Preparation and Properties of Polyhydroxybutyrate Blended with Different Types of Starch

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ABSTRACT: This study examines the properties of polyhydroxybutyrate (PHB) when blended with two types of maize starch, Starch 1 (containing 70% amylose) and Starch 2 (containing 72% amylopectin). The PHB/starch blends were prepared by melt compounding at a ratio of 70/30 by weight and characterized in terms of their morphology, structure, thermal, rheological, and mechanical properties. The results show that starch granules act as a filler in PHB/starch blends and also act as a nucleating agent causing a very significant reduction in the size of the PHB spherulites. There were found to be significant improvements in thermal, rheological, and mechanical properties, and these were greater for blends containing Starch 1 than those containing Starch 2. These improvements are attributed to enhanced hydrogen bonding between PHB and Starch 1 with high-amylose content. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 688–694, 2010

Key words: Polyhydroxybutyrate; maize starch; blends; biodegradable; hydrogen bonding

INTRODUCTION

With the increasing price of crude oil and concerns over the environmental impact of plastic waste, there is increasing interest in polymers that are both derived from renewable resources and are biodegradable. One such biopolymer is polyhydroxybutyrate (PHB) (Fig. 1). PHB is made by controlled bacterial fermentation.[1] It is a semicrystalline polymer with a high melting temperature and a high degree of crystallinity. It is perfectly isotactic and does not include any chain branching and therefore flows easily during processing. It is 100% biodegradable and insoluble in water.

PHB has a number of drawbacks that have restricted its use. First, the fermentation and extraction process is inefficient and expensive.[2] Second, PHB has very low melt viscosity, poor formability, and poor mechanical properties.[2] The large spherulites in its structure give rise to cracking and brittleness. Third, its thermal decomposition temperature of 210°C is just above its melting temperature of 170°C, therefore leaving a narrow temperature window for processing. The degradation of PHB, in a temperature range of 180–200°C, is due to random chain scission causing a gradual decrease in molecular weight. Hence, the basic problem with PHB is that it has too high a rate of chain scission at its melting point.[3–5]

Efforts have been made to improve the thermal and mechanical properties of PHB. The most economical and commonly used method is blending of PHB with other polymers,[6–13] such as starch, polycaprolactone (PCL), poly (vinyl acetate) (PVAc), and cellulose derivatives.

Starch is considered to be an attractive biopolymer due to its low cost, low density, nonabrasive nature, and biodegradability.[14,15] It is composed of a linear polymer (amylose) and a branched polymer (amylopectin) (Fig. 2). Thermoplastic starch (TPS) is obtained by mixing starch powder, water, and/or plasticizers, such as polyols, mono-, di-, or oligosaccharides, fatty acids, lipids, and derivatives, through a "gelatinization" process.[16]

Some efforts have been made to produce PHB/starch blends with improved mechanical properties. Up to now, blends with PHB has been prepared either by a conventional solvent casting method, usually from chloroform solution, or by melt processing methods, such as injection molding and compression molding, after compounding. The thermal and mechanical properties of solvent-cast films of PHB and starch/thermoplastic starch (TPS) have been studied by Godbole et al.[6] They found that blends with a PHB : TPS ratio of 0.7 : 0.3 showed the best properties and had reduced cost compared with other blends. Innocentini-Mei et al.[7] studied blends of PHB with starch and starch derivatives produced by injection molding. They reported that the blends containing natural starch and starch
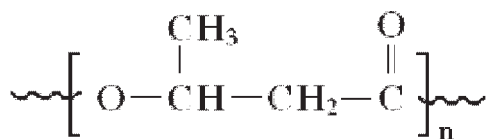
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Figure 1 Structure of polyhydroxybutyrate (PHB).

adipate resulted in brittle materials. Thire' et al.[17] processed PHB/starch blends by compression molding. They also observed that the addition of starch decreased the mechanical properties of PHB and decreased the degree of crystallinity without affecting the PHB crystalline lattice. Lai et al.[18] have studied the mechanical properties and biodegradability of solvent-cast films of TPS as the matrix reinforced with PHB (at addition levels of 1, 3, 5, and 7 wt %).

