-2,6-diisopropyl phenyl carbodiimide); ≤ 1 wt.% low molecular weight compounds (lactic acid, lactide and lactyl lactate)	JP2001261797 A (2001, TORAY IND INC)
PLLA (fibers)	Functional group-capping agent	Polycarbodiimide	JP2003301327 A (2003, TORAY IND INC)

Table 7.1 Suppression of biodegradability (*Continued*)

Biopolymers	Ways of suppressing biodegradability	Conditions/compounds	Patents
PGA	Carboxyl group-capping agent & thermal stabilizer	Carboxyl group-capping agent: carbodiimide compound, epoxy compound; Thermal stabilizer: cyclic neopentane-tetra- <i>il</i> -bis(2,6-di- <i>tert</i> -butyl-4-methylphenyl) phosphite, cyclic neopentane-tetra- <i>il</i> -bis(2,4-di- <i>tert</i> -butylphenyl) phosphite, cyclic neopentane-tetra- <i>il</i> -bis(octadecyl) phosphite; alkyl phosphates, alkyl phosphites having an alkyl group of 8–24 carbons; mono-or di-stearyl acid phosphate or a mixture of these; metal carbonates: calcium carbonate, strontium carbonate.	WO2007060981 A1 (2007, KUREHA CORP)
PLA, PHB, PBS, PBA	Functional group-capping agents	Lignophenol	CN101130627 A (2008, FUJI XEROX CO LTD)
PGA	Carboxyl group-capping agent & polymerization catalyst-deactivation agent	Carboxyl group-capping agent: carbodiimide, oxazoline, oxazine, epoxy, isocyanurate; Polymerization catalyst-deactivation agent: hydrazine compounds such as bis[2-(2-hydroxybenzoyl)hydrazine] dodecanoic acid; <i>N,N'</i> -bis[3-(3,5-di- <i>t</i> -butyl-4-hydroxyphenyl) propionyl]-hydrazine; 3-(<i>N</i> -salicyloyl)amino-1,2,4-triazole; triazine compounds	WO2007063941 A1 (2007, KUREHA CORP)
Aliphatic polyester, cellulose derivative, polypeptide, PVOH naturally occurring polymer	Grafting a vinyl carboxylate to the biopolymer	Vinyl acetate, vinyl propionate, vinyl butyrate	JP2007112827 A (2006, JAPAN ATOMIC ENERGY AGENCY; UNIVERSITY OF GUNMA)
Polyphosphazene	Inserting hydrophobic side groups	Aryloxy side groups	US6077916 A (2000, PENN STATE RES FOUND)
PLA	Polymerization catalyst-deactivation agent	Hydrazine compound	JPH09124778 A (1997, SHIMADZU CORP)

(Continued)

Table 7.1 Suppression of biodegradability (*Continued*)

Biopolymers	Ways of suppressing biodegradability	Conditions/compounds	Patents
PLA (Lacea [®] H-100J)	Physical aging & hydrolysis stabilizer & inorganic filler	15°C + T _g ≤ T ≤ 120°C & RH ≥ 60% carbodiimide & mica	US2002030305 A1 (2002, SONY CORP); JP2002173583 (2002, SONY CORP)
PLA (fibers)	Processing conditions	Lowering of spinning temperature	JPH0921017 A (1997, TOYOBO CO LTD)
PLA, PBSA	Hydrolysis stabilizer	(Poly)carbodiimide: 4,4'-dicyclohexylmethanecarbodiimide	JPH1180522 A (1999, NISSHIN SPINNING)
PLA (Lacty [®] 9000, NatureWorks 4031D) (film)	Hydrolysis stabilizer	Polycarbodiimide: poly(4,4'-diphenylmethane carbodiimide), poly(<i>p</i> -phenylene carbodiimide), poly(<i>m</i> -phenylene carbodiimide), poly(tolyl carbodiimide), poly(diisopropyl phenylene carbodiimide), poly(methyl-diisopropylphenylene carbodiimide), poly(triisopropylphenylene carbodiimide) (Stabaxol [®] P100)	JP2003003052 A (2002, MITSUBISHI PLASTICS IND)
PLA, PHB, PCL (Tone [®]), PES (Lunarle SE [®]), PBS, PBSA (Bionolle [®]), PBST (Biomax [®]), PBAT (Ecoflex [®] , EnPol [™]) (fibers)	Hydrolysis stabilizer	Aliphatic carbodiimide & fiber	EP1564316 A1 (2005, NISSHIN SPINNING)
PLA, PHB, PCL (Tone [®]), PES (Lunarle SE [®]), PBS, PBSA (Bionolle [®]), PBST (Biomax [®]), PBAT (Ecoflex [®] , EnPol [™])	Hydrolysis stabilizer	PLA-modified carbodiimide	WO2007091427 A1 (2007, NEC CORP)
Poly(ester amide)s: BAK [®] 1095 BAK [®] 2195; aliphatic polyester(s); aliphatic-aromatic polyester(s); poly(ester carbonate)s; poly(ester urethane)s	Hydrolysis stabilizer(s) and/or antimicrobial agent(s)	Aromatic polycarbodiimide: Stabaxol [®] P (Stabaxol [®] P100, Stabaxol [®] P200) and/or antibacterial organic compounds: thiurams, thiophthalimides, sulfamides, urea derivatives, triazole derivatives, triazoline derivatives, benzimidazole derivatives, benzimidazolylcarbamic acid derivatives, aryl sulfones, sulfonylsulfamides, phenols, phenolates, thiobenzothiazole derivatives, aminoalcohols, isothiazolinones, benzothiazoles, pyrethroids	DE19754418 A1 (1999, BAYER AG)

Table 7.1 Suppression of biodegradability (*Continued*)

Biopolymers	Ways of suppressing biodegradability	Conditions/compounds	Patents
PLA: PLLA, PDLA, PLGA (adhesive film)	UV absorber(s)/light stabilizer(s)	Benzophenones, benzotriazoles, sebacates	EP0587069 A1 (1994, MITSUI TOATSU CHEMICALS INC)
PLA, PGA, PCL, PHP, PHB, PHV, PES, PBS, PESA, PBSA (mulch film)	UV absorber/optical stabilizer	UV absorber: benzophenone-type absorber, triazine-type absorber, phenolic-acid ester-type absorber, benzotriazole-type absorber; optical stabilizer: hindered amine-type, benzoate-type compound	JP2005089537 (2005, DAICEL CHEM IND LTD)
PLA	UV absorber/light stabilizer(s) & plasticizer	2-Hydroxy-4- <i>n</i> -octoxybenzophenone & glycerol triacetate	JPH06184417 A (1994, MITSUI TOATSU CHEM INC)
PLA	Antioxidant	Phenol phosphite compound	JP2001049097 A (2001, MITSUI CHEMICALS INC)
PLA	Oxidation stabilizer	Hydrophobic rutile-type TiO ₂ surface-treated with an organic substance	JP2004075727 A (2004, AICHI PREFECTURE; TSUJI HIDETO; UNITIKA LTD)
PLA, PHB, PCL (Tone [®]), PES (Lunare SE [®]), PBS, PBSA (Bionolle [®])	Hydrolysis stabilizer & antioxidant	Carbodiimide & hindered phenol & phosphite	EP1354917 A1 (2003, NISSHIN SPINNING)
PLA, PHB, PCL (Tone [®]), PES (Lunare SE [®]), PBS, PBSA (Bionolle [®]), PBST (Biomax [®]), PBAT (Ecoflex [®] , EnPol [™])	UV absorbers/light stabilizer(s) & hydrolysis stabilizer	Benzotriazole, triazine, hydroxylamine & carbodiimide (Carbodilite [®] HMV-10B, Carbodilite [®] HMV-8CA, Stabaxol [®] P)	EP1418201 A1 (2004, NISSHIN SPINNING)
PLA, PHB, PCL (Tone [®]), PES (Lunare SE [®]), PBS, PBSA (Bionolle [®]), PBST (Biomax [®])	Hydrolysis stabilizer & antioxidant	Aliphatic carbodiimide & phosphite organic compound (e.g., bis(2,4-di- <i>tert</i> -butylphenyl) pentaerythritol-diphosphite)	US2005054755 A (2005, NISSHIN SPINNING)
PLA (Lacea [®] H-400), PHB, PHBHP, PHBHV, PES (Lunare SE [®]), PCL (Tone [®] , Placcell [®]), PBS, PBSA (Bionolle [®]), PBST (Biomax [®]), PBAT (Ecoflex [®] , EnPol [™])	Hydrolysis stabilizer & UV absorbent & antioxidant	Aliphatic polycarbodiimide & UV absorbent: benzotriazole-based compound, a triazine-based compound, hydroxylamine-based compound; Antioxidant: hindered phenol-based, phosphite organic compound	EP1854837 A2 (2007, NISSHIN SPINNING)

(Continued)

Table 7.1 Suppression of biodegradability (*Continued*)

Biopolymers	Ways of suppressing biodegradability	Conditions/compounds	Patents
PLA	Hydrolysis stabilizer & antioxidant(s)	Layered silicate & carbodiimide & phosphite organic compound (e.g., bis(2,4-di- <i>tert</i> -butylphenyl) pentaerythritol-diphosphite)	WO2006118096 A1 (2006, UNITIKA LTD; SHISEIDO CO LTD)
Aliphatic polyesters, aliphatic-aromatic copolyesters (PBAT)	Antioxidant resin	Phenol-terpene resin (NIREZ [®])	WO0222737 A2 (2002, EASTMAN CHEM CO)
PHBHV	Antibacterial (antibiotic) compounds	Antibacterial metal compounds: silver, copper, zinc	JPH0551073 A (1993, TOPPAN PRINTING CO LTD)
PHA, PHBHV (Biopole [®] 530), PCL (Placel [®]), PVOH, starch, chitin-chitosan	Antibacterial compounds	β -Lactam type compounds: penicillin, cephalosporin; puromycin, tetracycline erythromycin; azacerine, acridine, actinomycin; phenols, quaternary ammonium salts, cyclic peptides; silver ions and its complex compounds	GB2281709 A (1995, FUJITSU LTD)
Polyalkylene alkanoates, PCL	Blending with other polymers	Blending polyalkylene alkanoates or PCL with PHB	JP2000129105 A (2000, MITSUBISHI GAS CHEMICAL CO)
PLA	Blending with other polymers	Blending PLA with phosphine-based polymer	US2010144979 A1 (2010, IND TECH RES INST)
PBS, PBSA, PCL	Blending with other polymers	PLA	WO02094935 A (2002, DAICEL CHEM)
PLLA, PGA, PCL, PES and PBS (Bionolle [®])	Blending with hydrophobic or hydrophilic polymers; suppression or acceleration of biodegradation	Non-biodegradable polymer: polyesters, aliphatic polyamides (nylon), polystyrene, polyolefins & compatibilizer: ionomer resin, oxazoline-based compatibilizer, elastomer-based compatibilizer, reactive compatibilizer, copolymer-based compatibilizer	JP2005220238 A (2005, OSAKA GAS CO LTD)
PLA	Photocatalyst coated with inorganic compound	Titanium oxide, zinc oxide, zirconium oxide, strontium titanate, titanium hydroxyapatite, or mixtures	WO2008038350 A1 (2008, FUJITSU LTD)
PVOH	Encapsulated microorganisms or enzymes	<i>Pseudomonas vesicularis</i> sealed in a polyamide microcapsule	JP2002356623 A (2002, TOYOTA MOTOR CORP)

Table 7.1 Suppression of biodegradability (*Continued*)

Biopolymers	Ways of suppressing biodegradability	Conditions/compounds	Patents
Aliphatic polyesters, aliphatic-aromatic polyesters, poly(ester urethane)s, poly(ester carbonate)s, poly(ester amide)s (BAK [®] 403-004, BAK [®] 404-002)	Coating	Cellulose esters: cellulose acetate, cellulose butyrate, cellulose propionate, cellulose nitrate (N ₂ content > 12.6%) & plasticizers	DE19911209 A1 (2000, WOLFF WALSRODE AG)
PDLA	Hydrophobic coating	PLLA, PTMG	US2002123546 A1 (2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC); WO9406866 A1 (1994, BIOPAK TECHNOLOGY LTD)
PDLA	Surface halogenation	Fluorine gas and a light catalyst	US2002123546 A1 (2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC); WO9406866 A1 (1994, BIOPAK TECHNOLOGY LTD)
PDLA	Thin surface layer of highly cross-linked material formed by plasma polymn.	Hydroxycarboxylic acid monomer exposed to ionizing radiation	US2002123546 A1 (2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC); WO9406866 A1 (1994, BIOPAK TECHNOLOGY LTD)

Abbreviations: PHB, Poly(3-hydroxybutyrate); P3HB4HB, Poly(3-hydroxybutyrate-co-4-hydroxybutyrate); P4HB, Poly(4-hydroxybutyrate); P4HB2HB, Poly(4-hydroxybutyrate-co-2-hydroxybutyrate); PBA, Poly(butylene adipate); PBAT, Poly(butylene adipate-co-terephthalate); PBS, Poly(butylene succinate); PBSA, Poly(butylene succinate-co-adipate); PBST, Poly(butylene succinate-co-terephthalate); PCL, Poly(ϵ -caprolactone); PDLA, Poly(D-lactide); PES, Poly(ethylene succinate); PESA, Poly(ethylene succinate-co-adipate); PGA, Polyglycolide; PHA, Poly(hydroxyalkanoate); PHP, Poly(3-hydroxypropionate); PHBHD, Poly(3-hydroxybutyrate-co-3-hydroxydecanoate); PHBHP, Poly(3-hydroxybutyrate-co-3-hydroxypropionate); PHBHx, Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); PHBO, Poly(3-hydroxybutyrate-co-3-hydroxyoctanoate); PHBHV, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PHV, Poly(3-hydroxyvalerate); PLA, Polylactide; PLGA, Poly(lactide-co-glycolide); PLLA, Poly(L-lactide); PVOH, Poly(vinyl alcohol).

A general trend is that the higher the T_m , the lower the biodegradation of the aliphatic polyester [1,5,6].

Crystalline PLA (PLLA or L,L-PLA) is less susceptible to degradation than PDLA or D,L-PLA. The amorphous content of PLA can be regulated by increasing the ratio of D- and L-lactide. The rate at which a highly crystalline PLA degrades is typically about two to three times longer than the rate at which an amorphous PLA degrades (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD).

The degradation rate depends not only on the crystallinity, but also on the molecular orientation of the biopolymer. It has been found that poly(butylene succinate) (PBS) and poly(butylene succinate-co-lactide) (PBSL) fiber samples have poorer degradability than the corresponding film samples. The poorer degradability is attributed to the higher molecular orientation of the polymer chains rather than to the difference in crystallinity. Even in the amorphous region of the drawn fibers, the polymer chains should have a stretched and oriented conformation. The ester linkages in these polymer chains

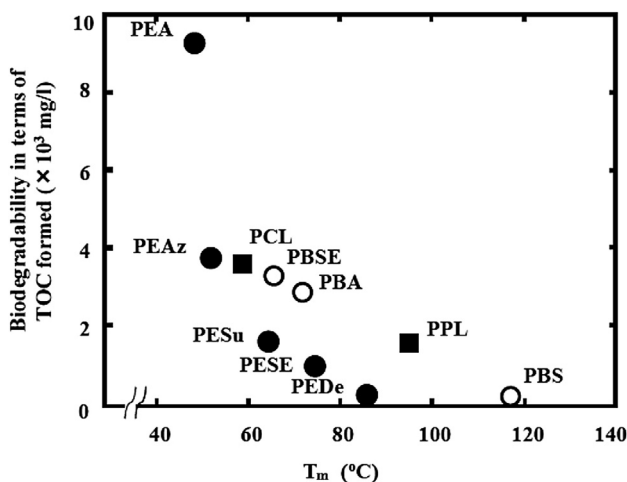


Figure 7.1 Relationship between T_m and biodegradability of aliphatic polyesters by *Rhizopus arrhizus* lipase in terms of TOC (total organic content) [4].

Abbreviations: PEA, Poly(ethylene adipate); PESu, Poly(ethylene suberate); PEAz, Poly(ethylene azelate); PESE, Poly(ethylene sebacate); PEDe, Poly(ethylene decamethylate); PBS: Poly(butylene succinate); PBA, Poly(butylene adipate); PBSE, Poly(butylene sebacate); PCL, Poly(ϵ -caprolactone); PPL, Poly(β -propiolactone).

are difficult for enzymes to attack. Particularly in PBS fibers, the ester linkages are more resistive to enzymatic hydrolysis [7]. According to **WO2007060981 A1** (2007, KUREHA CORP) the hydrolysis resistance of PGA can be enhanced by increasing the molecular orientation of PGA through stretching.

7.2.1.3 Composition (reduced number of impurities or residues)

The presence of residual monomer (ca. 2–8% of unreacted cyclic ester) in an aliphatic polyester shortens the useful life of the material; it is desirable to reduce the residual monomer to as small an amount as possible. For this reason, several methods have been proposed for reduction of the residual monomer in aliphatic polyesters. **JPH07316272 A** (1995, TOYOBO CO LTD) discloses a PLA and/or its copolymer containing 2 wt.% or less of low molecular weight compounds having an average molecular weight of 1000 or less. **JPH0921018 A** (1997, TOYOBO CO LTD) discloses a biodegradable fiber for nonwoven fabric consisting of PLA and/or a copolymer composed mainly of PLA with the

content of low molecular weight compounds (lactic acid, lactide, and lactyl lactate) brought to 1 wt.% or less (preferably ≤ 0.3 wt.%). According to **CA2411004 A1** (2003, KURARAY CO), these two inventions are for retarding the biodegradation of the fibers while in use, but they take nothing into consideration relating to promoting the biodegradation of the fibers after use, or for controlling or retarding the biodegradation rate of the fibers while in use. In addition, the biodegradability of the fibers and nonwoven fabrics that have such stabilized physical properties is on the level that they may lose their strength in a period of time from a half year to one year after they are buried in the ground. This means that fibrous wastes of this type require a long period of time (possibly years) until they biodegrade once buried in the ground. They are therefore unsuitable for land reclamation.

The hydrolyzability of PGA is also related to the residual glycolide content. When it contacts with water, the residual glycolide in PGA is decomposed into glycolic acid dimer and dissociated to function as a terminal carboxyl group concentration in a proportion of a little more than 60% thereof (**WO2005090438 A1**, 2005, KUREHA CORP).

US3565869 A (1971, AMERICAN CYANAMID CO) discloses a method for removing monomers and low molecular weight volatile substances from PGA by contacting particles of PGA (milled product) with a high temperature inert gas, thereby providing PGA with a reduced residual monomer (down to possibly ca. 0.2 wt.%). **EP0368571 A2** (1990, MITSUI TOATSU CHEMICALS) claims that the method of **US3565869 A** cannot effectively remove the volatile substances such as monomers because the polymer is solid. It takes more than several tens of hours to reduce the amount of residual monomer to 2% or less. The polymer decomposes during the treatment and the molecular weight decreases.

EP0368571 A2 (1990, MITSUI TOATSU CHEMICALS) proposes instead a reduced pressure treatment of the resultant polymer in a molten state. **JPH0912690 A** (1997, TOYOBO CO LTD) proposes an alternative method of reducing the pressure of the inside of the polymerization reaction system in the molten state of the polymer to obtain an aliphatic polyester substantially free from low molecular weight compounds. **JPH0912688 A** (1997, TOYOBO CO LTD) and **JP2005023218 A** (2005, TOYOBO CO LTD) also disclose methods for the extension of the degradation period of an aliphatic

polyester (PLA) by reducing unreacted monomers, impurities, and low molecular weight compounds such as linear or cyclic oligomers in the biopolymer (PLA). To remove impurities in the polyester, the resin is brought into contact with a supercritical fluid extractant in combination with water and/or an organic solvent. Preferably, the extractant is carbon dioxide and the organic solvent is one or more of the following: alcohols, ethers, ketones, or esters.

However, according to the methods in these patents, the reduction of residual monomer was insufficient. It was difficult to obtain an aliphatic polyester with a residual monomer of 0.3 wt.% or less, so adverse effects to the lowering in properties of the aliphatic polyesters remained at a non-ignorable level (WO2005090438 A1, 2005, KUREHA CORP).

WO2005090438 A1 (2005, KUREHA CORP) discloses a method for producing an aliphatic polyester with a reduced content of residual cyclic ester, more specifically a securely reduced amount of less than 0.2 wt.%, of residual monomer. According to invention described, an aliphatic polyester obtained by ring-opening polymerization of a cyclic ester (a glycolide or a mixture of glycolide and lactide), wherein the latter half of the polymerization period is preceded by solid-phase polymerization, is subjected to a residual monomer removal step (i.e., a step that removes the residual cyclic ester by releasing it to a gas phase). More specifically, the aliphatic polyester in a solid or molten state is brought into contact with a heated dry gas or is subjected to reduced pressure. In order to suppress depolymerization of the polyester that might also occur in this step, it is preferable to perform the polymerization in a solid particle state rather than in a molten state.

7.2.1.4 Form (less porosity, smaller surface area, higher density)

The role of porosity, surface area, and density is analyzed in [Section 7.3.1.4](#).

7.2.1.5 Condition of the article (physical aging, processing conditions)

JPH0921017 A (1997, TOYOBO CO LTD) discloses a technique to decrease the concentration of terminal carboxylic groups in a PLA fiber by lowering spinning temperature and capping terminal carboxylic groups with an aliphatic alcohol (see also [Section 7.2.3: Functional Group-Capping Agents and](#)

Catalyst-Deactivation Agents; **JPH07316273 A**). However, because the melt viscosity of an aliphatic polyester (PLA) has a relatively high dependency on temperature, there has been a problem: in order to spin at low temperature, it is necessary to decrease the molecular weight of the polymer sufficiently, which makes it difficult to obtain a PLA fiber with high strength.

US2002030305 A1 and **JP2002173583 A** (2002, SONY CORP) disclose a method for improving the elastic modulus of a biodegradable resin composition used for molded products. The biodegradable resin composition is placed in a humidifying environment maintained above the glass transition temperature (T_g) for a predetermined period, preferably in the temperature range $15^\circ\text{C} + T_g \leq T \leq 120^\circ\text{C}$ and at a relative humidity (RH) from 60 to 80%. The “aging” period (heat treatment) is selected to raise the elastic modulus of the biodegradable resin composition as high as 10^8 Pa (80°C), and is within a range from 5 min to 3.5 h. The biodegradable resin composition contains PLA (Lacea[®] H100J), and optionally 0.1–2 wt.% carbodiimide for suppressing hydrolysis, and mica as an inorganic filler. The method provides a simple and rapid procedure for improving the heat resistance (by measuring the elastic modulus before and after aging) of a biodegradable resin composition while retaining an ample strength, waterproof property, and moldability, as well as ensuring a rapid degradability (upon disposal) by common soil microorganisms.

7.2.2 Modification of the Polymer Backbone (Hydrophobic Bonds, Grafting)

JP2006225427 A (2006, JAPAN ATOMIC ENERGY AGENCY; UNIVERSITY OF GUNMA) discloses a method to suppress the biodegradability of a biopolymer used for agricultural film by grafting a hydrophilic monomer to the biopolymer. By treating the biopolymer with heat, the biodegradability is recovered and the biopolymer is decomposed by subterranean microorganisms after it is discarded. The hydrophilic monomer is one of the following: acrylic acid, methacrylic acid, hydroxyethyl acrylate, hydroxyethyl methacrylate, acrylamide or acrylamide derivative, or vinyl acetate. The biodegradable polymer is an aliphatic polyester such as poly-(3-hydroxybutyrate) (PHB), cellulose derivative,

polypeptide, poly(vinyl alcohol) (PVOH), or a naturally occurring polymer.

In a related publication by the same inventors [8], radiation-induced graft polymerization of acrylic acid (AAc) was carried out on a PHB and the resulting film was thermally remolded. The PHB films grafted with AAc (PHB-g-AAc) and a degree of grafting higher than 5% completely lost the enzymatic degradability. The enzymatic degradability of the grafted film was recovered by thermal remolding. The highest enzymatic degradation rate was observed at a degree of grafting of 10% after thermal remolding. The enzymatic degradability of PHB-g-AAc films was lost by the grafted AAc, which covered the surface of PHB film. The acceleration of enzymatic degradation in the remolded PHB-g-AAc films was mainly caused by a decrease of PHB crystallinity by disperse of the grafted AAc during thermal remolding.

In an alternative method the biodegradability of the biopolymer is suppressed by grafting a vinyl carboxylate to the biopolymer. The biodegradability of the biopolymer is recovered after discarding by hydrolysis using an alkaline solution. The carboxylic acid vinyl ester is preferably vinyl acetate, vinyl propionate, or vinyl butyrate (JP2007112827 A, 2006, JAPAN ATOMIC ENERGY AGENCY; UNIVERSITY OF GUNMA).

The hydrophobicity of polyphosphazenes can be increased by adding hydrophobic side groups, such as aromatic groups, to the backbone. For example, the degradation rate of these polymers can be modulated by incorporating aryloxy side groups, which are known to retard polyphosphazene backbone hydrolysis (US6077916 A, 2000, PENN STATE RES FOUND) [9].

7.2.3 Functional Group-Capping Agents and Catalyst-Deactivation Agents

Functional group-capping agents are compounds that cap functional terminal groups. They are known as hydrolysis-suppressing agents for improving the moisture-resistance of biodegradable biopolymers. Hydrolysis-suppressing agents exhibit reactivity with active hydrogen contained in the biodegradable biopolymers. Active hydrogen means hydrogen bonded with oxygen or nitrogen (an O—H or N—H bond). This hydrogen is higher in reactivity than hydrogen in the carbon-hydrogen bond (C—H). More specifically, such active hydrogen is present in

a carboxylic group (—COOH), a hydroxy group (—OH), an amino group (—NH₂), or in an amido linkage (—NHCO—) in the biodegradable biopolymer. By adding these suppressing agents, it becomes possible to reduce the amount of active hydrogen in the biodegradable biopolymer, thus preventing the molecular chain from being catalytically hydrolyzed by the active hydrogen. As a result, the hydrolysis of the biodegradable polymer is delayed and the mechanical properties of the material, such as tensile strength and impact strength, are maintained for a prolonged period of time.

A technique to cap the terminal carboxylic groups of PLA by condensation with an aliphatic alcohol is disclosed in JPH07316273 A (1995, TOYOBO CO LTD). However, this capping technique is a condensation reaction that requires the removal of reaction byproducts, which presents problems. For example: polymerization rate is low, so industrial production is impossible; or many unreacted materials with low molecular weight remain, and since they vaporize in molding, appearance of the molded article is inferior; or thermal resistance of the article is poor. Another problem is that during remelting and molding of a polymer with capped terminals (obtained by a condensation reaction), terminal carboxylic groups are regenerated, which creates uncapped terminal ends. This makes hydrolysis resistance of molded articles insufficient (EP1564316 A1, 2005, NISSHIN SPINNING).

Other compounds that have reactivity to the active hydrogen in the biodegradable biopolymer are carbodiimides, isocyanates, and oxazolines. In particular, the carbodiimide compound (—N=C=N—) is preferred since this compound may be melted and kneaded with a biodegradable high molecular weight biopolymer; it is sufficient to add a small amount thereof to suppress hydrolysis more effectively. The carbodiimide controls the hydrolysis in the initial reaction after the addition by reacting with the hydroxyl or carboxyl groups remaining in the biodegradable biopolymer, or after that, by bonding to the linkages of a biodegradable polymer cleaved by hydrolysis, thus recombining them (EP1564316 A1, 2005, NISSHIN SPINNING).

JPH1180522 A (1999, NISSHIN SPINNING) discloses a biodegradable biopolymer composition with an adjustable biodegradation rate and usefulness as a material for agriculture, forestry, and fisheries. These materials include such articles as a film and a planting pot, and earthwork items such as

a water-retaining sheet for a plant. They are made by incorporating a carbodiimide compound into the biodegradable polymer. The biodegradable biopolymer composition comprises 100 parts by weight of an aliphatic polyester such as poly(butylene succinate-*co*-adipate) (PBSA) or PLA, and a compound having one or more carbodiimide groups in it, such as 4,4'-dicyclohexylmethanecarbodiimide (preferably 0.01–10 parts by weight). The mixing method is exemplified by melt-kneading with an extruder. However, the composition does not improve hydrolysis resistance to a sufficient extent. Furthermore, the composition has the additional problem of reduced transparency. In particular, an attempt to enhance the hydrolysis resistance of a PLA-based product by increasing the amount of the carbodiimide resulted in loss of transparency (EP1354917 A1, 2003; EP1854837 A2, 2007, NISSHIN SPINNING). Furthermore, a compound with a low molecular weight (e.g., monocarbodiimide) has problems such as causing environmental pollution by generating a component with an offensive odor, or losing the addition effect thereof by vaporization because of the tendency for easy thermal decomposition during processing.

JP2001261797 A (2001, TORAY IND INC) discloses an aliphatic polyester such as PLLA and a molded article such as a fiber or a film comprising the same. These are characterized in that some or all of the terminal carboxyl groups of the aliphatic polyester are capped with an aromatic monocarbodiimide compound such as *N,N'*-di(2,6-diisopropyl phenyl)carbodiimide; a 5% weight reduction measured by TG-DTA is exhibited at a temperature $\geq 170^\circ\text{C}$ (for instance, the concentration of terminal carboxyl groups is not higher than 10 equivalents per 10^3 kg of aliphatic polyester). According to EP1564316 A1 (2005, NISSHIN SPINNING), fibers of PLLA wherein the terminal carboxyl groups are capped with an aromatic monocarbodiimide compound as disclosed in JP2001261797 (2001, TORAY IND INC), have poor weatherability to sunshine.

JP2003301327 A (2003, TORAY IND INC) discloses a PLLA fiber improved in hydrolysis resistance and having a good color tone by blocking the carboxylic terminals with a polycarbodiimide compound. The PLLA fiber exhibits a b^* value, which is an index of color tone, of not higher than 7. In fibers of PLLA wherein the terminal carboxyl groups are capped with a polycarbodiimide compound as disclosed in JP2003301327 A (2003,

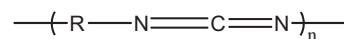
TORAY IND INC), the problem of poor thermal stability (or thermal resistance) in fiber production is adjusted by spinning conditions and by the addition of an amount of a polycarbodiimide compound. However, this method still had the problem that the appropriate condition range was narrow, resulting in a non-stable quality, and additionally, insufficient levels of color hue stability (e.g., yellowing) and hydrolysis resistance, which yielded no durability in dye processing of a fiber article. There was also a problem of insufficient durability after producing an article (EP1564316 A1, 2005, NISSHIN SPINNING).

In general an aliphatic polyester compounded with a carbodiimide shows yellowing progressed by heat, thermal oxidation, and the like. Yellowing becomes more significant with an increase in the amount of carbodiimide compounded into the aliphatic polyester.

JP20033003052 A (2002, MITSUBISHI PLASTICS IND) provides an aliphatic polyester composition for producing a biodegradable film comprising 100 parts by mass of aliphatic polyester such as PLA (e.g., Lacty[®] 9000, NatureWorks 4031D), 0.05–10 parts by mass of a polycarbodiimide compound, and optionally, a plasticizer. The aliphatic polyester composition exhibits enhanced hydrolysis resistance without substantially deteriorating the biodegradability inherent in the aliphatic polyester. The polycarbodiimide compound contains a group with the formula shown in Scheme 7.1.

When n is 10–100, the polycarbodiimide improves the hot humid hydrolysis resistance of the resin composition. When $n < 10$, the polycarbodiimide has the tendency to deactivate quickly at high temperature. When $n > 100$ it becomes easily cloudy at the time of addition, or there is hardly any improvement to the hydrolysis resistance of the resin composition.

DE19754418 A1 (BAYER, 1999) also discloses a method aiming at an extension of the degradation period by compounding an aromatic (poly)carbodiimide as a hydrolysis stabilizer and/or an antibacterial agent to the biodegradable polymer.



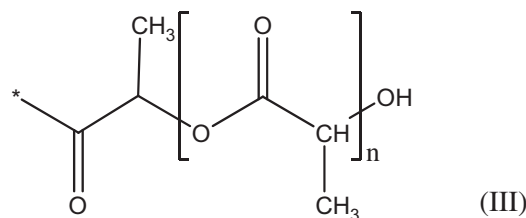
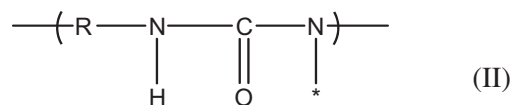
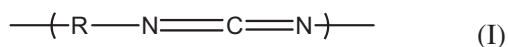
Scheme 7.1 Polycarbodiimide.

n : 1 or more; and R: aliphatic, alicyclic or aromatic bonding unit.

Suitable polymers are aliphatic polyesters, aliphatic-aromatic polyesters, poly(ester carbonate)s, poly(ester urethane)s, and poly(ester amide)s; the most preferable are poly(ester amide)s (e.g., BAK[®] 1095 and BAK[®] 2195). Recommended commercial aromatic (poly)carbodiimides are Stabaxol[®] P, Stabaxol[®] P100, and Stabaxol[®] P200. Suitable antibacterial organic compounds are thiurams, thiophthalimides, sulfamides, urea derivatives, triazole derivatives, triazoline derivatives, benzimidazole derivatives, benzimidazolylcarbamic acid derivatives, aryl sulfones, sulfonylsulfamides, phenols and phenolates, thiobenzothiazole derivatives, amino alcohols, isothiazolinones, benzothiazoles, and pyrethroids. However, the method had a problem of losing transparency of biodegradable polymer products irrespective of the addition amount (EP1354917 A1, 2003; EP1854837 A2, 2007, NISSHIN SPINNING).

EP1564316 A1 (2005, NISSHIN SPINNING) provides a fiber structure with enhanced hydrolysis resistance composed of 10 to 90 wt.% of a fiber (A) comprised of a biodegradable polymer formulated with a carbodiimide compound as a stabilizer against hydrolysis and 10 to 90 wt.% by weight of at least one fiber (B) selected from a natural fiber, a regenerated fiber, a semi-synthetic fiber, and a synthetic fiber. Fiber structures have been subjected to at least one processing treatment selected from scouring processing, bleaching processing, liquid ammonium processing, mercerization processing, biological processing, dyeing processing, and resin treatment. Concentration of total terminal carboxyl groups derived from fiber (A) in said fiber article is not higher than 30 equivalents/ton, and preferably not higher than 1 equivalent/ton, based on fiber (A). The stabilizer against hydrolysis is preferably an aliphatic polycarbodiimide and formulated in a ratio of 0.01 to 5 parts by weight based on 100 parts by weight of the biodegradable biopolymer; optionally, an antioxidant is added such as hindered phenol or phosphite organic compound.

WO2007091427 A1 (2007, NEC CORP) discloses a polylactic acid-modified polycarbodiimide compound that imparts hydrolysis resistance by formulation with PLA and also improves mechanical properties. The PLA-modified polycarbodiimide compound is a grafted copolymer obtained through the addition reaction of the carboxyl group in the PLA (III) with some carbodiimide groups comprising



Scheme 7.2 Polylactic acid-modified polycarbodiimide compound obtained by grafting polylactic acid (III) to carbodiimide groups comprising the structural unit (I) in the molecular chain of a polycarbodiimide compound and thereby forming the structural unit (II) bound with the polylactic acid group (III); wherein in the formulas (I) and (II), R is a divalent aliphatic, alicyclic, or aromatic hydrocarbon skeleton comprising C and H; the moiety * in the formula (II) is bound with the moiety * in the formula (III); n is any integer of 6 to 210.

the structural unit (I) in the molecular structure of a polycarbodiimide compound and thereby forming the structural unit (II) with the PLA (III) (Scheme 7.2). This reaction does not involve removing redundant by-products from the system. Therefore, for example, the polycarbodiimide compound (e.g., CARBODILITE[®] LA-1) and the PLA can be melt-mixed in a solvent such as chloroform and tetrahydrofuran and subjected to reflux to almost quantitatively obtain the PLA-modified polycarbodiimide compound.

The invention claims to overcome the problems of related arts by improving the compatibility between a polycarbodiimide compound and PLA. Specifically, when a PLA-modified polycarbodiimide compound (which comprises a polycarbodiimide compound partially linked to PLA) having a particular range of molecular weight is formulated with a PLA, the obtained PLA composition maintains high hydrolysis resistance and is largely improved in mechanical properties as compared with the addition of a conventional polycarbodiimide compound.

The hydrolyzability of PGA is also related to the concentration of terminal carboxyl groups, and its

hydrolysis resistance can be enhanced by adding a carboxyl group-capping agent selected from mono- and polycarbodiimide compounds (WO2005090438 A1, 2005, KUREHA CORP).

WO2007060981 A1 (2007, KUREHA CORP) discloses a method of controlling the moisture resistance of PGA at a good accuracy by controlling the contribution of both terminal carboxyl group concentration and residual glycolide content. The following are examples of carboxyl group-capping agents: carbodiimide compounds including monocarbodiimides and polycarbodiimides, such as *N,N*-bis(2,6-diisopropylphenyl)carbodiimide; oxazoline compounds, such as 2,2'-*m*-phenylene-bis(2-oxazoline), 2,2'-*p*-phenylene-bis(2-oxazoline), 2-phenyl-2-oxazoline, and styrene-isopropenyl-2-oxazoline; oxazine compounds, such as 2-methoxy-5,6-dihydro-4*H*-1,3-oxazine; and epoxy compounds, such as *N*-glycidylphthalimide, cyclohexene oxide, and tris(2,3-epoxypropyl) isocyanurate. Among these, carbodiimide compounds and epoxy compounds are preferred. Aromatic carbodiimide compounds are particularly preferred. These carboxyl group-capping agents can be used in combinations of two or more species as desired, and may be used in the following proportions of increasing preference: 0.01–10, 0.1–2, or 0.2–1 parts by weight per 100 parts by weight of PGA.

Residual glycolide in PGA is decreased by adding a thermal stabilizer. Preferred thermal stabilizers include: phosphoric acid esters having a pentaerythritol skeleton, such as cyclic neopentane-tetra-*il*-bis(2,6-di-*tert*-butyl-4-methylphenyl)phosphite, cyclic neopentane-tetra-*il*-bis(2,4-di-*tert*-butylphenyl)phosphite, and cyclic neopentane-tetra-*il*-bis(octadecyl)phosphite; alkylphosphates or alkylphosphites having an alkyl group of preferably 8–24 carbon atoms; mono- or di-stearyl acid phosphate or a mixture of these; and metal carbonates, such as calcium carbonate and strontium carbonate. These thermal stabilizers may be used in the following proportions of increasing preference: 3 (at most), 0.003–1, or 0.01–0.05 weight parts per 100 weight parts of aliphatic polyester. By adding such a thermal stabilizer to a PGA composition, depolymerization of the PGA resin during the glycolide elimination step is suppressed so that it becomes easier to control the residual glycolide and reduce it.

A further study by the same inventors to find combinations of a carboxyl group-capping agent and various thermal stabilizers resulted in **WO2007063941 A1** (2007, KUREHA CORP). This patent discloses

a system comprised of a carboxyl group-capping agent and a polymerization catalyst-deactivation agent used as a thermal stabilizer; this combination provides a PGA composition with a remarkably improved moisture resistance compared to its total carboxyl group concentration. More specifically, it has been disclosed that the combined system obstructs the function of residual glycolide functioning as a carboxyl group source in PGA as proposed in WO2007060981 A1, so that the moisture resistance can be remarkably improved. The result is assumed to be attributable to deactivation of a residual polymerization catalyst by the polymerization catalyst-deactivation agent, which results in suppression of glycolide hydrolysis, thus depriving the glycolide of its function as a carboxyl group source. The PGA composition is based on knowledge of the remarkable improvement in moisture resistance attained by a combined system of a polymerization catalyst-deactivation agent and a carboxyl group-capping agent for a PGA containing residual glycolide. The carboxyl group-capping agent is understood to act on terminal carboxyl groups in the PGA resin to obstruct their hydrolysis-promoting action, thereby improving the moisture resistance of the PGA resin.

A compound that deactivates metal-based polymerization catalysts is used as the polymerization catalyst-deactivation agent. The so-called heavy metal-deactivating agents that show a deactivation function toward heavy metal-based polymerization catalysts (such as tin compounds) are preferred. Preferred compounds are meltable, compatible (i.e., mutually soluble) with PGA, do not cause thermal decomposition, and are capable of forming a complex with a metal at a melt-mixing (extrusion in particular) temperature of ca. 270°C. Specific examples of the polymerization catalyst-deactivation agent include: hydrazine compounds having a –CONHNH–CO– unit, such as bis[2-(2-hydroxybenzoyl)hydrazine] dodecanoic acid, and *N,N'*-bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyl]-hydrazine; 3-(*N*-salicyloyl)amino-1,2,4-triazole; and further triazine compounds. Hydrazine compounds are preferred because they more easily form of a complex with a metal.

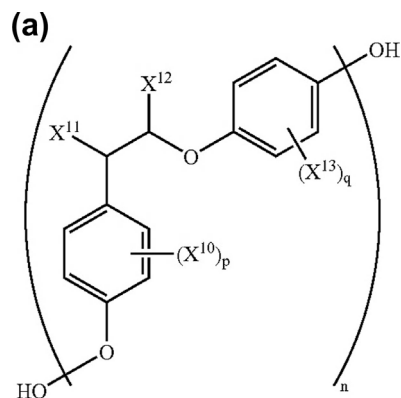
The resistance to thermal degradation of PLA around its melting point can be increased by adding a polymerization catalyst-deactivation agent (**JPH09124778 A**, 1997, SHIMADZU CORP). A high molecular weight PLA free from discoloration, decomposition products, and lactide, having a form suitable for molding and enhanced heat stability, is

obtained by adding a heavy metal deactivator in the latter half or after completion of polymerization. In this process for producing PLA by copolymerizing and/or blending lactic acid as the main minimum constituent unit with another resin, polymerization is conducted at 140–160°C to prevent the racemization of the lactide and the discoloration due to decomposition; the polymerization temperature can also be 120–250°C. The catalyst used is comprised of at least one metal selected from groups IA, IVA, IVB, and VA, or a compound thereof. The molecular weight of the final polymer can be adjusted based on the amount of the catalyst used. The heavy metal deactivator is added in an amount of 0.5- to 10-fold by weight of the catalyst in the latter half, or after completion of polymerization. The heavy metal deactivator comprises, for example, a hydrazine compound. The deactivator is added and low molecular components are removed by reducing the pressure and/or by an inert gas stream (while the polymerization mixture is in a molten state or solid-phase state) to give a high molecular weight PLA with low monomer content.

CN101130627 A (2008, FUJI XEROX CO LTD) discloses a biodegradable resin composition comprising an aliphatic polyester and a lignophenol compound. Examples of the aliphatic polyesters include PLA, PHB, PBS, and poly(butylene adipate) (PBA); of those, the commercially available PLA and PHB are preferred, with PLA of highest preference. The use of lignophenol suppresses polyester hydrolysis and the deterioration of mechanical properties such as impact strength. It is understood that when the lignophenol compound and the polyester react, the terminals of the aliphatic polyester are capped, thereby developing the hydrolysis suppression effect. Examples of the chemical bond formed between the lignophenol compound and the aliphatic polyester compound include an ester bond and an ether bond. Examples where the chemical bond is an ester bond include copolymers obtained by reacting the lignophenol compound represented by the formula in [Scheme 7.3a](#) and the aliphatic polyester compound represented by the formula in [Scheme 7.3b](#).

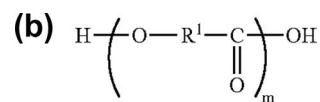
The biodegradable resin composition has improved properties such as oxidation resistance, heat resistance, surface hardness, abrasion resistance, weather resistance, and recycling efficiency.

Caffeine is another compound known to slow polymer degradation. Polymer medical devices highly loaded with caffeine reduce degradation due



Scheme 7.3a Lignophenol.

X^{10} and X^{13} , which may have a substituent, each independently represents an alkyl group, an aryl group, or an alkoxy group; X^{11} and X^{12} each independently represents an alkyl group, an aryl group, an alkyl-substituted aryl group or a group of an alkyl group, an aryl group or an alkyl-substituted aryl group each having a hydroxyl group, a carboxylic acid group or a carboxylic acid derivative group bonded thereto as a substituent; p and q each independently is an integer from 1 to 4; n is an integer from 1 to 10.



Scheme 7.3b Aliphatic polyester.

R^1 represents a linear or branched alkylene group; and m is an integer of 1 or more.

to neutralization of carboxyl end-groups, while caffeine-free polymer implants exhibit accelerated degradation due to autocatalysis (CA2605791 A1, 2008, CORDIS CORP).

7.2.4 Desiccants (Blotting Compounds)

Another possibility for the retardation of the degradation rate in biopolymers involves the use of desiccants (blotting compounds). Desiccants are compounds that attract and absorb substances that promote degradation, such as moisture and degradation products (e.g., acidic groups). As such, desiccant compounds can retard the rate at which disposable materials degrade. However, once the desiccant compounds are saturated, the degradation rate will accelerate. Use of an appropriate amount of

a desiccant compound allows for desiccant compound saturation to occur soon after the beginning of the disposal stage, which leads to an accelerated disposal degradation rate relative to the operative degradation rate. Desiccant compounds are particularly useful for stabilizing disposable materials during processing stages, such as packaging manufacture, when the materials are exposed to high temperatures and/or water. Preferred desiccant compounds are essentially not volatile at the temperatures at which polymer formation or packaging occurs. Desiccant compounds can also be used to absorb moisture into the disposable material from the environment, such as rainfall in a landfill.

Suitable desiccant compounds include water grabbers, alkaline compounds capable of neutralizing acid, dry mineral fillers, and mixtures thereof. Suitable water grabbers include dry silica, talc, clays, calcium sulfate, calcium chloride, sodium sulfate, carbodiimides, and mixtures thereof. Suitable alkaline desiccant compounds include sodium bicarbonate, sodium acetate, sodium phosphate, and mixtures thereof. Preferred desiccant compounds include dry silica gel and calcium sulfate. Desiccant compounds can be either incorporated directly into the disposable materials or microencapsulated in capsules that degrade in the presence of water and acid. For example, since soluble alkaline desiccant compounds may actually promote polymer degradation if they are present in the disposable material in free form, such compounds can be incorporated into the disposable material as coated solids that solubilize in the presence of acid. Alternatively, they can be microencapsulated in a capsule that is susceptible to acid and/or water degradation, so that the desiccant compound is released at a rate effective for promoting neutralization of the acid. Suitable capsular formulations include aliphatic polyesters, amyloses, ethyl cellulose and cellulose acetate butyrate. Desiccants can also be used to stabilize or heal polymers because they can remove water formed during an esterification reaction (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD).

7.2.5 Antibacterial (Antibiotic) Compounds

A biopolymer is likely to be degraded or decomposed by bacteria during its use. To prolong the

useful life of a biodegradable biopolymer, the degradation by bacteria must be restricted. An attempt has been made to retard biodegradation by adding an antibacterial (antibiotic) material to the biopolymer. To this purpose **JPH0551073 A** (1993, TOPPAN PRINTING CO LTD) discloses a multilayer plastic container where the inner layer is poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBHV) and the outermost superficial layer is the antibacterial layer, PHBHV kneaded with antibacterial materials. Antibacterial metals or metal compounds such as silver, copper, and zinc are used as antibacterial materials. Gradually effective antibacterial chemicals are used to control the speed of biological decomposition. The container is designed not to be decomposed during use, but to be decomposed after disposal. However, direct addition of an antibacterial material to a biodegradable polymer has the problem that control of release of the antibacterial material is difficult. In other words, if release of the antibacterial materials occurs too quickly, the effect of the antibacterial material will be insufficient. If it is too slow, the period before the start of biodegradation will be too long (GB2281709, 1995, FUJITSU LTD).

GB2281709 A (1995, FUJITSU LTD) discloses a biopolymer-molded article that does not undergo degradation by bacteria during its use. This is achieved by compounding a small amount of antibacterial material into the biopolymer. Suitable antibacterial materials include those that impede biosynthesis of peptidoglycan of a cellular membrane (β -lactam types compounds such as penicillin, cephalosporin), biosynthesis of protein of bacteria (puromycin, tetracycline erythromycin, etc.), and biosynthesis of nucleic acid (azacrine, acridine, actinomycin, etc.). They also include those that change ion permeability and destroy a cellular membrane (phenols, quaternary ammonium salts, cyclic peptides, etc.). Metal ions (silver and its complex compounds) are also suitable. An alkali or acid component may be added to neutralize the acidic or alkaline impurities and retard the hydrolysis of the biopolymer. Biodegradability can be suppressed for a predetermined period until the antibacterial materials are decomposed and inactivated or are caused to flow out (e.g., by moisture). According to a preferred embodiment, the outermost layer of a biodegradable molded article shaped into a laminar structure is formed by a coating composition comprising a photolytic resin (e.g., ethylene-carbon monoxide copolymer or polyisobutylene oxide) and an antibacterial material. When the molded article

becomes unnecessary, it is irradiated with visible or ultraviolet (UV) rays to decompose and remove the photolytic resin.

7.2.6 Antioxidants, UV and Light Stabilizers

JP2001049097 A (2001, MITSUI CHEMICALS INC) discloses a method for enhancing the heat stability of an aliphatic polyester by adding a phenol phosphite compound. This aliphatic polyester composition is obtained by compounding 0.005–5 parts by weight of a phenol phosphite compound to 100 parts by weight of an aliphatic polyester (such as PLA) in which a retention rate of molecular weight after heating fusion at 230°C for 5 min is 90–100% of the molecular weight before the heating fusion. Although the addition of the phenol phosphite to PLA improves the color tone, it does not solve problems such as the strength reduction and the deposited substances observed during the long-term storage (WO2006118096 A1, 2006, UNITIKA LTD; SHISEIDO CO LTD).

In an attempt to solve the aforementioned problems **WO2006118096 A1** (2006, UNITIKA LTD; SHISEIDO CO LTD) discloses a biodegradable biopolymer composition containing 100 parts by mass of a biodegradable polyester containing not less than 50% by mass of PLA, 0.1–10 parts by mass of a layered silicate, 0.1–5 parts by mass of a carbodiimide compound, and 0.01–5 parts by mass of a phosphite organic compound. The biodegradable polymer composition may contain at least one additive selected from the group consisting of hindered phenol compounds, benzotriazole compounds, triazine compounds, and hindered amine compounds.

The layered silicate is one type of a swellable lamellar clay mineral, and specific examples thereof include smectite, vermiculite, and swellable fluoromica. The layered silicate enhances the strength and gas-barrier property of the biodegradable biopolymer composition. The phosphite organic compound suppresses the coloration of the biodegradable biopolymer composition and improves its heat resistance and moisture heat resistance. Preferred phosphite organic compounds include: pentaerythritol diphosphite, bis(2,6-di-*tert*-butyl-4-methylphenyl)pentaerythritol-diphosphite, tris(2,4-di-*tert*-butylphenylphosphite), hydrogenated bisphenol A-pentaerythritol phosphite polymer, and the like.

The disclosed composition is claimed to retain the initial color tone, and to suppress the strength reduction and the generation of deposited substances under a high-temperature moisture condition.

JPH06184417 A (1994, MITSUI TOATSU CHEM INC) discloses a PLA compounded with at least one type of additive selected from UV absorbers and light stabilizers (e.g., 2-hydroxy-4-*n*-octoxybenzophenone) at 0.001 to 5 parts by weight per 100 parts by weight of the polymer. The composition also preferably contains 1–50 parts by weight of a plasticizer such as glycerol triacetate. An article prepared from this composition has enhanced weather resistance and decomposes readily in the natural environment as soon as it is discarded after use. However, the object of this disclosure is control of biopolymer decomposition by solar rays, not hydrolysis control.

EP1418201 A1 (2004, NISSHIN SPINNING) attempts to solve these problems by compounding an aliphatic polyester with 0.01 to 10 parts by weight of a carbodiimide compound (including a polycarbodiimide compound) and 0.01 to 10 parts by weight of at least one compound selected from the group consisting of benzotriazole-, triazine-, and hydroxylamine-based UV absorbers. Commercial products of polycarbodiimides include Carbodilite[®] HMV-10B, Carbodilite[®] HMV-8CA, and Stabaxol[®] P. The biodegradable biopolymer composition is capable of adjusting its own biodegradation rate, has greatly improved resistance to hydrolysis (in particular) and weather, and durability that results from the improved resistances.

EP1354917 A1 (2003, NISSHIN SPINNING) discloses a biodegradable polymer composition that enables stable adjustment of biodegradation rate, improves hydrolysis resistance and heat resistance, retains transparency of molded articles thereof, and provides a method for controlling the biodegradation rate of the biodegradable polymer. This composition is made by compounding 100 parts by weight of a biodegradable polymer in particular, an aliphatic-type polyester with 0.01 to 5 parts by weight of a carbodiimide compound and 0.01 to 3 parts by weight of an antioxidant; the antioxidant is a hindered phenol-type antioxidant with a molecular weight of not less than 400 alone, or a mixed antioxidant of a hindered phenol-type antioxidant and a phosphite-type antioxidant. Suitable aliphatic polyesters are PLA, PHB, PCL, and polyalkylene alkanates. Typical examples of polyalkylene alkanates are PBS, PBSA, and poly(ethylene succinate)

(PES). Commercially available products of PBSA, PCL, and PES are Bionolle® (Showa Highpolymer), Tone® (Dow Chemical) and Lunare SE® (Nippon Shokubai), respectively.

US2005054755 A1 (2005, NISSHIN SPINNING) discloses a biodegradable biopolymer composition comprised of an aliphatic polyester compounded with an aliphatic carbodiimide compound and a phosphorus antioxidant; optionally a second phosphorus antioxidant and a hindered phenol antioxidant are compounded in the composition. The stabilizer system provides an aliphatic polyester composition with superior hue stability that prevents yellowing ($YI < 20$) and high stability against hydrolysis. The phosphorus antioxidant preferably has a pentaerythritol structure for improvement in stability against hydrolysis, and more preferably an aromatic hydrocarbon group with a *tert*-butyl group in addition to the pentaerythritol structure (e.g., bis(2,4-di-*tert*-butylphenyl)pentaerythritol-diphosphite).

EP1854837 A2 (2007, NISSHIN SPINNING) discloses a biodegradable polymer composition in which a biodegradable polymer is blended with three kinds of specific additives so that its biodegradation rate is controlled, its hydrolysis rate is retarded, and its weatherability is significantly improved by the synergistic effect of the additives. In particular, the biodegradable polymer composition comprises a carbodiimide compound, a UV absorbent, and an antioxidant as essential ingredients. The carbodiimide compound is an aliphatic polycarbodiimide compound. The UV absorbent is selected from the group consisting of a benzotriazole-based compound, a triazine-based compound, and a hydroxylamine-based compound. The antioxidant is at least one of a hindered phenol-based antioxidant and a phosphite-based antioxidant. Typical examples of the aliphatic polyester are PLA, PHB, poly(3-hydroxybutyrate-*co*-3-hydroxypropionate) (PHBHP), PHBHV, PCL, PES, PBS, PBSA, poly(butylene succinate-*co*-terephthalate) (PBST), and poly(butylene adipate-*co*-terephthalate) (PBAT). The commercial products include Lacea® H-400, Tone® (Nippon Unicar; Dow Chemical), Placel® (Daicel Corporation), Lunare SE® (Nippon Shokubai), Bionolle® (Showa Highpolymer), EnPol™ (Ire Chemicals), BioMax® (Du Pont), and Ecoflex® (BASF).

JP2004075727 A (2004, AICHI PREFECTURE; TSUJI HIDETO; UNITIKA LTD) discloses a PLA composition for films which enables control of suppression or acceleration of the biodegradation rate

(see Section 7.3.4: Compounds Which Can Initiate and/or Propagate Depolymerization) without much change to mechanical properties such as tensile strength and modulus. The PLA composition with a suppressed biodegradation rate comprises 100 parts PLA and 5–40 parts hydrophobic rutile-type titanium oxide having a particle diameter of 0.005–1 μm ; it is surface-treated with an organic substance.

JP2005089537 A (2005, DAICEL CHEM) discloses an aliphatic polyester composition and a mulch film for agriculture prepared from the same, wherein the part buried in soil does not degrade or deteriorate earlier than necessary. The aliphatic polyester composition is obtained by adding one or more types of additives, chosen from a UV absorber and optical stabilizer, to the aliphatic polyester. The aliphatic polyester is PLA, PGA, PCL, poly(3-hydroxypropionate) (PHP), PHB, poly(3-hydroxyvalerate) (PHV), PES, PBS, poly(ethylene succinate-*co*-adipate) (PESA), or PBSA. The UV absorber is a benzophenone-type absorber, triazine-type absorber, phenolic acid ester-type absorber, and/or benzotriazole-type absorber; the UV absorber is preferably 2-hydroxy-4-*n*-octoxy-benzophenone and/or 2-(2-hydroxy-4-hexyloxy phenyl)-4,6-diphenyl-1,3,5-triazine. The optical stabilizer is a hindered amine-type and/or benzoate-type compound. The resin composition contains 0.2–7 wt.% of ultraviolet absorber.

EP0587069 A1 (1994, MITSUI TOATSU CHEMICALS INC) discloses a degradable adhesive film wherein the substrate of the adhesive film is obtained from a PLA composition comprising 0.001 to 5 parts by weight of one or more additives selected from an ultraviolet absorber and light stabilizer for 100 parts by weight of PLA. The additives are one or more compounds selected from benzophenones, benzotriazoles, and sebacates. The PLA is one or more (co)polymers selected from PLLA, PDLA, or poly(lactide-*co*-glycolide) (PLGA). The addition of a specific amount of ultraviolet absorbers and/or light stabilizers confers excellent weatherability to the degradable PLA composition. The degradable product can maintain the essential mechanical properties of PLA during its use period and then degrade after use on the basis of its essential hydrolytic properties; it is therefore useful for making throwaway, formed products for use outdoors.

