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Investigation on compatibility of PLA/PBAT blends modified by epoxy-terminated branched polymers through chemical micro-crosslinking

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Abstract: In this study, a type of epoxy-terminated branched polymer (ETBP) was used as an interface compatibilizer to modify the poly lactic acid (PLA)/poly(butylene adipate-co-butylene terephthalate) (PBAT) (70/30) blends. Upon addition of ETBP, the difference in glass transition temperature between PLA and PBAT became smaller. By adding 3.0 phr of ETBP, the elongation at break of the PLA/PBAT blends was found increased from 45.8% to 272.0%; the impact strength increased from 26.2 kJ·m⁻² to 45.3 kJ·m⁻². In SEM analysis, it was observed that the size of the dispersed PBAT particle decreased with the increasing of ETBP content. These results indicated that the compatibility between PLA and PBAT can be effectively enhanced by using ETBP as the modifier. The modification mechanism was discussed in detail. It proposes that both physical and chemical micro-crosslinking were formed, the latter of which was confirmed by gel content analysis.

Keywords: compatibility; ETBP; PLA; PBAT; micro-crosslinking

1 Introduction

Poly(lactic acid) (PLA) is a type of bio-based polymer with fascinating properties such as great biocompatibility, biodegradability and processibility (1). It has found widespread applications in the area of packaging and medical materials (2-5). However, the disadvantages of PLA, such as high fragility, high hardness and low impact strength, limit its application in many other potential areas (6,7). As a result, it is common blending PLA with tough biodegradable polymers, for example, polycaprolactone (PCL) (8), polyhydroxybutyrate (PHB) (9-11), poly(propylene carbonate) (PPC) (12), poly(butylene succinate) (PBS) (13) and poly(butylene adipate-co-terephthalate) (PBAT) (14-18).

To date, many investigations on PLA/PBAT blends have concluded that the interfacial compatibility between PLA and PBAT is poor (19). Consequently, the introducing of a compatibilizer is usually necessary. Kumar et al. used glycidyl methacrylate (GMA) to improve the interfacial compatibility between PLA and PBAT. It is found that the impact strength of the blends is increased (20). Ding et al. added two types of triblock copolymers, i.e. PLA-PBAT-PLA and PLA-PEG-PLA, to the PLA/PBAT blends, aiming to improve the interfacial interaction between PLA and PBAT (21,22). Carbonell-Verdu group modified the PLA/PBAT blends using cottonseed oil-based derivatives. It shows that the addition of cottonseed oil-based derivatives can effectively enhance the interphase fusion of the blends (23). In order to increase the thermal properties of the PLA/PBAT blends, Coban's team added volcanic rock particles (VPS) to the blends. The results show that when the VPS is added in an amount of 5 wt%, the thermal properties of the blends are at an optimum state (24). Li et al. found that nanoclay can improve the interfacial adhesion between PLA and PBAT. Furthermore, the addition of nanoclay can significantly affect the crystallization of the PLA/PBAT blends and increase the tensile strength and modulus of the solid and microporous components (25).

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Among all types of compatibilizers for the PLA/PBAT blends, ones with terminal epoxy groups have been widely used because of their high reactivity. These substances act as chain extenders due to the ring-opening reaction between the peripheral epoxy groups and the terminal hydroxyl groups within the molecular chains of PLA/PBAT. Ren and his co-workers used an epoxy-functional styrene-acrylic acid copolymer (ESA) to modify the PLA/PBAT blends. It is found that ESA is only reactive for PLA matrix. The results show that the toughness and the melt elasticity of the PLA/PBAT blends are improved (26). Similarly, Al-Itry et al. investigated the modification of the PLA/PBAT blends by polyfunctional epoxides (27,28). Adrar group added organo-montmorillonites/epoxy functionalized graphene mixture into the PLA/PBAT blends aiming to improve the rheological and mechanical properties (29). Mehmet Kodal et al. investigated the compatibilization of the PLA/PBAT blends by using different Epoxy-POSS types to improve the mechanical properties (30).