The objective of this study is to investigate the effect of blending maize starch with polyhydroxybutyrate to improve its properties and cost effectiveness. Two types of maize starch, Starch 1 (containing 70% amylose) and Starch 2 (containing 72% amylopectin), were blended with PHB. The morphological, thermal, and rheological properties were examined. The results are interpreted in terms of the interfacial bonding between PHB and the different types of starch.

EXPERIMENTAL

Materials

Pure bacterial polyhydroxybutyrate (PHB), in the form of a white powder, was purchased from Biomer, Germany. Its weight average molecular weight (M_w) was found to be 283×10^3, determined by Gel Permeation Chromatography (GPC). Starch 1 (HYLON VII, native food starch refined from high-amylose maize containing 70% amylose) and Starch 2 (ECO-MAIZE, regular maize starch containing 72% amylopectin) were both obtained from National Starch & Chemical Company, UK. No plasticizer or other additive was used for processing the PHB/starch blends.

Preparation and processing of the blends

Table I shows the formulations of the different samples prepared. Formulations of PHB and starch were mixed in a Haake Polylab Rheomix at 175°C for 10 min at a constant rotor speed of 50 rpm. These materials were used for differential scanning calorimetry (DSC) and capillary rheometry tests. Further processing was performed by hot pressing using a 20-Ton Lab Press CO1123/1. After hot pressing at 180°C, the mold assembly was cooled down to 70°C and held for 3 min before cooling down to room temperature. Materials prepared in this way were characterized by optical microscopy, Fourier transform infrared (FTIR), wide angle X-ray diffraction (WAXD), dynamic mechanical thermal analysis (DMTA), and tensile testing.

Characterization of polymer blends

A Leica DMLM optical microscope, equipped with a FP82 hot stage and a FP90 control unit, was used to study the spherulites in a PHB sample and in the PHB/starch blends. A scanning electron microscope (SEM), LEO 1530 VP, was used to examine the fracture surfaces of PHB/starch blends.

Fourier transform infrared (FTIR) spectra were obtained at room temperature on a FTIR-8400S spectrometer. The scanned wavenumber range was 4000–600 cm^{-1}.

Wide angle X-ray diffraction (WAXD) patterns were recorded for 2θ between 0 and 40° using a Bruker AXS D8 X-ray diffractometer equipped with a copper tube operating at 40 kV and 40 mA producing CuKα radiation of 0.154 nm wavelength.

Dynamic mechanical thermal analysis (DMTA) measurements were performed using TA Instrument DMA Q800 apparatus in the flexure (Dual Cantilever) mode ($L_0 = .35$ mm). The rectangular specimens of dimensions $50 \times 10 \times 3$ mm were heated from -50 to 100°C at 3°C/min, at a flexure frequency of 10 Hz.

Differential scanning calorimetry (DSC) measurements were performed on a TA Instrument DSC 2010 apparatus fitted with an autosampler and mechanical cooler. Samples of approximately 10–15 mg
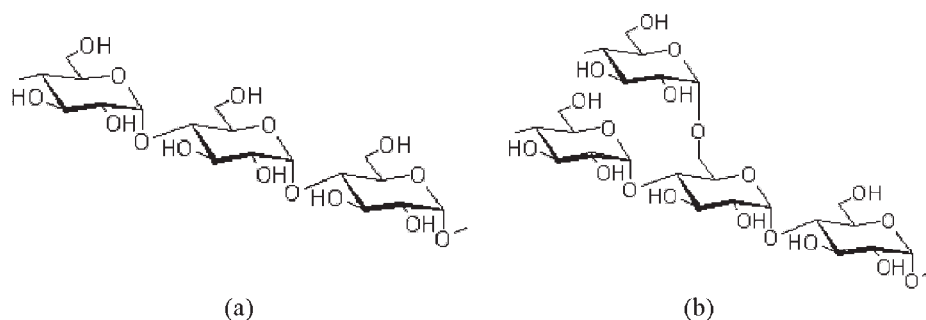

Figure 2 (a) Structure of amylose and (b) structure of amylopectin.