The proposed degradable composition overcomes the disadvantages of the prior art. For example, a PLA film which had been expected to hold its strength for at least six months at room temperature

(based on its rate of hydrolysis information) was embrittled after about a month of outdoor use and could not perform its functions any more. Furthermore, the rate of acceleration of its decomposition could not be anticipated, which resulted in a widely varying decomposition period.

The degradable adhesive film can be used as surface protection in the transportation and storage of metal plates such as stainless steel and aluminum, or their workpieces, which can include such items as synthetic resin plates, synthetic resin molded articles, resin-coated wood boards, decorative laminates, wood and metal furniture, and measuring instruments such as watches and automotive bodies.

WO0222737 A2 (2002, EASTMAN CHEM CO) discloses a method for slowing the degradation rate of a biodegradable biopolymer or biodegradable biopolymer composition by adding a sufficient amount of a phenol-containing compound comprised of a phenol-terpene resin into a biodegradable biopolymer or biodegradable polymer composition. The amount of phenol-containing compound introduced into a biodegradable biopolymer or biodegradable biopolymer composition ranges from about 0.1 to about 10%, preferably from about 0.5 to about 5%, or, more preferably, from about 1 to about 3 wt.%. Phenol-terpene resin is food-safe and would not harm someone (e.g., a child) who ingests a material containing it. A commercial product of phenol-terpene resin is NIREZ[®] (Arizona Chemical Co.). Suitable biopolymers include aliphatic polyesters and aliphatic-aromatic copolyesters such as PBAT.

7.2.7 Cross-linking

Conventional cross-linking of biodegradable biopolymers causes a significant decrease in both the degradability and chemical recyclability [10]. In **JP2003034734 A** (2003, SONY CORP) and **JP2008223023 A** (2008, SONY CORP) degradation rate is lowered by adding a cross-linking agent to a biodegradable biopolymer and then irradiating it with actinic rays. The biodegradable polymer is an aliphatic polyester, preferably PLA. The cross-linking agent is a carbodiimide compound, isocyanate compound, or oxazoline compound, preferably *N,N'*-dicyclohexylcarbodiimide or *N,N'*-diisopropylcarbodiimide. These compounds also function as hydrolysis-suppressing agents (see Section 7.2.3: Functional Group-Capping Agents and Catalyst-Deactivation Agents). Molded articles prepared from this

biodegradable biopolymer composition, such as electric appliance housings, have enhanced durability after irradiation.

7.2.8 Plasticizers

Plasticizers can increase or decrease polymer degradation rates; thus, addition of plasticizers to a disposable biodegradable biopolymer can be used to control the operative degradation rate of the material. Internal or external plasticizers can be used for this purpose. Internal plasticizers either form part of the polymeric backbone itself or are chemically bonded to the polymer backbone, whereas external plasticizers are discrete compounds that are not chemically bonded to the polymer. Plasticizers introduce pliability, flexibility, and toughness into a polymer to an extent not typically found in a disposable material containing only a biopolymer. Introduction of plasticizers into the biopolymer reduces the melt viscosity of the polymer and lowers the temperature, pressure, and shear rate required to melt-form the polymer. Plasticizers also prevent heat build-up and consequent discoloration and molecular weight decrease during processing steps, such as production and packaging. Furthermore, plasticizers add impact resistance to the polymer (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD).

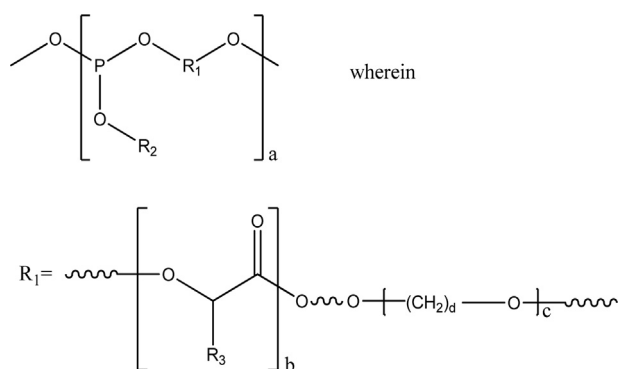
One of the embodiments of **US2002123546 A1** (2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC) or **WO9406866 A1** (1994, BIOPAK TECHNOLOGY LTD) is the use of hydrophobic plasticizers to control the rate at which water penetrates into the disposable material. The plasticizers can be added at a variety of concentrations. Preferably, disposable materials containing hydrophobic plasticizers contain from about 5 to about 50% plasticizer. The plasticizers, depending on their characteristics, may be added before or during formulation of the disposable material. Hydrophobic plasticizers can be used in the presence of hydrophilic plasticizers such as lactide and/or lactic acid oligomers as long as the overall hydrophilic/lipophilic balance (HLB) is low enough to impart sufficient hydrophobicity to keep the water concentration below a critical concentration, generally less than about 200 ppm by weight. Suitable plasticizers include, but are not limited to: esters of relatively long chain acids, such as ethyl laurate; esters of relatively long chain alcohols, such as lauryl acetate; low molecular weight polyesters, such as

polypropylene glycol adipate; glyceryl triacetate; ketones, such as 2-undecanone, isophorone, and cyclododecanone; aromatic ethers or esters, such as alkylated polyglycol ethers or poly(ethylene adipate); and mixtures thereof. The more preferred hydrophobic plasticizers include stearyl esters, low-toxicity phthalates, phenyl ethers, phenyl esters, and mixtures thereof. A hydrophobic plasticizer, such as diethyl phthalate, endows the biodegradable biopolymer with enhanced plasticization and slow degradation rate prior to disposal, with at least several years of shelf life before there is a noticeable change in physical properties.

7.2.9 Blending with other Polymers

JP2000129105 A (2000, MITSUBISHI GAS CHEMICAL CO) discloses a method for suppressing the biodegradation rate of an aliphatic polyester (A) synthesized from a glycol and an aliphatic dicarboxylic acid or a PCL by blending component A with PHB (B) ($M_w \geq 100,000$); preferably, component B is mixed with component A at 20–80%. The blend is melted and kneaded in the temperature range 130–250°C. In a multilayered molding with outer layers that consist of the same mixture as at both surfaces of an inner layer, and by changing the mixing ratio of component B, it is possible to control the biodegradation rate of the multilayered molding.

According to **US2010144979 A1** (2010, IND TECH RES INST) PLA is blended with a phosphine-based polymer of **Scheme 7.4** in order to suppress the degradation of PLA during processing.



Scheme 7.4 Phosphine-based polymer.

R_2 : $-\text{OCH}_3$ or $-\text{OCH}_2\text{CH}_3$; R_3 : $-\text{CH}_3$; a : 2–20; b : 1–8; c : 1–5; and d : 2–6.

When PLA is blended with the phosphine-based polymer in a weight ratio of 0.05–10 (preferably 2–3) parts by weight based on 100 parts by weight of PLA and processed, lowering of the PLA molecular weight is effectively inhibited. Specifically, the molecular weight (M_w) ratio: M_w (after processing)/ M_w (before processing) of PLA blended with the phosphine-based polymer is not less than 80%. Compared to conventional trinonylphenyl phosphine (TNPP) monomers, the phosphine-based polymer has a high boiling point, capable of avoiding evaporation and leakage when being processed. Additionally, compared to TNPP containing nonylphenol, the phosphine-based polymer without nonylphenol acts more like an environmental protection-type plasticizer. Additionally, the blend of PLA with a high phosphine-based polymer content (e.g., 10 wt.%) possesses fire retardation (self-extinguishing properties following direct exposure to flames).

JP2001049115 A (2001, OKURA IND CO LTD) discloses a garbage bag that scarcely decomposes when used for the disposal of garbage, but quickly decomposes when charged in a composting apparatus; the bag is composed of a biodegradable composition that is comprised of a blend of a specific aliphatic polyester (A) and PLA (B). The aliphatic polyester (A) is obtained by polymerizing a polyester pre-polymer, obtained from 1,4-butanediol and an aliphatic dicarboxylic acid (such as succinic acid), with a polyisocyanate. Component (B) is preferably a copolymer of 94–6 wt.% L-lactic acid and 6–94% D-lactic acid. The preferred amounts of (A) and (B) 90–50 and 10–50 wt.%, respectively. The raw waste bags that consist of biodegradable resins decompose very little during use because of slow decomposition at ordinary temperature, and decompose rapidly in composting devices by fast hydrolysis at a relatively high temperature; they can be buried in the earth and put into composting devices.

WO02094935 A (2002, DAICEL CHEM) discloses a thermoplastic resin composition comprised of an aliphatic polyester (A) and a PLA (B), the amount of PLA (B) being 1 to 20 parts by weight (excluding 20 parts by weight) per 100 parts by weight of the sum of both. The aliphatic polyester (A) can be PBS, PBSA, PCL, or a mixture of two of the polyesters. The composition gives a biodegradable film with a controlled biodegradation rate, in particular, a biodegradable agricultural mulch film, which is suitable for compost sacks, bin bags, bottles, etc.

JP2005220238 A (2005, OSAKA GAS CO LTD) discloses a method for controlling hydrolyzability of a biodegradable polymer that comprises blending a biodegradable polymer (A) with a non-biodegradable polymer (B) and/or at least one compatibilizer (C) selected from the following group: an ionomer resin, an oxazoline-based compatibilizer, an elastomer-based compatibilizer, a reactive compatibilizer, and a copolymer-based compatibilizer. Polymer (B) is selected from polyesters, aliphatic polyamides (nylon), polystyrene, and polyolefins. Examples of biodegradable polymer (A) are PLLA, PGA, PCL, PES, and PBS (Bionolle®). When compatibilizer (C) is blended with biodegradable polymer (A), generally the hydrolysis of biodegradable polymer (A) will be suppressed. When compatibilizer (C) is used in combination with a hydrophobic polymer as said polymer (B), the hydrolysis of biodegradable polymer (A) is heavily suppressed. On the other hand, when compatibilizer (C) is used in combination with a hydrophilic polymer as said polymer (B), the hydrolysis enhancement effect by the hydrophilic polymer (B) will be balanced by the hydrolysis inhibitory effect of compatibilizer (C).

Furthermore, it was found that the degradability of several aliphatic polyesters with non-biodegradable polymers could be controlled depending on their phase structure [4]. In particular, blends of PCL and low density polyethylene (LDPE), and PCL and polypropylene (PP), retained the high biodegradability of PCL. In contrast, the degradability of the PCL part in the blends of PCL and polystyrene (PS), PCL and poly(ethylene terephthalate) (PET), and PCL and PHB dropped off markedly. In the case of blends of PCL and nylon 6 or PS, the biodegradability of PCL did not change much. According to Tokiwa and Iwamoto, the higher the miscibility of PCL and conventional polymers, the harder the degradation of PCL on their blends by *Rhizopus arrhizus* lipase [4,11]. The degradabilities of PCL/LDPE [12] and PCL/PP [13] blends by the lipase could also be controlled depending on their phase structure.

Blends of PHB and PCL, and PHB and PBA, were immiscible in the amorphous state, while blends of PHB and poly(vinyl acetate) (PVAc) were miscible [4]. Enzymatic degradation studies of these blends with PHB depolymerase from *Alcaligenes faecalis* T1 showed that the weight loss of these blends decreased linearly with an increase in the amount of PBA, PVAc, or PCL [14]. In blends of PHB and PLA the rate of enzymatic surface erosion decreased with increasing PLA content in the blend [15].

7.2.10 Physical Separation of Degradation Additives (e.g., by Encapsulation or Coating)

WO2008038350 A1 (2008, FUJITSU LTD) discloses a biodegradable resin composition (1) containing a biopolymer and a photocatalyst (3) coated with an inorganic material (2); 0.1 to 20 parts by weight of photocatalyst is contained per 100 parts by weight of biopolymer (see Figure 7.2). The resin composition is used for molded products such as electronic device housings, domestic electrical appliances, furniture, toys, and tableware. The molded products can be decomposed easily by grinding, while the degradation of the resin composition during service life is suppressed. The photocatalyst is titanium oxide, zinc oxide, zirconium oxide, strontium titanate, titanium hydroxyapatite, or mixtures; preferably, titanium hydroxyapatite is used. The inorganic material is a hard-coat silicone system. The resin

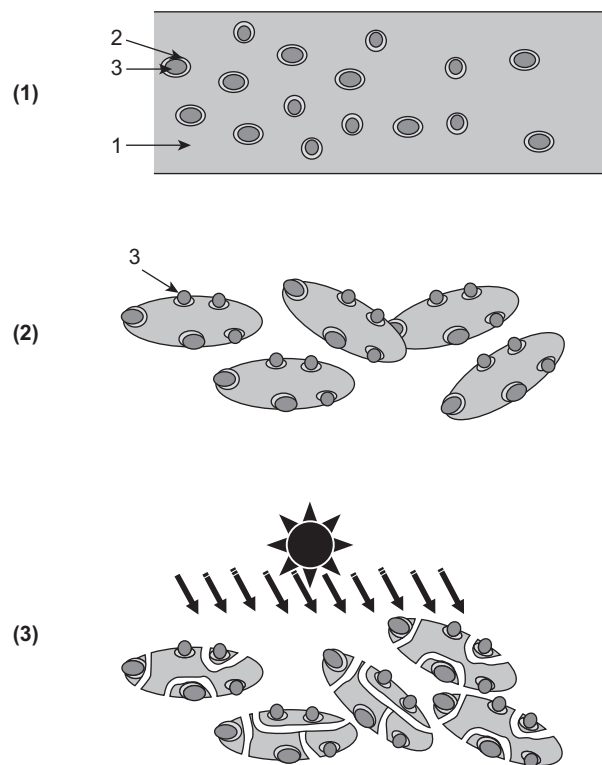


Figure 7.2 The drawing shows a photocatalyst in a biodegradable resin composition.

1: Biodegradable resin composition; 2: Inorganic material; 3: Photocatalyst (WO2008038350 A1, 2008, FUJITSU LTD).

composition further contains 0.1–10 wt.% of surface-active agent. The preferred biopolymer is PLA.

JP2002356623 A (2002, TOYOTA MOTOR CORP) discloses a biodegradable polymer such as PVOH containing microorganisms (e.g., *Pseudomonas vesicularis*) or an enzyme sealed in a polyamide microcapsule. The biodegradable polymer contains 0.1–20 volume% of the microcapsule; it is designed not to decompose while in use, but after disposal. The disposal involves a step of destroying the microcapsules by grinding the polymer before discarding in a natural environment where the resin is easily decomposed.

7.2.11 Coatings

DE19911209 A1 (2000, WOLFF WALSRÖDE AG) discloses semi-finished products consisting of biodegradable, compostable polymers with improved hydrolytic stability and stress-cracking resistance, and the use thereof. Hydrolysis susceptibility is reduced by completely or partially coating the semi-finished product on at least one surface with cellulose ester and plasticizer. Recommended plasticizers include cellulose esters such as cellulose acetate, cellulose butyrate, cellulose propionate, and preferably cellulose nitrate (N_2 content > 12.6%). The biodegradable biopolymers are selected from aliphatic polyesters, aliphatic-aromatic polyesters, poly(ester urethane)s, poly(ester carbonate)s, and poly(ester amide)s (BAK[®] 403-004, BAK[®] 404-002).

In yet another embodiment **US2002123546 A1** (2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC) and **WO9406866 A1** (1994, BIOPAK TECHNOLOGY LTD) disclose a disposable biodegradable biopolymer, such as PDLA, which is coated with at least one coating compound capable of retarding the degradation of the disposable material. The coating compound can be applied to the surface or can be mixed with the biopolymer and bloom (i.e., migrate) to the surface. The coating compound should be compatible with the biopolymer. A particularly preferred coating is one that is prone to abrasion so that it can protect the disposable material during the operative stage, but will still be penetrable to moisture during the disposal stage. Also preferred is a coating that has a high contact angle when the objective is to delay the onset of hydrolytic degradation. A coating with a high contact angle (e.g., at least about 90 degrees) is hydrophobic; it causes water and other hydrophilic substances to bead on the surface, thereby

reducing penetration of the disposable material by such substances. Suitable coating compounds include polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), nitrocellulose, PLA, poly(tetramethyl glycolide) (PTMG), polyurethanes (PUs), aliphatic polyamides (PAs), and PET. The two preferred coating compounds are PLLA and PTMG.

The application of a hydrophobic coating on the surface of a biopolymer article alters water uptake by the polymer and decreases the degradation rate (WO0056376 A1, 2000; US2003236320 A1, 2003, METABOLIX INC).

JP2002219779 A (2002, KANAZAWA INST OF TECHNOLOGY) discloses a biodegradable resin laminate whose degradation period is controlled; it is characterized in that at least one biodegradable resin layer, the degradation rate of which is low, is formed on a biodegradable resin composition sheet.

7.2.12 Surface Modification

Surface halogenation with a small amount of fluorine gas and a light catalyst can modify the surface of a disposable biopolymer such as PDLA by increasing the contact angle. Another example of surface modification/coating involves plasma polymerization, in which a hydroxycarboxylic acid monomer is exposed to an ionizing field in order to apply a thin surface layer of highly cross-linked material to the surface of PDLA (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD).

7.3 Promotion of (Bio)-degradability

Many biodegradable biopolymers are not easily hydrolyzed; PLA, polyhydroxyalkanoates (PHAs), PCL, PBS, and cellulose acetate are such examples. Therefore, there is a need to find ways to accelerate or trigger the degradability of environmentally disposable biopolymers after the end of their service life (see Table 7.2).

Triggered degradation has a number of advantages:

- (1) The degradation is initiated on a discretionary basis by treatment of the material with chemical, enzymatic, or microbial agents.
- (2) The timing of degradation is subject to the discretion of the user and not dependent on weather or soil conditions.

Table 7.2 Promotion of biodegradability

Biopolymers	Ways of promoting biodegradability	Conditions/compounds	Patents
PDLA	Lower molecular weight	< 5000 Da	US2002123546 A1 (2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC); WO9406866 A1 (1994, BIOPAK TECHNOLOGY LTD)
PLA, PCL, PVOH, PBS, PHB (foam)	Increasing surface area	Grinding under freezing	JP2002355819 A (2002, TOYOTA MOTOR CORP)
Aliphatic-aromatic copolyesters	Modification of polymer backbone	Greater amounts of aliphatic dicarboxylic acids, sulfonated compounds	US6368710 B1 (2002, DU PONT)
PHA	Modification of polymer's pendant groups	Conversion to acidic and basic groups, such as carboxylic acids and amines	WO9839453 A1 (1998, MONSANTO CO)
PLA	Lowering the molecular weight	Compounds containing a nucleophilic nitrogen atom	JP2003221461 A (2003, TOYOTA CENTRAL RES & DEV LAB INC)
PHA, P4HB, P3HB4HB, P4HB2HB, PHBHx, PHB, PHBO, PHBHD	Pore forming agents	Salt crystals, proteins (gelatin, agarose), starches, polysaccharides, alginate	WO9932536 A1 (1999, METABOLIX INC); US2003236320 A1 (2003, METABOLIX INC)
PLA, PCL, or mixture with starch	Promoting degradation	Coconut powder	JPH09263700 A (1997, SUGIMOTO I); JPH1036684 A (1998, SUGIMOTO I)
PHA, P4HB, P3HB4HB, P4HB2HB, PHBHx, PHB, PHBO, PHBHD	Depolymerization agents	Inorganic acids: ammonium sulfate, ammonium chloride; Organic acids: citric acid, benzoic acids, peptides, ascorbic acid; Inorg. bases: sodium carbonate, potassium carbonate, calcium carbonate, zinc carbonate, zinc hydroxide; Org. bases: protamine sulfate, spermine, choline, ethanolamine, diethanolamine, triethanolamine; Surfactants: Tween™, Pluronic™	WO9932536 A1 (1999, METABOLIX INC); US2003236320 A1 (2003, METABOLIX INC)
PLA, PGA, PLGA	Depolymerization-enhancing agents	Quaternary ammonium compounds	US5278256 A (1994, DU PONT)

Table 7.2 Promotion of biodegradability (*Continued*)

Biopolymers	Ways of promoting biodegradability	Conditions/compounds	Patents
PCL, PLA, poly(sebacic anhydride), poly(valeric anhydride), PTMC, poly orthoester, polysaccharide ester, PU, polyglutamate, PHB, PHV, cellulosic ester, starch ester, poly-(carboxyphenoxypropane-sebacic acid), poly(fumaric acid-sebacic acid)	Degradation-triggering agent	Chemical agent, enzymatic agent, biological agent (preferably microbes or fungi)	WO0075259 A1 (2000, EASTMAN CHEM CO)
PCL, PPL	Depolymerization initiators	Alkali metal compound or an alkali-earth metal compound (NaOH), and an alcohol (methyl alcohol)	JPH08253619 A (1996, MATSUSHITA DENKI SANGYO KK)
PLA, copolymer of D-glucose and adipic acid	Depolymerization initiators by exposure to heat, electromagnetic radiation (e.g., UV), water	Triphenylsulfonium trifluoromethylsulfonic acid salt; diphenyliodonium hexafluoroantimonate; hydrochloric acid salts; octamethylcyclotetrasilazane; carboxymethylcellulose ammonium salt	EP1207181 A (2002, CANON KK)
PHA: PHB, P3HB4HB, PHV, PHBHx	Grafting	Maleic anhydride and its ester, fumaric acid anhydride and its ester, styrene and its derivative, acrylic acid and its ester, methacrylate, acrylonitrile, long chain unsatd. carboxylate	CN101747476 A (2010, SHANDONG YIKEMAN TECHNOLOGY CO)
Poly(ester amide)s, poly(ester urethane)s (Degranil® DLN, Bionolle® 1010 and 3030) aliphatic-aromatic copolyesters PLA	Enzymes/microorganisms	Lipase (<i>Candida antarctica</i> , <i>Mucor miehei</i> , <i>Aspergillus niger</i>), cutinase (<i>Humicola insolens</i>)	DE19706023 A1 (1998, BAYER AG; NOVOZYMES AS)
Aliphatic polyester (fibers)	Enzymes	Lipases, polyesterases	WO9733001 A1 (1997, UNIVERSITY OF CALIFORNIA; GENENCOR INT); US6254645 B1 (2001, GENENCOR INT)
Sulfonated aliphatic-aromatic copolyesters	Enzymes/microorganisms	Proteases, lipases, cutinases, esterases	US2005261465 A1 (2005, DU PONT); WO2005118693 A1 (2005, DU PONT)
Sulfonated aliphatic-aromatic copolyesters	Microorganisms	Microbial consortium (SPDC-1; ATCC PTA-6129)	WO2006084261 A (2006, DU PONT; BRAMUCCI M G; NAGARAJAN V)

(Continued)

Table 7.2 Promotion of biodegradability (*Continued*)

Biopolymers	Ways of promoting biodegradability	Conditions/compounds	Patents
PLA	Enzymes/ microorganisms	Lipase, amylase, cellulase, lactate dehydrogenase	JPH04168149 A (1992, SHIMADZU CORP)
PLA, PGA, PBS, PBSL (mulch film)	Enzymes/ microorganisms	Enzymes: hydrolase, oxidative degradation enzyme; Genera: <i>Pseudomonas</i> , <i>Bacteroides</i> , <i>Mucor</i> and <i>Humicola</i>	JP2002348406 A (2002, MITSUBISHI CHEM CORP)
PLA, PDLLA, poly(L- lactide- <i>co</i> -D,L-lactide), poly(ester amide)s	Nutrients of microorganisms	Sources of carbohydrate, nitrogen, phosphate, sulfate, metals; vitamins, growth promotants	US6323307 B1 , (2001, CARGILL DOW POLYMERS LLC)
Biodegradable biopolymers (generic)	Nutrients of microorganisms	Alcohol, oil, fat (e.g., glycerol ester of fatty acid)	JP2006225518 A (2006, INOUE TADAO)
PLA	Coating material contg. proliferation accelerating agent of microbes	Carbohydrates, amino acids	US2007082202 A1 (2007, FUJITSU LTD)
PLA, PCL, PVOH, starch, starch deriv., cellulose, cellulose derivative	Nutrients of microorganisms	Nutrient salts, trace elements, minerals	DE29619016U U1 (1998, MUELLER W R; SCHOENBERGER D)
Polyanhydride, biodegradable polyester, cellulose derivatives, starch-based polymers, lignin, chitin	Biodegradability enhancement additive (microbial attractant)	Sugar, starch, furanone	US2010115836 A1 (2010, JULIAN B J)
PLA	Degradation additive(s)	Non-surface treated anatase- type TiO ₂ ; rutile-type TiO ₂ surface- treated with an inorganic substance	JP2004075727 A (2004, AICHI PREFECTURE; TSUJI HIDETO; UNITIKA LTD)
Biopolymer (A): PLA, PGA, PCL, poly(<i>p</i> -dioxanone), PTMC, polyoxaesters, polyoxaamides, PLLA, PLAGA, poly(glycolide- <i>co</i> - caprolactone) (75/25), poly(glycolide- <i>co</i> - trimethylene carbonate), poly(DTH carbonate)s, poly(imino-carbonate)s, polyphosphoesters, polyphosphazenes, PMA, poly(ester amide), polyalkanoates, PHB, poly(3-hydroxyvalerate) copolymers (medical device)	Specially selected additives	Degradation additives (enzymes): Proteinase K, bromelain, lipase-type enzymes, <i>Rhizopus delemar</i> lipase, <i>Rhizopus arrhizus</i> lipase, <i>Pseudomonas</i> lipase, microorganism-type enzymes, <i>Amycolatopsis</i> -type enzymes, poly(hydroxybutyrate) depolymerases; Coating biopolymer (B): PGA, polyanhydrides such as poly(carboxyphenoxy hexane- sebacic acid), poly (fumaric acid-sebacic acid), poly(carboxyphenoxy hexane-sebacic acid), poly(imide-sebacic acid) (50-50), poly(imide-	CA2605791 A1 (2008, CORDIS CORP)

Table 7.2 Promotion of biodegradability (*Continued*)

Biopolymers	Ways of promoting biodegradability	Conditions/compounds	Patents
		carboxyphenoxy hexane) (33-67); polyorthoesters such as diketene acetal based polymers; polyphosphoesters, polyphosphazenes; poly(DTH carbonates); poly(p-dioxanone)	
PHB, PCL, PEA, PTEMA	Specially selected additives	Silica, starch ($V=4.2 \times 10^{-3} - 65.4 \mu\text{m}^3$)	JPH04146953 A (1992, AGENCY IND SCIENCE TECHN; HUO KAGAKU KK)
PLA (90–50 wt.%)	Blending with other polymers	Poly(ethylene oxalate) (10–50 wt.%) & biodegradable plasticizer (5–25 wt.%)	JPH11116788 A (1999, MITSUI CHEM INC)
PLA (LACEA® H-100), PBS	Blending with other polymers	Poly(ethylene oxalate), poly(neopentyl oxalate) (PNOx), polyethylene maleate	WO2008038648 A1 (2008, TOYO SEIKAN KAISHA LTD)
PLA (NatureWorks 4031D)	Blending with other polymers	PGA (0.01–30 parts by weight) & ester degradation acceleration adjuvant (28–200 parts by weight): alkali metal, alkaline earth metal zeolite	WO2012046709 A1 (2012, TOYO SEIKAN KAISHA LTD; KUREHA CORP)
PCL	Mixture of biodegradation promotion (1) and suppression (2) agents	(1) Organic matter derived from plant such as rice bran, old rice, straw of rice, bean husk, rice hull, soybean hull, wheat bran, coffee hull, tea hull, coconut hull, bagasse, wooden powder, used paper, starch type polymer residue and/or plant fiber; (2) Organic antimicrobial agents such as herbs, extracts of wood, polyphenol compounds, mugwort, chitosan and polylysine	JP2001323177 A (2001, MIYAGI PREFECTURE)
PHBHV, PCL, PHB, PLA, acetylated starch	Oxodegradable technology; mix. biodegradation promotion (1) and suppression (2) agents	(1) Pro-degradant: transition metal salt selected from tartrate, stearate, oleate, citrate and chloride; (2) Free radical scavenging agent: hindered phenols, thiosynergists, phosphites, metal deactivators, monomeric, low and high mol. wt. oligomeric and block oligomeric hindered amines, benzophenone absorbers, benzotriazoles, benzotriazines, vitamin E, NORs	GB2464285 A (2010, WELLS PLASTICS LTD)

(Continued)

Table 7.2 Promotion of biodegradability (*Continued*)

Biopolymers	Ways of promoting biodegradability	Conditions/compounds	Patents
Aliphatic polyesters (Bionolle®)	Mix. biodegradation promotion & retarding agents	Alkaline earth metal oxides: (BeO, MgO, CaO, SrO or BaO) & coconut husks	JPH10273582 A (2005, OKURA IND CO LTD)
PLA (Lacea® H-100J)	Irradiation & cross-linking agent	Radiation: actinic rays, electron beam; Cross-linking agent: carbodiimide, isocyanate, oxazoline cpd. (preferably dicyclohexyl carbodiimide or diisopropyl carbodiimide)	JP2003034734 A (2003, SONY CORP); JP2008223023 A (2008, SONY CORP)
Chitosan, carboxymethylcellulose, hyaluronan, dextran, alginate, pectine, pullulan, amylopectin, dextrin, xanthan, guar gum, carrageenan, gelatin	Irradiation	Ultrasonic irradiation	FR2938265 A1 (2010, UNIV CLAUDE BERNARD LYON)
PLA fibers	Surface modification; creation of cracks	≥ 1 wt.% of an alkaline fiber-processing agent (pH ≥ 7.8); e.g., organic phosphate salts, unsaturated fatty acids and unsaturated alcohols	CA2411004 A1 (2003, KURARAY CO); JP2003213521 A (2003, KURARAY CO)
Polyalkanoates, PCL	Surface modification	Corona, plasma, flame treatment	JP2002256088 A (2002, KANAZAWA INST OF TECHNOLOGY)

Abbreviations: PHB, Poly(3-hydroxybutyrate); P3HB4HB, Poly(3-hydroxybutyrate-co-4-hydroxybutyrate); P4HB, Poly(4-hydroxybutyrate); P4HB2HB, Poly(4-hydroxybutyrate-co-2-hydroxybutyrate); PBA, Poly(butylene adipate); PBAT, Poly(butylene adipate terephthalate); PBS, Poly(butylene succinate); PBSA, Poly(butylene succinate-co-adipate); PBSL, Poly(butylene succinate-co-lactide); PBST, Poly(butylene succinate-co-terephthalate); PCL, Poly(ϵ -caprolactone); PDLA, Poly(D-lactide); PDLLA, Poly(D,L-lactide); PES, Poly(ethylene succinate); PGA, Polyglycolide; PHA, Polyhydroxyalkanoate; PHBHD, Poly(3-hydroxybutyrate-co-3-hydroxydecanoate); PHBHP, Poly(3-hydroxybutyrate-co-3-hydroxypropionate); PHBHx, Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); PHBO, Poly(3-hydroxybutyrate-co-3-hydroxyoctanoate); PHBHV, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PLA, Polylactide; PLGA, Poly(lactide-co-glycolide); PLLA, Poly(L-lactide); PMA, Poly(α -malic acid); PTeMA, Poly(tetramethylene adipate); PTMC, Poly(trimethylene carbonate); PVOH, Poly(vinyl alcohol).

(3) The degradation of an article in place eliminates the labor required for transportation of the material for off-site disposal and also the cost of disposal (WO0075259 A1, 2002, EASTMAN CHEM CO).

Ways of promoting the biodegradation of biopolymers are:

- (1) Control of the physical features of the biopolymer (lower molecular weight, less crystallinity, reduced stereoisomerism, low density, increased

porosity and higher surface area, no orientation, no physical aging).

- (2) Modification of the polymer backbone (hydrophilic bonds, functional end-groups, grafts with hydrophilic groups).
- (3) Enzymes and microbial nutrients.
- (4) Compounds that can initiate and/or propagate depolymerization.
- (5) Especially selected additives; e.g., capsules, (nano)particles.

- (6) Plasticizers.
- (7) Blending with other polymers.
- (8) Mixtures of biodegradation-promotion and -retarding agents.
- (9) Environmental conditions (temperature, moisture, radiation dose and time of exposure).
- (10) Surface modification.

7.3.1 Control of the Physical Features of Biopolymers

7.3.1.1 Structure (chemical structure, lower molecular weight)

The degradation rate of a biopolymer is increased by lowering the molecular weight of the polymer. For example, a PDLA having a molecular weight of more than about 5000 daltons (Da) is typically rigid and hard, whereas a PDLA having a molecular weight of less than about 5000 Da is typically semisolid and soft, which allows increased water penetration compared to high molecular weight polymers. In addition, low molecular weight PDLA polymers (i.e., polymers having shorter chain length) have more acid groups (i.e., free ends) per unit length than do high molecular weight polymers (i.e., polymers having a long chain length); such acid groups can catalyze hydrolysis (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD). Furthermore, PLA of relatively lower molecular weight shows higher rates of enzymatic degradation due to, for example, the high concentration of accessible chain groups [16,17].

7.3.1.2 Morphology (reduced stereoisomerism, less crystallinity)

Decrease of crystallinity leads to an increase of degradation. The amorphous phase of a biodegradable polymer is more susceptible to degradation than the crystalline phase. The molecules in the amorphous region are loosely packed and have more “free volume” into which water and/or enzymes can penetrate, which leads to accelerated hydrolysis and biodegradation (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD).

The amorphous content of PLA can be regulated by changing the ratio of D- and L-lactide. Less

crystalline PDLA (D,L-PLA) is more prone to degradation than PLLA (L,L-PLA).

Plasticizers may also be added to increase the biopolymer's amorphous character. For instance, citrate esters or atactic PHAs are added to PHA.

Copolymers of L-lactide and D,L-lactide have therefore been prepared to disrupt crystallinity and accelerate degradation. A copolymer of 50% glycolide and 50% D,L-lactide degrades faster than either homopolymer. Copolymers of L-lactide with 25–70% glycolide are amorphous due to the disruption of the regularity of the polymer chain by the other monomer.

Similarly, since PCL has a degradation time of about 2 years, copolymers have been synthesized to accelerate the rate of bioabsorption. For example, copolymers of ϵ -caprolactone with D,L-lactide have produced materials with more rapid degradation rates. A block copolymer of ϵ -caprolactone with glycolide (which offers reduced stiffness compared to pure PGA) is marketed as a monofilament suture by Ethicon Inc. under the commercial name Monocryl®.

JP2003221461 A (2003, TOYOTA CENTRAL RES & DEV LAB INC) discloses a method of efficiently lowering the molecular weight of an aliphatic polyester, such as PLA, and improving its biodegradability by heating and hydrolyzing the aliphatic polyester in the presence of one or more kinds of compounds containing a nucleophilic nitrogen atom to render it lower in molecular weight and thereby preventing the increase of crystallinity which takes place upon lowering the molecular weight by a simple heating hydrolysis. The easily biodegradable aliphatic polyester thus obtained is further subjected to enzymatic monomer decomposition by microorganisms.

7.3.1.3 Form (increased porosity, higher surface area, higher density)

Since the depolymerization of polyhydroxy acids (PHAs) is a surface reaction, increasing the surface area, such as by shredding or pulverizing the biopolymer, expedites depolymerization degradation (US5278256 A, 1994, DU PONT). In **JP2002355819 A** (2002, TOYOTA MOTOR CORP) the biodegradable biopolymer (PLA, PCL, PVOH, PBS, or PHB) is ground under freezing to form small particles before discarding. Grinding a biodegradable foam, which is incapable of being ground into small particles by

a usual method or the like, accelerates biodegradation. The crushed material decomposes at a rate dependent upon the size of ground particles.

Similarly, increasing the porosity area will increase the rate of degradation. It has been shown that the presence of pores in PCL and PHB films enhanced their biodegradation in seawater [18]. The rate of degradation can also be enhanced by additives which form pores or otherwise increase the surface area in the polymer or increase the amorphous content of the biopolymer. Pore-forming agents are generally added as particulates, and include water-soluble compounds such as inorganic salts and sugars, which are removed by leaching. Suitable particles include salt crystals, proteins such as gelatin and agarose, starches, polysaccharides such as alginate, etc. The most suitable diameter of the particles is between several nanometers and 500 μm . Pore-forming agents can be included in an amount of between 0.01 and 90% weight to volume, preferably at a level between 1 and 30% to increase pore formation in biopolymers (WO9932536 A1, 1999, METABOLIX INC; US2003236320 A1, 2003, METABOLIX INC).

It has also been shown that the creation of cracks on the surface of PLA fibers promotes the biodegradation of the fibrous products. The cracks serve as capillaries through which a fiber-processing agent may enter the fibers. The fiber-processing agent assists the propagation of biodegrading enzymes into the fibers, thereby promoting biodegradation of the fibers (CA2411004 A1, 2003, KURARAY CO).

7.3.1.4 Composition (increased number of impurities or residues)

The role of impurities or residues on the degradability of aliphatic polyesters has been analyzed in Section 7.2.1.3.

7.3.1.5 Condition of the article (processing conditions, no orientation, no physical aging)

As mentioned in Section 7.3.1.2, as a biodegradable biopolymer loses crystallinity and orientation, the material becomes less ordered and has more “free volume” into which water can penetrate, which accelerates hydrolysis and degradation.

7.3.2 Modification of the Polymer Backbone

Modification of the polymer backbone to increase its susceptibility to hydrolytic cleavage is an important key to enhancing the breakdown of aliphatic-aromatic copolyesters. It has been generally found that the biodegradation rate of aliphatic-aromatic copolyesters can be enhanced through the addition of greater amounts of aliphatic dicarboxylic acids. Another option for enhancing the biodegradation rate is through the incorporation of a sulfonated compound. The sulfonated compound is selected from the group consisting of sulfosuccinic acid, 3-sulfobenzoic acid, 4-sulfobenzoic acid, 5-sulfosalicylic acid, sulfophthalic acid, sulfoterephthalic acid, and 5-sulfoisophthalic acid; or an ester or salt thereof. The sulfo groups may be introduced in any desired manner (e.g., in aliphatic or aromatic monomers such as sulfonated aliphatic or aromatic dicarboxylic acids) or as end-groups by including monofunctional components containing a sulfonic acid moiety as a substituent (US6368710 B1, 2002, DU PONT). This modification makes the polymer less resistant to hydrolysis due to the activating effect exerted by the strong electron-withdrawing substituent [19]. At the same time, it has been generally found that the incorporation of greater amounts of aliphatic dicarboxylic acids and/or sulfonated compounds into the copolyester backbone tend to degrade the thermal properties of the copolyester composition; one such property is the glass transition temperature (T_g). In US6368710 B1 (2002, DU PONT) it is disclosed that sulfonated aliphatic-aromatic copolyesters which incorporate isosorbide (1,4:3,6-dianhydro-D-sorbitol) avoid the aforementioned shortcomings.

Additionally, it is well established that the degradation of biopolymers such as PLA and PGA is catalyzed by carboxyl end-groups formed by chain cleavage, and that amorphous regions are preferentially degraded [20] (see also Section 7.2.1.3). In general, cleavage of an ester bond yields a carboxyl end-group and a hydroxyl end-group; the carboxyl end-groups are capable of catalyzing hydrolysis of other ester bonds (autocatalysis).

The rate of hydrolysis can be enhanced by changing the chemical nature or reactivity of ester linkages between monomers. The rate of degradation of a PHA backbone can be altered by incorporating chemical linkages that are more susceptible to

hydrolysis or enzymatic attack. Examples of monomers that can be incorporated into the PHA backbone to alter the rate of degradation of the polymer are 2-hydroxycarboxylic acids (α -hydroxycarboxylic acids), such as glycolic acid and lactic acid, and other hydroxycarboxylic acids that modulate the reactivity of the ester linkage, such as 2-hydroxyethoxy acetic acid. Besides the aforementioned hydroxycarboxylic acids, which yield esters that are more susceptible to hydrolytic or enzymatic attack, other types of functionality may be incorporated into a PHA backbone. For example, one or more of the ester linkages can be replaced by groups such as amides, anhydrides, carbonates, or carbamates. Examples of monomers that can be incorporated into the PHA backbone are aminoacids and aminoalcohols. Moreover, multi-functional monomers can be incorporated into the PHA backbone (e.g., triols or tetraols). These types of monomer units can also be used to increase or maintain the molecular weight of PHA by interchain cross-linking, or can be used to modify crystallinity of the biopolymer (WO9932536 A1, 1999, METABOLIX INC; US2003236320 A1, 2003, METABOLIX INC).

Another method for altering the degradation rate involves the modification of the PHA pendant groups. These may be modified in whole or in part. For example, pendant groups can be converted to acidic and basic groups such as carboxylic acids and amines. These types of groups can enhance degradation by altering local pH values. Alternatively, the pendant groups can be converted into reactive groups such as alcohols and amines, which can cleave the polymer backbone either by an intramolecular or intermolecular reaction. In addition to these conversions, the pendant groups can also be converted to hydrophilic groups to increase uptake of hydrolytic agents such as water, or they can be converted to groups that increase the amorphous nature of the polymers. Suitable pendant groups in PHA polymers that will alter the rate of degradation can also be derived directly by fermentation.

CN101747476 A (2010, SHANDONG YIKE-MAN TECHNOLOGY CO) discloses a PHA graft prepared from 100 weight parts PHA, 0.1–15 parts grafting monomer, 0–5 parts initiator, and 0–5 parts antioxidants. The grafting monomer can be maleic anhydride and its ester, fumaric acid anhydride and its ester, styrene and its derivative, acrylic acid and its ester, methacrylate, acrylonitrile, long-chain unsaturated carboxylate, and mixtures of these. The PHA graft polymer changes the molecular structure of

PHA, improves the heat stability thereof, and further accelerates biodegradation rate. In addition, the compatibility of the PHA graft polymer to inorganic filling materials, such as calcium carbonate and talcum powder, is improved. Suitable PHAs include PHB, poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB), PHV, and PHBHx.

7.3.3 Enzymes and Microbial Nutrients

Biodegradation by microbial action can occur in almost any waste context; however, the extent to which it occurs depends especially upon humidity, air content, and temperature of the waste content. Numerous enzymes known in the art can degrade polymers containing hydrolyzable groups such as esters, amides, etc. (see also Chapter 4: Disposal; Section 4.3.3: Microbes and Enzymes). **DE19706023 A1** (1998, BAYER AG; NOVOZYMES AS) discloses the use of a cutinase from *Humicola insolens* and lipases from *Aspergillus niger*, *Mucor miehei* (Lipozyme 20,000 L), and *Candida antarctica* (lipase component B) to degrade substrate polymers that are aliphatic polyesters, aromatic poly(ester amide)s, or partially aromatic poly(ester urethane)s. **WO9733001 A1** (1997, UNIVERSITY OF CALIFORNIA; GENENCOR INT) and **US6254645 B1** (2001, GENENCOR INT) describe the use of lipases or polyesterases to modify polyester fibers to enhance wettability and absorbency of textiles. **US2005261465 A1** and **WO2005118693 A1** (2005, DU PONT) disclose a method for accelerating the biodegradation of sulfonated aliphatic-aromatic copolyesters having more than 60 mol% aromatic acid content based on the total acid in the copolyester. The method works by contacting at least one hydrolytic enzyme in aqueous solution to the copolyester. The hydrolytic enzymes are selected from the group consisting of proteases, lipases, cutinases, esterases, or a combination of these.

An alternative way to increase the biodegradation rate of copolyesters with a high aromatic content has been disclosed by **WO2006084261 A** (2006, DU PONT; BRAMUCCI M G; NAGARAJAN V). It provides a microbial consortium SPDC-1 with ATCC accession number PTA-6129 for the biodegradation of sulfonated aliphatic-aromatic copolyesters having greater than 60 mol% aromatic acid content based on the total acid content of the copolyester. The invention is claimed to be economical, to foster the use of

composting as a workable waste process, to help eliminate the need for source separation of waste, to provide commercially valuable fertilizer-quality compost, and to help accelerate the rate of degradation of polyesters with aromatic content disposed of in landfills.

JP2006104262 A (2006, MITSUBISHI CHEM CORP) discloses a method for decomposing an aliphatic polyester molding. The method enables the polyester molding to be decomposed in a short time by accelerating its biodegradation after its service life, and is influenced less by the weather, soil quality, season, etc., of the area where it is decomposed. The method comprises bringing a *Humicola insolens*-derived hydrolase, with an amino acid sequence modified so as to increase the decomposition rate of ester linkages, into contact with the surface of the molding at the time of its decomposition; this is done under temperature conditions of 15 to 65°C.

JPH04168149 A (1992, SHIMADZU CORP) discloses a method for shortening the degradation period of a biodegradable polymer (e.g., PLA) by the addition of 1 ppm to 1 wt.% of a hydroxylase (e.g., lipase, amylase, cellulase, or lactate dehydrogenase). The biopolymer has high mechanical strength when in service in a dried state; after it is out of service and disposed of in a wet environment, the enzyme will be activated and will promote hydrolysis of the biopolymer. The biopolymer is useful as a garbage bag.

JP2002348406 A (2002, MITSUBISHI CHEM CORP) provides a method for the disposal of an agricultural mulch film made from a biodegradable biopolymer. The biopolymer is typically lying in soil with little fluctuation in biodegradability, and is dependent upon climate and the nature of the soil in the area where it is disposed of. The method works by promoting biodegradation to enable short-term degradation after end-of-service life. According to the landfill disposal method, enzymes and/or microorganisms capable of degrading the biodegradable biopolymer are brought into contact with the surface of the mulch film lying in the soil; the mulch film is then plowed into the soil. The biopolymer is an aliphatic or an alicyclic polyester polymer such as PLA, PGA, PBS, or PBSL. The enzyme, which decomposes the biopolymer in a short period of time, is a hydrolase or an oxidative degradation enzyme; the microorganisms belong to the genera *Pseudomonas*, *Bactericides*, *Mucor*, and *Humicola* (see also Chapter 4: Disposal; Section 4.3.1.1: Biodegradation in Soil).

One way to enhance the rate at which the microorganisms grow and degrade disposable biopolymers is by adding at least one source of microbial nutrients. Suitable nutrients include, but are not limited to, sources of carbohydrate, nitrogen, phosphate, sulfate, metals, and other salts. Typically, microorganisms can obtain carbon from the disposable materials, but in most cases, the disposable materials do not supply nitrogen, metals, or salts. Thus, the preferred source of nutrients includes at least one of the following: a nitrogen source, a salt source, and a metal source. Complex nutrients such as vitamins and growth promotants are also preferred, particularly for microorganisms not capable of producing such compounds from simple nutrients. Sources of nutrients can be incorporated into the polymer, grafted to the polymeric backbone of the disposable material, be microencapsulated, or be coated onto the surface of the disposable material. Other nutrients include compounds such as hydroxycarboxylic acids with long aliphatic or fatty acid chains and isocyanates, which are added to the disposable material to control degradation in other ways (**US6323307 B1**, 2001, CARGILL DOW POLYMERS LLC).

JP2006225518 A (2006, INOUE TADAO) discloses a method of decomposing a biodegradable polymer, even under low-temperature conditions, by mixing oil and fat or alcohol in an amount of 1 to 10 parts by weight to 10 parts by weight of biodegradable polymer and 10 to 500 parts by weight of organic waste. The oil and fat or alcohol are consumed as a nutrient for the microorganism decomposing the biodegradable polymer and activating the microorganisms remaining inert at low temperatures. The fat and oil are a glycerol ester of fatty acid.

In one of its embodiments **US2007082202 A1** (2007, FUJITSU LTD) discloses a method for disposing of a molded article including a molded substrate containing a biodegradable biopolymer such as PLA. In one step a coating material is applied to the article; the coating contains an agent for accelerating proliferation of microorganisms. Since the proliferation-accelerating agent is contained in the applied coating that covers a surface of the molded substrate, it can dissolve in soil or water and become food (substrate) for microorganisms living therein; this accelerates microorganism proliferation even further. As a result, the number of microorganisms can be increased and the rate of biodegradation of the molded substrate containing a biodegradable polymer can be increased so that the

molded substrate can be biodegraded in a short time. The proliferation-accelerating agent is selected from carbohydrates and amino acids and may contain both of them. The carbohydrates and amino acids can be utilized by the microorganisms in the soil, and accelerates their proliferation. The coating material also contains a natural material. From the viewpoint of reducing environmental effects, an aqueous coating material is preferable.

DE29619016U U1 (1998, MUELLER W R; SCHOENBERGER D) discloses a biodegradable biopolymer composition containing nutrient salts, trace elements, and minerals so that biodegradation is not limited by diffusion. The biodegradable biopolymer contains additive(s) selected from nutrient salts, trace elements, and minerals to assist biodegradation, so that the biodegradability is independent of the medium. The biodegradable biopolymer is selected from PLA, PCL, PVOH, starch, and starch derivatives, cellulose and cellulose derivatives (especially cellulose acetate and cellulose diacetate), and/or biodegradable copolymer(s). The composition is used for consumer or industrial products, e.g., bags, foils, films, molded packaging, fishing nets, etc. It is also useful for treating (especially denitrifying) ground- and surface water to produce water for drinking or aquariums.

US2010115836 A1 (2010, JULIAN B J) discloses an agricultural growth management tool, useful for plant identification, that comprises a biodegradable polymer body including a synthetic polymer and a biodegradability enhancement additive including a microbial attractant. The microbial attractant is a sugar, starch, and/or a furanone. The biodegradability enhancement additive comprises 0.5–5 wt.% of the biodegradable polymer body, and also includes an organic carboxylic acid. Optimal microbial attractants can vary for particular microbial environments and can include any material that acts to increase microbial growth over a composition without the attractant. For example, certain microbes may be either repelled or attracted by certain sugars or furanones. The biodegradation of the agricultural tool or system can be accelerated by exposing the system to a dosage of an optimized microbial population. This can be provided in a solid or solution form that is sprayed over the system and/or infused or flushed through the system.

The biodegradable polymer body is any of the following: plant stake, branch tag, drip tubing, blister pack, plantable container, agrifilm, drip tubing connectors, drip tubing accessories, market trays, plug

and propagation trays, flats and inserts, transfer pots, transfer trays, landscape ribbon, landscape twine/rope, landscaping bags, pot wraps, floral wraps, hanging basket assemblies, or greenhouse films/sheets. The synthetic polymer is an inherently non-biodegradable polymer or a biodegradable polymer; suitable biodegradable polymers include polyanhydride, biodegradable polyester, cellulose derivatives, starch-based polymers, lignin, chitin, and/or their copolymers.

7.3.4 Compounds Which Can Initiate and/or Propagate Depolymerization

According to **WO9932536 A1** (1999) and **US2003236320 A1** (2003, METABOLIX INC) the degradation of PHAs is accelerated at acidic or basic pHs and thus the inclusion of acidic or basic additives can be used to regulate the rate of degradation of PHAs. Additives which enhance the rate of degradation include inorganic acids such as ammonium sulfate and ammonium chloride; organic acids such as citric acid, benzoic acids, peptides, and ascorbic acid; inorganic bases such as sodium carbonate, potassium carbonate, calcium carbonate, zinc carbonate, and zinc hydroxide; organic bases such as protamine sulfate, spermine, choline, ethanolamine, diethanolamine, and triethanolamine; and surfactants such as Tween[™] and Pluronic[™]. Such additives are preferably used at concentrations between 0.1 and 30 wt.% of polymer. Preferred PHAs comprise polymers selected from the group consisting of poly(4-hydroxybutyrate) (P4HB), poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB), poly(4-hydroxybutyrate-co-2-hydroxybutyrate) (P4HB2HB), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx), poly-3-hydroxybutyrate-co-3-hydroxyoctanoate (PHBO), poly(3-hydroxybutyrate-co-3-hydroxydecanoate) (PHBHD), and copolymers and blends thereof.

WO0075259 A1 (2000, EASTMAN CHEM CO) discloses a method for enhancing the biodegradability of a shaped article (e.g., agricultural mulch film) by contacting the article with a degradation-triggering agent. The degradation-triggering agent is a chemical agent, enzymatic agent, or biological agent (preferably microbes or fungi). Chemical triggers include alkaline chemicals, such as metal oxides, metal hydroxides, agricultural lime, amines, and acidic materials such as mineral acids or organic acids. Enzymatic triggers include hydrolases such as esterases, lipases, cellulases, etc. Biological agents

include microbes, bacteria, fungi, and spores. The triggering may be applied to a shaped article by spraying, dipping, or immersing the article in a bath containing the triggering agent. The triggering agent may include additives for facilitating the penetration of the triggering agent into the article. One convenient way is to treat the object in place with a triggering agent after it has completed its useful life. A suitable triggering agent applied on an aliphatic polyester film would initiate hydrolysis of the ester bond and chain cleavage of the polymer chain. This could be useful in degrading objects such as films that are quite large and bulky and would have applications in agriculture (mulch films and silage bags). The shaped article is made of PCL, PLA, polyanhydrides such as poly(sebacic anhydride) or poly(valeric anhydride), PTMC, polyorthoester, polysaccharide ester, polyurethane (PU), polyglutamate, PHB, PHV, cellulosic ester, starch ester, or copolymer, preferably poly(carboxyphenoxypropane-sebacic acid) or poly(fumaric acid-sebacic acid).

US5278256 A (1994, DU PONT) discloses a method of enhancing the depolymerization of polyhydroxy acid compositions and articles in a liquid medium by using an ammonium salt or a quaternary ammonium compound. The polyhydroxy acid is selected from the group consisting of PLA, PGA, copolymers of lactide and glycolide, and polymers containing a major proportion of lactide or glycolide units or combinations thereof. These are polymerized with up to 30% of at least one of the following monomers: ϵ -caprolactone, δ -valerolactone, 1,5-dioxepan-2-one, 1,4-dioxan-2-one, β -butyrolactone, β -propiolactone, 6-methyl-2,5-morpholinedione. Although the mechanism by which the quaternary ammonium compound enhances polyhydroxy acid hydrolysis is not completely understood, it is thought that the overall effect of the quaternary ammonium compound is to expedite hydrolysis of the ester bond. The amount of quaternary ammonium compound depends on the particular depolymerization medium, such as water, acid, alcohol, amide, and the like. It also depends on the temperature, pressure, and time of depolymerization. Higher temperature, pressure, and longer time of depolymerization permit the use of lower quantities of a particular quaternary ammonium compound. The amount of depolymerization medium used affects the time of depolymerization and the percent depolymerization in a given time. The inclusion of a surfactant along with the quaternary ammonium compound has been found to further speed

up depolymerization. Preferably a nonionic surfactant such as a lauryl alcohol/ethylene oxide surfactant in an amount of 0.1–1% is used. When the quaternary ammonium compound is put into the depolymerization medium (water) instead of in the polymer in accordance with the invention described, the quaternary ammonium compound has little or no effect on the rate of depolymerization (see also Chapter 4: Disposal; Section 4.2.1: Pretreatment Before Disposal).

JPH08253619 A (1996, MATSUSHITA ELECTRIC IND CO LTD) discloses a method for disposing of molded polymer articles comprising an aliphatic polyester (e.g., PCL) by contacting the molded product (A) with a solution containing at least an alkali metal compound or an alkaline earth metal compound (B), and an alcohol (e.g., methyl alcohol) (C). The addition of alcohol to the treating solution accelerates the decomposition of the ester bonds with no heating and no pressure. It is preferable that the molded product (A) be immersed in a solution containing both the components B and C and added with (D) inorganic compound particles (e.g., alumina particles); agitation follows.

EP0573042 A1 (1993, MITSUI TOATSU CHEM INC) discloses a process for decomposing a biopolymer composition comprising an aliphatic hydroxycarboxylic acid-derived polyester as a primary component in an alkaline solution of pH 10, recovering hydroxycarboxylic acid from the solution by electrodialysis or acid-precipitation, and using the recovered hydroxycarboxylic acid as the raw material of a new polymer. Hydroxycarboxylic acids which can be used include, for example, lactic acid, glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 4-hydroxyvaleric acid, 5-hydroxyvaleric acid, and 6-hydroxycaproic acid. When an aqueous sodium hydroxide solution is used as the alkaline solution, an aqueous hydroxycarboxylic acid solution can be efficiently obtained by electrodialysis. When the hydroxycarboxylic acid is lactic acid, an aqueous solution or suspension of calcium hydroxide is used as an alkaline solution.

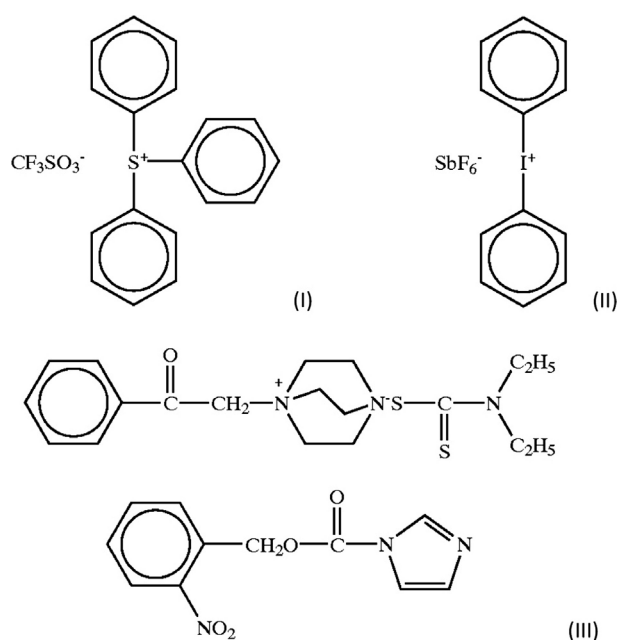
AU3521984 A (1985, ICI PLC) discloses disposable bags for body waste comprising a PHB polymer and a basic material, preferably sodium hydroxide or sodium carbonate, to modify the pH of the bag contents to at least 12. The modification of the pH of the contents increases the rate of the polymer's degradation.

