

Study of Biodegradable Polylactide/Poly(butylene carbonate) Blend

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ABSTRACT: Polylactide (PLA) was melt blended with poly(butylene carbonate) (PBC) in an effort to improve the toughness of the PLA without compromising its biodegradability and biocompatibility. The miscibility, morphology, thermal behavior, and mechanical properties of the blends were investigated. The blend was an immiscible two-phase system with PBC uniformly dispersed within the PLA matrix. Because of the interfacial function, the incorporation of PBC accelerated the crystallization rate of PLA. By the incorporation of PBC, a polylactide-based material with high stiffness and toughness was achieved. Even at 10% of PBC, high elongation at break of 139% was obtained, while the tensile strength remained as high as 50.7 MPa. The Pukanszky model gave credit to modest interfacial adhesion between PLA and PBC although PLA/PBC is an immiscible blend. The plastic deformation, occurring via debonding process, is an important energy-dissipation process and leads to a toughened, biodegradable polymer blend. The important point is that the toughening mechanism requires only modest level of adhesion between particles and the polymer. The molecular mobility is a crucial factor for yield stress and plastic flow. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: immiscible blends; polylactide; mechanical properties; toughness

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INTRODUCTION

Plastic materials have found wide applications in every aspect of life and industries. However, most of the conventional plastics are nonbiodegradable, and their accumulation in the environment has been a threat to the planet. Environmental concerns and a shortage of petroleum resources have driven efforts aimed at the production of biodegradable materials.^{1,2} Polylactide (PLA) is biodegradable and biocompatible thermoplastic which can be fermented from renewable resources. It has proved to be a cost-effective alternative to traditional, commodity plastics for various end-use applications, due to its good mechanical properties, thermal plasticity, and facile fabrication.^{3–6} However, it exhibits brittleness and its fracture strain is only about 5% in the tensile test, which results in poor impact and tear resistance. The inherent brittleness has been a great bottleneck for its large-scale commercial applications. Accordingly, a PLA-based material with high stiffness and toughness is still elusive.

The development of methods for PLA toughening is a master topic since the advent of PLA. Blending PLA with other polymers is one approach of modifying the desired properties. Compared with copolymerization method, blending may be a much

more practical and economic measure to obtain toughened PLA products. Up to recently, PLA has been melt processed with many flexible polymers to improve its toughness and flexibility.^{7–20} Some interesting and noteworthy results have been reported. In general, when the softer component forms a second phase within the more brittle continuous phase, it may act as a stress concentrator which enable ductile yield and prevents brittle failure. These PLA blends displayed improved elongation-at-break and impact strength but reduced strength and modulus due to the addition of ductile phase. However, most of the blends are immiscible and may need compatibilizers to increase their compatibility to access the desired mechanical properties. In addition, most of the added polymers have no biodegradability, which clearly limits the applications of the prepared blends.

Poly(butylene carbonate) (PBC) is a biodegradable aliphatic polycarbonate and the final degradation products are 1,4-butanediol, carbon dioxide, and di(4-hydroxybutyl) carbonate.^{21–23} It can be synthesized either by polycondensation of PBC oligomer or by transesterification between dimethyl carbonate and 1,4-butanediol in the presence of a heterogeneous catalyst.^{24–26} The PBC supplied by our collaborator is a flexible plastic with excellent impact strength and melt processibility.

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Besides, the soft segments of PBC are expected to have good compatibility with PLA because PLA has been reported to be miscible with some polyester.^{1,28} In the view of its nice mechanical properties and biodegradability, PBC was considered to be a good candidate for the toughening of PLA. Our overall goal is to produce blends of PLA and PBC with increase toughness without sacrificing biodegradability. The specific objectives of this research are to assess the miscibility, phase morphology, and the mechanical properties of PLA/PBC blends.

EXPERIMENTAL

Materials and Sample Preparation

The PLA (4032D) sample was purchased from Cargill Dow company with a weight-average molecular weight of 2.07×10^5 , and polydispersity of 1.71 (GPC analysis). PBC exhibits a weight-average molecular weight of 1.30×10^5 and polydispersity of 1.83, which was kindly provided by our collaborator (Institute of Chemistry Chinese Academy of Science). All of the polymers were dried in a vacuum oven at 50°C for at least 12 h before processing. The composition ratios of PLA/PBC system were 0, 5, 10, 20, and 30 wt %. Dried pellets of PLA and PBC were mixed in a container and blended in a melt mixer (Rheomix 600p, Haake, Germany) at a fixed temperature of 175°C and rotation speed of 60 rpm for 5 min. The sheet specimens for measurements were hot-pressed at 185°C and 5 MPa with a thickness of about 1 mm, followed by quenching at room temperature.

