Comparing the Degradation of Poly-β-(hydroxybutyrate), Poly-β-(hydroxybutyrate-co-β-valerate)(PHBV) and PHBV/Cellulose Triacetate Blend

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ABSTRACT: The hydrolytic degradation of poly-β-(hydroxybutyrate) PHB, poly-β-(hydroxybutyrate-co-β-valerate) (PHBV) and PHBV/cellulose triacetate blend was studied under different pH at 37 °C. PHBV showed a similar trend of degradation to PHB but at higher rates in alkaline medium. The presence of cellulose triacetate in the blend increased the water uptake and permeability which favoured the hydrolytic degradation especially in lower pH medium. In the surface hydrolysis of PHB and its blends, the overall degradation rate was increased with higher pH values. The melting temperature, crystallinity and tensile properties were also determined. The blend, PHBV/CTAc had the lowest crystallinity values and PHB the highest. However, the blends were mechanically better in strength and toughness.

Keywords: Hydrolytic degradation, biodegradable polymers, Poly-β-(hydroxybutyrate), Poly-β-(hydroxybutyrate-co-β-valerate), Cellulose triacetate

1.0 INTRODUCTION

Large amount of plastic waste generated by industries poses serious environmental problems which may require up to hundred years for total degradation [1]. An approach to decrease the solid waste is to substitute conventional material with biodegradable materials [2,3,4] to reduce costs and to enhance the degradation of the final product [5].

Poly-β-(hydroxybutyrate) is one of the best known biodegradable polymers which can be produced from renewable resources via biosynthesis by bacterial fermentation [6,7]. It can also be produced by chemical synthesis from the polymerization of β-butyrolactone [8]. Poly-β-(hydroxybutyrate-co-β-valerate), PHBV is a copolymer of PHB containing segmens of
Comparing the Degradation of Poly-β-(hydroxybutyrate), PHB, and their similar melting temperature and crystallinity [8, 12]. However, it has a very narrow processability window and a low impact resistance. From previous work, PHB mixed with HV filler in the form of blends with cellulose triacetate (CTAc), showed miscible behaviour in the melt [9]. The blended polymer also showed improvement in processability and impact resistance. The aim of the present study is to investigate the biodegradable properties by examining the mode of hydrolytic degradation of this polymer blend. This is important to verify if the biodegradable properties are retained and the degree of the hydrolytic reaction could be intensified.

2.0 EXPERIMENTAL

2.1 Materials

PHB was supplied in powder form by Aldrich Chemical Company. The polymer has weight average molecular weight ($M_w$) of 279,000 contained 0.2% nitrogen and 0.66% ash (w/w). It is a commercial grade synthesized by the continuous fermentation of a strain of Alcaligenes eutrophus. The poly-hydroxyvalerate, PHV was also supplied in powder form by Aldrich Chemical Co. The content of hydroxyvalerate in PHV is 20%. Cellulose triacetate is soluble in tetrachlorometane aqueous, analytical grade 99% with boiling point at 61.2°C, was obtained from Fluka Chemie, Switzerland.

2.2 Preparation of Blend Films

Blend of PHBV and CTAc was prepared in the aqueous form using chloroform as solvent. The ratio of PHV as internal plasticiser in the formulation of PHBV was not more than 40% of overall blends whereas the PHBV:CTAc ratio used was 36:64. Blends were prepared by slowly casting films from chloroform. The resulting films were dried under vacuum at 80°C until they reached constant weight. The best ratios of PHBV:CTAc were selected according to the lowest melting point of blends obtained.

2.3 Differential Scanning Calorimetry

Thermal analysis of PHB and its PHBV/CTAc blend films were done using a differential scanning calorimeter (model DSC-7 Perkin Elmer, USA) under a nitrogen atmosphere, heating rate of 20°C min$^{-1}$. Two heating cycles were used for each polymer. PHB, PHBV and PHBV/CTAc were first heated from room temperature to 200°C to eliminate the thermal history of the samples, and then cooled to room temperature and immediately reheated to...
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200 °C. The second scan was done using the same heating rate as the first. All experiments were done in duplicate.

Crystallinity was determined using the following heat of fusion values for 100% materials: $H_0^{\text{PHB}} = 146,000 \text{ J/kg}$. The $H_0$ for PHBV was assumed to be the same as that for PHB [7].

2.4 Determination of Tensile Properties

Tensile test were carried out according to ASTM D-638-99 [10] on Type I specimens of films using universal testing machine Model Lloyd 1000S at a cross-head speed of 3 mm/min.

