Mechanical Properties, Crystallization and Biodegradation Behavior of the Polylactide/Poly(3-hydroxybutyrate-co-4-hydroxybutyrate)/Poly(butylene adipate-co-terephthalate) Blown Films

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Abstract Poly(lactide) (PLA), poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P(3HB-co-4HB)), and poly(butylene adipate-co-terephthalate) (PBAT) ternary blends were prepared by extrusion blending. The biodegradable PLA/P(3HB-co-4HB)/PBAT films were successfully obtained by using blown films technique. Excellent stiffness-toughness balance was achieved for 55/10/35 PLA/P(3HB-co-4HB)/PBAT film. The tensile strength reached 33.0 MPa (MD) and 23.5 MPa (TD), the elongation at break exceeded 130 %, and tear strength exceeded 110 kN/m. The Young’s modulus as low as about 1800 MPa also met packaging applications. SEM observations revealed rough and long ligaments, indicating that the tear specimens were broken yieldingly. The addition of PBAT elastomers was the main reason for the improved toughness of the film. From DMA and SEM analysis, it was demonstrated that PLA, P(3HB-co-4HB), and PBAT were partially compatible. With increasing P(3HB-co-4HB) content, the melt and cold crystallization of PLA was promoted. The enzymatic degradation experiments indicated that the films had good biodegradability. These findings gave important implications for designing and manufacturing biodegradation package of high biological carbon content.

Keywords Poly(lactide); Poly(3-hydroxybutyrate-co-4-hydroxybutyrate); Blown films; Mechanical properties; Biodegradability

INTRODUCTION

Biodegradable aliphatic polyesters are getting more and more attractive due to their large application prospects in the field of packaging and single-use disposable items for their great biocompatibility, biodegradable, and renewable characteristics. As one of the most prominent polymers, poly(lactide) (PLA) has good biocompatibility, biodegradability, and high mechanical strength, and PLA films for packaging applications including food packaging, trashcan liners, shrink films, stretch films, and merchandise packaging are commonly made through a blown film process.[1-7]

Unfortunately, compared to polyolefins, neat PLA is not well suited for the blowing extrusion due to its relatively low melt strength as well as oxidative and hydrolytic degradation.[8,9] Many strategies have motivated considerable research efforts. The film blowing processability and mechanical properties of PLA can be improved by grafting reaction or blending with other polymers, plasticizers or nucleating agents. Blending PLA in an extruder with other flexible polymers is an excellent method for increasing the toughness of the resulting material particularly.[10-18] Poly(butylene adipate-co-terephthalate) (PBAT) is a commercially available biodegradable aliphatic-aromatic co-polyester and it exhibits excellent elongation at break with 700% in the tensile test, which results in a high impact and tear resistance.[19] PBAT is also a common polymer to be combined with PLA by melt blending. The PLA/PBAT blends are particularly interesting since they can offer a much wider range of applications and thus have significant commercial potential.[19-21] Yeh et al.[22] studied the compatibility and crystallization properties of PLA/PBAT blends, pointing out that 2.5% PBAT could effectively improve the toughness of the blend. Li et al.[23] studied the dynamic rheological behavior and morphology of PLA/PBAT blends, indicating that the PBAT content was 30 wt% and appeared in the elongated fibrous structure form in the blends. In addition, a co-continuous phase structure was observed when the PBAT content was 50 wt%. Zhang et al.[24] studied the PLA (70 wt%) blends with PBAT (30 wt%), obtaining samples with impact strength exceeding 30 kJ/m².