Characterization Methods

Dynamic mechanical analysis (DMA) was carried out with a DMA/SDTA861e apparatus (Mettler-Toledo, Switzerland) in the tensile mode. All tests were conducted at a frequency of 1 Hz and a heating rate of 3°C/min as a function of temperature from -65 to 125°C.

The morphology of the blends was observed by field-emission scanning electron microscopy (SEM; XL30, Philips) at an accelerating voltage of 15 kv. All of the samples were fractured after immersion in liquid nitrogen for about 5 min. The fracture surface after the impact tests and the different zones of the specimens after tensile tests were also observed using the same SEM apparatus.

The thermal properties of the blends were investigated by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7). All samples were first heated at 195°C for 2 min to erase previous thermal history before rapidly cooled to 45°C at 45°C/min. Subsequently, the samples were scanned at 5°C/min to observe cold crystallizations.

The mechanical properties of the blends were measured using Instron 1121 tensile testing machine (Canton, MA) at a rate of 5 mm/min at room temperature. Oar-shaped specimens with 20.0-mm gauge length and width of 4.0 mm were used for this test. The V-notched specimens were tested to measure the impact strength according to GB1843-93 using an impact testing machine (CEAST, Chengde, China). All tests were carried out at room temperature and 50% relative humidity. At least three samples of each type were drawn to fracture.

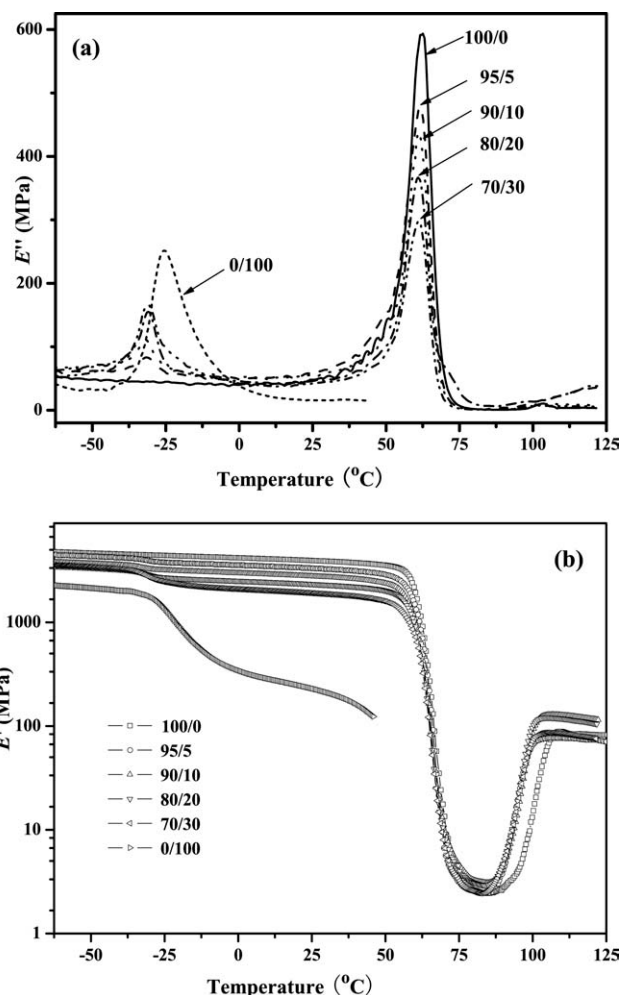


Figure 1. Dynamic viscoelastic curves for PLA/PBC blends: (a) loss modulus versus temperature; (b) storage modulus versus temperature.

RESULTS AND DISCUSSION

Miscibility and Morphology

The dynamic viscoelastic curves for pristine polymers and blends are shown in Figure 1. As shown in Figure 1(a), each pristine polymer showed one peak (glass transition). All of the blends exhibited two distinct glass transitions, revealing a typical two-phase system, one for PBC at about -32°C and one for PLA at about 62°C. It was noticed that the glass transition temperatures are almost independent of PBC concentrations, indicating the lack of significant molecular interactions between PLA and PBC. As shown in Figure 1(b), the storage modulus (E') at room temperature for PLA/PBC blends gradually decreased with increasing content of PBC. The E' of pure PLA dropped sharply at about 50°C due to the glass transition and then increased at around 100°C due to the cold crystallization. Moreover, the temperature at which the E' started to increase, due to the cold crystallization of PLA, shifted to a lower temperature with the addition of PBC. This result suggested that the incorporation of PBC enhanced the cold-crystallization ability PLA and therefore decreased the cold-crystallization temperature of PLA in the blend.