Compared to linear polymers, branched polymers have plenty of active terminal functional groups present in the molecular chain, which enable strong hydrogen bonding and certain types of chemical reactions with other polymers. Apart from that, they are also of high degree of branching which can effectively prevent the entanglement between molecular chains and lead to low viscosity. Consequently, it is possible to enhance the compatibility between PLA and PBAT by using branched polymers.

In this study, a type of epoxy-terminated branched polymer (ETBP) was used to enhance the interfacial compatibility and physical properties of the PLA/PBAT blends for the first time. The impact of the addition of ETBP on the thermal properties, mechanical properties, rheological properties and gas barrier properties of the PLA/PBAT blends was investigated in detail. The modification mechanism was also proposed. It concluded that ETBP can effectively enhance the interfacial compatibility between PLA and PBAT, through micro-crosslinking effect.

2 Experiment

2.1 Materials

PLA (4032D, $\bar{M}_w = 1.1 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$, DI = 2.5) was provided by NatureWorks® Co. LLC, USA; PBAT ($\bar{M}_w = 1.0 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, DI = 2.3) was provided by Hangzhou Xinfu Pharmaceutical Co., Ltd.; ETBP (Generation 8.0, $\bar{M}_w = 7.0 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$, Epoxy Equivalent = 300 $\text{g}\cdot\text{mol}^{-1}$) was synthesized in our laboratory (31). The Chemical structure of ETBP was shown in Figure 1 as below.

2.2 Sample preparation

PLA and PBAT were completely dried prior to use to avoid any undesirable hydrolysis reaction during processing.

Figure 1: Chemical structure of ETBP.

The weight ratio of PLA/PBAT was kept consistently at 70/30; the ETBP loadings were selected at 0, 0.5, 1.0, 3.0 and 5.0 phr respectively. The blends were prepared through the twin-screw extruder (TS35, Nanjing T&S Extrusion Machinery Co., Ltd., China) and melted for granulation. The extrusion temperature profile was 180–195°C, and the rotation speed was 50 r/min. Through injection molding (TY-400, Hangzhou TAYU Machinery Co., Ltd., China), the resulting particles were made into strips for performance testing.

2.3 Sample characterization

2.3.1 DMA

DMA measurement was conducted from −70°C to 120°C, with a heating rate of 3°C/min (242C, NETZSCH, Germany). The frequency is set to 1 Hz and the amplitude is set to 25 m.

2.3.2 Mechanical properties

Electronic universal testing machine controlled by computer (CMT6104, MTS Industry System Co., Ltd.) was used to test the tensile strength and the elongation at break of the PLA/PBAT/ETBP blends as a dumbbell shaped specimen. The tensile rate was set to be 30 mm/min. The length of the specimen is 150 mm while the depth of the specimen is 4 mm.

An electronic Izod impact testing machine (XJUD-5.5, JinJian Testing Instrument Co., Ltd. ChengDe) was used to test the impact strength of the PLA/PBAT/ETBP blends as the A-type notched specimen. The size of the specimen is 80 mm × 10 mm × 4 mm. Impact pendulum energy is 2.75 J.

2.3.3 Gel content

The PLA/PBAT/ETBP blends were mixed with chloroform at 60°C for 14 h. All undissolved materials were filtered and dried at 80°C for 2 h. The gel content of PLA/PBAT blends with different content of ETBP was calculated by Eq. 1.

$$\text{Gel content} = \frac{m_1}{m_2} \times 100\% \quad (1)$$

where m_1 and m_2 are the mass of the PLA/PBAT/ETBP blends after and before dissolution, respectively.

2.3.4 TGA

The thermal decomposition performance of specimens was tested by TG (TA-Q50 Instrument Company, USA) under a nitrogen atmosphere, and the testing temperature ranged from RT to 600°C at a speed of 20°C/min.

