Preparation and characterization of biodegradable poly-3-hydroxybutyrate–starch blend films

S. Godbole a, S. Gote b, M. Latkar b, T. Chakrabarti a,*

a Environmental Biotechnology Division, National Environmental Engineering Research Institute, Nehru Marg, Nagpur 440 020, India
b Vishweshwaraiya Regional College of Engineering, Nagpur 440 011, India

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Abstract

Bacterial polyesters have attracted much attention as biodegradable biocompatible polymers. Poly-3-hydroxybutyrate, a microbially produced thermoplastic, has similar material properties to polypropylene. Its potential application as biodegradable and biocompatible plastics is well documented. However, due to high cost it is used mainly in biomaterials for medical applications. Materials with useful properties may result from blending bacterial polyhydroxybutyrate (PHB) with other polymers.

In this paper, the compatibility of PHB with starch for improved properties and cost reduction is discussed. The thermal and mechanical properties of the blended films were studied by means of thermogravimetry, differential scanning calorimetry and an automated material testing system. The results revealed that blend films had a single glass transition temperature for all the proportions of PHB:starch tested. The nature of all combinations was found to be crystalline. The tensile strength was optimum for the PHB:starch ratio of 0.7:0.3 (wt/wt). The variation in tensile strength, Young’s modulus, extension needed to break, thermal stability, glass transition temperature, melting temperature, for the different proportions of PHB:starch are discussed.

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1. Introduction

In response to increasing public awareness over the environmental hazards caused by plastics, research is underway on producing biodegradable plastic materials. An eco-friendly alternative to this biodegradable material is poly-3-hydroxybutyrate (PHB) which is 100% biodegradable and can be produced from renewable resources. PHB, whose physical properties are similar to polypropylene, has attracted industrial attention as an environmentally degradable plastic for a wide range of agricultural, marine and medical applications. The physical properties of polylactic acid have been reviewed by Koning. PHB has been found to degrade within a few weeks in soil and other environments. However PHB is not widely used because of its high cost as compared to synthetic plastics. At present, its use is restricted to medical applications. However, research is going on to bring down the cost of production of PHB by employing various strategies such as development of better bacterial strains, more efficient fermentation/recovery process and use of low cost renewable resources as substrates. Some attempts have also been made to improve its physical properties by blending with other biodegradable polymers such as polyethylene oxide (Avella and Martuscelli, 1988; Greco and Martuscelli, 1989; Kumagai and Doi, 1992a), cellulose esters (Scandola et al., 1992; Ceccorulli et al., 1993), and starch (Pearce et al., 1992; Kumagai and Doi, 1992b; Abe et al., 1994; Verh cogt et al., 1995) as these materials have been found to be miscible with bacterial PHB. Blending with polylactic acid has been studied by Koyama and Doi (1995). Application of starch to make biodegradable plastics by blending with LDPE and HDPE has also been investigated (Wool et al., 1991; Corti et al., 1991). As starch is abundantly and cheaply available, its use in blending with PHB will result in completely biodegradable material which can have desired physical properties with concomitant reduction in cost.

In this paper we investigated the miscibility, film formation and thermal and mechanical properties of binary blends of bacterial PHB with starch.
2. Methods

2.1. Materials

The bacterial PHB samples were purchased from Aldrich chemical company. Soluble potato starch and chloroform were purchased from Qualigens Chemical Company.

2.2. Preparation of blend films

PHB and Starch were mixed in different ratios (wt/wt) of 0.1:0.9, 0.2:0.8, 0.3:0.7, 0.4:0.6, 0.5:0.5, 0.6:0.4, 0.7:0.3, 0.8:0.2, 0.9:0.1, and 1.0:0.0. The mixtures were then mixed with hot chloroform and blend films were prepared by conventional solvent-casting technique from the chloroform solutions of PHB and starch using glass petri dishes as casting surfaces.

2.3. Blending of PHB with thermoplastic starch

Thermoplastic starch (TS) was obtained by mixing starch powder, water, and glycerol in the composition 50:15:35 (wt/vol/vol), respectively according to Ramsay et al. (1995), with some modifications. The contents were mixed for 15–30 min. to obtain a paste. The paste was transformed into TS by heating at 100 °C in water bath with continuous stirring for 15 min. This product so obtained was mixed with PHB in different ratios and solvent cast films were obtained from chloroform.

