Thermal and Mechanical Behavior of Injection Molded Poly(3-hydroxybutyrate)/Poly(ε-caprolactone) Blends

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Received: December 2, 2004; Revised: July 13, 2005

Aiming the development of high-performance biodegradable polymer materials, the properties and the processing behavior of poly(3-hydroxybutyrate), P(3HB), and their blends with poly(ε-caprolactone), PCL, have been investigated. The P(3HB) sample, obtained from sugarcane, had a molecular weight of 3.0 × 10^5 g.mol⁻¹, a crystallinity degree of 60%, a glass transition temperature (T_g), at -0.8 °C, and a melting temperature at 171 °C. The molecular weight of PCL was 0.8 × 10^5 g.mol⁻¹. Specimens of 70/30 wt. (%) P(3HB)/PCL blends obtained by injection molding showed tensile strength of 21.9 (± 0.4) MPa, modulus of 2.2 (± 0.3) GPa, and a relatively high elongation at break, 87 (± 20%). DSC analyses of this blend showed two T_g’s, at -10.6 °C for the P(3HB) matrix, and at -62.9 °C for the PCL domains. The significant decrease on the T_g of P(3HB) evidences a partial miscibility of PCL in P(3HB). According to the Fox equation, the new T_g corresponds to a 92% wt. (%) P(3HB)/PCL composition.

Keywords: P(3HB), cold compaction, injection molding, mechanical behavior

1. Introduction

The family of microbial polyesters known as polyhydroxyalkanoates (PHAs) has been receiving considerable attention due to their potential use as environmentally friendly thermoplastics. These polymers undergo hydrolytic and enzymatic degradation. Poly(3-hydroxybutyrate), P(3HB), is a well known example of the PHAs. This polymer has properties similar to those of polypropylene, possesses low thermal stability, and can be produced by bacterial fermentation. It is not only biodegradable that makes PHAs so fascinating; it is also their synthesis from renewable carbon sources, based on agriculture or even on industrial wastes, allowing a sustainable closed cycle process. However, some characteristics of P(3HB) limit its applications, such as high crystallinity, poor processability and high fragility. In order to obtain a material with better characteristics, PHB can be modified, or physical mixtures can be prepared with other biodegradable polymers, enhancing the range of applications of the polymer and controlling his profile of biodegradation. Biodegradation of polymer blends is mainly determined by the degradability of the blend components, the blend composition, the phase structure (miscibility and crystallinity of the components) and the surface blend composition. P(3HB) has been found to be miscible with various polymers, including poly(ethylene oxide), poly(epichlorohydrin) and poly(vinyl acetate) PVAc. The study of systems with immiscible binary blends with P(3HB) are also important in controlling the profile of biodegradation. P(3HB)/poly(propiolactone), P(3HB)/poly(ethylene adipate) and P(3HB)/poly(3-hydroxybutyric acid-co-hydroxyvaleric acid) blends showed that they degrade faster than the pure components and the acceleration occurred due to the phase-separated structure.

On the other hand, poly(ε-caprolactone) (PCL) is an aliphatic polyester also degradable in the environment by hydrolytic or enzymatic degradation. It is a semi-crystalline polymer with crystallinity degree that lies at approximately 50% and glass transition temperature of -70 °C. In general, PCL acts as a polymeric plasticizer (it lowers the elastic modulus) enhancing the processability of the blend. In the present work mixtures of commercial biodegradable polymers, P(3HB) and PCL, were prepared, attempting to obtain a material with high flexibility and good biodegradability to be applied in packaging. These blends were then characterized by thermal (DSC, TGA) and mechanical (tensile tests) methods.

2. Material and Methods

2.1. Materials

The P(3HB) samples used in this study were supplied by PHB Industrial S.A., Brazil (batch L-57-2) as a white fibrous powder. The material was produced from sugarcane by bacterial fermentation and had a number average molecular weight of 3.0 × 10^5 g.mol⁻¹. Poly(ε-caprolactone) was purchased from Solvay (CAPA 6806) with a nominal molecular weight of 80,000 g.mol⁻¹.

