Improvement in Toughness and Heat Resistance of Poly(lactic acid)/Polycarbonate Blend Through Twin-Screw Blending: Influence of Compatibilizer Type

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ABSTRACT: The thermal mechanical properties and morphological changes of modified poly(lactic acid) (PLA) and polycarbonate (PC) polymer blends based on the equal weight fraction of each component were investigated. Several blend samples were prepared by melt processing with a twin screw extruder using both poly(butylene succinate-*co*-lactate) (PBSL) and epoxy (EP) as compatibilizers for the PLA/PC binary system. Differential scanning calorimetry (DSC) of PLA/PBSL and PC/PBSL binary blends showed that individual components were immiscible. Scanning electron microscopy (SEM) analysis of these blends revealed the domain size of PBSL was ~ 0.5–1 μm in PLA/PBSL blend, and reduced to around 0.1 μm in PC/PBSL blend. The notched Izod impact strength (IS) of PLA/PC/PBSL ternary blends increased with PBSL content up to 10 phr PBSL due to enhanced interfacial interaction and proper domain size of the dispersed phase on the basis of DMA, DSC, and SEM analysis. The heat deflection temperature (HDT) showed a maximum at 5 phr PBSL, and it dropped with increasing PBSL content which is a ductile polymer. However, the HDT of PLA/PC/EP ternary blends increased considerably with 10 phr EP due to rigid interphase formation, and it increased further with 1 phr quaternary amine catalyst, however, the IS dropped nearly the same as that of unmodified PLA/PC blend. To take advantage of the two compatibilizers, PBSL and EP were added to the PLA/PC blend at 10 phr each plus 1 phr catalyst and both IS and HDT were improved significantly over unmodified PLA/PC pair. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polymer blends; melt processing; poly(lactic acid); polycarbonate; compatibilizer; toughness; heat deflection

INTRODUCTION

The poly(lactic acid) (PLA) polymer is made through a fermenting process from annually renewable and carbon neutral resources. Due to its environmentally benign characteristics, it has generated wide interest amongst both the academia and the industry. Factors such as fast depletion of petroleum-based raw materials, growing consumer awareness, global warming, and increasing concerns over solid waste disposal would continue to drive the worldwide demand for biodegradable polymers. PLA is linear polyester that is biodegradable and aims to replace commodity synthetic polymers. It has an excellent balance of mechanical and rheological properties[1]; however, the inherent brittleness and low heat deflection temperature (HDT) of this polyester reduce its use to very limited applications in the packaging industry.[2–5] To overcome those drawbacks, new and enhanced grades with improved processability and end-use properties are being developed to make PLA suitable for a wider range of applications. Two recent publications[6,7] summarized the latest development in the modification and processing of PLA. The presence of a sizable potential market for high performance engineered and durable applications may open up a significant amount of opportunities for companies within the chemical, agricultural, and plastic sectors.

Many strategies, including plasticization, addition of rigid fillers, copolymerization, and blending with a variety of flexible polymers or rubbers, have been proposed to alter the thermal and mechanical characteristics of PLA in a hope to further extend the range of properties achievable and thus optimize the material for specific end use applications.[8–10] However, blending PLA with plasticizer generally increases the elongation and toughness through glass transition temperature (T_g) lowering and reduction of tensile strength. On the contrary, adding fibers or inorganic fillers generally increases heat resistance and stiffness at the expense of toughness and ductility. Further, properties including tensile and impact performances of a PLA copolymer can be tailored in a versatile way by manipulating the architecture of the participating molecule, sequence of monomers, and composition. Unfortunately, none

of these copolymerization processes is currently economically viable. Therefore, processing approaches that incorporate another polymer or filler have found wide utility, especially in industrial settings. Melt blending of polymers is a much more economic and convenient methodology than synthesizing new copolymers to achieve the properties unattainable with existing polymers. In addition, the largest amount of research on the toughening of PLA has occurred in the blending field; however, only few of them[11–13] has considered the balance between heat resistance and toughness, which should be an integral part of blend design, especially for those blends involving rigid polymers such as PLA. PLA has been blended with a variety of biodegradable and nonbiodegradable polymers for different purposes.[14,15] While it is desirable for researchers to pursue viable eco-friendly solutions to address the brittleness problem of PLA materials, blending PLA with nonbiodegradable but readily available petroleum-based thermoplastic polymers to modify the properties of PLA materials has gained momentum in recent years.

Polycarbonate (PC) has been widely used as an engineering plastic that has high thermal stability, impact resistance, and compatibility with aliphatic or aromatic copolyesters and epoxy (EP) resin.[16–18] To improve the properties of PLA, several PLA/PC blends have been investigated.[16,17] Some of such blends are also commercially available.[18,19] Although the thermal stability and impact strength (IS) of PLA could be improved by the addition of over 45 wt % PC, the heat resistance and the brittleness of PLA was not changed much.[16] However, various aliphatic and aliphatic-aromatic polyesters with low T_g, such as poly(butylene succinate) (PBS),[20–22] poly(butylene succinate-co-lactate) (PBSL),[23] and poly(butylene adipate-co-terephthalate) (PBAT),[24–26] all containing butylene unit in the main chain, are incompatible with PLA; however, it could improve the toughness and enhance the recrystallization behavior of PLA. In particular, the compatibility between PLA and PBSL may be altered due to the lactate moiety. Therefore, there is a possibility that the poor mechanical properties of PLA could be altered by the addition of PC, and further modified with various compatibilizing agents. The modified PLA/PC blends could also be a new environmentally benign material consisting of over 50 wt % biodegradable polymers.

There have been a huge amount of the literature investigating PLA blending and property modification, with effects on characteristics such as biocompatibility or miscibility. To improve the compatibility between two immiscible components, a third component is added as a compatibilizer in most cases. The compatibilizer can be either premade or *in situ* formed during melt blending. One successful application of reactive blending is the addition of peroxides to several PLA blends, such as PLA/poly(ε-caprolactone),[27,28] PLA/PBS,[29] PLA/poly(butylene succinate-co-adipate) (PBAT),[17] by simultaneous melt blending. It was shown that the addition of peroxides to those polymer blends forms crosslinked and/or branched structures by heteroradical coupling reactions, which improve the compatibility of the polymer blends, the melt tensions and the extrusion stability. The other reactive application is principally based on the reactions between end functional groups (i.e., —OH or —COOH) of PLA and other complementary functional groups (mainly epoxide groups) of the compatibilizers, for example, PLA/PBAT blend modified with glycidylmethacrylate (GMA),[30,31] PLA/poly(ethylene octane) (POE) blend with POE-g-GMA modifier,[32] and chain extension of PLA with multifunctional epoxide.[33] As a result, improved interfacial adhesion and hence fine dispersion were achieved.