2.3.5 DSC

The differential scanning calorimeter (DSC) (Q100, TA, USA) of the PLA/PBAT blends with various ETBP contents were measured under the protection of nitrogen gas. The sample (5.0–10.0 mg) was heated from room temperature to 190°C, pre-annealed at 190°C for 3 min, followed by cooling to −50°C at 20°C/min and then reheated to 190°C at 10°C/min.

2.3.6 SEM

The SEM images of the impacted fracture surface morphology, the fractured surface morphology after immersion in liquid nitrogen for 10 min, and tensile fractured surface morphology were observed under SEM (QUANTA250, FEI, USA). Before observation, gold spraying was carried out under a working voltage of 15 kV. The impacted fracture surface, the fractured surface after immersion in liquid nitrogen for 10 min, and tensile fractured surface of the PLA/PBAT/ETBP samples was sputter-coated with gold; and then SEM images of the blends were obtained using an accelerating voltage of 10 kV to magnify the sectional morphology.

2.3.7 Gas permeability

PLA/PBAT blends and PLA/PBAT/ETBP blends were compressed into 200 µm thick sheet by tablet press (lp-s-50, Lab Tech, Sweden) at 150°C respectively, and then specimens with size of 10 cm × 10 cm × 200 µm were obtained. The O₂ and CO₂ transmission property of the prepared specimens were tested by a permeation tester (VAC-V2, Ji'nan Languang Mechanical and Electrical Technology Co., Ltd., Shandong Province, China) according to GB 1038-2000. Samples of each group were tested three times.

2.3.8 Rheological analysis

The rheological test was conducted by Rotary Rheometer (MARS, Thermo Scientific Co., Ltd.,) at 165°C. The angular velocity range was set between 0.01 and 100 rad·s^{−1}.

3 Results and discussion

3.1 DMA

Figure 2 shows the loss factor ($\tan \delta$)-temperature relation curves for the PLA/PBAT blends with different content of ETBP. The T_g values of PBAT and PLA were denoted as T_{g1} and T_{g2} , respectively; the difference between T_{g1} and T_{g2} was denoted as ΔT_g .

As shown in Table 1, ΔT_g of the neat PLA/PBAT blends is 93.1°C, indicating that PLA and PBAT are immiscible as each phase shows relatively independent thermodynamic property. Upon addition of ETBP, ΔT_g of the blends is found decreased. The lowest ΔT_g at 87.1°C was obtained for the blends with 3 phr of ETBP. It proposes that the epoxy groups of ETBP reacted with the terminal carboxyl groups of PLA and/or PBAT, to enhance the interaction between the two phases.

It is worth noting that, compared to that with 3.0 phr of ETBP, ΔT_g of the blends with 5.0 phr of ETBP increased unexpectedly. The reason for this phenomenon may be due to the agglomeration of ETBP occurring under the action of hydrogen bonding after adding excessive ETBP (more than 3.0 phr).

3.2 Mechanical properties

Figure 3 shows the mechanical properties of the PLA/PBAT blends with different content of ETBP, including tensile strength, elongation at break and impact strength. At first glance, it is apparent that the tensile strength of the blends

fluctuated a little bit but stayed more or less the same, along with different content of ETBP, as shown in Figure 3a. On the other hand, the elongation at break of the blends showed a trend of firstly increase and then decrease, with the increasing of ETBP content, as illustrated in Figure 3b. The elongation at break for the neat PLA/PBAT blends was 45.8%. When 3 phr of ETBP was added, the peak value of the elongation at break was reached at 272%, which is 5.9 times of that of the neat blends. Unexpectedly, when adding excessive ETBP (5 phr), the elongation at break was decreased from 272% to 167%.