TABLE I
Formulations of Samples (wt %)

	PHB	Starch 1	Starch 2
PHB[a]	100	0	0
Blend 1	70	30	0
Blend 2	70	0	30

[a] For better comparison, the PHB used in this study has the same heating history as the blends.

in mass were sealed in aluminium pans and loaded into the autosampler. First, samples were heated from −25 to 200°C at 10°C/min and left for 1 min to measure the melting point of the as-formed sample, and then they were cooled down at the same heating rate to −25°C to determine the crystallinity. Then, the samples were reheated to 200°C at 10°C/min, so that the melting and degradation could be studied. All DSC analysis was performed in a nitrogen atmosphere.

The shear rheology of the pure PHB and PHB/starch blends was studied using a twin bore Rosand RH7 capillary rheometer. One bore of the rheometer was fitted with a long capillary die (L/D ratio = 16),

and the other bore was fitted with a short die. The diameter of both capillary dies was 1 mm. Melt viscosity was determined at shear rates of 20, 63, 200, 633, and 2000 s^{-1}. The Bagley correction was applied for the PHB/starch blends.

Tensile testing was performed on a LLOYD INSTRON L10000 Tensometer. The dumbbell-shape specimens (width ∼ 4 mm, thickness ∼ 3 mm, $L_0 =$ 25 mm) were extended at a crosshead speed of 5 mm/min. Charpy impact testing was carried out on a RAY-RAN universal pendulum impact system with a maximum impact energy of 7.5 J. The specimen size was 10 × 55 × 3.3 mm with a V-notch (2 mm deep, with a 45° angle and 0.25 mm radius along the base). The weight of the hammer and the impact velocity were 1.039 kg and 3.8 m/s, respectively.

RESULTS AND DISCUSSION

Morphological study

Figure 3 shows the dark field optical micrographs of the spherulites of PHB in pure PHB and PHB/starch
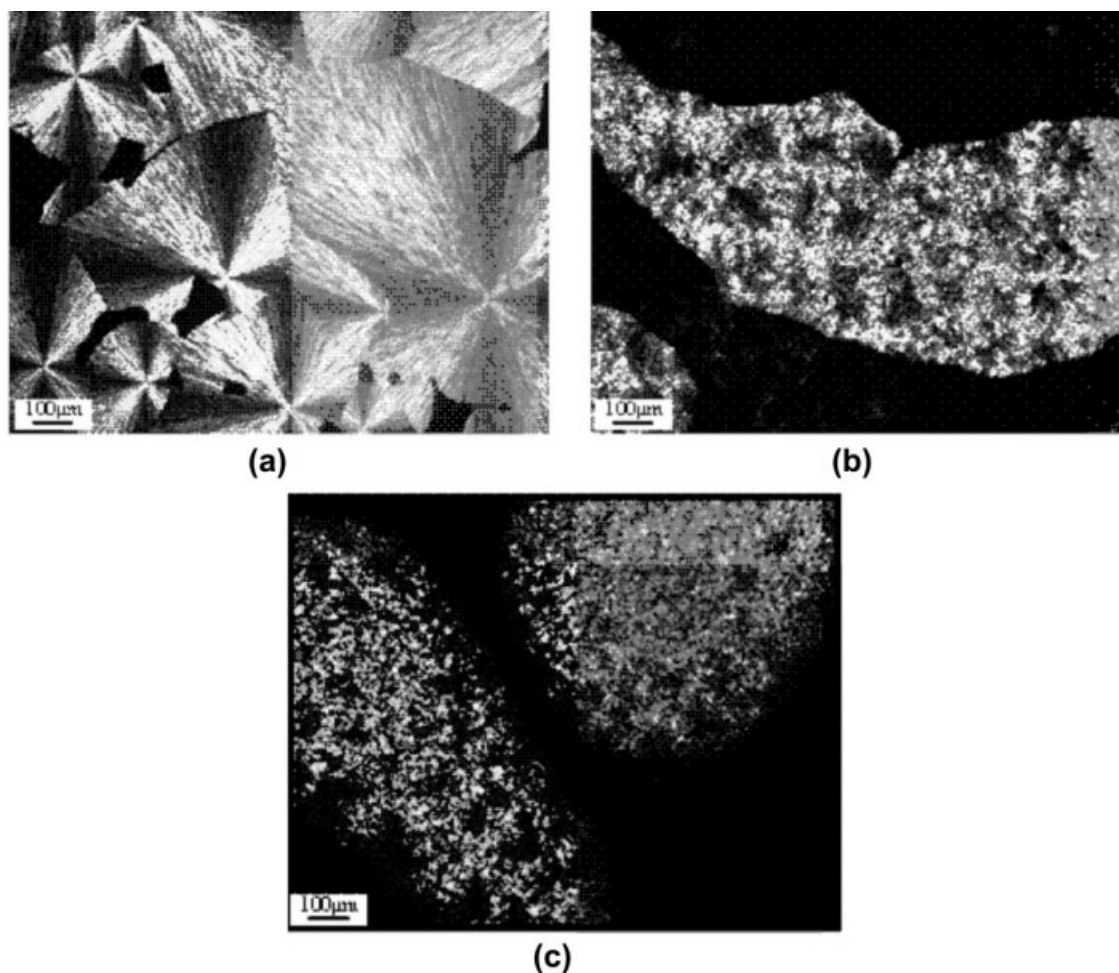