To enlarge its property (processing) window and thereby its applications field, PLA needs to be toughened and heat resistant. It has been demonstrated that reactive blending is an effective way in improving the toughness of PLA blends, particularly IS. In most of these blends, however, the achievement of superior impact relies on the addition of a large amount of nonbiodegradable petroleum-based polymers (>20 wt %), which is usually accompanied by a great loss in heat resistance and stiffness. Thus, how to enhance significantly toughness and heat resistance while minimizing the reductions in stiffness of the PLA materials, still remains a challenge. This work is based on two types of modifiers to modify the PLA/PC blend through twin-screw extrusion. We shall investigate improvement of the toughness and the heat resistance of PLA/PC blends by (1) balancing the toughness and thermal resistance of the ternary blends with EP or PBSL, (2) examining the morphological changes of the modified polymer blends, and (3) elucidating the mechanism for improvement of the physical properties of the blends.

EXPERIMENTAL

Materials

The PLA 2002D was obtained from NatureWorks, which consists of 92% L-lactide and 8% meso-lactide contents. The average molecular weight of 78,000 was determined by size exclusion chromatography (SEC) in chloroform at 25°C. The PLA pellets were transparent and amorphous, with a T_g of 58°C. The PC 110 was obtained from Chi Mei. Two types of modifiers, Shell Epon 1010 and Mitsubishi poly(butylene succinate-co-L-lactate) (PBSL), were selected for the study. The EP equivalent of Epon 1010 was

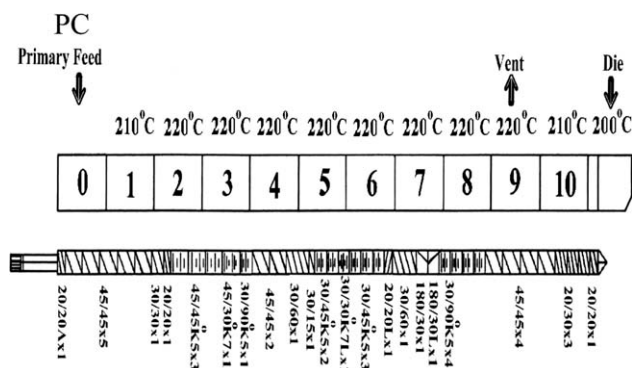**Figure 1** Schematics of twin screw configuration and barrel temperature profiles of PSM30 (hopper feed).

4000 from supplier. PBSL (GS Pla® AZ-type, lactate unit about 3 mol %, melt flow rate (190°C; 2.16 kg) 25 g/10 min, specific gravity 1.26, was supplied from Mitsubishi Chemical Corporation (Japan). The choice of these compatibilizers was based on requisites such as nontoxicity and biocompatibility. The catalyst tetrabutylammonium bromide (TBAB), analytical grade, was obtained from Acros. All the regents were used as received without further purification.

Preparation of modified PLA/PC blends

To seek the proper compositions for the PLA/PC blends with compatibilizers and critically compare the performance of various formulations, the reactive blending of PLA/PC blends was carried out with a corotating self-wiping twin-screw extruder. The PSM-30 machine was manufactured by Sino-Alloy Machinery, with a screw diameter of 31.2 mm, the distance between screw axes was 26.2 mm, the screw tip clearance was 0.25 mm and the length to the diameter ratio $L/D = 45$. The screw consisted of 10-segmented barrels with three kneading zones. The first kneading zone started at the second barrel consisting of high shear disk blocks, and ended with neutral blocks. The second zone started at the fifth barrel also consisting of high-shear elements with reverse elements at the end. The third zone started at the eighth barrel with only neutral elements. It is expected that the filler particles would experience a high intensity of dispersive mixing in the first and the second kneading zones; and the distributive mixing action would dominate in the third kneading zone. The details of the screw configuration and element geometries are shown in Figure 1. A standard pelletizing die plate was installed at the screw end. The strand was solidified in a water bath and pelletized. The screw speed was fixed for all experimental runs at 160 rpm. In general, there were 10°C rises from the first barrel to the fifth, and the temperatures remained the same for the rest of the barrels. The throughput rate was fixed at 20 kg/h. Equal

weight fractions of both PLA and PC components were maintained in all the blends modified with two types of compatibilizer: EP and poly(butylene succinate-co-L-lactate).

Characterization

The extruded strands were cooled in a water bath, pelletized, and dried in vacuum at 80°C for 4 h. Injection molding was carried out by an injection machine (NP7 Real Mini, Nissei) to obtain the bar specimen of 3.2 mm thick, 12.7 mm width, and 64 mm length for Izod impact test and 127 mm for HDT test. The barrel temperature was set at 230°C.

Notched Izod impact test was performed according to ASTMD 256, using DG-1B (Toyo Seiki) after notching (sharp notches of 2.5 mm depth obtained with a diamond cutter). An average value of five replicated specimens was taken for each composition.

HDT was measured by an HDT tester, 6M-2 (Toyo Seiki) at flatwise mode under a load of 0.455 MPa at a heating rate of 2°C/min according to ASTM D648. HDT was the temperature at which the specimen distortion increased to 0.25 mm during the heating process. Both impact and HDT tests were carried out for the as-mold samples.

Differential scanning calorimetry (DSC) was carried out under nitrogen flow at a heating rate of 10°C/min using PerkineElmer DSC-7 and a tiny as-extruded sample (ca. 10 mg) for DSC over a temperature range from 30 to 200°C. Dynamic mechanical relaxation was measured with a Perkin Elmer model 7e DMTA working in bending mode at constant stress. The complex modulus, $E^* = E' + iE''$, of each sample was determined over a temperature range from 0 to 150°C at a constant frequency of 1 Hz. The experiments were carried out at a heating rate of 5°C/min. The dimension of the specimen samples was about 12 × 12 × 3 mm. The specimen was cut from a core part of the injection-molded dumbbell specimen.

Scanning electron microscopy (SEM) images of the morphology of modified PLA/PC blends were observed by field-emission scanning electron microscope (FESEM) JSM-6400 (JEOL, Japan) with accelerating voltage at either 5 or 10 kV and working distance from 8.8 to 15.1 mm. The dispersed PC domain within the PLA matrix was also studied by SEM. Both the freeze-fractured and the impact-fractured sample surfaces were sputter-coated with platinum using an ion coater IB-3 (Giko, Japan).