EP1207181 A (2002, CANON KK) discloses a decomposable polymer composition comprising

an agent that generates an acid or base by light irradiation (UV) or heat together with a hydrolyzable and biodegradable polymer. The combination of a proper acid- or base-generating agent with a decomposable polymer can promote decomposition by carrying out light irradiation or heating at the desired time; the decomposition speed of the polymer can be controlled by the amount of acid- or base-generating agent.

Preferred agents for generating acid by light are sulfonium salts such as triphenylsulfonium trifluoromethylsulfonic acid salt represented by formula (I) and iodonium salts such as diphenyliodonium hexafluoroantimonate represented by formula (II) of Scheme 7.5. Agents for generating base by light are compounds represented by formula (III). The amount of an acid- or base-generating agent is preferably 1 to 5 wt.% in a decomposable resin.

Examples of compounds for generating acids by heat are hydrochloric acid salts. Compounds for generating bases by heat include, for example, silazane compounds such as octamethylcyclotetrasilazane



Scheme 7.5 Acid-generating agents by light: (I) sulfonium salts such as triphenylsulfonium trifluoromethylsulfonic acid salt; (II) iodonium salts such as diphenyliodonium hexafluoroantimonate; (III) base-generating agents by light (EP1207181 A, 2002, CANON KK).

and ammonium salts such as carboxymethylcellulose ammonium salt. The amount of such a compound is preferably 0.1 to 20 wt.% and especially 1 to 5 wt.% in a decomposable resin. The heating temperature is preferably 50 to 150°C and the heating duration is preferably 30 to 120 min.

Suitable biopolymers include PLA and copolymers of saccharides and dicarboxylic acids such as copolymer of D-glucose and adipic acid.

JPH09263700 A (1997) and **JPH1036684 A** (1998, SUGIMOTO I) disclose a biodegradable film showing improved biodegradability in a composting environment by mixing a biodegradable polymer with a dry powder of fibers contained in the mesocarp of a coconut. Fine pieces of fibers obtained by soaking the mesocarp in fresh water to dissolve the sarcocarp are dried and then compressed at a compression ratio of (5–6):1. The compressed powder is ground to obtain a dry powder having a particle diameter of 1–80 μm ; 98–60 wt.% biodegradable biopolymer is mixed with 2–40 wt.% of the dry powder to obtain a biodegradable plastic composition. This composition is melt-kneaded and then pelletized. The pellets are molded into a film, and this film is stretched and formed into a compost bag having a thickness of 10–2000 μm . When the articles produced by this method are buried in the ground after use, the dry coconut powder therein absorbs water in the ground and the buried articles are thereby swollen and biodegraded. To that effect, the method is unique in that it provides biodegradation control of the buried articles. However, the coconut powder to be mixed with the polymer is large, preferably from 20 to 80 μm . According to CA2411004 A1 (2003, KURARAY CO), the method is not applicable to fibers with a diameter of only 14 to 30 μm .

JP2004075727 A (2004, AICHI PREFECTURE; TSUJI HIDETO; UNITIKA LTD) discloses a PLA composition for films that enables control of the acceleration or suppression of biodegradable rate (see Section 7.2.6: Antioxidants, UV and Light Stabilizers) without much change in mechanical properties such as tensile strength and modulus. The PLA composition with an accelerated biodegradation rate comprises 100 parts PLA and 5–40 parts anatase-type titanium oxide with a particle diameter of 0.05–1 μm which is non-surface treated, or rutile-type titanium oxide with a particle diameter of 0.005–1 μm which is surface-treated with an inorganic substance.

7.3.5 Specially Selected Additives (e.g., Capsules, (Nano)particles Acting as Degradation Agents)

Polymer nanocomposites are not only suitable for the significant improvement of mechanical and various other material properties of virgin materials, they are also suitable to enhance the rate of biodegradation of biodegradable polymers such as PLA. Since the biodegradability of PLA in nanocomposites depends upon both the nature of pristine layered silicates and surfactants used for the modification of layered silicate, the biodegradability of PLA can be enhanced via judicious choice of organically modified layered silicate [17].

CA2605791 A1 (2008, CORDIS CORP) discloses a medical device that is made of biodegradable biopolymer (A) including blends, coatings, or layers having encapsulated degradation additives that accelerate degradation of the structures or components of the medical device after the medical device has achieved its desired functional effect or achieved the end of its functional purpose or useful life. The degradation additive is encapsulated by another biodegradable and/or bioabsorbable biopolymer (B) forming a nanoparticle or microparticle. The biodegradable and/or bioabsorbable material of the nanoparticle or microparticle has a degradation rate that is faster than the degradation rate of biopolymer (A). The degradation rate for biopolymer (A) is 3–48 months, and the degradation rate for biopolymer (B) is between 1 day and 3 months. The medical device experiences a period of accelerated degradation upon release of the degradation additive from the nanoparticle or microparticle.

Biopolymer (A) is selected from the group consisting of PLA, PGA, PCL, poly(*p*-dioxanone), poly(trimethylene carbonate) (PTMC), polyoxaesters, polyoxaamides, PLLA, PLAGA, poly(glycolide-*co*-caprolactone) (75/25), poly(glycolide-*co*-trimethylene carbonate), tyrosine-derived poly(amino acid)s such as poly(DTH carbonate)s, poly(imino-carbonate)s, phosphorus-containing polymers such as polyphosphoesters and polyphosphazenes, poly(α -malic acid) (α -PMA), poly(ester amide), polyalkanoates, PHB, poly(3-hydroxyvalerate) copolymers, etc.

Biopolymer (B) is selected from the group consisting of PGA, polyanhydrides such as poly(carboxyphenoxy hexane-sebacic acid), poly(fumaric acid-sebacic acid), poly(carboxyphenoxy

hexane-sebacic acid), poly(imide-sebacic acid) (50:50), poly(imide-carboxyphenoxy hexane) (33:67); polyorthoesters (diketene acetal-based polymers); phosphorus-containing polymers such as polyphosphoesters, polyphosphazenes, tyrosine-derived poly(amino acid)s such as poly(DTH carbonate)s, poly(*p*-dioxanone), etc.

The degradation additive is preferably an enzyme selected from Proteinase K, bromelain, lipase-type enzymes, *Rhizopus deleamar* lipase, *Rhizopus arrhizus* lipase, *Pseudomonas* lipase, *Amycolatopsis*-type enzymes, and poly(hydroxybutyrate) depolymerases.

JP2001302891 A (2001, TOYOCO LTD) discloses a method for accelerating or controlling the degradation of a biodegradable molded product. The biodegradation rate is accelerated by forming the biodegradable molded product comprising fibers consisting essentially of an aliphatic polyester having 0.1–50 μm average fiber diameter and capable of deliberately regulating the strength retention to $\leq 50\%$ in a short period and laminating a fibrous sheet-like material, a metal-coated sheet-like material, etc., having a fluorine-based resin component supporting photocatalyst particles onto the biodegradable molded product.

JP2002256142 A (2002, UNITIKA LTD) discloses a biodegradable resin composition which can be degraded more rapidly in the natural environment or in an accelerated degradation apparatus, and also provides a method for degrading the resin composition. The biodegradable composition contains 99.99–95 parts by mass PLA and 0.01–5 parts by mass organic carboxylic acid compound and/or organic carboxylate compound. The method allows the organic carboxylic acid compound and/or the organic carboxylate compound to act on PLA as a biodegradable resin composition.

JPH04146953 A (1992, AGENCY IND SCIENCE TECHN; HUO KAGAKU KK) discloses a method for preventing biodegradation and disintegration during the use of a biodegradable polymer molding made of a biodegradable aliphatic polyester; this is done by specifying the amount and mean volume of an inorganic and/or an organic filler compounded into the polyester when producing the molding. The biodegradable aliphatic polyester is compounded with 10–50 vol.% filler comprised of an inorganic filler (e.g., silica) and/or an organic filler (e.g., starch) to yield a composition. In addition, the mean volume of the filler is changed in the range of 4.2×10^{-3} to $65.4 \mu\text{m}^3$ and thereby the

biodegradation rate per unit volume of the filler is adjusted to 90–10% of that of the polyester. The biodegradable aliphatic polyester is preferably PHB, PCL, PEA, poly(tetramethylene adipate) (PTeMA), poly(cyclohexylene dimethyl adipate), etc. The inorganic filler can be talc, calcium carbonate, clay, silica, or alumina. The organic filler is, for example, various starches; a starch copolymer with vinyl acetate, acrylic acid, acrylate, etc.; wood powder; cellulose powder; thermosetting resin powder; etc. The composition is molded into the desired shape by extrusion molding, injection molding, etc., to give a molding that is prevented from biodegradation and disintegration during use, that is easily degraded and disintegrated by microorganisms after disposal, and is hence suitable for use as a pot, sheet, etc., for afforestation.

7.3.6 Plasticizers

Plasticizers are also used to modify and/or control the rate at which disposable materials degrade such that the disposal degradation rate is accelerated relative to the operative degradation rate.

Another embodiment of **US2002123546 A1** (2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC) or **WO9406866 A1** (1994, BIOPAK TECHNOLOGY LTD) is the use of at least one plasticizer to modify and/or control the rate at which

disposable materials degrade such that the disposal degradation rate is accelerated relative to the operative degradation rate. Preferred hydrophilic plasticizers include lactic acid, L-lactide, D-lactide, D,L-lactide, glycolide, glycolic acid oligomers, lactic acid oligomers, glycolide oligomers, L-lactide oligomers, D-lactide oligomers, D,L-lactide oligomers, butyl lactate, ethyl lactate, diethyl adipate, polyethylene glycol succinate, ϵ -caprolactone, valerolactone, adipic acid esters, citric acid esters, glycol-alkyl esters, and mixtures thereof. Oligomers are typically from about 2 to about 35 monomeric units. The disposable material usually contains from about 5 to about 50 wt.% plasticizer. A preferred amount of plasticizer in the disposable material is from about 10 to about 30 wt.%.

In one example, a poly(L-lactide-co-D,L-lactide) (with a weight ratio of L-lactide/D,L-lactide of 90/10) was plasticized with a lactide plasticizer (see [Table 7.3](#)). Copolymers either with a lactide plasticizer or with an activator (fumaric acid) showed more severe degradation after 9–12 weeks than did the copolymer sample with L-PLA (PLLA).

7.3.7 Blending with other Polymers

JPH11116788 A (1999, MITSUI CHEM INC) discloses a biodegradable resin composition and

Table 7.3 Tensile properties of a PLA film after seawater exposure¹

Sample composition	Exposure time, weeks	Elastic modulus, psi (MPa)	1% Secant modulus, psi (MPa)	Tensile strength, psi (MPa)
95% 90/10 L-/D,L 5% L-PLA	0	304,722 (2101)	292,020 (2013)	7649 (52.7)
	6	317,050 (2186)	317,050 (2186)	7314 (50.4)
	9	227,644 (1570)	230,284 (1588)	6214 (42.8)
	12	355,302 (2450)	343,061 (2365)	3881 (26.8)
90/10 L-/D,L 10% plasticizer (lactide)	0	274,521 (1893)	274,521 (1893)	6113 (42.2)
	3	291,181 (2008)	280,762 (1936)	6806 (46.9)
	6	246,050 (1697)	246,050 (1697)	3856 (26.6)
	9	110,864 (764)	105,251 (726)	1444 (10.0)
	12	360,000 (2482)	353,846 (2440)	3308 (22.8)
90/10 L-/D,L 1% fumaric acid	0	299,597 (2066)	297,546 (2052)	7053 (48.6)
	3	291,759 (2012)	291,439 (2009)	6471 (44.6)
	6	318,313 (2195)	318,313 (2195)	6896 (47.5)
	9	225,828 (1557)	223,310 (1540)	6142 (42.3)
	12	69,979 (483)	139,957 (965)	807 (5.6)

¹Exposure at Daytona Beach, Florida. Temperature range of seawater is 20–29°C. Salinity range of seawater is 33.4–38.4. pH range is 7.2–7.9. Values are the average of six specimens. Strain rate is 1.0 in./in./min. (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC; WO9406866 A1, 1994, BIOPAK TECHNOLOGY LTD).

a film formed thereof obtained by compounding 50–90 wt.% PLA, 10–50 wt.% of another biodegradable aliphatic polyester such as poly(ethylene oxalate), and 5–25 wt.% biodegradable plasticizer; if necessary, an inorganic filler (e.g., silica), a lubricant (e.g., an aliphatic carboxamide), an antioxidant, a heat stabilizer, an ultraviolet absorber, etc., can be added to the composition. The biodegradable plasticizer is selected from among triacetylene, acetyltributyl citrate, dibutyl sebacate, and the like. Blending PLA with poly(ethylene oxalate) facilitates hydrolysis of the biodegradable composition. Hydrolysis of poly(ethylene oxalate) releases an acid that functions as an ester degradation promoter. The released acid accelerates hydrolysis and promotes decomposition of the biodegradable composition by enzymes.

WO2008038648 A1 (2008, TOYO SEIKAN KAISHA LTD) discloses a readily degradable resin composition including an aliphatic polyester (A) which is biodegradable, and an aliphatic polyester (B). The aliphatic polyester (B) is biodegradable at a higher degradation rate than that of the aliphatic polyester (A) and has a melt viscosity of 50 Pa s or less at 190°C and a shear rate of 1 rad/s or a solution viscosity of 0.25 dl/g or less measured using 0.4 g/dl of the polyester (B) in mixed solvent containing *m*-chlorophenol and 1,2,4-trichlorobenzene in the weight ratio of 4:1 at 30°C. Preferred examples of the biodegradable aliphatic polyester (A) include PLA and PBS. Examples of the readily degradable aliphatic polyester (B) include poly(ethylene oxalate), poly(neopentyl oxalate) (PNOx), polyethylene maleate, and the like.

Upon hydrolysis, the aliphatic polyester (B) releases an acid showing a pH of 2.0 or less when dissolved in water at a concentration of 0.005 g/ml. Examples of the released acid are oxalic acid and maleic acid. By use of such aliphatic polyester (B), the aliphatic polyester (A) degrades rapidly. This is presumably because when water enters and elutes the aliphatic polyester (B), the eluted acid component hydrolyzes the aliphatic polyester (A) (such as PLA), which causes a large number of cracks inside the aliphatic polyester (A) that further increase the surface area on which an enzyme acts. The composition can be used for packaging materials such as films, pouches, pillow packaging bags, and cover material of tray cups.

However, when a readily degradable resin composition containing an aliphatic polyester (B), which releases an acid upon hydrolysis as described

above, is enzymatically degraded in a degradation liquid, the degrading rate decreases for the following reasons. Specifically, the acid is released from the readily degradable resin composition over time; this lowers the pH of the degradation liquid, which leads to a decrease in activity of the enzymatic degradation (see also Chapter 6: Chemical Recycling; Section 6.4: Enzymatic Depolymerization).

In addition, when a biodegradable resin is degraded with an enzyme, the enzyme and oligomers and/or a monomer produced by the degradation form aggregates; this eventually makes it difficult to recover the oligomers and/or the monomer. Since the aggregates are not dissolved again, the oligomers and/or the monomer cannot be recovered. Moreover, in the method for depolymerizing PLA to produce oligomers mainly composed of repolymerizable cyclic products, the oligomers cannot be recovered in high yield because of the low water content in the reaction system (WO2010050482 A, 2010, TOYO SEIKAN KAISHA LTD).

WO2012046709 A1 (2012, TOYO SEIKAN KAISHA LTD; KUREHA CORP) discloses an alternative solution for the rapid decomposition of a biodegradable resin composition that comprises a hardly hydrolyzable biodegradable resin such as PLA. The biodegradable resin composition comprises 100 parts by weight PLA, 0.01–30 parts by weight PGA and 28–200 parts by weight of an ester degradation adjuvant comprising inorganic particles that can accelerate the hydrolysis of PGA. The inorganic particles are basic compounds containing alkali metal or alkaline earth metal, preferably CaCO₃ and/or Na₂CO₃.

Furthermore, it was found that the addition of PHBHV to a film forming PHB could decrease the level of crystallinity in the blend, and the lower the initial crystallinity of the films, the higher the rate of hydrolytic degradation [21].

7.3.8 Mixtures of Biodegradation-Promoting and -Retarding Agents

A special case is the mixture of biodegradation-promoting and -retarding agents. **JP2001323177 A** (2001, MIYAGI PREFECTURE) discloses a biodegradable polymer composition prepared by mixing a biodegradation-promoting matter and a biodegradation-retarding matter, each at a definite mixing ratio to a biodegradable resin (e.g., PCL). The

biodegradation-promoting substance comprises an organic matter derived from plants such as rice bran, old rice, straw of rice, bean husk, rice hull, soybean hull, wheat bran, coffee hull, tea hull, coconut hull, bagasse, wood powder, used paper, starch-type polymer residue, and/or plant fiber. The biodegradation-retarding agent comprises an organic antimicrobial agent such as herbs, extracts of wood, polyphenol compounds, mugwort, chitosan, and polylysine. The resin composition is suitable in agriculture, forestry, and fishery applications; for example, mulch films, pots for nursery plants, packaging containers for raw garbage, etc. The biodegradation rate of the biodegradable polymer composition can be controlled according to usage, and will not pollute the soil after it is discarded.

GB2464285 A (2010, WELLS PLASTICS LTD) applies oxodegradable technology to (hydro)biodegradable polymers to enhance the biodegradability of biopolymers such as PHA. It does this by using an additive comprising a transition metal salt selected from tartrate, stearate, oleate, citrate, and chloride as pro-degradant. The additive can further comprise a free radical scavenging system and one or more inorganic or organic fillers such as chalk, talc, silica, wollastonite, starch, cotton, reclaimed cardboard, and plant matter. The free radical scavenging systems are used in order to postpone the reactivity of the transition metal salt pro-degradant so that the polymer does not fall apart immediately or prematurely. Examples of possible free radical scavenging systems include hindered phenolics, thiosynergists, phosphites, metal deactivators, monomeric, low and high molecular weight oligomeric and block oligomeric hindered amines, benzophenone absorbers, benzotriazoles, benzotriazines, natural antioxidants such as vitamin E, and other systems such as NORs (e.g., *N*-hydroxycarboxy-substituted hindered amines). The additive can also comprise an enzyme, a bacterial culture, a swelling agent, CMC, sugar, or other energy sources. The types of (hydro)biodegradable polymers include PHBV, PCL, PHB, PLA, acetylated starch, and related compounds, amongst other possibilities. The (hydro)biodegradable polymers comprising the additive can be used for bottles, containers, packages, films, agricultural mulch films, disposable garbage bags, drinking cups, cutlery, pens, and food container packaging. Oxidative degradation causes chain scission at C—C bonds (see Chapter 2: Definitions and Assessment of (Bio) degradation; Section 2.4: Types and Mechanisms of (Bio) degradation). The metal ion catalyst is

regenerated, which allows the reaction to continue and chain lengths to become progressively smaller. When the molecular weight is sufficiently reduced, fragmentation, hydrolysis, and subsequent breakdown (e.g., by microbial attack) are promoted.

JPH10273582 A (2005, OKURA IND CO LTD) developed a resin composition with a controllable biodegradation rate and reduced cost by mixing an aliphatic polyester with a specified amount of a vegetable fiber and an alkaline earth metal oxide. This composition comprises 79–99 parts by weight aliphatic polyester, 1–30 parts by weight vegetable fiber, and an alkaline earth metal oxide. Examples of the alkaline earth metal oxide are BeO, MgO, CaO, SrO, or BaO. The amount of the alkaline earth metal oxide added is larger on the basis of the amount stoichiometrically equivalent to the moisture which the vegetable fiber carries into the composition when the molding temperature is high or when the required biodegradation rate is high. It is smaller when the molding temperature is low or when the required biodegradation rate is low. The most desirable vegetable fiber is one derived from coconut husks.

7.3.9 Environmental Conditions (Temperature, Moisture, Radiation, and Time of Exposure)

Biodegradation is affected by temperature, moisture, and time of exposure. The hydrolysis of a biodegradable polymer is promoted by exposure to a high-temperature and high-humidity environment. However, this method of exposing fibers to a high-temperature and high-humidity environment is environmentally undesirable. The method requires that the used products be collected and transported to a place where they can be exposed to high temperature and high humidity. Thus, this method is troublesome, and the collection, transport, and treatment of the used products have a negative environmental impact (CA2411004 A1, 2003, KURARAY CO).

JP2003034734 A (2003, SONY CORP) and **JP2008223023 A** (2008, SONY CORP), which were commented on in Section 7.2.7, disclose the irradiation of an aliphatic polyester such as PLA with actinic rays. The actinic radiation is performed during molding of the biodegradable polymer composition, or when a molded product is discarded. The decomposition speed is controlled by changing the amount of irradiation. A more effective control of the

decomposition speed is achieved by using actinic rays in combination with a cross-linking agent.

FR2938265 A1 (2010, UNIV CLAUDE BERNARD LYON) discloses a process and an installation for the control of the depolymerization treatment of a water-soluble biopolymer — such as protein including hydrosoluble collagen, or polysaccharides and their hydrosolubles including chitosan — in which a given volume of a solution of the biopolymer is subjected to the action of ultrasonic waves produced by an ultrasonic probe penetrating the solution.

7.3.10 Surface Modification

Surface modification includes chemical treatment or coating of shaped articles made of biodegradable biopolymers. Surface modification is effective in varying the hydrophilicity and biodegradability of biodegradable biopolymers without altering their bulk physical properties.

Alkaline surface treatment has been reported to enhance the enzymatic degradation of biodegradable polyesters in soil and seawater [18,22,23]. It is expected that the hydrophilic surface will attract environmental microbes and their enzymes, resulting in rapid degradation [24]. Numerous microbes were observed on the alkali-treated PCL film [23]. On the other hand, it has been asserted that the treatment of PLA fibrous products with a strong alkali, such as aqueous sodium hydroxide solution having a pH of 10 or more, is effective for promoting fiber hydrolysis; however, it kills biodegrading enzymes that are not resistant to alkali, and therefore retards the biodegradation of the fibrous products. For example, even if used PLA fibers and their products are buried in ground into which sugar-containing water or the like has been infiltrated in order to promote the growth of microorganisms, biodegradation of fibers so treated may not be promoted. In addition, such a method of treating used fibrous products with a strong alkali is environmentally undesirable (CA2411004 A1, 2003, KURARAY CO).

CA2411004 A1 and **JP2003213521 A** (2003, KURARAY CO) disclose fibers comprised of a PLA having a number-average molecular weight of from 50,000 to 150,000, wherein the alkali solubility of an interior portion of each fiber is greater than the alkali solubility of the outer, peripheral portion of the fiber, and the surface of each fiber has from 5 to 50 cracks/10 cm. The biodegradation of the PLA fibers is accelerated by treating the fibers with

a fiber-processing agent comprised of at least 1 wt.% of at least one component selected from the group consisting of organic phosphate salts, unsaturated fatty acids, and unsaturated alcohols. After the fibers are processed with an alkaline solution, the processing agent penetrates into the center part of the cross-section of each fiber through the cracks, and significantly promotes the degradation of the fibers. The outer skin of each fiber remains essentially intact, while the inside of the fiber is eroded.

JP2002256088 A (2002, KANAZAWA INST OF TECHNOLOGY) provides a molded product of an aliphatic polyester — whose surface is chemically modified with corona, plasma, or flame treatment — promoted in biodegradation without deteriorating its strength. The surface treatment introduces oxygen-containing functional groups to the surface of the molded product, which promotes the biodegradation rate. The aliphatic polyester is either the reaction product of an aliphatic diol and an aliphatic dicarboxylic acid (polyalkanoate), or PCL.

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8 Developments and Trends in Patenting

OUTLINE

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8.1 Biopolymers and Patents

A patent is a legal title granting its holder the right to prevent third parties from commercially using an invention without authorization. In return for this protection, the holder has to disclose the invention to the public. Protection is granted for a limited period, generally 20 years, for a specific geographic area.

Users of patent documents often encounter difficulties in identifying the bibliographic data associated with patent documents. A list of approximately 60 distinct bibliographic data is widely used on the first page of patent documents or in Patent Gazettes (see Figure 8.1). They are identified through code numbers, the so-called “INID Codes” or “INID Numbers.” (“INID” is an acronym for “Internationally agreed Numbers for the Identification of (bibliographic) Data”) [1]. The bibliographic data covered in the recommendation section ranges from data for the document identification, filing data, priority data, publication data, data concerning technical information, and data related to International Patent Conventions. The following codes are used in the European Patent Bulletin [2] in addition to the INID codes to identify the kind of publication:

A1: Publication of the European patent application with search report.

A2: Publication of the European patent application without search report.

A3: Separate publication of the European or international search report.

B1: Publication of the European patent specification.

B2: Publication of the new European patent specification.

A distinction has to be made between a patent application and a granted patent. A patent application is an invention, which has been published but not granted yet (“pending”) and is indicated by the symbol “A” (A1 or A2 or A3) following the patent’s application number (e.g., EP2 348121 A1). A granted patent is indicated by the symbol “B” (B1 or B2) following the patent number (e.g., EP0726325 B1).

To be patentable, an invention must fulfill four requirements:

- Have a technical character (e.g., comprise a product, process or apparatus).
- Be novel.
- Involve an inventive step.
- Be industrially applicable.

(19)  (11)  **EP 2 022 818 A1**

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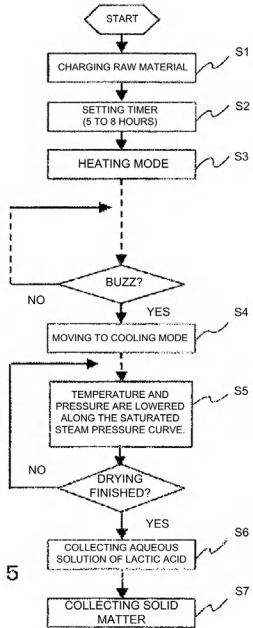
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(54) **PROCESS FOR THE DECOMPOSITION AND RECLAMATION OF SYNTHETIC RESINS HAVING ESTER-LINKAGE STRUCTURES**

(57) The synthetic resin having ester bond in the composition structure is subjected to the hydrolysis treatment to reclaim the raw material component before polymerization. Provided is a method for decomposing and reclaiming a synthetic resin having ester bond in the composition structure thereof, executing the hydrolysis treatment and the separation collection treatment in this order. The hydrolysis treatment is a treatment in which an article to be treated containing a synthetic resin to be decomposed and reclaimed is exposed to a water vapor atmosphere filled at or below the saturation water vapor pressure at a treatment temperature specified by the condition of treatment temperature of at or below the melting point of the synthetic resin, and the synthetic resin in the article to be treated is hydrolyzed by the water vapor generated at the treatment temperature, thus a decomposition product before polymerizing to the synthetic resin containing ester bond in the composition structure thereof is generated. The separation collection treatment is a treatment in which the decomposition product generated by the hydrolysis treatment is separated into liquid component and solid component to be collected individually.

FIG. 5



```

graph TD
    START([START]) --> S1[CHARGING RAW MATERIAL S1]
    S1 --> S2[SETTING TIMER 5 TO 8 HOURS S2]
    S2 --> S3[HEATING MODE S3]
    S3 --> S4{BUZZ? S4}
    S4 -- NO --> S3
    S4 -- YES --> S4_1[MOVING TO COOLING MODE S4]
    S4_1 --> S5[TEMPERATURE AND PRESSURE ARE LOWERED ALONG THE SATURATED STEAM PRESSURE CURVE S5]
    S5 --> S6{DRYING FINISHED? S6}
    S6 -- NO --> S4_1
    S6 -- YES --> S6_1[COLLECTING AQUEOUS SOLUTION OF LACTIC ACID S6]
    S6_1 --> S7[COLLECTING SOLID MATTER S7]
  
```

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Figure 8.1 First page of an example European patent application depicting bibliographic data.

Some innovations are not patentable. For example, mathematical methods or formulas, computer programs, and business methods are as such not regarded as inventions. New plant or animal varieties and inventions whose commercial exploitation would be contrary to “ordre public” or morality (e.g., the cloning of human life) are examples of inventions excluded from patentability.

Many researchers are not familiar with patents. However, patents can give new insights into research, provide supplementary information on the state of the art, show industrial trends, and monitor activity in technical fields. After all, more than 80% of all technical information is recorded in patents.

In the past several years there has been substantial focus on environmental issues. This interest has

been reflected in patents. The number of patents on waste treatment technologies, new biodegradable materials, alternative energy sources (e.g., photovoltaic panels, aeolian energy, and geoenery harnessing unexploited forms of energy), and sequestration of carbon dioxide is growing. The European Patent Office, in response to the challenges of the day and in an effort to keep pace with new developments and embrace the growing number of patents, has introduced new classification groups such as climate change (Y02). This class covers selected technologies, which control, reduce, or prevent anthropogenic gases (GHG), as controlled by the Kyoto Protocol.

Biodegradable materials are one of the fastest growing technical areas. Biodegradable polymers in particular, with many applications in packaging.

8.2 Patent Analysis

It is widely accepted that patent statistics are a reliable (although not perfect) indicator of innovative activity. Therefore, it has become standard practice to use patent statistics for monitoring innovative activities and the development of new technologies. However, when using patent statistics as an indicator of inventive activity, the following points should be taken into consideration:

- Not all inventions are patented. There are other alternatives available to inventors for protecting their inventions, such as trade secrecy or technical know-how.
- Use of the patent system for protecting inventions varies across countries and industries. Applicants' different filing strategies or filing preferences may render direct comparison of patent statistics difficult.
- Differences in patent systems may influence the applicant's patent filing decisions in different countries.
- Due to the increase in the internationalization of research and development (R&D) activity, R&D may be conducted in one location, but the protection for the invention might be sought in a different one.
- Cross-border patent filings depend on various factors, such as trade flows, foreign direct investment, market size of a country, etc.

Notwithstanding the points mentioned above, patent statistics do provide valuable information about innovative activity.

The number of patents and rate of patenting are some of the indicators used to estimate industrial activity. One problem with patent count is that it assumes that all patents are equal in their economic and technological values. Other measures used to estimate industrial activity include the number of important patents and the sales of new products. An empirical way to measure the number of important patents is by counting the so-called triadic patents.

Triadic patents are a series of corresponding patents filed at the European Patent Office (EPO), the United States Patent and Trademark Office (USPTO), and the Japan Patent Office (JPO), for the same invention and by the same applicant or inventor. Triadic patents form a special type of patent family. Triadic patents reflect a select group of inventions of which the owner expects to collect most of the profits, as she is willing to incur the relatively high patent filing and patent maintenance costs at all three patent offices [3].

A company's patent portfolio can represent a significant fraction of the overall value of the company. There are several tools for the evaluation and management of patents, for example, EPO's patent evaluation software, Ipscore [4].

One has to be careful when analyzing patent data. Patents related to biopolymers are spread across several technical fields and their retrieval is not straightforward. Quite often different keywords or codes are used to describe biopolymers. Furthermore, in the same technical field classification is quite often incomplete, erroneous, or even not updated. As one example, poly(butylene succinate) (PBS) can be classified either as an aliphatic polyester or as a biodegradable biopolymer, but it can be found also in many applications under its most common commercial name, BionolleTM (Showa Denko KK). There is extra difficulty with the non-biodegradable, bio-based biopolymers, such as bio-based polyethylenes or polyamides, for which there is not yet a separate classification scheme. These have to be searched within the corresponding conventional polymer classification schemes. Therefore, no reliable conclusions can be drawn by blindly following these data. This can have a serious impact on future development and investment. Last but not least, a substantial part of the available patent literature is in Japanese, with only a short abstract in English.

On the basis of the abstract, an English speaker may consult an online machine translation of the text, which is a very tedious and not always reliable procedure. In the present review, every effort was made to overcome these obstacles, to minimize their possible effects, and to enable the retrieval of every patent related to the waste treatment of biopolymers. This has been done by taking into account all possible ways of classifying, coding, and naming various biopolymers.

8.2.1 Distribution of Patent Applications Per Category of Waste Treatment

Waste biopolymers can be disposed of, reused, or recycled. As seen in Figure 8.2 and Table 8.1, 103 patent inventions relate to disposal, and 109 relate to

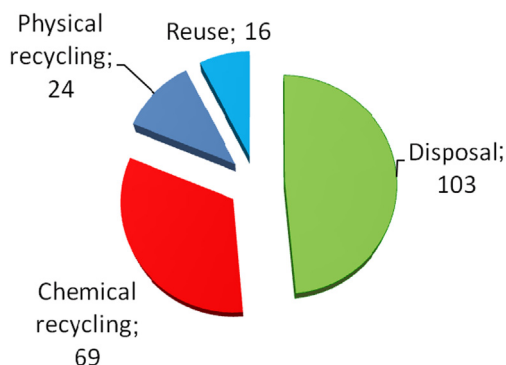


Figure 8.2 Distribution of patent inventions per category for waste treatment during the period January 1, 1990 to August 31, 2012.

recycling. Of the recycling patents, 69 relate to chemical recycling.

The patent counts on chemical recycling are distributed further as follows:

Chemical recycling: **69**

- Dry heat depolymerization: **10**
- Hydrolysis/Alcoholysis: **21/8**
- Hydrothermal: **19**
- Enzymatic depolymerization: **10**
- Miscellaneous: **1**

The importance of these patents as expressed by the number of triadic patents is rather limited. Notably, most patent inventions on all types of waste treatment are patent applications (“A” type). In other words, they are pending, and only few are granted (“B” type).

8.2.2 Geographical Distribution of Patent Applications on Waste Treatment

As shown in Figure 8.3, Japan leads patent applications on biopolymers when expressed as either country of publication or as country of priority. Japan also has the highest number of patent applications worldwide relating to the waste treatment of biopolymers (66% of all patents). Only two non-Japanese companies are actively involved on a large scale with the recycling of biopolymers or bioplastics, namely NatureWorks LLC in the United States and Galactic S.A. in Europe. However, in view

Table 8.1 Number of patent inventions per category of waste treatment

	Patent inventions	Patent inventions % (of sum/of total)	Patent inventions + patent family members	Triadic patents
Disposal	103	48.6%/52.3%	242	9
Reuse	16	7.5%/8.1%	73	4
Physical recycling	24	11.3%/12.2%	95	1
Chemical recycling	69	32.5%/35.0%	158	5
Sum/Total	212 /197*		568 (500*)	

*The total number of patents is different from the sum of the individual types because there is overlap between waste treatment classifications. For example, an integrated waste treatment system of biopolymers can comprise a combination of physical and chemical processes, or a patent invention can be categorized under both reuse and physical recycling.

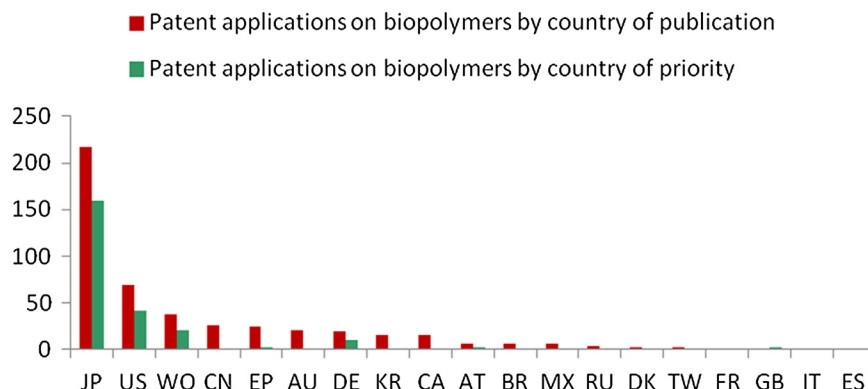


Figure 8.3 Geographical distribution of patent applications (including family members) for the waste treatment of biopolymers during the period January 1, 1990 to August 31, 2012.

Abbreviations: AT, Austria; AU, Australia; BR, Brazil; CN, China; DE, Germany; DK, Denmark; EP, European Patent Office; ES, Spain; FR, France; GB, Great Britain; IT, Italy; JP, Japan; KR, Republic of Korea; MX, Mexico; RU, Russian Federation; TW, Taiwan; US, United States of America; WO, World Intellectual Property Organization (WIPO).

of the large number of patent applications for the recycling of biopolymers, future commercial implementation are expected.

Also of note, most of the Chinese (CN), Australian (AU), Korean (KR), and Canadian (CA) published patents originate from other countries, as evidenced by their priority dates.

As seen in Figure 8.4, the first patent applications on the waste treatment of biopolymers appeared in the early 1990s. Since then, the general trend seems to follow the trend of biopolymers, where for roughly 240 patent applications on biopolymers, there corresponds approximately one patent application for the waste treatment of biopolymers.

The drop in the number of patents over the 2010–2012 time period is attributable to the global

recession, which affected both economies and capital markets.

Table 8.2 shows the major patent applicants involved in the waste treatment of biopolymers. As can be seen, 66% (132/198) of the retrieved patent inventions are from companies and organizations in Japan.

8.3 Prospects and Limitations of the Waste Treatment Options of Biopolymers

Waste biopolymers can be disposed of, reused, or recycled. As explained in Chapters 3 through 6, all three options for the waste treatment of biopolymers are controversial.

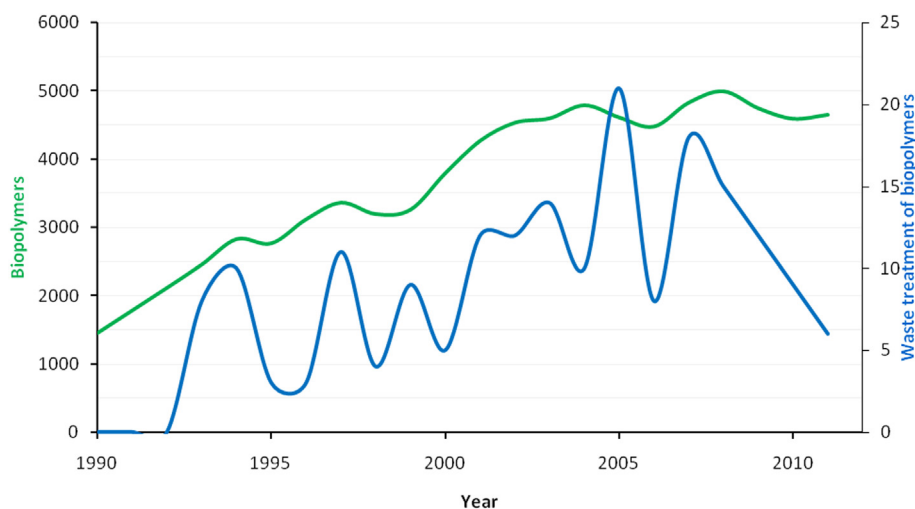


Figure 8.4 Patent applications on biopolymers and their waste treatment worldwide during the period January 1, 1990 through August 31, 2012.

Table 8.2 Major patent applicants in the waste treatment of biopolymers

Applicants (companies, institutions, universities, individuals)	No. patent inventions
NAT INST ADN IND SCI TECHN	30
TEIJIN FIBERS LTD	14
DU PONT	11
MITSUBISHI	12
MITSUI TOATSU CHEM, MITSUI SHIPBUILDING	12
SHIMADZU CORP	10
UNIV KEIO	9
TOKIWA Y	7
NAKAMURA K	6
FUJIXEROX, FUJI ELECTRIC, FUJIFILM	6
GALACTIC SA	5
UNIV TOYOHASHI TECHNOLOGY	5
KANEBO SYNTHETIC FIBERS LTD	4
SHARP CORP	4
ALMIGHTY KK	3
BAYER AG	3
CANON KK	3
JAPAN STEEL WORKS LTD	3
KITAKYUSHU FOUNDATION	3
KYUSHU INST OF TECHNOLOGY	3

The main problems faced with each of these options are as follows:

Disposal

- Most commercial biopolymers, such as polylactide (PLA), are not degraded under ordinary conditions, even in presence of microorganisms.
- Disposal of biopolymer articles has the disadvantage of discarding valuable raw materials (e.g., polyhydroxy acids).

- Landfill disposal is not recommended for the disposal of biopolymers, and domestic and municipal composting of biopolymers are even less favored.
- Few waste haulers and landfills are able to accommodate the composting of biodegradable biopolymers.
- Although industrial composting is considered by many specialists to be the best suited end-of-life disposal method for biopolymers, there is not an adequate number of large-scale industrial composting facilities to implement it.
- Large amounts of disposed of PLA may create new environmental problems in the future.

Reuse

- Most biodegradable polymers, such as PLA, are highly susceptible to thermal deterioration, and reuse of such materials as they exist is liable to cause coloration, degeneration, and decrease in molecular weight of the polymer. Therefore, it is difficult to reuse biodegradable polymers.

Recycling

- Biodegradable biopolymers constitute a serious problem when they enter a conventional mechanical plastics recycling facility. For example, PLA contaminates the waste stream of PET due to its low thermal resistance.
- Mechanical recycling of rigid biopolymers can be handled at present only as a sideline in existing recycling facilities, provided the value of the recycled product exceeds incurred costs.

8.4 Conclusions

The following conclusions can be drawn from the current state of patents:

- Waste treatment of biopolymers is an unresolved issue.
- 51.8% of retrieved patent inventions are related to disposal and 48.2% to recycling.
- The majority of patents relate to enzymatic decomposition of biopolymers followed by hydrolysis treatment.

- Hydrolysis in the melt (hydrothermal) and dry heat depolymerization are promising methods for the depolymerization and recycling of rigid biopolymers, especially PLA.
- Most of the retrieved patents relate to waste treatment of PLA and only a small fraction to polyhydroxyalkanoates (PHAs).
- Degradation rates of biopolymers during use or after disposal can be controlled by chemical, thermal, or enzymatic means.
- Japan has the highest number of patent applications worldwide relating to the waste treatment of biopolymers (66% of all patents).
- In view of the large number of patent applications (198), future commercial implementations are to be expected.

Industrial composting is currently the preferred end-of-life disposal method for biopolymers, especially soft packaging (e.g., films). Domestic and municipal composting is less favored, while landfill disposal is not recommended at all.

Japan has put a greater emphasis on biodegradable biopolymers, and their use is encouraged not only by the private sector but also by the government. In 2002 Japan ratified the Kyoto Protocol, which requires countries to reduce their emissions of carbon dioxide and other greenhouse gases, and Japanese corporations will have to play their part in achieving this goal. This means that the use of biopolymers, seen as an effective way of cutting carbon dioxide emissions, is likely to continue to expand. Even though the cost of these new polymers is high, many Japanese plastics producers, car manufacturers, consumer electronics manufacturers, and even retailers have already based some parts of their products on biopolymers.

8.5 Development of New Waste Treatment Processes/Materials

The production of biopolymers, while still representing a small portion of total plastic use, will continue to grow, and the accompanying generation of waste is anticipated to rise proportionally. This trend is likely to impact the generation and management of biopolymers. Most commercial biopolymers, such as PLA, do not degrade under ordinary conditions, and the increased use of

biopolymers may have implications for the recycling of conventional polymers by contaminating existing (e.g., PET) recycling streams.

New technologies are currently being investigated in an effort to mitigate the above problems. Patent trends and technological developments will impact the waste treatment of biopolymers. These new developments can be summarized as follows:

- New enzymes for the depolymerization and/or recycling of biopolymers (e.g., genetically modified enzymes).
- Advances in industrial composting.
- New recycling techniques such as hydrothermal, dry heat, and enzymatic depolymerization.
- Control of degradation rate (promotion or suppression of degradability on demand).

Besides technological innovations to the recycling and disposal of biopolymers, other research efforts are focused on the development and design of new biopolymer products. The main issues for the next generation of biopolymers are:

- Use of alternative non-food-based feedstocks.
- Saving energy resources.
- Reduction of production costs.
- Reduction of carbon dioxide emissions.
- Disposal/recycling.

A future process for the production and degradation of biopolymers should consume low amounts of energy, have a full life-cycle, and satisfy the following requirements: (1) the polymer should be degraded into low molecular weight compounds without consuming much energy, such as fossil fuel energy; (2) the low molecular weight compounds should be effectively reutilized; and (3) the original polymer should be obtainable from the low molecular weight compound without similarly consuming much energy.

The main trend in biopolymers is the development of conventional polymers, such as polyolefins (e.g., PE, LDPE, PP) and aromatic polyesters (e.g., PET), from renewable resources, so the biopolymer industry is dividing its products into single-use disposable or compostable materials, and durable products, which are not designed to be compostable [5].

The challenges with recycling PLA bottles, in combination with the poor barrier properties of PLA, has in part led many major bottle producers like Coca-Cola to avoid their use. Instead, Coca-Cola is trying to develop and introduce a new generation of bio-based PET bottles based on a 100% bio-based PET wherein both the glycol and terephthalic acid are derived from renewable resources. This bio-based PET could be recycled together with PET derived from fossil-derived fuel without problem [6].

Another trend is the substitution of conventional PET with poly(ethylene furanoate) (PEF) (see Chapter 1: Introduction to Biopolymers; Section 1.3.2.3: Aromatic polyesters (bio-based)), which is 100% bio-based and is claimed to have better gas barrier properties. This brings substantial savings to fossil fuel consumption, and reduces carbon dioxide emissions.

An innovation already in use is the combination of different technologies without compromising biodegradability properties. Two examples are hybrid biopolymer production from the copolymerization of fossil fuel- and plant-based monomers (e.g., Ecoflex[®] of BASF), and biocomposite production by compounding biopolymers with different additives.

An even more economical solution is the blending of biopolymers with conventional polymers or other biopolymers (e.g., Ecovio[®] from BASF).

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9 Regulatory Aspects Framework

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9.1 Standards

A standard is a document that provides requirements, specifications, guidelines, or characteristics that can be used consistently to ensure that materials, products, processes, and services are fit for their purpose (ISO) [1].

The main international and national organizations that have established standards are the following:

- International Organization for Standardization (ISO) [1]
- European Committee for Standardization (Comité Européen de Normalisation) (CEN) [2]
- American Society for Testing and Materials (ASTM) [3]
- German Institute for Standardization (Deutsches Institut für Normung) (DIN) [4]
- Japanese Standards Association (JSA) [5]
- British Standards Institution (BSI) [6]

- Organization of Economic Co-operation and Development (OECD) [7]
- Standards Australia (AS) [8]

ISO, ASTM, and CEN are actively involved in developing and issuing standards related to biopolymers or bioplastics, wherein the main focus is devoted to biodegradability, compostability, and content of renewables. In addition, DIN, BSI, and the Japan BioPlastics Association (JBPA), contribute to the development and issuing of standards on biodegradable and/or compostable biopolymers. Recently, there has been interest in developing national standards related to compostability and biodegradation testing in other regions of the world (e.g., China, Taiwan, and Australia).

OECD developed a series of standardized tests called “Guidelines for the Testing of Chemicals.” The OECD guidelines described the first laboratory tests for evaluating the biodegradability of chemicals in aquatic environments and formed the basis for several of the modern standards; however, the OECD tests were meant for low-molecular-weight chemical

compounds at low concentrations, and therefore are less suitable for biopolymers.

9.1.1 Standards Related to the Recycling of Biopolymers

There are no standards dedicated to the recycling of biopolymers. However, the same standards that are used for fossil-fuel derived polymers can be applied to polymers derived from renewable resources (bio-based) as there are no specific requirements for biopolymers. For example, bio-based polyethylenes have the same properties as fossil fuel-based polyethylenes and can be recycled in the same way as their fossil-based counterparts (see Chapter 1: Introduction to Biopolymers; Section 1.11: Vinyl Polymers).

Plastic recyclates are generally dealt with by the standards of the EN 1534x series. These standards define minimum quality criteria of recycled plastics made of PE, PP, PS, PVC, and PET. There are no specific requirements for biopolymers or bioplastics.

EN 15342:2007

Title: Recycled Plastics — Characterization of polystyrene (PS) recyclates.

Scope: This European standard defines a method of specifying delivery condition characteristics for PS recyclates. It gives the most important characteristics and associated test methods for assessing a single batch of PS recyclates intended for use in the production of semi-finished/finished products. It is intended to support parties involved in the use of recycled PS to agree on specifications for specific and general applications. This standard does not cover the characterization of plastics wastes (see EN 15347). This standard is applicable without prejudice to any existing legislation.

EN 15343:2007

Title: Recycled Plastics — Plastics recycling traceability and assessment of conformity and recycled content.

Scope: This European standard specifies the procedures needed for the traceability of recycled plastics. This gives the basis for the calculation procedure for the recycled content of a product. This standard is applicable without prejudice to any existing legislation.

Note: The procedures are needed to formulate or describe the traceability, while the traceability can be used as a basis for calculating the recycled content.

EN 15344:2007

Title: Recycled Plastics — Characterization of polyethylene (PE) recyclates.

Scope: This European standard defines a method of specifying delivery conditions for polyethylene (PE) recyclates. It gives the most important characteristics and associated test methods for assessing PE recyclates intended for use in the production of semi-finished/finished products. It is intended to support parties involved in the use of recycled PE to agree on specifications for specific and generic applications. This standard is applicable without prejudice to any existing legislation. This standard does not cover the characterization of plastics wastes (see EN 15347).

EN 15345:2007

Title: Recycled Plastics — Characterization of polypropylene (PP) recyclates.

Scope: This European standard defines a method of specifying delivery conditions for PP recyclates. It gives the most important characteristics and associated test methods for assessing a single batch of PP recyclates intended for use in the production of semi-finished/finished products. It is intended to support parties involved in the use of recycled PP to agree on specifications for specific and general applications. This standard does not cover the characterization of plastics wastes (see EN 15347). This standard is applicable without prejudice to any existing legislation.

EN 15346:2007

Title: Recycled Plastics — Characterization of poly(vinyl chloride) (PVC) recyclates.

Scope: This European standard defines a method of specifying delivery conditions for PVC recyclates. It gives the most important characteristics and associated test methods for assessing PVC recyclates intended for use in the production of semi-finished/finished products. It is intended to support parties involved in the use of recycled PVC to agree on specifications for specific and generic applications. This standard does not cover the characterization of plastics wastes (see EN 15347). This standard is applicable without prejudice to any existing legislation.

EN 15347:2007

Title: Recycled Plastics — Characterization of plastics wastes.

Scope: This European standard provides a scheme for the characterization of plastics wastes, laying out those properties for which the supplier of the waste shall make information available to the purchaser, and identifying test methods where applicable. The scheme provides for a division of information between “Required Data,” where a statement is required, even if it is “unclassified,” and additional “Optional Data” which the supplier may choose to

provide if it adds value to the waste. This standard is applicable without prejudice to any existing legislation. Note: This standard does not cover the characterization of plastics recyclates.

EN 15348:2007

Title: Recycled Plastics — Characterization of poly(ethylene terephthalate) (PET) recyclates.

Scope: This European standard gives guidelines for the characterization of PET recyclates. It gives the most important characteristics and associated test methods for assessing PET recyclates intended to be used for the production of semi-finished/finished products. It is intended to assist the supplier and purchaser of such materials in agreeing on specifications. This standard was produced in accordance with the guidance produced by CEN on Environmental Aspects and in accordance with CEN/TR 15353.

CEN/TR 15353:2007

Title: Recycled Plastics — Guidelines for the development of standards for recycled plastics.

Scope: This technical report provides a format for the drafting of standards for recycled plastics. It is intended for use by those preparing drafts for consideration by the Technical Committee. The guide provides information for the development of standards (guides, practices, test methods, and specifications) relating to the proper use of recycled plastics.

ASTM D1972-97(2005)

Title: Standard practice for generic marking of plastic products.

Scope: This practice covers a system for uniform marking of products that have been fabricated from polymeric materials. Provision for the process or processes to be used for marking is outside the scope of this practice.

This marking system is to provide assistance in identification of products for making subsequent decisions as to handling, recycling, or disposal.

ASTM D5203-07

Title: Standard specification for polyethylene plastics molding and extrusion materials from recycled postconsumer (HDPE) sources.

Scope: This specification provides for the identification of recycled postconsumer HDPE molding and extrusion materials, from specified sources, in pellet or chip form so that the supplier and the user can agree on the acceptability of lots or shipments. This specification covers postconsumer HDPE materials from the following: (1) blow molded

household chemical containers, (2) blow molded milk, juice, and water containers, (3) materials from the spunbonded process, (4) thermoformed packaged food containers and personal care packages, (5) injection molded packaged food containers and beverage bottle base cups, and (6) injection molded house wares and industrial articles such as pails, crates, totes, and pallets. Other postconsumer HDPE materials may be added to this specification when such material streams are characterized.

ASTM D5577-94(2010)e1

Title: Standard guide for techniques to separate and identify contaminants in recycled plastics.

Scope: This guide is intended to provide information on available methods for the separation and classification of contaminants such as moisture, incompatible polymers, metals, adhesives, glass, paper, wood, chemicals, and original-product residues in recycled plastic flakes or pellets. Although no specific methods for identification or characterization of foam products are included, foam products are not excluded from this guide. The methods presented apply to postconsumer plastics.

ASTM D5814-10

Title: Standard practice for determination of contamination in recycled poly(ethylene terephthalate) (PET) flakes and chips using a plaque test.

Scope: This practice covers an indication of the quality of recycled transparent PET by examination of a wafer or plaque formed by melting a representative sample and quenching it to prevent crystallization.

ASTM D5991-09

Title: Standard practice for separation and identification of poly(vinyl chloride) (PVC) contamination in poly(ethylene terephthalate) (PET) flake.

Scope: This practice covers four procedures for separation and qualitative identification of PVC contamination in PET flakes.

ASTM D6265-09

Title: Standard practice for separation of contaminants in polymers using an extruder filter test.

Scope: This practice covers a means to separate the unmolten particles, gels, and impurities contaminating a polymer sample. The procedure may be used to remove gels and incompatible materials that may cause imperfections in the final extruded product. Under pressure, most gels will break up or deform and pass through a wire mesh filter; however, high-molecular-weight gels may not break up or deform.

ASTM D6288-09

Title: Standard practice for separation and washing of recycled plastics prior to testing.

Scope: This practice describes a procedure for separating recycled plastics based on their color (for example, green versus colorless) and a procedure for washing dirty, ground plastic which results in separation of light materials (density $< 1.00 \text{ g/cm}^3$). This practice is not intended to represent generic washing procedures used in the plastics recycling industry. The described procedures are solely for preparation of plastic samples for use in other analytical tests. The procedure includes a room temperature wash step to facilitate separation of paper (for example, labels) followed by washing at an elevated temperature.

ASTM D7209-06

Title: Standard guide for waste reduction, resource recovery, and use of recycled polymeric materials and products.

Scope: This guide provides information for the development of standards (guides, practices, terminology, test methods, or specifications) relating to plastics recycling and other means of waste reductions and resource recovery.

ASTM D7611/D7611M-10

Title: Standard practice for coding plastic manufactured articles for resin identification.

Scope: This practice stipulates the types, names, and sizes of codes for those material types specified in Table 1 of the practice (see the full text of the standard).

Resin Identification codes are used solely to identify the plastic resin used in a manufactured article.

Resin Identification Codes are not “recycle codes.” The use of a Resin Identification Code on a manufactured plastic article does not imply that the article is recycled or that there are systems in place to effectively process the article for reclamation or reuse. The term “recyclable” or other environmental claims shall not be placed in proximity to the code.

9.1.2 Standards Related to the Disposal of Biopolymers

The regulatory framework for the disposal of biopolymers includes standards or norms, certifications, and legal aspects. The various standards are divided into two groups:

- Standard specifications describing product requirements and setting a test scheme

combining different tests, criteria, and pass levels.

- Testing standards describing detailed procedures for the execution of the test methods as well as the evaluation of tests and the permissible limiting values.

9.1.2.1 Standard specifications on compostability

A specification is a kind of standard that defines two requirements:

- A set of scientific tests that can be used to measure the properties of a biopolymer.
- A set of criteria (threshold values) that these measurements must meet for the biopolymer to be considered “compostable.”

The specification standards defining the requirements for compostability of biopolymers (materials and products) are listed in [Table 9.1](#):

ISO 17088:2012

Title: Specifications for compostable plastics.

ISO 17088:2012 describes the same test scheme as EN 13432:2000, EN 14995:2006, and ASTM D6400-12.

EN 13432:2000

Title: Requirements for packaging recoverable through composting and biodegradation — Test scheme and evaluation criteria for the final acceptance of packaging.

Scope: This European Standard specifies requirements and procedures to determine the

Table 9.1 Standard specifications for testing compostability

ISO 17088:2012
EN 13432:2000
EN 13432:2000/AC:2005
EN 14995:2006
ASTM D6400-12
ASTM D6868-11
DIN V54900
AS 4736-2006
AS 4736-2006/Amdt 1-2009
AS 5810-2010
BNQ — 9011-911/2007

compostability and anaerobic treatability of packaging and packaging materials by addressing four characteristics: (1) biodegradability; (2) disintegration during biological treatment; (3) effect on the biological treatment process; and (4) effect on the quality of the resulting compost. In case of a packaging formed by different components, some of which are compostable and some others which are not, the packaging itself as a whole is not compostable.

EN 13432:2000/AC:2005

Title: Packaging — Requirements for packaging recoverable through composting and biodegradation — Test scheme and evaluation criteria for the final acceptance of packaging.

Scope: No scope available.

EN 14995:2006

Title: Evaluation of compostability — Test scheme and specifications.

Scope: This European standard specifies requirements and procedures to determine the compostability or anaerobic treatability of plastic materials by addressing four characteristics: (1) biodegradability; (2) disintegration during biological treatment; (3) effect on the biological treatment process; and (4) effect on the quality of the resulting compost.

Note: For packaging, EN 13432 applies, while EN 14995:2006 applies to plastic material in general. Both European standards define requirements and methods for establishing compostability and anaerobic treatment.