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The copolymer poly(3-hydroxybutyrate-co-4-hydroxybutyr-ate) (P(3HB-co-4HB)), a member of the poly(hydroxy alkanoates) (PHAs) produced by various many Archaea, has good biodegradability and biocompatibility. By changing the molar ratio of 3HB to 4HB, P(3HB-co-4HB) can be adjusted from highly crystalline plastics to soft elastomers. Neat poly(4-hydroxybutyrate) homopolymer has an elongation at break of about 1000%. Blending PLA and PHAs also provides an effective method for modifying the blends properties. Wang et al. studied the degradation behavior of PLA/P(3HB-co-4HB) blends in real soil, pointing out that P(3HB-co-4HB) had better degradation performance. Han et al. studied the mechanical properties of PLA/P(3HB-co-4HB) blend films, pointing out that P(3HB-co-4HB) can effectively improve the toughness of PLA. The elongation at break of the films exceeded 200%. Compared to binary blends, multicomponent polymer materials usually exhibit better balance performance. Zhang et al. studied ternary blends of PLA/PHBV/PBS, pointing out that PHBV/PLA/PBS 60/30/10 showed the optimum balance of mechanical performance.

Based on the above discussion, 35 wt% of PBAT was blended with PLA and P(3HB-co-4HB) was used to further improve the toughness of the PLA/PBAT films. In addition, P(3HB-co-4HB) can be used to improve the biobased content of films, which means highly biorenewable films. Mechanical properties, compatibility, crystallization behavior, and biodegradability of the PLA/P(3HB-co-4HB)/PBAT films were investigated in detail.

EXPERIMENTAL

Materials
All materials used in the study were commercial grade. PLA resin of 4032D was obtained from NatureWorks (USA), with a density of 1.24 g/cm³, a weight-average molecular weight (Mw) of 2.07 × 10⁵ g/mol, polydispersity of 1.73, and the melt flowing ratio (MFR, 210 °C, 2.16 kg) of 7 g/10min. PBAT was supplied by Xinjiang Blue Ridge Tunhe Polyester Co. Bioresource-based P(3HB-co-4HB) was provided by Tianjin Guoyun Biotech (Tianjin, China). It possessed a number-average molecular weight (Mn) of 3.24 × 10⁴ g/mol and polydispersity of 1.22 as determined by gel permeation chromatography (GPC). The content of 4HB in the co-polymer was 9.6 mol% determined by ¹H-nuclear magnetic resonance (NMR) spectroscopy.

Preparation of the Blend Films
Before compounding, PLA, P(3HB-co-4HB), and PBAT were dried at 65 °C for 12 h to remove moisture. The preparation of samples was carried out in a twin-screw extruder. The screw rotation speed was set at 100 r/min. The temperature profile was set at 150 °C (feeding zone), 190 °C (melting zones). After melt blending, each extrudate was quenched in cold water bath and granulated and the blends were dried at 65 °C for 6 h in a vacuum oven.

Then, all the PLA/P(3HB-co-4HB)/PBAT blend films were blown using a 3.00-mm smooth-bore single-screw extruder having an aspect ratio of 30:1 and fitted with a 64.5 mm diameter blown film die. The mold used external cooling air at a temperature of 20 °C. The barrel temperatures in different areas were between 170 and 190 °C and the screw speed was kept at 40 r/min. When the process was initiated, air was introduced at the bottom of the die to expand the tube and form bubbles. Moreover, the blow-up ratio (BUR) was 3, the frost line height (distance from die exit) was 15 cm, and the winding speed was 7.0 m/min.

Mechanical Properties Test
The blown films were cut into a dumbbell shape (W × H × L = 4 mm × 1 mm × 20 mm) for testing in the machine direction (MD) and transverse direction (TD), respectively. The measurements were performed using a tensile-testing machine (Instron-1121, Canton, MA) according to ASTM D638-2008 at a crosshead speed of 50 mm/min. All tests were carried out at room temperature and 53.0% relative humidity.

The right-angle tearing strength was measured at 23 ± 2 °C on an Instron 1121 testing machine. The measurements were conducted at a cross-head speed of 50 mm/min at room temperature according to QB/T 1130–91 in MD and TD, respectively. At least five runs for each sample were performed, and the results were averaged.

Scanning Electron Microscopy (SEM)
The tear fractured surfaces of the PLA/P(3HB-co-4HB)/PBAT films were analyzed with a scanning electron microscope (model Japan JXA-840 ESEMFE). A layer of gold was uniformly applied to all fractured surfaces prior to SEM observation.