RESULTS AND DISCUSSION

IS and HDT of modified PLA/PC blends

The notched Izod IS and the HDT of PLA/PC binary system and modified ternary PLA/PC blends with

Sample composition PLA/PC/PBSL/EP/TBAB	Notched Izod IS (J/m)	HDT (°C)
100/0/0/0/0	7.5 ± 0.1	57.8 ± 0.9
0/100/0/0/0	853.0[a]	136[a]
50/50/0/0/0	10.2 ± 0.6	80.3 ± 0.7
50/50/5/0/0	36.6 ± 0.9	94.8 ± 0.4
50/50/10/0/0	65.1 ± 2.3	76.8 ± 2.9
50/50/20/0/0	50.0 ± 1.5	61.2 ± 1.9
50/50/0/10/0	10.8 ± 0.9	104 ± 4.4
50/50/0/10/0.5	9.6 ± 0.6	107 ± 7.2
50/50/0/10/1.0	7.2 ± 0.5	129 ±0.5
50/50/10/10/0	25.5 ± 0.9	82.5 ± 1.1
50/50/10/10/1.0	34.0 ± 0.1	94.2 ± 4.5

[a] Provided by Chi-Mei Co.

either PBSL or EP are shown in Table I. The properties of the neat PLA and PC are included for comparison. Note that the weight fractions of both PLA and PC were equivalent. We first look at the IS of the blends modified with PBSL. It can be seen that unmodified PLA/PC blend showed an IS of 10.2 J/m, only about 40% increase relative to that (7.5 J/m) of neat PLA. As expected, the IS of PLA/PC blend substantially increased with PBSL compatibilizer. Notably, the IS increased to 65.1 J/m with 10 phr PBSL, which was six times higher than that of unmodified PLA/PC blend. However, with 20 phr PBSL the IS decreased to 50.0 J/m, which was still five times that of the unmodified system. In fact, the fracture behavior changed from brittle to ductile with PBSL modification, as to be discussed later from the morphological observation. However, as shown in Table I, the HDT of the blend with 20 phr PBSL dropped to 61.2°C, which was much lower than the unmodified pair. It is expected that the HDT of the PLA/PC/PBSL ternary blend would decreased with increasing PBSL content. Moreover, it is interesting to see that the HDT of the PLA/PC blend with 5 phr PBSL rose to 94.8°C, which was nearly 20% increase compared with the unmodified blend (80.3°C). The increase in HDT may be due to the improvement in interfacial adhesion between PC and PLA and the increase in the crystallinity of the PLA component with the addition of PBSL.[23]

Next, we examine the PLA/PC blend modified with EP resin. The EP content was fixed at 10 phr after several trials, and we only focus on the effect of the quaternary amine, TBAB, which has been widely used as a catalyst for ring-opening of the epoxide group.[34] It can be seen from Table I, varying the TBAB content from 0 to 1.0 phr, the IS monotonically decreased from 10.8 to 7.2 J/m; however, the HDT increased significantly from 104 to 129°C. The drop in IS may be attributed to the brittle nature of the EP resin with high EP equivalent weight. How-

ever, the drastic rise in the HDT with increasing catalyst content indicated that the improved interfacial adhesion due to accelerated ring opening of the epoxide with the carboxylic end of PLA.[30,31] Finally, we also modified the PLA/PC blend with both PBSL and EP at 10 phr each. We also considered the effect of TBAB on the four-component blend. The blend without TBAB apparently showed less improvement than that with 1 phr TBAB. However, with IS increased to 34.0 J/m and HDT to 94°C, the properties of the quaternary blend with 1 phr TBAB was merely comparable to that of PLA/PC/PBSL ternary blend with 5 phr PBSL.

PLA/PC blend modified with PBSL

Thermal behaviors of PLA/PBSL and PC/PBSL binary blends by DSC

Before we investigate the properties of the PLA/PC/PBSL ternary blend, it is necessary to study first the miscibility of PLA/PBSL and PC/PBSL binary systems. These two blends were prepared in a Brabender internal mixer with a weight fraction of 85/15. The heating behavior of these two blends at the first heating stage was studied using the as-extruded pellets. Figure 2 shows the heating scan for both PLA/PBSL and PC/PBSL blends at a heating rate of 10°C/min. First, in the PLA/PBSL blend, there were two distinctive melting peaks at 109.9 and 155.2°C for PBSL and PLA, respectively. Note that these melting temperatures are nearly the same as that of the neat resins. It clearly indicated a phase-separated blend. In addition, the recrystallization peak of PLA disappeared in the PLA/PBSL blend; however, the melting enthalpy of the PLA component was 23 J/g corrected for the weight fraction of PLA, which was higher than that of the neat PLA at 19 J/g. Indeed, it has been reported that the
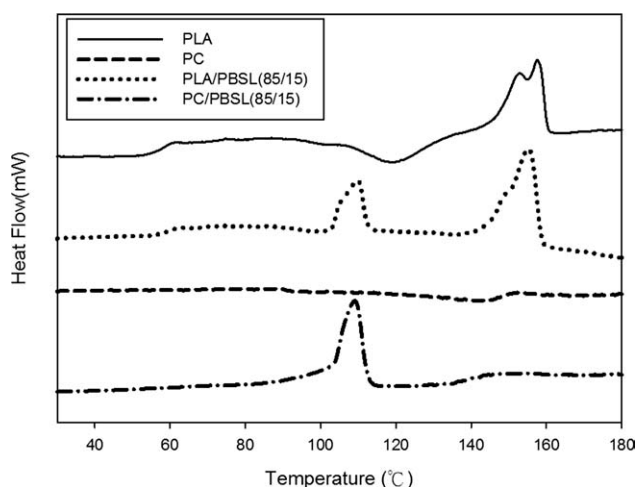

Figure 2 First heating scans of neat PLA, PC, PLA/PBSL, and PC/PBSL blends prepared from Brabender.
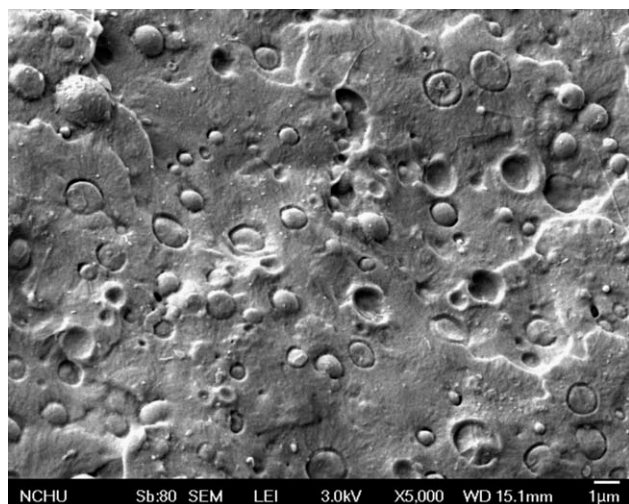
Figure 3 SEM micrograph of the cryofractured surface of PLA/PBSL blend.

addition of PBSL enhances the crystallization of the PLA component.[23] Regarding the PC/PBSL blend, we could only observe the melting peak of PBSL at 109.1°C, which was nearly the same as that of the neat PBSL. Further, the glass transition of PC is clearly broadened, and the T_g at 142.4°C, determined from the half height of the step change in heat capacity, is also lower than that of neat PC (148°C). It was thought that some interaction between PBSL and PC in the amorphous region contributed to the broadening of the glass transition and the shifting of the T_g of PC component to the lower temperature.

