

Improvement in Toughness of Polylactide by Melt Blending with Bio-based Poly(ester)urethane

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Abstract Polylactide (PLA) was successfully toughened by blending with bio-based poly(ester)urethane (TPU) elastomers which contained bio-based polyester soft segments synthesized from biomass diols and diacids. The miscibility, mechanical properties, phase morphology and toughening mechanism of the blend were investigated. Both DSC and DMTA results manifested that the addition of TPU elastomer not only accelerated the crystallization rate, but also increased the final degree of crystallinity, which proved that TPU has limited miscibility with PLA and has functioned as a plasticizer. All the blend samples showed distinct phase separation phenomenon with sea-island structure under SEM observation and the rubber particle size in the PLA matrix increased with the increased contents of TPU. The mechanical property variation of PLA/TPU blends could be quantitatively explained by Wu's model. With the variation of TPU, a brittle-ductile transition has been observed for the TPU/PLA blends. When these blends were under tensile stress conditions, the TPU particles could be debonded from the PLA matrix and the blends showed a high ability to induce large area plastic deformation before break, which was important for the dissipation of the breaking energy. Such mechanism was demonstrated by tensile tests and scanning electron microscopy (SEM) observations.

Keywords: Poly(ester)urethane; Polylactide; Toughness; Morphology.

INTRODUCTION

Polylactide (PLA) has attracted tremendous attention in recent years as a biodegradable and bio-based polymer. It could be derived from biomass materials, such as corn, potato and beet^[1–3], and possesses high biocompatibility, good biodegradability and excellent mechanical properties. It has been widely used for biomedical applications such as degradable sutures and drug delivery devices and has also become an alternative to petroleum based plastics for daily applications.

Generally, PLA has high mechanical strength and modulus, but its inherent brittleness with very low impact resistance, restricts its application as a common commodity plastic. Therefore, some researchers attempted to tailor the required properties of PLA by using various methods, such as plasticizing, blending and copolymerizing. For example, commercial plasticizers, such as polyethylene glycol (PEG), tributyl citrate (TBC), triethyl citrate (TEC), acetyltri butyl citrate (ATBC) and acetyltriethyl citrate (ATEC)^[4, 5] were used to increase the toughness of PLA, which all show effective improvement in elongation. Unfortunately, results of these tensile tests also showed a dramatic decrease in modulus and strength. Besides, these plasticizers would migrate from the PLA matrix to the surface, and resulted in embrittlement of the blends during the application.

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PLA-*b*-PEG and poly(CL-*co*-LA) block copolymers were synthesized^[6–9]. The copolymer showed microphase separation and resulted in better mechanical properties compared to those of neat PLA. However, the above-mentioned PLA copolymers are usually very expensive for wide application.

Considering the disadvantages of plasticizers and copolymers in toughening PLA, it seems to be a more practical and economical way the blending of PLA with other polymers. Researchers have reported several PLA/flexible bio-degradable polymer systems, in which poly(ϵ -caprolactone) (PCL) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) were used to toughen the PLA^[10–12]. Other biodegradable polymers like poly(propylene carbonate) (PPC)^[13, 14], poly(butyleneadipate-*co*-terephthalate) (PBAT)^[15, 16] and poly(butylene succinate) (PBS)^[17, 18] were also taken as a second phase polymer to improve the toughness of PLA. On the other hand, non-biodegradable polymers like poly(ethylene oxide) (PEO)^[19], polyethylene (PE)^[20], poly(ethylene-glycidylmethacrylate) (EGMA) and acrylonitrile-butadiene-styrene copolymer (ABS) were also adopted to toughen the PLA^[21–24]. But most of the added polymers have no biocompatibility, which clearly limit the biomedical applications of the prepared blends. In addition, most of these blends are strongly incompatible systems, and frequently resulted in fairly poor mechanical properties with noticeable reduction in strength and modulus.

Thermoplastic polyurethane elastomers (TPU) have great features of toughness, flexibility, biocompatibility and biological stability, which make them to be one of the research trends in polymer science. TPU chains are normally made up of soft segments (SS) and hard segments (HS), and with SS providing elastic nature and HS contributing mechanical stability, TPU materials obtain unique properties and claim a big market share. The soft segments are usually composed of polyester or polyether, both of them are considered to have good compatibility with PLA^[25–28]. To the best of our knowledge, the physical and mechanical properties of PLA/TPU blends have received only little attention^[29, 30], and bio-based TPU is newly developed materials and researchers have just started to employ it in different application fields. What's more, polyester polyurethane plays a predominant role as biodegradable plastics due to their potentially hydrolysable ester bonds and keeps the biodegradation of PLA/TPU blends.