2.5 Water Uptake and Permeability Studies

Water uptake and permeability studies were carried out according to previous work done by Kester and Fennema [11]. The water uptake value was calculated using this following equation:

$$\text{Water uptake (\%)} = \frac{M_2 - M_1}{M_1} \times 100 \quad \text{(1)}$$

Where $M_2$ is the mass of sample after immersion (g) and $M_1$ is the mass of sample before immersion (g).

2.6 Degradation of Polymer Films in the Presence of Aqueous Solutions

For the degradation study, cast films were prepared and cut into pieces measuring approximately 2 cm x 1 cm. Each piece was weighed individually and stored. Degradation experiments were conducted as follows: 20 films of the cut films were divided into four groups, each group containing five pieces. The average weight loss was taken as the average of the four groups. Each piece of the film was placed in a screw capped specimen tube in the presence of 50 ml of the buffer solution. The degradation experiment was performed at 37 °C in pH 2.3, 7.4, 10 and 13.

3.0 RESULTS AND DISCUSSION

3.1. Differential Scanning Calorimetry
Table 1 summarizes the melting temperatures and crystallinity of the polymers. The melting temperatures agreed with values in the literature. PHB is a thermoplastic material with a melting temperature around 180°C, crystallizes to form large spherulites when cooled slowly after melting [12]. The equilibrium melting temperature of an infinite PHB crystal has been reported to be 197 ± 2°C [12]. The melting temperatures of PHBV and the blend film of PHBV/CTAc were much lower than PHB. These could be explained by the decrease in crystallinity and overall structure of the resultant blends.

Table 1: Melting temperatures and crystallinity of PHB, PHBV and PHBV/CTAc

<table>
<thead>
<tr>
<th>Properties</th>
<th>PHB</th>
<th>PHBV</th>
<th>PHBV/CTAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Temperature (°C)</td>
<td>179.9</td>
<td>172.9</td>
<td>169.4</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td>71.9</td>
<td>51.1</td>
<td>19.5</td>
</tr>
</tbody>
</table>

### 3.2 Tensile Properties

Table 2 shows the fundamental physical properties of PHB and its blends with PHV and CTAc compared with those of common polymer isotactic polypropylene as reference. The tensile strength (40 MPa) of PHB film was quite close to those of isotactic polypropylene. However, the elongation at break of PHB (6%) was markedly lower than that of polypropylene, though the Young’s modulus was higher. Thus, PHB was stiffer and more brittle than polypropylene. Previous report showed that the brittleness of PHB film is due to cracks within the spherulites that form under conditions of no externally applied stress [13]. Interestingly, the blend film of PHBV/CTAc showed a slightly increase in Young’s modulus (5.3 GPa) and the tensile strength (52 MPa) which result in a stiffer material. From previous work, increasing the HV content as plastisicer does help in getting a more flexible polymer [8].

Moreover, the extension to break (15%) has input some reduction in the brittleness of PHB film.

Table 2: Physical and mechanical properties of PHB, PHBV, PHBV/CTAc including isotactic polypropylene at 25°C.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PHB</th>
<th>PHBV</th>
<th>PHBV/CTAc</th>
<th>Polypropylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elongation at Break (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
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<table>
<thead>
<tr>
<th></th>
<th>CTAc</th>
<th>(PP30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (GPa)</td>
<td>3.5</td>
<td>4.7</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>52</td>
<td>38</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>6</td>
<td>15</td>
</tr>
<tr>
<td>Water uptake(wt %)</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Water permeability</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

a after 24 hours (all samples in similar thickness)

b at 25°C and relative humidity 90%

3.3 Water Vapour Permeability

Water vapour permeability (at 25 °C, RH gradient 90%) through PHB and its blends PHBV and PHBV/CTAc was compared to permeability data of polypropylene. PHB and PHBV exhibited good barrier properties to moisture vapour transmission. This property was slightly decreased with the incorporation of CTAc into the copolymer. In addition, the blending of cellulose triacetate into the polymer showed an increase in the water uptake properties. Such behavior is common for hydrophilic polymer which molecules bonded tightly by hydrogen bonding with H2O molecules and results in more active permeance. This caused a significant increase in the solubility of water in the films due to the sigmoidal shape of the sorption isotherms for polar materials [1].