Comparison of morphologies of PLA/PBSL and PC/PBSL binary blends

To confirm the previous discussions, the morphology of the blends was studied. We first examine the SEM images of the cryofractured surfaces of PLA/PBSL and PC/PBSL blends, with the weight fraction of 85/15, as shown in Figures 3 and 4, respectively. The binary systems behaved, as expected, as immiscible polymer blends. For PLA/PBSL blend in Figure 3, large dispersed phase particles of PBSL with mean diameter about 1 μm, which was a typical sea-island formation in an immiscible blend, was observed. In addition, the PLA/PBSL blend showed that large droplets of PBSL were barely embedded in the PLA matrix. The poor adhesion between PLA and PBS was evidenced by the large number of oval cavities left after cryogenically fracturing. However, there were few particles adhering well with the PLA matrix without visible gap at the boundary, which may indicate partial adhesion at the interfaces. For PC/PBSL blend in Figure 4, the cryofractured surface seemed rather smooth. The PBSL domain can be seen as finely dispersed droplets with mean diameter

<0.5 μm, which is much smaller than that of the PLA/PBSL blend. Further, most droplets embedded in the continuous PC network, indicating strong interfacial interaction between the two components.

Thermal and dynamic mechanical properties of PLA/PC/PBSL ternary blends

Next, we look at the thermal behavior of the PLA/PC/PBSL ternary blends from twin-screw extrusion. Figure 5(a) showed the DSC traces of the ternary blend with PBSL loading varying from 5 to 20 phr. The heating scan was performed at a heating rate of 10°C/min. The melting peaks of PBSL and PLA, similar to the PLA/PBSL binary blend, appeared at about 108 and 155°C, respectively. These distinctive melting peaks again indicated the immiscible nature of PLA and PBSL components. Further, the recrystallization peak of PLA also disappeared, and the melting enthalpy ΔHm of PLA increased from 22.8 to 25.1 J/g corrected for PLA weight fraction (corresponding to PBSL content from 0 to 20 phr), which clearly indicated the enhancement of PLA crystallization with PBSL.[23] In addition, the glass transition of PC about 145°C was masked by the melting of PLA, which cannot be observed from the heating scan. We then investigated the non-isothermal cooling behaviors of the ternary systems cooled from the molten state at 220°C. Figure 5(b) showed the cooling scans at a rate of 10°C/min. While the T_g of PLA component remained unchanged, broadening of PC glass transition with T_g peak shifting to lower temperature were also clearly observed in the cooling scans. Further, the crystallization peaks of PBSL during cooling were unaffected with PBSL content, but the crystallization enthalpy increased with increasing PBSL content.
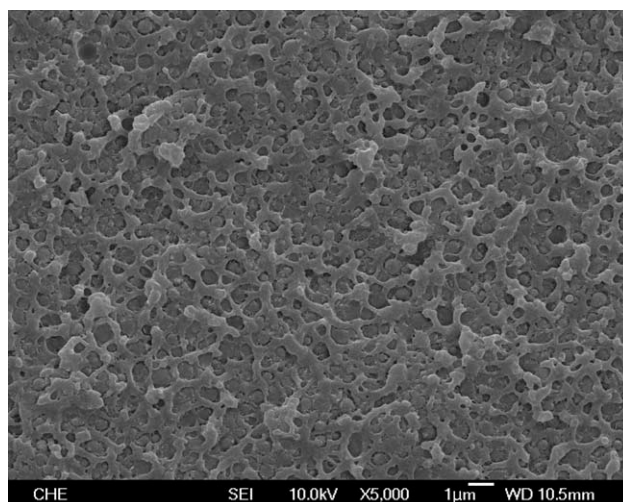

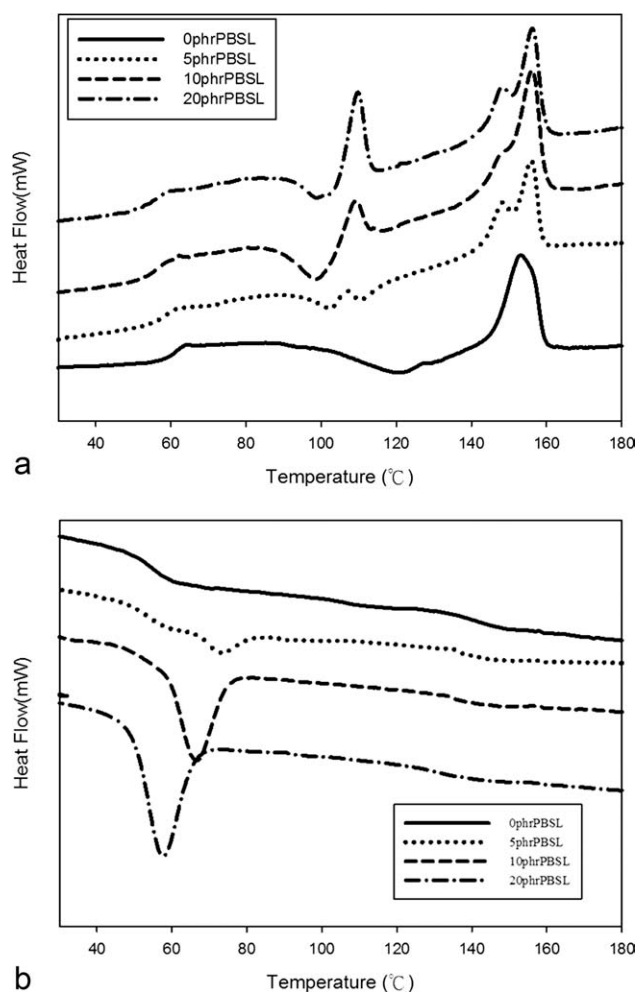**Figure 4** SEM micrograph of the cryofractured surface of PC/PBSL blend.

a

b

Figure 5 (a) First heating scans of as-extruded PLA/PC/PBSL ternary blends. (b) Cooling scans of as-extruded PLA/PC/PBSL ternary blends.