Dynamic Mechanical Analysis (DMA)
Dynamic mechanical properties were measured using a dynamic mechanical analyzer (DMA, 850, TA Instruments, USA), which provided the plots of the loss tangent (tanδ) and the storage modulus (E′) versus temperature. The size of the sample was L × W × H = 12 mm × 4 mm × 1 mm. The experiment was performed in a tension mode at a constant heating rate of 3 °C/min and a frequency of 1 Hz. The temperature ranged from −60 °C to 125 °C for samples.

Differential Scanning Calorimetry (DSC)
Thermal properties of the films were studied by differential scanning calorimetry (TA Instruments Co., DSC Q20, USA) under a nitrogen atmosphere. First, the films were heated from 0 °C to 190 °C at a heating rate of 10 °C/min and held at 190 °C for 3 min to eliminate thermal history. Then the melt was cooled to −60 °C at 10 °C/min and again heated to 190 °C at 10 °C/min. Heat of fusion values (ΔHf) of the films were obtained from the second heating scans using the following formula:

\[
x = \frac{\Delta H_m}{\Delta H_{f0} \times W_{PLA}}
\]

where \(x\) is the degree of crystallinity of the samples, \(\Delta H_m\) is the heat of fusion of the blends, \(\Delta H_{f0}\) is the heat of fusion for 100% crystalline PLA (93 J/g), and \(W_{PLA}\) is the weight fraction of PLA in the blend films.

Wide-angle X-ray Diffraction (WAXD)
WAXD experiments were performed on a D8 advance X-ray diffractometer (Bruker, Germany) at room temperature in the range of 5°–55° at a scanning rate of 4 °C/min. The Cu Ka radiation (λ = 0.15418 nm) source was operated at 40 kV and 200 mA. Wide-angle X-ray diffraction measurements were carried out on the film samples to characterize the crystal structure and orientation.

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Polarized Microscopy (POM)
The crystalline morphology of blend films was observed with a Leica DMLP polarized microscope equipped with a Linkam TM600 hot stage and a camera controlled by computer. A small amount of sample with a thickness of approximately 0.05 mm was sandwiched between two microscope cover glasses and then placed on the hot stage. The samples were heated from room temperature to 185 °C at a rate of 30 °C/min, held there for 3 min to eliminate previous thermal history, and then rapid cooled under the action of liquid nitrogen to 90 and 130 °C for isothermal crystallization. The morphology changes were recorded during crystallization.

Enzymatic Degradation of Films
The enzymatic degradation of the blend films was carried out in phosphate buffer (pH = 8.0) containing 0.2 mg/mL of proteinase K (Genview) at 45 °C with shaking at 150 r/min. Sample films (8 mm × 8 mm × 0.1 mm) were placed in small glass bottles filled with phosphate buffer containing protease. The film was taken out periodically, washed with distilled water, and dried under vacuum to constant weight. Then, the weight of the film was measured. The surfaces of the PLA/P(3HB-co-4HB)/PBAT films were analyzed with a scanning electron microscope (model Japan JXA-840 ESEMFE). A layer of gold was uniformly applied to all surfaces prior to SEM observation.

RESULTS AND DISCUSSION

Mechanical Properties
Table 1 lists the tensile strength, elongation at break, tear strength, and Young’s modulus of PLA/P(3HB-co-4HB)/PBAT blown films. The addition of P(3HB-co-4HB) and PBAT changed the tensile behavior of the PLA/P(3HB-co-4HB)/PBAT films significantly as shown in Fig. 1. In MD, that is, in the stretching direction of the films, the elongation at break of neat PLA was 3.6%, the tensile strength of neat PLA film was 51.5 MPa, and no obvious yield was observed from the strain-stress curves, which showed brittle fracture upon tensile load. While 35% PBAT was added to the PLA matrix, because of PBAT having a relatively flexible segment comparing with the rigid chain structure of PLA, these parameters changed markedly to 116.4% and 37.1 MPa. As the P(3HB-co-4HB) content increased from 5 wt% to 25 wt%, the elongation at break was also increased from 116.4% to 294.1%, and the tensile strength was decreased from 37.1 MPa to 19.5 MPa. All of the PLA/P(3HB-co-4HB)/PBAT films showed clear yielding behavior upon stretching. After yielding, the strain developed continuously while the stress remained almost constant. The area under the stress-strain curves could also be seen to increase with increase of P(3HB-co-HB), reflecting greater enhancement of the toughness due to the relatively flexible segment of P(3HB-co-4HB).