Figure 3 Polarizing optical micrographs of the spherulites of PHB during cooling in (a) pure PHB, (b) Blend 1, and (c) Blend 2.
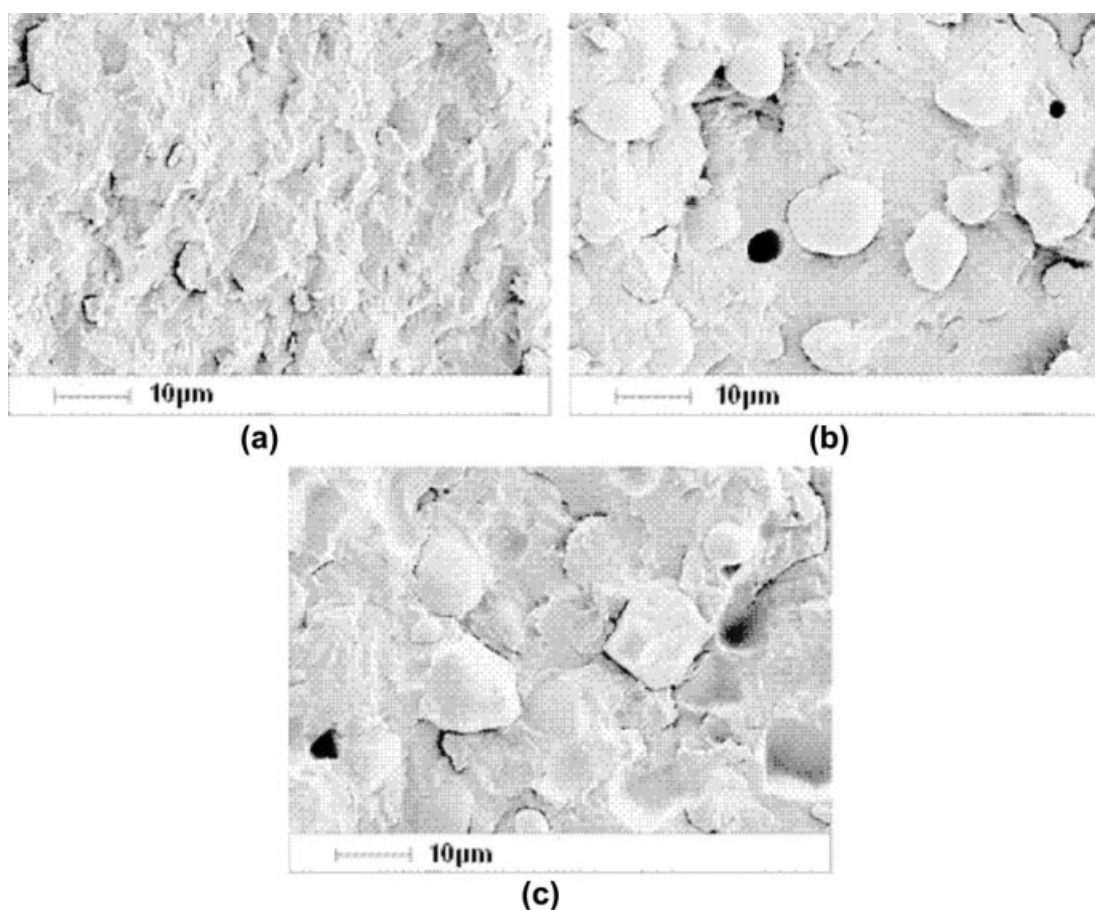
Figure 4 Scanning electron micrographs of fracture surfaces of (a) pure PHB, (b) Blend 1, and (c) Blend 2.