Before processing, the P(3HB) was grinded in a high speed impact mill, Netzsch CUM-300, to decrease and homogeneize the grain size. The granulometric analysis was carried out in a Horiba LA-910 laser scattering particle size equipment, showing that, after milling, the average grain size of P(3HB) was 181.3 µm (10% < 60 µm and 98% < 600 µm).

The identity of the samples was confirmed on the basis of the infrared spectrum, recorded on a Perkin Elmer Spectrum One B spectrometer, and X ray diffractometry data, obtained using a Shimadzu XRD 6000 diffractometer, which provided consistent data to the reported in literature. Differential scanning calorimetry, performed...
on a Netzsch STA 409C calorimeter, showed, for powder P(3HB) samples, glass transition and melting temperatures of -0.8 °C and 171 °C, respectively, and 60.6% of crystallinity degree.

2.2. Injection molding

Dogbone-shaped specimens of P(3HB) and 70/30 wt. (%) P(3HB)/PCL blends were obtained in a Battenfeld 250 Plus injection molding machine, with a clamping force of 25 tons, plasticizing capacity of 9.5 g.s⁻¹, and L/D = 16. Standard processing conditions were screw speed of 250 rpm and zone temperatures rising from 135 °C in the first barrel zone to 165 °C in the die zone. Prior to processing, the material was dried under vacuum at 60 °C overnight.

2.3. Characterization

2.3.1. Scanning Electron Microscopy (SEM)

The fracture behavior was investigated by carrying out scanning electron microscopy on fracture surfaces from specimens submitted to mechanical tests and cryo-fractured specimens, using a Zeiss DSM 940 A at 10 kV. The samples were coated with a thin layer of gold (ca. 15 nm), under vacuum, using a BAL-TEC SCD 050 Sputter Coater.

2.3.2. Mechanical characterization

Tensile tests were performed according to the ISO 527 standard test method, on a computer-controlled Kratos testing machine at a constant cross-speed of 50 mm.min⁻¹. The tests were done in sevenfold.

2.3.3. Thermal analysis

Differential Scanning Calorimetry (DSC) analysis was carried out on a NETZSCH STA 409C instrument. The samples for DSC measurements had an average weight of 10 mg and were scanned at a heating rate of 10 °C.min⁻¹ under helium. Thermogravimetric analyses (TGA) were carried out under nitrogen atmosphere, from 25 to 600 °C at the heating rate of 10 °C.min⁻¹ on a NETZSCH STA 449C equipment.

3. Results and Discussion

Specimens of 100% P(3HB) obtained by injection molding shows tensile strength of 24.5 (± 0.8) MPa, elongation at break of 18 (± 2)% and Young modulus of 3.8 (± 0.1) GPa. These results are in agreement to those reported in literature for injection molded P(3HB)¹²,¹³. Other works with P(3HB) specimens prepared by casting or compression molding present lower Young moduli (ca. 1.5 GPa)⁸,¹⁴. SEM micrographs of the fractured surface of injection molded P(3HB) shows a typical brittle behavior (Figure 1). After processing the material takes on a light brownish color, revealing some thermal degradation even with optimal processing parameters.

The DSC analysis of injected P(3HB) gives, in the first heating, a Tₓ at -4.4 °C, a Tₘ at 172.5 °C and a melting enthalpy (ΔHₘ) of 42.8 J.g⁻¹. The degree of crystallinity was 30.2%, calculated by considering the melting enthalpy of 100% crystalline P(3HB) equal to 142 J.g⁻¹¹⁵. It is observed that the injection molding decreases by half the degree of crystallinity, when compared to the initial powder P(3HB). This decreasing, from 60.6% to 30.2%, is probably associated with the rapid cooling in the mold. This behavior was also verified in compression molded P(3HB)⁶. The increase of the amorphous phase causes a decrease in the stiffness, giving a more flexible material, and facilitates the attack of microorganisms.