However, due to the orientation of polymer chains in the blown film process, the films exhibited completely different mechanical properties in two mutually perpendicular directions. In TD, as the P(3HB-co-4HB) content increased, the elongation at break of the films had worse properties, showing the characteristics of gradual transforming from ductile fracture to brittle fracture. Especially when the P(3HB-co-4HB) content increased from 10 wt% to 15 wt%, the elongation at break decreased sharply from 147.2% to 39.1%. This difference could be ascribed to that in the process of blown film, the orientation of polymer chains in the blown film process, the films exhibited completely different mechanical properties in two mutually perpendicular directions.

Fig. 1  Tensile behavior of PLA/P(3HB-co-4HB)/PBAT films: (a) in the machine direction (MD); (b) in the transverse direction (TD).

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nip rolls produced traction for films and the film oriented in MD. Thus, the molecular chains were more easily to re-arrange in MD. When the content of P(3HB-co-4HB) was relatively low (less than 10%), it mainly dispersed in the PLA matrix and did not form a continuous phase structure, so the orientation effect in the film blowing process only made the toughness of the film in MD only slightly better than that in TD. When the content of P(3HB-co-HB) increased to more than 15%, the phase transition of the blend film occurred, resulting in a co-continuous phase structure. In TD, the phase-interface bonding became worse due to the smaller deformation than that in MD during film blowing, so a significant decrease in toughness appeared.

Corresponding to the tensile properties, the tear properties of the film also showed the same trend. After the addition of the flexible material, the tear strength of the film increased from 84 kN/m of neat PLA to more than 100 kN/m in TD, but in MD, it decreased from 149.5 kN/m to 24.8 kN/m due to factors such as orientation.

Measuring Young’s modulus was the common method of determining stiffness. From Table 1, neat PLA film exhibited a modulus value of about 2400 MPa. With the addition of PBAT and the content of P(3HB-co-4HB) increasing from 0% to 25%, the modulus decreased to about 1050 MPa. This indicated that PBAT and P(3HB-co-4HB) improved the flexibility of PLA/P(3HB-co-4HB)/PBAT blown films. Generally, by adjusting the blend content ratio, a film with uniform performance and excellent properties could be obtained, such as 55/10/35 PLA/P(3HB-co-4HB)/PBAT film.

SEM Analysis

SEM micrographs of the tearing fracture surface in MD of PLA/P(3HB-co-4HB)/PBAT films are given in Fig. 2. Tear strength of films ranged from 149.5 kN/m to 24.8 kN/m. The tear fracture surface of neat PLA is shown in Fig. 2(a), which is smooth and indicates that little plastic deformation had taken place during the tearing test. As can be seen from Figs. 2(b)–2(g), the tear fracture surfaces of the 65/0/35 to 40/25/35 PLA/P(3HB-co-4HB)/PBAT films exhibited rough and long ligaments, indicating that the tear specimens were broken yieldingly. For PLA/P(3HB-co-4HB)/PBAT films, some cavitation and significant matrix deformation could be clearly identified. As the P(3HB-co-4HB) content increased, cavities increased. These cavities were formed when the volumetric strain energy released by the formation of the voids was greater than the surface energy required to form the new surface plus the energy required to stretch the surrounding rubber to make room for the voids. In particular, the 45/20/35 and 40/25/35 PLA/P(3HB-co-4HB)/PBAT films showed significant ductile fractures on which a crumpled surface was visible (Figs. 2f and 2g). The pleats were parallel to the notches of the highly drawn material. The appearance of wrinkles could be attributed to the considerable tearing before the crack tip. These structures were created by extensive deformation in front of the crack tip. In particular, extensive plastic deformation of the PLA matrix could be clearly observed, which means that shear yielding of the PLA matrix has occurred. This was a typical feature of ductile fracture.