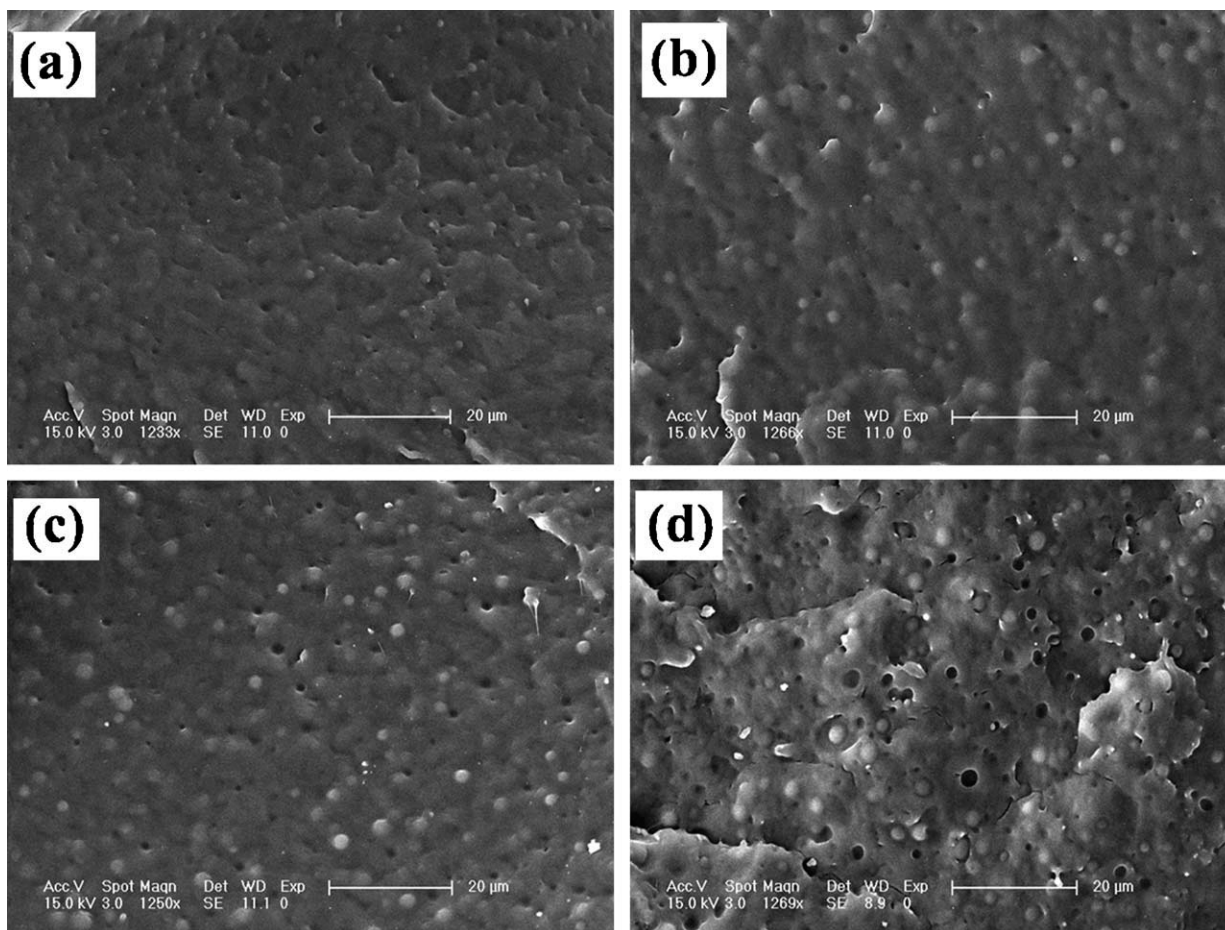


Figure 2. Phase morphologies of the PLA/PBC blends with various weight ratio: (a) 95/5, (b) 90/10, (c) 80/20, and (d) 70/30 (20- μ m scale bar).

Figure 2 shows the SEM micrographs of the PLA/PBC blends. All the blends appeared a clear, phase-separated morphology with PBC dispersed in the PLA matrix. As shown in the graphs, PBC phase domains dispersed in the PLA matrix with distinct interface. With increasing content of PBC, there was a corresponding increase in the PBC particles size due to the coalescence phenomena. This phase-separated structure of the blends is in agreement with the result obtained from DMA measurements.