Similar phenomenon can be observed for the impact strength of the PLA/PBAT/ETBP blends, as demonstrated in Figure 3c. The impact strength of the PLA/PBAT/ETBP blends is found to be increased firstly and decreased in the following, with the increasing of ETBP content. The optimum addition level of ETBP was also found at 3.0 phr. As shown in Figure 2c, the impact strength of the PLA/PBAT blends with 3.0 phr of ETBP is 45.3 kJ·m⁻², much higher than that of the neat blends (26.2 kJ·m⁻²). When the content of ETBP is higher than 3 phr, i.e. 5 phr, it decreased from 45.3 to 41.4 kJ·m⁻².

Table 1: Glass transition points of the PLA/PBAT blends with different content of ETBP.

ETBP content (phr)	T_{g1} (°C)	T_{g2} (°C)	ΔT_g (°C)
0	-20.7	72.4	93.1
0.5	-19.7	73.0	92.7
1	-17.4	74.3	91.7
3	-16.2	70.9	87.1
5	-15.7	72.2	87.9

Figure 2: DMA curves of the PLA/PBAT blends with different content of ETBP: (a) $\tan \delta$ -temperature curve of PBAT; (b) $\tan \delta$ -temperature curve of PLA.

Figure 3: Tensile strength (a), elongation at break (b) and impact strength (c) of the PLA/PBAT blends with different content of ETBP.

The enhancement of the elongation at break and the impact strength was ascribed to the strong physical hydrogen bonding and chemical micro-crosslinking reaction between the terminal epoxy functional groups of ETBP and the terminal groups ($-OH$ and/or $-COOH$) within PLA and/or PBAT. Firstly, this reaction promoted the two-phase compatibility at a molecular level, making the PLA/PBAT blends more similar to elastomer. In such a system, PLA could act as the rigid segment; PBAT could act as the flexible segment, so as to increase the elongation at break and the impact strength of the blends. Secondly, the physical hydrogen-bonding and chemical bonding effects between ETBP and PLA/PBAT enhanced the adhesion at the interface between PLA and PBAT, increasing the thickness of the PLA/PBAT interaction layer. The absorption capacity of the stress between the PLA continuous phase and the PBAT dispersed phase was subsequently increased, leading to the enhancement of the toughness of the PLA/PBAT blends. Thirdly, the combined action of the strong physical and chemical

micro-crosslinking make the structure of the PLA/PBAT blends changed from linear structure to 3-D micro-crosslinked network structure. It helps the improvement of the elasticity and the impact strength of the blend system. When the ETBP content was less than 3.0 phr, the elongation at break and the impact strength of the PLA/PBAT blends increased with ETBP content increasing. However, when the content of ETBP was more than 3.0 phr, the elongation at break and the impact strength began to decrease. The reason lies in: When the content of ETBP was more than 3.0 phr, the excessive physical hydrogen bonding and chemical bonding reaction between ETBP and the PLA/PBAT blends restrict the movement and rotation of the macro-molecular chains. Under this situation, the movement of the PLA and PBAT molecular chains is not feasible, only if the chemical bonding between PLA and PBAT is broken. It causes the decrease of the elongation at break and the impact strength of the PLA/PBAT/ETBP blends. The above results conclude that the mechanical properties (elongation at break and impact strength)

Figure 4: Proposed modification mechanism of ETBP on the PLA/PBAT blends.

of the blends can reach the peak value when the added content of ETBP is 3.0 phr.

The proposed modification mechanism is illustrated in Figure 4.

3.3 Gel content

The gel content of the PLA/PBAT blends with different content of ETBP was measured to give evidence of the formation of the chemical micro-crosslinking network. During the dissolution, macro-molecular chains with solely physical micro-crosslinking structures can be soluble completely in the solvent; whilst macro-molecular chains with chemical micro-crosslinking structures are insoluble but only swelled.

As shown in Table 2, the neat PLA/PBAT blends cannot be dissolved in the solvent completely due to the existence of additives in PLA and PBAT. It is found that the gel content of the neat blends is 1.8%. The reason lies in that PLA contained a small amount of inorganic nucleating agent which is insoluble. Upon addition of ETBP, the gel content of the PLA/PBAT blends increased with the ETBP content increasing. When the content of ETBP is 5.0 phr, the gel content of PLA/PBAT blends is about 17.8%. The gel content analysis confirms that the chemical micro-crosslinking structure is formed upon addition of ETBP.