ASTM D6400-12

Title: Standard specification for labeling of plastics designed to be aerobically composted in municipal or industrial facilities.

Scope: This specification covers plastics and products made from plastics that are designed to be composted in municipal and industrial aerobic composting facilities. The properties in this specification are those required to determine if plastics and products made from plastics will compost satisfactorily, including biodegrading at a rate comparable to known compostable materials. The purpose of this specification is to establish standards for identifying products and materials that will compost satisfactorily in commercial and municipal composting facilities.

ASTM D6868-11

Title: Standard specification for labeling of end items that incorporate plastics and polymers as

coatings or additives with paper and other substrates designed to be aerobically composted in municipal or industrial facilities.

Scope: Requirements for labeling of materials and products (including packaging), wherein a biodegradable plastic film or coating is attached (either through lamination or extrusion directly onto the paper) to compostable substrates and the entire product or package is designed to be composted in municipal and industrial aerobic composting facilities. This specification, however, does not describe the contents of the product or their performance with regards to compostability or biodegradability. In order to compost satisfactorily, the product must demonstrate each of the three characteristics as follows: (1) proper disintegration during composting; (2) adequate level of inherent biodegradation; and (3) no adverse impacts on the ability of composts to support plant growth.

The standards EN 13432:2000, EN 14995:2006, ISO 17088:2012, and ASTM D6400-12 define the same test scheme for the characterization of a product as compostable. All four standards state that in order for a product to be compostable, the following criteria must be considered closely: characterization of material composition, disintegration, biodegradation, and compost quality.

- (1) Characterization of material composition: identification of the different constituents (e.g., by IR), organic matter content, and heavy metal concentration level. In the EN standards the organic matter content determined as volatile solids must be at least 50%; there are maximum concentrations defined for 11 elements. ASTM D6400-12 does not define a minimum content of organic matter and permits higher values for heavy metals in the material than the EN standards [9].
- (2) Disintegration: the ability to fragment into indistinguishable pieces after screening and safely support bio-assimilation and microbial growth. The disintegration requirements are similar in all four standards. At least 90% of original dry weight disintegrates into particles having a size of less than 2 mm (maximum of 10% of original dry weight may remain after sieving on a 2.0 mm sieve) after a specified time; namely, 12 weeks in the EN standards, 45 days or 5 weeks (with the option of extension) in ASTM D6400-12, and 45 days (with the option

of extension of up to six months) in ISO 17088:2012 [10].

- (3) Biodegradation: conversion of the material to carbon dioxide, water, and biomass within a period of six months to the extent of 90% for EN 13432:2012, EN 14995:2006, and ISO 17088:2012. The standard ASTM 6400-12 sets a less stringent threshold of 60% biodegradation within six months for homopolymers or random copolymers, and 90% for copolymers and polymer blends.
- (4) Compost quality: performance of ecotoxicity tests in finished compost. In all four standards the ecotoxicity tests are performed in accordance with OECD 208 ("Terrestrial Plants: Growth Test," 1984). In EN 13432:2012 at least two kinds of plants from two different categories of the total three categories in OECD 208 have to be tested. In the standard ASTM 6400-12 three types of plant species including watercress are tested. ISO 17088:2012 refers to EN 13432:2012 [10].

EN 13432:2000 and EN 14995:2006 also describe an anaerobic degradation test. In EN 13432 it is stated that anaerobic biodegradation and disintegration can be verified as an option. The degree of biodegradation (biogas production) has to be at least 50% after two months as anaerobic fermentation is followed by aerobic composting, during which biodegradation can continue. With regard to disintegration, the standard requires that after five weeks of combined anaerobic and aerobic treatment, at most 10% of the original sample may remain after sieving over 2 mm mesh size [11].

DIN V54900

Title: Testing of Compostability of Plastics

Scope: This German compostability standard was the first standard of its kind and although it has been replaced by EN 13432, several materials are still certified according to DIN V54900. In order to meet the specifications of DIN V54900, a product must be capable of 60% degradation in six months with no adverse effect on the composting process or end product. This standard is currently the strictest in terms of heavy metal allowance; however, it is not as widely used as other standards such as EN 13432 and ASTM D6400.

AS 4736-2006

Title: Biodegradable plastics — Biodegradable plastics suitable for composting and other microbial treatment.

This Australian standard provides requirements and procedures for determining the compostability of packaging and packaging materials. It is similar to EN 13432:2000.

AS 4736-2006/Amdt 1-2009

Title: Biodegradable plastics — Biodegradable plastics suitable for composting and other microbial treatment.

AS 5810-2010

Title: Biodegradable plastics — Biodegradable plastics suitable for home composting.

Scope: This standard specifies requirements and procedures to determine whether a plastic material is biodegradable in home composting conditions and provides the basis to allow labeling of materials and products made from plastics as "home compostable" for use in home composting systems.

This standard stipulates pass/fail criteria addressing biodegradability, disintegration during biological treatment, effect on the biological treatment process, and effect on the quality of the resulting home compost.

Home composting systems vary considerably in their design, construction and operation, hence their performance also varies considerably compared to commercial composting facilities. Consequently, this standard, in comparison to AS 4736, uses lower temperatures in test environments and a longer test duration to account for such variations in home composting performance.

AS 5810-2010 is the only known standard for home composting. This standard applies the principles of AS 4736-2006, which is related to industrial composting operating at temperatures of at least 60°C.

BNQ — 9011-911/2007

Title: Compostable plastic bags; approach, criteria and contents are similar to the EN standards.

This Canadian standard is similar to ISO 17088:2012.

9.1.2.2 Biodegradation testing standards

A testing standard or test method is a kind of standard that defines two things:

- An exact scientific experimental procedure that can be applied to a material to produce a test result.
- An exact way of measuring and calculating the results of the test.

The testing standards contain detailed descriptions of test methods which must be performed according to the stipulations of the aforementioned standard specifications. The biodegradation testing standards are subdivided in various categories depending on the environmental conditions during the biodegradation tests and are displayed in [Table 9.2](#).

9.1.2.2.1 Aquatic, aerobic biodegradation standards

ISO 9408:1999

Title: Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium by determination of oxygen demand in a closed respirometer.

ISO 9408:1999 is similar to OECD 301 F.

ISO 9439:1999

Title: Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium — Carbon dioxide evolution test.

Scope: ISO 9439:1999 is based on the Sturm test and is similar to OECD 301 B. Both tests refer to low-molecular-weight compounds, at low concentrations and are less suitable for biopolymers [9,12].

ISO 9887:1992

Title: Evaluation of the aerobic biodegradability of organic compounds in an aqueous medium — Semi-continuous activated sludge (SCAS) method.

Scope: The method specified applies to organic compounds which are soluble, nonvolatile (or which have a negligible vapor pressure), not lost by foaming from the test solution, not significantly adsorbable on glass and activated sludge, and not inhibitory to the test microorganisms. Its principle is comparison with the comparison of dissolved organic carbon in the effluent from a control unit. Annex A gives examples of results of the test on various compounds, Annex B typical control values.

ISO 9887:1992 is similar to OECD 302 A.

ISO 9888:1999

Title: Water quality — Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium — Static test (Zahn-Wellens method).

ISO 9888:1999 is similar to OECD 302 B.

ISO 10634:1995

Title: Guidance for the preparation and treatment of poorly water-soluble organic compounds for the subsequent evaluation of their biodegradability in an aqueous medium.

Scope: Restricted to the description of the four techniques for introducing the poorly soluble organic test compounds for a subsequent test on biodegradability in an aqueous medium. The techniques are: direct addition, which is restricted to nonvolatile compounds; ultrasonic dispersion of nonvolatile liquid and solid compounds; adsorption on an inert support; and dispersions or emulsions with an emulsifying agent. Volatile chemicals may not be tested.

ISO 14851:1999

Title: Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium — Method by measuring the oxygen demand in a closed respirometer.

ISO 14851:1999 is similar to EN 14048:2002. Predecessors of ISO 14851:1999 are OECD 301 C and ISO 9408.

ISO 14851:1999/Cor 1:2005

ISO 14852:1999

Title: Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium — Method by analysis of evolved carbon dioxide.

The principle of the test procedure is similar to ISO 14851. The main difference is the parameter for measuring the biodegradation. Instead of oxygen consumption the evolved carbon dioxide is measured.

ISO 14852:1999 is similar to EN 14047:2002. ISO 14852:1999 was also similar to ASTM D5209 (withdrawn in 2004).

ISO/TR 15462:2006

Title: Selection of tests for biodegradability.

Scope: ISO/TR 15462:2006 gives an overview of biodegradation tests for the aquatic environment standardized by ISO and provides recommendations on their use. The biodegradation tests listed are designed to determine the biodegradability of chemical substances or wastewaters under standardized conditions. Inhibitory tests with bacteria and mixed bacterial inocula are included because a possible toxicity on the inoculum is important information for the choice and performance of biodegradation tests.

EN 14047:2002

Title: Packaging — Determination of the ultimate aerobic biodegradability of packaging materials in an aqueous medium — Method by analysis of evolved carbon dioxide.

Scope: This standard specifies a method to evaluate the ultimate biodegradability of packaging

Table 9.2 Biodegradation testing standards

Aquatic aerobic	Aquatic anaerobic	High solids (landfilling)	Compost	Soil	Marine	Other
ISO 9408:1999	ISO 11734:1995	ISO 15985:2004 (anaerobic)	ISO 14855-1:2005	ISO 11266:1994	ISO 16221:2001	ASTM D6954-04
ISO 9439:1999	ISO 13975:2012	ISO 15985:2004/Cor 1:2007	ISO 14855-1:2005/Cor 1:2009	ISO 17556:2012	ASTM D6691-09	ISO 11721-1:2001
ISO 9887:1992	ISO 14853:2005	ASTM D5511-12	ISO 14855-2:2007	CEN/TR 15822:2009	ASTM D7081-05	ISO 11721-2:2003
ISO 9888:1999	ISO 14853:2005/Cor 1:2009	ASTM D5526-12	ISO 14855-2:2007/Cor 1:2009	ASTM D5988-12	ASTM D7473-12	ASTM G21-09
ISO 10634:1995	ASTM D5210-92(2007)	ASTM D7475-11	ISO 20200:2004		OECD 306	
ISO 14851:1999			EN 14806:2005			
ISO 14851:1999/Cor 1:2005			ASTM D5338-11			
ISO 14852:1999			ASTM D6002-96(2002)e1 (withdrawn in 2011)			
ISO/TR 15462:2006						
EN 14047:2002			ASTM D6340-98(2007) (aqueous or compost)			
EN 14048:2002			JIS K 6952:2008			
ASTM D5209-92			JIS K 6953-1			
ASTM D6340-98(2007) (aqueous or compost)			JIS K 6953-2			
JIS K 6950:2000 (ISO 14851:1999)						
JIS K 6951:2000 (ISO 14852:1999)						
OECD 301 A						

Table 9.2 Biodegradation testing standards (*Continued*)

Aquatic aerobic	Aquatic anaerobic	High solids (landfilling)	Compost	Soil	Marine	Other
OECD 301 B						
OECD 301 C						
OECD 301 D						
OECD 301 E						
OECD 301 F						

materials and their constituents by measurement of CO₂ evolution.

EN 14047:2002 is similar to ISO 14852:1999.

EN 14048:2002

Title: Packaging — Determination of the ultimate aerobic biodegradability of packaging materials in an aqueous medium — Method by measuring the oxygen demand in a closed respirometer.

EN 14048:2002 is similar to ISO 14851:1999.

ASTM D5209-92

Title: Standard test method for determining the aerobic biodegradation of plastic materials in the presence of municipal sewage sludge (withdrawn in 2004).

ASTM D6340-98(2007)

Title: Standard test methods for determining aerobic biodegradation of radiolabeled plastic materials in an aqueous or compost environment.

Scope: These test methods directly determine the rate and degree of biological oxidation of carbon in plastic materials when placed in a composting environment containing simulated municipal solid waste or an aqueous environment under laboratory conditions.

JIS K 6950:2000

Title: Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium — Method by measuring the oxygen demand in a closed respirometer.

This Japanese standard is similar to ISO 14851:1999.

JIS K 6951:2000

Title: Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium — Method by analysis of evolved carbon dioxide.

This Japanese standard is similar to ISO 14852:1999.

OECD 301 A

Title: DOC die-away test.

Scope: OECD 301 A is a 28-day test that evaluates biodegradation by measuring the dissolved organic carbon.

OECD 301 A is similar to ISO 7827:2010.

OECD 301 B

Title: CO₂ evolution test (modified Sturm test).

Scope: OECD 301 B is a 28-day test of a measured volume of inoculated mineral medium containing a known concentration of the test substance. The primary analytical method used in OECD 301 B is respirometry based on CO₂ evolution. It is suitable for both poorly soluble and absorbing material sample.

OECD 301 B is similar to ISO 9439:1999.

OECD 301 C

Title: Modified MITI (I) (Ministry of International Trade and Industry, Japan) test.

Scope: OECD 301 C is a 28-day respirometry test that measures oxygen consumption. It is suitable for poorly soluble materials and can be used with volatile material sample. OECD 301 C is similar to 301 F differing mainly in the inocula employed.

OECD 301 C is predecessor of ISO 14851.

OECD 301 E

Title: Modified OECD screening test.

OECD 301 E is a 28-day test that evaluates biodegradation by measuring dissolved organic carbon. It can be used with absorbing material sample. In general, OECD 301 A and the OECD 301 E are not suitable for testing the biodegradability of poorly soluble substances.

OECD 301 F

Title: Manometric respirometry test.

OECD 301 F is a 28-day test that measures oxygen consumption. It is suitable for poorly soluble, volatile and adsorbing materials. OECD 301 F is similar to 301 C differing mainly in the inocula employed.

OECD 301 F is similar to ISO 9408:1999.

ISO 7827:2010

Title: Evaluation of the “ready,” “ultimate” aerobic biodegradability of organic compounds in an aqueous medium — Method by analysis of dissolved organic carbon (DOC).

Scope: ISO 7827:2010 specifies a method for the evaluation of the “ready” and “ultimate” biodegradability of organic compounds at a given range of concentrations by aerobic microorganisms. In this context, ISO 7827:2010 also gives specific definitions for the terms “ready” and “ultimate.”

The method applies to organic compounds which are: (a) soluble at the concentration used under the conditions of the test, dissolved organic carbon (DOC) concentrations of 10 mg/l to 40 mg/l; (b) nonvolatile or having a negligible vapor pressure under the conditions of the test; (c) not significantly adsorbable on glass and activated sludge; (d) not inhibitory to the test microorganisms at the concentration chosen for the test.

The method is not suitable for wastewaters, as they usually contain significant amounts of water-insoluble organic carbon, which is not included in DOC measurements.

ISO 7827:2010 is similar to OECD 301 A.

ASTM E1279-89(2008)

Title: Standard test method for biodegradation by a shake-flask die-away method.

OECD 301 D

Title: Closed bottle test.

Scope: OECD 301 D determines biodegradation by dissolved oxygen in a 28-day test. It can be used with poorly soluble materials and is suitable with volatile and absorbing material samples.

OECD 301 D is similar to ISO 10707:1994.

OECD 302 A

Title: Inherent biodegradability — Modified SCAS test.

Scope: This test guideline describes a method which is an adaptation of the Soap and Detergent Association semi-continuous activated sludge (SCAS) procedure for assessing the primary biodegradation of alkyl benzene sulfonate. The test does not simulate those conditions experienced in a sewage treatment plant.

OECD 302 A is similar to ISO 9887:1992.

OECD 302 B

Title: Inherent biodegradability — Zahn-Wellens test.

Scope: In the Zahn-Wellens test, biodegradation is measured by monitoring chemical oxygen demand (COD) elimination.

OECD 302 B is similar to ISO 9888:1999.

9.1.2.2.2 Aquatic, anaerobic biodegradation standards**ISO 11734:1995**

Title: Evaluation of the “ultimate” anaerobic biodegradability of organic compounds in digested sludge — Method by measurement of the biogas production.

Scope: Gives a method for the evaluation of the ultimate biodegradability of organic compounds in digested sludge at a given concentration by anaerobic microorganisms.

ISO 13975:2012

Title: Determination of the ultimate anaerobic biodegradation of plastic materials in controlled slurry digestion systems — Method by measurement of biogas production.

Scope: This standard specifies a method of evaluating the ultimate anaerobic biodegradability of plastic materials in a controlled anaerobic slurry digestion system with a solids concentration not exceeding 15%, which is often found for the treatment of sewage sludge, livestock feces, or garbage. The test method is designed to yield a percentage and rate of conversion of the organic carbon in the test materials to carbon dioxide and methane produced as biogas.

The method applies to the following materials, provided they have a known carbon content:

- Natural and/or synthetic polymers, copolymers, or mixtures.
- Plastic materials that contain additives such as plasticizers, colorants, or other compounds.
- Water-soluble polymers.

It does not apply to materials that exhibit inhibitory effects on the test microorganisms at the concentration chosen for the test.

ISO 14853:2005

Title: Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system — Method by measurement of biogas production.

Scope: This standard specifies a method for the determination of the ultimate anaerobic biodegradability of plastics by anaerobic microorganisms. The

conditions described in the standard do not necessarily correspond to the optimum conditions for the maximum degree of biodegradation to occur. The test calls for exposure of the test material to sludge for a period of up to 60 days, which is longer than the normal sludge retention time (25 to 30 days) in anaerobic digesters, though digesters at industrial sites can have much longer retention times.

The method applies to the following materials:

- Natural and/or synthetic polymers, copolymers, or mixtures thereof.
- Plastic materials which contain additives such as plasticizers, colorants, or other compounds.
- Water-soluble polymers.
- Materials which, under the test conditions, do not inhibit the microorganisms present in the inoculum.

ISO 14853:2005/Cor 1:2009

ASTM D5210-92(2007)

Title: Standard test method for determining the anaerobic biodegradation of plastic materials in the presence of municipal sewage sludge.

Scope: This test method determines the degree and rate of anaerobic biodegradation of synthetic plastic materials (including formulation additives) on exposure to anaerobic-digester municipal sewage sludge from a wastewater plant under laboratory conditions.

ASTM D5210-92(2007) and the equivalent ISO 14853:2005 are aquatic biodegradation tests (total solid or TS in the range 0.1–0.3% or > 0.1%) at a mesophilic temperature (about 35°C) in a synthetic growth medium with a mixed microbial population derived from a compost or wastewater treatment facility. In these tests, the sludge is diluted with a mineral salts medium, so only microorganisms utilizing the polymer as a carbon source in the mineral salts medium grow. The microbial population is thought not to reflect the original sludge [13].

9.1.2.2.3 High-solids anaerobic biodegradation standards

ISO 15985:2004

Title: Determination of the ultimate anaerobic biodegradation and disintegration under high-solids

anaerobic-digestion conditions — Method by analysis of released biogas.

Scope: This standard specifies a method for the evaluation of the ultimate anaerobic biodegradability of plastics based on organic compounds under high-solids anaerobic-digestion conditions by measurement of evolved biogas and the degree of disintegration at the end of the test. This method is designed to simulate typical anaerobic digestion conditions for the organic fraction of mixed municipal solid waste. The test material is exposed in a laboratory test to a methanogenic inoculum derived from anaerobic digesters operating only on pretreated household waste. The anaerobic decomposition takes place under high-solids (more than 20% total solids) and static non-mixed conditions. The test method is designed to yield the percentage of carbon in the test material and its rate of conversion to evolved carbon dioxide and methane (biogas).

ISO 15985:2004/Cor 1:2007

ASTM D5511-12

Title: Standard test method for determining anaerobic biodegradation of plastic materials under high-solids anaerobic-digestion conditions.

Scope: This test method covers the determination of the degree and rate of anaerobic biodegradation of plastic materials in high-solids anaerobic conditions. The test materials are exposed to a methanogenic inoculum derived from anaerobic digesters operating only on pretreated household waste. The anaerobic decomposition takes place under high-solids (more than 30% total solids) and static non-mixed conditions.

ASTM D5511-12 is equivalent to ISO 15985:2004. Both standards describe tests using over a 20% TS concentration (a high-solid condition) sludge at a thermophilic temperature (about 52°C in ISO 15985) or mesophilic temperature (about 35°C in ASTM D5511) with mixed inocula derived from anaerobic digesters operating only on pretreated household waste.

ASTM D5526-12

Title: Standard test method for determining anaerobic biodegradation of plastic materials under accelerated landfill conditions.

Scope: This test method covers determination of the degree and rate of anaerobic biodegradation of plastic materials in an accelerated-landfill test environment. This test method is also designed to produce mixtures of household waste and plastic

materials after different degrees of decomposition under conditions that resemble landfill conditions. The test materials are mixed with pretreated household waste and exposed to a methanogenic inoculum derived from anaerobic digesters operating only on pretreated household waste. The anaerobic decomposition occurs under dry (more than 30 % total solids) and static non-mixed conditions. The mixtures obtained after this test method can be used to assess the environmental and health risks of plastic materials that are degraded in a landfill.

There is no known ISO equivalent to this standard.

ASTM D5526-12 is equivalent to ISO 15985:2004. Both standards ISO 15985 and ASTM D5526 are tests using over a 20% TS concentration (a high-solid condition) sludge at a thermophilic temperature (about 52°C in ISO 15985) or mesophilic temperature (about 35°C in ASTM D5526) with mixed inocula derived from anaerobic digesters operating only on pretreated household waste [13].

ASTM D7475-11

Title: Standard test method for determining the aerobic degradation and anaerobic biodegradation of plastic materials under accelerated bioreactor landfill conditions.

Scope: This modification of test method D5526, which only considered anaerobic degradation, is used to determine the degree and rate of aerobic degradation (as indicated by loss of tensile strength, molecular weight, possibly resulting in disintegration and fragmentation) and anaerobic biodegradation of plastic materials in an accelerated bioreactor landfill test environment. It simulates the change from aerobic to anaerobic environments over time as landfill depth increases. Plastic materials found in landfills include discarded plastic products such as bags and wrappers and also deliberately applied plastic covers as inter-layer sealers between daily refuse fills to prevent wind-blown scatter of garbage overnight or at other down times. This modification is a two-tiered test method in which the two tiers, which address aerobic degradation and anaerobic biodegradation, are most preferably run sequentially to more closely resemble the real world condition of a biologically active landfill, or a bioreactor landfill, but are functional independently and separately depending on the plastic under evaluation and the information sought: either aerobic degradation or anaerobic biodegradation or both.

There is no ISO equivalent to this standard.

9.1.2.2.4 Compost biodegradation (compostability) standards

ISO 14855-1:2005

Title: Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions — Method by analysis of evolved carbon dioxide — Part 1: General method.

Scope: ISO 14855-1:2005 specifies a method for the determination of the ultimate aerobic biodegradability of plastics, based on organic compounds, under controlled composting conditions by measurement of the amount of carbon dioxide evolved and the degree of disintegration of the plastic at the end of the test. This method is designed to simulate typical aerobic composting conditions for the organic fraction of solid mixed municipal waste. The test material is exposed to an inoculum that is derived from compost. The composting takes place in an environment wherein temperature, aeration, and humidity are closely monitored and controlled. The test method is designed to yield the percentage conversion of the carbon in the test material to evolved carbon dioxide as well as the rate of conversion.

Also specified is a variant of the method, using a mineral bed (vermiculite) inoculated with thermophilic microorganisms obtained from compost with a specific activation phase, instead of mature compost. This variant is designed to yield the percentage of carbon in the test substance converted to carbon dioxide and the rate of conversion.

ISO 14855-1:2005/Cor 1:2009

ISO 14855-2:2007

Title: Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions — Method by analysis of evolved carbon dioxide — Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test.

Scope: ISO 14855-2:2007 specifies a method for determining the ultimate aerobic biodegradability of plastic materials under controlled composting conditions by gravimetric measurement of the amount of carbon dioxide evolved. The method is designed to yield an optimum rate of biodegradation by adjusting the humidity, aeration, and temperature of the composting vessel.

The method applies to the following materials:

- Natural and/or synthetic polymers and copolymers, and mixtures of these.

- Plastic materials that contain additives such as plasticizers or colorants.
- Water-soluble polymers.
- Materials that, under the test conditions, do not inhibit the activity of microorganisms present in the inoculum.

ISO 14855-2:2007/Cor 1:2009

ISO 16929:2002

Title: Plastics — Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test.

Scope: This standard is used to determine the degree of disintegration of plastic materials in a pilot-scale aerobic composting test under defined conditions. The test method laid down in the standard can also be used to determine the influence of the test material on the composting process and the quality of the compost obtained. It cannot be used to determine the aerobic biodegradability of a test material. Other methods are available for this (for example, see ISO 14851, 14852 or 14855).

ISO 20200:2004

Title: Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test.

Scope: ISO 20200:2004 specifies a method of determining the degree of disintegration of plastic materials when exposed to a laboratory-scale composting environment. The method is not applicable to the determination of the biodegradability of plastic materials under composting conditions. Further testing is necessary to be able to claim compostability.

EN 14806:2005

Title: Packaging — Preliminary evaluation of the disintegration of packaging materials under simulated composting conditions in a laboratory scale test.

Scope: This laboratory-scale test method using synthetic waste aims at simulating the environmental conditions found in industrial composting plants. Packaging materials exposed to this environment can be preliminarily assessed for disintegrability. A negative result does not necessarily mean that the test material is not disintegrating under industrial composting conditions. This test does not replace the acceptance disintegration test as specified in EN 14045, in accordance with EN 13432.

ASTM D5338-11

Title: Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions, incorporating thermophilic temperatures.

Scope: This test method determines the degree and rate of aerobic biodegradation of plastic materials on exposure to a controlled-composting environment under laboratory conditions, at thermophilic temperatures. This test method is designed to yield reproducible and repeatable test results under controlled conditions that resemble composting conditions, where thermophilic temperatures are achieved. The test substances are exposed to an inoculum that is derived from compost from municipal solid waste. The aerobic composting takes place in an environment where temperature, aeration, and humidity are closely monitored and controlled.

ASTM D6002-96(2002)e1

Title: Standard guide for assessing the compostability of environmentally degradable plastics (withdrawn 2011, no replacement).

ASTM D6340-98(2007)

See Section 9.1.2.2.1 Aquatic, aerobic biodegradation standards.

JIS K 6952:2008

Title: Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test.

This Japanese standard is similar to ISO 16929:2002.

JIS K 6953-1

Title: Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions — Method by analysis of evolved carbon dioxide.

This Japanese standard is similar to ISO 14855-1:2005.

JIS K 6953-2

Title: Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions — Method by analysis of evolved carbon dioxide — Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test.

This Japanese standard is similar to ISO 14855-2:2005.

JIS K 6954:2008

Title: Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test.

This Japanese standard is similar to ISO 20200:2004.

AS 4454-2003

Title: Composts, soil conditioners and mulches.

This Australian standard is based on AS 4736 and provides specifications and lists requirements as to compost quality, soil properties, and soil depth [10].

There are no OECD tests for composting environment.

9.1.2.2.5 Soil biodegradation standards

ISO 11266:1994

Title: Guidance on laboratory testing for biodegradation of organic chemicals in soil under aerobic conditions.

Scope: Guidance on laboratory testing for biodegradation of organic chemicals in soil under aerobic conditions.

ISO 17556:2012

Title: Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved.

Scope: This standard specifies a method for determining the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a closed respirometer or the amount of carbon dioxide evolved. The method is designed to yield an optimum degree of biodegradation by adjusting the humidity of the test soil.

CEN/TR 15822:2009

Title: Biodegradable plastics in or on soil — Recovery, disposal, and related environmental issues.

Scope: This technical report is intended to summarize the current state of knowledge and experience in the field of biodegradable plastics which are used on soil or end up in soil. It also addresses the links between use, disposal after use, degradation mechanisms, and the environment. Therefore, this document is intended to provide a basis for the development of future standards. Its aim is to clarify the ideas and ensure a level playing field, without hiding possible needs for further research or areas of disagreement among experts.

ASTM D5988-12

Title: Standard test method for determining aerobic biodegradation of plastic materials in soil.

Scope: This test method covers determination under laboratory conditions of the degree and rate of aerobic biodegradation of plastic materials, including formulation additives, in contact with soil.

JIS K 6955:2006

Title: Determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved.

This Japanese standard is similar to ISO 17556:2003.

9.1.2.2.6 Marine biodegradation standards

ISO 16221:2001

Title: Guidance for determination of biodegradability in the marine environment.

ISO 16221:2001 is similar to OECD 306.

ASTM D6691-09

Title: Standard test method for determining aerobic biodegradation of plastic materials in the marine environment by a defined microbial consortium or natural seawater inoculum.

Scope: This test method is used to determine the degree and rate of aerobic biodegradation of plastic materials (including formulation additives) exposed to a pre-grown population of at least ten aerobic marine microorganisms of known genera or the indigenous population existing in natural seawater. The test method is conducted under controlled laboratory conditions.

This test method is designed to index polymer materials that are possibly biodegradable, relative to a positive reference material, in an aerobic environment.

This test method is applicable to all polymer materials containing at least 20% carbon that are not inhibitory to the microorganisms present in a marine environment.

There is no similar or equivalent ISO standard.

ASTM D7081-05

Title: Standard specification for non-floating biodegradable plastics in the marine environment.

Scope: This specification covers products made from plastics (including packaging and coatings) that are designed to be biodegradable under the marine environmental conditions of aerobic marine waters, or anaerobic marine sediments, or both. (Possible environments are shallow and deep salt water and brackish water.)

ASTM D7473-12

Title: Standard test method for weight attrition of plastic materials in the marine environment by open system aquarium incubations.

Scope: This test method is used to determine the weight loss as a function of time of non-floating plastic materials (including formulation additives), when incubated under changing, open, marine aquarium conditions, which is representative of aquatic environments near the coasts and near the bottom of a body of water in the absence of sunlight, particularly UV and visible portions of the spectrum. The goal of this test is to obtain data that will predict real world experiences based on the extent and rate of biodegradation data of the same materials obtained from laboratory test method D6691. The aquarium-incubated films are examined for visual degradation and dry weight loss over time. This test is not a replacement for ASTM D6691, but rather an additional ASTM method for weight attrition. The standard addresses weight loss of the plastics in a marine environment and cannot be used for demonstrating biodegradation for which specification D7081 needs to be used.

OECD 306

Title: Biodegradability in seawater.

Scope: The OECD TG 306 includes seawater variants of the closed bottle test (OECD 301 D) and of the modified OECD screening test (OECD 301 E). Degradation of organic chemicals in seawater has generally been found to be slower than that experienced in freshwater, activated sludge, and sewage effluent; therefore, a positive result obtained during 28 days in a biodegradability in seawater test (>60% ThOD; >70% DOC) can normally be regarded as an indication of ready biodegradability.

OECD 306 is similar to ISO 16221:2001.

9.1.2.2.7 Other (bio)degradation standards

ISO 11721-1:2001

Title: Determination of resistance of cellulose-containing textiles to micro-organisms – Soil burial test – Part 1: Assessment of rot-retardant finishing.

ISO 11721-2:2003

Title: Determination of the resistance of cellulose-containing textiles to micro-organisms – Soil burial test – Part 2: Identification of long-term resistance of a rot retardant finish.

Scope: ISO 11721-2:2003 describes a test procedure for identification of the long-term resistance of a rot-retardant finish against the attack of microorganisms in the soil.

It permits a distinction to be made between rot-retardant finishes with no long-term resistance, with

regular long-term resistance, and with increased long-term resistance, in order to assess the suitability for use in the tropics.

ASTM D6954-04

Title: Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation.

Scope: This guide is a sequential assembly of extant but unconnected standard tests and practices for the oxidation and biodegradation of plastics, which will permit the comparison and ranking of the overall rate of environmental degradation of plastics that require thermal or photo-oxidation to initiate degradation. Each degradation stage is independently evaluated to allow a combined evaluation of a polymer's environmental performance under a controlled laboratory setting. This enables a laboratory assessment of its disposal performance in soil, compost, landfill, and water and for use in agricultural products such as mulch film without detriment to that particular environment.

This standard has been at the center of a controversy between the oxodegradable and the bioplastics industries (see Chapter 2: Definitions and Assessment of (Bio)degradation; Section 2.3: Biopolymers versus Oxodegradable Polymers). Presently, the testing done on oxodegradable polymers refers to ASTM D6954. ASTM D6954-04 is not a standard specification, but a standard guide.

ASTM D6954-04 is analogous to the recently published British standard BS 8472:2011, "Methods for the assessment of the oxo-biodegradation of plastics and of the phytotoxicity of the residues in controlled laboratory conditions."

There is no ISO standard that is the equivalent of this standard guide.

ASTM G21-09

Title: Standard practice for determining resistance of synthetic polymeric materials to fungi.

Scope: The synthetic polymer portion of these materials is usually fungus-resistant in that it does not serve as a carbon source for the growth of fungi. It is generally the other components, such as plasticizers, cellulosics, lubricants, stabilizers, and colorants that are responsible for fungus attack on plastic materials. To assess materials other than plastics, use of this test method should be agreed upon by all parties involved. It is important to establish the resistance to microbial attack under conditions favorable for such attack, namely, a temperature from 2 to 38°C (35 to 100°F) and a relative humidity from 60 to 100%.

As the soil burial test is a biological process and the test soil not accurately defined, ISO 11721-2:2003 only covers the comparison of finished and unfinished specimens.

ISO 11721 (Parts 1 and 2) and ASTM G21-09 show a susceptibility to biological attack, but they are totally unsuitable to demonstrate a far-reaching, let alone complete, biodegradation or mineralization.

9.1.3 Determination of Bio-Based Content

CEN/TS 16137:2011

Title: Determination of bio-based carbon content.

Scope: This Technical Specification specifies a calculation method for the determination of the bio-based carbon content in monomers, polymers and plastic materials and products, based on the ^{14}C content measurement. It also specifies three test methods to be used for the determination of the ^{14}C content from which the bio-based carbon content is calculated:

- Method A: Proportional scintillation-counter method (PSM);
- Method B: Beta-ionisation (BI);
- Method C: Accelerator mass spectrometry (AMS).

The bio-based carbon content is expressed by a fraction of sample mass, as a fraction of the total carbon content or as a fraction of the total organic carbon content. This calculation method is applicable to any polymers containing organic carbon, including biocomposites.

Note: This Technical Specification does not provide the methodology for the calculation of the biomass content of a sample.

CEN/TS 16295:2012

Title: Declaration of the bio-based carbon content.

Scope: This technical specification provides requirements for the declaration, including statements and labels, of the bio-based carbon content of items such as polymers, plastic materials, semi-finished plastic products, and finished plastic products, including composites.

Note 1: This document does not override, or in any way change, legally required environmental information, claims, or labeling, or any other applicable legal requirements.

Note 2: This document addresses the bio-based content of plastic items, expressed as a fraction of the total organic carbon content. The declaration of biomass content (i.e., the total amount of raw materials of biogenic origin contained in a plastics item, expressed as a percentage of the total mass) is out of the scope of this document, as there is currently no well-established method to determine the biomass content of polymers or plastics materials.

Note 3: Since bio-based polymers can be biodegradable or non-biodegradable, and the origin of the materials renewable or non-renewable, (see CEN/TR 15932), the declaration of the bio-based carbon content is not an indication of the biodegradability of an item.

ASTM D6866-12

Title: Standard test methods for determining the bio-based content of solid, liquid, and gaseous samples using radiocarbon analysis.

Scope: These test methods are applicable to any product containing carbon-based components that can be combusted in the presence of oxygen to produce carbon dioxide (CO_2) gas. The overall analytical method is also applicable to gaseous samples, including flue gases from electrical utility boilers and waste incinerators.

These test methods do not address environmental impact, product performance and functionality, determination of geographical origin, or assignment of required amounts of bio-based carbon necessary for compliance with federal laws.

There are no ISO test methods that are equivalent to the test methods outlined in this standard.

ASTM D7026-04

Title: Standard guide for sampling and reporting of results for determination of bio-based content of materials via carbon isotope analysis.

Scope: This guide provides a framework for collecting and handling samples for determination of bio-based content of materials by means of the carbon isotope method described in ASTM D6866. Tests for sampling adequacy based on the standard statistical tools are provided. In addition, reporting of the results, including sampling techniques, handling procedures, and chain-of-custody issues, are discussed.

There is no similar or equivalent ISO standard.

ASTM WK35315

Title: New specification for calculating and reporting bio-based content of complex products.

Scope: This Technical Specification provides requirements for calculating and reporting bio-based

carbon content of complex products using ASTM D6866 as the test method for measuring bio-based (carbon) content. The standard helps define the technical specifications and guidance on how to calculate and report bio-based carbon content of complex products. It will be used to label and communicate to the stakeholders the percent bio-based carbon content of a complex products because of the value proposition bio-based carbon offers in terms of material carbon footprint reductions and implementing sustainability principles.

9.1.4 Ecotoxicity

ISO 11268-1:2012

Title: Soil quality — Effects of pollutants on earthworms — Part 1: Determination of acute toxicity to *Eisenia fetida*/*Eisenia andrei*.

ISO 11268-2:2012

Title: Soil quality — Effects of pollutants on earthworms — Part 2: Determination of effects on reproduction of *Eisenia fetida*/*Eisenia andrei*.

ISO 11268-3:1999

Title: Soil quality — Effects of pollutants on earthworms — Part 3: Guidance on the determination of effects in field situation.

ISO 11269-1:2012

Title: Soil quality — Determination of the effects of pollutants on soil flora — Part 1: Method for the measurement of inhibition of root growth.

ISO 11269-2:2012

Title: Soil quality — Determination of the effects of pollutants on soil flora — Part 2: Effects of contaminated soil on the emergence and early growth of higher plants.

ISO 11348-1:2007

Title: Water quality — Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test) — Part 1: Method using freshly prepared bacteria.

ISO 11348-2:2007

Title: Water quality — Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test) — Part 2: Method using liquid-dried bacteria.

ISO 11348-3:2007

Title: Water quality — Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test) — Part 3: Method using freeze-dried bacteria.

OECD 202

Title: *Daphnia* sp., acute immobilisation test.

Scope: This Test Guideline describes an acute toxicity test to assess effects of chemicals towards daphnids (usually *Daphnia magna* Staus)

OECD 207

Title: Earthworm, acute toxicity tests.

Scope: This test guideline includes two kinds of tests, a paper contact toxicity test and an artificial soil test. The recommended species is *Eisenia fetida* (Michaelson).

A simple paper contact toxicity test is described as an optional initial screen to indicate those substances likely to be toxic to earthworms in soil and which will require further, more detailed, testing in an artificial soil.

The simple contact test is easy to perform and gives reproducible results with the recommended species. The artificial soil test gives toxicity data more representative of natural exposure of earthworms to chemicals.

OECD 207 is similar to ISO 11268-1.

OECD 208

Title: Terrestrial plants growth test.

Scope: This test guideline is designed to determine possible toxic effects of soil-incorporated solid or liquid chemical substances on the emergence of seedlings and the early stages of growth of a variety of terrestrial plants after a single application.

9.1.5 Sample Preparation

ISO 10210:2012

Title: Methods for the preparation of samples for biodegradation testing of plastic materials.

Scope: This standard describes methods for the preparation of test samples used in the determination of the ultimate aerobic and anaerobic biodegradability of plastic materials in an aqueous medium, soil, controlled compost, or anaerobic digesting sludge. The methods described are designed to provide dimensional consistency of test samples, resulting in improved reproducibility of test results during the determination of the ultimate biodegradability of the product.

These methods apply to the following materials:

- Natural and/or synthetic polymers, copolymers, or mixtures of these.

- Plastic materials that contain additives, such as plasticizers or colorants.
- Plastic composite materials that contain organic or inorganic fillers.
- Products made from the above materials.

ASTM D6288-09

See [Section 9.1.1](#): Standards Related to the Recycling of Biopolymers.

ASTM D7026-04

See [Section 9.1.3](#): Determination of Bio-Based Content.

9.1.6 Terminology

ISO 1043-1:2011

Title: Symbols and abbreviated terms — Part 1: Basic polymers and their special characteristics.

Scope: This standard defines abbreviated terms for the basic polymers used in plastics, symbols for components of these terms, and symbols for special characteristics of plastics. It includes only those abbreviated terms that have come into established use, and its aim is both to prevent the occurrence of more than one abbreviated term for a given plastic, and to prevent a given abbreviated term from being interpreted in more than one way.

ISO 1043-2:2011

Title: Plastics. Symbols and abbreviated terms — Part 2: Fillers and reinforcing materials.

Scope: This standard specifies uniform symbols for terms referring to fillers and reinforcing materials for plastics. It includes only those symbols that have come into established use, and its main aim is both to prevent the occurrence of more than one symbol for a given filler or reinforcing material, and to prevent a given symbol from being interpreted in more than one way.

ISO 1043-3:1996

Title: Symbols and abbreviated terms — Part 3: Plasticizers.

Scope: This standard provides uniform symbols for components of terms relating to plasticizers for plastics in terms of abbreviations. Contains in general only those abbreviations that have come into established use in practice. Replaces the first edition.

Guidance for the preparation of new abbreviated terms, reference lists of symbols for the components of plastics terms used to form the abbreviated terms for plastics, and a classification of

abbreviated terms for polymers grouped by type are given in annexes.

ISO 1043-4:1998

Title: Symbols and abbreviated terms — Part 4: Flame retardants.

EN 13193

Title: Packaging and the environment — Terminology.

Scope: This standard defines terms used in the field of packaging and the environment.

CEN/TR 15932:2010

Title: Recommendation for terminology and characterization of biopolymers and bioplastics.

Scope: This technical report gives recommendations for bioplastic and biopolymer-related terminology. These recommendations are based on a discussion of commonly used terms in this field. This technical report also briefly describes the current test methods state of the art in relation to the characterization of bioplastics and products made thereof.

ASTM D883-11

Title: Standard terminology relating to plastics.

Scope: This terminology covers definitions of technical terms used in the plastics industry. Terms that are generally understood or adequately defined in other readily available sources are not included.

ASTM D1600-08

Title: Standard terminology for abbreviated terms relating to plastics.

Scope: The purpose of this terminology is to provide uniform contractions of terms relating to plastics. Abbreviated terminology has evolved through widespread common usage. This compilation has been prepared to avoid both the occurrence of more than one abbreviated term for a given plastics term and multiple meanings for abbreviated terms.

The scope of these abbreviated terms includes plastics terms pertaining to composition and relating to type or kind according to mode of preparation or principal distinguishing characteristics. Also included are abbreviated terms for terms relating to copolymers, blends and alloys of plastics, and additives such as plasticizers, fillers, etc.

9.1.7 Life Cycle Assessment (LCA) Related Standards

ISO 14001:2004

Title: Environmental management systems — Requirements with guidance for use.

Scope: This standard specifies requirements for an environmental management system to enable an organization to develop and implement a policy and objectives which take into account legal requirements and other requirements to which the organization subscribes, and information about significant environmental aspects. It applies to those environmental aspects that the organization identifies as those that it can control and those that it can influence. It does not itself state specific environmental performance criteria.

ISO 14001:2004 is applicable to any organization that wishes to establish, implement, maintain, and improve an environmental management system, to assure itself of conformity with its stated environmental policy, and to demonstrate conformity with ISO 14001:2004 by doing one of the following:

- (1) Making a self-determination and self-declaration.
- (2) Seeking confirmation of its conformance by parties having an interest in the organization, such as customers.
- (3) Seeking confirmation of its self-declaration by a party external to the organization.
- (4) Seeking certification/registration of its environmental management system by an external organization.

All the requirements in ISO 14001:2004 are intended to be incorporated into any environmental management system. The extent of the application will depend on factors such as the environmental policy of the organization, the nature of its activities, products and services, and the location where, and the conditions in which, it functions.

ISO 14001:2004 also provides, in Annex A, informative guidance on its use.

ISO 14001:2004/Cor 1:2009

ISO 14040:2006

Title: Environmental management — Life cycle assessment — Principles and framework.

Scope: This standard describes the principles and framework for life cycle assessment (LCA), including definition of the goal and scope of the LCA, the life cycle inventory analysis (LCI) phase, the life cycle impact assessment (LCIA) phase, the life cycle interpretation phase, reporting and critical review of the LCA, limitations of the LCA, the relationship between the LCA phases, and conditions for use of value choices and optional elements.

ISO 14040:2006 covers LCA studies and LCI studies. It does not describe the LCA technique in detail, nor does it specify methodologies for the individual phases of the LCA.

The intended application of LCA or LCI results is considered during definition of the goal and scope, but the application itself is outside the scope of the standard.

ISO 14044:2006

Title: Environmental management — Life cycle assessment — Requirements and guidelines.

Scope: This standard specifies requirements and provides guidelines for LCA, including definition of the goal and scope of the LCA, the LCI analysis phase, the LCIA phase, the life cycle interpretation phase, reporting and critical review of the LCA, limitations of the LCA, relationship between the LCA phases, and conditions for use of value choices and optional elements.

ISO 14044:2006 covers LCA studies and LCI studies.

ISO 14045:2012

Title: Environmental management — Eco-efficiency assessment of product systems — Principles, requirements and guidelines.

Scope: ISO 14045:2012 describes the principles, requirements, and guidelines for eco-efficiency assessment for product systems, including:

- The goal and scope definition of the eco-efficiency assessment.
- The environmental assessment.
- The product-system-value assessment.
- The quantification of eco-efficiency.
- Interpretation (including quality assurance).
- Reporting.
- Critical review of the eco-efficiency assessment.

Requirements, recommendations, and guidelines for specific choices of categories of environmental impact and values are not included. The intended application of the eco-efficiency assessment is considered during the goal and scope definition phase, but the actual use of the results is outside the scope of ISO 14045:2012.

ISO/TR 14047:2012

Title: Environmental management — Life cycle assessment — Illustrative examples on how to apply ISO 14044 to impact assessment situations.

Scope: The purpose of ISO/TR 14047:2012 is to provide examples to illustrate current practice of LCIA according to ISO 14044:2006. These examples are only a sample of all possible examples that could satisfy the provisions of ISO 14044. They offer “a way” or “ways” rather than the “unique way” of applying ISO 14044. They reflect the key elements of the LCIA phase of the LCA. The examples presented in ISO/TR 14047:2012 are not exclusive, and other examples exist to illustrate the methodological issues described.

ISO/TS 14048:2002

Title: Environmental management — Life cycle assessment — Data documentation format.

Scope: This technical specification provides the requirements and a structure for a data documentation format to be used for transparent and unambiguous documentation and exchange of LCA and LCI data, thus permitting consistent documentation of data, reporting of data collection, data calculation, and data quality, by specifying and structuring relevant information.

The data documentation format specifies requirements on division of data documentation into data fields, each with an explanatory description. The description of each data field is further specified by the structure of the data documentation format.

This technical specification is applicable to the specification and structuring of questionnaire forms and information systems. However, it can also be applied to other aspects of the management of environmental data.

This technical specification does not include requirements on completeness of data documentation. The data documentation format is independent of any software or database platform for implementation.

This technical specification does not require any specific sequential, graphic, or procedural solutions for the presentation or treatment of data, nor does it describe specific modeling methodologies for LCI and LCA data.

ISO/TR 14049:2012

Title: Environmental management — Life cycle assessment — Illustrative examples on how to apply ISO 14044 to goal and scope definition and inventory analysis.

Scope: ISO/TR 14049:2012 provides examples about practices in carrying out an LCI analysis as a means of satisfying certain provisions of ISO 14044:2006. These examples are only a sample of the possible cases satisfying the provisions of ISO 14044.

They offer “a way” or “ways” rather than the “unique way” for the application of ISO 14044. These examples reflect only portions of a complete LCI study.

ISO 17422:2002

Title: Environmental aspects — General guidelines for their inclusion in standards.

Scope: This standard provides a structure for inclusion of environmental aspects in standards for plastics products. It proposes an approach that is directed at minimizing any adverse environmental impact without detracting from the primary purpose of ensuring adequate fitness for use of the products under consideration.

Note: This standard is intended to promote the following practices:

- (1) The use of techniques for identifying and assessing the environmental impact of technical provisions in standards, and for minimizing their adverse effects.
- (2) The adoption of good practices, such as:
 - (a) Procedures for pollution avoidance.
 - (b) Material and energy conservation in the light of the intended use (and foreseeable misuse) of the product.
 - (c) Safe use of hazardous substances.
 - (d) Avoidance of technically unjustifiable restrictive practices.
 - (e) Promotion of performance criteria rather than exclusion clauses such as are based, for example, only on chemical composition criteria.
- (3) The adoption of a balanced approach in standards development to issues such as environmental impact, product function and performance, health and safety, and other regulatory requirements.
- (4) The regular review and revision of existing standards in the light of technical innovations, permitting improvement in the environmental impact of products and processes.
- (5) The application of life cycle analytical approaches wherever applicable and technically justifiable.

ASTM D7075-04

Title: Standard practice for evaluating and reporting environmental performance of bio-based products.

Scope: Environmental performance shall be measured using the LCA approach. LCA is a “cradle-to-grave” approach that evaluates all stages in the life of a product, including raw material acquisition, product manufacture, transportation, use, and ultimately, recycling (that is, “cradle-to-cradle” and waste management).

JIS Z 7001:2007

Title: Environmental aspects — General guidelines for their inclusion in standards.

This Japanese standard is similar to ISO 17422:2002.

JIS Z 7121:2007

Title: Methods of life cycle inventory studies on plastics including recycling stages.

JIS Q 14040:2010

Title: Environmental management — Life cycle assessment — Principles and framework

Scope: This Japanese Industrial Standard describes the principles and framework for LCA.

JIS Q 14040:2010 is similar to ISO 14040:2006.

JIS Q 14044:2010

Title: Environmental management — Life cycle assessment — Requirements and guidelines.

Scope: This Japanese Industrial Standard specifies requirements and provides guidelines for LCA, including: (a) goal and scope definition of LCA; (b) LCI phase; (c) LCIA phase; (d) life cycle interpretation phase; (e) reporting and critical review of LCA; (f) limitations of the LCA; (g) relationship between LCA phases; and (h) conditions for use of value choices and optional elements.

JIS Q 14044:2010 is similar to ISO 14044:2006.

9.1.8 Eco-Labeling

ISO 14020:2000

Title: Environmental labels and declarations — General principles.

Scope: This standard establishes guiding principles for the development and use of environmental labels and declarations. It is intended that other applicable standards in the ISO 14020 series be used in conjunction with this standard.

This standard is not intended for use as a specification for certification and registration purposes.

Note: Other standards in the series are intended to be consistent with the principles set forth in this standard. Other standards currently in the ISO 14020 series are ISO 14021, ISO 14024, and ISO/TR 14025.

ISO 14021:1999

Title: Environmental labels and declarations — Self-declared environmental claims (Type II environmental labelling).

ISO 14021:1999/Amd 1:2011

ISO 14024:1999

Title: Environmental labels and declarations — Type I environmental labelling — Principles and procedures.

ISO 14025:2006

Title: Environmental labels and declarations — Type III environmental declarations — Principles and procedures.

Scope: ISO 14025:2006 establishes the principles and specifies the procedures for developing type III environmental declaration programs and type III environmental declarations. It specifically establishes the use of the ISO 14040 series of standards in the development of type III environmental declaration programs and type III environmental declarations.

ISO 14025:2006 establishes principles for the use of environmental information, in addition to those given in ISO 14020:2000

Type III environmental declarations as described in ISO 14025:2006 are primarily intended for use in business-to-business communication, but their use in business-to-consumer communication under certain conditions is not precluded.

The group of certified eco-labels, defined by the ISO standards 14024 (type I), 14021 (type II), and ISO 14025 (type III) enable the manufacturers to develop/create/design a logo by themselves (type II, declaration by themselves) or to prove the environmental compatibility of their products by a life cycle assessment (type III). The certification by a third party, however, is only requested with type I. So, the statements of the eco-labels should always be scrutinized.

9.2 Certification

Certification is a well-defined process in which a certification organization establishes the credibility of claims made regarding the biodegradability of a polymer material, intermediate, or product, and is necessary for the acceptance of the polymer as biodegradable. Certification is normally based on an established international or national standard, although it can also rely on less widely accepted criteria.

The certification process is carried out on a voluntary basis. It begins with an application that

Table 9.3 Main certification organization

Certification organizations	Country
DIN CERTCO [14]	EU/DE
Vinçotte [15]	EU/BE
Biodegradable Products Institute (BPI) [16]	USA
Japan BioPlastics Association (JBPA) [17]	JP
Keurmerkinstituut [18]	NL
Association for Organics Recycling (Afor) [19]	UK
Consorzio Italiano Compostatori (CIC) [20]	IT
Polish Packaging Research and Development Centre (COBRO) [21]	PL
Avfall Norge [22]	NO
Finnish Solid Waste Association (JLY) [23]	FI
Bureau de normalisation du Québec [24]	CA
Australasian Bioplastics Association (ABA) [25]	AU

includes information about the material or product that is to be certified. This then undergoes appropriate laboratory tests at an approved laboratory (which is normally not operated by the certification organization). The laboratory reports the results, and the certification organization uses these to decide whether to issue a certificate.

A certificate gives the producer of the product the right to mark it with an approved logo that is accompanied with the serial number of the certificate. In addition, the certification body maintains a publicly available list of issued certificates. A certificate has defined limitations. For example, it is valid for the defined product that was tested, has a validity period, requirements for periodic verification, etc. The main certification organizations are listed in Table 9.3. Each one of them issues independent certificates for biodegradable and/or compostable materials.

9.2.1 Certification Systems

Most certification systems relate to the evaluation of compostability. Other systems relate to environmental fate and safety (e.g., the Japanese GreenPla), or to biodegradation in water or soil (e.g.,

OK Biodegradable). All these systems differ from each other with regard to technical content, geographical coverage, application, and administration. The bioplastics industry is trying to develop a single, international certification and logo system for compostability that is valid throughout the world. In 2002, DIN CERTCO, the JBPA, and the Biodegradable Products Institute (BPI) reached an agreement to mutually recognize the test results of their respective laboratories [10].

The certification system “Products made of compostable materials” is a system under which products made of compostable materials that meet the identification standards prescribed by DIN EN 13432 — as well as, if applicable, the standards of ASTM D 6400, DIN EN 14995, and ISO 17088 — are authorized to use the “seedling” logo (see section 4 according to the procedure described in this certification scheme) [26]. The certification system “Products made of compostable materials” has been owned by European Bioplastics since 2012, and was created and continuously refined in collaboration with DIN CERTCO and a dedicated committee of experts. It makes a distinction between the registration of materials, intermediates and additives, and the certification of (end) products. It is continuously being developed under the auspices of European Bioplastics in consensus with the involved stakeholders. The certification work is performed by both DIN CERTCO (DE) and Vinçotte (BE). Certification clients can choose either of the certification bodies for proving the conformity of products with the underlying standards. The association is owner of the seedling mark shown in Figure 9.1, which is protected by trademark law.

DIN CERTCO issues certificates for compostable plastics based on the EN 13432 standard, while Vinçotte issues certificates for compostable plastics based on EN 13432 (“OK compost”), as well as certificates for plastics that can be composted in home



Figure 9.1 The “seedling” logo (European Bioplastics) [27].



Figure 9.2 The various “OK” logos of Vinçotte [15].

composting (“OK compost HOME”), and plastics that biodegrade in soil (“OK biodegradable SOIL”) and water (“OK biodegradable WATER”). Both organizations issue certificates for bio-based materials based on the ASTM 6866 standard (Vinçotte’s “OK bio-based”). The various logos of Vinçotte are displayed in Figure 9.2. Currently, there is no obligatory label requiring producers to disclose the amount of bio-based materials in their products. Producers provide this information to consumers voluntarily.

In Germany and many other countries of the EU, compostable bioplastics which have been successfully certified according to EN 13432 have the “seedling” symbol printed on them. In Great Britain and the Benelux countries, the logo “OK COMPOST” has prevailed.

Laboratory testing and inspection of routine production are performed on behalf of DIN CERTCO and Vinçotte either by testing laboratories which are officially approved by the two certification organizations, or by independent laboratories which are accredited according to ISO 17025 or recognized by a similar certification body [14].

The BPI certification scheme is based on the ASTM D6400 and ASTM D6868 standards. The BPI certifies compostability test results from BPI-approved testing laboratories, then licenses the BPI compostable logo (Figure 9.3) to the company concerned [16].

The JBPA has established two identification systems related to biodegradable plastics products and biomass-based plastics products [17]: the GreenPla Identification System, and the BiomassPla Identification System. The logo marks for these two systems are shown in Figure 9.4.

The GreenPla Identification System is a system under which GreenPla products that meet the

identification standards prescribed by the JBPA are authorized to use the GreenPla logo (specified separately by the JBPA), in order to ensure that ordinary consumers can easily identify GreenPla. The term GreenPla as used here refers to materials or products that include in their components biodegradable organic materials that are broken down by the action of microorganisms in the natural environment, and which ultimately become carbon dioxide or water.

The BiomassPla mark certification system is an identification system for products of biomass origin. Under this system, the products that meet the stipulated standards are certified as BiomassPla and are authorized to use the BiomassPla logo. The degree of biomass plastics in a product shall be a plastics

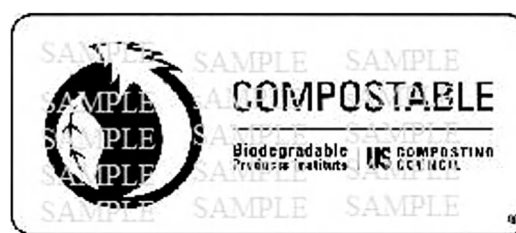


Figure 9.3 BPI compostable logo [28].

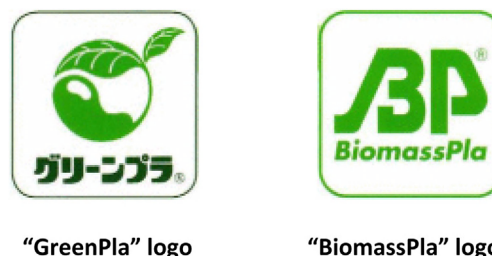


Figure 9.4 Certification identification systems of JBPA [17].