Thermal Behavior

It is well known that the solid-state morphology and crystallinity have great effect on the physical and mechanical properties of PLA.^{29–31} Consequently, it is important to study the influence of existence of the PBC on the crystallization of PLA. Figure 3 shows the DSC heating curves of neat PLA and the PLA/PBC blends after melt-quenched, with a heating rate of 5°C/min. Neat PLA exhibited the glass transition at about 61.7°C and displayed a cold crystallization exotherm at 117.5°C. The melt of these crystallized domains occurred at 165.6°C. The T_g of PLA in the blends almost unchanged with increasing PBC content, suggesting that the blends were totally immiscible. It was consistent with the results from DMA and SEM analysis. However, the cold-crystallization exothermic peak of the blend was significantly different from that of neat PLA. Compared to neat PLA,

the incorporation of PBC decreased cold crystallization temperature by approximate 7°C and narrowed the peak width, indicating an enhanced crystalline ability of PLA. Thus, the cold

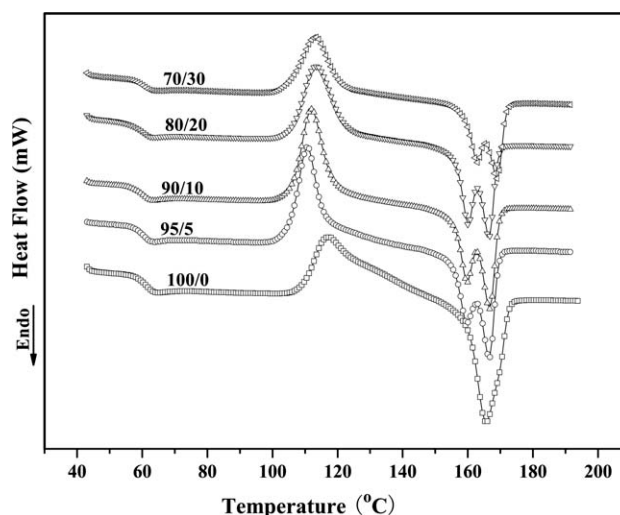


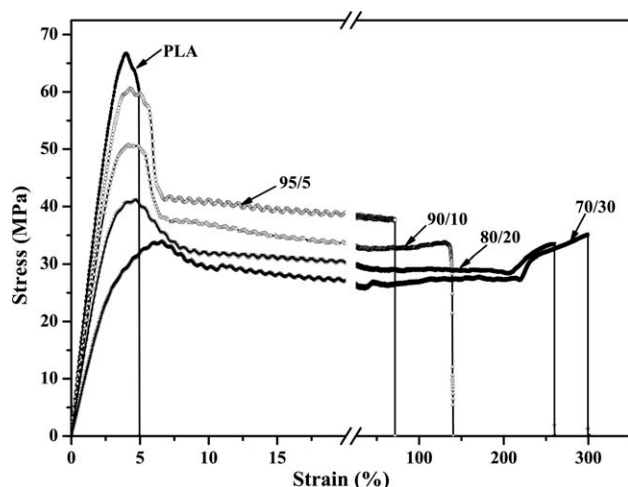
Figure 3. DSC heating curves of the PLA/PBC blends with a heating rate of 5°C/min.

Table I. Thermal Properties of PLA/PBC Blends

Samples	T_g (°C)	T_{cc} (°C)	T_{mPLA} (°C)		ΔH_{cc} (J/g)	ΔH_m (J/g)
			T_{m1} (°C)	T_{m2} (°C)		
100/0	61.7	117.5	-	165.6	41.3	40.8
95/5	60.8	110.8	159.6	166.5	37.6	40.0
90/10	60.8	112.0	160.0	166.7	35.5	39.6
80/20	60.6	113.6	160.5	166.5	33.0	41.0
70/30	60.5	113.5	161.8	168.7	28.0	40.0

crystallization of PLA can be promoted by the addition of PBC, as it occurs at a lower temperature with respect to pure PLA. However, a further increase in the PBC content had little effect on the cold crystallization of PLA in the blend.