DMA Analysis

It is well known that DMA is an effective method for assessing the miscibility of the polymer blend. Fig. 3(a) shows the storage modulus curves of neat PLA, PBAT, P(3HB-co-4HB), and the ternary blends. The samples were compression molded into sheets with thicknesses of 1.0 mm at 185 °C. The storage modulus ($E'$) of PLA was about 3.7 GPa in the regions between −20 and 55 °C, and decreased sharply because of the glass transition of PLA. After the glass transition zone, $E'$ of PLA decreased more than 2 orders of magnitude, reaching a value below 10 MPa. With the temperature continuing to increase, the cold crystallization happened at around 120 °C, and as the result of the cold crystallization, the storage modulus increased rapidly. Neat PBAT and P(3HB-co-4HB) showed the highest storage modulus at the temperature range below $T_g$. When the temperature increased above $T_g$, $E'$ decreased rapidly. In particular, in the case of the ternary blends, the blends showed a high storage modulus near room temperature and increased with increasing PLA content. However, after $T_g$, $E'$ of the blends decreased with increasing PLA content. Moreover, it was interestingly found that the temperature at which $E'$ started to increase due to the fact that the cold-crystallization of PLA component shifted to a lower temperature with the addition of PBAT and P(3HB-co-4HB). This result suggested that the incorporation of
PBAT and P(3HB-co-4HB) enhanced the cold-crystallization ability of PLA. Tangent delta (tanδ) is the ratio of loss modulus (E′′) to storage modulus (E′). And the data for tanδ of the blends are shown in Fig. 3(b). A sharp tanδ peak was observed around 64.5 °C for neat PLA. Around 64.5 °C, it was obvious that the glass transition temperature peak height of the PLA/P(3HB-co-4HB)/PBAT blends gradually dropped compared with that of neat PLA. It was attributed to the gradually increased flexibility of the blends. Meanwhile, it could be clearly observed that with the addition of PBAT, tanδ peaks of blends dropped from 64.5 °C to 59 °C and with the increasing concentration of P(3HB-co-4HB), tanδ peaks of blends dropped from 59 °C to 52 °C. Tg of PBAT in the blends did not move toward high temperature. For Tg of P(3HB-co-4HB), it was hardly to find the tanδ peak of blends when the content of P(3HB-co-4HB) was less than 25 wt%. However, when the content of P(3HB-co-4HB) was reaching 25 wt%, it could be observed that a small peak appeared, increasing to 10 °C compared to neat P(3HB-co-4HB). This result demonstrated that the system showed partial miscibility between PLA and P(3HB-co-4HB).

**Thermal Properties**

PLA, P(3HB-co-4HB), and PBAT are all typical semi-crystalline polymers. The mechanical properties of these polymers are greatly dependent on the solid-state morphology and crystallinity. Accordingly, it is very important to study the influence of the existence of other minor components on the crystallization of matrix polymers in the blend. The thermal properties of samples were investigated by DSC and the results are shown in Fig. 4. The glass transition temperature (Tg), cold crystallization temperature (Tc), melting temperature (Tm), and crystallinity of samples are presented in Table 2. In Fig. 4(a), neat PLA showed no exothermic peak corresponding to the crystallization of the PLA component at this cooling rate, indicating that neat PLA had weak crystallinity and could not be crystallized at the faster cooling rate. However, obvious exothermic peaks could be observed for neat P(3HB-co-4HB) and PBAT from the thermograms. The crystallization peak temperature (Tc) of neat P(3HB-co-4HB) was around 89.1 °C, whereas Tc of neat PBAT was around 44.3 °C at a cooling rate of 10 °C/min. Comparing the curves of the blend with neat polymers, it could be observed that PBAT component in the blends was difficult to crystallize, and the content of P(3HB-co-4HB) was less in the films, making it difficult to observe the crystallization of P(3HB-co-4HB). For the PLA/P(3HB-co-4HB)/PBAT blends, the crystallization at around 80 °C was attributed to the crystallization of PLA component, and the crystallization temperature gradually increased with increasing P(3HB-co-4HB) content, indicating that the addition of PBAT and P(3HB-co-4HB) promoted crystallization of PLA. Fig. 4(b) presents the second heating thermograms of the neat polymer and the ternary films at 10 °C/min. As shown in Table 2, neat PLA showed an obvious