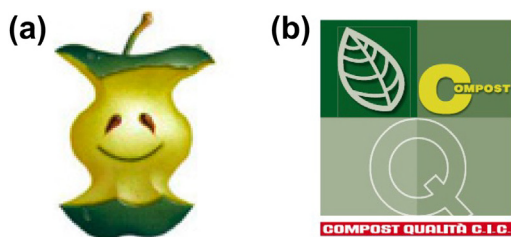


Figure 9.5 Finnish [23] (a) and Italian [20] (b) compostable logos.

product of 25.0 wt.% or more in one of the authentication conditions of the above-mentioned system.

Additional logos for certifying compostable materials include the “apple” logo developed by the Finnish Solid Waste Association (Jätelaitosyhdistys, JLY), and the Italian “compostabile” logo developed by the Consorzio Italiano Compostatori, both shown in Figure 9.5.

No specific certificates or labels exist for anaerobic biodegradation, nor are any foreseen for the near future [11].

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10 Economic Evaluation and Environmental Impacts

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10.1 Economic Evaluation

There are hardly any studies on the economic analysis of the recycling of waste biopolymers or bioplastics so far. There are good reasons for this. Because biopolymers make up less than 1% of the global plastics market, they lack economies of scale and their waste streams have not yet reached an adequate level. Secondly, in view of the general belief that biopolymers are biodegradable or compostable, there is no need to recycle them. However, as has been mentioned elsewhere in the book (see for example Chapter 5: Physical Recycling; Section 5.1: General), most biopolymers are not decomposed spontaneously in nature, but only under specific conditions, such as in industrial composting. Furthermore, not all biopolymers are compostable because they are defined either as polymers from renewable origin (but not necessarily biodegradable), or as polymers from fossil origin that are compostable (see Chapter 2: Definitions and Assessment of (Bio)degradation; Section 2.1: Define the Terms). This makes managing biopolymer waste streams very complex and costly.

Polylactide (PLA), and to a lesser degree polyglycolide (PGA), may well become a commodity product, so the question of disposal or recycling of large quantities of this material, such as empty bottles, must be addressed. It has been established that biodegradable biopolymers pose a serious problem when they enter either conventional plastics recycling or green-waste composting streams. Early attempts to physically recycle waste PLA bottles with mainstream poly(ethylene terephthalate) (PET) bottles was met with strong resistance from PET recyclers and recycling associations; it was claimed that PLA contaminates the existing PET recycling streams, causing the production of inferior recycled material. PLA and PET bottles look alike and their sorting is not always straightforward.

Cornell [1] developed two scenarios for the physical or mechanical recycling of PLA bottles from a mixed stream with PET:

Scenario #1

If the cost of automatic sorting was 0.010 \$/lb of material sorted and biopolymer was present in 2% of the stream, the cost of examining all 100% of the material should be borne by the 2% that is causing this to happen. Then, the added cost to recycle the

biopolymer over the general cost to recycle plastic bottles would be as follows:

$$(0.010 \text{ \$/lb bottles sorted}) \div (0.02 \text{ lb biopolymer/lb bottles sorted}) = 0.50 \text{ \$/lb biopolymer cost}$$

If the biopolymer bottle arrived in a stream of PET bottles, its approximate cost as recycled flake would be the cost of PET recycled flake plus the added sorting cost. When PET postconsumer flake costs approximately 0.40 \\$/lb, in this scenario the biopolymer postconsumer flake would cost ca. 0.90 \\$/lb and require end uses that would pay at least that much for the value received. Finding such high-value uses for recycled flake is a daunting task.

Scenario #2

If the biopolymer was removed from the stream of PVC bottles that is currently formed as a reject stream from PET bottle recycling, the concentration of biopolymer bottles might be eventually as high as 20%, for which the added cost would be a more tolerable 0.05 \\$/lb biopolymer; for the resulting flake, an end use is required that would pay at least 0.45 \\$/lb. In any case, since the inclusion of minor resin bottles into the current collection and sorting system means extra cost must be borne by the minor resin, it is sought for recycling.

Cornell [1] estimates the use of biopolymers for all packaging purposes in the USA to be around 30 million pounds (Mlbs). By doubling this amount and assuming the public's efficiency in recycling to be 50% — a high value for the different types of bottles the consumer would have to recognize — the amount of biopolymer to be recycled would be at most:

$$\begin{aligned} & (60 \text{ Mlbs}) \times (60\% \text{ availability}) \\ & \quad \times (50\% \text{ public's participation}) \\ & \quad \times (50\% \text{ public's efficiency}) \\ & = 9 \text{ Mlbs biopolymer} \end{aligned}$$

This amount is not adequate to support even one independent bottle reclamation facility. Such a facility needs to process at least 10 Mlbs, preferably 40 Mlbs annually, to be sustainable. Cornell [1] estimates that a critical mass of virgin biopolymers used in bottles of at least 400 Mlbs annually is necessary for an independent rigid packaging recycling to be profitable. Till then the physical (or mechanical) recycling of rigid biopolymers could be handled as a sideline in existing

recycling facilities provided the value of the recycled product exceeds incurred costs (see for example Chapter 5: Physical Recycling; Section 5.1: General).

It can therefore be concluded that a successful recycling scheme of biopolymers should fulfill four basic requirements:

- Adequate quantities of waste biopolymers.
- Existence of a network of collecting waste biopolymer articles.
- Proper biopolymer recycling facilities.
- Economical profitability (i.e., the value of the products made in whole or part from the recycled material exceeds the recycling costs).

Kuppens et al. [2] investigated the economic benefits resulting from the flash co-pyrolysis of short-rotation coppice, such as willow, with waste biopolymers, via cost-benefit analysis and Monte Carlo simulations that took into account uncertainties. The biopolymers under investigation were polyhydroxybutyrate (PHB), Eastar[®] Bio[poly(butylene adipate-co-terephthalate), PBAT], potato starch, PLA, cornstarch, and Solanyl[®] (starch-based resin). The disposal problem associated with phyto-extraction of farmland polluted with heavy metals by means of willow requires a biomass conversion technique that meets both ecological and economic needs. Combustion and gasification of willow require special and costly flue gas treatment to avoid re-emission of the metals into the atmosphere, whereas flash pyrolysis mainly results in the production of (almost) metal-free bio-oil with a relatively high water content. Flash co-pyrolysis of biomass and waste biopolymers synergistically improved the characteristics of the pyrolysis process (e.g., reduction of the water content of the bio-oil, more bio-oil and less char production, and an increase of the higher heating value (HHV) of the bio-oil). Besides bio-oil, crystals of crotonic acid (a source of valued added chemicals) were formed during co-pyrolysis of willow with PHB.

Flash co-pyrolysis led to better economic results as compared to flash pyrolysis of pure willow. The net present value (NPV) of cash flows has been increased to at least 0.405 million euros (M€) for the willow/cornstarch blend. Flash co-pyrolysis of willow and PHB even increased the NPV to 49.156 million euros (M€) due to the high value of crotonic acid. Except for the willow/PHB blend, the economics, however, depend largely on the presence

of green current certificates that make up more or less 44% percent of total revenues for each blend. Because of the currently small supply of biopolymers, however, it was not possible to determine the exact costs for collecting and transporting biopolymer waste to the pyrolysis plant. For this reason the maximum cost for the biopolymer feedstock has been calculated for different scenarios taking into account several uncertainties. In the most expected scenario the maximum prices for all biopolymers except PHB were negative, meaning that flash co-pyrolysis was only profitable if the stream of biopolymer waste generated an income for the investor in the pyrolysis reactor. Flash co-pyrolysis can be seen as an alternative technology for processing waste biopolymers (PLA, PHB, Bio-pearls, Eastar® Bio, and potato starch), as it is cheaper than composting, which costs 80 euros per oven dry ton (€/odt). Only for waste of cornstarch and Solanyl®, however, was composting cheaper. Until the current system of green certificates is phased out without some other compensation, composting will always (except for PHB waste) be preferred above flash co-pyrolysis as the latter costs between 172 €/odt for the disposal of Eastar® Bio waste and 237 €/odt for disposal of cornstarch waste. If biopolymers make their full entry into the plastic industry, flash co-pyrolysis of willow and PHB is the only commercial option in the short term with a value for PHB waste between 2.151 and 2.749 €/kg.

10.2 Life Cycle Assessment (LCA)

Several tools and metrics have been developed to measure the environmental impact of a product in the life cycle of the whole product chain. One of the most prominent tools is life cycle assessment (LCA), also known as life cycle analysis or eco-balance. LCA provides a way of measuring and comparing the environmental credentials of products, such as biopolymers. Its principles and framework have been standardized by the ISO 14040 series, namely ISO 14040:2006 and ISO 14044:2006.

ISO/TR 14047:2012 and ISO/TR 14049:2012 provide illustrative examples on how to apply ISO 14044 to impact assessment situations and to goal and scope definition and inventory analysis, respectively (see Chapter 9: Regulatory Aspects Framework; Section 9.1.7: Life Cycle Assessment (LCA) Related Standards).

The basis of any LCA is the creation of a model that contains the amounts of all process inputs and outputs that occur during the product life cycle. This includes the production phase, distribution, use, and final disposal or recycling of the product. Depending on the goal and scope of the assessment, the boundaries can be set differently; for instance, a “cradle-to-gate” assessment might be adequate when comparing two alternative processes to the same product; or a “gate-to-grave” assessment may suffice when comparing two different end-of-life technologies. The results of these assessments can be reported as direct inventory data (e.g., life cycle energy, life cycle mass, life cycle emissions), measures of individual potential impacts (such as global warming or acidification), or as an aggregate score or index for high-level comparison (for example Eco-Indicator 99) [3]. LCA methodologies provide a directly applicable framework to assess the sustainability of processes. In addition to the traditional environmental life cycle assessment, which has increasingly included health and safety impacts, life cycle costing [4], and the more recent social life cycle assessment [5,6] attempt to complete the holistic view of sustainability [3]; however, the proposed LCA frameworks for assessing social and economic impacts are not well developed [7].

The two most commonly used systems chosen in LCA studies are “cradle-to-gate” and “cradle-to-grave.” A cradle-to-gate LCA study includes all steps from the extraction of raw materials and fuels, followed by all conversion steps up and until the product is delivered at the factory gate. Cradle-to-gate analyses are often published by material producers. The cradle-to-grave system covers all steps of the cradle-to-gate system, as well as the usage and disposal phases.

Cradle-to-grave analyses have the advantage of covering all phases of the life cycle. Since waste management differs by country and not all waste treatment options can be taken into account, cradle-to-grave analyses for a given product can lead to very different results depending on the type of waste management. If comparisons across the various waste management options are not available, cradle-to-gate analyses can provide first insight into the environmental impacts [8].

A recently introduced LCA system, the so-called “eco-efficiency assessment,” consists of a cradle-to-grave analysis combined with an assessment of all life cycle costs [4]. BASF has also proposed

a cradle-to-grave LCA called SEEBALANCE[®] which includes life cycle costs and social aspects (Figure 10.1) [9].

LCA has been considered an important tool for the evaluation of biopolymer environmental profiles. The LCA assesses the interactions that a product or service has with the environment, and considers its whole life cycle, including the pre-production points (extraction and production of raw materials), production, distribution, use (including reuse and maintenance), recycling, and final disposal. The impact categories most used in LCAs of biopolymers are global warming, acidification, eutrophication, ozone layer depletion, smog, and fossil resource depletion. Recently, extra categories have been added, such as land use change (including aesthetic impact) and impact on biodiversity and soil productivity. These categories lead to a more detailed, and therefore more realistic, assessment of biopolymers [10].

The LCA provides major benefits to manufacturers, policy makers, legislators, researchers and end users. These benefits can be summarized as follows:

- Quantification of emissions into air, water, and land that take place in every life cycle phase and estimation of the environmental consequences on humans and the ecosystem.
- Detection of significant changes in the environmental effects between the life cycle phases.
- LCA studies can be used in drafting environmental and waste management policies as well as for regulatory and legislative measurements.
- LCA results are increasingly being considered as a key input in decision-making. For instance, LCA can be used internally within an industry

for process and product improvement, and for selection of technology, feedstock, energy carriers, and production locations, etc. Externally LCA can be used for promotion purposes.

- LCA results enable users and the final consumers to make more informed choices.

Despite the obvious benefits, LCA tools for the study of biopolymers have several limitations:

- An LCA study is economically prohibitive for most of the companies interested in applying it. This is because a holistic LCA is a data-intensive and time-consuming procedure.
- There is not a universally accepted LCA methodology. As a result inconsistency problems with different background databases can affect LCA comparisons and give misleading results and interpretations due to the varying level of details and accuracy of the respective databases [11].
- Some LCA studies do not refer to the overall life cycle of the product, but to specific stages.
- The results of most LCA studies focus on the national and regional levels. This means that the results of such studies may not be applicable in different regions or countries.
- The accuracy of an LCA study depends on the quality and availability of the relevant data.
- Occasionally, the presented environmental performance of the product is not realistic and consequently the reliability and usefulness of the results is controversial.
- LCA is too complex to be used to communicate the environmental performance of products to final consumers.

Figure 10.1 Depiction of the SEEBALANCE[®] tool developed by BASF [9] (courtesy of BASF). Matryoshka principle: each step “nests” the previous one.



- Most LCAs have failed to count the carbon emissions that occur as farmers worldwide convert forest and grassland to new cropland to replace the corn diverted to biopolymers. By excluding emissions from land use change, most previous accountings were one-sided because they counted the carbon benefits of using land for biopolymers but not the carbon costs, the carbon storage, and sequestration sacrificed by diverting land from its existing uses. From an environmental standpoint, accounting for emissions from land use changes can limit the attractiveness of LCAs [12].
- The LCAs generally do not consider the availability, consistency, and stability of various raw material under consideration, nor do they consider how these factors determine material costs. In the case of bio-based biopolymers, key suppliers are still ramping up production, and most of the producers have limited capacity. Even if an LCA determines a biopolymer is the most sustainable choice for a product, its use may not even be feasible at the required volumes [13].
- Despite growing interest in biopolymers, there is little research available as to environmental, health, and safety impacts throughout their life cycles.
- The application of LCA methodology can be misleading if only applied as a comparison of the environmental impact of alternative products.
- An LCA approach focused on an “isolated” product does not take into account the possible role the product can play in a complex system and the overall impact on different systems. A biodegradable product can be just “eco-advertising” or part of a chain whose benefit and consequences are much larger than the single product [14].
- An LCA of today will not necessarily be valid in the future. For example, a biopolymer which is disposed of by landfilling or incineration today could have alternative waste management options in the future, such as chemical recycling [14].

In conclusion, LCA results should be treated with caution. While the information they provide to interested parties is scientifically correct, it can at the same time be potentially misleading.

10.2.1 LCA of Biopolymers

LCA has been performed on several biopolymers, including starch; PLA; various PHAs, such as PHB; aliphatic-aromatic polyesters, such as PBAT; aliphatic polyamides, such as polyamide 11 (PA 11); etc. However, the majority of these studies are estimates comparing the energy requirements of CO₂ or greenhouse gas (GHG) emissions. The only available full LCA study is provided by NatureWorks LLC for their PLA manufacturing [15]. The available data for other biopolymers are incomplete and often based on semi-industrial or even laboratory-scale manufacturing conditions. At the same time, the available data for certain biopolymers exhibit a wide degree of variation, as in the case of PHAs [16]. Biopolymers are in an early stage of development and are produced in small-scale or individual facilities; their conversion into final products is often not yet optimized. This also means that their life cycle inventory (LCI) datasets often derive from relatively new and more accurate sources, which results in higher inventory quality and broader coverage of inputs and outputs (e.g., measurements of substances not measured in other datasets) [11].

10.2.1.1 Starch

Dinkel et al. [17] prepared a cradle-to-grave LCA study comparing starch to low density polyethylene (LDPE). Two types of waste management were distinguished: (1) a combination of combustion in municipal solid waste incineration plants and landfilling; and (2) composting. The waste management assumed for LDPE consists of 80% incineration and 20% landfilling. Based on these assumptions, Dinkel et al. came to the conclusion that thermoplastic starch performs better than LDPE in all impact categories, including energy resources, GHG emissions, human toxicity, acidification, and salinization. Eutrophication was the only exception. GHG emissions are reported to be dominated by CO₂, while N₂O emissions (from agriculture) and methane emissions (from energy supply) are of minor importance (5 and 1–2%, respectively, of the total GHG emissions potential). The impact on biodiversity depends on the type of land. A negative impact is determined if natural areas are displaced [17,18].

Patel et al. [19] compared various types of thermoplastic starch with polyethylene (PE). The

thermoplastic starches varied from 100% pure starch to different blends with different shares of petrochemical copolymers (PVOH, PCL). It was assumed that both the starch polymers and PE are incinerated in municipality solid waste incineration (MSWI) plants after their useful life. No credits have been assigned to steam and/or electricity generated in waste-to-energy facilities. The results of this analysis are restricted to energy and CO₂. According to this comparison, starch polymers offer saving potentials relative to PE in the range of 28–55 MJ/kg polymer and 1.4–3.9 t CO₂/t plastic depending on the share of petrochemical copolymers. LCA data for PCL and PVOH are generally considered to be subject to major uncertainties [19].

James and Grant conducted a comparative LCA of biodegradable grocery bags made from starch polymers/blends, paper, cotton, and conventional polymers [20]. All LCA studies report that, per kilogram, starch polymers require less non-renewable energy use (NREU) than petrochemical polymers. According to Patel et al. [21], the energy savings of starch polymers ranges from 23 to 52 MJ/kg ($\pm 15\%$) depending on whether LDPE or LLDPE is chosen. However, due to the low density of starch polymers, usually larger amounts of them are needed to produce a final product that fulfils the same function (e.g., loose fills, packaging films, and bags) than their petrochemical counterparts. For the cases studied, thermoplastic elastomer starch (TPS) is nevertheless at least comparable to petrochemical products, and in some cases the NREU savings are substantial. For example, the TPS film requires half the energy to produce compared to the PE film [8]. Landfilling without methane capture, which is another common waste treatment method in some regions, can cause higher GHG emissions for starch polymer products than for petrochemical products due to the methane emissions from biodegradation.

Morken and Nyland [22] performed a cradle-to-grave LCA study that compared Mater-Bi[®] bags to PE bags. The LCA system boundaries encompassed raw materials all the way through to bag disposal by landfill and composting (cradle-to-grave excluding land application of the resultant compost). Raw material production and transportation, granulate production, and bag manufacture, were analyzed and the fuel inputs considered. Transportation, end-of-life composting, and energy from waste or landfill options were also assessed. The overall results of this study showed that the LCA of Mater-Bi[®] bags was

more energy intensive and produced more GHG emissions than the LCA cycle of PE bags (disposed of by composting or landfill). The incineration of Mater-Bi[®] bags for heat and power generation produced a global warming potential only slightly higher than incinerated PE due to the oil saved by burning Mater-Bi[®] bags [4].

A more recent cradle-to-grave LCA study of Mater-Bi[®] (provided by Novamont) compared Mater-Bi[®] bags with equivalent paper and PE bags. The stages considered in this study were crop production through to bag manufacture and disposal by composting or incineration. Unlike the 2002 Mater-Bi[®] bag study, this LCA did not incorporate transportation. The results indicated that Mater-Bi[®] bag manufacture uses slightly less energy than equivalent PE bags and significantly less than paper bags. Novamont also stated that the GHG output/global warming potential for the life of Mater-Bi[®] bags is significantly lower (over 60% reduction) than that for PE bags. The disparity observed between the results of these two LCAs can probably be attributed to different LCA specifications, manufacturing procedures, and plant efficiency [4].

10.2.1.2 PLA

PLA is the most studied biopolymer.

Using LCA, Detzel et al. [23] compared the environmental performance of clamshells made from PLA (Ingeo[™]) with clamshells made from polypropylene (PP), oriented polystyrene (PS), and PET. In addition, the authors examined the potential environmental effects of improved PLA polymer production and a number of individual end-of-life options for PLA packaging waste. The comparison of the PLA packaging system against the alternative systems revealed the following:

- The PLA system shows advantages compared to all three systems with conventional polymers in the categories fossil resource consumption, global warming, and summer smog (POCP). Similar results regarding human toxicity (carcinogenic risk) are of limited reliability due to existing data quality issues.
- For the remaining impact categories, comparisons of the PLA system with the alternative systems do not show a clear trend. The LCA results for acidification, terrestrial eutrophication, and human

toxicity (PM10) show the disadvantages of PLA when compared to PS and PP systems.

- On the other hand, with the exception of terrestrial eutrophication, advantages in these categories are found when compared to the PET system. However, the latter observation has been found to depend on the choice of PET inventory datasets.
- As for aquatic eutrophication, clam shells from PLA show environmental advantages if compared to PP and disadvantages in comparison with PS and PET.

The use in the agricultural area is a feature intrinsic to PLA given its origin from corn, an agricultural feedstock. When including this renewable feedstock, the total cumulative energy demand of the PLA system is in the range of that of fossil-based polymers. However, when looking at the non-renewable energy demand only, the PLA systems score best.

The authors emphasize that in all the packaging systems examined, it is the polymer production step which strongly influences the overall LCA results for most environmental impact indicators. In addition, greenhouse gas emissions are generated in the end-of-life phase to a considerable degree, though these emissions are partly compensated for by the credits achieved through recycling and energy recovery.

In the addendum of 2009, clamshells made from PLA (Ingeo™) were compared to clamshells made partly or completely from recycled PET (rPET) under a European and US framework [24]. Relevant settings within the given framework are the final waste treatment options, the supplied grid electricity, and the raw material transport. The main difference between the two geographical frameworks, besides the differences in the energy grid, is that there is no Ingeo™ production in Europe. In the latter case the required Ingeo™ has to be transported overseas from the USA to Europe.

In both scenarios clamshells made from Ingeo™ showed lower potential environmental impacts than clamshells made from either PET or rPET for the following indicators: fossil resources, climate change, summer smog, human toxicity (carcinogenic risk), and non-renewable and total primary energy. On the other hand, PET (and rPET), has a better score for use of nature: farmland, terrestrial and aquatic eutrophication, human toxicity (PM10), renewable energy. PET also often has a better score for acidification.

From a climate change point of view the best end-of-life option for any clamshell is landfill (assuming 0% degradation) followed by incineration with energy recovery and composting. From a non-renewable energy point of view the best choice is incineration with energy recovery; both other options show an equal score.

Assuming landfill as the best end-of-life scenario, for the comparison of Ingeo™ and PET (100% rPET), Ingeo™ shows a lower score for the following indicators: fossil resource use, climate change, summer smog, human toxicity (carcinogenic risk), and non-renewable energy. For other indicators like acidification, terrestrial and aquatic eutrophication, and human toxicity (PM10), PET scores lower. The same conclusions are valid for incineration as the end-of-life option. The only waste treatment option examined under the US framework is landfill. The results are similar to the results for clamshells which end up on European landfills; except for the indicator acidification the net results for clamshells made from Ingeo™ material show lower potential environmental impacts than clamshells made from virgin PET. This is due to the avoidance of overseas transport of Ingeo™ pellets in the US framework. The comparison of clamshells made from Ingeo™ and clamshells made from 100% rPET shows a similar result pattern as the results for the European framework. Lower environmental indicator results are found for clamshells made from Ingeo™ for fossil resources, climate change, summer smog, human toxicity (carcinogenic risk), and renewable primary energy. Lower environmental indicator results are found for clamshells made from 100% rPET for acidification, terrestrial and aquatic eutrophication, and human toxicity (PM10) [24].

Vink et al. described a cradle-to-gate LCA study of PLA manufactured by NatureWorks LLC [15]. Their LCA encompassed (1) corn (maize) production and transport; (2) corn milling for starch; (3) starch conversion to dextrose sugar; (4) conversion of dextrose to lactic acid; (5) conversion of lactic acid to lactide; and (6) polymerization of lactide into PLA. For corn production, various inputs were considered, including seed, fertilizer, limestone, electricity and fuels, irrigation, and energy used by the crop for herbicide and pesticide manufacture. Various farm outputs were also considered, including nitrogen compound, phosphate compound, and farm vehicle emissions. At the stage of corn processing, considered activities included the separation of corn kernel

components, starch hydrolysis to sugars, and the production of useful co-products. For the manufacture of PLA several inputs were considered, including electricity, fuels, steam, water, and chemicals. Outputs included were gypsum and other co-products, wastewater, air emissions, and solid waste. The results of this study showed an 85% reduction in GHG output and a 50% reduction in fossil fuel-based energy requirements for PLA production in 2006 compared to PLA manufacture in 2003.

Murphy et al. conducted an LCA study of super-market carrier bags made of biopolymers and synthetic polymers [25]. In this study both oxodegradable and non-degradable high density polyethylene (HDPE) bags were compared to starch-based Mater-Bi® bags and PLA/fossil fuel-based polymer mix bags. The system boundaries incorporated raw material, and carrier bag production, distribution, use, and end-of-life options such as landfill, incineration, recycling, and industrial composting. A comparison of the four bag types tested showed that using and recycling HDPE bags produced the least environmental impact. The Mater-Bi® bags disposed of by incineration were shown to be second best with only a slightly higher impact than HDPE bags. The following conclusions were drawn from this study: (1) the major source of environmental impact was the extraction and production of materials for all four bag types; (2) there was no evidence of energy savings in the production of bioplastic bags; (3) waste management options greatly influence the outcome of an LCA; (4) incineration is the best option for the disposal of bioplastic bags; (5) landfill of bioplastic bags results in the least global warming potential due to slow breakdown of the bags; and (6) composting is not a clear winner for the disposal of bioplastic bags. However, it must be noted that bioplastic bags are sustainable and are made using renewable raw materials that are biodegradable, which can help reduce waste sent to landfill.

Contradictory conclusions were drawn in a review study by Davis and Song [26] on the potential impact of biodegradable packaging materials on waste management in terms of landfill, incineration, recycling/reuse, composting, and anaerobic digestion. The most favored end-of-life disposal options for these materials are domestic and municipal composting in place of landfill as the worst disposal option, the second worst option being incineration, with anaerobic digestion falling somewhere in the middle. Techniques for recycling conventional

polymers are generally not suitable for biodegradable biopolymers [26].

Piemonte [27] used cradle-to-gate and cradle-to-grave LCA methodologies to compare PLA and Mater-Bi® with conventional polymers (PE, PET) by assessing the actual energy and GHG savings resulting from the production of these biopolymers. Also taken into consideration were the final scenarios of composting, incineration, anaerobic digestion, and mechanical recycling. The analysis showed that incineration, composting, and anaerobic digestion processes clearly underperform from an environmental point of view, and with respect to the mechanical recycling process. Due to the uncertainties associated with the LCI data reliability and LCA method used, the results reported in this paper can be useful to draw first conclusions about the environmental reliability of biopolymers, but cannot be taken as guidelines for the market use of PET or PE as compared to PLA or Mater-Bi®. It is noted that the extra costs involved in sorting PLA from a mixed recycling stream have not been taken into consideration during physical (mechanical) recycling [27].

10.2.1.3 Polyhydroxyalkanoates (PHAs)

There are no full LCAs for polyhydroxyalkanoates (PHAs). The only available studies are estimates comparing energy requirements and CO₂ or GHG emissions [28–32]. These studies compare the LCA data of PHAs with the corresponding data of conventional polymers derived from fossil fuel, such as PS, HDPE, LDPE, and PP. Comparing the energy requirements for the production of PHA and PS, the study by Gerngross [31] showed that the production of 1 kg of PHA requires 50.4 MJ (2.39 kg of fossil fuel equivalent) and exceeds the 47.6 MJ (2.26 kg of fossil fuel equivalent)¹ required to produce an equal amount of PS. The energy requirements for the production of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx) and polyolefins in the study by Akiyama et al. [33] showed that between 50 and 59 MJ/kg-polymer is needed. Nonato et al. [32] reported

¹ PHA production requires the combustion of the entire 2.39 kg for energy production, whereas polystyrene production combusts only 1 kg of the 2.26 kg fossil fuel required for its manufacture, the balance being used as feedstock.

Table 10.1 CO₂ emissions and energy requirements for the production of polyhydroxyalkanoates (PHAs) and some conventional polymers (cradle-to-gate)

Polymer	CO ₂ emissions (kg CO ₂ /kg-polymer)	Energy requirements (MJ/kg-polymer)	Reference
PHA	2.4	50.4	[31]
PHA (from corn plants)		90	[29]
PHA (bacterial fermentation)		81	[29]
PHA	2.0		[30]
PHA	0.26–0.45	50–59	[33]
PHB		113.7	[32]
PHB	2.6	42.9	[34]
PP	3.4	85.9	[35]
HDPE	2.5	73.7	[35]
HDPE		80	
LDPE	3.0	81.8	[35]
HDPE		80	[36]
PET		77	[36]
PS		87	[36]
PS		47.7	[31]

Abbreviations: HDPE, high density polyethylene; LDPE, low density polyethylene; PET, poly(ethylene terephthalate); PHA, polyhydroxyalkanoate; PHB, poly(3-hydroxybutyrate); PP, polypropylene; PS, polystyrene.

a total energy requirement of 113.7 MJ/kg-polymer for the production of PHB. These studies included an electricity credit from biomass used for energy needs as each author deemed relevant. Harding et al. [34] reported a total cradle-to-gate energy for the production of PHB of 42.9 MJ/kg-polymer. In Table 10.1 these data are compared to LCA data for conventional polymers derived from fossil fuel. As can be seen, the total cradle-to-gate energy requirements of PHAs, with the exception of the study by Nonato et al., are either lower than, or comparable with, those of polyolefins and PET.

The CO₂ emissions reported by Akiyama et al. [33] that take the carbon neutral status of agricultural processes into account were between 0.26 and 0.45 kg/kg-polymer. Gerngross [31] reported net CO₂ emissions of 2.4 kg/kg-polymer mainly as a result of the combination of fossil fuel used to generate energy for the process, similar to the 2.0 kg/kg-polymer reported by Kurdiyar et al. [30]. These values compare with 2.6 kg/kg-polymer reported by Harding et al. [34], which resulted from the production of steam (55.4%), electricity (30.8%), combustion of natural gas (6.7%), production of

hydrogen peroxide (2.7%), fertilizer (2.5%), and other processes (1.9%).

Gerngross and Slater [29] calculated that the process energy requirements for the production of 1 kg of PHA from genetically modified corn plants would require about three times more energy than the 29 MJ needed to manufacture an equal amount of fossil fuel-based PE. On the basis of these results it was concluded that PHAs do not offer any advantages for emission reduction [29,31]. This finding is valid for certain system boundaries (e.g., the cradle-to-gate system which outputs pellets). Patel et al. [18] commented that the conclusion is correct if all PHA waste is deposited in landfills, and the finding is incorrect if other types of waste management processes are assumed within the cradle-to-grave analysis. Furthermore, Patel et al. [18] demonstrated that the total fossil energy requirements are practically the same for PE and PHA manufactured by bacterial fermentation. If combusted in a waste incinerator (without energy recovery), both polymers result in comparable CO₂ emissions throughout the life cycle [18].

Yu and Chen [37] performed a simulated cradle-to-gate LCA study of the manufacture of PHAs from

the “black syrup” byproduct of biomass-based bioethanol with two important categories, the GHG emissions and the fossil energy requirement per kilogram of biomass produced. The analysis indicates that PHA contributes clearly to the goal of mitigating GHG emissions with only 0.49 kg CO₂ being emitted from production of 1 kg of PHA. Compared with 2–3 kg CO₂ of fossil fuel-derived counterparts, it is about 80% reduction of the global warming potential. The fossil energy requirement per kg of PHA is 44 MJ, lower than the 78–88 MJ/kg of PHA produced from fossil fuel resources. About 62% of fossil energy is used for processing utilities and wastewater treatment, and the rest is required for raw materials in different cycle stages. The LCA study has shown that it is theoretically feasible to produce PHAs on a commercial scale with a significant reduction in global warming potential.

Akiyama et al. [33] found that pure culture production from soybean oil and corn glucose contributes markedly less to GHG emissions than conventional polymers. However, Gerngross [31] and Kim and Dale [38] have concluded that PHA production from corn-based glucose does not have an environmental advantage over conventional polymer production from crude oil. These assessments pinpointed the high levels of energy consumption throughout the production process (from cradle-to-gate) as the most important contributing processes. They also found that pure culture PHA production, based on processed agricultural feedstocks (such as corn-based glucose), will still not provide better profiles for other environmental impacts (i.e., photochemical smog, acidification, and eutrophication) than polystyrene production. Harding et al. [34] reported also that the impacts of PHB in acidification and eutrophication are higher than polyethylene. Kim and Dale [38] suggested that one of the primary reasons for high impacts of PHA in photochemical smog, acidification, and eutrophication are the environmental burdens associated with corn cultivation.

10.2.1.4 Polyethylene (PE)

Braskem S.A. and Toyota Tsusho Corporation concluded a joint study of LCA for polyethylene derived from Brazilian sugarcane (“Green Polyethylene”), and found that the biopolyethylene emits less GHG when compared to fossil fuel-based

polyethylene even with transportation half a world away [39].

The University of Tokyo conducted the analysis under the collaborative study with the parties using the preliminary eco-efficiency study performed by Fundação Espaço Eco in Brazil (2007/2008), which shows that 1 kg of biopolyethylene emits 1.35 kg of CO₂ equivalents of GHG when it is produced in Brazil, shipped to Japan, used by consumers as container and packaging, and then incinerated. Meanwhile, traditional fossil fuel-based polyethylene emits 4.55 to 5.10 kg in its overall life cycle. As a result, the study demonstrates that 70–74% of GHG can be reduced by the substitution of biopolyethylene for traditional PE.

Many LCAs of bio-based and biodegradable biopolymers neglect the postconsumer waste treatment phase because of a lack of consistent data, even though this stage of the life cycle may strongly influence the conclusions. Hermann et al. [40] attempted to approximate carbon and energy footprints of the waste treatment phase and to find out what the best waste treatment option for biodegradable materials is by modeling home and industrial composting, anaerobic digestion, and incineration. They compiled datasets for the following biodegradable materials: paper, cellulose, starch, PLA, starch/polycaprolactone (Mater-Bi®), PBAT (Ecoflex®), and PHA on the basis of an extensive literature search, experiments, and analogies with materials for which there have been significant experience. During biological waste treatment, the materials are metabolized so a part of their embodied carbon is emitted into air, with the remainder stored as compost or digestate. The compost or digestate can replace soil conditioners supporting humus formation, which is a benefit that cannot be achieved artificially. Experimental data has also shown that home and industrial composting differ in their emissions of nitrous oxide and methane, but it should be noted that data availability on home composting is limited. The results show that anaerobic digestion has the lowest footprint for the current level of technology, but incineration may become better in the future if energy efficiency in waste incineration plants improves significantly. Home composting is roughly equal to incineration with energy recovery in terms of carbon and energy footprint when carbon credits are considered. The same applies to industrial composting if carbon credits are assigned for compost to replace straw. Carbon credits can therefore considerably affect the results, but there are

significant uncertainties in how they are calculated. Incineration may become better than home composting in the future if the average energy efficiency in waste incineration plants improves significantly. However, biological waste treatment options should be chosen when soil carbon is a limiting factor [40].

Industrial composting is often argued to be the best option for the disposal of biodegradable biopolymers, as an LCA might also indicate, but this assumes falsely that the required large-scale industrial composting facilities actually exist in most municipalities. Here, the LCA's conclusion would have limited applicability [13].

Tabone et al. [41] conducted an LCA study on the environmental impact of both fossil fuel and bio-based biopolymers, assessing them using metrics which included economy, mass from renewable sources, biodegradability, percent recycled, distance of furthest feedstock, price, life cycle health hazards, and life cycle energy use. It was found that biopolymers are the more eco-friendly material in terms of energy use and emissions created. However, it was also found that biopolymers could have greater environmental impact in terms of eutrophication and ecotoxicity. These impacts would be caused by fertilizer use, pesticide use, and land use change required for agriculture production, as well as from fermentation and other chemical processing steps.

Several bioplastic manufacturers have commissioned or conducted LCA studies. These or similar studies will provide a clearer picture of the potential effects of the transition from fossil fuel- to bio-based polymers, and permit material selection decisions to be made with greater confidence.

10.3 Environmental Impacts

An extended review on the subject has been written by Álvarez-Chávez et al. [7]. This study has cast doubt on the sustainable credentials of bio-based biopolymers. It indicates that no bio-based biopolymers are sustainable owing to practices that include pesticide use. However, the authors consider that this could change with further technological developments [7].

The potential negative environmental impacts of biopolymers can be summarized as follows:

- Litter and pollution of the environment
- Source and production of feedstocks

- Energy requirements
- Catalysts
- Solvents
- Recalcitrant residues (additives and modifiers)

10.3.1 Litter and Pollution of Environment

A debate is ongoing as to whether biopolymers actually degrade spontaneously in natural habitats as compared to specific experimental conditions such as in industrial composting, particularly if they are present in large amounts [42,43]. There is also doubt as to whether they will degrade in a marine environment where heat and pressure conditions are significantly different [44]. Biopolymers like PLA, which biodegrade slowly under environmental conditions, can litter the landscape, enter streams and rivers, and eventually end up in the sea. This can aggravate things in the future, with the current trend of substituting conventional polymers with durable bio-based biopolymers. Consumer products made from bio-polyethylene or bio-PET can be disposed of in an uncontrolled manner in the environment due to considerable misunderstanding among the general public about the biodegradation credentials of these bio-based biopolymers.

The biodegradation of biopolymers may also influence the types and concentrations of soil microflora in disposal areas. Enrichment of soil with certain microflora could have unanticipated risks, such as an outbreak of a new microbial disease [45].

10.3.2 Source of Feedstocks

The bulk of biopolymers are produced from ethanol using corn and sugar as their feedstocks. The production of biopolymers from ethanol appears to have the same disadvantages associated with bio-fuels (i.e., raised food costs and deforestation for the creation of extra fields for corn cultivation, a phenomenon observed in Brazil and in some South East Asian countries). There is also concern about using land for biopolymer production that could be used to grow crops for human consumption. If biopolymers are to be produced on a large scale, there could be competition between feedstock crops and food crops for land, which could raise food prices [46]. Estimates say that agricultural product supplies would be affected even if only 10% of all polymers were starch-based, potentially making

food less affordable [13]. In addition, with the current rate of increase in the human population, it seems unlikely that there will be sufficient land available to grow crops for food, let alone for biopolymers [47]. On the other hand, European Bioplastics points out that there are significant differences between the use of agricultural feedstocks for biofuel production and for the production of biopolymers [48,49]:

- Biofuel production has reached a multi-million ton level in the EU, but the biopolymers market is still in its infancy.
- The cultivation area needed to supply the biopolymers industry is currently very small. About 2–3 tons of biopolymers can be produced from one hectare of corn or wheat (using their starch), thus the area cultivated for the production of biopolymers can be estimated at approximately 30,000 ha in Europe compared with a total agricultural area of more than 162,000,000 ha according to the European Commission.
- There is a range of biopolymers that already use alternative feedstocks which are not competing with food markets, such as agricultural residues (cellulosics) and other waste streams, and the so-called second- and third-generation feedstocks [50] (see also Chapter 1: Introduction to Biopolymers; Section 1.16: Sources of Biopolymers).

However, even these alternative feedstocks are not problem-free. The advantages and disadvantages of using second-generation feedstocks can be summarized as follows [51]:

- Second-generation feedstocks can be derived from many different sources, including forestry waste (e.g., straw, corn stover), paper and municipal waste, and dedicated energy crops such as switchgrass, miscanthus, or short-rotation poplar.
- Second-generation feedstocks exclude direct land use change and minimize indirect land use change.
- The technology of converting lignocellulose to ethanol is ripe as a result of recent breakthroughs.
- The conversion of lignocellulose byproducts to ethanol is a highly energy-intensive process.

The industry is still in a nascent state, with most second-generation biorefinery plants that use

cellulose material only expected to be ready for large-scale commercial production in a few years.

10.3.3 Production Methods of Feedstocks

Bio-based feedstocks are generally grown using industrial agricultural production methods and therefore significant amounts of energy, water, land, genetically modified organisms (GMOs), toxic pesticides, and fertilizers are used. These deplete natural resources and can pollute water, air, and soil. Advances in biotechnology make it possible to produce biopolymers directly in microorganisms or in genetically modified crops such as corn [7].

One common hazard for most bio-based polymers is the use of GMOs in crops [52]. They can also be used during fermentation of substrates to produce building blocks for polymers. Environmental concerns about GMOs are increased pest resistance, development of weed tolerance, decreased genetic diversity, and undesirable crop or weed species development [53]. Canola/rapeseed and soy feedstocks are predominantly GMO (with some estimates now at 90%), which is prohibited by organic standards.

The use of toxic compounds such as herbicides to cultivate the feedstock (e.g., corn, soy) might pose environmental trade-offs.

The use of fertilizers on the plants from which the biopolymers are made causes eutrophication of water and acidification of soil to a much greater extent than the production of conventional polymers.

10.3.4 Polymerization/Processing

10.3.4.1 Catalysts

Monomers are generally polymerized in the presence of certain catalytic metals in order to achieve sufficient commercial productivity. Tin-based catalysts are used for the polymerization of PLA [54]. Remnants of the catalysts remain in the final polymers. In non-biodegradable polymers, these catalyst residues remain encapsulated with the polymer matrix and are not mobile or leachable. In biodegradable biopolymers these catalyst residues are liberated and can enter the disposal environment. Small residues of organic tin (tin octanoate) in PLA products can be a concern during disposal because they have lipophilic properties and can build up in aquatic organisms and plants; they have also been found in human tissues [7,55].

10.3.4.2 Solvents/chemicals

The various raw materials that are extracted from plants are separated using organic solvents, and then isolated from the extraction solvent through a series of purification steps. Several other solvents are also used during the production and processing of biopolymers. 1-Octanol is used in the lactide ring opening catalysis step to control molecular weight and accelerate the reaction [54,56]. 1-Octanol is slightly toxic to fish and zooplankton [7].

10.3.5 Disposal/Recycling Methods

Though biopolymers address the carbon emissions posed by polymer production, they neglect the second half of society's trouble with polymers. For the polymer to be truly green, it has to be recyclable. Where the biopolymers arrive at the end of the life cycle is the part of the equation that most biopolymer producers do not address [57]. LCA studies, which do not include the impact effects of recycling, incineration, biodegradation, and other factors, are of limited scope.

According to Vink et al. [58], burning and land-filling of PLA does not generate toxic emissions and leachates [59]. An LCA carried out on PLA used 30–50% less fossil energy and lowered CO₂ emissions by 50–70% compared to fossil fuel-based polymers. More recently, a new eco-profile showed 85% fewer CO₂ emissions and 50% less fossil fuel use compared with data from 2003 [15].

Landfilling biodegradable biopolymers can result in methane emissions (unless landfill gas is captured), which may make the system unattractive in terms of reducing greenhouse gas emissions [60].

An independent study carried out on behalf of the Federal Environmental Agency, or *Umweltbundesamt* (UBA, the German EPA), by the Institute for Energy and Environment Research (IFEU) evaluated a total of 85 life cycle assessment studies and professional articles, with an eye toward the environmental pros and cons of packaging made of biopolymers [61]. The main conclusion of this study was that the climate impact of biopolymers scores better than conventional polymers. In particular, CO₂ emissions and fossil fuel consumption are lower. On the other hand, these polymers place greater strains on other environmental areas, particularly through the use of fertilizers. Moreover, they cause high levels of particulate emissions.

There is substantial room for improvement in terms of optimization of the production process (e.g., PLA). This includes increasing the efficiencies of the various unit processes involved and enhancing process integration.

In response to this article, it is important to note that future improvements in feedstock selection and production will undoubtedly help reduce the environmental impacts observed in the study, while optimization of the various process stages in biopolymer production will help reduce costs. After all, it took the fossil fuel-based plastics industry 50 years to mature. To achieve a comprehensive alternative, the biopolymer industry, which is still at a very early stage of development, may need just as much time.

10.4 Health and Safety Impacts

Álvarez-Chávez et al. [7] used an LCA to conduct a qualitative evaluation of the occupational and environmental hazards posed by bio-based biopolymers. PHAs, PLA, and starch do not present any recognized serious safety or health hazards. Nevertheless, it has been reported that the production of PHA may expose workers to various hazardous chemicals, especially solvents used during physical extraction or chemical digestion phases [7,62].

10.4.1 Catalysts

During the industrial manufacture of PLA, an organotin-based catalyst system (tin octanoate) is used in very low concentrations (100–1000 ppm) [63], which is an issue for the health and safety of workers. Organotin compounds have shown neurotoxic effects in animals, and cytotoxic effects in humans and animals, and could have toxic effects on the hormonal system [7,55,64].

10.4.2 Solvents/Chemicals

PLA production uses sulfuric acid during the recovery of lactic acid from the fermentation broth [58,65]. Sulfuric acid is a highly corrosive mineral acid, and its use poses safety hazards.

1-Octanol used in the lactide ring-opening catalysis is a volatile and combustible liquid that can be absorbed into the body by contact, inhalation, and ingestion. It causes irritation to tissues [7].

10.4.3 GMOs

The potential health hazards related to the use of GMOs in the production of biopolymers have not been established with certainty. It has been reported, however, that the use of GMOs may cause allergic reactions, that there may be an inherent toxicity of the novel gene and its products, and that GMOs may alter metabolic pathways [7,52,53].

Furthermore, fears similar to those that have slowed down the uptake of genetically modified food crops in Europe could stall the adoption of GMOs for feedstock crops.

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Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
AU3521984 A	19850523	EP0142950 A2 19850529; JPS60122527 A 19850701; US4620999 A 19861104; EP0142950 A3 19870805; AU576795 B2 19880908; EP0142950 B1 19901010	GB19830030414 19831115	HOLMES P A	ICI PLC	Disposable bags.
AU2010237249 A1	20110818	KR20120015440 A 20120221	WO2009BE00231 20090414; WO2010EP54280 20100331	COSZACH P; BOGAERT J-CH; WILLOCQ J	GALACTIC SA	Chemical recycling of PLA by alcoholysis.
CA2098220 A1	19941211	EP0628533 A1 19941214; JPH0711044 A 19950113	JP19930143107 19930615; CA19932098220 19930611; EP19930109098 19930607	ROOREN D B; NARAAYANAN S S; NEBIRU E D; BRAKE L D; DRYSDALE N E; SUBRAMANIAN N S	DU PONT	Recovery of hydroxy acid from waste.
CN101130627 A	20080227	US2008048365 A1 20080228; JP2008050446 A 20080306; US7598305 B2 20091006; CN101130627 B 20120502	JP20060226967 20060823	YAO K	FUJI XEROX CO LTD	Resin composition, resin molding, package, production method of resin molding, and recycling method of resin molding.
CN101230129 A	20080730		CN20071173495 20071228	PENG T; XIAO M; XU Y	SHANGHAI NEW SHANGHUA POLYMER	Recrystallization method of polylactic acid (PLA) and PLA acquired thereby.
CN101275009 A	20081001	JP2008274222 A 20081113; CN101275009B B 20120222	JP20070092711 20070330; JP20070321186 20071212	YAO K; MORIYAMA M; SUZUKI F; MOCHIZUKI T; KAWASAKI H	FUJI XEROX CO LTD; FUJIFILM CORP	Resin composition, resin compact, production method of resin compact and recycling method of resin compact.
DE102008025758 A1	20091203		DE200810025758 20080529	WALDAU C; ROSE D	BERNDT & PARTNER GMBH	“Device, useful for producing compost (e.g., from biodegradable packaging) that comprises many chambers, where first chamber is a feeding chamber, other chambers are real composting areas and final chamber is opened to remove end product.”

DE19637404 A1	19970320	JP9077904 A 19970325; US5728847 A 19980317; JP3503127 B2 20040302; DE19637404 B4 20060511	JP19950236278 19950914	OKAMOTO T; OHARA H	SHIMADZU CORP; TOYOTA MOTOR CO LTD	Verfahren zur Rückgewinnung von Lactid mit hohem Molekulargewicht. "Method for recovering lactide from high molecular weight PLA."
DE19706023 A1	19980820	WO9836086 A1 19980820; CA2281109 A1 19980820; AU6099398 A 19980908; EP0968300 A1 20000105; AU734738 B2 20010621; US6255451 B1 20010703; JP2001512504 A 20010821; NZ337239 A 20010928; EP0968300 B1 20080305; CA2281109 C 20090922; JP4463331 B2 20100519	DE19971006023 19970217; WO1998EP00585 19980204	KOCH R; LUND H	BAYER AG	Abbau von biologisch abbaubaren Polymeren mit Enzymen. "Degradation of biodegradable polyester amides with enzymes."
DE19754063 A	19990610	WO9929885 A1 19990617; AU1875599 A 19990628	DE19971054063 19971205	KOCH R; WIEGAND S	BAYER AG	Abbau von biologisch abbaubaren Polymeren. "Degradation of biodegradable polymers."
DE19816881 A1	19991021	DE19816881 B4 20120105	DE19981016881 19980417	FEY D; BOHLEBERJ; DAUSELN M; KRIEG G	KRIEG G	Verfahren und Vorrichtung zur Detektion und Unterscheidung zwischen Kontaminationen und Gutstoffen sowie zwischen verschiedenen Farben in Feststoffpartikeln. "Method and device for detecting and differentiating between contaminations and accepts as well as between different colors in solid particles."
DE19848873 A1	20000427	WO0024819 A1 20000504; NO20011910 A 20010418; EP1129131 A1 20010905; JP2002528585 T 20020903	DE19981048873 19981023; WO1999EP07677 19991013	WITT U; SKUPIN G; DELAVER P	BASF AG	Zusammensetzungen aus biologisch abbaubare Polymeren und Fluoreszenzfarbstoffen. "Compositions consisting of biodegradable polymers and fluorescent dyes."
DE3842072 C1	19891228	EP0373372 A2 19900620; JP2202403 A 19900810; US5009586 A 19910423; EP0373372 A3 19910502; EP0373372 B1 19930908; JP6013176 B 19940223	DE19883842072 19881214	PALLMANN W	PALLMANN MASCHINENFABRIK GMBH & CO. KG	Vorrichtung zum kontinuierlichen Regranulieren von thermoplastischen Kunststoffabfällen, insbesondere von Folien, Fäden und dgl.

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
						"Agglomerating apparatus for the continuous regranulation of thermoplastic wastes, especially films, filaments, and the like."
EP0573042 A1	19931208	EP0573042 B1 19961204; DE69306308 T2 19970619; US5780704 A 19980714	JP19920143940 19920604	AJIOKA M; ENOMOTO K; ENOMOTO T; SUZUKI K; YAMAGUCHI A; YAMAGUCHI T	mitsui toatsu chem inc	Process for treating plastic product.
EP0679412 A1	19951102	DE4415127 A1 19951102; JPH0838587 A 19960213	DE19944415127 19940429	BATZ H G; SLUKA P; JENDROSSEK D	BOEHRINGER MANNHEIM GMBH	Degradable polymers.
EP1241231 A1	20020918	US2002130436 A1 20020919; JP2002275379 A 20020925; US2006035860 A1 20060216; US7064113 B2 20060620; JP3902916 B2 20070411; US7608593 B2 20091027	JP20010076559 20010316; US20020096016 20020313; US20050251790 20051018	MAEHARA H	CANON KK	Method for forming monomer of biodegradable polyester.
EP1741536 A1	20070110	WO2007003659 A1 20070111; EP1907182 A1 20080409; US2008315020 A1 20081225; US7762482 B2 20100727; BRPI0612775 A2 20101130	EP20050106142 20050706; WO2006EP63965 20060706		PURAC BIOCHEM BV	Method for comminuting polymeric shaped articles by milling.
GB2107320 A	19830427		GB19810029314 19810929	SEMP B A; MING-YI T D; KERITSIS D	PHILIP MORRIS INC	Method for recycling cellulosic waste materials from tobacco product manufacture.
JPH1036553 A	19980210		JP19960215061 19960726	OTA M	SHIMADZU CORP	Treatment of waste aliphatic polyester.
JPH10108669 A	19980428	JP3742825 B2 20060208	JP19960262073 19961002	JIKUYA H; NAGAI N; TOKIWA Y	NAT INST ADV IND SCI TECHN; SHIMADZU CORP	Microorganism capable of decomposing polylactate resin and microbial decomposition of polylactate resin.
JPH10108670 A	19980428	JP3742826 B2 20060208	JP19960262074 19961002	JIKUYA H; NAGAI N; TOKIWA Y	NAT INST ADV IND SCI TECHN; SHIMADZU CORP	Bacteria capable of decomposing polylactate resin and microbial decomposition of polylactate resin.

JPH10117768 A	19980512		JP19960280562 19961023	ISHIOKA R; NAKANO K; NISHIOKA M	SHOWA DENKO KK	Decomposition of aliphatic polyester and microbial preparation.
JPH114680 A	19990112	JP3734118 B2 20060111	JP19970160230 19970617	TOKIWA Y; NAGAI N; JIKUYA H	NAT INST ADV IND SCI TECHN; SHIMADZU CORP	Bacteria decomposing PLA resin and microbial degradation of PLA resin.
JPH1146755 A	19990223	JP3897261 B2 20070322	JP19970210829 19970805	JIKUYA H; NAGAI N; TOKIWA Y	NAT INST ADV IND SCI TECHN; SHIMADZU CORP	Actinomyces capable of degrading PLA resin and biodegradation of PLA resin.
JPH11127850 A	19990518		JP19970316616 19971104	KONNO M; NISHIDA H; TOKIWA Y	NAT INST ADV IND SCI TECHN; TOKUYAMA SODA KK	Degradation of PLA.
JPH11225755 A	19990824		JP19980037435 19980219	KANBE T; NAKAHARA T	MITSUBISHI CHEM CORP	Biodegradable polymer decomposition enzyme and its production.
JPH11349729 A	19991221		JP19980201054 19980611	KIMURA N; KUMA H; OZAWA K	SEIKO SANGYO	Device for dissolving alkali-soluble biodegradable synthetic resin.
JP2000060540 A	20000229	JP3692455 B2 20050907	JP19980236009 19980821	IGURA Y; KUDO T	RIKAGAKU KENKYUSHO	New microorganism having PLA resin-decomposing ability and decomposing treatment of PLA resin.
JP2000290428 A	20001017		JP19990096608 19990402	MIHARA C	CANON KK	Method for degrading biodegradable resin and device for degrading biodegradable resin.
JP2001040078 A	20010213		JP19990219688 19990803	MINAMI M	CANON KK	Sugar chain polymer compound and its thermoformed product.
JP2001128667 A	20010515	JP3326495 B2 20020924	JP20000158973 20000529	TOKIWA Y	NAT INST ADV IND SCI TECHN; TOKIWA Y	Decomposition method of PLA resin.
JP2001128668 A	20010515	JP3326608 B2 20020924	JP20000158974 20000529	TOKIWA Y	NAT INST ADV IND SCI TECHN; TOKIWA Y	Decomposition method of PLA resin.
JP2001128669 A	20010515	JP3326496 B2 20020924	JP20000158975 20000529	TOKIWA Y	NAT INST ADV IND SCI TECHN; TOKIWA Y	Decomposition method of PLA resin.
JP2001128670 A	20010515	JP3326497 B2 20020924	JP20000158976 20000529	TOKIWA Y	NAT INST ADV IND SCI TECHN; TOKIWA Y	Decomposition method of PLA resin.
JP2001128671 A	20010515	JP3326498 B2 20020924	JP20000158977 20000529	TOKIWA Y	NAT INST ADV IND SCI TECHN; TOKIWA Y	Decomposition method of PLA resin.

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
JP2001128693 A	20010129	JP3128577 B1 20010129; WO0132902 A1 20010510; CA2385726 A1 20010510; EP1227158 A1 20020731; US2005032181 A1 20050210; EP1227158 A4 20060201; US7235398 B2 20070626	JP19990313578 19991104; US20040942463 20040916; US20020089120 20020322; WO2000JP02113 20000331	TOKIWA Y	NAT INST ADV IND SCI TECHN	Method for degrading polylactide resins.
JP2001205233 A	20010731		JP20000013763 20000124	NOMOTO M; MORISHITA M	EBARA CORP	Method and apparatus for treating biodegradable plastic bag containing garbage.
JP2001226518 A	20010821	JP32929872 B2 20020617	JP20000038317 20000216	TOKIWA Y	NAT INST ADV IND SCI TECHN	Method for decomposing polybutylene succinate resin with microorganisms.
JP2002017384 A	20020122		JP20000198867 20000630	MATSUMURA S	UNIV KEIO	Method for producing trimethylene carbonate.
JP2002017385 A	20020122	JP4140804 B2 20080827	JP20000198866 20000630	MATSUMURA S	UNIV KEIO	Method for producing dicaprolactone and caprolactone polymer.
JP2002226623 A	20020814		JP20010028034 20010205	YAMAMOTO M; KUBO T; YAMA S; NAKAE T; HASHIMURA T	KANEBO LTD	Reclaimed foam and regenerating method of foam.
JP2002226624 A	20020814		JP20010021948 20010130	KAWAHARA A; KONNO Y; MATSUNAGA A; YOSHIDA N	UNITIKA LTD	Degradation method of aliphatic polyester-based molded article.
JP2002255675 A	20020911		JP20010107787 20010302	NEZU K	NEZU KIYOMI; SHIMIZU K	Composting circulating method of food and tableware.
JP2002293982 A	20021009		JP20010103684 20010402	SUGIHARA Y	KANEBO LTD	Agent and method for accelerating degradation of biodegradable polymer and method for degrading polymer.
JP2002320499 A	20021105		JP20010131768 20010427	MATSUMURA S	UNIV KEIO	Depolymerization method for oligomer consisting essentially of ring compound of polyalkylene alkanoate or poly(3-hydroxyalkanoate), and method for polymerizing the cyclic oligomer.