3.4 TGA

Figure 5 shows the TGA and DTG curves for the PLA/PBAT blends with different content of ETBP.

Table 2: Gel content of the PLA/PBAT blends with different content of ETBP.

ETBP content (phr)	Gel content (%)
0	1.8
0.5	8.4
1.0	8.9
3.0	11.4
5.0	17.8

As shown in Figure 5, the initial weight-loss temperature ($T_{50\%}$) and the 50% weight-loss temperature ($T_{50\%}$) of the PLA/PBAT blends containing different content of ETBP were basically consistent with that of the neat PLA/PBAT blends. The detailed results are also shown in Table 3. It shows that the addition of ETBP did not reduce the thermal stability of the PLA/PBAT blends obviously. The thermal stability of the blends remained basically stable, indicating that the addition of ETBP did not affect the hot-working performance of the PLA/PBAT blends evidently.

3.5 DSC

The DSC curves and parameters of the PLA/PBAT blends with different content of ETBP by the first heating cycle can be found in Figure 6 and Table 4. As shown in Figure 6 and Table 4, the cold crystallization temperature of the PLA/PBAT blends decreases firstly and then increases with the gradual increasing of ETBP content. The decrease of cold crystallization temperature of the PLA/PBAT/ETBP (0.5 phr) blends was presumed to be caused by the lubrication effect of ETBP. ETBP is a branched polymer

Figure 5: TGA (a) and DTG (b) curves of the PLA/PBAT blends with different content of ETBP.

Table 3: Decomposition temperature of the PLA/PBAT blends with different content of ETBP.

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)
PLA/PBAT	361.8	395.7
PLA/PBAT/0.5 phr ETBP	359.7	394.9
PLA/PBAT/1.0 phr ETBP	360.6	395.3
PLA/PBAT/3.0 phr ETBP	358.8	394.8
PLA/PBAT/5.0 phr ETBP	357.8	399.3
PLA	353.7	380.9
PBAT	383.0	413.8

without intermolecular entanglements and of low viscosity. The lubrication effect of ETBP on the PLA/PBAT blends would increase the movement and orientation arrangement of macromolecular chain segments. It leads to the ease of crystallization of the blends, which causes the decrease of the cold crystallization temperature. Also, as illustrated in Figure 6 and Table 4, there is no significant change in melting temperature of the PLA/PBAT blends upon addition of ETBP.

The percentage crystallinity (X_c) values of PLA in the blends were estimated using baselines drawn from 95°C to 190°C and a perfect heat of fusion (ΔH_m^0) of PLA of 93 J·g⁻¹ (32). In which, X_c values of PLA in the blends are evaluated according to Eq. 2 as below:

$$X_c = \frac{\Delta H_c}{(1-\Phi)\Delta H_m^0} \quad (2)$$

where ΔH_c is the net melting enthalpy of crystallization of the blends obtained by subtracting the enthalpy values of those of the re-crystallization exotherms and Φ is the weight fraction of PBAT (30%) in the PLA/PBAT blends.

As shown in Table 4, with the increasing of ETBP content (from 0 to 3.0 phr), the percentage crystallinity (X_c) values of PLA in the blends increased from 3.0% gradually to 7.3%, indicating parts of the amorphous regions of PLA changed into crystalline regions. However, when the content of ETBP in the PLA/PBAT blends is more than 3.0 phr, X_c began to decrease, indicating that parts of the crystalline regions of PLA started changing back to the amorphous regions.

3.6 SEM

The SEM images of the impacted fracture surface morphology, the fractured surface morphology (immersion in liquid nitrogen) and the tensile fractured surface morphology of the PLA/PBAT/ETBP blends were shown respectively in Figure 7, Figure 9 and Figure 11 as below. The size of PBAT particles in the PLA/PBAT blends with different content of ETBP was shown in Figure 8 and Figure 10.