As observed from DSC thermogram, neat PLA shows a melting peak at 165.6°C. The addition of PBC clearly separated the melting peaks of neat PLA into two individual peaks. The peaks at low temperature were around 5°C lower than the peak of neat PLA, whereas the peaks at high temperature almost unchanged. The very similar ΔH_c and ΔH_m values for each sample (Table I) indicate that the crystals cannot form during cooling from melt. The exothermal peaks during heating of the samples due to the cold crystallization indicate the formation of crystals. Thus, the double melting behavior can be well explained by the melting, recrystallization, and remelting mechanism.^{32–34} Therefore, it could be concluded that compared with neat PLA, the addition of PBC increased the crystallization rate of PLA but did not affect the final crystallinity of the PLA in the blends if given enough time. This finding may be related to the immiscibility of the blend. Considering the immiscibility of the PLA/PBC blends, the interface between the phase-separation domains may play a favorable nucleation sites for cold crystallization of PLA in the blend. Accordingly, the addition of PBC greatly increased the crystallization rate of PLA and this likely occurred through the increase in the nucleation rate.

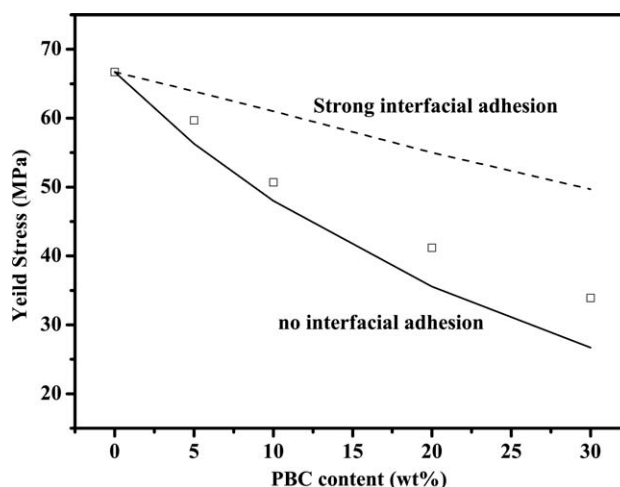
**Figure 4.** Tensile stress–strain curves of the blends with different PBC contents.**Table II.** Mechanical Properties PLA/PBC Blends

Samples	Storage modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m ²)
100/0	2091	66.7	4.9	5.6
95/5	1805	59.7	70.4	6.7
90/10	1649	50.7	139.3	7.6
80/20	1409	41.2	260.1	12.5
70/30	988	33.9	299.3	25.1

However, the nucleation effect of the interface did not simply increase with increasing PBC content due to coalescence phenomena. Thus, a further increase in the PBC content had little effect on the cold crystallization of PLA in the blend. The similar phenomena were also reported in other immiscible PLA blends such as PLA/PCL and PLA/PBAT.^{35,36}

Mechanical Properties

The addition of PBC significantly changed the tensile behavior, from brittle fracture of neat PLA to ductile fracture of the blends. Figure 4 shows the stress–strain curves of neat PLA and PLA/PBC blends. Neat PLA is very rigid and brittle with tensile strength around 66.7 MPa, and the elongation at break only about 4.9%. Neat PLA showed a distinct yield point with subsequent failure by neck instability. In contrast, all the blends showed clear yielding and stable neck growth through cold drawing. The samples were finally broken at a drastically increased elongation and the elongation continuously increased with increasing PBC content. Surprisingly, it was interesting to notice that even at 10% of PBC, high elongation at break of 139% was obtained, whereas the tensile strength remained as high as 50.7 MPa (Table II). On the other hand, the tensile strength and modulus of the PLA/PBC blends decreased with increasing PBC content. The tensile strength decreased from 66.7 MPa (neat PLA) to 33.9 MPa (20% PBC), whereas modulus decreased from 2091 MPa (neat PLA) to 988 MPa (20%