In this work, several bio-based TPUs were synthesized to improve the toughness of PLA. Biomass diols and diacids were used to synthesize polyesters, which functioned as soft segments in TPUs and offered the bio-based feature. It is quite often that the strength and stiffness of PLA will be largely depressed by the blended elastomers, but we are delighted to find that with our bio-based TPUs the PLA material retains relatively good mechanical behavior.

EXPERIMENTAL

Raw Materials

Adipic acid (ADA, purity of 98%), itaconic acid (IA, purity of 99%), 1,10-decanediol (purity of 98%), 1,4-butanediol (BDO, purity of 99%), isophoronediiisocyanate (IPDI, purity of 99%), dibutyltin dilaurate (DBTDL, purity of 95%), *p*-toluenesulfonic acid (*p*-TSA), tetra-*n*-butyltitanate (TBT, purity of 98%) and hydroquinone were purchased from Aladdin (Shanghai, China) and used as received. Solvents (chloroform, methanol and methyl ethyl ketone) of analytic grade were also obtained from Aladdin. Polylactide (PLA, 4032D, D-isomer content = 1.2%–1.6%) was provided by Natureworks Co. Ltd, USA. It has a density of 1.25 g/cm³, weight-averaged molecular weight (M_w) of 204 kDa, and polydispersity of 1.7, respectively.

Synthesis of Polyester Polyol and Preparation of Bio-based TPUs

Our bio-based polyester polyol was synthesized according to two-step method^[31, 32]. In brief, we charged 1,10-decanediol (20.9000 g, 0.1210 mol), IA (6.5100 g, 0.0520 mol), ADA (7.3200 g, 0.0500 mol), inhibitors hydroquinone (0.1315 g) and *p*-TSA (0.0521 g) into a 250 mL three-neck flask. The mixture was purged with nitrogen and then heated at 160 °C for 2 h. In the second phase, after adding TBT (0.02 g) as the catalyst, the mixture was heated to 180 °C under reduced pressure (< 500 Pa) for 4–5 h. The polymer was dissolved in chloroform, precipitated in cold methanol filtered, and vacuum dried. Titration methods were applied to determine the acid value (AV) and the hydroxy value (HV) according to HG/T 2709-1995. In order to calculate

the number average molecular weight, the equation of $M_n = 56.1 \times 2000 / (AV + HV)$ was used. The accuracy of resulted M_n values through this method was 1020 ± 25 g/mol and its glass transition temperature was -20 °C (DSC analysis).

TPU was synthesized *via* a two-step process (so-called prepolymer method), which is schematically depicted in Fig. 1. The reaction was conducted at the molar ratio of NCO/OH = 1. A certain ratio of bio-based polyol and IPDI were dissolved in methyl ethyl ketone, added to a three-neck flask, and stirred at 65 °C for 3 h. The reaction was catalyzed by TBT. The pre-polymer was then chain extended to form a high molecular weight polymer by adding BDO to the reaction mixture and stirring at 85 °C for 3–4 h. The disappearance of the isocyanate peak (2260 cm^{-1}) was confirmed according to Fourier transform infrared spectroscopy (FTIR), suggesting that the reaction finished. Finally, the resulting viscous liquid was quickly poured into a rectangular mold made of polytetrafluoroethylene (PTFE) and was cooled inside the mould until room temperature was reached. The weight-average molecular weight (M_w) and poly-dispersity index of the polymer were 66000 g/mol and 1.8 respectively, which were evaluated by gel permeation chromatography (GPC).

