

Cost-Effective Synthesis of Environmentally Benign Materials on the Basis of Poly-3-Hydroxybutyrate

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Abstract: As an example for an environmentally benign and low-cost material we prepared blends from 1. copolyester-urethanes (PEU) and 2. cellulose acetate recycling material (CAR). The copolyester-urethanes were prepared by joining blocks of α , ω -(poly-(R)-3-hydroxybutyrate)-diol and poly-butylenglycol-adipate-diols with hexamethylene diisocyanate. Fibrous CAR was transformed into a short-fiber felt by textile technology and calendared into the PEU melt. The processing of the blends was done at 80 - 100 °C mainly by injection molding. The mechanical properties of the tough-elastic materials were studied with respect to the influence of the PEU composition and the ratio of CAR admixture. The starting materials, (R)-PHB and cellulose derivatives are obtained from agrarian resources. Therefore, the resulting polymers are stable under conditions of usage, yet readily bio-degradable on soil deposition. Mixing with cellulose acetate waste material allows for cost-effective production of such blends.

Keywords: *Blends, copolyester-urethane, cellulose acetate, recycling material.*

Introduction

Bacterial poly-(R)-3-hydroxybutyrate ((R)-PHB) is, in many instances, a nearly ideal eco-material: It is obtained from renewable resources. It is readily bio-degradable on soil deposition (composting)^[1]. It is biocompatible, thus, can be the basis of medical implants^[2] or the substrate for growth of cell cultures^[3]. It has a stereoregular structure and, thus, can give rise to stereoregular building blocks for organic chemistry^[4].

All these aspects of a sustainable technology have stimulated the NASA space agency to investigate on the preparation, application and disposal of (R)-PHB under simulated extraterrestrial conditions^[5].

Unfortunately, the technical exploitation and commercialization of this polymer has been seriously hampered mainly by two adverse aspects:

1. Due to its high crystallinity, (R)-PHB has some unfavorable material properties: Since the melting point is at ca. 177 °C^[6] and thermal degradation starts beyond 200 °C^[7], there is only a narrow "window" for thermoplastic processing. Films are rather inelastic, brittle and opaque. Biodegradation proceeds at a given rate, too fast for some potential applications.

2. The cost of production and processing of (R)-PHB is too high, as compared with commodity polymers like polyethylene or polypropylene, which are based on fossile

carbon sources.

These problems could not be completely eliminated (a) by controlling the crystallization process^[8], since the material may deteriorate on ageing, or (b) by the biosynthesis of copolymers e.g. with 3-hydroxyvalerate or 4-hydroxybutyrate^[9], since the productivity often decreases with the introduction of unusual substrates.

We have now overcome these difficulties by combining two novel developments: (a) We have prepared segmented polyester-urethanes by combining diol-terminated blocks ("macrodiols") of bacterial PHB with blocks of diol-terminated biodegradable co-components and joining these pre-polymers by reaction with hexamethylenediisocyanate^[10]. (b) We have prepared blends^[11] with a readily available biodegradable recycling material.

Experimental

Bacterial poly-(R)-3-hydroxybutyrate ((R)-PHB) was obtained from PHB Inc., Serrana, S.P., Brazil, and from Biomer Co., Krailling, Germany^[12]. α , ω -Dihydroxy-poly(butylene glycol adipate) (PBA-diols, $M_n \cong 1260$) was purchased from Aldrich. Dibutyltindilaurate, zirconium acetylacetonate, p-toluene sulfonic acid and 1,6-hexamethylene diisocyanate were supplied by Merck KGaA.

Cellulose acetate recycling material was obtained from EFKA Co., Trossingen, Germany. This material contained

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ca. 83% cellulose triacetate, ca. 10% paper and ca. 7% additives (glue, binder).

Preparation of PHB-diol-prepolymer

α , ω -Dihydroxy-poly[(R)-3-hydroxybutyrate] (PHB-diol) was obtained by transesterification of (R)-PHB with 1,4-butanediol in CHCl_3 at 65° in the presence of *p*-toluenesulfonic acid as a catalyst according to literature^[13]. During this procedure the initial molecular weight of the starting material $\overline{M}_n = \text{ca. } 30\,000$ for (R)-PHB from PHB Inc. resp. ca. 73 500 for (R)-PHB from Biomer) is broken down to ca. 1500 - 5500 for PHB-diol. The prepolymers were collected by filtration of the precipitate obtained after addition of cyclohexane to the reaction mixture. The yields were up to 94% based on PHB educt.