**Figure 5.** Yield stress versus the composition for PLA/PBC blends.

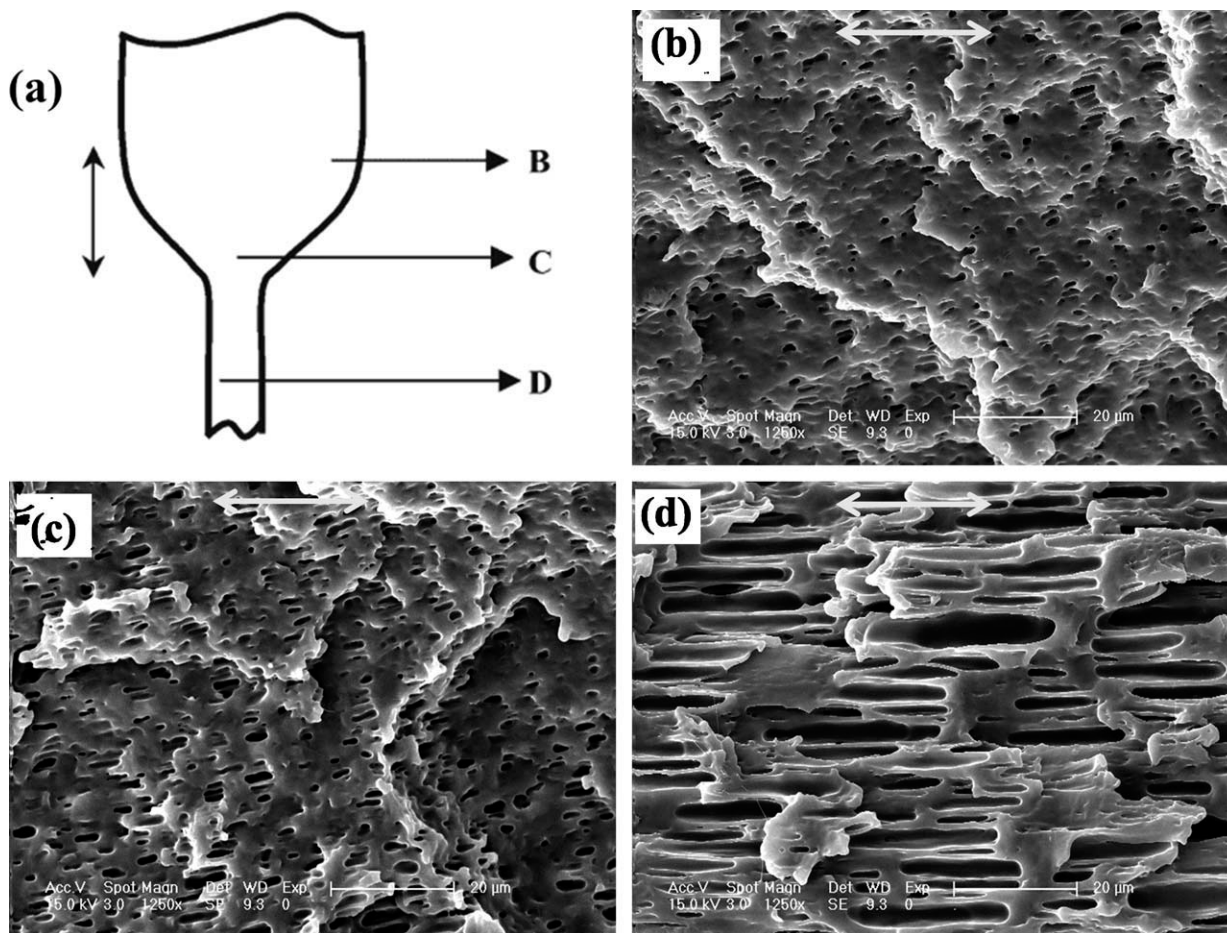


Figure 6. (a) Schematic diagram of the measurement locations B, C, and D of the SEM micrographs of the PLA/PBC blend (80/20) during the tensile testing; (b) morphology in region B; (c) morphology in region C; and (d) morphology in region D. The arrow indicates the stretching direction (20- μ m scale bar).

PBC). This consequence can be ascribed to the difference of tensile and modulus between PLA and PBC.

According to the literatures, the yield behavior of polymer blends is affected by the interfacial adhesion. When the interfacial adhesion is strong enough for stress transfer to occur between two phases, the yield stress obeys the law of mixtures:

$$\sigma_b = \sigma_1\phi_1 + \sigma_2\phi_2 \quad (1)$$

where b is the blend, σ is the yield stress and subscripts 1 and 2 refer to component 1 (PLA) and component 2 (PBC), respectively. While in the case of a lack of interfacial adhesion, the yield stress calculated with eq. (2):

$$\sigma_b^0 = \sigma_m \frac{1 - \phi_d}{1 + 2.5\phi_d} \quad (2)$$

where superscript 0 denotes zero interfacial adhesion, subscript m is the matrix or continuous phase, and d is the dispersed phase. Figure 5 shows the comparison of the experimental data with the prediction for extreme interfacial adhesion. The PLA/PBC blends have a significant positive deviation with respect to the predictions by eq. (2). The Pukanszky model gave credit to

modest interfacial adhesion between PLA and PBC although PLA/PBC is an immiscible blend. According to literatures, the interfacial adhesion has a great influence in the