For 70/30 wt. (%) P(3HB)/PCL blends, it was observed a small decrease on the tensile strength, 21.9 (± 0.4) MPa, and modulus, 2.2 (± 0.3) GPa. On the other hand, the elongation at break, 87 (± 20)%, was highly increased (80% in comparison with pure P(3HB)). The lowering of the stiffness by adding PCL to P(3HB) was also verified by Gassner & Owen¹⁰ for compression molded 60/40 P(3HB)/PCL blends. It was attributed to the plasticizing effect of PCL. SEM analysis of the fractured surfaces of 70/30 wt. (%) P(3HB)/PCL blends evidences phase separation (Figure 2).

The DSC data for the glass transition (Tₓ) and melting temperatures (Tₘ) are summarized in Table 1. The DSC analysis of the 70/30 P(3HB)/PCL blend showed two Tₓ´s, one at -10.6 °C, corresponding to the P(3HB) matrix, and another at -62.9 °C, attributed to the PCL domains. The significant decrease on the Tₓ of P(3HB) evidences a partial miscibility of PCL in P(3HB). According to the Fox equation¹⁷, the new Tₓ corresponds to a 92/8 wt. (%) P(3HB)/PCL composition.
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Table 1. DSC data (T_g and T_m) for P(3HB), PCL and 70/30 P(3HB)/PCL.

<table>
<thead>
<tr>
<th>Material</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(3HB)</td>
<td>-61.0</td>
<td>171.0</td>
</tr>
<tr>
<td>Injected P(3HB)</td>
<td>-64.0</td>
<td>172.5</td>
</tr>
<tr>
<td>70/30 wt. (%) P(3HB)/PCL</td>
<td>-10.3 PHB</td>
<td>62.6</td>
</tr>
</tbody>
</table>

Table 2. Thermogravimetric data - onset (T_i) and maximum degradation (T_max) temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>T_i (°C)</th>
<th>T_max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(3HB)</td>
<td>283.4</td>
<td>307.2</td>
</tr>
<tr>
<td>PCL</td>
<td>389.8</td>
<td>432.6</td>
</tr>
<tr>
<td>Injected P(3HB)</td>
<td>280.2</td>
<td>301.5</td>
</tr>
<tr>
<td>70/30 wt. (%) P(3HB)/PCL</td>
<td>277.2</td>
<td>298.6</td>
</tr>
<tr>
<td>P(3HB)</td>
<td>390.3</td>
<td>429.5</td>
</tr>
</tbody>
</table>

On the other hand, the T_g for PCL does not vary significantly, as well as the T_m values.

Thermal degradation studies were carried out by thermogravimetric methods, showing that the thermal degradation of P(3HB) occurs in only one step and that the presence of oxygen does not interfere in the degradation process. A decrease on the onset and the maximum degradation temperatures for injection molded P(3HB), in comparison with virgin P(3HB), shows that some degradation took place on the processing. PCL is much more thermally stable than P(3HB). It was also observed that the addition of PCL slightly decreases the onset temperature of the P(3HB) degradation. A summary of the TGA data is shown in Table 2.

4. Conclusions

Specimens of P(3HB) obtained by injection molding showed mechanical properties of a rigid thermoplastic, with tensile strength and modulus compatible to diverse type of applications. The crystallinity of P(3HB) is highly decreased after processing, allowing a faster microbiological degradation.

Adding PCL to P(3HB) it is obtained a very flexible material. DSC analysis of injection molded 70/30 wt. (%) P(3HB)/PCL blends showed a partial miscibility of PCL in P(3HB), with a new T_g corresponding to a 92/8 wt. (%) P(3HB)/PCL composition.

Acknowledgments

The authors would like to thank CAPES and CNPq for scholarship support to MATD, RGH and ESM, PGCEM-UDESC for financial support, Prof. Eliana A. R. Duque (PUC-SP) for DSC analyses, and PHB Industrial S. A. for P(3HB) supply.

References