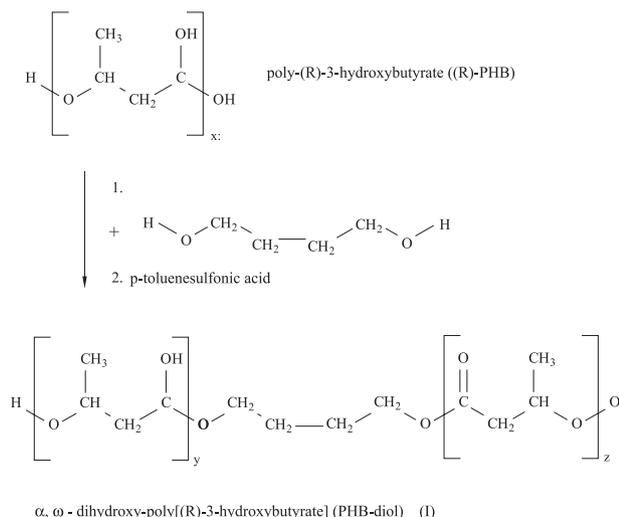
Synthesis of copolyester-urethanes

The synthesis of copolyester-urethanes was done initially, as described by G.R. Saad et al^[10], by dissolving PHB-diol and PBA-diol together with 0.5% dibutyltin dilaurate as a catalyst in dry 1,2-dichloroethane, and then adding an equivalent amount of 1,6-hexamethylene-diisocyanate. After 5 - 6 hours at 75°C a >95% yield of copolyesterurethane was obtained.

Recently, this procedure was significantly improved by 1. substituting dry 1,4-dioxane as a solvent for 1,2-dichloroethane, and 2. using organometallic acetylacetonates as catalysts instead of the environmentally toxic organotin compounds (results see "Results and Discussion").

Preparation of blends of polyester-urethane and recycling material

Smaller quantities of cellulose acetate recycled material (CAR) were mixed with copolyester-urethane on a hot plate, then, after cooling, ground into a fine powder. For kilogram batches the fibrous CAR was treated with a card, thus producing a fleece. This fleece was calendared into the copolyester-urethane melt by heated rolls at $120\text{-}140^\circ\text{C}$, and the material was granulated.



Scheme 1. Preparation of PHB-diol

Injection molding

Smaller test samples (ca. 50 g) were processed in a piston-equipped injection molding machine. Initially this was done at beyond 130°C , in later batches the temperature could be lowered to $80 - 100^\circ\text{C}$.

For kilogram batches an injection molding machine with a screw conveyor was used.

The samples obtained in this way and their properties are described in the following paragraph.

Results and Discussion

Preparation of copolyester-urethanes

The preparation of copolyester-urethanes was done by further developing previous procedures^[10]. The first step is the preparation of diol-terminated pre-polymers by acid-catalyzed transesterification in the presence of a diol, e.g. butane-1,4-diol^[13] (Structure I, Scheme 1).

The correct structure of compounds I was established by NMR spectroscopy (Figure 1).

The copolyester-urethanes were initially prepared by mixing PHB-diol and PBA-diol in a given ratio, addition of dibutyltin dilaurate as a catalyst, finally admixture of a stoichiometric amount of 1,6-hexamethylene diisocyanate. Reaction for 5 - 6 hours at 75° (Scheme 2) resulted in a nearly quantitative (>95%) yield of copolyester-urethane (compound II).

In view of the environmental toxicity of organotin compounds we recently developed a new procedure for the preparation of copolyester-urethanes, using acetylacetonates of non-toxic metals as catalysts and dioxane instead of chlorinated hydrocarbon as a solvent. Using this new procedure, the most satisfactory results were obtained with zirconium-acetylacetonate (Table 1), which was then applied for the following experiments.