blends after heating to 200°C and cooling at 10°C/min. In general, the presence of starch significantly reduced the size of the PHB spherulites due to the nucleating effect of starch.

The scanning electron micrographs of Figure 4(b,c) show that the starch granules do not gelatinize or melt during processing. Hence, the starch granules act as a filler for PHB. There is also evidence of poor interfacial bonding between starch granules and PHB. Similar results were obtained by Thiré et al.[17]

Analysis of structure: FTIR and WAXD results

Typical FTIR spectra of PHB, starch, and PHB/starch blends are shown in Figure 5. The spectra of Starch 1 and Starch 2 are very similar. In the spectrum of Starch 1, the band at 3400 cm^{-1} is a strong and broad peak, which is related to the hydroxyl vibration. The changes in the peak in both width and intensity indicate the intensity of intermolecular and intramolecular hydrogen bonding occurring in starch. In the spectrum of pure PHB, there is a strong and sharp peak at 1724 cm^{-1}, which is attributed to the stretching vibrations of crystalline carbonyl groups; the amorphous carbonyl vibration

of PHB at 1750 cm^{-1} is very weak and cannot clearly be observed in the spectrum. It is found that the FTIR spectra of PHB/starch blends are different from the vibration peaks of the components.

As shown in Figure 5, the spectra of PHB/starch blends show an obvious decrease in the intensity of the band of the hydroxyl group at 3400 cm^{-1} compared with the pure starch. Furthermore, the center of the band of the hydroxyl group in PHB/starch blends shifts to a higher wavenumber compared with pure starch, and this suggests the formation of intermolecular hydrogen bonds between PHB and starch. There is an obvious broadening of the peaks in the carbonyl region of the blends compared with pure PHB. The peak at 1724 cm^{-1} has become weak, and the ratio of the peak at 1750 cm^{-1} to that at 1724 cm^{-1} has increased (see insert in Fig. 5). The band centered at 1709 cm^{-1}, which is attributed to the vibration of the hydrogen-bonded carbonyl groups,[19] increases on addition of starch. These results indicate that intermolecular hydrogen bonding occurs between the two components of the blends and the hydroxyl groups in the starch chains and the carbonyl groups in the PHB participate in the intermolecular interactions. Moreover, the
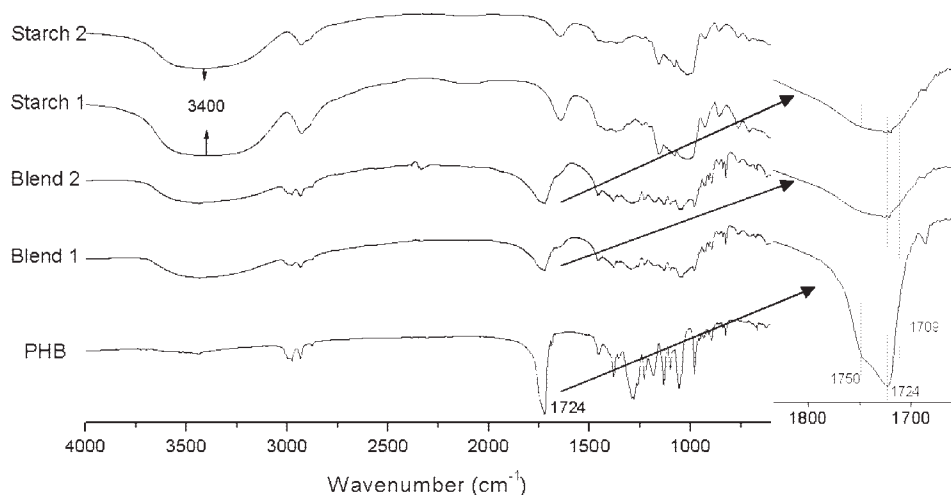
Figure 5 FTIR spectra of PHB, PHB/starch blends, Starch 1, and Starch 2.