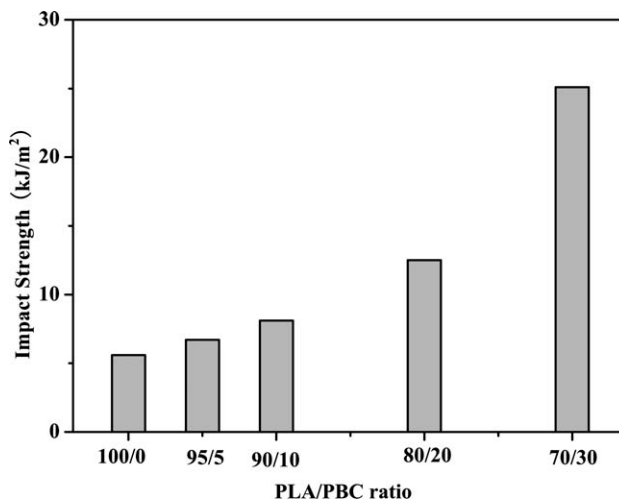


Figure 7. Effect of the PBC contents in the blends on their impact strength.

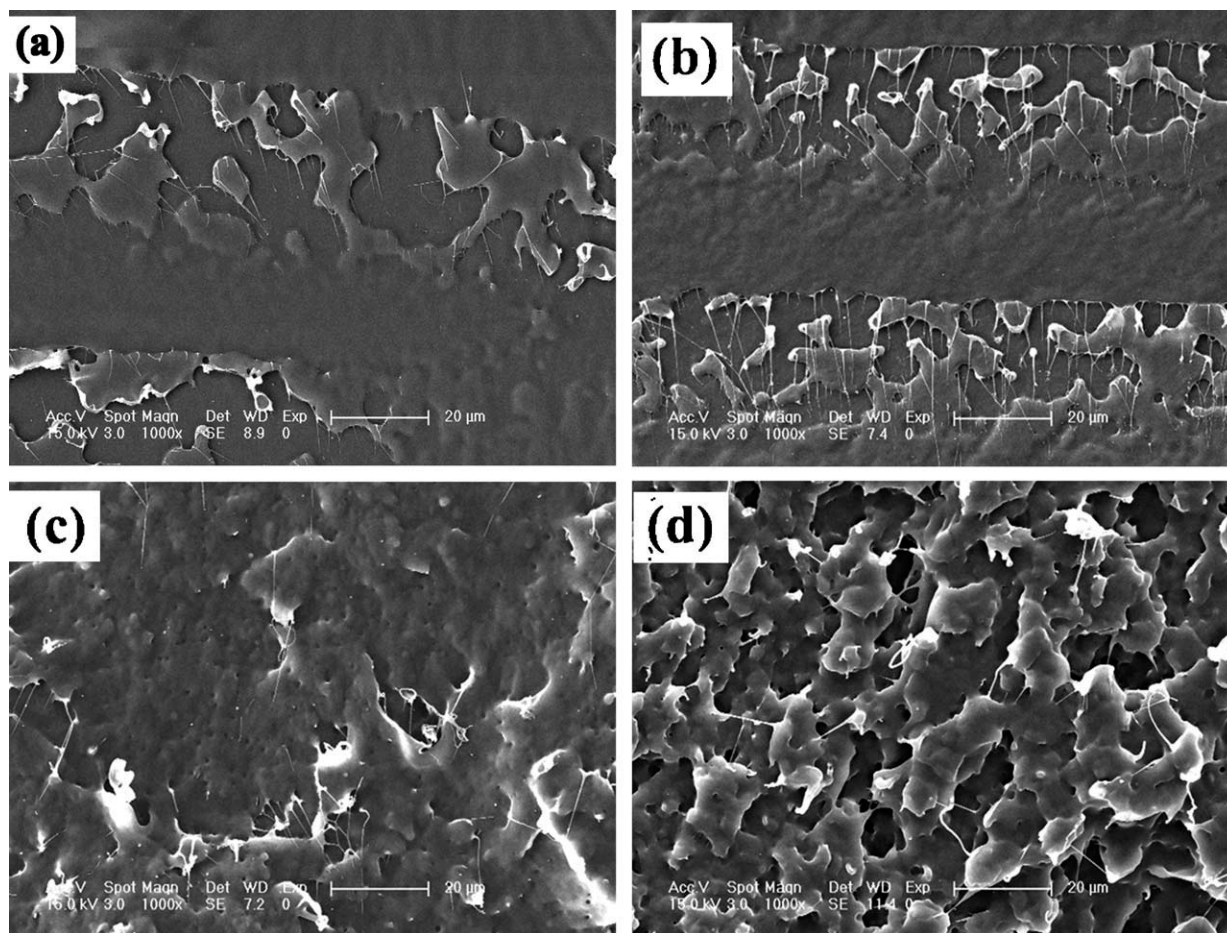


Figure 8. SEM micrographs of the fracture surfaces of the PLA/PBC blends: (a) 100/0, (b) 90/10, (c) 80/20, and (d) 70/30 (20- μ m scale bar).