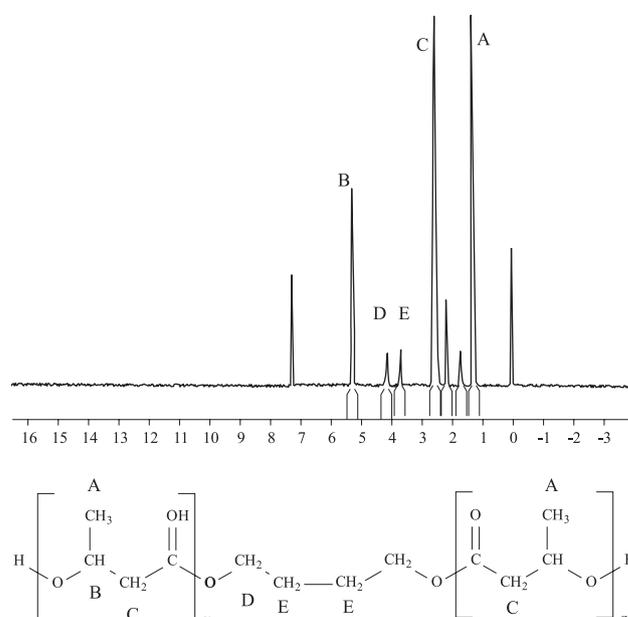
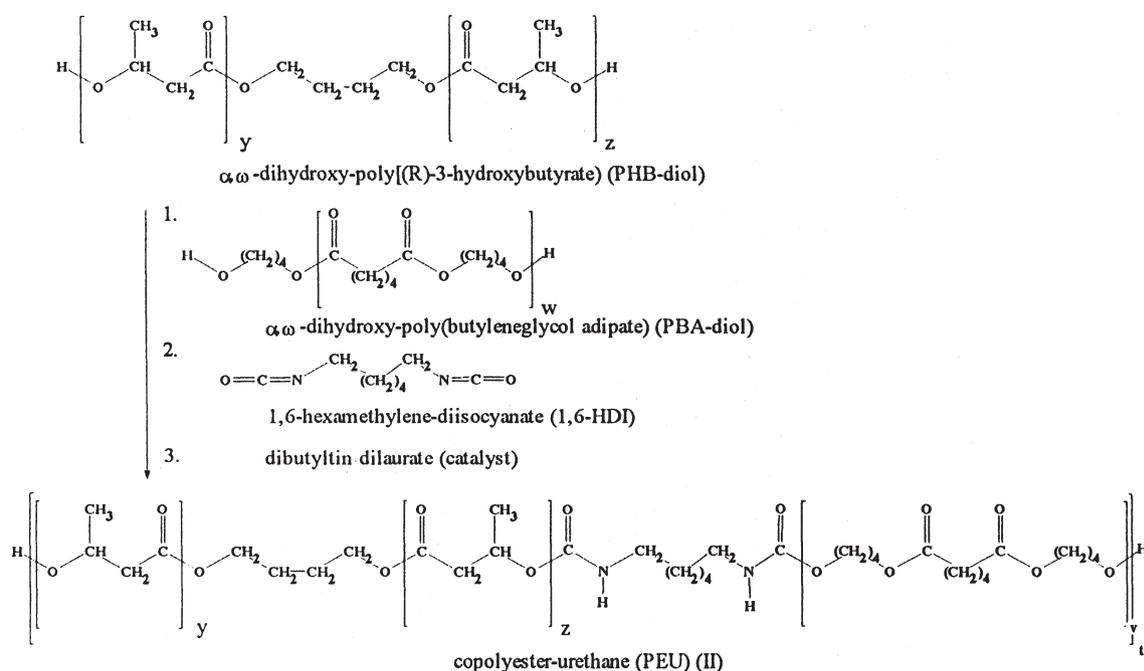


Figure 1. ¹H-NMR-Spectrum (400MHz) of PHB-diol



Scheme 2. Preparation of copolyester-urethane

Table 1.

Catalyst	$\overline{\text{Mn}}$
manganese (II) acetylacetonate	6300 g/mol
aluminum (III) acetylacetonate	16000 g/mol
zirconium (IV) acetylacetonate	43000 g/mol

The expected composition of the polyester-urethane was again proven by $^1\text{H-NMR}$ spectroscopy.

Blends of copolyester-urethane and cellulose acetate recycling material

Cellulose acetate was obtained as a recycling material (CAR) containing ca. 13% paper and additives. Due to the high melting point (ca. 280 °C) and the fibrous nature of this material homogeneous blends could not be achieved. The best results were obtained, when textile technology was applied to obtain a felt-like mass, which could be combined with copolyester-urethane as described in "Experimental". The compounds obtained in this way are described in Table 2.

Processing of PEU/CAR blends

The blends listed in Table 2 were generally processed by injection molding using appropriate machines for small-scale tests and larger-scale batches (see Experimental). Initially, the processing temperatures were adjusted to 130 - 170 °C, i.e. to the melting temperature of the PHB-diol "hard segments". While the injection molding proved relatively easy, when the samples contained not more than 25 - 40% CAR, the test objects obtained with higher CAR content were brittle and had bad material properties. However, experimental sheets could be obtained in a hot-press even from samples C4 and C5 containing 70% CAR.

Table 2.