As shown in Figure 7a, PLA in the sample was the continuous phase, whereas PBAT was dispersed in a continuous phase in droplets form. Phase separation structure between PLA and PBAT could be seen clearly. The interface image between the two phases was clear and loosely bonded, showing a sea-island structure. The average size of PBAT particles in PLA/PBAT blends was 2.87 μm (as shown in Figure 8). It indicates that the PLA/PBAT blend system was a typical thermodynamically immiscible system.

After the addition of different content of ETBP, the size of the dispersed PBAT particle decreased obviously. For example, in Figure 7e, the average size of PBAT particles reduced to 0.38 μm (as shown in Figure 8, island structure

Figure 6: DSC curve of the PLA/PBAT blends with different content of ETBP by first heating cycle.

Table 4: DSC parameters of the PLA/PBAT blends with different contents of ETBP.

Content	ΔH_m (J·g ⁻¹)	ΔH_c (J·g ⁻¹)	X_c (%) ^a
PLA/PBAT	16.9	15.1	3.0 ± 0.2
PLA/PBAT/0.5 phr ETBP	18.1	15.3	4.2 ± 0.3
PLA/PBAT/1.0 phr ETBP	18.2	14.8	5.1 ± 0.2
PLA/PBAT/3.0 phr ETBP	17.0	12.2	7.3 ± 0.6
PLA/PBAT/5.0 phr ETBP	18.8	12.5	5.1 ± 0.3
PLA	36.1	0	38.8 ± 0.1

^a For each sample, the test was performed three times under the same condition (at a rate of 10°C/min).

almost disappeared). Also, as illustrated in Figures 7b-e, the interface between PLA and PBAT becomes fuzzy, more PLA and PBAT were combined together. In Figures 7a-c, mixtures of two incompatible or partially compatible phases can be observed, showing obvious sea-island structure. In Figures 7d and 7e, only one phase can be observed, indicating that PLA and PBAT have better compatibility after adding enough ETBP. It concludes that the addition of ETBP improved the interfacial compatibility between PLA and PBAT, which is consistent with the results of the above sections.

The SEM images and the PBAT particle size distribution of the fractured surface morphology (immersion in liquid nitrogen) of the PLA/PBAT/ETBP blends were shown respectively in Figures 9 and 10 as below. The average PBAT particle size in the PLA/PBAT blends is 1.48 μm; the average PBAT particle size in the PLA/PBAT/3.0 phr ETBP blends decreased to 0.75 μm, indicating a better dispersion of PBAT in PLA matrix upon addition of 3.0 phr of ETBP.

The SEM images of the tensile fractured surface morphology of the PLA/PBAT/ETBP blends were shown in Figures 11 as below. As can be seen from Figures 11a and 11b, the tensile fractured surface morphology presented brittle fracture characteristics and distinct sea island structure. As can be seen from Figures 11c-e, the tensile fractured surface morphology presented ductile fracture characteristics and obvious wire drawing state, the sea island structure nearly disappeared, indicating that the addition of more than 1.0 phr of ETBP in the PLA/PBAT blends can significantly improve the compatibility between PLA and PBAT and the toughness of PLA/PBAT blends.

3.7 Rheological performance analysis

Figure 12 shows the storage modulus (G')-angular frequency (ω) relation curves and the loss modulus (G'')-angular frequency (ω) relation curves of the PLA/PBAT blends with different contents of ETBP. The PLA/PBAT blends with different content of ETBP presented the typical behavior of linear polymers having a fast relaxation process of the chains, G' and G'' values increased steadily with the increasing of the shear frequency.