2.4. Determination of density of the blended films

The diameters of the films were determined with the help of a scale and the average thickness was determined with the help of a micrometer. Each film was weighed on a Mettler balance, and the density of the samples was determined by the formula

\[
\text{Density (D)} = \frac{\text{Mass (M)}}{\text{Volume (V)}} \text{ in g/cm}^3
\]

\[
\text{Volume (V)} = \text{area (A)} \times \text{thickness of the film (T)}
\]

\[
V = \frac{\pi \times D^2}{4} \times T
\]

2.5. Evaluation of mechanical properties of the blend films

The mechanical properties analysed were tensile strength, Young’s modulus, and extension needed to break. The testing was done on the Instron corporation series IX automated material testing system. The samples were cut into rectangular shape and duplicate samples were analysed for each film type. The samples were subjected to tests on the instrument and rate of pull applied was 5 mm/min. The instrument was connected to a computer which automatically interprets the graphical output and computes the tensile strength, Young’s modulus and extension needed to break.

2.6. Evaluation of thermal properties of the blend films

The thermal stability of the blended films was determined by Thermogravimetric analysis (TGA). Melting temperature (\(T_m\)) and glass transition temperature (\(T_g\)) were determined by differential scanning calorimetry (DSC). Thermogravimetry was carried out with the Mettler TC-11 thermogravimetry analyzer. The mass of each sample was 10–12 mg and the reaction environment was flowing nitrogen (45 ml/min). Heating range was 20 °C/min. The thermogravimetric curves were recorded in the course of heating from room temperature to 900 °C. The DSC data of film samples were recorded in the temperature range of 0–200 °C, under a nitrogen flow of 30 ml/min on a Mettler DSC-25 instrument. The films were encapsulated in aluminum pans and heated at a rate of 10 °C/min. \(T_m\) was determined from the DSC endotherm, which was taken as the peak temperature of the melting endotherm. \(T_g\) was taken as the midpoint of the stepwise increase of the specific heat associated with the transition. The software used for these analyses was Graphware-72.

3. Results and discussion

Blending is a common practice in polymer science to improve unsatisfactory physical properties of the existing polymer and has been applied to PHB in recent years. The techniques most commonly adopted to blend polymers are either melt blending (direct mixing of the component polymers in the molten state), or film casting from a common solvent. While the former method tends to mimic industrial processing conditions, the latter is a simple laboratory approach. In this study the latter approach was adopted to study the effect of blending starch on the physical properties of PHB.

Out of the various proportions studied, film formation started at a PHB:starch ratio of 0.3:0.7. The density of films of different ratios of PHB:starch, was found to be more than water for most of the combinations indicating that the material would sink to the bottom of water-bodies and get degraded in the sediments when disposed of.

The tensile strength of the blend film with the ratio of 0.7:0.3 PHB:starch was maximum i.e. 31.45 MPa as compared to virgin PHB (18.29 MPa). The variation in tensile strength, Young’s modulus and extension needed to break for different combinations of PHB:starch are represented in Table 1. The nature of all the combinations was found to be crystalline as determined by DSC. The thermal stability, as determined by TGA was in the range of 203–223 °C, whereas the thermal stability was
increased by 30 °C for the blends of PHB with TS as compared to the blends with starch powder alone (Table 2). Fig. 1 depicts the DSC thermogram showing the thermal stability at 259.6 °C for PHB:(TS) ratio of 0.7:0.3. The melting point for all the films ranged between 165 and 168 °C (Table 2), it was also reported by Ramsay et al. (1995), that there is no shift in the melting point of the polyesters, suggesting that there is no interaction between the two polymers. The advantage of use of TS containing glycerol as compared to native starch granules is that it can be reprocessed at elevated temperatures retaining its flexibility. Thermal analysis of the blends showed no indication of any interaction between the two polymers. The glass transition temperature was in the range of 63.1–87.4 °C (Table 2). The DSC data also revealed that PHB and starch blends had a single glass transition temperature for all proportions of the components. It has been reported earlier by Scandola et al. (1994) that if the $T_g$ is higher than the room temperature it implies that at room temperature the corresponding blends are stable homogeneous mixtures. Generally the physical properties were found to be optimum for the ratio of 0.7:0.3 PHB:starch. In another study by Ramsay et al. (1992) it was reported that by blending starch with Polyhydroxybutyrate-co-hydroxyvalerate (PHB-co-HV) even at 0.5:0.5 the blend exhibited useful thermoplastic properties. The values of the tensile strength, Young’s modulus and extension needed to break obtained in the present study were in concurrence with those reported earlier by Ramsay et al. (Table 3). When compared to synthetic plastics, this blended bioplastic has properties comparable to other thermoplastics. Table 4 shows the comparison of physical properties of the PHB and blend films with other thermoplastics.