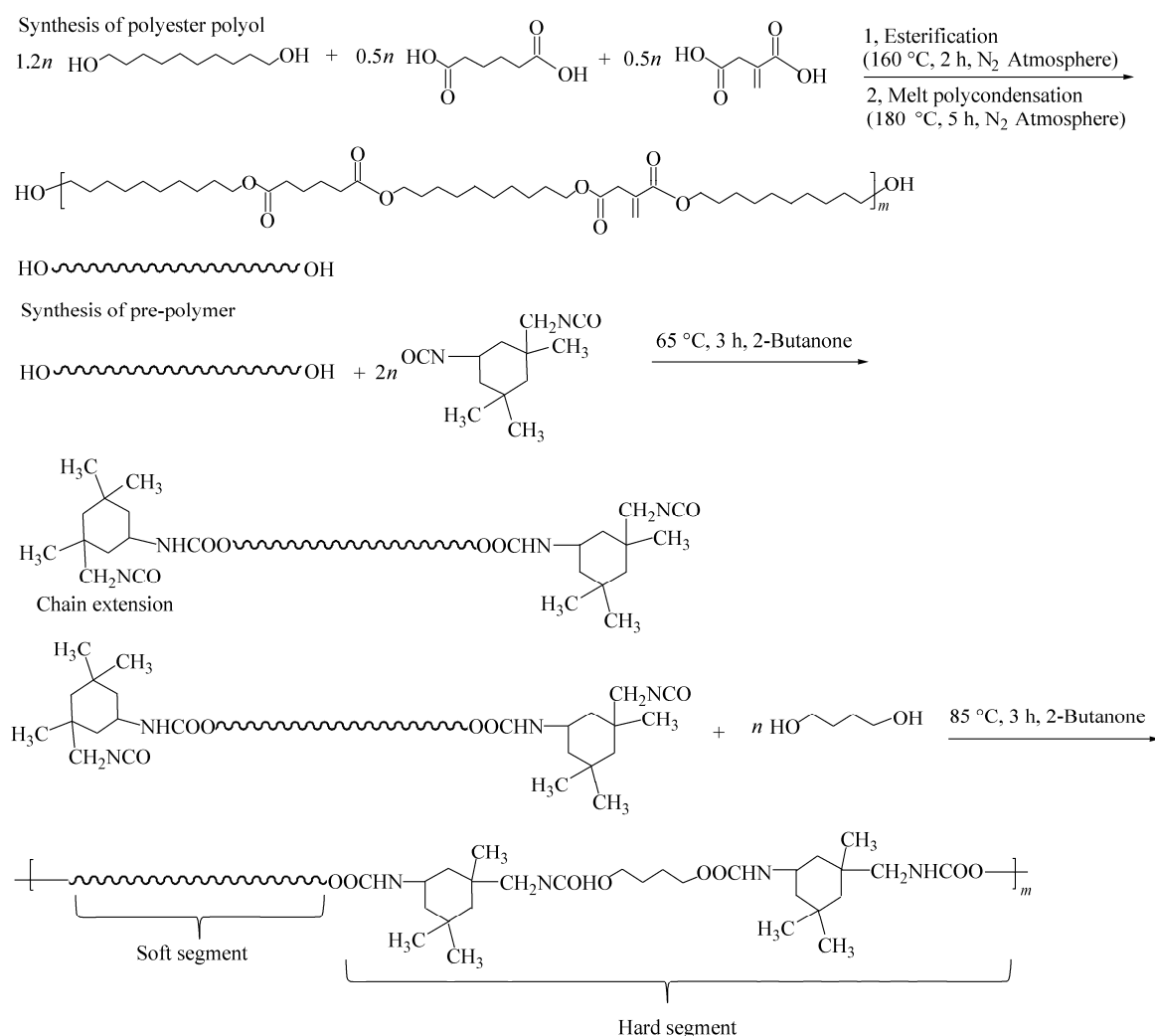


Fig. 1 Synthesis of hydroxyl terminated polyester and segmented polyurethane from polyester, BDO, and IPDI

Sample Preparation

PLA and TPU were dried in a vented oven at 80 °C for 12 h prior to processing. The blends were melt blended in a Brabender mixer at 180 °C with a rotary speed of 60 r/min for 8 min. The obtained blends were hot-pressed into flat sheets with approximately 0.5 mm and 4 mm thickness at 190 °C under 10 MPa. For convenience, we use symbol TPU_x to represent the sample in which TPU weight content is *x*%. For example, TPU10 means a blend with 90 wt% of PLA and 10 wt% of TPU.

Characterization

Gel permeation chromatography tests

Gel permeation chromatography was performed at 80 °C on a PL-GPC 220 instrument equipped with two PL Mixed-B-LS columns, a MALLS (DAWN EOS, Wyatt Technology) and a RI Detector. Chloroform (HPLC) was used as the eluent with a normal flow rate of 1.0 mL/min. Polystyrene standards in the range 500–1800000 g/mol were used for calibration.