As can be seen from Figures 12a and 12b, it clearly shows that G' and G'' for the PLA/PBAT/ETBP blends increased with the increasing of the ETBP contents. It is well known that the mobility of the macro-molecular depends on the speed of the segment transition and the frequency of the macro-molecular chains translation. The former is related to the intermolecular friction, and the latter is related to the molecular structure of polymers. Upon addition of ETBP, the formed micro-crosslinking network structure strengthened the macro-molecular chains entanglement and interweaving of PLA and PBAT, leading to the change of molecular structure (from linear structure to micro-crosslinking structure) and the increase of intermolecular friction, thus the elasticity and melt viscosity increased (G' and G'' of the PLA/PBAT/ETBP blends increased) (33).

It is worth noting that, under higher shear frequency, the slope (G' vs ω and G'' vs ω) of the curves decreased drastically with the increasing of ETBP content. It is well known that under higher shear frequency, the change of G' and G'' actually reflects the movement of chain molecular segment. The addition of ETBP can give rise to the generation of chemical micro-crosslinking between ETBP and PLA/PBAT. However, apart from the segments which locate closed to the micro-crosslinking point, in most cases, the structure of the molecular chain segments stay nearly unchanged. Consequently, the slope (G' vs ω

Figure 7: SEM images of the impacted fractures of the PLA/PBAT blends with different content of ETBP: (a) neat, (b) 0.5 phr, (c) 1.0 phr, (d) 3.0 phr and (e) 5.0 phr.

Figure 8: Particle size distribution of the impact fracture surface of the PLA/PBAT blends with different ETBP content: (a) neat, (b) 0.5 phr, (c) 1.0 phr, (d) 3.0 phr and (e) 5.0 phr.

Figure 9: SEM images of the fractured surface morphology (immersion in liquid nitrogen) of the PLA/PBAT blends with different content of ETBP: (a) neat, (b) 0.5 phr, (c) 1.0 phr, (d) 3.0 phr and (e) 5.0 phr.

Figure 10: Particle size distribution of the fractured surface morphology (immersion in liquid nitrogen) of PLA/PBAT blends with different content of ETBP: (a) neat, (b) 0.5 phr, (c) 1.0 phr, (d) 3.0 phr and (e) 5.0 phr.

Figure 11: SEM images of the tensile fracture surface morphology of the PLA/PBAT blends with different content of ETBP: (a) neat, (b) 0.5 phr, (c) 1.0 phr, (d) 3.0 phr and (e) 5.0 phr.

Figure 12: G' - ω relation curves (a) and G'' - ω relation curves (b) of the PLA/PBAT/ETBP blends.

and G'' vs ω) of the curves decreased drastically with the increasing of ETBP content.

3.8 Gas transmission

As can be seen from Table 5, upon addition of ETBP, the transmission coefficient of CO_2 and O_2 both decreased significantly. When the content of ETBP is 3.0 wt% (mechanical property is best), the carbon dioxide and oxygen permeability coefficient of the PLA/PBAT/ETBP blends decreased by 16.2% and 14.9%, respectively. It indicates that the addition of ETBP helps to improve the gas barrier property of the PLA/PBAT blends, which is important in preservation of food by packaging.

The gas transmission of amorphous polymers is chiefly based on the model of free volume (34). The decline of the gas transmission coefficient of PLA/PBAT after addition of ETBP (no more than 3.0 phr) attributes to the increase of crystallinity of PLA and the formation of the strong chemical micro-crosslinking function between ETBP and PLA/PBAT.

On one hand, with the increasing addition of ETBP (from 0 to 3.0 phr), X_c values of the blends increased from 3.0% gradually to 7.3%, indicating parts of the amorphous regions of PLA changed into crystalline regions. The increase in crystallinity limited the movement of the molecular chain, resulting in the weakening of the gas (O_2 and CO_2) transport effect. However, when the content of ETBP in the PLA/PBAT blends is more than 3.0 phr, X_c began to decrease, indicating that parts of the crystalline regions of PLA started changing back to the amorphous regions. Consequently, the gas (O_2 and CO_2) transport effect is enhanced.