![Fig. 3](image-url) **Fig. 3** DMA traces of PLA/P(3HB-co-4HB)/PBAT ternary blends at various concentrations: (a) storage modulus versus temperature; (b) tanδ versus temperature.

![Fig. 4](image-url) **Fig. 4** DSC thermograms for the PLA/P(3HB-co-4HB)/PBAT films: (a) in the cooling run, (b) in the second heating run.
near the interface may play an important role in the early stages of crystallization in poly(dimethyl siloxane) composites.\[37,38] These regions may offer a different pathway for crystallization by allowing the system to bypass kinetic barriers that delay crystallization. In poly(ethylene terephthalate) (PET), a kind of semi-crystalline polymers, it was found that enhanced surface mobility combined with local alignment results in lower cold crystallization temperatures and increased free surface kinetics.\[42]

These results have important implications for our understanding of the behavior of polymer systems near interfaces. Similar to the PLA/PCL blend, PLA/P(3HB-co-4HB)/PBAT ternary blend films were also a system with some degree of compatibility. Therefore, it was reasonable to speculate that the presence of P(3HB-co-4HB) and PBAT phase could play a role in crystallization of PLA.

**Wide-angle X-ray Diffraction Analysis**

From the perspective of structural research, a variety of techniques have been used to study the crystal structure and morphology. X-ray diffraction is one of the most accurate and representative techniques. Therefore, to get further information about the crystal structure of PLA/P(3HB-co-4HB)/PBAT blends, wide-angle X-ray diffraction experiment was performed in this study. Fig. 5 demonstrates the WAXD patterns of neat PLA/PB/4HB, and its blend films. The WAXD patterns of neat PBAT and PLA samples were very wide, and the center of the diffraction peak was not obvious, indicating that the PLA matrix in the film was amorphous, and the crystallization of

![Fig. 5 WAXD patterns of neat P(3HB-co-4HB) and PLA/P(3HB-co-4HB)/PBAT blend films.](https://doi.org/10.1007/s10118-020-2418-6)
PBAT was also very difficult. Neat P(3HB-co-4HB) and its blends exhibited the variation trend of the main characteristic diffraction peaks at around 13.4°, 16.9°, 22.0°, 25.5°, and 27.0°, corresponding to (020), (110), (111), (121), and (040) planes of P(3HB-co-4HB) crystal, respectively.[41] As the P(3HB-co-4HB) content increased, the intensity of each diffraction peak gradually increased, which indicated that P(3HB-co-4HB) could be crystallized in the PLA/PBAT blends, but the crystallinity was not high, so it had little effect on the mechanical properties, otherwise it would lead to a decrease in toughness. The crystal diffraction peak position of P(3HB-co-4HB) did not shift, indicating that its crystal structure was not affected by PLA and PBAT.