Figure 6 shows dynamic mechanical curves of PLA/PC/PBSL ternary blends. Since PBSL is the minor component, and we were interested in the
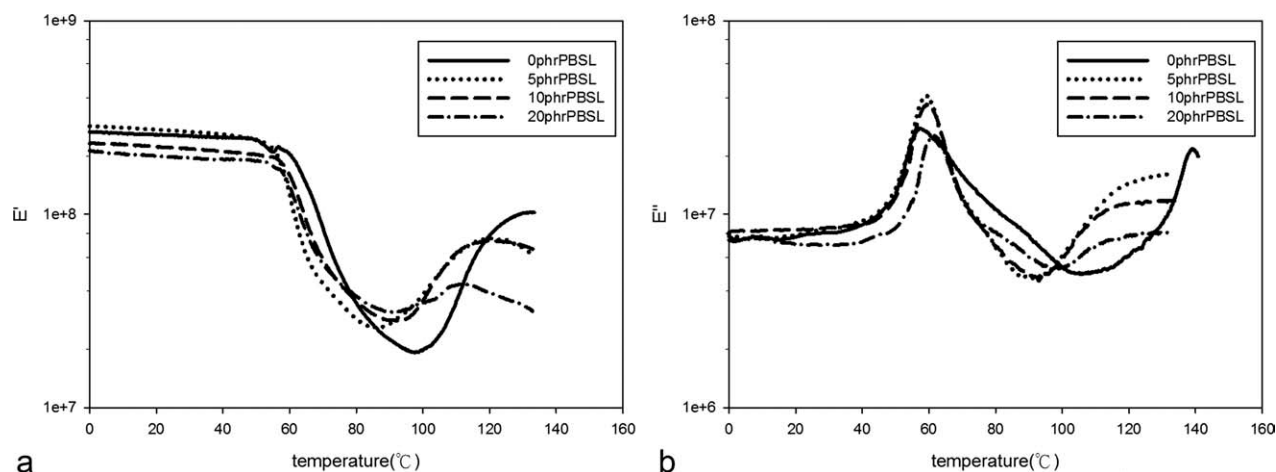
variation of the glass transition of both PLA and PC, the DMA scan started at 0°C. Figure 6(a) shows the storage moduli E' of the ternary blends with PBSL content varying from 0 to 20 phr. At 25°C, E' decreased from about 250 to 192 MPa with increasing PBSL content. Further, it has been reported that E' of the PLA component increased right after the glass transition zone mainly due to the PLA recrystallization. It can be seen that the temperature beyond which E' started to increase was shifted lower with increasing PBSL content. The promotion of PLA recrystallization with the addition of PBSL may be responsible for such shift and further, as expected, for temperatures over about 100°C, the magnitudes of E' of the blends also decreased with increasing PBSL content.

Figure 6(b) presents the loss moduli E'' of ternary blends. The T_g corresponding to PLA and PC components for the blends can be explicitly determined from the E'' peak temperature. As is obvious from the E'' curves, the ternary blends showed two T_g's for PLA and PC, respectively. This result indicated that their blends were immiscible in the amorphous phase. The T_g's of the PLA components of the blends varying from 61 to 62°C were slightly higher than that (ca. 60°C) of the unmodified system. However, the T_g of the PC component apparently decreased from 140 to about 125°C with increasing PBSL content. The shifting in T_g also indicated partial improvement in the interfacial interaction between PLA and PC with PBSL addition.

Morphological observation for PLA/PC/PBSL ternary blends

The cryofractured surfaces of the PLA/PC/PBSL ternary blends with PBSL loading at 0, 5, 10, and 20 phr were shown in Figure 7(a–d), respectively. In Figure 7(a), the dispersed PC domains tend to connect
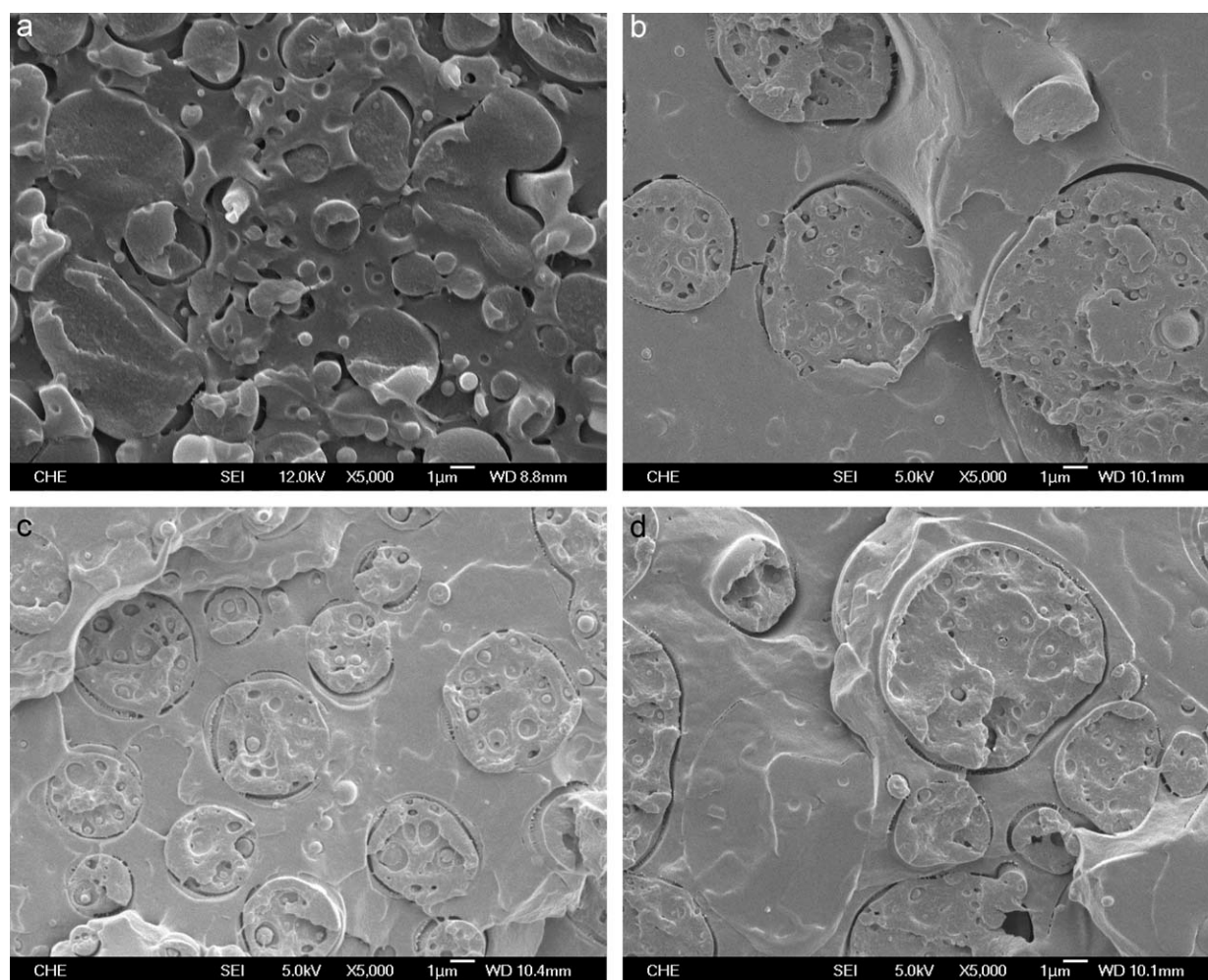

a

b

Figure 6 DMA curves of storage and loss moduli of injection-mold PLA/PC/PBSL ternary blends. (a) Storage moduli (E'); (b) loss moduli (E'').