micromechanical deformation processes.^{14,37,38} The cavitations form within the cores of rubber particles when there is a strong interfacial bonding between the components and relatively weak strength of rubber phase itself. Although when there is not sufficient interfacial adhesion, interfacial debonding will take place.

To further investigate the toughening mechanism of PLA/PBC blends, the morphology of different necking regions of the tensile specimen was cryofractured longitudinally to verify the interfacial adhesion effect on the micromechanical deformation processes. Neat PLA had almost the same smooth fracture surface for different regions without visible plastic deformation in the stress direction. However, the PLA/PBC blends showed different behaviors under tensile testing and the different deformation stages of the blend (20% PBC) during stretching are presented in Figure 6(a). The PBC particles act as stress concentrators because they have an elastic property that differed from the PLA matrix. The consequent stress concentration leads to the development of a triaxial stress in the PBC particles. Because of the lack of phase adhesion, debonding can easily take place at the particle matrix interface in the perpendicular external stress direction. Thus, the cavities arise and are clearly observed in the initial stage of the stretching, which is shown in Figure 6(b). Once the voids are formed, the hydrostatic stress state caused by stress concentration is released with the stress

state in the ligaments of PLA between the voids being converted from a triaxial to more biaxial or uniaxial tensile stress state. With the continuous growth of voids, weak shear bands form in the matrix between the PBC particles. At this stage, these cavities are enlarged along the stress direction, as shown in Figure 6(c). With the continuous plastic growth of voids, PLA matrix between the PBC particles deforms more easily and therefore shear yielding is achieved. The oriented cavities in the stress direction along with the deformation of the matrix are shown in Figure 6(d). The plastic deformation, occurring via debonding process, is the important energy-dissipation process and leads to a toughened, biodegradable polymer blend. The conclusion is that the compatibility between the dispersed PBC phase and PLA matrix in the blending process is not necessary for toughness, but for obtaining a fine dispersion of the dispersed phase. The important point is that the toughening mechanism requires only modest level of adhesion between particles and the polymer. The molecular mobility is a crucial factor for yield stress and plastic flow.

The impact strength of the PLA/PBC blends was also significantly increased, from 5.6 kJ/m² for neat PLA to 25.1 kJ/m² for the blend containing 30% PBC, as shown in Figure 7. The SEM micrographs of the impact-fracture surface, shown in Figure 8, can also confirm the toughening mechanism that the plastic

deformation occurs via a single cavitations process inside the rubber particles. The neat PLA shows typical brittle fracture and the surface is very smooth. With increasing PBC content, the impact-fracture surfaces show more evidence of ductile fractures as more and longer fibrils can be observed. The important energy dissipation processes, involved in the impact fracture of toughened polymer, include crazing, cavitation, shear banding, crack bridging, and shear yielding. For the composites with 20 and 30% PBC contents, the impact caused not only fibers but also cavitations and a clear matrix deformation. Moreover, the extensive plastic deformation implied that the shear yielding of the PLA matrix has taken place.

CONCLUSIONS

PLA and PBC were blended by melt mixing to prepare a biodegradable polymer blend materials with improved mechanical properties. The PLA/PBC blends are finely dispersed immiscible blends with distinct interface. Considering the immiscibility of the PLA/PBC blends, the interface between the phase-separation domains may play a favorable nucleation site for cold crystallization of PLA in the blend. Accordingly, the addition of PBC greatly increased the crystallization rate of PLA and this likely occurs through the increase in the nucleation rate. A PLA-based material with high stiffness and toughness was achieved by incorporation of PBC. All the blends showed considerably increased elongation at break as well impact strength, compared with neat PLA. SEM micrographs revealed that the plastic deformation took place in the PLA matrix. The shear yielding, initiated by the stress concentration, occurred via debonding process. The conclusion is that the compatibility between the dispersed PBC phase and PLA matrix in the blending process is not necessary for toughness, but for obtaining a fine dispersion of the dispersed phase. The important point is that the toughening mechanism requires only modest level of adhesion between particles and the polymer. The molecular mobility is a crucial factor for yield stress and plastic flow.

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