Fourier transform infrared spectroscopy

The polymerization was monitored by Fourier transform infrared spectroscopy (FTIR) (Nicolet FTIR 6700 infrared spectrophotometer, KBr powder). Spectra of the samples were recorded at various reaction times after averaging 32 scans in the range 400–4000 cm⁻¹.

Mechanical tests

Type-V specimens were shaped with a dumbbell-shaped cutter and measured at room temperature according to ASTM D638, by using an Instron 5567 Tensile Instrument (Wuhan, China) at 20 mm/min. An average value of five replicated measurements was taken for each sample. The notched Izod impact strength was performed on a mechanical impact tester (XJ-50Z, Chengde Dahua Testing Machine Co. Ltd., Chengde, China) according to GB/T 1843-2008. The bar samples A-shaped notches with a radius of about 0.2 mm in the bar samples (dimensions L × W × H = 80 mm × 10 mm × 4 mm) were made. At least five specimens for each composite were tested for an average value.

Differential scanning calorimetry (DSC) tests

A DSC instrument (Mettler-Toledo) was used to study the thermal properties (*T_g*, *T_m*) of the blends. Each DSC specimen was heated from room temperature to 190 °C at a rate of 10 K/min and hold for 3 min to eliminate any thermal history, then quenched to -20 °C, following by heating to 190 °C at a heating rate of 10 K/min. The degree of crystallinity (*X_c*) of the PLA/TPU blends were determined using the relationship:

$$X_c = \frac{\Delta H_m - \Delta H_c}{w_{PLA} \Delta H_m^0} \times 100\% \quad (1)$$

ΔH_m and ΔH_c , the enthalpies of melting and cold crystallization, respectively; ΔH_m^0 , the enthalpy of fusion assuming 100% crystalline PLA (93.7 J/g)^[33]; w_{PLA} , the weight fraction of PLA in the blend.

Characterization of the blend morphology

The microstructural morphology of the blends was characterized by environmental scanning electron microscopy (SEM, Hitachi TM-1000) at 10 kV. After immersing in liquid nitrogen for 10 min, notched samples were fractured by a vice, and then surface-coated with gold prior to observation. The number-average particle diameter (*d_i*) was determined by a Nano Measurer 1.2 (Fudan University, China) and 120 particles were analyzed per sample. The average particle diameter (*d*) and its distribution (*σ*) were calculated by the following equations^[34]:

$$\ln d = \sqrt{\frac{\sum_{i=1}^N n_i \ln d_i}{\sum_{i=1}^N n_i}} \quad (2)$$

$$\ln\sigma = \sqrt{\frac{\sum_{i=1}^N n_i (\ln d_i - \ln d)^2}{\sum_{i=1}^N n_i}} \quad (3)$$

n_i , the number of droplets whose diameter is d_i ; N , the number of all of the droplets; d , the mean particle diameter; σ , the polydispersity of particle diameter.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) was carried out on a DMA-SDTA861e apparatus (Mettler-Toledo). The dimension of test bars was $W \times H \times L = 0.5 \text{ mm} \times 0.5 \text{ mm} \times 2.5 \text{ mm}$. The experimental temperature ranged from -70°C to 150°C , at a heating rate of 3 K/min . The amplitude was set at $15 \mu\text{m}$, with a frequency of 1 Hz . Loss modulus, storage modulus, and $\tan\delta$ were recorded as a function of temperature.

RESULTS AND DISCUSSION

The FTIR Analysis of Polyester Polyol and TPU

The structure of polyester polyol was confirmed by FTIR. The FTIR spectrum (Fig. 2) displays strong absorptions at 1730 cm^{-1} , which are due to the stretching vibrations of $\text{C}=\text{O}$ in the ester groups. The curve also shows a bimodal between $3400\text{--}3500 \text{ cm}^{-1}$, which corresponds to the stretching vibration of hydrogen bonded and free hydroxyls. From the FTIR results, it could be concluded that the desired polyol were obtained. The infrared spectra of synthesized TPU are also shown in Fig. 2. They do not show the stretching vibration band of isocyanate ($-\text{N}=\text{C}=\text{O}$) group at 2266 cm^{-1} . This manifests that all the isophorone diisocyanates have reacted with the polyol and the chain extender. The spectra of TPUs also display a characteristic band of urethane group 1540 cm^{-1} , which corresponds to the NH of amide bonds. These results indicate that the bio-based TPUs were successfully synthesized.