change in the peak shoulder at 1750 cm^{-1}, attributed to the PHB amorphous carbonyl vibration,[20,19] indicates that the intermolecular hydrogen bonding is mainly due to the interactions between PHB and starch in the amorphous phase. These interactions may affect the crystal structure of the components. This is further investigated in the WAXD analysis later.

Similar changes in the FTIR spectra of PHB/chitosan blends were reported in the work of Chen et al.[20] Using FTIR and WAXD, they found the existence of hydrogen bonding between PHB and chitosan.

As shown in the WAXD patterns of Figure 6, the diffraction peak for (020) in PHB is located at $2\theta = 13°$ and that for (110) is located at $2\theta = 17°$[17]. In both PHB/starch blends, the (020) and (110) diffraction peaks are lower in intensity compared with those of pure PHB. The intensity ratio values $I_{(020)}/I_{(110)}$ for PHB and the PHB/starch blends are shown
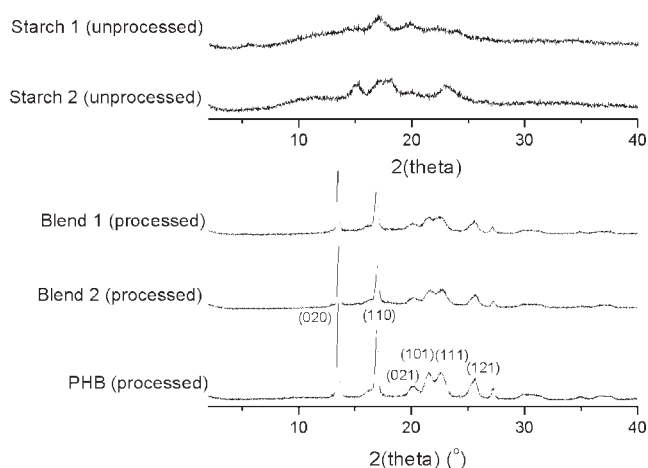
in Table II. It is seen from Table II that the addition of starch increases the $I_{(020)}/I_{(110)}$ ratio compared with pure PHB. This indicates that the original crystal structure of PHB has been disturbed, and this is thought to be due to the hydrogen bonding between PHB and the starch granules. The change in the $I_{(020)}/I_{(110)}$ ratio is greater for Blend 1 than Blend 2, and this implies that the hydrogen bonding effect is stronger in Blend 1 than in Blend 2. This result is further supported by the DMTA data.

Dynamic mechanical thermal analysis (DMTA)

The tan δ peak obtained from DMTA measurements can be used to assess interfacial bonding in polymer composites.[21,22] Figure 7 shows the plots of tan δ versus scan temperature for PHB/starch blends. Because of its poor formability and brittleness, the tan δ measurement was not obtained for pure PHB. Blend 1 gives a lower peak height compared with Blend 2. This result indicates that the Blend 1 dissipates less energy than Blend 2, i.e., that Blend 1 has a stronger interface. Moreover, Blend 1 shows a narrower tan δ peak than Blend 2, also indicating that Blend 1 has better interfacial bonding. This may be due to the linear structure of Starch 1 facilitating hydrogen bonding with PHB.

The tan δ peak temperature of Blend 1 (35°C) is slightly lower than that of Blend 2 (37°C), which may be due to the linear structure of Starch 1 having a less restricting effect compared with regular maize starch, which has a crosslinked structure.

Figure 6 WAXD profiles of Starch 1, Starch 2, PHB, and PHB/starch blends.