JP2002348405 A	20021204		JP20010160026 20010529	FURUSAWA K	SUMITOMO CHEM CO LTD	Degradation method for plastic.
JP2002348406 A	20021204		JP20010153397 20010523	DEGUCHI J; MARUYAMA K; TSUKAHARA T; SHIRAHAMA R	MITSUBISHI CHEM CORP	Disposition method for agricultural mulching film.
JP2002355819 A	20021210		JP20010163098 20010530	TSUTSUGI T; SATAKE S; KAGEYAMA Y; INAO T; YAMASHITA S; ISOBE Y; MITSUNE K	TOYOTA MOTOR CORP	Treatment method for biodegradable resin.
JP2003009846 A	20030114		JP20010248341 20010817; JP20010133588 20010427	TOKIWA Y; AMUNATTO J; TSUCHIYA A	NAT INST ADV IND SCI TECHN; ALMIGHTY KK	Inducer of PLA-decomposing enzyme-producing microbe or proteinase K-like protease-producing microbe and method for decomposing PLA therewith.
JP2003009855 A	20030114	JP4729684 B2 20110720	JP20010248343 20010817; JP20010133588 20010427	TOKIWA Y; AMUNATTO J; TSUCHIYA A	NAT INST ADV IND SCI TECHN; ALMIGHTY KK	Method for PLA splitting enzyme and/or proteinase K-like protease production.
JP2003012858 A	20030115		JP20010204156 20010705	UEDA K; YANO T; NISHIMURA H	UNITIKA LTD	Decomposition method for biodegradable polyester resin.
JP2003041047 A	20030213	JP4092942 B2 20080528	JP20020129788 20020501; JP20010153394 20010523	DEGUCHI J; MARUYAMA K; TSUKAHARA O; SHIRAHAMA R	MITSUBISHI CHEM CORP	Method for disposal treatment of biodegradable resin molding.
JP2003079388 A	20030318	JP4171823 B2 20081029	JP20020193114 20020702; JP20010204999 20010705	MATSUMURA S	UNIV KEIO	Method for depolymerizing polyester or polycarbonate by using supercritical fluid and method for producing polyester or polycarbonate.
JP2003128900 A	20030508	JP3583097 B2 20041027	JP20010324849 20011023	TAKAGI J	MITSUBISHI PLASTICS IND LTD	Lactic acid resin articles and its recycling process.
JP2003221461 A	20030805		JP20020022697 20020131	ASAMI O; TANAKA T; KAJINO T; TAKAHASHI H	TOYOTA CENTRAL RES & DEV LAB INC	Degradation controlling method for aliphatic polyester and biodegradable aliphatic polyester.

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
JP2003250527 A	20030909		JP20020059039 20020305	YAMANE H; TAKAHASHI A; NISHIYAMA N; MATSUMOTO K	KAO CORP	Method for degrading PVA.
JP2003252966 A	20030910	JP4065990 B2 20080326	JP20020057906 20020304	TOKIWA Y; TOTANI T; SHIMAKAWA H	NAT INST ADV IND SCI TECHN; KONAN CHEMICAL MFG	Copolymerization-type easily decomposable PLA and decomposition method of PLA.
JP2003300927 A	20031021	JP4177992 B2 20081105	JP20020109918	FUJIE K; TSUJI H; DAIMON H	INST NAGOYA IND SCI RES	Method for forming monomer of biodegradable polyester.
JP2003310248 A	20031105		JP20020125101 20020426	HAYASE N; TSUTSUMI K; NAKAGAWA K; MIYAHARA Y; TANAKA K; TANAKA S	OKURA INDUSTRIAL CO LTD	Microorganism degrading biodegradable polymer and method for degrading biodegradable polymer by using the same.
JP2004058010 A	20040226		JP20020223237 20020731	HATTORI S; SUGIYAMA H	TOYOBO CO LTD	Method of treating organic waste containing molded article made of biodegradable resin.
JP2004075905 A	20040311	JP3762990 B2 20060405	JP20020239878 20020820	IEFUJI H; IWASHITA K; MUKAI N; MASAKI K	NAT RES INST OF BREWING	Agent for decomposing biodegradable plastic and decomposing method.
JP2004123810 A	20040422		JP20020286546 20020930	YANO Y	KANEBO LTD; KANEBO SYNTHETIC FIBERS LTD	Biodegradable foam and its volume reduction method.
JP2004166542 A	20040617	JP4214372 B2 20090128	JP20020334162 20021118	KANBE T; SHIGENO Y	JAPAN SCI & TECHNOLOGY AGENCY	New plastic decomposing bacterium.
JP2004216378 A	20040805		JP20040111029 20040405	TAKAGI J	MITSUBISHI PLASTICS IND	Shredder dust for recycling, lactic acid resin molding using the same, and method for its recycling.
JP2004223470 A	20040812		JP20030016920 20030127	TOMIUCHI Y	FUJI ELECTRIC CO LTD	Method and apparatus for methane fermentation of organic waste.
JP2004290130 A	20041021		JP20030089915 20030328	ABE S; KATO S; DEGUCHI J	MITSUBISHI CHEM CORP	Method for recovering monomer constituting polyester.
JP2004292705 A	20041021	JP4059395 B2 20080312	JP20030089212 20030327	TAKASAGO H; TOGO Y; YOSHIDA T	KAJIMA CORP	Method for processing biodegradable plastic and processing system.

JP2004308077 A	20041104		JP20030106187 20030410	HONNA H; MITA T; MOTOMIYA T	TEIJIN FIBERS LTD	Polyester fiber product meeting the demands of recycling society and recycling method.
JP2005075865 A	20050324	JP4066027 B2 20080326	JP20030305278 20030828	YOSHIDA T; YOSHIDA S	SHIMIZU CONSTR CO LTD	System for treating biodegradable plastic member, apparatus for reducing volume of biodegradable plastic member, and method for reducing volume of biodegradable plastic member.
JP2005095729 A	20050414		JP20030330538 20030922	MIURA M; YAMAMOTO KI; TANAKA Y; KAMIMURA M	KOBE STEEL LTD; AICELLO CHEMICAL CO	Treatment method and treatment apparatus for organic type waste containing biodegradable plastic.
JP2005131480 A	20050526		JP20030368398 20031029	NAKAMURA K; HIRANO K; YOKOYAMA S; INOUE K; TAIRA T	NAKAMURA K; HIRANO K; YOKOYAMA S; INOUE K; TAIRA T	Method and apparatus for recycling biodegradable waste.
JP2005131856 A	20050526		JP20030368541 20031029	ISHIHARA K; HORIUCHI H	TEIJIN FIBERS LTD	Method for removing different material from aliphatic polyester.
JP2005132901 A	20050526		JP20030368542 20031029	ISHIHARA K; HORIUCHI H	TEIJIN FIBERS LTD	Method for removing foreign material from aliphatic polyester.
JP2005162832 A	20050623		JP20030401909 20031201	AMUNATTO J; JALERAT A; NAKATSUKA H; TOKIWA Y; TSUCHIYA A	ALMIGHTY KK; NAT INST ADV IND SCI TECHN	Method for degrading PLA.
JP2005206735 A	20050804		JP20040016218 20040123	KONO T; WADA K; SHISHIDA K; MATSUMOTO T; TAKEDA M	TAKUMA KK; HITACHI SHIPBUILDING ENG CO	Method for recovering energy from PLA-based biodegradable plastic.
JP2005232336 A	20050902	JP4231801 B2 20090304	JP20040043905 20040220	KONO T; WADA K; SHISHIDA K	TAKUMA KK	Method of solubilization of PLA-base biodegradable plastic.
JP2005298401 A	20051027		JP20040116653 20040412	TSUJI H; FUJIE K; DAIMON H	UNIV TOYOHASHI TECHNOLOGY	Method for converting biodegradable polyester into monomer.

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
JP2005298565 A	20051027		JP20040113148 20040407	SAKAI D; IIZUKA T	NIPPON ESTER CO LTD	Method for decomposing and treating molded product containing biodegradable resin.
JP2005304388 A	20051104	JP4441639 B2 20100331	JP20040126178 20040422	MAEDA H; ABE T; GOMI K; YAMAGATA Y; HASEGAWA F; NAKAJIMA Y	TOHOKU TECHNO ARCH CO LTD	New plastic-degradative enzyme and its use.
JP2005330211 A	20051202		JP20040149151 20040519	FUJIE K; HORIUCHI H; ISHIHARA K; OKADO H; SAEKI T; TSUJI H	UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD	Method for hydrolyzing biodegradable polyester into monomer, and apparatus for treating biodegradable polyester.
JP2006008780 A	20060112	JP4765273 B2 20110907	JP20040185586 20040623	SHINTANI N	MITSUBISHI CHEM CORP	Decomposition treatment method for polyester resin.
JP2006036899 A	20060209	JP4543211 B2 20100915	JP20040217971 20040726	TOKIWA Y; RAKU T	NAT INST ADV IND SCI TECHN	Biodegradable resin composition, its molded article and method for biodegrading.
JP2006124677 A	20060518		JP20040290261 20041001 ; JP20050282389 20050928	SHINTANI N; KATO S; SAKAGUCHI H; UYAMA N	MITSUBISHI CHEM CORP; NOVOZYME AS	Decomposition treatment liquid for biodegradable resin and disposal treatment method using the same.
JP2006124678 A	20060518		JP20040290260 20041001; JP20050282390 20050928	SHINTANI N; SHIRAHAMA R; KATO S; UYAMA N; SAKAGUCHI H	MITSUBISHI CHEM CORP; NOVOZYME AS	Decomposition treatment method of biodegradable resin and decomposition treatment liquid used for the same.
JP2006137892 A	20060601	JP4665073 B2 20110406	JP20040330154 20041115	SAEKI T; DAIMON H; TSUJI H; FUJIE K; NAKAJIMA M; ISHIHARA K	UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD	Method for regeneration of waste PLA.
JP2006193357 A	20060727		JP20050005053 20050112	NIWA Y; KANEKO H	NISSAN MOTOR	Hydrogen-producing method, polymer material used for the same and hydrogen-producing system.

JP2006271367 A	20061012	JP4670048 B2 20110413	JP20050058588 20050303; JP20050142231 20050516	NAKAJIMA T; SHIGENO Y	UNIV TSUKUBA	Method for acquiring gene encoding biodegradable plastic-degrading enzyme and new gene and enzyme obtained therefrom.
JP2007001940	20070111		JP20050184757 20050624	MATSUBARA W; OMOTO S; YAMAMOTO I	MITSUBISHI HEAVY IND LTD	Method for recycling polyalkylene succinate, and method for recycling.
JP2007002160 A	20070111	JP4647413 B2 20110309	JP20050186223 20050627	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Depolymerization process for biodegradable polyester.
JP2007023176 A	20070201		JP20050208434 20050719	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Method for depolymerizing biodegradable polyester.
JP2007031538 A	20070208	JP4486561 B2 20100623	JP20050215630 20050726	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Method for removing foreign material from PLA stereo-complex polymer.
JP2007051202 A	20070301		JP20050236656 20050817	NAKAMURA K; AKATSU S; NAGAHAMA M; YOKOSUKA M	NAKAMURA K; AKATSU S; NAGAHAMA M; YOKOSUKA M	Method for regenerating lactic acid-based biodegradable plastic.
JP2007099663 A	20070419		JP20050290614 20051004	SAEKI T; DAIMON H; TSUJI H; FUJIE K; NAKAJIMA M; ISHIHARA K	UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD	Separating and recovering method of waste of PLA.
JP2007177247 A	20070712	JP4766266 B2 20110907	JP20070001576 20070109	TOKIWA Y; SHIMAKAWA H	NAT INST ADV IND SCI TECHN; KONAN CHEMICAL MFG	Copolymer-type easily decomposable PLA and method.
JP2007210889 A	20070823		JP20060029128 20060207	FUJIE K; ISHIHARA K; NAKAJIMA M; OKADO H; SHIMBO T; TSUJI H	UNIV TOYOHASHI TECHNOLOGY; TEIJIN FIBERS LTD	Method for monomerizing stereocomplex type PLA.
JP2007224113 A	20070906		JP20060045058 20060222	ISHIHARA KI; NAKAJIMA M	TEIJIN FIBERS LTD	Method for recovering effective components from recovered.
JP2007238691 A	20070920	JP4006457 B2 20071114	JP20060060529 20060307	NAKAMURA K	NAKAMURA K	Process of regenerating lactic acid based biodegradable plastic.
JP2007277389 A	20071025	JP4747366 B2 20110817	JP20060105070 20060406	AKAMATSU K; KONISHI N; NAKAMURA K	AKAMATSU K; KONISHI N; NAKAMURA K	Recovery process of plastic waste by type.

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
JP2007284495 A	20071101		JP20060111038 20060413	KAWAGUCHI Y; SUMIDA N; FUKUSHIMA Y; OTA T; ISHIGAMI Y	SHARP CORP	Recycling method for thermoplastic resin, raw material of thermoplastic resin, thermoplastic resin member, and manufacturing method thereof.
JP2007319078 A	20071213		JP20060152729 20060531	TOKUYAMA S	UNIV SHIZUOKA NAT UNIV CORP	Method for degrading PLA and microorganism.
JP2007319092 A	20071213		JP20060153643 20060601	TOYAMA M	TOYO SEIKAN KAISHA LTD	Method for degrading biodegradable resin.
JP2008007611 A	20080117		JP20060178853 20060629	SASHI A; SHINOHARA R	KUMAMOTO TECH & IND FOUND	Method for collecting lactic acid and/or water-soluble oligomer from PLA.
JP2008050351 A	20080306		JP20060204174 20060727; JP20070194291 20070726	KAWAI N	VICTOR COMPANY OF JAPAN	Method of recovering lactic acid.
JP2008100413 A	20080501		JP20060283988 20061018	FUKUSHIMA Y; SUMIDA N; UCHIUMI Y; KOSAKA H; MATSUMOTO K	SHARP CORP	Method for recycling waste plastic material, method for producing plastic raw material, method for producing plastic member, plastic raw material, and plastic member.
JP2008167701 A	20080724		JP20070004654 20070112	KITPRICHAWANI V; TOKUYAMA S	UNIV SHIZUOKA	Method for decomposing PLA, PLA-decomposing composition, and microorganisms used therefore.
JP2008179713 A	20080807		JP20070014951 20070125	NAKAMURA K	REAL PLASTIC KK	Method for recycling polylactic resin.
JP2008201679 A	20080904		JP20070036034 20070216	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Method for producing lactide from PLA.
JP2008201680 A	20080904		JP20070036035 20070216	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Method for producing lactide from PLA.
JP2008231048 A	20081002		JP20070074639 20070322	NISHIDA H; MOTOYAMA T; SHIRAI Y	KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION	Method for recovering lactide.
JP2009029757 A	20090212		JP20070197628 20070730	ISHIHARA K; NAKAJIMA M	TEIJIN FIBERS LTD	Depolymerization method of PLA.

JP2009039095 A	20090226	JP4625900 B2 20110202	JP20070188577 20070719; JP20080145029 20080602	KAWAI F; EBISO K	KURABO IND LTD; UNIV OKAYAMA	Thermophilic polyester-decomposing bacterium.
JP2009072759 A	20090409		JP20070224542 20070830; JP20080026060 20080206	MATSUMURA S; TSUNEIZUMI Y; OKAMOTO K; KUROSAKI H	UNIV KEIO; KUROSAKI H; KOGYO KK; MIZUSAWA IND CHEM LTD	Catalyst for depolymerizing PLA and depolymerization method.
JP2009091463 A	20090430		JP20070263423 20071009	NAKAMURA K	SHIMIZU CONSTR CO LTD	Volume reduction method for PLA.
JP2009154125 A	20090716	JP4767245 B2 20110907	JP20070337542 20071227	TSUBOTA J	OSAKA GAS CO LTD	Method of solubilizing PLA and biologically gasifying method.
JP2009161655 A	20090723		JP20080000609 20080107	NIIZAKI M; SUMIDA N; FUKUSHIMA Y; KAWAGUCHI Y	SHARP CORP	Method for recycling biomass-based thermoplastic resin waste, method for producing biomass-based thermoplastic resin molded article and biomass-based thermoplastic resin molded article.
JP2009207424 A	20090917		JP20080054082 20080304	TAKAKU H; NASHIMOTO M; TAKAGI M	KANEKA CORP	Method for decomposing polyhydroxyalkanoic acid, microbial preparation.
JP2009242545 A	20091022		JP20080090256 20080331	FURUKAWA T; FUKUNAGA S	KANEKA CORP	Treatment method for PLA based foam before recycling.
JP2009249508 A	20091029		JP20080099486 20080407	ADNAN A F M; NISHIDA H; SHIRAI Y; TANIGUCHI M	KYUSHU INST OF TECHNOLOGY; MUSASHINO KAGAKU KENKYUSHO	Method for oligomerizing PLA product efficiently.
JP2010005948 A	20100114		JP20080168671 20080627	NIIZAKI MI; SUMIDA N; FUKUSHIMA Y; KAWAGUCHI Y	SHARP CORP	Method for manufacturing biomass-based plastic molded form and biomass-based plastic molded form.
JP2010116481 A	20100527		JP20080290600 20081113	KATAYAMA T; KOGURE M; YOSHIKAWA S	TOYO SEIKAN KAISHA LTD	Decomposition method for easily decomposing resin composition.
JP2010131528 A	20100617		JP20080310161 20081204	KATAYAMA T; KOGURE M; YOSHIKAWA S	TOYO SEIKAN KAISHA LTD	

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
JP2010168595 A	20100805	JP4811772 B2 20111109	JP20100109650 20100511	TOKIWA Y; RAKU T	NAT INST ADV IND SCI TECHN	Method for biodegradation of poly-D-hydroxybutyric acid.
JP2010248516 A	20101104	JP4811771 B2 20111109	JP20100109649 20100511	TOKIWA Y; RAKU T	NAT INST ADV IND SCI TECHN	Method for biodegrading biodegradable resin composition or its molded product.
JP2011162480 A	20110825		JP20100027084 20100210	NISHIDA; SHIRAI Y	KITAKYUSHU FOUNDATION	Method of recovering lactide.
JP4118313 B1	20080716	JP2008208258 A 20080911	JP20070047535 20070227	NAKAMURA K	NAKAMURA K	Decomposition recycling method of synthetic resin having constitution structure of ester bond.
JPH05178977 A	19930720		JP19910361580 19911227	ITO K; MURATA M; MOROHASHI N; OKABAYASHI A	TOYO INK MFG CO	Method for treating molded polymer article.
JPS5282773 A	19770711	JPS5444749 B2 19791227	JP19750159530 19751226	TOKIWA Y; SUZUKI T; TAKAHARA Y	KOGYO GIJUTSUIN	Polyester decomposing agent.
JPS5282774 A	19770711	JP57009354 B2 19820220	JP19750159531 19751226	TOKIWA Y; SUZUKI T; TAKAHARA Y	KOGYO GIJUTSUIN	Decomposition of polyesters.
JPH05344897 A	19931227	JP3194792 B2 20010806	JP19920179032 19920612	HAYASHI T; IKADA Y	AMANO PHARM KK	Method for degrading a biodegradable high molecular weight polymer and a method for treating the surface of the high molecular weight polymer.
JPH0649266 A	19940222	JP3356825 B2 20021216	JP19930131852 19930602; JP19920143940 19920604	AJIOKA M; ENOMOTO K; ENOMOTO T; SUZUKI K; YAMAGUCHI A; YAMAGUCHI T	mitsui chem inc; mitsui toatsu chem inc	Treatment of plastic article.
JPH06240004 A	19940830	JP3267369 B2 20020318	JP19930031657 19930222	AJIOKA M; KAWASHIMA N; YAMAGUCHI T	mitsui toatsu chem inc	Method for fractionating degradable polymer composition.
JPH06253865 A	19940913	JP2869838 B2 19990310	JP19930043740 19930304	TOKIWA Y; ITO A	NAT INST ADV IND SCI TECHN; mitsui shipbuilding eng	Decomposition of aliphatic polyester with anaerobic bacteria.

JPH06297458 A	19941025	JP3487608 B2 20040119	JP19930089678 19930416	AJIOKA M; YAMAGUCHI T	mitsui toatsu chem inc	Separating method for decomposable polymer composition.
JPH06315935 A	19941115		JP19930105557 19930506	AJIOKA M; YAMAGUCHI T	mitsui toatsu chem inc	Method for separating degradable polymer composition.
JPH06319532 A	19941122		JP19930113070 19930514	OKUMA K; KURACHI K	SUMITOMO METAL IND	Novel microbe and method for decomposing waste using the same.
JPH06319533 A	19941122		JP19930113069 19930514	OKUMA K; KURACHI K	SUMITOMO METAL IND	Novel microbe and method for decomposing waste using the same.
JPH07132272 A	19950523	JP3368363 B2 20030120	JP19930260565 19931019	TOKIWA Y; ITO A	NAT INST ADV IND SCI TECHN; MITSUI SHIPBUILDING ENG	Method for decomposing aliphatic polyester by anaerobe.
JPH07309863 A	19951128	JP2821986 B2 19981105	JP19940103091 19940517		JAPAN STEEL WORKS LTD	Method for recovering lactide from PLA product.
JPH08151476 A	19960611	EP0726325 A2 19960814; US5674740 A 19971007; EP0726325 A3 19980204; EP0726325 B1 20020327; DE69526062 T2 20021114	JP19940292658 19941128	SUYAMA T; TOKIWA Y	NAT INST ADV IND SCI TECHN	Enzymatic decomposition of polycarbonate resin.
JPH08187090 A	19960723	JP2640630 B2 19970813	JP19940316083 19941128	TOKIWA Y; YOSHIDA Y; IWAMOTO A	NAT INST ADV IND SCI TECHN; JSP CORP	Decomposing method of aliphatic polycarbonate resin.
JPH08253619 A	19961001		JP19950058948 19950317	ONISHI H; TERADA T; YAMAGATA Y	MATSUSHITA DENKI SANGYO KK	Method for treating plastic molded form.
JPH0937776 A	19970210	JP3697639 B2 20050921	JP19950160501 19950627	TOKIWA Y; TANAKA H; HARUDANIN P; YAHATA M	NAT INST ADV IND SCI TECHN; SHIMADZU CORP	Bacterium hydrolyzing PLA resin, and bacterium hydrolysis of PLA resin.
JP9191887 A	19970428		JP19950269580 19951018	NAKAMURA N; TOKUSHIGE Y; UEDA S	SHINETSU CHEMICAL CO	Disposal treatment of biodegradable polyester resin molded product.
JPH09191887 A	19970729		JP19960301671 19961113; JP19950294346 19951113	KATO N; KITA K; ISHIMARU K	KYOTO DAIICHI KAGAKU CORP	Depolymersae of biodegradable polymer and its production.
JPH09201579 A	19970805		JP19960011846 19960126	MIYOSHI R; SAKAI T	JAPAN STEEL WORKS LTD	Method for separating and recovering paper from biodegradable plastic-coated paper.

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
JPH09241417 A	19970916		JP19960057586 19960314	TAKAHASHI A	DAINIPPON INK & CHEM INC	Recovery of raw material for lactic acid-based polymer.
JPH09249474 A	19970922		JP19960058905 19960315	NAGAI T; OTANI T; FUKUSHIMA K; HATTORI K; ONO A; YOKOTA M	JAPAN STEEL WORKS LTD	Composting treatment of organic waste containing biodegradable plastic.
JPH09249475 A	19970922		JP19960058904 19960315	NAGAI T; OTANI T; FUKUSHIMA K; HATTORI K; ONO A; YOKOTA M	JAPAN STEEL WORKS LTD	Composting treatment of biodegradable plastic and apparatus thereof.
JPH09252791 A	19970930		JP19960090530 19960319	TOKIWA Y; TANAKA H; HARUDANIN P	NAT INST ADN IND SCI TECHN; SHOWA DENKO KK	Polybutylene succinate-based resin decomposing bacterium, biological decomposition of polybutylene succinate-based resin and production of 4-hydroxy- <i>N</i> -butyric acid.
JPH09263653 A	19971007	JP2889953 B2 19990510	JP19960097584 19960327	TOKIWA Y; SHIBATANI S	NAT INST ADV IND SCI TECHN; CHIKYU KANKYO SANGYO GIJUTSU; TOYOBO CO LTD	Degradation of microorganism- produced aliphatic polyester with anaerobic bacterium.
US2001045518 A1	20011129	US6610981 B2 20030826	US20010841519 20010424; US20000200720P 20000427	SOMMER E. J	SOMMER E J; NATIONAL RECOVERY TECHNOLOGIES INC	Method and apparatus for near-infrared sorting of recycled plastic waste.
US2005250931 A1	20051110	US2007100051 A1 20070503	US20040838223 20040505	TAKAGI J	MITSUBISHI PLASTICS INC	Shredder dust for recycling, molding for shredder dust and a method for recovering lactide from the shredder dust as well as molding formed from the lactide.
US2005261465 A1	20051124	US7053130 B2 20060530	US20040852403 20040524	NAGARAJAN V	DU PONT	Method to accelerate biodegradation of aliphatic- aromatic co-polyesters by enzymatic treatment.

US2005286398 A1	20051229		JP20040187315 20040625	HIGUCHI M; FUKUNO Y; KODAMA Y; KUSAFUKA T; MAENO Y	SANYO MAVIC MEDIA CO LTD	Optical disc and discarding method thereof.
US2006283340 A1	20061221	DE102005027861 A1 20061228; DE102005027861 B4 20120802; US7467585 B2 20081223	DE200510027861 20050616	PALLMANN H	PALLMANN MASCHINENFABRIK GMBH & CO KG	Apparatus for converting free- flowing feed material into granules, agglomerates, pellets, compacts, and the like.
US2007259413 A	20071108		JP20030376269 20031105; WO2004JP16436 20041105	TOKIWA Y	TOKIWA Y	Method of decomposing polyhydroxyalkanoate resin.
US2008237910 A1	20081002	US7767744 B2 20100803	JP20070092711 20070330; JP20070321186 20071212	YAO K; MORIYAMA M; SUZUKI F; MOCHIZUKI T; KAWASAKI H	FUJI XEROX CO LTD; FUJIFILM CORP	Resin composition, resin compact, production method of resin compact and recycling method of resin compact.
US2010175691 A1	20100715	WO2010083356 A1 20100722; KR20110094345 A 20110823; MXPA11007535 A 20110831; EP2376538 A1 20111019; CN102239185 A 20111109	US20100686619 20100113; US20090144775P 20090115; US20100686619 20100113; US20090144775P 20090115	COMBS M T; WOODSON B R	CELANESE ACETATE LLC	Process for cycling cellulose acetate ester waste.
US2011071235 A1	20110324	WO2011038071 A1 20110331; CN102498151 A 20120613; EP2480589 A1 20120801; KR20120099384 A 20120910	US20100823629 20100625; US20090245073P 20090923	KANNAN G; ALIDEDEOGLU H A; GALLUCCI R R	SABIC INNOVATIVE PLASTICS US LLC	Biodegradable aliphatic- aromatic copolyesters, methods of manufacture, and articles thereof.
US4298013 A	19811103	FR2481081 A 19811030; DE3116655 A 19820401; CA1133686 A 19821019	US19800144227 19800428	SEMP B A; MING-YI T D; KERITSIS D	PHILIP MORRIS INC	Method for recycling cellulosic waste materials from tobacco product manufacture.
US5229528 A	19930720		US19910796273 19911122	BRAKE L D; SUBRAMANIAN N S	DU PONT	Rapid depolymerization of polyhydroxy acids.
US5264614 A	19931123		US19910796274 19911122	BRAKE L D	DU PONT	Recovery of polyhydroxy acids.

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
US5264617 A	19931123		US19910797502 19911122	BRAKE L D	DU PONT	Preparation of alkyl esters by depolymerization.
US5264626 A	19931123		US19910797503 19911122	BRAKE L D	DU PONT	Rapid depolymerization of polyhydroxy acids.
US5268507 A	19931207		US19910796272 19911122	BRAKE L D	DU PONT	Preparation of amide derivatives of hydroxy acids.
US5278256 A	19940111	CA2106168 A 19940317	US19920945853 19920916	BELLIS H E	DU PONT	Rapidly degradable poly(hydroxyacid) compositions.
US5342969 A	19940830		US19930025923 19930303	FORD T M; HOCKESSIN J V	DU PONT	Recovery of hydroxycarboxylic acid values from poly(hydroxycarboxylic acids).
US5925556 A	19990720		JP19960262073 19961002; JP19960262074 19961002	TOKIWA Y; JIKUYA H; NAGAI N	NAT INST ADV IND SCI TECHN; SHIMADZU CORP	Method of degrading PLA resin using <i>Staphylococcus hominis</i> and <i>S. epidermidis</i> .
US6066492 A	20000523		JP19960262073 19961002; JP19960262074 19961002; US19970942361 19971002; US19990233041 19990120	TOKIWA Y; JIKUYA H; NAGAI N	NAT INST ADV IND SCI TECHN; SHIMADZU CORP	Microorganism capable of degrading PLA resin and method of degrading PLA resin using said microorganism.
US6191176 B1	20010220		US20000504824 20000216; US19990358348 19990721; US19980204338 19981202; US19970067514P 19971204	TADROS R M; TIMM D C	UNIV NEBRASKA	Degradable polyesters, a mixed culture of microorganisms for degrading these polyesters, and methods for making these substances.
WO0070331 A1	20001123	EP1105715 A1 20010613; US6509537 B1 20030121;	WO1999EP03325 19990514	KRIEG G; FEY D BOHLEBER J; DAUSCH M	KRIEG G	Verfahren und Vorrichtung zur Detektion und Unterscheidung zwischen Kontaminationen und Gutstoffen sowie zwischen verschiedenen Farben in Feststoffpartikeln. "Method and device for detecting and differentiating between contaminations and accepts as well as between different colors in solid particles."

WO0107166 A1	20010201	DE19934259 A1 20010208; EP1200194 A1 20020502; SK962002 A3 20020604; CZ20020269 A3 20020717; HU0201525 B 20020828	DE19991034259 19990727	HOLLEY W; HUBER K; KATZSCHNER G; PFEIFFER T	FRAUNHOFER GES FORSCHUNG	Verfahren zur selektiven Abtrennung von vorgebbaren Stoffen aus Stoffgemischen. "Method for selectively separating predetermined materials in mixtures of materials."
WO0236675 A2	20020510	AU2571302 A 20020515; WO0236675 A3 20020906; EP1332173 A2 20030806; WO0236675 A8 20031030; BR0115158 A 20031021; KR20030068147 A 20030819; US2003208034 A1 20031106; CN1473171 A 20040204; JP2004513200 A 20040430; AU2002225713 A8 20050915; KR100566707 B1 20060403; CA2423601 C 20070522	US20000246158P 20001106; WO2001US43853 20011106; US20030430793 20030506	NODA I	PROCTER & GAMBLE CO	Plastic articles digestible by hot alkaline treatment.
WO03035753 A1	20030501	US2003108701 A1 20030612; EP1436350 A1 20040714; AU2002341940 A1 20030506; KR20040063126 A 20040712; BR0213422 A 20041214; JP2005507018 A 20050310; AU2002341940 B2 20050929; CN1692140 A 20051102; US7077994 B2 20060718; KR100611536 B1 20060810; CN1974203 A 20070606; CA2463806 C 20071211; HK1084684 A1 20071207; CN1326940 C 20070718; EP1436350 B1 20090325; AT426640 T 20090415	US20020080042 20020219; US20010343569P 20011019	BOND E B; ISAO N; NODA I	PROCTER & GAMBLE CO; MEREDIAN INC	Polyhydroxyalkanoate copolymer/starch compositions for laminates and films.

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
WO03091238 A1	20031106	AU2003231482 A1 20031110; JP4458422 B2 20100428	JP20020124375 20020425	NISHIDA H; FAN Y; SHIRAI Y	NISHIDA H; FAN Y; SHIRAI Y	Process for producing lactide.
WO03097468 A1	20031127	CA2486312 A1 20031127; AU2003242308 A1 20031202; KR20040104742 A 20041210; EP1555209 A1 20050720; US2005175801 A1 20050811; CN1652976 A 20050810; CN100436271 C 20081126; US2009030094 A1 20090129; JP4476803 B2 20100609; AT469035 T 20100615; US7799837 B2 20100921	US20080232365 20080916; JP20020146095 20020521; US20040514048 20041110; WO2003JP06134 20030516	YAMANE K; KATO R; SATO H	KUREHA CHEM IND CO LTD	Bottle excellent in recyclability and method for recycling the bottle.
WO2004013217 A1	20040212	AU2003252345 A1 20040223; EP1548053 A1 20050629; US2005233425 A1 20051020; US7396667 B2 20080708; JP4359718 B2 20091104	JP20020227644 20020805	MATSUMURA S	UNIV KEIO	Method of enzymatic depolymerization of PLA, and process for producing PLA from depolymerization product.
WO2005026245 A1	20050324	JP2005082710 A 20050331	JP20030316611 20030909	MATSUMURA S; OSANAI Y	UNIV KEIO	Method of continuously depolymerizing polyester, polycarbonate, or PLA with supercritical fluid and apparatus for continuous depolymerization.
WO2005045017 A1	20050519	JP4649593 B2 20110309; CN1902309 A 20070124	JP20030376263 20031105	TOKIWA Y	NAT INST ADV IND SCI TECHN; TOKIWA Y	Method of decomposing polyhydroxyalkanoate resin.
WO2005049710 A1	20050602	CA2546071 A1 20050602; EP1707593 A1 20061004; KR20060120074 A 20061124; CN1882647 A 20061220; US2007095957 A1 20070503; CN100412119 C 20080820;	WO2004JP17107 20041111; JP20030392497 20031121	YAMANE K; WAKAMATSU A; KATO Y	KUREHA CHEM IND CO LTD	Method of recycling laminated molding.

		JP4571587 B2 20101027 US8119699 B2 20120221				
WO2005105775 A1	20071001	EP1741707 A1 20070110; CN1926126 A 20070307; KR20070009625 A 20070118; US2008004454 A1 20080103; KR100830022 B1 20080515; EP1741707 A4 20090225; CN100475808 C 20090408; US7557224 B2 20090707; JP4517069 B2 20100804	WO2005JP07813 20050425; JP20040135476 20040430	NISHIDA H; FAN Y; SHIRAI Y	KYUSHU INST OF TECHNOLOGY; KITAKYUSHU FOUNDATION; UNIV KINKI	Method of recovering lactide from PLA or derivative thereof.
WO2005105908 A1	20051110	DE112005000965 T5 20070322; US2007293591 A1 20071220; JP4817321 B2 20111116	JP20040133594 20040428; WO2005JP08241 20050428	MATSUMURA S	UNIV KEIO	Depolymerization method for polymer containing ester bond in main chain, and method for producing polymer containing ester bond in main chain from depolymerization product.
WO2005118693 A1	20051215	JP2008500424 A 20080110	WO2004US16349 20040525	NAGARAJAN V	DU PONT	Method to accelerate biodegradation of aliphatic- aromatic copolyesters by enzymatic treatment.
WO2007102488 A1	20070913	KR20080109010 A 20081216; EP2022818 A1 20090211; US2009099270 A1 20090416; US7985778 A1 20090416	JP20060060529 20060307; JP20070014951 20070125	NAKAMURA K	NAKAMURA K	Process for the decomposition and reclamation of synthetic resins having ester-linkage structures.
WO2008045516 A1	20080417	JP2010506965 A 20100304; EP2079767 A1 20090722; EP2079767 A4 20100127; CA2666341 A1 20080417; CA2666341 C 20120103	US20060850744P 20061011	MOORE L; NORTON R	QLT USA INC	Preparation of biodegradable polyesters with low-burst properties by supercritical fluid extraction.
WO2008058303 A1	20080522	CA2668902 A1 20080522; AU2007321746 A1 20080522; MX2009004892 A 20090521; KR20090092806 A 20090901; EP2101974 A1 20090923;	AT20060001880 20061113; WO2007AT00515 20071113	WENDELIN G; HACKL M; FEICHTINGER K	EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT MBH	Method for the pretreatment , reprocessing, or recycling of thermoplastic material.

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
		CN101535018 A 20090916; AT505462 A1 20090115; JP2010509413 A 20100325; US2010216902 A1 20100826; KR20110007259 A 20110121; RU2009122359 A 20101220; RU2412804 C1 20110227; EP2295218 A1 20110316; AU2007321746 B2 20110818; CN102357943 A 20120222; JP2012066588 A 20120405; AT552958 T 20120415; ES2385105 T3 20120718; DK2101974 T3 20120723				
WO2009081362 A1	20090702	IT1380839 B 20100913	IT2007TO00923 20071220	MUSO SI; ZANETTI M; TAGLIAFERRO A; LUDA M P	TORINO POLITECNICO; UNIV DEGLI STUDI TORINO	Process for recycling organic materials with the production of carbon nanotubes.
WO2009100473 A1	20090820	AU2009214810 A1 20090820; CA2715048 A1 20090820; AT506489 A1 20090915; CN101945743 A 20110112; EP2252440 A1 20101124; KR20100120212 A 20101112; MX2010008248 A 20100823; AT506489 B1 20101215; US2011049763 A1 20110303; JP2011514850 A 20110512; RU2010137909 A 20120320	AT20080000245 20080214	HACKL M; FEICHTINGER K; WENDELIN G	EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT MBH	Method and a device for injection-molding plastic material.

WO2010050482 A1	20100506	JP2010132886 A 20100617; JP2010138389 A 20100624; JP2010138390 A 20100624; EP2348122 A1 20110727; US2011201069 A1 20110818; CN102264912 A 20111130	WO2009JP68433 20091027; JP20080275738 20081027; JP20080290320 20081112; JP20080290321 20081112	YOSHIKAWA S; KATAYAMA T; KOGURE M	TOYO SEIKAN KAISHA LTD	Method for producing oligomer and/or monomer by degrading biodegradable resin.
WO2010118954 A1	20101021	BE1018716 A3 20110705; AU2010237248 A1 20101021; MXP A11010716 A 20111031; CN102348673 A 20120208; EP2419395 A1 20120222; US2012142958 A1 20120607; KR20120012810 A 20120210	BE20090000232 20090414; WO2010EP54274 20100331	COSZACH P; BOGAERT J-CH; WILLOCQ J	GALACTIC SA	Chemical recycling of PLA by hydrolysis.
WO2010118955 A1	20101021	US2012029228 A1 20120202; CN102348672 A 20120208; EP2419396 A1 20120222	BE20090000231 20090414	COSZACH P; BOGAERT J-CH; WILLOCQ J	GALACTIC SA	Chemical recycling of PLA by alcoholysis.
WO2011015433 A1	20110210	WO2011015433 A9 20110721; BE1018850 A3 20111004; AU2010280940 A1 20111215; MX2012001088 A 20120314; CN102482447 A 20120530; US2012116049 A1 20120510; EP2462189 A1 20120613	BE20090000475 20090806; WO2010EP60142 20100714	COSZACH P; WILLOCQ J.	GALACTIC SA	Purification of a conventional polymer flow contaminated with PLA.
WO2011029648 A1	20110317	BE1018882 A3 20111004; MX2012002137 A 20120314; CN102482369 A 20120530; US2012165554 A1 20120628	BE20090000554 20090910	COSZACH P.; WILLOCQ J.	GALACTIC SA	Procédé de recyclage stéréospécifique d'un mélange de polymères à base de PLA; "Method for stereospecifically recycling a PLA polymer mixture."

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TABLE I Patents related to recycling, reuse, and disposal of biopolymers (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
WO2011146562 A2	20111124	WO2011146562 A3 20120518; US2012128924 A1 20120524	US20100345698P 20100518	LENGES G M; MADELEINE D G; SAMANT K	DU PONT	Recycled poly(trimethylene) terephthalate and processes thereof.
WO2012001784 A1	20120105		WO2010JP61182 20100630	TSUBOTA J	OSAKA GAS CO LTD	PLA decomposition method.
WO9743014 A1	19971120	DE19619236 A1 19971120; CA2254094 A1 19971120; AU2774997 A 19971205; EP0912214 A1 19990506; JP2000511567 A 20000905; US6071711 A 20000606; TW426735 A 20010321; EP0912214 B1 20011004; DE59704803 G 20011108; DK912214 T3 20020128; TW426735 B 20010321;	DE19961019236 19960513; WO1997EP02211 19970430	KOCH R	BAYER AG	Abbau von biologisch abbaubare Polyesteramiden mit Enzymen. "Degradation of biodegradable polyester amides with enzymes."
WO9928366 A1	19990610	AU1709099 A 19990616; US5990266 A 19991123; US6121033 A 20000919	US19980204338 19981202; US19970067514P 19971204; US19990358348 19990721; US20000504824 20000216	TADROS R M; TIMM D C	UNIV NEBRASKA	Novel degradable polyesters useful in packaging, agricultural, and biomedical applications.

TABLE II Patents related to degradation on demand

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
AU3521984 A	19850523	EP0142950 A2 19850529; EP142950 A3 19850529; JPS60122527 A 19850701; US4620999 A 19861104; AU576795 B2 19880908; EP0142950 B 19901010; DE3483387 G 19901115; JP5052223 B 19930804	GB19830030414 19831115	HOLMES P A	ICI PLC	Disposable bags.
CA2605791 A1	20080406	US2008085297 A1 20080410; KR20080031842 A 20080411; EP1911472 A1 20080416; AU2007216921 A1 20080424 ; BRPI0703731 A 20080527; JP2008110205 A 20080515; CN101195046 A 2008061; MX2007012485 A 20090216		DAVE V; LANDAU G	CORDIS CORP	Bio-absorbable device having encapsulated additives for accelerating degradation.
CN101130627 A	20080227	US2008048365 A1 20080228; JP2008050446 A 20080306; US7598305 B2 20091006	JP20060226967 20060823	YAO K	FUJI XEROX CO LTD	Resin composition, resin molding, package, production method of resin molding, and recycling method of resin molding.
CN101747476 A	20100623		CN20081218167 20081215	LI M; ZHANG X	SHENZHEN ECOMANN TECHNOLOGY CO LTD	Polyhydroxyalkanoate graft polymer prepared from polyhydroxyalkanoate, graft monomer, initiator, and antioxidant (WPI).
DE19754418 A1	19990610	ZA9811205 A 19990609; WO9929768 A1 19990617; CA2313192 A1 19990617; AU1876399 A 19990628; CN1281482 A 20010124; NO20002947 A 20000703; EP1037943 A1 20000927; JP2001525473 T 20011211	DE19971054418 19971209; WO1998EP07690 19981128	VOIGT M; JESCHKE K; ECKERT A; MUELLER V	BAYER AG	Stabilisierte Formmassen biologisch abbaubarer Materialien. "Stabilized molding compounds comprised of biologically degradable materials."
DE19911209 A1	20000914	WO0055240 A1 20000921; AU3553100 A 20001004	DE19991011209 19990313	KLEEMIS M; HOPPE L; WEBER G	WOLFF WALSRÖDE AG	Halbezeuge aus biologisch abbaubaren Polymeren mit verbesserter Hydrolysestabilität und Spannungsrissbeständigkeit. "Semi-finished products consisting of biodegradable polymers with improved hydrolytic stability and stress-cracking resistance."

DE29619016U U1	19980312		DE19962019016U 19961101	MUELLER W R; SCHOENBERGER D	MUELLER W R; SCHOENBERGER D	Biologisch abbaubares Kunststoffprodukt. "Biologically degradable plastic material."
EP0587069 A1	19940316	JPH06330001 A 19941129; US5489474 A 19960206; US5663288 A 19970902; EP0587069 B1 19981202; DE69322333 E 19990114; KR100209818 B1 19990715	JP19930218259 19930902; JP19920237288 19920904	SHINODA H; OHTAGURO M; FUNAE A; MORIYA S; IIMURO S	MITSUI TOATSU CHEM INC	Degradable adhesive film and degradable resin composition.
EP1207181 A1	20020522	JP2002155216 A 20020528; US2002091172 A1 20020711; US6653364 B2 20031125; US2004010051 A1 20040115; EP1207181 B1 20040630; DE60104074 E 20040805; US7019043 B2 20060328; JP3848077 B2 20061122	JP20000353417 20001120	MAEHARA H	CANON KK	Decomposable resin composition and method for producing the same.
EP1354917 A1	20031022	JP2003313436 A 20031106; US2003228478 A1 20031211; KR20030082908 A 20031023; US6846860 B2 20050125; EP1354917 B1 20060614; DE60306013 E 20060727; DE60306013 T2 20061221; JP4084953 B2 20080430; KR100958855 B1 20100520	JP20020116092 20020418	TAKAHASHI I; IIDA H; NAKAMURA N; TAKEUCHI T	NISSHIN SPINNING	A biodegradable plastic composition, a molded article thereof, and a method for controlling biodegradation rate.
EP1418201 A1	20040512	CA2448469 A1 20040508; JP2004155993 A 20040603; US2004132860 A1 20040708; KR20040041047 A 20040513; EP1418201 B1 20070822; DE60315780 E 20071004; US7361701 B2 20080422; DE60315780 T2 20080605; JP4245333 B2 20090325	JP20020325201 20021108; EP20030024523 20031027	IIDA H; NAKAMURA N; TAKAHASHI I; TAKEUCHI T; YAMAZAKI Y	NISSHIN SPINNING	Biodegradable plastic composition, shaped article and method for controlling biodegradation speed utilizing the same.
EP1564316 A1	20050817	US2005233142 A1 20051020; CN1654721 A 20050817; JP2005226183 A 20050825; KR20060042925 A 20061031; US7129190 B2 20061031; CN100398709 C 20080702; EP1564316 B1 20090401;	JP20040034941 20040212	TAKAHASHI I; IIDA H	NISSHIN SPINNING	Fiber article comprising a biodegradable plastic.

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TABLE II Patents related to degradation on demand (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
EP1854837 A2	20071114	EP1854837 A2 20071114; JP2007302758 A 20071122; US2007265371 A1 20071115; KR20070109891 A 20071115; EP1854837 A3 20090930	JP20060131031 20060510	IIDA H; TAKAHASHI I	NISSHIN SPINNING	Biodegradable plastics composition, molded article of the composition, and method of controlling biodegradation rate.
FR2938265 A1	20100514	WO2010055250 A1 20100520	FR20080057656 20081112	DOMARD A; DAVID L; POPA NITA S	UNIV CLAUDE BERNARD LYON; CNRS CENT NAT RECH SCI	Procédé pour le pilotage d'un traitement de dépolymérisation par ultrasons d'un biopolymère hydrosoluble. "Process for controlling an ultrasound depolymerization treatment of a water-soluble biopolymer."
GB2281709 A	19950315	DE4418634 A1 19950316; JPH07133435 A 19950523; JPH07196903 A 19950801; US5545485 A 19960813; GB2281709 B 19980408; US5744516 A 19980428; DE4447884 A1 20000831; DE4418634 C2 20010830; JP3377844 B2 20030217; JP2003138110 A 20030514; JP2003138148 A 20030514; JP3585475 B2 20041104; JP3729794 B2 20051221	JP19930229265 19930914 JP19930336070 19931228 JP19930332493 19931227	HASHITANI T; FUJITA S; IIJIMA M; ASANO K	FUJITSU LTD	Biodegradable resin molded article.
JPH1036684 A	19980210		JP19960212192 19960724	SUGIMOTO I	SUGIMOTO I	Biodegradable film and compost bag made thereof.
JPH10273582 A	19981013	JP3634937 B2 20050330	JP19970077268 19970328	TANAKA S	OKURA IND CO LTD	Biodegradable resin composition.
JPH1180522 A	19990326	JP3776578 B2 20060517	JP19970333542 19971117; JP19970200803 19970709	IMASHIRO Y; TAKAHASHI I; HORIE T; SUZUKI J	NISSHIN SPINNING	Biodegradable plastic composition and control of biodegradation rate of biodegradable plastic.
JP2000129105 A	20000509		JP19980307295 19981028	HARADA M; MATSUSHITA H; YOSHIDA S	MITSUBISHI GAS CHEM CO INC	Control of biodegradation rate and biodegradable multi-layered molding.
JP2001049115 A	20010220		JP19990227628 19990811	MIYAHARA Y; TANAKA K; KURAMOTO Y	OKURA IND CO LTD	Bag for garbage.
JP2001261797 A	20010926	JP3440915 B2 20030825	JP20000070098 20000314	MATSUMOTO H; MASUDA T; MAEDA Y	TORAY IND INC	Aliphatic polyester resin and molded product.

JP2001302891 A	20011031		JP20000121169 20000421	TANAKA S	TOYOBO CO LTD	Method for controlling degradation of biodegradable molded product and biodegradable molded product used thereof.
JP2001323177 A	20011120	JP3646193 B2 11052005	JP20000147610 20000519	SATO I	MIYAGI PREFECTURE	Biodegradable resin composition with controlled biodegradation rate and method of its manufacturing.
JP2001329082 A	20011127		JP20000155174 20000525	OSAWA S; OGAWA T	UNIV KANAZAWA KOGYO	Polylactic acid (PLA) resin molded product having controlled biodegradation period and its manufacturing method.
JP2002219779 A	20020806		JP20010018328 20010126	OGAWA T; OSAWA S	KANAZAWA INST OF TECHNOLOGY	Biodegradable resin laminate whose degradation period is controlled.
JP2002256088 A	20020911		JP20010059359 20010305	OGAWA T; OSAWA S	KANAZAWA INST OF TECHNOLOGY	Molded product of aliphatic polyester-based resin, improved in biodegradation rate, and production method thereof.
JP2002256142	20020911		JP20010056964 20010301	MIYAKE M; NISHIMURA H; SAKAKI T; YANO T	UNITIKA LTD	Colored resin composition and method for recovering non-biodegradable colorant.
JP2002266340 A	20020918		JP20010065046 20010308	YAMAMOTO A; TAKAHASHI T	UNITIKA LTD	Drain material and method for accelerating decomposition thereof.
JP2002348406 A	20021204		JP20010153397 20010523	DEGUCHI J; MARUYAMA K; TSUKAHARA T; SHIRAHAMA R	MITSUBISHI CHEM CORP INC	Disposition method of agricultural mulching film.
JP2002356623 A	20021213		JP20010163107 20010530	TSUTSUGI T; SATAKE S; KAGEYAMA Y; INAO T; YAMASHITA S; ISOBE Y; MITSUNE K	TOYOTA MOTOR CORP	Biodegradable resin containing microorganism.
JP2003003052 A	20030108		JP20010186528 20010620	TAKAGI J	MITSUBISHI PLASTICS IND LTD	Resin composition, film and method of disposal.

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TABLE II Patents related to degradation on demand (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
JP2003034734 A	20030207		JP20010222216 20010723	FUJIHIRA H; NOGUCHI T; MORI H; OGASAWARA J	SONY CORP	Method of controlling decomposition speed of biodegradable resin.
JP2003221461 A	20030805		JP20020022697 20020131	ASAMI O; TANAKA T; KAJINO T; TAKAHASHI H	TOYOTA CENTRAL RES & DEV LAB INC	Degradation controlling method for aliphatic polyester and biodegradable aliphatic polyester.
JP2004075727 A	20040311	JP4289841 B2 20090701	JP20020234239 20020812	FUKUDA N; ONISHI Y; TSUJI H; YAMADA K	AICHI PREFECTURE; TSUJI H; UNITIKA LTD	PLA resin composition having controlled biodegradation rate and its molded product.
JP2005089537 A	20050407		JP20030322332 20030912	UMEMOTO K; YUGAMI Y	DAICEL CHEM IND, LTD	Biodegradable resin composition, mulch film for agriculture, shaped article, and method for suppressing degradation in soil.
JP2005220238 A	20050818	JP4486829 B2 20100623	JP20040030142 20040206	NISHIMURA H; KATO M; KAWASAKI S; KAWAGUCHI T; SAKAMOTO H; KONDO Y	OSAKA GAS CO LTD	Method for controlling hydrolyzability of biodegradable polymer material.
JP2006104262 A	20060420		JP20040290259 20041001	SHINTANI N; KATO S; NAKAJIMA Y; SAKAGUCHI H	MITSUBISHI CHEM CORP; NOVOZYME AS	Method for decomposing polyester resin molding.
JP2006225427 A	20060831		JP20050037636 20050215	MITOMO H; NAGASAWA N; TAMADA M	JAPAN ATOMIC ENERGY AGENCY; UNIV GUNMA	Method for recovering biodegradability of biodegradable polymer whose biodegradability has been made lower or lost.
JPH04168149 A	19920616	JP3077704 B2 20000814	JP19900295121 19901030	TAWARA O	SHIMADZU CORP	Biodegradable plastic.
JPH0551073 A	19930302		JP19910209338 19910821	TANIGUCHI M; NAKAGAWA Y; TERAUCHI Y; HACHIFUSA K	TOPPAN PRINTING CO LTD	Plastic container.
JPH06184417 A	19940705	JP3256350 B2 20020212	JP19930218259 19930902; JP19920237288 19920904	SHINODA N; OTAGURO M; IIMURO S; MORIYA S	MITSUMI TOATSU CHEM INC	Lactic acid-type polymer composition.

JPH0912688 A	19970114	JP3319553 B2 20020903	JP19950160607 19950627	YUUCHI M; ITO T; AOYAMA T; UNO K	TOYOBO CO LTD	PLA resin composition.
JPH09124778 A	19970513		JP19950283856 19951031	FUJII Y	SHIMADZU CORP	Production of PLA.
US2002030305 A1	20020314	EP1188530 A2 20020320; JP2002088161 A 20020327; CN1343734 A 20020410; KR20020021322 A 20020320; EP1188530 A3 20030319; TW570868 B 20040111; CN1204195 C 20050611; KR100792533 B 20080109	JP20000279169 20000914	FUJIHIRA Y; NOGUCHI T; MORI H	SONY CORP	Method for improving elastic modulus of biodegradable resin composition.
US2002123546 A1	20020905	US6740731 B2 20040525	US20010782183 20010212; US19990244324 19990203; US19920949675 19920922; US19900579000 19900906; US19900579005 19900906; US19900579460 19900906; US19900579465 19900906; US19890387676 19890731; US19890387678 19890731; US19890386844 19890731; US19890387670 19890731; US19880229894 19880808; US19880229896 19880808; US19890317391 19890301; US19880229939 19880808	BIGG D M; SINCLAIR R G; LIPINSKY E S; LITCHFIELD J H; ALLEN B R	ECOPOL LLC; CARGILL DOW POLYMERS LLC	Degradation control of environmentally degradable disposable materials.
US2003092338 A1	20030515	CA2411004 A1 20030514; CN1421555 A 20030604; EP1312702 A1 20030521; JP2003213521 A 20030730; KR20030040174 A 20030522; US6699581 B2 20040302; TW568964 B 20040101; KR100467115 B 20050124; TW200300467 A 20030601; CN1206394 C 20050615	JP20010348141 20011114; US20020293305 20021114	SHIMICHI S; ANDO Y; HOKIMOTO A	KURARAY CO	Biodegradable fiber, cloth, and method for controlling biodegradability of fiber.
US2003236320 A1	20031225	US6867248 B1 20050315; US6878758 B2 20050412	US20030403942 20030328; US19980218575 19981222; US19980076198 19980512; US19970068455P 19971222; US19970046211P 19970512; US19970054289P 19970731; US19970063501P 19971024; US19970065921P 19971117		METABOLIX INC	Polyhydroxyalkanoate compositions having controlled degradation rates.