The possible advantage of using TS containing glycerol as compared to native starch granules lies in that it can be deformed and distributed in the blending process. In addition, this type of TS can be reprocessed at elevated temperature, as it retains its flexibility.
4. Conclusion

The results indicate that blending of starch with PHB in a ratio of 30:70% could be advantageous for cost reduction with improved properties than the virgin PHB. Application of starch in biodegradable plastics (as a filler or as a bioester) has been studied greatly with other non-biodegradable polymers such as HDPE, LDPE etc., in order to make the plastic biodegradable.

The primary aim of the study was to determine the feasibility of blending starch with PHB. As the cost of PHB is very high as compared to synthetic plastics and as starch is abundantly available at a very low cost, blending of starch up to 30% in PHB would help in substantially reducing the cost of bioplastic, without compromising the physical properties. This material might also be used as a coating material on paper or cardboard used for food packaging etc.

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References


Table 3

<table>
<thead>
<tr>
<th>Composition</th>
<th>Yield stress (MPa)</th>
<th>Elongation to yield (mm)</th>
<th>Strength at break (MPa)</th>
<th>Elongation to break (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE 100%</td>
<td>24 ± 0.2</td>
<td>7.2 ± 0.2</td>
<td>35.4 ± 3.4</td>
<td>759 ± 65</td>
<td>1004 ± 37</td>
</tr>
<tr>
<td>(PHB-co-HV) starch granules 50:50%</td>
<td>12.5</td>
<td>0.7</td>
<td>7.7</td>
<td>1.0</td>
<td>2498 ± 120</td>
</tr>
<tr>
<td>(PHB-co-HV) starch granules 75:25%</td>
<td>17.5</td>
<td>1.4</td>
<td>8.6 ± 2.6</td>
<td>5.1</td>
<td>2132 ± 36</td>
</tr>
<tr>
<td>(PHB-co-HV) starch granules 100:0%</td>
<td>24.4</td>
<td>5.9</td>
<td>17.7 ± 3.9</td>
<td>25 ± 8</td>
<td>1525 ± 114</td>
</tr>
<tr>
<td>PHB:starch 50:50%</td>
<td>12.46</td>
<td>–</td>
<td>2.7</td>
<td>2.8</td>
<td>1712</td>
</tr>
<tr>
<td>PHB:starch 70:30%</td>
<td>18.07</td>
<td>–</td>
<td>31.9</td>
<td>11.7</td>
<td>3334</td>
</tr>
</tbody>
</table>

HDPE: High density polyethylene; (PHB-co-HV): polyhydroxybutyrate-co-hydroxyvalerate.

aData from Ramsay et al. (1995).

Table 4

<table>
<thead>
<tr>
<th>Composition</th>
<th>TS (Mpa)</th>
<th>Tm (°C)</th>
<th>Tg (°C)</th>
<th>Th.S (°C)</th>
<th>Y.M. (MPa)</th>
<th>Density (g/cm³)</th>
<th>E.B. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>18.29</td>
<td>168.0</td>
<td>63.1</td>
<td>223.0</td>
<td>1708</td>
<td>0.984</td>
<td>3.32</td>
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<tr>
<td>PHB:starch 0.7:0.3</td>
<td>32.0</td>
<td>167.0</td>
<td>71.3</td>
<td>260.0</td>
<td>3340</td>
<td>1.142</td>
<td>11.70</td>
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<tr>
<td>PP</td>
<td>38.0</td>
<td>176.0</td>
<td>10.0</td>
<td>–</td>
<td>–</td>
<td>0.905</td>
<td>–</td>
</tr>
<tr>
<td>PET</td>
<td>70.0</td>
<td>267.0</td>
<td>69.0</td>
<td>–</td>
<td>2900</td>
<td>1.38</td>
<td>–</td>
</tr>
<tr>
<td>HDPE</td>
<td>35.4</td>
<td>–</td>
<td>–</td>
<td>1004</td>
<td>1.14</td>
<td>759 ± 65</td>
<td>–</td>
</tr>
<tr>
<td>Nylon-6,6</td>
<td>83</td>
<td>265.0</td>
<td>50.0</td>
<td>–</td>
<td>2800</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Tm: Melting temperature; Tg: glass transition temperature; TS: tensile strength; Th.S: thermal stability; Y.M.: Young’s modulus; E.B: extension needed to break; PP: polypropylene; PET: polyethylene terephthalate; HDPE: high density polyethylene.

aData obtained in the present study.

bData from Ramsay et al. (1993).