TABLE II
Ratio of $I_{(020)}/I_{(110)}$ in PHB and PHB/Starch Blends

	PHB	Blend 1	Blend 2
$I_{(020)}/I_{(110)} \pm 0.01$	1.33	1.49	1.42

Figure 7 Plot of tan δ vs. scan temperature for PHB/starch blends.
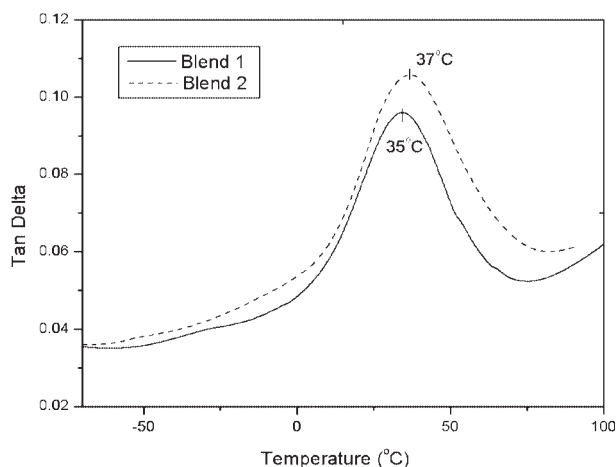
Figure 9 Plot of log (shear viscosity) vs. log (shear rate) from capillary rheometer for PHB and PHB/starch blends.

Thermal stability (DSC) study

Figure 8 shows the DSC curves of PHB and PHB/starch blends heated at a rate of 10°C/min. During the first heating run, the melting temperatures of PHB and PHB/starch blends are very similar, about 171°C. However, during the second heating run, the melting temperature for pure PHB shifts to significantly lower temperature due to chain scission. The melting point of Blend 2 is not reduced as much as that of pure PHB during the second heating run, showing less degradation. The blend of PHB and Starch 1 (Blend 1) shows virtually no degradation during the second heating run.

Improvement in the thermal stability of PHB is thought to be due to the hydrogen bonding between the hydroxyl groups of starch and the carbonyl groups of PHB. According to the work of Grassie et al.,[3–5] thermal degradation of PHB is due to chain scission through a widely accepted ring ester decomposition mechanism involving a six-membered ring transition state. Hydrogen bonding between starch and PHB
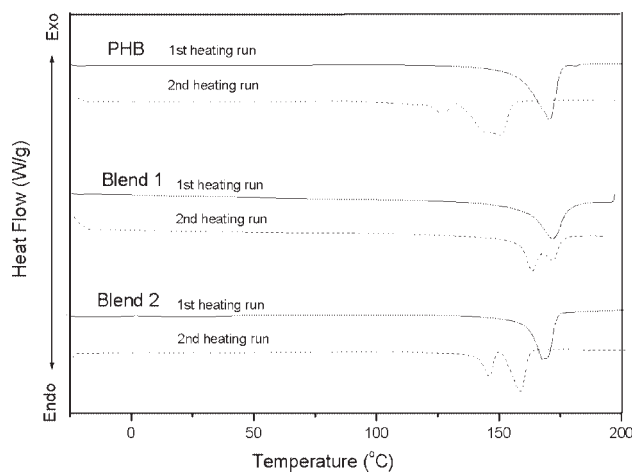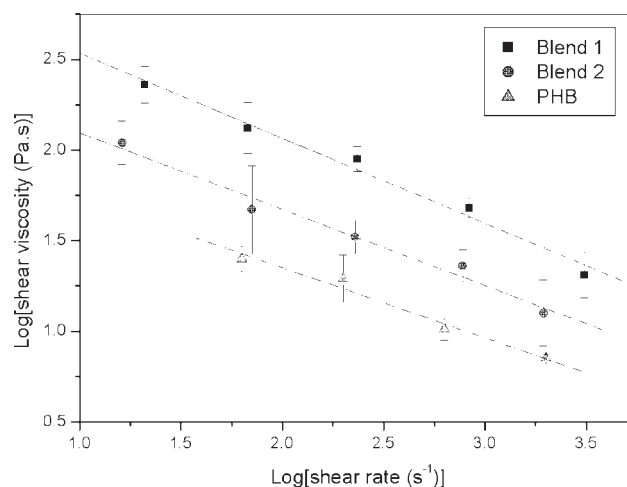
may inhibit the formation of the six-membered ring and hence improve the thermal stability of PHB.