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TABLE II Patents related to degradation on demand (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
US2005054755 A1	20050310	CA2480380 A1 20050305; EP1514897 A1 20050316; JP2005082642 A 20050331; CN1603357 A 20050406; KR20050025066 A 20050311; US7273902 B2 20070925	JP20030313602 20030905; US20040929774 20040831		NISSHIN SPINNING	Hydrolysis resistance stabilizer for ester group-bearing resin and thermoplastic composition.
US2005261465 A1	20051124	WO2005118693 A1 20051215; US7053130 B2 20060530; JP2008500424 T 20080110	US20040852403 20040524; WO2004US16349 20040525; JP20070515006 20040525	NAGARAJAN V	DU PONT	Method to accelerate biodegradation of aliphatic-aromatic copolyesters by enzymatic treatment.
US2007082202 A1	20070412	EP1775328 A1 20070418; JP2007106783 A 20070426; CN1948370 A 20070418; US7361408 B2 20080422	JP20050296071 20051011; US20060337646 20060124	CYOURAKU K; NAGARA K; TAKAHASHI H; YAMAGUCHI S; YUI Y	FUJITSU LTD	Resin-molded product and electronic equipment using the same, and method for treating resin-molded product.
US2008166789 A1	20080710	US20080049668 20080317; CA2675487 A1 20090917; WO2009117022 A1 20090924; US2009275111 A1 20091105; CN101657499 A 20100224	US20050041322 20050124; US20070747481 20070511; US20080049668 20080317; US20080098613 20080407; US20090500805 20090710	GROSSMAN R F	BIOTECH PROD LLC	Compostable vinyl acetate polymer compositions, composites, and landfill biodegradation.
US2010115836 A1	20100513		US20090618204 20091113; US20080114197P 20081113; US20090227709P 20090722	BRANDON J J	BRANDON J J	Biodegradable agricultural growth management tools.
WO0075259 A1	20001214	EP1183319 A1 20020306; BR0011380 A 20020305; CN1354777 A 20020619; US2002132884 A1 20020919; US6462120 B2 20021008; MXPA01012545 A 20030701; JP2003529625 T 20031007; EP1183319 B1 20041027; DE60015326 E 20041202	US19990137978P 19990607; US20000534727 20000324; WO2000US12259 20000505	OFFERMAN R J	EASTMAN CHEM CO	Agricultural mulch films with triggered degradation.
WO02094935 A1	20021128	KR20030011358 A 20030207; CN1462296 A 20031217; CN1246385 C 20060322; JP4127648 B2 20080730; HK1060894 A1 20060804	JP20010153121 20010522	NAKATA K; OMAE H	DAICEL CHEM IND, LTD	Biodegradable resin composition with controlled biodegradation rate, film, and agricultural mulch film.
WO0222737 A2	20020321	WO0222737 A3 20020530; EP1317506 A2 20030611; JP2004509205 T 20040325;	US20000662965 20000915; WO2001US20065 20010622	IRICK G J R; LIGHT R R	EASTMAN CHEM CO	Methods for slowing the degradation rate of biodegradable polymer and

		US6767972 B1 20040727; EP1317506 B1 20051214; DE60115922 T2 20060706; AT312876 T 20051215				biodegradable polymer compositions and compositions thereof.
WO2005090438 A1	20050929	EP1736498 A1 20061227; CN1930211 A20070314; EP1736498 B1 20100714; US2007244293 A1 20071018; EP1736498 A4 20080507; AT474008 T 20100715	JP20040078306 20040318; WO2005JP04771 20050317	SATO H; KOBAYASH F; KAWAKAMI Y; YAMANE K; AMANO Y; SATO T	KUREHA CORP	Process for producing aliphatic polyester reduced in residual cyclic ester content.
WO2006084261 A2	20060810	WO2006084261 A3 20061123; US2006177930 A1 20060810	US20050650446P 20050204; US20060347447 20060203	BRAMUCCI M G; NAGARAJAN V	DU PONT; BRAMUCCI M G; NAGARAJAN V	Method to enhance biodegradation of sulfonated aliphatic-aromatic co-polyesters by addition of a microbial consortium.
WO2006118096 A1	20061109	EP1876205 A1 20080109; CN101163743 A 20080416; KR20080000594 A 20080102; JP2007514731 T2 20081218; TW200641042 A 20061201; US2009270530 A1 20091029; EP1876205 B1 20100317; DE602006012956 E 20100429	JP20050128054 20050426	NAKAI M; KAWAHARA M; UEDA K; TAKAHASHI S; KUSUMOTO T; TANAKA M	UNITIKA LTD; SHISEIDO CO LTD	Biodegradable resin composition, and molded body and production method thereof.
WO2007060981 A1	20070531	EP1958976 A1 20080820; CN101316877 A 20081203; US2009298979 A1 20091203	JP20050338304 20051124; WO2006JP323301 20061122	SATO HI; HOKARI Y; YAMANE K; KOBAYASHI F	KUREHA CORP	Method for controlling degradation water resistance of polyglycolic acid resin.
WO2007063941 A1	20070607	EP1958987 A1 20080820; CN101321829 A 20081210; US2009171039 A1 20090702	JP20050349812 20051202; WO2006JP323937 20061130	SATO H; AKUTSU F; KOBAYASHI F	KUREHA CORP	Polyglycolic acid resin composition.
WO2008038350 A1	20080403	JP2008536230 T2 20100128	WO2006JP319174 20060927	KIMURA K; NISHII K	FUJITSU LTD	Resin composition, pulverized matter and method of discarding resin.
WO9406866 A1	19940331	CA2144310 A1 19940331; AU4923793 A 19940412; MX9305814 A 19940429; EP0662107 A1 19950712; EP0662107 A4 19950927	US19920949675 19920922; WO1993US08717 19930915	BIGG D M; SINCLAIR R G; LIPINSKY E S; LITCHFIELD J H; ALLEN B R	BIOPAK TECHNOLOGY LTD	Degradation control of environmentally degradable disposable materials.

TABLE III Supplementary patents

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
AU2006294414 A1	20070329	AU2006294414 B2 20120524	AU20050905192 20050920; WO2006AU01380 20060920; AU20060294414 20060920	MOORE T G; GUNATILLAKE P A; ADHIKARI R	POLYNOVO BIOMATERIALS PTY LTD	Chain extenders.
AU3521984 A	19850523	EP0142950 A2 19850529; JPS60122527 A 19850701; US4620999 A 19861104; EP0142950 A3 19870805; AU576795 B2 19880908; EP0142950 B1 19901010	GB19830030414 19831115	HOLMES P A	ICI PLC	Disposable bags.
AU5560680 A	19800828	EP0015123 A1 19800903; EP0015123 B1 19821222; EP0036699 A1 19810930; EP0036699 B1 19830202; EP0036699 B2 19870902; ES8103169 A1 19810516; DK73380 A 19800822; AU529981 B2 19830630	GB19790006076 19790221; GB19790006077 19790221; GB19790015858 19790508	HOLMES P A; WRIGHT L F; ALDERSON B; SENIOR P J	ICI PLC	A process for the extraction of poly-3-hydroxybutyric acid from microbial cells.
AU5560780 A	19800828	EP0015669 A2 19800917; EP0015669 A3 19810429; EP0015669 B1 19830525; AU537572 B2 19840705	GB19790006078 19790221; GB19790006079 19790221	POWELL K A; COLLINSON B A; RICHARDSON K R	ICI PLC	Microbiological process for the production of poly (β -hydroxybutyric acid), and microorganisms for use therein.
BE837935 A1	19760514	FR2299356 A1 19760827; ZA7600493 A 19770727; US4138344 A 19780606; SE7600760 A 19760920; SE418189 B 19810511; NL7600881 A 19760730; NL174728 C 19840801; MX142986 A 19810203; JPS51100194 A 19760903; IT1057070 B 19820310; IL48799 A 19790131; GB1502082 A 19780222; ES444484 A1 19770916; DK32076 A 19930413; DK166360 B 19930413; DE2602994 A1 19760729; DE2602994 C2 19820826;	US19750544808 19750128	CHOI NAM SOK; HELLER J	ALZA CORP	Drug delivery devices manufactured from poly(orthoesters) and poly(orthocarbonates).

		CH635355 A5 19830331; CA1087345 A1 19801007; BR7600499 A 19760831; US4093709 A 19780606; AU1041676 A 19770818; AT356903 B 19800610; AR213619 A1 19790228				
CA2202676 A1	19981014	US5955068 A 19990921	CA19972202676 19970414	GOUIN S; ZHU X-X	UNIV MONTREAL	Biodegradable polyanhydrides derived from dimers of bile acids, and use thereof as controlled drug release systems.
CA2541366 A	20061006	US2006229375 A1 20061012; KR20060107330 A 20061013; EP1712576 A1 20061018; CN1847279 A 20061018; JP2006291205 A 20061026; SG126853 A1 20061129; BRPI0601137 A 20061205; RU2006110878 A 20071010; SG161236 A1 20100527; CN1847279 B 20120118; CN102585200 A 20120718	US20050100221 20050406	HSIAO Y-L; SKORPENSKIE R G; KAUSHIVA B D; MCDANIEL K G; PAZOS J F; HAGER ST L; HAIDER K W	BAYER MATERIALSCIENCE AG	Polyurethane foams made with alkoxyated vegetable oil hydroxylate.
CA2568765 A1	20070526	EP1790678 A1 20070530; DE102005056432 A1 20070531; US2007123725 A1 20070531; KR20070055956 A 20070531; CN1974526 A 20070606; JP2007146163 A 20070614; SG132645 A1 20070628; BRPI0605169 A 20070904; MXPA06013551 A 20081009; EP1790678 B1 20091007; AT444983 T 20091015; ES2333038 T3 20100216; CN1974526 B 20120118	DE200510056432 20051126	LORENZ K	BAYER MATERIALSCIENCE AG	Process for the production of polyols based on natural oils.
CH250077 A	19470815		CHT250077 19460924	HOLZER T	HOLZER T	Verfahren zur Herstellung von Formartikeln. "Method for producing molded bodies."
CN101628972 A	20100120	CN101628972 B 20111005	CN20081132792 20080714		QINGDAO INST OF BIOMASS ENERGY	Method for preparing poly(ethylene succinate).

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TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
				NING K; YUHONG L; JIANZHONG L		
CN102002148 A	20110406	CN102002148 B 20120418	CN20101547712 20101117	JIAN D; ZHONGHUA B	ZHANGJIAGANG CHAINENG BIOLOG SCIENCE CO LTD	Method for preparing biodegradable poly(malic acid) material.
DE10151386 A1	20030508	DE10151386 C2 20031016	DE20011051386 20011018		TECNARO GES ZUR IND ANWENDUNG	Zusammensetzung für die thermoplastische Verarbeitung zu Formkörpern und Verfahren zur Herstellung einer solchen Zusammensetzung. "Composition for thermoplastic processing into molded bodies and method for producing such a composition."
DE19522147 A1	19970102	DE19522147 C2 19970507	DE19951022147 19950619	KOEHNLECHNER R	HAMOS ELEKTRONIK GMBH	Vorrichtung zum elektrostatischen Sortieren von Gemischen aus Teilchen unterschiedlicher Kunststoffe. "Electrostatic sorter for comminuted particles of differing types, especially plastics."
DE19530449 A1	19970220	EP0759451 A2 19970226; JPH0959337 A 19970304	DE19951030449 19950818	EIER H-M; SENG F; BECKER A; KUCKERT E; BOECKER T; LUTTERMANN K	BAYER AG	Polymere Fluoreszenzmarker. "Polymeric fluorescence markers."
DE19700902 A1	19980716		DE19971000902 19970114	HUETTERMANN A; RAUN-LUELLEMANN A; MAJCHERZCYK A; NOETZOLD S; KHARAZIPOUR A; HUETTERMANN J	HUETTERMANN A	Zwischenprodukt für die Herstellung von Polymerisaten aus Ligninderivaten. "Activated lignin intermediates for lignin polymers preparation" (no official title).

DE19700903 A1	19980716		DE19971000903 19970114	HUETTERMANN A; RAUN-LUELLEMANN A; MAJCHERZCYK A; NOETZOLD S; KHARAZIPOUR A; HUETTERMANN J	HUETTERMANN A	Zwischenprodukt für die Herstellung von Polymerisaten aus Ligninderivaten. "Activated lignin intermediates for lignin polymers preparation" (no official title).
DE19700905 A1	19980716		DE19971000905 19970114	HUETTERMANN A; GOES C; HOEPPNER M; MAJCHERCZYK A; BRAUN-LUELLEMANN A	HUETTERMANN A	Zwischenprodukt für die Herstellung von Polymerisaten aus Ligninderivaten. "Activated lignin intermediates for lignin polymer preparation" (no official title).
DE19700907 A1	19980716	CA2277279 A1 19980723; WO9831825 A1 19980723; AU5664098 A 19980807; EP0960206 A1 19991201; CZ9902516 A3 19991117; PL334520 A1 20000228; SK94299 A3 20000516; BR9806955 A 20000321; CN1250482 A 20000412; ID23445 A 20000420; HU0001972 A2 20001028; NZ336663 A 20010427; US6280855 B1 20010828	DE19971000907 19970114	VIKARI L; HASE A; QVINTUS-LEINO P; NIKU-PAAVOLA M-L	NESTE OY	Zwischenprodukt für die Herstellung von Ligninpolymerisaten und dessen Verwendung zur Herstellung von Holzwerkstoffen. "Intermediate product for preparation of lignin polymers and use thereof for production of wood materials."
DE19701015 A1	19980716		DE19971001015 19970114	KHARAZIPOUR A; HUETTERMANN A; HUETTERMANN J	WIBMER GMBH U. CO. KG PAPIER- FORMTECHNIK	Zwischenprodukt für die Herstellung von Polymerisaten aus Ligninderivaten, sowie die Verwendung dieser Zwischenprodukte für die Herstellung von Beschichtungsmitteln für die Beschichtung von pflanzlichen Fasern für die Herstellung von Pflanztöpfen. "Intermediate products for the preparation of polymers based on lignin derivatives, and the use of these intermediate products for

(Continued)

TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
						the coating of plant fibers for the preparation of plant pots."
DE19739992 A1	19990826		DE19971039992 19970911	KOEHNLECHNER R	HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK	Verfahren, Anlage, Vorrichtungen und Vorrichtungsanordnung zur triboelektrischen Trennung von unterschiedlich Stoffgemischen aus Nichtleitern, insbesondere aus Kunststoffen. "Triboelectric separation of differently composed material mixtures of non-conducting materials, especially plastics."
DE19740027 A1	19990318		DE19971040027 19970911	KOEHNLECHNER R	HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK	Verfahren und Vorrichtung zur Bestimmung triboelektrischer Eigenschaften von Nichtleitern. "Electrostatic separation of mixture of different nonconductive materials."
DE19829200 A1	20000105		DE19981029200 19980630	KOEHNLECHNER R	HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK	Verfahren, Anlagen und Vorrichtungen zur elektrostatischen Separation von unterschiedlich zusammengesetzten Nichtleitergemischen, insbesondere von Kunststoffgemischen. "Automatic electrostatic separation of nonconductive material mixtures, use of process, process plant and electrostatic separating unit."
DE19829200 A1	20000105		DE19981029200 19980630			Verfahren, Anlagen und Vorrichtungen zur

					HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK	elektrostatischen Separation von unterschiedlich zusammengesetzten Nichtleitergemischen, insbesondere von Kunststoffgemischen. "Automatic electrostatic separation of nonconductive material mixtures, use of process, process plant, and electrostatic separating unit."
DE19852034 C1	20000420	WO0027924 A1 20000518; AU1552200 A 20000529; EP1129139 A1 20010905; EP1129139 B1 20020605; AT218601 T 20020615; JP2002529568 A 2002090; ES2178491 T3 20021216; US6706106 B1 20040316; CA2350418 C 20090929; JP4843141 B2 20111221	DE19981052034 19981111	NAEGELE H; EYERER P; PFITZER J; EISENREICH N; INONE E; ECKL W	FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG	Zusammensetzung zur Herstellung von Formkörpern und Verfahren zur Herstellung von Formkörpern aus einer solchen Zusammensetzung. "Composition for producing molded bodies and method for producing molded bodies from such a composition."
DE19901743 A1	20000720		DE19991001743 19990118		HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK	Verfahren, Anlage, Vorrichtungen und Vorrichtungsanordnung zur triboelektrischen Aufladung und anschliessenden elektrostatischen Trennung von unterschiedlich chemisch zusammengesetzten Stoffgemischen aus Nichtleitern, insbesondere unterschiedlich chemisch zusammengesetzten Kunststoffen. "Triboelectric charging and electrostatic separation of diverse, non-conductive mixed waste, especially plastic; employs enclosed

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TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
						vibro-conveyor followed by in-flight separation influenced by non-linear electrostatic field."
DE3842072 C1	19891228	EP0373372 A2 19900620; JPH02202403 A 19900810; US5009586 A 19910423; EP0373372 A3 19910502; EP0373372 B1 19930908; JP6013176 B 19940223	DE19883842072 19881214	PALLMANN W	PALLMANN MASCHINENFABRIK GMBH & CO KG	Vorrichtung zum kontinuierlichen Regranulieren von thermoplastischen Kunststoffabfällen, insbesondere von Folien, Fäden und dgl. "Agglomerating apparatus for the continuous regranulation of thermoplastic wastes; especially, films, filaments and the like."
DE4029167 A	19920319	EP0476416 A 19920325; JPH04246425 A 19920902; US5201921 A 19930413; EP0476416 A3 19930217	DE19904029167 19900914	LUTTERMANN K; CLAUSSEN U; SAYED AZIZ EL; RIESS R	BAYER AG	Verfahren zur Kennzeichnung von Kunststoffen. "Method for the masking of plastics."
DE4231477 A1	19940324		DE19924231477 19920919	HAN KYUNG TAE; KOELLNER M; SAUER M; SEEGER S; WOLFRUM J; SCHMITT C; SCHULZ A	HAN KYUNG TAE; KOELLNER M; SAUER M; SEEGER S; WOLFRUM J; SCHMITT C; SCHULZ A	Verfahren zur optischen Sortierung von Kunststoffen mittels zeitaufgelöster Laserspektroskopie. "Sorting of plastics by time-resolved laser spectroscopy."
DE4327024 A1	19950216	EP0641817 A2 19950308; JPH07102061 A 19950418; EP0641817 A3 19960807; US5644020 A 19970701; EP0641817 B1 20001227; ES2154655 T3 20010416; JP3493472 B2 20040203	DE19934327024 19930812	TIMMERMANN R; DUJARDIN R; KOCH R	BAYER AG	Thermoplastisch verarbeitbare und biologisch abbaubare aliphatische Polyesteramide. "Thermoplastically processable and biologically degradable aliphatic polyester amides."
DE4331747 A1	19950323	WO9508594 A1 19950330; EP0720634 A1 19960710; CZ9600822 A3 19960911; HUT75658 A 19970528; EP0720634 B1 19980218; AT163304 T 19980315;	DE19934331747 19930920; WO1994EP03131 19940917	WUENNING P; WUENNING M	WUENNING P	Extrudiertes, faserverstärktes Naturstoff-Granulat zur thermoplastischen Weiterverarbeitung, sowie Verfahren zu seiner Herstellung.

		ES2115258 T3 19980616; DK720634 T3 19981123				"Extrudable, fiber-reinforced natural substance granulate for thermoplastic processing, and process for its production."
EP0046335 A2	19820224	EP0046335 A3 19820310; JPS57174094 A 19821026	GB19800026882 19800818	HOLMES P A; JONES E	ICI PLC	Extraction of poly(β -hydroxybutyric acid).
EP0046344 A2	19820224	EP0046344 A3 19820303; EP0046344 B1 19850619; US4433053 A 19840221; SU1303035 A3 19870407; JPS5774084 A 19820510; AU7355281 A 19820225; AU542807 B2 19850314	GB19800027004 19800819	HUGHES L; RICHARDSON K R	ICI PLC	Fermentation process.
EP0052459 A1	19820526	EP0052459 B1 19851204; JPH0515383 A 19930126	GB19800036967 19801118; GB19810020991 1981070	HOLMES P A; WRIGHT L F; COLLINS S H	ICI PLC	β -Hydroxybutyrate polymers.
EP0069497 A2	19830112	AU8410882 A 19830113; EP0069497 A3 19830216; NZ201054 A 19851108; AU560653 B2 19870416; EP0069497 B1 19870415; JPH06172501 A 19940621; JP7047623 B 19950524	EP19810305186 19811030; GB19810020991 19810707; GB19820013697 19820512	HOLMES P A; WRIGHT L F; COLLINS S H	ICI PLC	Copolyesters and process for their production.
EP0260415 A2	19880323	US4757128 A 19880712; EP0260415 A3 19880518; EP0260415 B1 19961127; NL990036 I1 19991201; LU90462 A 20000103; JPS63258924 A 19881026; GR3022577 T3 19970531; GR88300163 T1 19890131; ES2006417 T3 19970701; DEE260415 19890216; DE3751964 T2 19970605; CA1274339 A1 19900918; AT145657 T 19961215	US19860892809 19860801	DOMB AB; LANGER R	MASSACHUSETTS INST TECHNOLOGY	High molecular weight polyanhydride and preparation thereof.
EP0261572 A1	19880330	JPS63101378 A 19880506; BR8704814 A 19880517	DE19863632103 19860920; DE19873708915 19870319	MUELLER M	BOEHRINGER INGELHEIM KG; BOEHRINGER INGELHEIM INT	Process for the production of lactide.

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TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
EP0266603 A1	19880511	US4789724 A 19881206; KR960006410 B1 19960515; JPS63199227 A 19880817; DE266603 T1 19890216; DE3752381 T2 20051110; A1278141 C 19901218; AT285432 T 20050115	US19860920724 19861017	DOMB AB; LANGER R	MASSACHUSETTS INST TECHNOLOGY	Preparation of anhydride copolymers.
EP0349505 A2	19900103	WO9000067 A1 19900111; CA2314151 A1 19990701; AU3843889 A 19900123; DK46690 A 19900222; NO900878 A 19900514; JPH03500139 A 19910117; AU636570 B 19930506; IL90714 A 19940624; NO302999 B1 19980518; EP0349505 B1 19980916; DE68928817 T2 19990408; ES2121741 T3 19981216; JP2842649 B2 19990106; CA1340634 C 19990706; AT171076 T 19981015	SE19880002414 19880627	BOWALD S F; JOHANSSON E G	ASTRA MEDITEC AB	A novel surgical material.
EP0460608 A2	19911211	JPH0439400 A 19920210; EP0460608 A3 19920422; US5258446 A 19931102; EP0460608 B1 19950412; DE69108778 T2 19951130	JP19900149140 19900606	ENOMOTO M; ITO N	SEIKOH CHEMICALS CO, LTD; AJINOMOTO COMPANY, INC	Suede touch surface finishing composition.
EP0566948 A1	19931027	DE4213323 A1 19931028; JPH0673191 A 19940315; US5329127 A 19940712; EP0566948 B1 19960911	DE19924213323 19920423	BECKER A; LUTTERMANN K; CLAUSSEN U; ORTH P; HEILIGER L; EL SAYED AZIZ	BAYER AG	Improved method for marking plastics.
EP1029890 A2	20000823	KR20000058110 A 2000092; US6544607 B1 20030408; EP1029890 B1 20040728; TW574309 B 20040201; DE60012381 T2 20050504	JP19990039449 19990218	KUROKI T; IKADO S; IWATA M; WANIBE H	MITSUI CHEMICALS INC	Aliphatic polyester composition and stretched film obtained from said composition.
EP1106640 A2	20010613	EP1106640 A3 20020116; US2001007899 A1 20010712;	KR19990056991 19991211	CHUNG H S; LEE J W;	IRE CHEMICAL LTD	

		US6713595 B2 20040330; KR20010055721 A 20010704; JP2001187818 A 20010710		KIM D H; KIM D Y; LEE S W		Biodegradable copolyesters and their preparation.
EP1108737 A2	20010620	US2001004665 A1 20010621; EP1108737 A3 20020116; US6399716 B2 20020604; JP2001187817 A 20010710; KR20010057068 A 20010704	KR19990058816 19991217	CHUNG H S; LEE J W; KIM D H; KIM D Y; LEE S W	IRE CHEMICAL LTD	Biodegradable copolyesters and their preparation.
EP1564235 A1	20050817	US2005182204 A1 20050818; EP1564235 B1 20070411	JP20040037556 20040216	OTOME S; IWAI K; SOHGAWA Y-H	NIPPON CATALYTIC CHEM IND	Biodegradable film.
EP1728818 A1	20061206	JP2006335874 A 20061214; US2006276575 A1 20061207; CN1872902 A 20061206	JP20050162189 20050602	KAO CORP	KAO CORP	Plasticizer for biodegradable resin.
EP327505 A2	19890809	AU2887689 A 19890803; IE890281 L 19890803; NO890361 A 19890804; DK36789 A 19890804; PL277424 A1 19890904; GB2214918 A 19890913; BR8900350 A 19890919; PT89556 A 19891004; CN1036215 A 19891011; ZA8900692 A 19891227; JPH0214228 A 19900118; NZ227762 A 19900828; PH25687 A 19910904; EP0327505 A3 19901010; AU617411 19911128; DE327505 T1 19920813; GR92300067 T1 19920831; IL89096 A 19920906; HU206510 B 19921130; PL159070 B1 19921130; ES2039315 T1 19931001; MX172659 B 19940106; PT89556 B 19940729; IN174313 A1 19941105; AR247411 A1 19941229; RU2026321 C1 9950109; CA1334224 C 19950131; JPH0757827 B 19950621; CN1034872 C 19970514; EP0327505 B1 19970730; AT156166 T 19970815;	GB19880002313 19880203	LAY G; REHM J; STEPTO RT F T; THOMA M	WARNER LAMBERT CO	Polymeric materials made from destructureized starch and at least one synthetic thermoplastic polymeric material.

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TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
		ES2039315 T3 19980116; FI100977 B 19980331; KR0139046 B1 19980501; FI890406 A 19890804; DE68928209 T2 19980903; NO307521 B1 200004017; EP0327505 B2 20011114; ES2039315 T5 20020601; DE68928209 T3 20020822; DK174534 B1 20030512				
FR2782999 A1	20000310	WO0014154 A1 20000316; CA2342723 A1 20000316; AU5523499 A 20000327; EP1112319 A1 20010704; US2001031297 A1 20011018; FR2782999 B1 20020510; EP1112319 B1 20030319; AT234894 T 20030415; DE69906099 E 20030424; US7148272 B2 20061212	FR19980011269 19980909	REYNES P; MESSAGE A	ULICE SA	Biodegradable material based on polymer and cereal flour, method for making same and uses
FR2786098 A1	20000526	WO0030618 A1 20000602; AU1278000 A 20000603; EP1131056 A1 20010912; JP2002530323 A 20020917; US6630171 B1 20031007; EP1131056 B1 20051019; AT306905 T 20051115; ES2251236 T3 20060416; DE69927841 T2 20060713; JP4927256 B2 20120509	FR19980014863 19981120; WO1999FR02859 19991119	HUILLE S; NICOLAS F; BRISON N; SOULA G	FLAMEL TECH SA	Particles based on polyamino-acid(s) and methods for preparing same.
GB1590261 A	19810528		GB19780003002 19780125	SHALABY W S; JAMIOLKOWSKI D D	ETHICON INC	Isomorphic copolyoxalates and sutures thereof.
GB2284477 A	19950607	DE4340914 A1 19950608; GB2284477 B 19971210; US5510619 A 19960423	DE19934340505 19931127; DE19934340914 19931201	ZACHMANN G; GAST J; SIMON A; SCHUEBEL R	BRUKER ANALYTISCHE MESSTECHNIK	Identification of plastics by infrared spectroscopy.
GB2464285 A	20100414	US2011200771 A1 20110818; MX2011003798 A 20110729; WO2010041063 A2 20100415; WO2010041063 A3 20100916;	GB20080018407 20081008	BARCLAY A	WELLS PLASTICS LTD	Transition metal additives for enhancing polymer degradation.

		EP2334723 A2 20110622; CN102177196 A 20110907				
JP2000302956 A	20001031	JP3383256 B2 20030304	JP20000024209 20000201; JP19990039449 19990218	KUROKI T; IMON S; IWATA M; WANIBE H	mitsui chemicals inc	Aliphatic polyester composition and oriented film thereof.
JP2001098065 A	20010410	JP3647689 B2 20050518	JP19990278020 19990930	KIDAI O; SHIRAHAMA R	mitsubishi chem corp	Method for preparation of aliphatic polyester.
JP2004175999 A	20040624	JP3680136 B2 20050810	JP20020346209 20021128	KOBAYASHI H; KAJIYAMA T; TAGUCHI T; TANAKA J	NAT INST FOR MATERIALS SCIENCE	Method for producing poly(malic acid).
JP2005211041 A	20050811		JP20040025685 20040202	MUKOYAMA M	NIPPON CATALYTIC CHEM IND	Method for producing succinic acid.
JP2005264155 A	20050929		JP20040037556 20040216; JP20050038953 20050216	OTOME S; IWAI K; SAGAWA Y	NIPPON CATALYTIC CHEM IND	Biodegradable film.
JP2005320426 A	20051117	JP4621885 B2 20110126	JP20040139173 20040507	KOBAYASHI H; KAJIYAMA T; TAGUCHI T; TANAKA J	NAT INST FOR MATERIALS SCIENCE	Manufacturing process of poly(malic acid) copolymer.
JP2011219736 A	20111104		JP20100065873 20100323; JP20110031495 20110217		TORAY IND INC	Polyalkylene terephthalate resin composition and fiber comprising same.
JPH0413710 A	19920117	JPH0749459 B 19950531	JP19900116146 19900502	TORII H	REGURUSU KK	Polyurethane-based resin.
JPH05148352 A	19980615	JP3079716 B2 20000821	JP19910335579 19911126	DOI Y; TAKIYAMA E	SHOWA HIGHPOLYMER, CO LTD	Production of polylactide containing urethane bond.
JPS63251424 A	19881018	JP2507731 B2 19960619	JP19870085262 19870407	SASAKI S; SUMI T	UNITIKA LTD	Production of butylene adipate.
JPH083302 A	19960109	JP3342579 B2 20021111	JP19940162621 19940620	MUKAI K; KASAI M; IWAYA Y	UNITIKA LTD	Production of aliphatic polyester.
JPH08301996 A	19961119		JP19950129216 19950427	YAGI T; YAMAMOTO M; MURAFUJI Y	KANEBO LTD	Method for polymerizing polyester.
JPH0931174 A	19970204	JP3390571 B2 20030324	JP19950178758 19950714	MUKAI K; YAMADA Y; IWAYA Y	UNITIKA LTD	Polyethylene succinate of high molecular weight and production thereof.
JPH0931176 A	19970204	JP3434622 B2 20030811	JP19950184271 19950720	TAKIYAMA E; FUJIMAKI T;		

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TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
				HATANO Y; ISHIOKA R	SHOWA HIGHPOLYMER CO, LTD; SHOWA DENKO KK	Production of biodegradable aliphatic polyester.
NL1007186C C2	19990407	WO9916810 A1 19990408; CA2305364 A1 19990408; AU9190298 A 19990423; EP1036106 A1 20000920; CN1281478 A 20010124; KR20010030837 A 20010416; JP2001518539 A 20011016; US2002055609 A1 20020509; AU746623 B2 20020502; US6387496 B1 20020514; US6392006 B1 20020521; EP1036106 B1 20030813; AT247143 T 20030815; ES2205543 T3 20040501; TW588069 B 20040521; DE69817216 T2 20040609; JP3643032 B2 20050427; IL135396 A 20050725; KR100524455 B1 20051026	NL19971007186 19971001	BENTHEM VAN R A; RIETBERG J; STANSSENS D A W	DSM NV	Condensation polymers containing hydroxyalkylamide groups.
SU1016314 A1	19830507		SU19792854648 19791217	ZAALISHVILI M M; KATSARAVA R D; KARTVELISHVILI T M	INST FIZIOL IM I S BERITASHVIL	Process for producing polyester urethanes.
US2001045518 A1	20011129	US6610981 B2 20030826	US20010841519 20010424; US20000200720P 20000427	SOMMER E J	SOMMER E J; NATIONAL RECOVERY TECHNOLOGIES INC	Method and apparatus for near-infrared sorting of recycled plastic waste.
US2004023028 A1	20040205	US6884432 B2 20050426	US20030423209 20030425; US20020375453P 20020425	ASZEMSKI M J; CURRIER B L; LU L; ZHU X; JABBARI E	MAYO FOUNDATION	Blend, cross-linkable poly(propylene fumarate) for immobilization and controlled drug delivery.
US2005095679 A1	20050505	US7364875 B2 20080429	US20040974442 20041027; US20030515879P 20031030; US20040590727P 20040723	PRESCOTT A G; STOCK L R II	CRESCENT INNOVATIONS INC	Method for producing medical and commercial grade poly- γ -glutamic acid of high molecular weight.

US2006283340 A1	20061221	DE102005027861 A1 20061228; DE102005027861 B4 20120802; US7467585 B2 20081223	DE200510027861 20050616	PALLMANN H	PALLMANN MASCHINENFABRIK GMBH & CO KG	Vorrichtung zum Umwandeln von schüttfähigem Ausgangsmaterial zu Granulaten, Agglomeraten, Pellets, Presslingen und dergleichen. "Apparatus for converting free-flowing feed material into granules, agglomerates, pellets, compacts, and the like."
US2008103232 A1	20080501	WO2008055240 A1 20080508; EP2087033 A1 20090812; AU2007313630 A1 20080508; CN101589097 A 20091125; JP2010508425 A 20100318	US20060855430P 20061031	LAKE J A; ADAMS S D	BIO TEC ENVIRONMENTAL LLC	Chemical additives to make polymeric materials biodegradable.
US2008166789 A1	20080710	WO2009117022 A1 20090924; CA2675487 A1 20090917; MXPA09009083 A 20091031; CN101657499 A 20100224; EP2254942 A1 20101201; KR20100137343 A 20101230; JP2011514427 A 20110506; US7939582 B2 20110510; CA2675487 C 20120508	US20050041322 20050124; US20070747481 20070511; US20080049668 20080317	GROSSMAN R F	BIOTECH PRODUCTS LLC	Compostable vinyl acetate polymer compositions, composites, and landfill biodegradation prodegradant.
US2010028512 A1	20100204		US20090577480 20091012; US20080210208 20080914; US20080040349P 20080328	KRIEGEL R M; HUANG X; SCHULTHEIS M W; BIPPERT D A; INSOLIA G E; KOLLS B; SUMMERVILLE S	COCA COLA CO	Bio-based polyethylene terephthalate packaging and method of making thereof.
US2010175691 A1	20100715	WO2010083356 A1 20100722; KR20110094345 A 20110823; MXPA11007535 A 20110831; EP2376538 A1 20111019; CN102239185 A 20111109	US20100686619 20100113; US20090144775P 20090115; US20100686619 20100113; US20090144775P 20090115	COMBS M T; WOODSON B R	CELANESE ACETATE LLC	Process for cycling cellulose acetate ester waste.

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TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
US2010272940 A1	20101028	WO2010125490 A2 20101104; WO2010125490 A3 20110414; AU2010243295 A1 20111020; MX2011011366 A 20111118; EP2424937 A2 20120307; KR20120023624 A 20120313; CN102414267 A 20120411	US20090430968 20090428	SHI BO; WANG J H	KIMBERLY-CLARK WORLDWIDE, INC	Algae-blended compositions for thermoplastic articles.
US2012135169 A	20120531		EP20090160670 20090519; WO2010EP56762 20100518	ANGELDER R; WEBER K; VAN DE MELJDEN J; PLIJTER J; SCHENNINK G	ANGELDER R; WEBER K; VAN DE MELJDEN J; PLIJTER J; SCHENNINK G	Bioplastics.
US2012214213 A1	20120823		US201113031350 20110221	CHEN G-Q; LI Z-J; GUO Y-Y; LU W-C; ZHOU Z-Z	TIANJIN GREENBIO MATERIAL CO LTD	Recombinant hosts and methods for manufacturing polyhydroxyalkanoate.
US2071251 A	19370216		US19330660778 19330314; US19310548701 19310703		DU PONT	Fiber and method of producing it.
US2111762 A	19380322		US19360057851 19360106	CARLETON E	ELLIS FOSTER CO	Resinous compositions from oxalic acid and polyhydric alcohols and process of making same.
US3619222 A	19711109		US19700008019 19700202	WERLE E E; MITCHELL T	DARLING & CO	Modified protein composition and method of forming insoluble seals.
US4057537 A	19771108		US19750544788 19750128	SINCLAIR R	GULF OIL CORP	Copolymers of L-(–)-lactide and ε- caprolactone .
US4078331 A	19780314		US19760680820 19760428	RAMUS J S	MOBIL OIL CORP	Process and culture composition for growth of algae and synthesis of biopolymer.
US4079038 A	19780314		US19760664127 19760305	CHOI NAM SOK; HELLER J	ALZA CORP	Poly(carbonates).
US4131648 A	19781226		US19750544805 19750128	CHOI NAM SOK; HELLER J	ALZA CORP	Structured orthoester and orthocarbonate drug delivery devices.

US4141087 A	19790227		US19770752374 19770119	SHALABY W S; JAMIOLKOWSKI D D	ETHICON INC	Isomorphic copolyoxalates and sutures thereof.
US4180646 A	19791225		US19780883123 19780303; US19750544808 19750128	CHOI NAM SOK; HELLER	ALZA CORP	Novel orthoester polymers and orthocarbonate polymers.
US4236349 A	19801202		US19780927698 19780724	RAMUS J S	MOBIL OIL CORP	Algae biopolymer production.
US4372311 A	19830208		US19800186429 19800912	POTTS J E	UNION CARBIDE CORP	Disposable articles coated with degradable water-insoluble polymers.
US4440921 A	19840403		US19820390350 19820621	ALLCOCK H R; NEENAN T X ; KOSSA W C	RESEARCH CORP	Coupling of polyorganophosphazenes to carboxylic acid.
US4450150 A	19840522		FR19740034307 19741011; US19730361182 19730517	SIDMAN K R	LITTLE INC A	Biodegradable, implantable drug delivery depots, and method for preparing and using the same.
US4490326 A	19841225		US19820433177 19821006; US19810288274 19810730	BEROFF H; THOMPSON D R; MERICLE R W; TRAVIS JR W C	ETHICON INC	Molding process for polydioxanone polymers.
US4495174 A	19850122		US19820390345 19820621	ALLCOCK H R; AUSTIN P E; NEENAN T X	RESEARCH CORP	Anesthetic polyorganophosphazenes.
US4673438 A	19870616		US19850796517 19851108; US19840579318 19840213	WITTWER F; TOMKA I	WARNER LAMBERT CO	Polymer composition for injection molding.
US4880622 A	19891114		US19860865504 19860520	ALLCOCK H R; AUSTIN P E	RES CORP TECHNOLOGIES INC	Water-soluble phosphazene polymers having pharmacological applications.
US4946938 A	19900807		US19890388539 19890801	MAGILL J H; MERKER R L	UNIV PITTSBURGH	A process for the catalytic synthesis of polyphosphazenes.
US5171308 A	19921215		US19920834794 19920213; US19900522134	GALLAGHER F G; HAMILTON C J; HANSEN S M;	DU PONT	Polyesters and their use in compostable products such as disposable diapers.

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TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
			19900511; US19910645849 19910125; US19910645995 19910125	SHIN H; TIETZ R F		
US5315010 A	19940524	WO9500479 A1 19950105; US5391764 A 19950221; JPH08512066 A 19961217; EP0746543 A4 19960912; EP0746543 A1 19961211; EP0746543 B1 20020918; DE69431408 T2 20030116	US19940219667 19940329; US19930080562 19930621; US19910660355 19910222	KOSKAN L P; LOW K C; MEAH A R Y; ATENCIO A M	DONLAR CORP	Polyaspartic acid manufacture.
US5362777 A	19941108		US19930115243 19930830; CH19880004083 19881103; US19900536683 19900711; US19910785931 19911031	TOMKA I	TOMKA I	Thermoplastically processable starch and a method of making it.
US5439688 A	19950808		US19910790033 19911112; CH19890002829 19890728; CH19900003616 19901114; US19900555973 19900720	ORSOLINI P; HEIMGARTNER F	DEBIO RECH PHARMA SA	Process for preparing a pharmaceutical composition.
US6077916 A	20000620		US19980090374 19980604; US19970048523P 19970604	LAURENCIN C; ALLCOCK H; IBIM S; AMBROSIO A; KWON M	PENN STATE RES FOUND	Biodegradable mixtures of polyphosphazene and other polymers.
US6428767 B1	20020806	US2003082756 A1 20030501; US7169588 B2 20070130	US19990369796 19990806; US19970966794 19971110; US19950440293 19950512	BURCH R R; DORSCH R R; LAFFEND L A; NAGARAJAN V; NAKAMURA C	DU PONT; GENENCOR INT	Method for identifying the source of carbon in 1,3-propanediol.
WO0027923 A1	20000518	E19852081 C1 20000727; AU1774700 A 20000529; EP1129140 A1 20010905; EP1129140 B1 20020724; DE59902150 G 20020829; JP2002529567 A 20020910; ZA200103577 A 20020925;	DE19981052081 19981111	NAEGELE H; PFITZER J; EISENREICH N; EYERER P; ELSNER P; ECKL W	FRAUNHOFER GES FORSCHUNG; TECNARO GES ZUR IND ANWENDUNG	Kunststoff-werkstoff aus einem polymer-blend. "Plastic material made from a polymer blend."

		US6509397 B1 20030121; ES2183631 T3 20030316; JP3725428 B2 20051214				
WO0062630 A1	20001026	WO0063263 A1 20001026; AU4351800 A 20001102; CA2369758 A1 20001026; CA2370330 A1 20001026; CA2370357 A1 20001026; US6306821 B1 20011023; AU4644700 A 20001102; AU4351800 A 20001102; AU4349600 A 20001102; EP1171006 A1 20020116; EP1194463 A1 20020410; EP1210379 A1 20020605; EP1194463 A4 20020925; EP1210379 A4 20020925; EP1171006 A4 20020925; JP2002542352 A 20021210; JP2002542339 A 20021210; JP2002542349 A 20021210; AU760358 B 20030515; AU770579 B2 20040226; AU775913 B2 20040819; EP1171006 B1 20060329; AT321803 T 20060415; DE60026983 E 20060518; EP1210379 B1 20070321; CA2369758 C 20070403; CA2370357 C 20070410; AT357468 T 20070415; DE60034045 T2 20071122; CA2370330 C 20090120; EP1194463 B1 20091111; AT448274 T 20091115; JP4644374 B2 20110302	US19990129577P 19990416; US19990146991P 19990803; US19990167328P 19991124; US19990167388P 19991124	HE S; YASZEMSKI M J; MIKOS A G	UNIV WM MARSH RICE	Poly(propylene fumarate) cross linked with poly(ethylene glycol).
WO0107166 A1	20010201	DE19934259 A1 20010208; EP1200194 A1 20020502; SK962002 A3 20020604; CZ20020269 A3 20020717; HU0201525 B 20020828	DE19991034259 19990727	HOLLEY W; HUBER K; KATZSCHNER G; PFEIFFER T	FRAUNHOFER GES FORSCHUNG	Verfahren zur selektiven Abtrennung von vorgebbaren Stoffen aus Stoffgemischen. "Method for selectively separating predetermined materials in mixtures of materials."
WO0111070 A2	20010215	EP1222303 A2 20020717; WO0111070 A3 20010830		BURCH R R; DORSCH R R; LAFFEND L A; NAGARAJAN V; NAKAMURA C	DU PONT	1,3-Propanediol and polymer derivatives from a fermentable carbon source.

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TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
WO0112833 A2	20010222	WO0112833 A3 20010830; BR0013315 A 20020402; EP1204755 A2 20020515; KR20020059364 A 20020712; US6514733 B1 20030204; CN1379818 A 20021113; JP2003507022 A 20030225; US2003157674 A1 20030821; EP1586647 A1 20051019; US7067300 B2 20060627; EP1204755 B1 20060809; PT1204755 E 20061130; DE60029971 T2 20070516; CN1298852 C 20070207; CN101024843 A 20070829; KR100785997 B1 20071214; CA2733616 A1 20010222; JP4716634 B2 20110706; CA2380616 C 20110524	US19990149534P 19990818	EMPTAGE M; HAYNIE S; LAFFEND L A; PUCCI J; WHITED G	DU PONT	Process for the biological production of 1,3-propanediol with high titer.
WO03097468 A1	20031127	CA2486312 A1 20031127; AU2003242308 A1 20031202; KR20040104742 A 20041210; EP1555209 A1 20050720; US2005175801 A1 20050811; CN1652976 A 20050810; CN100436271 C 20081126; US2009030094 A1 20090129; JP4476803 B2 20100609; AT469035 T 20100615; US7799837 B2 20100921	US20080232365 20080916; JP20020146095 20020521; US20040514048 20041110; WO2003JP06134 20030516	YAMANE K; KATO R; SATO H	KUREHA CHEM IND CO LTD	Bottle excellent in recyclability and method for recycling the bottle.
WO2004085533 A1	20041007	DE10313939 A1 20041014; EP1608700 A1 20051228; CN1809611 A 20060726; US2006264539 A1 20061123; JP2007524715 A 20070830; JP4277040 B2 20090610; CN100439439 C 20081203; EP1608700 B1 20110629	DE20031013939 20030327	MOSSEVELD H; WIERER K A; KOHLLHAMMER K	WACKER POLYMER SYSTEMS GMBH	Verwendung von Polymerisaten zur Stärkernodifizierung. "Use of polymers for starch modification."
WO2005054373 A1	20050616	JP2005162871 A 20050623; JP2005162872 A 20050623; JP2005162873 A 20050623; EP1690899 A1 20060816;	WO2004JP17728 20041129; JP20030403475 20031202;	HORIE T; YAMADA S; FUJIHIRA Y; MORI H	SONY CORP	Resin composition, molding thereof, and process for producing the resin composition.

		KR20060117961 A 20061117; CN1914278 A 20070214; US2007270527 A1 20071122; US7645823 B2 20100112; CN101864155 A 20101020	JP20030403477 20031202; JP20030403476 20031202			
WO2007020904 A1	20070222	EP1921098 A1 20080514; KR20080046655 A 20080527; CN101238161 A 20080806; US2009127915 A 20090521; EP1921098 A4 20101027; KR100944893 B1 20100303; CN101238161 B 20110706; JP4932721 B2 20120516; EP1921098 B1 20120808	JP20050234527 20050812; WO2006JP315967 20060811	NOZAWA K; SASAKI M; OHKUBO K	MITSUI CHEMICALS POLYURETHANES	Composition for polyurethane foam, polyurethane foam obtained from the composition, and use thereof.
WO2007033418 A1	20070329	EP1945690 A1 20080723; CN101296958 A 20081029; JP2009508598 A 20090305; EP1945690 A1 20080723; US2009175921 A1 20090709; US7964696 B2 20110621; US2011287102 A1 20111124; CN101296958 B 20120718	AU20050905192 20050920	GUNATILLAKE P A; MOORE T G; ADHIKARI R	POLYNOVO BIOMATERIALS PTY LTD; GUNATILLAKE P A	Chain extenders.
WO2008038648 A1	20080403	KR20090054454 A 20090529; EP2080787 A1 20090722; CN101541887 A 20090923; CN101541887 B 20120718; US2010086718 A1 20100408; US8048502 B2 20111101; KR110018895 B1 20120319	WO2007JP68633 20070926; JP20060260540 20060926	YOSHIKAWA S; YOSHIDA M; KOGURE M	TOYO SEIKAN KAISHA LTD	Readily degradable resin composition, and biodegradable container using the same.
WO2008067627 A2	20080612	AU2007329122 A1 20080612; BRPI0605173 A 20080722; WO2008067627 A3 20080724; EP2099735 A2 20090916; US2010069691 A1 20100318; JP2010511634 A 20100415	BR2006PI05173 20061205	MORSCHBACKER A L R D	BRASKEM SA	A method for the production of one or more olefins, an olefin, and a polymer.
WO2009070858 A1	20090611	AU2008331448 A1 20090611; EP2162475 A1 20100317; KR20100103783 A 20100928; JP2011506628 A 20110303; US2011213104 A1 20110901; EP2162475 B1 20111012; ES2372235 T3 20120117; US8222354 B2 20120717	BR2007PI04605 20071205	MORSCHBACKER A L R D	BRASKEM SA	Integrated process for the production of ethylene- butylene copolymer, an ethylene-butylene copolymer and the use of ethylene and 1-butylene, as comonomer, sourced from renewable natural raw materials.
WO2009095363 A1	20090806	MX2010007943 A 20100810; EP2238195 A1 20101013;	EP20080150748 20080129	MIJOLOVIC D; HAUNERT A;	BASF SE	Method for the production of polyether polyols.

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Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
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WO2009120457 A2	20091001	US2009246430 A1 20091001; WO2009120457 A3 20091126; TW201002756 A 20100116; AU2009229151 A1 20091001; MXPA10009905 A 20100930; EP2265659 A2 20101229; CA2718279 A1 20091001; CN101970530 A 20110209; JP2011527348 A 20111027; US2011262669 A1 20111027	US20080210208 20080914; US20080040349P 20080328	KRIEDEL R M; HUANG X; SCHULTHEIS M W	COCA COLA CO	Bio-based polyethylene terephthalate polymer and method of making the same.
WO2010123095 A1	20101028	WO2010123095 A1 20101028; JP2010254812 A 20101111; KR20120014243 A 20120216; CN102414247 A 20120411	JP20090106684 20090424	MATSUO T; KAMIKAWA M; OKA K; KONDO T; ITO H; SASE Y	HITACHI PLANT TECHNOLOGIES LTD	Method and device for synthesizing polyester.
WO2010133560 A1	20101125	CA2762988 A1 20101125; AU2010251208 A1 20111208; EP2432830 A1 20120328; CN102482461 A 20120530	EP20090160670 20090519; WO2009NL50730 20091201	WEBER K; VAN DER MEIJDEN J; PLIJTER J; VAN SOEST J; SCHENNINK G	WACKER CHEMIE AG; MENEBA B V	Bioplastics.
WO2010139056 A1	20101209	CA2763986 A1 20101209; US2012071591 A1 20120322	US20090213340P 20090601	MOHANTY A K; MISRA M; SAHOO S	UNIV GUELPH	Lignin based materials and methods of making those.
WO2011005664 A2	20110113	WO2011005664 A3 20110428; CN102471473 A 20120523; EP2451860 A2 20120516	WO2010US40829 20100701; US20090224134P 20090709; US20090223042P 20090705	SCOTT A	NOVOMER INC	Structurally precise poly(propylene carbonate) compositions.
WO2011066634 A2	20110609	WO2011066634 A3 20111006; BRPI0904979 A2 20110719	BR2009PI04979 20091204	PEREIRA G G; PEREZ J R; CARAZZOLLE M F; MORSCHBACKER A L R D; ROZA L; ANDRADE M H D S	BRASKEM SA; UNIV ESTADUAL CAMPINAS-UNICAMP	A method for the production of olefins, an olefin, a polyolefin, and use of the polyolefin.
WO2012004402 A1	20120112		GB20100011542 20100708	STEVENS M M; MAY J R; GENTILINI C	IMP INNOVATIONS LTD	Process for preparation of polymer body.

WO8103278 A1	19811126	US4304767 A 19811208; ZA8103269 A 19820630; SE8200068 A 19880808; SE455791 B 19880808; PT73035 A 1981061; PT73035 B 19841022; NZ197036 A 19840203; NL8120177 A 19820401; NL188166 C 19920416; JPS57500613 A 19820408; JPS60214745 A 19851028; JPS60221424 A 19851106; JPH02218719 A 19900831; JPH03732 A 19910107; IE811098 L 19811115; IE51287 B1 19861126; GR74902 A1 19840712; GB2086404 A 19820512; ES8207564 A1 19821216; EP0051667 A1 19820519; EP0051667 B1 19860305; DK16082 A 19820115; DE3148618 A1 19820715; CH657369 A5 19860829; CA1186438 A1 19850430; BE888829 A1 19810828; AU543991 B2 19850509; AT384615 B 19871210	US19800150052 19800515	HELLER J; HELWING R; PENHALE D	STANFORD RES INST INT	Polymers of di-ketene acetals (and higher functionality) and polyols.
WO9309172 A1	19930513	JP2003176289 A 20030624; TW211035 A 19930811; EP0616621 A1 19940928; US5397819 A 19950314; JPH07507074 A 19950803; US5461136 A 19951024; EP0700961 A2 19960313; EP0700961 A3 19960410; US5553714 A 19960910; EP0616621 B1 19961218; DE69216114 E 19970130; ES2095494 T3 19970216; MX184254 B 19970325; SG47881 A1 19980417; CA2121507 C 19980616; EP0875505 A2 19981104; EP0700961 B1 19981223; DE69228010 E 19990204	US19910789570 19911108; WO1992US08676 19921013; US19930156746 19931124	CUSHMAN M R; KRUTAK J J SR; PARHAM W W; COATES C A JR; WEAVER M A; PATONAY G	EASTMAN CHEM CO	Method for tagging thermoplastic materials with near-infrared fluorophores.

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TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
WO9514740 A1	19950601	AU8133694 A 19950613	US19930160561 19931124	GALLAGHER F G; GRAY D S; HAMILTON C J; TIETZ R F; WALLENBERGER F T	DU PONT	Apertured structures of biodegradable polyesters.
WO9529710 A1	19951109	AU2432295 A 19951129; US5733951 A 19980331	US19940234551 19940428	MIKOS A G; YASZEMSKI M J; PAYNE R G	RICE UNIVERSITY	Poly(propylene fumarate).
WO9625446 A1	19960822	WO9625448 A1 19960822; DE19505186 A1 19961031; EP0809664 A1 19971203; JPH11500157 A 19990106; US5889135 A 19990330; ES2147918 T3 20001001; EP0809664 B1 20000517; EP0809666 A1 19971203; EP0809666 B2 20020814; DK809664 T3 20000828;	DE19951005185 19950216	WARZELHAN V; PIPPER G; SEELIGER U; BAUER P; PAGGA U; YAMAMOTO M	BASF AG	Biodegradable polymers, process for producing them, and their use in preparing biodegradable moldings.
WO9806439 A1	19980219	CA2213368 A 19980216; EP0830859 A2 19980325; US5980948 A 19991109; EP1247522 A1 20021009; EP0830859 B1 20031210; AT255884 T 20031215; DE69726672 T2 20041007; DK830859 T3 20040405; EP1247522 B1 20040519; AT267006 T 20040615; DE69729228 T2 20050504; ES2212037 T3 20040716; PT830859 E 20040430; PT1247522 E 20041029; ES2221916 T3 20050116; CA2213368 C 20080401	US19960699896 19960816	BEZEMER J M; DE BRUIJN J D; FEIJEN J; GOEDEMOED J H; HENNINK W E; VAN BITTERSWIJK C A	OSTEOTECH INC	Polyether-ester copolymers as drug-delivery matrices.
WO9806785 A1	19980219	CA2263290 A1 19980219; EP0918825 A1 19990602; US6284838 B1 20010904; AT209669 T 20011215; ES2168652 T3 20020616; DK918825 T3 20020325;	CH19960001967 19960812; CH19960002687 19961031; CH19960003015 19961209; CH19970000013 19970106	SILBIGER J	SILBIGER J	Biodegradable composition.

WO9828080 A1	19980702		WO1996DE02510 19961223	KOEHNLECHNER R	HAMOS GMBH RECYCLING UND SEPARATIONSTECHNIK	Vorrichtung zum elektrostatischen sortieren von Gemischen aus Teilchen unterschiedlicher Kunststoffe. "Device for electrostatically sorting mixtures of particles of different plastic materials."
WO9828357 A1	19980702	CA2275033 A1 19980702; AU5472198 A 19980717; EP0946624 A1 19991006; US6042820 A 20000328; JP2000509428 A 20000725; NZ336718 A 20010126; BR9714065 A 20001024; AU729305 B2 20010201; US6287604 B1 20010911; US6312732 B1 20011106; JP2002138139 A 20020514; US6042820 A 20000328; EP0946624 B1 20030402; AT236207 T 20030415; DK946624 T3 20030714; PT946624 E 20030829; JP2003261661 A 20030919; ES2196385 T3 20031216; DE69720516 T2 20040219; CA2275033 C 20050802; US2005163745 A1 20050728	US19960770850 19961220	SOKOLL K K; CHONG P; KLEIN M H	CONNAUGHT LAB	Biodegradable copolymer containing α -hydroxy acid and α -amino acid units.
WO9851812 A2	19891119	AU7486798 A 19981208; WO9851812 A3 19990211; EP0981381 A2 20000301; US6245537 B1 20010612; US2001009769 A1 20010726; US6623749 B2 20030923; US2004053381 A1 20040318; EP0981381 B1 20070221; AT354600 T 20070315; PT981381 E 20070430; DK0981381 T3 20070604; US7244442 B2 20070717; DE69837141 T2 20071031; ES2285770 T3 20071116; US2007280899 A1 20071206; US7906135 B2 20110315; US2011135707 A1 20110609; US8231889 B2 20120731	US19970046211P 19970512; US19970054289P 19970731; US19970063501P 19971024; US19970065921P 19971117	WILLIAMS S F; MARTIN D P; GERNGROSS T; HOROWITZ D M	METABOLIX INC	Polyhydroxyalkanoates for <i>in vivo</i> applications.

(Continued)

TABLE III Supplementary patents (*Continued*)

Patent number	Pub. date	Family members	Priority number	Inventors	Applicants	Title
WO9925756 A1	19990527	EP0961805 A1 19991208; DE19750846 C1 20000127; US2002061943 A1 20020523; EP0961805 B1 20040414; AT264355 T 20040415; DK961805 T3 20040802; US6958369 B2 20051025	DE19971050846 19971117	BERGER W; JEROMIN L; MIERAU U; OPITZ G	BIOP BIOPOLYMER GMBH	Komponente zur Herstellung von Polymermischungen auf der Basis von Stärke und Verfahren zur Herstellung der Komponente. "Component for producing polymer mixtures on the basis of starch and a method for producing the same."
WO9929733 A1		NL1007735 C2 19990609; CA2313516 A1 19990617; AU1446599 A 19990628; NL1009449 C6 19991221; EP1040127 A1 20001004; EP1040127 B1 20020605; AT218585 T 20020615; PT1040127 E 20021031; DE69805848 T2 20021107; US6482341 B1 20021119; ES2175821 T3 20021116; HK1031887 A1 20021220; CA2313516 C 20080429; DK1040127 T3 20020708	NL19971007735 19971208; NL19981009449 19980619	JONGBOOM R O J; STUUT P I; RODENBURG J A	RODENBURG VEEVOEDERS B V	Biodegradable moldings.
WO9932536 A1	19990701	AU1942999 A 19990712; EP1042388 A1 20001011; JP2001527101 A 20011225; AU751610 B2 20020822; CA2314151 C 20041026; EP1659142 A1 20060524; DK1042388 T3 20061211; EP1042388 B1 20061115; AT345359 T 20061215; PT1042388 E 20070131; DE69836439 T2 20070524; ES2281147 T3 20070916; EP2258742 A1 20101208; EP2196484 A1 20100616; JP4376455 B2 20091202; AT461957 T 20100415; ES2356350 T3 20110407; EP2196484 B1 20120822	US19970068455P 19971222	MARTIN D P; SKRALY F A; WILLIAMS S F	METABOLIX INC	Polyhydroxyalkanoate compositions having controlled degradation rates.

Appendix IV

Databases Consulted

esp@cenet[®] of the European Patent Office (EPO): <http://espacenet.com>.

United States Patent and Trademark Office (USPTO): <http://patft.uspto.gov>.

Japanese Patent Office (JPO): http://www.ipdl.inpit.go.jp/homepg_e.ipdl.