Sample n°	Composition of copolyester-urethane (PEU)		Composition of compounds	
	% PHB-diol	% PBA-diol	% PEU	% CAR
C 1	40	60	75	25
C 2	50	50	75	25
C 3	40	60	60	40
C 4	40	60	30	70
C 5	50	50	30	70

An unexpected difficulty arose with samples C1 or C3 after injection molding at high temperature: the pressed objects, after cooling down, would adhere to the walls of the molding tool. This was prevented by using talcum powder as an additive. Later we learned, that the processing could just as well be done at lower temperature (80 - 100 °C, i.e. above the melt transition of the PBA-diol "soft segments") without such adverse effect, thus, omitting the addition of talcum.

Mechanical properties

In order to assess the mechanical properties, measurements were done of the tensile strength, impact strength and resistance to bending. The values obtained from these measurements are listed in Tables 3 - 5.

The data listed in Tables 3 - 5 demonstrate (1.) the influence of the PEU composition and (2.) the ratio of CAR admixture on the properties of the resulting blends. Ad (1.): With increasing content of PHB-diol in the PEU, the materials become generally harder and tolerate less admixture of CAR. Ad (2.): A higher content of CAR generally increases the

Table 3. Tensile properties of PEU/CAR blends

Sample n°	Tension E-modulus (N/mm ²)	Resistance to tensile stress (N/mm ²)	Max. extension on stress %
C 2	577.2 (33.6)	13.1 (0.2)	7.2 (0.6)
C 3	496 (108)	13.1 (0.8)	6.7 (0.5)
C 4	2033 (172)	16.1 (1.42)	1.12 (0.45)
C 5	1966 (154)	14.8 (1.22)	3.1 (0.5)

- Standard experimental deviations are listed in parentheses
 - Measurements on C 1 were not performed
 - n.d. = not determined

Table 4. Bending resistance of PEU/CAR blends

Sample n°	Tension E-modulus (N/mm ²)	Resistance to bending (N/mm ²)	Max. extension on bending %
C 2	532.7 (9.5)	21.9 (0.4)	8.8 (0.4)
C 3	444 (14. 7)	16.8 (1.2)	7.9 (0.9)
C 4	1763 (107)	26.1(0.2)	n. d.
C 5	2180 (194)	27.9 (2.23)	n.d.

- Standard experimental deviations are listed in parentheses
 - Measurements on C 1 were not performed
 - n.d. = not determined

Table 5. Impact strength of PEU/CAR blends

Sample n°	Impact resistance (mJ / mm ²)
C 2	28.4 (2.7)
C 3	26.0 (3.7)
C 4	16.4 (1.96)
C 5	15.6(1.9)

- Standard experimental deviations are listed in parentheses
 - Measurements on C 1 were not performed
 - n.d. = not determined

resistance to stress, however, the material becomes more and more brittle (compare Table 3 and 4 vs. Table 5). Ad (1.) and (2.): Interestingly, the properties of C 2 and C 3 are quite similar, thus, the two parameters can compensate each other to some extent. During earlier experiments^[10] it was found, that also the length of the “hard” (PHB-diol) and “soft” (PBA-diol) segments of the PEU has an influence on the mechanical properties. This should also influence the properties of the blends, and will be the subject of forthcoming studies.

In order to compare PEU/CAR blends to other blends of biological fibers with oil-based commodity polymers, we looked at composite materials obtained by filling flax fibers into polypropylene. For instance, a material containing 40% flax plus 60% polypropylene has 5.1% stress extension and a tension E-modulus of 2000 N/mm², thus, mechanical properties in a similar range.

Bio-degradation

Quantitative tests on the biodegradability of the polyesterurethanes have been done earlier measuring the oxygen uptake during degradation in a compost-inoculated medium (BODIS test)^[14,15]. These studies gave the surprising result, that copolymers composed of ca. 40 - 50% PHB-diol and 50 - 60% PBA-diol, as they are here used for blending, degrade at nearly the same rate as bacterial (R)-PHB homopolymer^[16].

Cellulose triacetate can be broken down to cellulose by soil bacteria, as reported in recent publications^[17,18]; the further bio-degradation of cellulose is common knowledge.

Studies on the biodegradability of PEU/CAR blends are in progress.

Economical aspects

So far, the main focus of our work has been to explore the scientific and technological feasibility of blending copolyester-urethanes with a recycling material. Economical aspects have not been in the foreground, but they are clearly a consequence. Cellulose acetate recycling material is just one example of a variety of polymers, which can be subject to materials recovery and, thus, potential blending partners for PEU. It is evident, that research on such kinds of polymer blends can not only bring the production cost of (R)-PHB based “eco-materials” to a level competitive with oil-based commodity polymers (calculating production and disposal), but it is also an investment with respect to a future scenario, where fossile carbon sources will not be as readily available as they are now.

Acknowledgment

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