Figure 7 (a) SEM micrographs of cryofractured surface of unmodified as-extruded PLA/PC blend. (b) SEM micrograph of cryofractured surface of as-extruded PLA/PC blend with 5 phr PBSL. (c) SEM micrograph of cryofractured surface of as-extruded PLA/PC blend with 10 phr PBSL. (d) SEM micrograph of cryofractured surface of as-extruded PLA/PC blend with 20 phr PBSL.

each other and shape of the phase clearly appeared as irregular droplets uniformly scattered in the PLA matrix. It can also be seen a lot of cavities and boundary defects between PLA and PC domain showing phase separated morphology. The detailed observation shows that PC domain is still dispersed in PLA matrix, which can be attributed to the higher PC viscosity than PLA even with the equal weight fraction of the two components. In Figure 7(b), when 5 phr of PBSL was added, the dispersed PC phase became nearly spherical, which seemed to adhere fairly with the PLA matrix except few gaps at the interface. Moreover, the interfacial debonding between PLA and PC was clearly observed as microfibril at the boundary between PLA and PC domains. In addition, some fine dispersions of PBSL component seemed to move inside the PC domain, indicating partial miscibility of PC and PBSL binary system. The uniformly dispersed PC/PBSL droplets with an average size of 1 μm can also be seen in Figure 7(c) for 10 phr PBSL

modified PLA/PC blend, and large aggregates of the dispersed phase probably due to the coalescence of PC/PBSL droplets can be seen in Figure 7(d) for 20 phr PBSL blend. Regardless of PBSL content, they all showed that improved interfacial adhesion between the dispersed PC phase and the PLA matrix with some droplets even embedded in the matrix. Note that interfacial interaction between PC and PLA phases due to the ductile PBSL compatibilizer gave rise to the microfibril formation at the domain boundaries.

To further investigate the toughening effect, the SEM micrographs of the impact fractured surface of PLA/PC/PBSL blends with PBSL content from 0 to 20 phr are shown in Figure 8(a–d), respectively. In Figure 8(a), the PLA/PC blend without PBSL showed that large droplets of PC were barely embedded in the PLA matrix. The adhesion between PLA and PC was poor as evidenced by the large number of oval cavities left after the impact fracture.
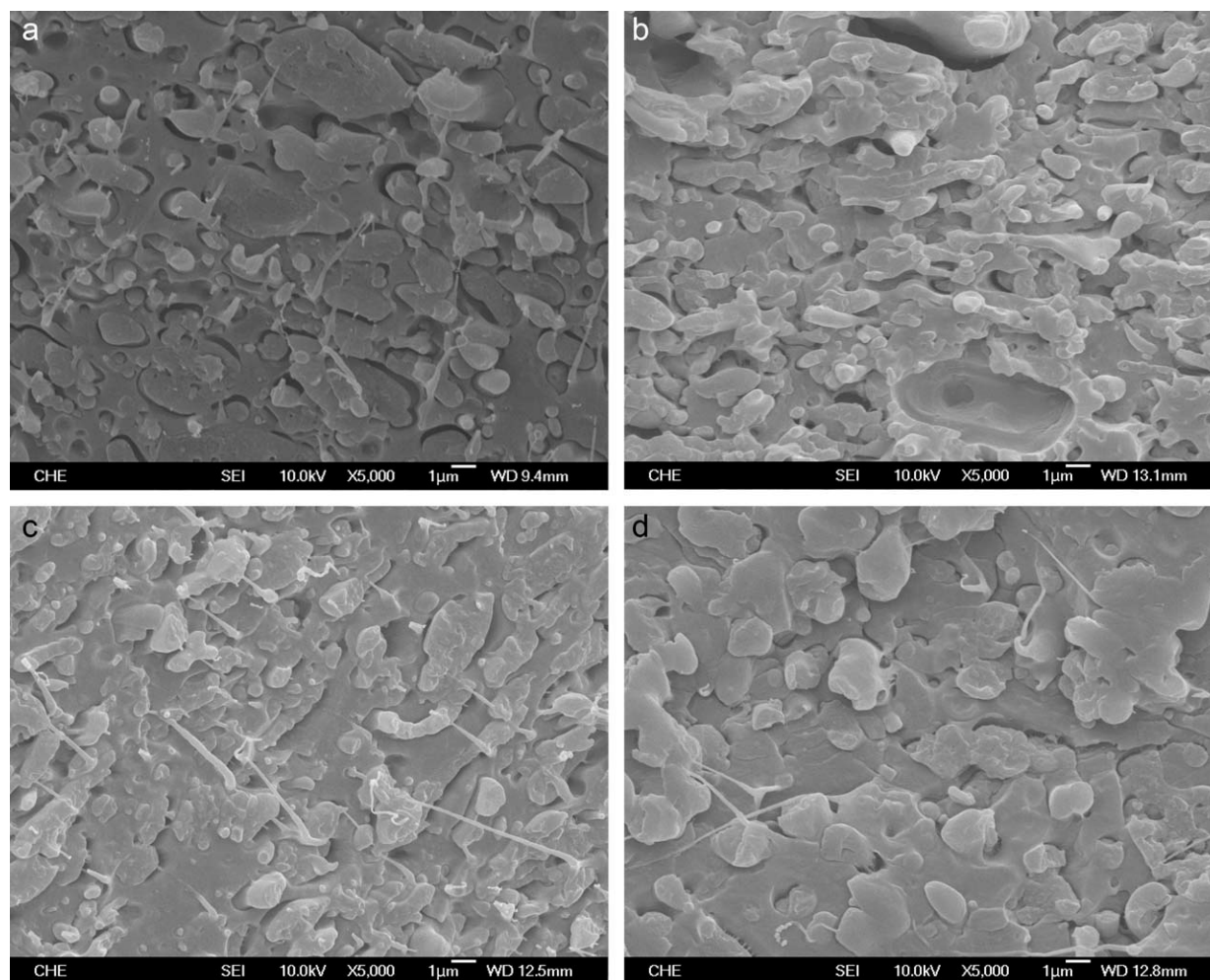
Figure 8 (a) SEM micrograph of impact-fractured surface of unmodified PLA/PC blend. (b) SEM micrograph of impact-fractured surface of PLA/PC blend with 5 phr PBSL. (c) SEM micrograph of impact-fractured surface of PLA/PC blend with 10 phr PBSL. (d) SEM micrograph of impact-fractured surface of PLA/PC blend with 20 phr PBSL.