Rheological behavior

Melt viscosity of pure PHB and PHB/starch blends was measured on a twin bore Rosand RH7 capillary rheometer. It was found that the melt viscosity of pure PHB was very low and the addition of starch made the polymer easier to process.

Figure 9 shows a plot of log (shear viscosity) vs. log (shear rate) and it is seen that the shear viscosity of PHB/starch blends is much higher than that of pure PHB, and the shear viscosity of Blend 1 was significantly improved compared with that of Blend 2.

The power law index (n) and consistency coefficient (K) were calculated according to the Power Law Equation[23]:

$$\log\eta = \log K + (n-1)\log\dot{\gamma} \qquad (1)$$

where, η is shear viscosity, $\dot{\gamma}$ is shear-strain rate, K is the consistency coefficient, and n is the power law index. The power law index is a measure of the deviation from Newtonian behavior of the fluid, and the consistency coefficient is the viscosity at a shear rate of 1 s^{-1}.

Figure 8 DSC curves of PHB and PHB/starch blends.

TABLE III
Power Law Index (n) and Consistency coefficient (K) Values for PHB and PHB/Starch Blends

	Power law index (n)	Consistency coefficient (K) Ns^n/m^2
PHB	0.6	132
Blend 1	0.6	1000
Blend 2	0.6	331

TABLE IV
Tensile Strength, Elongation at Break and Impact Strength of PHB/Starch Blends

	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m²)
Blend 1	12.5 ± 0.74	3.9 ± 0.49	0.9 ± 0.14
Blend 2	7.3 ± 1.06	2.8 ± 0.47	0.7 ± 0.11

As listed in Table III, the values of the power law index (n) for Blend 1, Blend 2, and PHB are the same. This implies that with increasing shear rate, the decrease in shear viscosity of PHB/starch blends is similar to that of PHB. The consistency coefficient (K) for Blend 2 is increased from 132 Ns^{n}/m^2 for pure PHB to 331 Ns^{n}/m^2. However, the K value for Blend 1, 1000 Ns^{n}/m^2 is significantly higher than that of pure PHB and Blend 2. These results can be attributed to the increased hydrogen bonding between PHB and starch with high-amylose content (Starch 1).

Formability and mechanical properties

The formability of pure PHB is very poor due to its low melt viscosity and brittleness. Thus, in this study, the mechanical data for pure PHB were not obtained. The addition of starch improved the formability of PHB.

It can be seen from Table IV that the mechanical properties of PHB/starch blends are still poor because the starch granules are acting as a filler in PHB (as shown in Fig. 4). However, tensile strength, elongation at break, and impact strength are greater for Blend 1 compared with Blend 2. Presumably this is due to the better hydrogen bonding between PHB and Starch 1.

CONCLUSIONS

A series of biodegradable PHB/starch blends were prepared by melt compounding and the morphology, structure, thermal stability, rheological behavior, and mechanical properties of the blends were investigated. The micrographs show that starch particles act as a nucleating agent for PHB crystallite formation. It is seen that PHB spherulites are significantly reduced in size. The SEM micrographs show that starch acts as a filler for PHB. The FTIR results indicate that intermolecular hydrogen bond occurs between PHB and both types of maize starch. As indicated from the WAXD results, the addition of starch affects the crystal structure of PHB. Compared with Starch 2, Starch 1 has stronger intermolecular hydrogen bonding with PHB due to its

high-amylose content and linear structure. This is also indicated by the DMTA results. The existence of hydrogen bonding improves the thermal stability, melt viscosity, and mechanical properties of PHB/starch blends. Hydrogen bonding between the hydroxyl groups of starch and carbonyl groups of PHB may inhibit chain scission degradation in PHB, and thus improve its thermal stability. The stronger hydrogen bonding effect between PHB and Starch 1 makes Blend 1 more stable than Blend 2. Furthermore, Blend 1 shows higher melt shear viscosity and better mechanical properties than Blend 2.

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