Derwent World Patents Index[®] (DWPISM), produced by Thomson Reuters Scientific: <http://library.dialog.com>.

Google Patents: <https://www.google.com/?tbn=pts>.

ScienceDirect of Elsevier: <http://www.sciencedirect.com>.

Wiley Online Library of Wiley-Blackwell: <http://onlinelibrary.wiley.com>.

Most relevant classification groups (IPC, EPC), ICO codes (EPO), FI terms (JPO), WPI codes (Derwent), and keywords were used for the retrieval of patent documents.

Biopolymer Database: <http://biopolymer.materialdatacenter.com/bo>.

This database origins from a research project between M-Base and the University of Applied Sciences Hannover, supported by the Agency for Renewable Resources (FNR).

Appendix V

Further Information Sources

Institutions/Organizations

BioEnvironmental Polymer Society (BEPS):
<http://www.beps.org>.

European Bioplastics:
<http://en.european-bioplastics.org>.

Japan BioPlastics Association (JBPA): <http://www.jbpaweb.net/english/english.htm>.

Centre for Sustainable Design (CfSD): <http://cfsd.org.uk>.

Australasian Bioplastics Association: <http://www.bioplastics.org.au/about>.

Belangenvereniging composteerbare producten Nederland (BCP): <http://www.bcpn.nl>.

Information/Magazines/Blogs

biopolymer.net: <http://www.biopolymer.net>.

Bioplastics Magazine:
<http://www.bioplasticsmagazine.com>.

Treehugger: <http://www.treehugger.com>.

bio-plastics.org: <http://www.bio-plastics.org>.

Bioplastic Innovation: <http://bioplastic-innovation.com>.

InnovativeIndustry.net:
<http://www.innovativeindustry.net/pla-recycling-infrastructure>.

α -Amino acid: Amino acid substituted on the α -carbon atom by the substituent R (i.e., $\text{H}_2\text{N}-\text{C}(\text{R})\text{H}-\text{COOH}$). Proteins and other polypeptides are derived from this monomer after the loss of water.

α -Hydroxy acid or 2-Hydroxy acid: Organic compound that consists of a carboxylic acid functional group substituted with a hydroxyl functional group on the adjacent carbon. Two common and simple examples of α -hydroxy acids are lactic acid and glycolic acid (see Figure G1).

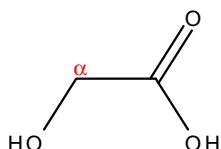


Figure G1 α -Hydroxy acid or 2-Hydroxy acid

β -Hydroxy acid or 3-Hydroxy acid: Organic compound that contains a carboxylic acid functional group and hydroxy functional group separated by two carbon atoms. It is closely related to α -hydroxy acid in which the two functional groups are separated by one carbon atom. Known examples of β -hydroxy acids are β -hydroxypropionic acid (3-hydroxypropionic acid) and β -hydroxybutyric acid (3-hydroxybutyric acid) (see Figure G2).

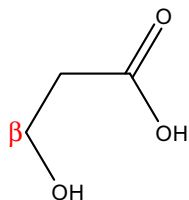


Figure G2 β -Hydroxy acid or 3-Hydroxy acid

γ -Hydroxy acid or 4-Hydroxy acid: Organic compound that contains a carboxylic acid functional group and hydroxy functional group separated by three carbon atoms. A known example of a γ -hydroxy acid is γ -hydroxybutyric acid (4-hydroxybutyric acid or 4-hydroxybutanoic acid) (see Figure G3).

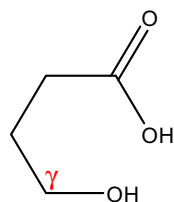


Figure G3 γ -Hydroxy acid or 4-Hydroxy acid

γ -PGA: see Poly(γ -glutamic acid).

ϵ -Poly(L-lysine) (ϵ -PL): Biodegradable and water-soluble natural homopolymer of the essential amino acid L-lysine. It is produced

by bacterial fermentation. ϵ -PL is represented by the chemical formula (see Figure G4):

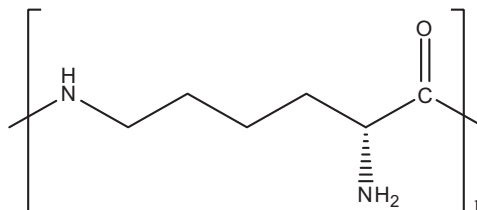


Figure G4 ϵ -Poly(L-lysine) (ϵ -PL)

Actinomyces: Genus of the actinobacteria class of bacteria. They are all Gram positive. All species grow best under anaerobic conditions.

Additive: Substance added to a material or product in order to generate certain properties.

Aerobic: "Requiring oxygen." Aerobic processes can only function in the presence of molecular oxygen (O_2).

Alicyclic compound: Organic compound that is both aliphatic and cyclic, but not aromatic.

Amino acid: Organic acid containing both an amino group and a carboxylic group with the general formula: $\text{H}_2\text{N}-\text{R}-\text{COOH}$. Polyamides are formed from this monomer by loss of water.

Anaerobic: "Deficient in oxygen." Describes environments where there is no molecular oxygen (O_2).

Anaerobic digestion: Degradation of organic matter by bacteria into biomass and biogas (a mixture of methane and carbon dioxide). Occurs in the absence of oxygen and takes place in four steps: (1) hydrolysis; (2) fermentation and acidification; (3) acetogenesis; and (4) methanogenesis. Also called biogasification.

ASTM International: Formerly known as the American Society for Testing and Materials (ASTM), this is an international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services.

Bacterial cellulose: Cellulose produced from certain types of bacteria such as *Acetobacter*, *Sarcina ventriculi*, and *Agrobacterium*. Bacterial cellulose has the same molecular formula as plant cellulose, but has significantly different macromolecular properties and characteristics. In general, microbial cellulose is more chemically pure and contains no hemicellulose or lignin.

Bagasse: Fibrous material that remains after sugarcane or stalks are crushed to extract their juice. It is currently used as a biofuel and in the manufacture of pulp and paper products, building materials, and, more recently, biopolymers.

Bio-based: Refers to a material or product that is (partly) derived from biomass (plants).

Biocompatible polymer: Polymer that does not cause substantial adverse health effects upon oral ingestion, topical or transdermal application, subcutaneous injection, intramuscular injection, inhalation, implantation, or intravenous injection.

Biocomposite: Biopolymers or synthetic polymers reinforced with natural fibers, such as sisal, flax, hemp, jute, banana, wood, and

various grasses, and/or fillers and additives. Novel biocomposites are based on a biodegradable matrix resin reinforced with natural fibers.

Biodegradable polymer: Polymer that can be broken down chemically by natural biological processes, such as digestion by bacteria or fungi into smaller components that are not harmful to the environment.

Biogasification: see Anaerobic digestion.

Biomass: The weight of all organisms in a given population.

Biomax®: Poly(butylene succinate-terephthalate) copolyester (PBST) marketed by Du Pont. It is a biodegradable polymer based on non-renewable (fossil) resources.

Bionolle™: Poly(ethylene succinate-co-butylene succinate) copolyester marketed by Showa High Polymer Company. Two different grades of Bionolle™ are commercially available: (1) polybutylene succinate (PBS), known as the 1000 series; and (2) polybutylene succinate/adipate (PBSA), known as the 3000 series.

Bioplastic: Substance that contains the biopolymer as an essential component.

Biopolymers: Polymers that are based on renewable raw materials as well as biological and petroleum-based biodegradable polymers.

Biorefinery: Facility that converts biomass – biological materials from living or recently living organisms – into fuels, energy, chemicals, materials, and feed.

Blend: Physical mixture of two or more materials without reactive interaction.

Candida antarctica lipase (Lipase CA): Granular immobilized enzyme that shows very high catalytic activity for the synthesis and degradation of aliphatic polyesters.

Carbon-14, ¹⁴C, or Radiocarbon: Radioactive isotope of carbon with a half-life of 5,730 years. Used in carbon dating and carbon labeling. Cosmic rays collide with the atmosphere to create secondary cosmic rays in the form of energetic neutrons. When these energetic neutrons collide with a ¹⁴N atom, it turns into a ¹⁴C atom and a hydrogen atom. Since nitrogen gas makes up about 78% of the Earth's air by volume, a considerable amount of ¹⁴C is produced. These ¹⁴C atoms combine with oxygen to form carbon dioxide, which is used by plants in photosynthesis, so new plant material will contain both ¹⁴C and ¹²C. A product made from renewable resources (biomass) will have a relatively high level of ¹⁴C, while a product made from fossil-based resources will have no ¹⁴C. The percentage of renewable carbon in a material (solid or liquid) can be measured with an accelerator mass spectrometer.

Carbon footprint (CP): The total amount of greenhouse gases emitted directly and indirectly to support human activities, usually expressed in equivalent tons of either carbon or carbon dioxide. Countries calculate carbon footprints as part of their reporting requirements, as do companies, regions, and individuals.

Casein: Natural polymer extracted from skim milk proteins.

Castor oil: Triacylglycerol composed of 85–90% 12-hydroxyoleic acid. Castor oil is a unique natural material and is obtained from the *Ricinus Communis* plant, which grows in tropical regions. Castor oil is the only commercially available natural oil that is produced directly from a natural source. It is used in the production of polyamides such as polyamide 11 (PA 11), polyamide 610 (PA 610), and polyamide 1010 (PA 1010). Also known as ricinoleic acid.

Cellulose: Crystalline polysaccharide of non-cross-linked long chain (C₆H₁₀O₅)_n whose glucose monomeric units are interlinked by β1-4 bonds. These bonds are harder to hydrolyze than the α1-4 bonds present between the glucose molecules that constitute the polymeric chain of the starch. Cellulose is the most common organic compound on Earth, and is the structural component of the primary cell wall of green plants and many forms of algae. About 33% of all plant matter is cellulose (the cellulose content of cotton is 90% and that of wood is 40–50%).

Cellulose acetate: The acetate ester of cellulose prepared by reacting cellulose with acetic acid and acetic anhydride in the presence of sulfuric acid.

Cellulose acetate butyrate: A mixed cellulose ester prepared by treating fibrous cellulose with butyric acid, butyric anhydride, acetic acid, and acetic anhydride in the presence of sulfuric acid.

Cellulose acetate propionate: A mixed cellulose ester prepared by treating fibrous cellulose with propionic and acetic acids and anhydrides in the presence of sulfuric acid.

Cellulose butyrate: The acetate ester of cellulose prepared by reacting cellulose with butyric acid and butyric anhydride in the presence of sulfuric acid.

Cellulose nitrate: The nitrate ester of cellulose prepared by treating fibrous cellulosic materials with a mixture of nitric and sulfuric acids.

CEN: see European Committee for Standardization.

Certification: Procedure by which a third party gives written assurance that a product, process, or service conforms to specified requirements (EN 45020:2006 Standardization and related activities – General vocabulary).

Chymopapain: Proteolytic enzyme isolated from the latex of the fruit papaya (*Carica Papaya*).

Compatibilizer: Polymer or copolymer that, when added to an immiscible polymer blend, modifies its interfacial character and stabilizes its morphology. Compatibilizers usually stabilize morphologies over distances of the order of micrometers or less (IUAPC).

Composite: Multicomponent material comprised of multiple different (nongaseous) phase domains in which at least one type of phase domain is a continuous phase (IUPAC).

Composite laminate: Laminate consisting of one or more layers of a substrate, often fibrous, impregnated with curable polymers or liquid reactants (IUPAC).

Composting: Process of degrading waste materials under conditions no higher than 70 °C (averaging more nearly 55–60 °C), at or near 100% relative humidity, and for durations ranging from two weeks to more than several months. The materials continue to degrade into low molecular weight fragments and/or monomers that can ultimately be completely biodegraded (metabolized) by microorganisms into biomass, biogas, and liquid leachate.

Country codes: Made up of two letters that indicate the country or organization where the patent application was filed or granted (e.g., GB (EPO)).

CP: see Carbon footprint.

“Cradle-to-gate”: LCA system that includes all steps from the extraction of raw materials and fuels, followed by all conversion steps up until the product is delivered to the factory gate. “Cradle-to-gate” analyses are often published by material producers.

“Cradle-to-grave”: LCA system that covers all steps of the “cradle-to-factory gate” system, and also the usage and disposal phases.

Crotonic acid: Unsaturated organic acid (CH₃-CH=CH-COOH) found in croton oil and having many industrial uses.

Cutinase: Hydrolytic enzyme that degrades cutin, the cuticular polymer of higher plants that is a polyester composed of hydroxy and epoxy fatty acids. The fatty acids of cutin are usually *n*-C₁₆ and *n*-C₁₈ and contain between one and three hydroxyl groups. Ester bonds predominate in cutins, although peroxide bridges and ether linkages may also be present.

DCL: see Dicaprolactone.

Deconstructed starch: Starch that has lost most of its crystalline order and so no longer has its natural structure. Since natural starch generally has a granular form, it needs to be deconstructed before it can be melted.

Dicaprolactone (DCL): The cyclic dimer of caprolactone (1,8-dioxacyclotetradecane-2,9-dione).

DIN: see German Institute for Standardisation (DIN).

Disposal: The Waste Framework Directive 2008/98/EC (Annex I, Official Journal of the European Union, 22.12.2008) distinguishes the following disposal operations:

D1: Deposit into or on to land (e.g., landfill, etc.).

D2: Land treatment (e.g., biodegradation of liquid or sludgy discards in soils, etc.).

D3: Deep injection (e.g., injection of pumpable discards into wells, salt domes, or naturally occurring repositories, etc.).

D4: Surface impoundment (e.g., placement of liquid or sludgy discards into pits, ponds, or lagoons, etc.).

D5: Specially engineered landfill (e.g., placement into lined discrete cells which are capped and isolated from one another and the environment, etc.).

D6: Release into a water body except seas/oceans.

D7: Release into seas/oceans; also includes sea-bed insertion.

D8: Biological treatment which results in final compounds or mixtures that are discarded by means of any of the operations D1 to D12.

D9: Physico-chemical treatment which results in final compounds or mixtures that are discarded by means of any of the operations D1 to D12 (e.g. evaporation, drying, calcination, etc.).

D10: Incineration on land.

D11: Incineration at sea¹(*)).

D12: Permanent storage (e.g. emplacement of containers in a mine, etc.).

D13: Blending or mixing prior to submission to any of the operations D1 to D12² (*).

D14: Repackaging prior to submission to any of the operations D1 to D13.

D15: Storage pending any of the operations D1 to D14 (excluding temporary storage and pending collection on the site where the waste is produced).³

Eastar Bio®: Poly(butylene adipate-terephthalate) copolyester (PBAT) produced by Eastman Chemicals. Eastar Bio® technology was bought by Novamont in 2004.

Eco-Indicator 99: A life cycle impact assessment tool developed by PRé Consultants B.V. (<http://www.pre-sustainability.com>). Eco-Indicator 99 helps designers make an environmental assessment of a product by calculating eco-indicator scores for materials and processes used. The resulting scores provide an indication of areas for product improvements. The Eco-Indicator is split into three sections: (1) production of raw materials (e.g., polystyrene), processing & manufacture (e.g. injection molding); (2) transportation of product (e.g., shipping), energy in use (e.g., electricity), and consumables in use (e.g. paper); and (3) disposal.

Ecoflex®: Poly(butylene adipate-terephthalate) copolyester (PBAT) produced by BASF. It is a biodegradable polymer based on non-renewable (fossil) resources and is synthesized from butane diol, adipic acid, and dimethyl terephthalate. Introduced in 1998, Ecoflex® has properties that mimic those of low density polyethylene (LDPE).

Ecotoxicity: Potential environmental toxicity of residues, leachate, or volatile gases produced by biopolymers during biodegradation or composting.

Ecovio®: Blend of Ecoflex® and PLA. Introduced in 2004 by BASF, Ecovio® has improved stiffness.

EnPol®: Series of biodegradable aliphatic and aliphatic–aromatic copolyesters produced through the polycondensation reaction

of glycols and dicarboxylic acids produced by Ire Chemical Ltd. (KR). The series of EnPol® contains the major grades EnPol® G4560, EnPol® G4560J (>MFI), and Enpol® G8060.

Enzymes: Catalytic proteins that decrease the level of activation energy of molecules that favor chemical reactions. Enzymes are named and numbered (EC numbers) according to rules adopted by the Enzyme Commission of the International Union of Pure and Applied Chemistry. The enzymes are grouped into six different classes according to the reaction catalyzed. The first number indicates the class of enzymes catalyzing a given chemical reaction: (1) oxidoreductases for catalyzing redox reactions; (2) transferases for catalyzing transfer of functional group reactions; (3) hydrolases for catalyzing hydrolysis; (4) lyases for catalyzing addition to double bond reactions; (5) isomerases for catalyzing isomerization; and (6) ligases for catalyzing formation of new bonds using ATP.

EPO: see European Patent Office.

Esterase: Enzyme that catalyzes the hydrolysis of an ester. The term is used interchangeably with polyesterase.

European Committee for Standardization (CEN): CEN (Comité Européen de Normalisation) contributes voluntary technical standards that promote free trade, the safety of workers and consumers, environmental protection, exploitation of research and development programs, and public procurement.

European Patent Office (EPO): Provides a uniform application procedure that enables inventors to seek patent protection in up to 40 European countries. Executive arm of the European Patent Organization (EPO).

European Patent Bulletin: Contains bibliographic data as well as data on the legal situation of European patent applications and patents. It is sold on subscription as a weekly PDF file. The corresponding data is also available via the European Patent Register, the ESPACE BULLETIN search and retrieval tool, or as raw data via Open Patent Services (EPO).

Enzymatic hydrolysis: Hydrolysis mediated by hydrolytic enzymes. Includes the breakage of ester and amide linkages from the polymer backbone by the addition of water and mediated by hydrolytic enzymes to yield the parent carboxylic acid group and the respective functional group, that is, the hydroxyl functional group for esters (i.e., alcohols such as methanol) and the appropriate amine for amides. This is also known as hydrolytic degradation of the polymer backbone.

Espacenet: Free online service that allows users to search the EPO's patent data collection.

Eutrophication: The enrichment of an aquatic environment with nutrients such as phosphoric and nitrogen compounds from agricultural fertilizing as well as from combustion processes and wastewater. Causes phytoplankton to grow and reproduce more rapidly, which results in algal blooms. The algae may use up all the oxygen in the water, leaving none for other marine life. This results in the death of many aquatic organisms such as fish, which need the oxygen in the water to live. The bloom of algae may also block sunlight from photosynthetic marine plants under the water surface. Some algae even produce toxins that are harmful to higher forms of life. This can cause problems along the food chain and affect any animal that feeds on them. The reference substrate for eutrophication is phosphate (PO₄), which is why the reference unit for eutrophication is the kilogram equivalent of PO₄.

FERM: Acronym derived from the former name of Fermentation Research Institute (FRI) in Japan, which later became the Patent Microorganism Depository of the National Institute of Bioscience and Human Technology (NIBH). The Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure requires deposition of the biological material be subject to a patent application. In Japan and some other countries, an applicant for a patent has to submit a receipt of that deposition to the Patent Office at filing. Under the established rules of the treaty, the

¹ This operation is prohibited by EU legislation and international conventions.

² If there is no other D code appropriate, this can include preliminary operations prior to disposal, including pre-processing such as, inter alia, sorting, crushing, compacting, pelletizing, drying, shredding, conditioning, or separating prior to submission to any of the operations numbered D1 to D12.

³ Temporary storage means preliminary storage according to point (10) of Article 3.

depository checks viability and furnishes a sample of the microorganism to a third party only for study and research.

Genetically modified organisms (GMOs): Organisms in which the genetic material (DNA) has been altered in a way that does not occur naturally.

German Institute for Standardization (DIN): DIN (Deutsches Institut für Normung) is the German national organization for standardization.

GMOs: see Genetically modified organisms.

GreenPla: The generic term for biodegradable polymers or plastics, raw materials, and products that contain biodegradable polymers or plastics, and that conform to the identification standards prescribed by the Japan Bioplastics Association (JBPA).

Hemicellulose: Branched short chain polysaccharide heteropolymer with an amorphous structure; easier to hydrolyze than cellulose.

HHV: see Higher heating value.

Higher (gross or upper) heating value (HHV): The amount of heat produced by the complete combustion of a unit quantity of fuel.

HLB: see Hydrophile-Lipophile Balance (HLB).

Hydrolysis: Process in which a molecule is cleaved in two by the addition of a molecule of water. This process can occur both chemically and enzymatically. In a hydrolysis reaction that involves breaking an ester bond, one hydrolysis product contains a hydroxyl functional group, and the other a carboxylic acid functional group. Amides hydrolyze to the parent carboxylic acid and the corresponding amine.

Hydrolytic enzymes: Class of hydrolases that include, but are not limited to, proteases, lipases, cutinases, and esterases. These enzymes have proven useful for a variety of industrial applications, including the enzymatic hydrolysis of aliphatic polyesters.

Hydrophile-Lipophile Balance (HLB): An expression of the relative amounts of the hydrophilic (water-loving or polar) and lipophilic (oil-loving or non-polar) groups in a disposable biopolymer without weighting their polarity strengths. A disposable material that is lipophilic (i.e., hydrophobic) in nature is assigned a low HLB (below 9 on a scale of 0 to 20 units). HLB measurements are useful in estimating whether a candidate additive will help to speed or retard water permeation. For example, the HLB value of PLA is approximately 10 and that of PGA is about 15. Lactide has an HLB of about 12 and glycolide has an HLB of about 15. A typical good plasticizer for PLA is dimethyl adipate (HLB about 10). However, this plasticizer does not function well with polyglycolic acid (from (US2002123546 A1, 2002, ECOPOL LLC; CARGILL DOW POLYMERS LLC).

Incineration: High-temperature dry oxidation process that reduces organic and combustible waste to inorganic, incombustible matter. Results in a very significant reduction of waste volume

and weight. This process is usually selected to treat wastes that cannot be recycled, reused, or disposed of in a landfill site.

Ingeo™: Trademark name for a range of polylactides (PLA) owned by NatureWorks LLC.

International Standards Organization (ISO): International standard-setting body composed of representatives from various national standards bodies.

IPscore: A Microsoft Access database designed to help with the evaluation and management of patent portfolios. In 2006 the EPO purchased IPscore from the Danish Patent Office who developed it in close co-operation with industry.

ISO: see International Standards Organization.

Isosorbide: The diol 1,4:3,6-dianhydro-D-sorbitol. Isosorbide is readily made from renewable resources, such as sugars and starches. For example, isosorbide can be made from D-glucose by hydrogenation followed by acid-catalyzed dehydration (Fleche G., et. al., Starch/Stärke, 38(1), 26-30, 1986).

Invention: New product, process, or apparatus, or any new use thereof. To be patentable, an invention must be novel, involve an inventive step (i.e., not be obvious to those having ordinary skill in the particular art of the invention) and be useful as an industrial application (EPO).

Japan Bioplastics Association (JBPA): Organization voluntarily founded by the major Japanese plastics-producing companies and others focused on plastics. Established with the aim of promoting the popularization of biodegradable plastics and biomass-based plastics, which play an important role in solving the recycling and technical problems (<http://www.jbpaweb.net/english/english.htm>; retrieved November 25, 2012).

Lactide: Ring closure of two lactic acid molecules. Three different stereoisomers of lactide are known depending on whether they consist of (1) two L-lactic acid molecules, L-lactide; (2) two D-lactic acid molecules, D-lactide; or (3) one L-lactic acid molecule and one D-lactic acid molecule, meso-lactide. Meso-lactide is characterized by a melting point (T_m) of around 50°C, whereas the melting point of L- and D-lactide isomers is 97°C (see Figure G5a). An equimolar mixture of L- and D-lactide results in LD-lactide (rac-lactide) (see Figure G5b).

Lacty®: Polylactide produced by Shimadzu Corp. The series of Lacty® contains three major grades, namely #5000, #9000, and #9800. Crystallinity of the resin decreases gradually in this order. Lacty® #5000 and #9000 have crystallinity, while #9800 has non-crystallinity. Melt flow rate, that indicates the mold property, increases in this order. The series of Lacty® are fitted for injection molding, fiber, film, and sheet. Crystalline Lacty® can be modified by blending it with other fatty ester plastics, while the non-crystalline one can be blended with wood powder or pulp.

Laminate: Material consisting of more than one layer, the layers being distinct in composition, composition profile, or anisotropy

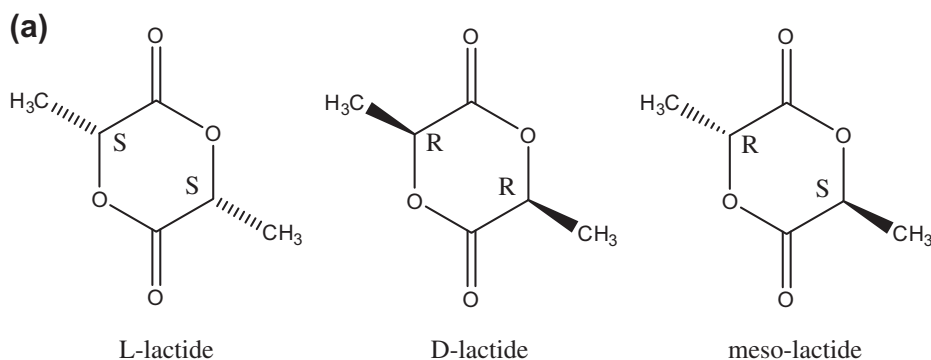
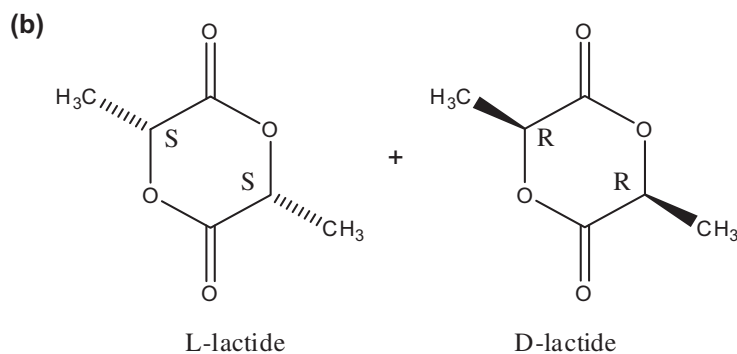


Figure G5a



LD-lactide (rac-lactide): equimolar mixture of L-lactide and D-lactide

Figure G5b

of properties. Laminates may be formed by two or more layers of different polymers (IUPAC).

Landfill: Specially structured solid waste pit lined with plastic and/or clay into which solid waste is dumped, isolated from ground water and air, and kept dry, thereby preventing microbial action from breaking down the waste. This results in the waste degrading slowly. A landfill is a solid waste context, generally in an anaerobic environment at the temperature of the ambient air or adjacent soil, and in relatively low humidity.

LCA: see Life Cycle Assessment (LCA).

LCI: see Life Cycle Inventory analysis (LCI).

Life cycle: Consecutive and interlinked stages of a product system from acquisition of raw material or generation from natural resources to final disposal (ISO 14040:2006).

Life Cycle Assessment (LCA): Compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a product system throughout its life cycle (ISO 14040:2006).

Life Cycle Inventory analysis (LCI): Phase of life cycle assessment involving the compilation and quantification of inputs and outputs for a product throughout its life cycle (ISO 14040:2006).

Lignin: Cross-linked macromolecule that is highly hydrophobic and comprised of aromatic elements derived from phenol. Lignin is a complex organic substance binding the cells, fibers, and vessels that constitute wood and the lignified elements of plants. After cellulose, it is the most abundant renewable carbon source on Earth.

Lipase: Enzyme that catalyzes the hydrolysis of fats into glycerol and fatty acids by hydrolyzing ester bonds.

***Lyophyllum ulmarium* (*Hypsizygus ulmarium*):** Strain of mushroom capable of forming a white fruiting body.

Masterbatch: Composition comprised of a carrier polymer and one or more ingredients (e.g., colorants) in higher concentration than occur in the final mixture, and whose composition is subsequently diluted with the remainder of the ingredients.

Mechanical recycling: see Physical recycling.

Micro-algae: Large and diverse group of unicellular photo- and heterotrophic organisms that have attracted attention in recent years due to their potential value as a renewable energy source. Focus has been on storage lipids in the form of triacylglycerols, which can be used to synthesize biodiesel via transesterification. The remaining carbohydrate content can also be converted to bioethanol via fermentation. Biopolymers derived from algae evolved as a byproduct of algae biofuel production.

Mater-Bi™: Product of Novamont derived from renewable raw materials of agricultural origin and non-genetically modified starch. Mater-Bi™ is reportedly completely biodegradable and compostable.

Mineralization: Conversion of a biodegradable polymer to CH₄ or CO₂ and H₂O, inorganic compounds, and biomass.

Net Present Value (NPV): The difference between the present value of the future cash flows from an investment and the amount of the investment. The NPV of the expected cash flows is computed by discounting them at the required rate of return.

Norrish mechanism: The fragmentation mechanism of organic carbonyl-containing compounds when subjected to ultraviolet radiation (UV). Both Norrish type I and type II mechanisms result in carbon-carbon bond dissociation of the excited state, producing chain scission in polymers.

Norrish type I reaction: A reaction step of carbonyl compounds according to the Norrish mechanism in which two free radicals are produced which can continue degradation reactions.

Norrish type II reaction: A reaction step of carbonyl compounds according to the Norrish mechanism in which chain scission occurs but no free radicals are produced, unlike the Norrish type I reaction.

NPV: see Net Present Value.

Octanol: A fatty alcohol with the molecular formula CH₃(CH₂)₇OH. The term usually refers to the isomer, 1-octanol. It is frequently in the lactide ring opening catalysis step to control molecular weight and accelerate the reaction.

Odt: see Oven dry ton.

OECD: see Organization of Economic Co-operation and Development.

OECD Test Guidelines: Collection of the most relevant internationally agreed upon test methods used by government, industry, and independent laboratories to determine the safety of chemicals and chemical preparations, including pesticides and industrial chemicals. They cover tests for the physical-chemical properties of chemicals, human health effects, environmental effects, and degradation and accumulation in the environment.

Organization of Economic Co-operation and Development (OECD): International economic organization of 34 countries founded in 1961 to stimulate economic progress and world trade.

Oven dry ton (odt): Unit used to express the dried weight of an agricultural commodity such as biomass that contained significant water weight when harvested.

P2HB: see Poly(2-hydroxybutyrate).

P3HB: see Poly(3-hydroxybutyrate).

P3HB4HB: see Poly(3-hydroxybutyrate-co-4-hydroxybutyrate).

PA 11: see Polyamide 11.

PA 12: see Polyamide 12.

Pancreatic lipase: An ester hydrolyase.

Patent: Legal title that gives inventors the right, for a limited period (usually 20 years), to prevent others from making, using, or

selling their invention without their permission in the countries for which the patent has been granted (EPO).

Patent application: Request for patent protection for an invention filed with a patent office (EPO).

Patent family: Set of interrelated patent applications filed in one or more countries to protect the same or similar inventions by a common inventor; linked by a common priority (or priorities). Used by those who wish, for example, to establish the geographical coverage of a particular patent (EPO).

Patent pending: Notice given that an application for a patent has been filed, and that legal protection (including retroactive rights) may be forthcoming (EPO).

PBS: see Poly(butylene succinate).

PBSA: see Poly(butylene succinate adipate).

PCL: see Poly(ϵ -caprolactone).

PEA: see Poly(ethylene adipate).

PES: see Poly(ethylene succinate).

PET: see Poly(ethylene terephthalate).

PGA: see Polyglycolide.

PHA: see Polyhydroxyalkanoate.

PHB: see Polyhydroxybutyrate.

PHBV: see Poly(3-hydroxybutyrate-co-3-hydroxyvalerate).

Physical or mechanical recycling: Recycling processes that involve the reduction in size (e.g., by grinding) and/or separation (e.g., by sorting) of different polymers from a waste mixture without significantly altering the chemical structure of the recovered polymer(s).

PLA: see Polylactide.

Plasmin: Proteolytic enzyme found in blood; serine protease.

Plastic: Substance that contains a polymer as an essential component.

PLGA: see Poly(lactide-co-polyglycolide)

PMA: see Poly(malic acid).

Poly(α -aspartic acid): Biodegradable polyamide synthesized from L-aspartic acid, a natural amino acid. It is also called polyaspartate. It is represented by the formula (see Figure G6):

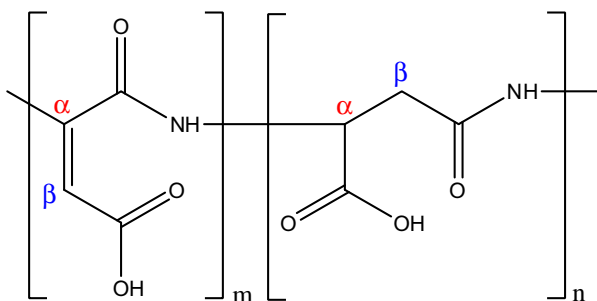


Figure G6 Poly(α -aspartic acid)

Poly(β -propiolactone) or Polypropiolactone (PPL): Aliphatic polyester of the chemical formula: $(-\text{OCH}_2\text{CH}_2\text{CO}-)_n$. It is a chemosynthetic biodegradable aliphatic polyester with good mechanical properties.

Poly(γ -glutamic acid) (γ -PGA): Poly(γ -glutamic acid) (also known as polyglutamate and γ -PGA) is a water-soluble, anionic, biodegradable polyamide consisting of D- and L-glutamic acid monomers connected by amide linkages between α -amino and γ -carboxyl groups (see Scheme 1.28). γ -PGA is synthesized by several bacteria and its molecular weight can vary anywhere from 20,000 to over 2 million Da depending on the method of production (see Figure G7).

Poly(ϵ -caprolactone) or Polycaprolactone (PCL): A poly(6-hydroxyhexanoic acid) of the chemical formula (see Figure G8):

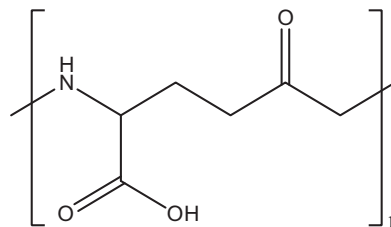


Figure G7 Poly(γ -glutamic acid) (γ -PGA)

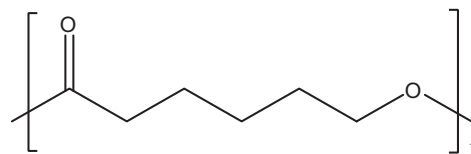


Figure G8 Poly(ϵ -caprolactone) or Polycaprolactone (PCL)

It is a biodegradable, synthetic, partially crystalline polyester with low melting point (60°C) and a glass transition temperature (T_g) of -60°C . Polycaprolactone is an important polymer due to its mechanical properties, miscibility with a large range of other polymers, and biodegradability. Two main pathways to produce polycaprolactone have been described in the literature: (1) the polycondensation of a hydroxycarboxylic acid, 6-hydroxyhexanoic acid; and (2) the ring-opening polymerization (ROP) of a lactone, ϵ -caprolactone.

Poly(2-hydroxybutyrate) (P2HB): Also called poly(2-hydroxybutyric acid) or poly(2-hydroxybutanoic acid). It can be synthesized from 2-hydroxybutanoic acid with a chiral α -carbon.

Poly(3-hydroxybutyrate) (PHB, P3HB): Polyhydroxyalkanoate of the chemical formula (see Figure G9): It is the most commonly occurring form of polyhydroxybutyrate with a chiral site in each molecular unit, all of which are in the D- (or R-) configuration. It is a natural polymer produced by many bacteria as a means to store carbon and energy. The polymer is also called poly(3-hydroxybutanoic acid) or poly(hydroxybutyric acid). The abbreviation P3HB is used interchangeably with PHB.

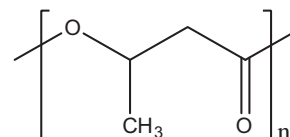


Figure G9 Poly(3-hydroxybutyrate) (PHB, P3HB)

Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB): Polyhydroxyalkanoate obtained by the incorporation of 4-hydroxybutyrate (4HB) units into poly(3-hydroxybutyrate) (P3HB or PHB). P3HB4HB is represented by the chemical formula (see Figure G10):

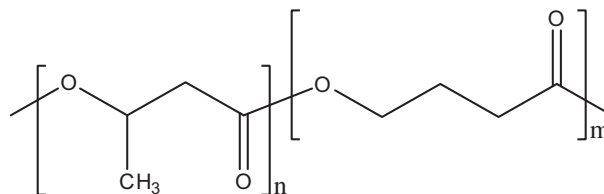


Figure G10 Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB)

Poly(3-hydroxybutyrate-co-3-hydroxyoctanoate) (PHBO or P3HB/3HO): Polyhydroxyalkanoate copolyester of 3-hydroxybutyrate (3HB) and 3-hydroxyoctanoate (3HO).

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV): Polyhydroxyalkanoate copolymer in which 3-hydroxyvalerate (HV) units are incorporated into the poly(3-hydroxybutyrate) (P3HB or PHB) backbone during the fermentation process (see Figure G11).

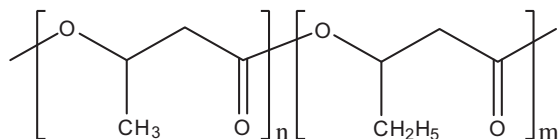


Figure G11 Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)

Poly(6-hydroxyhexanoic acid): see Poly(ϵ -caprolactone).

Poly(alkylene dicarboxylate): Polyester derived from a dicarboxylic acid and dihydroxy compound. See also Poly(alkylene alkanate).

Poly(alkylene alkanate): Polyester prepared from a dicarboxylic acid containing 4 to 10 carbon atoms and a diol containing 2 to 6 carbon atoms. Two or more kinds of dicarboxylic acids and diols may be employed.

Polyamide 11 or Nylon 11 (PA 11): Non-biodegradable polyamide derived from vegetable oil. It is produced by Arkema under the commercial name Rilsan[®] from castor beans.

Polyamide 12 or Nylon 12 (PA 12): Non-biodegradable polyamide derived from laurilactam, which itself is obtained from the trimerization of butadiene.

Poly(amino acid): Synthetic biopolymer made from α -amino acid repeating units (i.e., $-(NH-CHR-CO)_x-$). A poly(amino acid) is sometimes also called polypeptide.

Polyanhydride: Biodegradable polymer characterized by anhydride bonds that connect repeating units of the polymer backbone chain. It is represented by the chemical formula (see Figure G12):

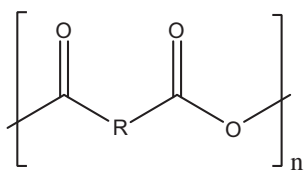


Figure G12 Polyanhydride

Polydioxanone or Poly-*p*-dioxanone (PDO): Biodegradable poly(ether-ester) polymer represented by the chemical formula (see Figure G13): It is obtained by ring-opening polymerization of *p*-dioxanone. Polydioxanone is used for biomedical applications, particularly the preparation of surgical sutures.

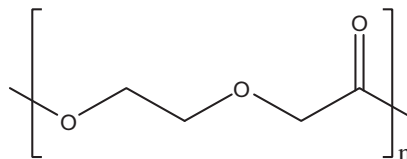


Figure G13 Polydioxanone or Poly-*p*-dioxanone (PDO)

Polyesterase: see Esterase.

Polyglycolide or Poly(glycolic acid) (PGA): Aliphatic polyester with a recurring unit represented by the chemical formula (see Figure G14):

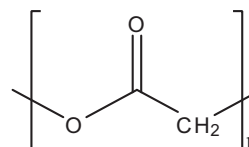


Figure G14 Polyglycolide or Poly(glycolic acid) (PGA)

Poly(hydroxylalkanoic acid): see Polyhydroxyalkanoate.

Polyhydroxyalkanoate or Polyhydroxylalkanoic acid (PHA):

Biodegradable aliphatic polyester commercially produced by several bacteria as intercellular carbon and energy storage materials in their cells. Examples of known commercially available forms of polyhydroxyalkanoates include polyhydroxybutyrate (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV).

Polyhydroxybutyrate: see Poly(3-hydroxybutyrate).

Poly(butylene adipate) (PBA): Poly(alkylene dicarboxylate) of the chemical formula (see Figure G15): PBA is synthesized from adipic acid and 1,4-butanediol.

Poly(butylene succinate) (PBS): Poly(alkylene dicarboxylate) of the chemical formula (see Figure G16): It has a melting point of 112–114°C. PBS is synthesized from succinic acid and 1,4-butanediol. Its mechanical properties are comparable to polypropylene and low density polyethylene (LDPE).

Poly(butylene succinate adipate) (PBSA): Poly(alkylene dicarboxylate) of the chemical formula (see Figure G17): PBSA is synthesized from succinic acid, adipic acid, and 1,4-butanediol. It is a biodegradable aliphatic polyester based on non-renewable (fossil) resources.

Poly(ethylene adipate) (PEA): Poly(alkylene dicarboxylate) of the chemical formula: $[-O-(CH_2)_4-O-CO-(CH_2)_4-CO-]_n$. It is synthesized from adipic acid and ethanol. It is a biodegradable aliphatic polyester based on non-renewable (fossil) resources. It is often blended with other polyesters to get specific desirable properties such as soft segments.

Poly(ethylene succinate) (PES): Poly(alkylene dicarboxylate) of the chemical formula (see Figure G18): Has a melting point of 103–106 °C. It is a biodegradable aliphatic polyester based on

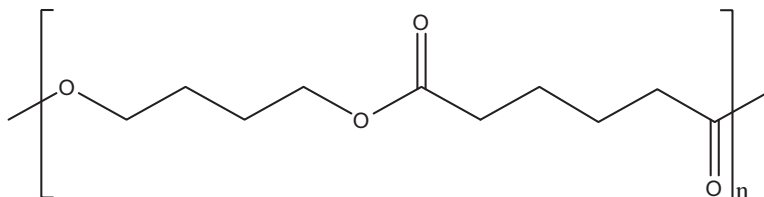


Figure G15 Poly(butylene adipate) (PBA)

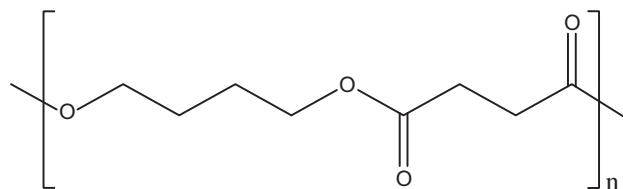


Figure G16 Poly(butylene succinate) (PBS)

non-renewable (fossil) resources and is synthesized from adipic acid and ethylene glycol. Its mechanical properties are comparable to polypropylene and low density polyethylene (LDPE).

Poly(ethylene furanoate) (PEF): Bio-based polyester made from ethylene glycol and 2,5-furan dicarboxylic acid (FDCA). Avantium (NL) developed a process using catalytic reactions to create FDCA, which reacts with ethylene glycol to make PEF (see [Figure G19](#)).

Poly(ethylene terephthalate), bio-based (PET): Bio-based polyester made from ethylene glycol and terephthalic acid or its ester-forming derivative, wherein at least one of the diol and/or terephthalate components are derived from at least one bio-based material (see [Figure G20](#)).

Poly(glycolic acid): see Polyglycolide.

Poly(hydroxy acid): Polyester, the monomers of which contain both a carboxylic acid group and a hydroxyl group. Examples of such polymers include polylactide (PLA), polyglycolide, polyhydroxybutyrate (PHB), and poly(ϵ -caprolactone) (PCL).

Poly(lactic acid): see Polylactide.

Polylactide or Poly(lactic acid) (PLA): Aliphatic polyester of the chemical formula (see [Figure G21](#)): The polymer can be produced by fermentation from renewable resources. It can also be synthesized either by condensation polymerization of lactic acid or by ring-opening polymerization of lactide in the presence of a catalyst. This polymer exists in the form of three stereoisomers: poly(L-lactide) (L-PLA), poly(D-lactide) (D-PLA), and poly(DL-lactide) (DL-PLA). The term poly(lactic acid) is misleading and does not comply with standard nomenclatures (such as IUPAC), which potentially leads to ambiguity. PLA is not a polyacid, but rather a polyester.

Poly(lactide-co-polyglycolide) (PLGA): Copolymer of hydrophobic PLA and hydrophilic PGA of the chemical formula (see [Figure G22](#)).

Poly(malic acid) (PMA): Biodegradable and bioabsorbable water-soluble polyester. PMA is known as polyhydroxyalkanoate with a carboxyl group in a side chain. A polymer of polymalic acid is known, by a manner of polymerization, in an α -type represented by the chemical formula (see [Figure G23a](#)): A β -type is represented by the chemical formula (see [Figure G23b](#)).

Polymer blend: Macroscopically homogeneous mixture of two or more different polymer species (IUPAC).

Polymer composite: Composite in which at least one component is a polymer (IUPAC).

Poly(ortho ester)s (POE)s: Hydrophobic biocompatible and bioerodible polymers potentially useful as a sustained drug delivery system. Four distinct families have been developed so far, designated POE I (see chemical formula), POE II, POE III, and POE IV. These polymers can be prepared by a transesterification reaction or by the addition of polyols to diketene acetals; the latter method has proven to be the preferred one (see [Figure G24](#)).

Polyphosphazene (PPHOS): Biodegradable polymer with alternating nitrogen and phosphorus atoms in the backbone of the chemical formula where R can be an alkoxy, aryloxy, or amino group (see [Figure G25](#)).

Poly(propylene carbonate) (PPC): Aliphatic polycarbonate obtained by the alternating copolymerization of ethylene oxide and carbon dioxide. It is represented by the chemical formula (see [Figure G26](#)).

Poly(propylene fumarate) (PPF): Biodegradable unsaturated linear polyester that can be modified or cross-linked through its fumarate double bonds (see [Figure G27](#)).

Poly(propylene terephthalate), bio-based (PPT): see Poly(trimethylene terephthalate).

Poly(trimethylene carbonate) (PTMC): Biodegradable polycarbonate with rubber-like properties. PTMC is obtained by ring-opening polymerization of trimethylene carbonate, and catalyzed with diethyl zinc. PTMC is represented by the chemical formula (see [Figure G28](#)).

Poly(trimethylene terephthalate), bio-based (PTT): Also called poly(propylene terephthalate) (PPT). Bio-based PTT is made by polycondensation of 1,3-propane diol derived from renewable sources and either terephthalic acid or dimethyl terephthalate. Bio-based PTT is marketed by DuPont Company as SORONA[®] fibers (see [Figure G29](#)).

Poly(vinyl alcohol) (PVOH): Water-soluble polymer prepared via the hydrolysis of poly(vinyl acetate). PVOH is represented by the chemical formula (see [Figure G30](#)).

Polyurethane (PU): Polymer that incorporates urethane groups (—NH—CO—O—) in the polymer backbone. Polyurethanes are commonly formed by the polyaddition reaction of a polyisocyanate (such as a diisocyanate) with a polyol (such as a diol) that results in the formation of linear, branched, or cross-linked polymers.

PPC: see Poly(propylene carbonate).

PPF: see Poly(propylene fumarate).

PPL: see Poly(β -propiolactone).

PPS: see Polypropylene succinate.

PPT: see Poly(propylene terephthalate); also called poly(trimethylene terephthalate) (PTT).

Priority: Right to file subsequent applications for the same invention at other offices. Valid for a period of 12 months from the date of first filing of a patent application. The first filing date is known as the priority date (EPO).

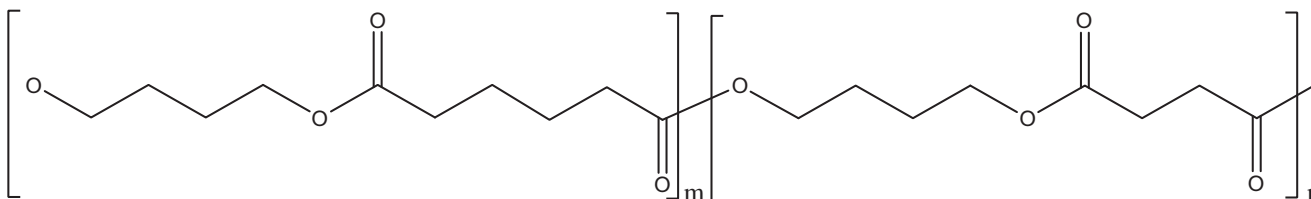
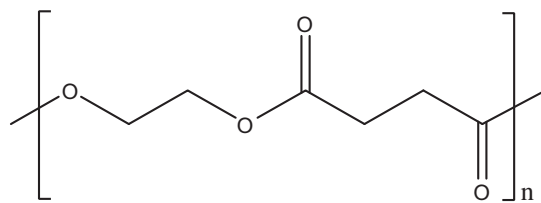
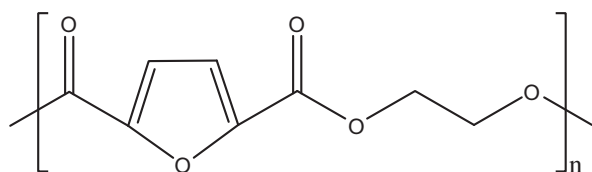
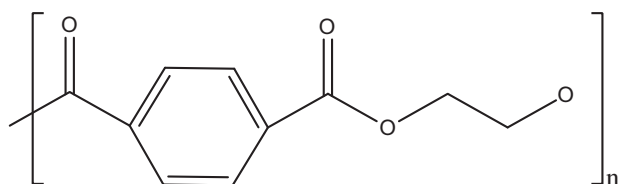
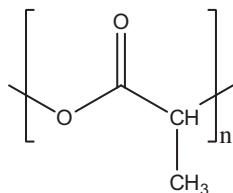
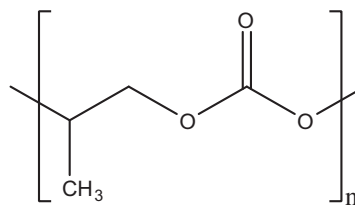
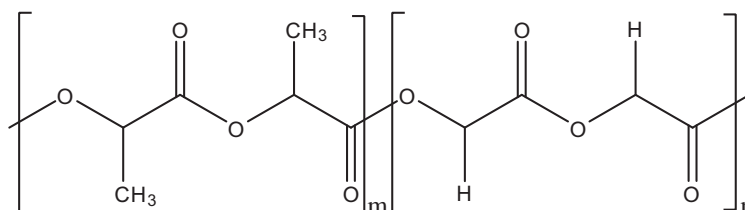
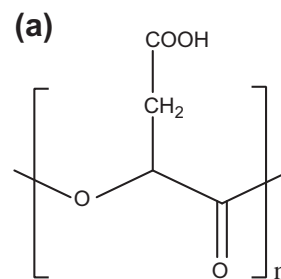
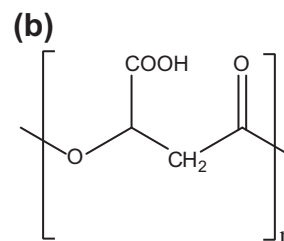
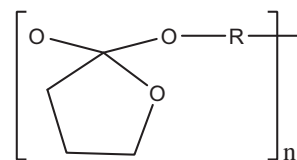
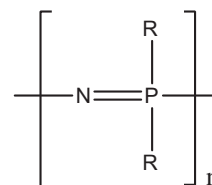


Figure G17 Poly(butylene succinate adipate) (PBSA)

**Figure G18** Poly(ethylene succinate) (PES)**Figure G19** Poly(ethylene succinate) (PES)**Figure G20** Poly(ethylene terephthalate), bio-based (PET)**Figure G21** Polylactide or Poly(lactic acid) (PLA)**Figure G26** Poly(propylene carbonate) (PPC)**Figure G22** Poly(lactide-co-polyglycolide) (PLGA)**Figure G23a** Poly(malic acid) (PMA), α-type**Figure G23b** Poly(malic acid) (PMA), β-type**Figure G24** Poly(ortho ester)s (POE)s**Figure G25** Polyphosphazene (PPHOS)

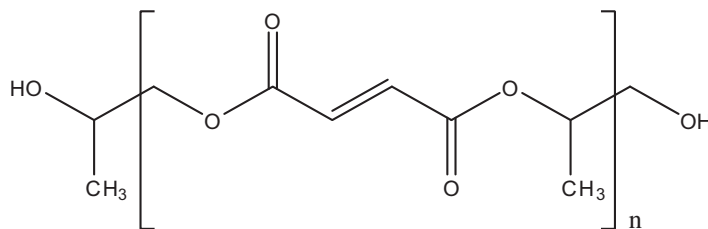


Figure G27 Poly(propylene fumarate) (PPF)

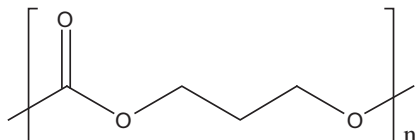


Figure G28 Poly(trimethylene carbonate) (PTMC)

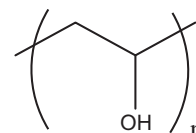


Figure G30 Poly(vinyl alcohol) (PVOH)

Priority date: Date of filing of a previous application for the same invention (EPO).

Protease: Enzyme that catalyzes the hydrolytic breakdown of proteins via hydrolysis of peptide bonds.

Proteins: Natural chains of α -amino acids joined by amide linkage.

Proteinase-K: Serine protease produced by *Tritirachium album*, a fungus that grows on native keratin as its sole carbohydrate and nitrogen source. The enzyme has been used to study degradation of PLLA and its copolymers.

PTMC: see Poly(trimethylene carbonate).

PTT: see Poly(trimethylene terephthalate).

Pyrolysis: Form of thermal treatment that chemically decomposes organic materials by heat in the absence of oxygen.

Rilsan®: Polyamide 11 (PA 11) or Nylon 11 derived from vegetable oil. It is produced by Arkema from castor beans. PA 11 is a bio-based non-biodegradable biopolymer.

scCO₂: see Supercritical carbon dioxide.

Septic tank system: An onsite system designed to treat and dispose of domestic sewage. A typical septic system consists of a tank that receives wastes from a residence or business. An anaerobic bacterial environment develops in the tank that decomposes or mineralizes the waste discharged into the tank.

Short Rotation Coppice (SRC): Coppice grown mainly as an energy crop. This woody solid biomass is used as biofuel and has also been proposed as a second-generation crop for bio-based biopolymers.

SKYGREEN®: Series of poly(butylene succinate) (PBS), poly(butylene succinate-adipate) (PBSA), and poly(butylene adipate-terephthalate) (PBAT) produced by SK Chemicals (KR). The SKYGREEN® series contains three major grades, namely SG100 (PBS), SG200 (PBSA), and SG300 (PBAT).

Standard: Official publications used in industry and trade to describe specifications and procedures. Standards provide rules and recommendations for quality, safety, performance and

construction, codes of practice, methods of testing, symbols and terminology.

Starch: Natural polymer composed of two types of α -D-glucose polymers: amylose, a substantially linear polymer with molecular weight of about 1×10^5 ; and amylopectin, a highly branched polymer with very high molecular weight of the order 1×10^6 . Depending on the origin of the starch, the ratio of amylose to amylopectin can vary significantly. Most starches contain 20–30% amylose and 70–80% amylopectin. Starch typically exists in small granules having a crystallinity that ranges from about 15–45%.

Sturm test: Aquatic, aerobic biodegradation test in which the conversion to CO₂ is measured and used to calculate the extent of biodegradation. It is named after the scientist who developed it (Sturm R. N. *Journal of American Oil Chemist's Society*, 50, 159, 1973).

Supercritical CO₂: Fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure. Carbon dioxide usually behaves as a gas in air at standard temperature and pressure (STP), or as a solid called dry ice when frozen. If the temperature and pressure are both increased from STP to be at or above the critical point for carbon dioxide, it can adopt properties midway between a gas and a liquid. More specifically, it behaves as a supercritical fluid above its critical temperature (31.1°C) and critical pressure (72.9 atm/7.39 MPa), and expands to fill its container like a gas, but with a density like that of a liquid (from Wikipedia).

Thermoplastic: Polymer that softens or melts when heated and solidifies when cooled.

Thermoplastic elastomer: Melt-processable polymer blend or copolymer in which a continuous elastomeric phase domain is reinforced by dispersed hard (glassy or crystalline) phase domains that act as junction points over a limited temperature range. The behavior of the hard phase domains as junction points is thermally reversible (IUPAC).

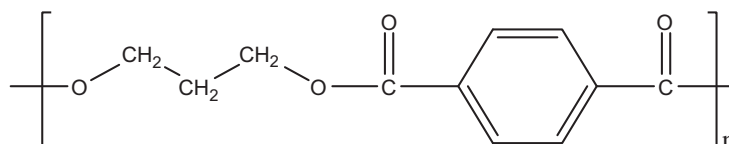


Figure G29 Poly(trimethylene terephthalate), bio-based (PTT)

Thermoset: Polymer that, when heated, is irreversibly hardened by forming a three-dimensional crosslinked structure between the chains.

Triadic patents: Series of corresponding patents filed at the European Patent Office (EPO), the United States Patent and Trademark Office (USPTO), and the Japan Patent Office (JPO) for the same invention by the same applicant or inventor. Triadic patents form a special type of patent family.

Trimethylene carbonate (TMC): Also known as 1,3-dioxan-2-one, and has the chemical formula (see [Figure G31](#)): Used as a monomer for the production of poly(trimethylene carbonate) (PTMC). It can also be used as a co-monomer for the production of poly(ester carbonate) using both enzyme and chemical catalysts.

Waste context: Includes composting, landfill, solid waste, wastewater treatment, septic tank, and garbage disposal systems.

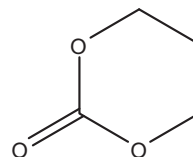


Figure G31 Trimethylene carbonate (TMC)

World Intellectual Property Organization (WIPO): Agency of the United Nations responsible for promoting the protection of intellectual property throughout the world by encouraging cooperation between nations.

Note: Page numbers followed by “f” or “t” indicate figure or table respectively

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