However, short fibril formation emanating from the PC droplet can be observed clearly. As the elasticity of PC was different from that of PLA, the PC particles could act as stress concentrators under stress in PLA/PC blend. In the procedure of debonding, PC particles could deform more easily to achieve the shear yielding, which would improve the PLA toughness.

As shown in Figure 8(b), the brittle to ductile transition under impact testing after the addition of PBSL was observed. PLA/PC showed a very nonhomogenous surface [Fig. 8(a)], indicating a typical brittle fracture behavior. In the PLA/PC blend with 5 phr PBSL [Fig. 8(b)], interfacial debonding between PLA and PC after impact was clearly observed, and some deformation of the PLA matrix occurred with smaller dispersed PC phase, which was in accordance with the improved interfacial adhesion between PLA and PC compatibilized by PBSL. For 10 phr PBSL blend [Fig. 8(c)], not only elongated fibrils and cavities but also the matrix deformation was clearly

observed, but also the PC/PBSL domain size was significantly decreased to 0.2–1 μm. Moreover, the PC/PBSL particles adhered well to the PLA matrix, much less, cavities can be seen after the impact fracture, indicating a dramatic increase in the interfacial adhesion between PLA and PC via compatibilization with PBSL, thus the shear yielding of the PLA matrix occurred during the interfacial debonding, and the toughness of the blend was significantly improved. Unfortunately, at high PBSL loading of 20 phr, the PLA weight fraction was reduced to near 40 wt %, and the PC/PBSL particles did not reduce further. Some big PC/PBSL particles clearly seen from Figure 8(d) may attribute to the coalescence of the dispersed phase [see Fig. 8(d)]. The number of elongated fibrils emanated from the PC droplets was less than the blend with 10 phr PBSL. Therefore, the IS of the blend dropped, though it was still higher than that of the 5 phr PBSL blend.

Since no influence is reasonably expected on the improvement of the miscibility between PLA and
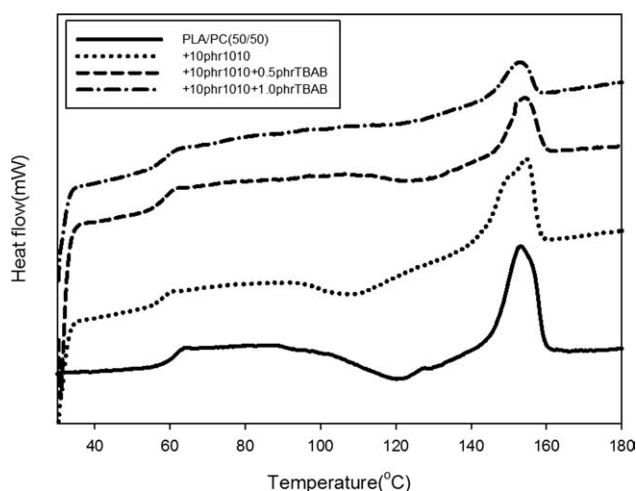
Figure 9 First heating scans of as-extruded PLA/PC/EP ternary blends with various TBAB loadings.

PC components, the reduction in dispersed phase should be due to the compatibilization by interfacial interactions.[35] Therefore, the improvement of the interfacial adhesion can be used as an indirect confirmation that compatibilizers were distributed in the PLA/PC blends. The compatibilizers located at the interface between PLA and PC, enhancing the interfacial adhesion and reducing the dimension of the PC/PBSL particles.

PLA/PC blend modified with EP

Thermal behaviors by DSC

The DSC first heating scans of the PLA/PC/EP (50/50/10 phr) ternary blends with TBAB loading at 0.5 and 1 phr are shown in Figure 9. The T_g's of PLA at about 59°C did not shift with the addition of EP, however, the melting enthalpy ΔHm decreased from 29 J/g without TBAB to 9.0 J/g with 1 phr

TBAB. In short, ΔHm of the PLA component decreased with the catalyst loading. The reactive compatibilization with EP may impede the crystallization and hence decrease the crystallinity of PLA. Moreover, the recrystallization of PLA also nearly disappears with the addition of catalyst. The interfacial reaction between the epoxide group and the carboxyl end group of PLA may occur at the interface,[33] which makes PLA chain rearrangement (motion) more difficult, and discourage the recrystallization.

Dynamic mechanical properties by DMA

By means of DMA measurements, it is possible to characterize the composite interfacial interactions in addition to the bulk chain motion on both crystalline and amorphous regions of the polymer.[36] The efficiency of the EP compatibilizers was also evaluated through DMA. The influence of the compatibilizer (Epon 1010) on the storage modulus (E') and loss modulus (E'') of the PLA/PC blends is shown in Figure 10(a,b), respectively. The DMA curve of unmodified PLA/PC at 50/50 shows a marked drop in E' and a sharp E'' peak at 60°C, corresponding to the glass transition of PLA. The rise of E' beyond 100°C is due to the presence of PC component showing T_g at 140°C as seen from the E'' peak. Note that the recrystallization process of neat PLA (not shown) is insignificant; thanks to a fast scan rate (5°C/min) and sinusoidal solicitation. Finally, as the temperature increases beyond the T_g of PC, the storage modulus dropped again as the material starts to flow.