3.4 Hydrolytic Degradation

Degradation of the polymers was monitored by gravimetric methods. Table 3 shows the degradation of PHB, PHBV and PHBV/CTAc relative to cellulose triacetate in high medium at 37 °C. (The t10 and t50 are the measured time for the hydrolysis of 10% and 50% of initial weight of polymer film respectively.)
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Table 3: The \( t_{10} \) and \( t_{50} \) weight loss parameters for polymers in a pH 2.3 buffer at 37 °C (thin films)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( t_{10} ) (days)</th>
<th>( t_{50} ) (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHB</td>
<td>310.0</td>
<td>n.d* (8.2% in 300d)</td>
</tr>
<tr>
<td>PHBV</td>
<td>313.0</td>
<td>138.0</td>
</tr>
<tr>
<td>PHBV/CTAc</td>
<td>62.0</td>
<td>100</td>
</tr>
<tr>
<td>CTAc</td>
<td>138.0</td>
<td>241.0</td>
</tr>
</tbody>
</table>

*n.d - not determined

The degradation rate of polymers was slow with weight reduction of 8.2% and 8.9% for PHB and PHBV, respectively after 300 days of ageing relative to CTAc. These were characterized by an initial slow weight loss, followed by an enhanced secondary phase \( t_{50} \). Interestingly, the degradation rate was increased with the incorporation of CTAc in the blend.

Figures 1 and 2 show the progressive weight loss from PHB, PHBV and PHBV/CTAc films as a function of hydrolysis time (storage) in pH 7.4, 10.0 and 13.0 at 37 °C. The weight loss from these films was noted to follow a zero-order pattern. It seems that degradation occurred through a constant surface area. This means that the degradation from the sides of the films was not significant as compared to the degradation from the planar surface [14].

This could be explained by surface erosion which results in the release of incorporated materials that reflects their relative positions in the film. The position of each component is determined by its ability to diffuse throughout the film architecture.

In Figure 1, both polymers showed a more rapid loss of mass in pH 10 and 13 at 37 °C than in pH 7.4, indicating greater degradation in alkaline medium. In this case, PHB and PHBV were totally degraded after 20-30 days of ageing in highly alkaline medium. The rate content of the PHBV copolymers act as plasticizer produced a small, but noticeable change in the overall rate of degradation. However, it did not change the form of the degradation profile compared to pure PHB degradation profile.

There was a significant difference in the degradation of polymer blends, with PHBV/CTAc showing a more consistent pattern. The mass loss was at intermediate rate but significantly slower than PHB and PHBV in pH 10 and 13 (Figure 2). This difference may reflect the higher susceptibility of PHB and PHBV to degradation in higher pH condition because of the presence of highly branched ester groups and a greater number of tertiary carbons which facilitate hydrolysis and cleavage of the films [15]. It seems that another factor that favoured the slightly faster degradation of PHBV than PHB was its lower crystallinity (refer to Table 1 and Figure 1) as the larger amorphous regions enhanced the permeation of water molecules and subsequent hydrolysis of ester bonds. However this seems not a prevailing factor for the degradation of PHBV/CTAc in the higher pH medium.

The rate constant values, as derived from the gradient of the slope (Figure 2) were 0.49%, 0.70% and 0.77% day\(^{-1}\) for pH 7.4, 10.0 and 13.0, respectively. The higher values of increase in the degradation rate of PHB and PHBV probably indicates that the degradation of the polymer is mediated by hydroxyl ion. Majid and co-researchers [14] reported that the degradation of PHB in the presence of water occurred through surface hydrolysis with no change in the molecular weight. Thus, the mechanism is thought to occur through hydrolysis.
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In comparison, when the CTAc was blended into the PHBV polymer matrix, a combination of physical and structural properties governs the rate of dissolution from the matrix. The fibrous nature of cellulose coupled with the mainly β1-4 glycosidic bonds together with the replacement of acetate groups for each hydroxyl molecules determine the hydrophilic properties and chemical reactions. The combination results in its elution from the matrix being much slower than that of the fine PHBV particles.

![Graph showing the weight percentage of PHB vs. time](image_url)
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Figure 1: Progressive weight loss of (a) PHB and (b) PHBV films in buffer solutions at 37 °C: (■) pH 7.4, (▲) pH 10.0, (●) pH 13.0.

Figure 2: Progressive weight loss of PHBV/CTAc blends films in buffer solutions at 37 °C: (■) pH 7.4, (▲) pH 10.0, (●) pH 13.0.

4.0 CONCLUSION

By employing weight loss measurement during aqueous degradation of the polymers, this study indicated that the degradation of the polymer in water most probably occurred by surface hydrolysis. The degradation rate was slow in acidic hydrolytic medium but increased when the pH of the medium was increased from pH 7.4 to pH 13.
5.0 ACKNOWLEDGEMENT

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6.0 REFERENCES


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