On the other hand, the movement of PLA and PBAT molecular chains is also attenuated due to the strong micro-crosslinking effect. Therefore the free volume of

Table 5: Gas permeability of different materials.

Sample	$\text{O}_2 \text{TR}^a$ ($\text{cm}^3/\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm}$)	$\text{CO}_2 \text{TR}^a$ ($\text{cm}^3/\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm}$)
PLA ^b	260	1200
PBAT ^b	600	260
PLA/PBAT	451.3 ± 1.9	410.5 ± 0.2
PLA/PBAT/0.5 phr ETBP	437.4 ± 2.8	396.4 ± 1.6
PLA/PBAT/1.0 phr ETBP	415.1 ± 1.2	379.6 ± 0.9
PLA/PBAT/3.0 phr ETBP	378.6 ± 1.4	349.3 ± 0.5
PLA/PBAT/5.0 phr ETBP	392.4 ± 2.8	354.1 ± 1.3

^a For each sample, the test was performed three times under the same condition.

^b Data provided by the corresponding manufacturer.

PLA and PBAT macromolecules and the transport of gas molecules (O_2 and CO_2) reduced with the increasing of ETBP content (from 0 to 3.0 phr). However, if the degree of micro-crosslinking is too high, there would be voids present in the micro-crosslinking network. It would cause the increase in the gas permeability. As shown in Table 5, when the content of ETBP is 5.0 phr, the carbon dioxide and oxygen transmission rates for the blends both increase, compared to those with 3.0 phr of ETBP.

On the other hand, the movement of PLA and PBAT molecular chains is also attenuated due to the strong micro-crosslinking, thereby the free volume of PLA and PBAT macromolecules and the transport of gas molecules (O_2 and CO_2) reduced with the increasing addition of ETBP (from 0 to 3.0 phr). However, if the degree of micro-crosslinking is too high, there would be voids present in the micro-crosslinking network. It would cause the increase in the gas permeability. As shown in Table 5, when the content of ETBP is 5.0 phr, the carbon dioxide and oxygen transmission rates for the

PLA/PBAT/ETBP blends both increase, compared to that with 3.0 phr of ETBP.

4 Conclusions

ETBP is used in order to enhance the interfacial compatibility between PLA and PBAT. The reaction of epoxy groups within ETBP and hydroxyl groups present in PLA/PBAT helps the generation of the chemical micro-crosslinking structure, and thus the improvement of the properties of PLA/PBAT (70/30) blends. When the content of ETBP was 3.0 phr, the elongation at break of the PLA/PBAT blends increased from 45.8% (neat PLA/PBAT) to 272%; the impact strength increased from 26.2 to 45.3 kJ·m⁻². DMA results showed that ΔT_g of the two phases in PLA/PBAT blends decreased with the ETBP content (no more than 3.0 phr) increasing, indicating that ETBP promoted the interfacial compatibility between the PLA and PBAT phases.

The formation of the chemical micro-crosslinking structure is confirmed by gel content analysis of the PLA/PBAT blends with different content of ETBP. It is found that when the content of ETBP is 5.0 phr, the micro-crosslinking degree is about 17.8%.

SEM results suggest that ETBP improved the dispersion of PBAT particles in PLA phase, blurring the interface morphology between the two phases.

Rheological analysis shows that upon addition of ETBP, G' value under lower shear frequency is increased with the increasing of ETBP content; whilst under higher shear frequency, G' is found nearly overlapped. On the other hand, it is found that G'' value for the blends is actually influenced by summation of two sets of effect: micro-crosslinking effect and the lubrication effect.

The increase of PLA crystallinity and the formation of the micro-crosslinking structure can effectively slow down the movement of PLA and PBAT molecular chains, which reduces the free volumes of PLA and PBAT macromolecules. Consequently, it decreases the transmission of gas molecules (O₂, CO₂) in the LA/PBAT blends with ETBP content no more than 3.0 phr.

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