When the PLA/PC blend was modified with 10 phr EP, the E' below T_g shows only a slight dependence on EP, however, the magnitude of E' increases significantly for temperatures beyond the T_g of PLA component, indicating the effect of the EP rigidity. The temperature at which E' started to drop again represented the glass transition of PC, which
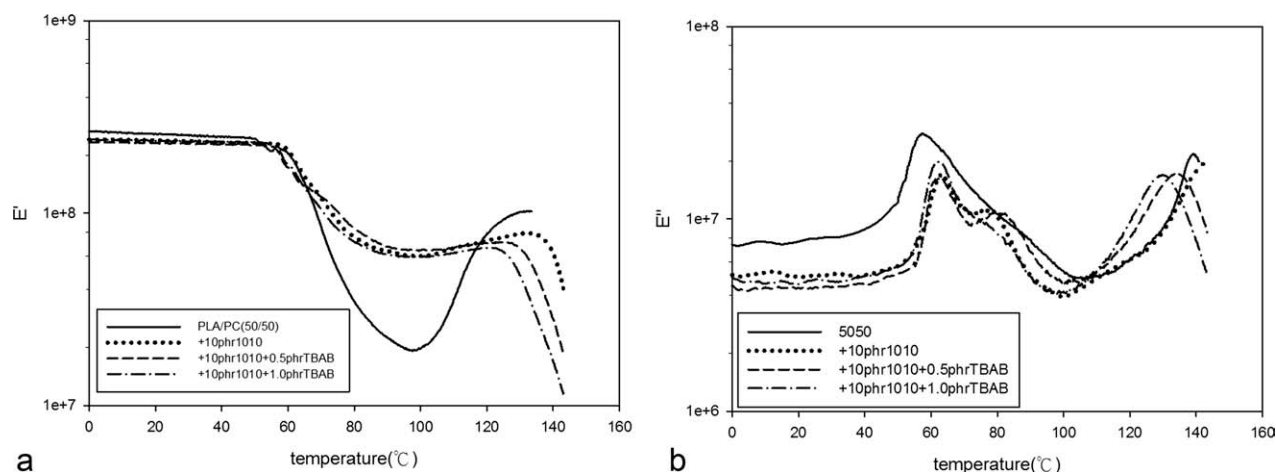

Figure 10 DMA curves of storage (E') and loss (E'') moduli of injection-mold PLA/PC/EP ternary blends with various TBAB loadings. (a) Storage moduli; (b) Loss moduli.
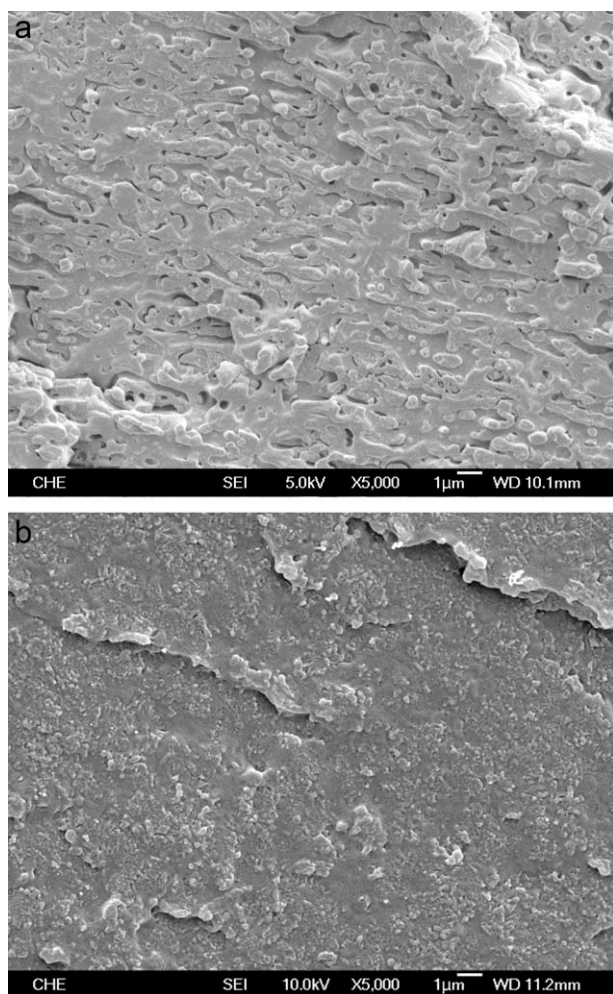
Figure 11 (a) SEM micrographs of impact-fractured surface of PLA/PC/EP ternary blend without TBAB. (b) SEM micrographs of impact-fractured surface of PLA/PC/EP ternary blend with 1 phr TBAB.

was clearly lower than that of PC in the unmodified binary blend. When the PLA/PC blend was further modified with EP and TBAB, it can be seen the glass transition of PC shifted to even lower temperature with increasing content of TBAB. As can be seen from the peak temperatures of E'', the T_g's of PC decreased from 140°C of unmodified blend to 129.5°C of PLA/PC blend modified with 10 phr EP and 1 phr TBAB, clearly showing the accelerated ring opening of epoxide by TBAB,[37] which primarily speeding up the interfacial reaction between EP groups and carboxyl groups of PLA. Further, the weak peaks appeared around 80°C in the E'' curves may represent the T_g of the rigid EP interphase. In fact, the T_g of EP 1010 was reported at 80°C from the supplier.

Morphological observation

SEM images of the cryofractured surfaces of the blends are shown in Figure 11. As afore-mentioned,

the binary blend behaved as expected for a highly immiscible polymer blend [see Fig. 6(a)]; large dispersed phase particles and smooth, distinct particle interfaces, indicating poor interfacial adhesion, were obtained. When Epon 1010 was added to the binary blend at 10 phr [Fig. 11(a)], the PC particle size decreased significantly with average size <0.5 µm. This is most likely attributable to the presence of the *in situ* compatibilization at the interface, suppressing the coalescence of the PC particles. The blend after the addition of 1 phr TBAB showed a much more uniform fractured surface [Fig. 11(b)], and it can be clearly seen that the PC domains were further reduced into tiny dispersed droplets due to effective compatibilization between PLA and PC phase by TBAB catalyst.

CONCLUSION

Novel PLA/PC blends that contain either PBSL or EP modifier were prepared successfully using the melt blending method. The PBSL modifier has been well known as a biodegradable toughening agent for PLA. Its partial miscibility with PC and the ductile interphase formation between PLA and PC domains can be seen from SEM. While the IS increased with PBSL modification, the HDT dropped significantly with increasing PBSL content.

Regarding the EP modified PLA/PC blend, the *in situ* compatibilization at the interface between PLA and PC can be seen clearly from SEM micrographs. The reduced size of PC domain demonstrated the effectiveness of EP as a compatibilizer. The addition of TBAB further catalyzed the reaction between the carboxyl group of PLA and the epoxide group of EP, and further reduced the domain size of the dispersed PC component. The increases in both storage modulus and HDT showed the efficiency of TBAB catalyst.

Finally, the proper combination of various modifiers can optimize the advantages and eliminate some of the disadvantages associated with the individual modifiers. A combination of PBSL and EP could facilitate both the toughness and heat resistance for PLA/PC blend. However, adding both modifiers with the amine catalyst in the PLA/PC blend only resulted in moderate improvement in both IS and HDT. Further refinement of the formulation and blending conditions will be pursued in the future to take full advantage of the two components.

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