Crystalline Morphology Analysis
To further reveal the crystallization behavior of neat PLA, P(3HB-co-4HB) and blend films, the nucleation and morphology of the spherulites were investigated by POM observation. Fig. 6 shows the polarized microscopy photographs of PLA/P(3HB-co-4HB)/PBAT films. The samples were heated from room temperature to 185 °C, held there for 3 min to eliminate previous thermal history, and then rapidly cooled to 90 and 130 °C under the action of liquid nitrogen for isothermal crystallization, respectively. The crystallization of PBAT could not be observed at 90 °C and the crystallization of both PBAT and P(3HB-co-4HB) could not also be observed at 130 °C, which was consistent with the DSC conclusion. The crystallization of neat PLA is given in Fig. 6(a), in which PLA formed large spherulites at 130 °C and dense small crystals at 90 °C. From Fig. 6(a), it could be seen that the well-developed spherulites grew to a size of about 50 μm in diameter, and the boundaries could be seen clearly for neat PLA samples. With the addition of 35 wt% PBAT in PLA, the number of spherulites was increased, while PBAT existed as small particles distributing around the PLA matrix in Fig. 6(b). As shown in Fig. 6(d), the presence of P(3HB-co-4HB) influenced the spherulitic morphologies, as island-like structures could be found in addition to the granular structure appearing in the blend system. As the P(3HB-co-4HB) content continued to increase, island-like structures could be more clearly observed, in which P(3HB-co-4HB) appeared in the island and spherulites became incomplete. At 90 °C for neat P(3HB-co-4HB), the spherulites showed an average radius over 100 μm in Fig. 6(e) and exhibited a typical ring-banded structure, which has also been reported before.[42] With the addition of PBAT and P(3HB-co-4HB), the number of PLA crystals in the form of small spherulites was reduced. P(3HB-co-4HB) crystals appeared on the island structure, but due to the influence of other components in the blend, complete spherulites could not be formed. With increasing P(3HB-co-4HB) content, the nucleation of the spherulites decreased, and PLA and P(3HB-co-4HB) formed the co-continuous phase morphologies with PBAT dispersed in the matrix. The formation of the co-continuous phase also explained to some extent the decrease in mechanical properties in TD. The addition of P(3HB-co-4HB) affected the morphology of the spherulites and crystallization of PLA.

Enzymatic Degradation of PLA/P(3HB-co-4HB)/PBAT Films
PLA, PBAT, and P(3HB-co-4HB) are all biodegradable plastics. The biodegradability of PLA/P(3HB-co-4HB)/PBAT blends is extremely important for the potential application of the materials in future. Here, we used proteinase K, which could degrade PLA but did not degrade P(3HB-co-4HB) and PBAT, to evaluate the biodegradability of PLA and its blended films. Fig. 7 shows the weight loss profiles of neat PLA and PLA/P(3HB-co-4HB)/PBAT blend films as a function of time during the enzymatic degradation. The rate of degradation of the enzyme could be determined from the slope of the weight loss over time. For all the samples, the weight losses of the films increased with time, and enzymatic degradation was the fastest at about the third day. When PBAT and a small amount of P(3HB-co-4HB) were added to PLA, the degradation rate of PLA kept at a high level, indicating that the dispersion of PLA in the blend was good and the contact area with the enzyme was increased. Considering that the enzyme hydrolyzed only the PLA phase,
not the PBAT or P(3HB-co-4HB) phase, PLA degraded still more than 40% in one week, which proved that the films maintained favourable biodegradability.

The surface morphology of neat PLA and PLA/P(3HB-co-4HB)/PBAT blends before and after enzymatic degradation is shown in Fig. 8. It is clearly found that the surfaces of all the blends were smooth before enzymatic degradation. However, after enzymatic degradation, the surfaces were apparently blemished by the function of protease; with increasing P(3HB-co-4HB) content, the degree of degradation decreased and the surface became smoother. Meanwhile, it could be found that the degradation of PLA in the blends was extended in a gully rather than appearing pores. This was also consistent with the co-continuous phase structure of the blends in a polarizing microscope.

CONCLUSIONS

In this work, we first reported a novel type of fully biodegradable PLA/P(3HB-co-4HB)/PBAT ternary blend films by extrusion blending and blown films technique with the aim of obtaining high performance materials. The ternary blend films exhibited unique synergistic mechanical properties which are not seen in either the homopolymers or their binary films. Mechanical analysis revealed that P(3HB-co-4HB) and PBAT improved remarkably the flexibility with reducing the elastic modulus of the PLA matrix slightly. More interestingly, a good balance of stiffness and toughness was attained for PLA/P(3HB-co-4HB)/PBAT ternary blends with PLA as matrix. The 55/10/35 PLA/P(3HB-co-4HB)/PBAT film had the most balanced mechani-
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