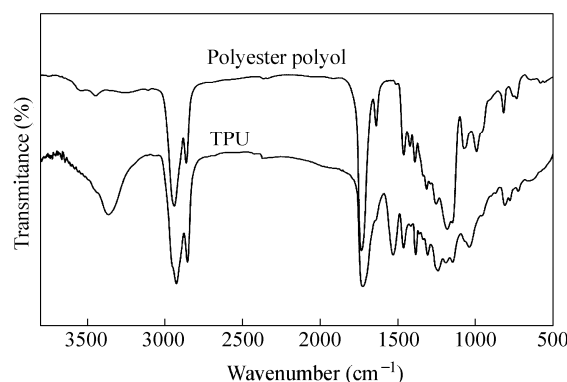


Fig. 2 The FTIR spectra of bio-based polyester polyol and TPU

Thermal Behavior

Figure 3 gives the DSC heating scans of the four PLA/TPU blends, and glass transition, cold crystallization and melting behavior can all be observed in these curves. Experimental results, like crystallinity X_c , are calculated and summarized in Table 1. From the DSC curves and Table 1, it could be found that the glass transition temperatures of the PLA phase were decreased with the increasing TPU content, which probably indicated some limited miscibility between the two components. Such weak compatibility can be attributed to the segmental interaction between the PLA chain and the soft segment (bio-based polyester polyols) of the TPU elastomer.

All of the samples had only one cold crystallization peak shifted to lower temperatures relative to that of neat PLA, which suggested that the crystallization ability of PLA was improved after introducing TPUs. In addition, the crystallinity X_c increased continuously upon increasing TPU elastomer content in the blends, suggesting that the addition of TPU increased the crystallinity of PLA. The result may be attributed to the decreased T_g of PLA, which made the PLA molecular chains more flexible.

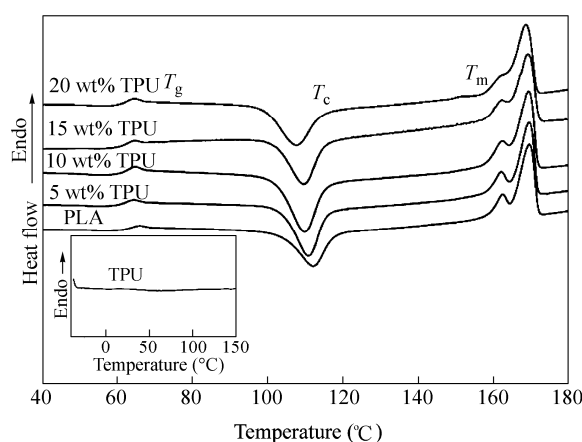


Fig. 3 DSC heating curves of PLA/TPU blends with different amounts of TPU

Table 1. Thermal properties of PLA/TPU blends

Sample	T_g^a (°C)	T_g^b (°C)	T_c (°C)	ΔH_c (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	X_c (%)
TPU0	64.5	56.4	113.0	26.5	162.2	169.0	34.2	8.2
TPU5	64.0	55.4	110.7	27.5	161.6	168.6	34.8	8.2
TPU10	64.0	54.8	109.1	28.3	161.7	168.7	35.4	8.4
TPU15	63.6	54.3	108.8	27.3	161.8	168.5	34.8	9.4
TPU20	63.5	53.0	107.8	27.1	161.9	168.5	34.3	9.6

^a Obtained from DSC measurements; ^b Obtained from DMTA measurements

Dynamic mechanical thermal analysis (DMTA) was used to directly investigate the phase interaction and miscibility of the PLA/TPU system. As shown in Fig. 4(a), the glass transition temperatures (T_g) were calculated from the $\tan\delta$ peak temperatures, and the results are summarized in Table 1. It is interesting to note that glass transition temperatures of the TPU phase were also exhibited in these curves, and as the TPU content increased the T_g of TPU phase decreased. Although the T_g obtained from DMTA was not the same as that obtained from DSC, the variation trend was the same. The T_g of both TPU and PLA phases shifted toward lower temperatures, indicating that TPU and PLA were partially miscible.

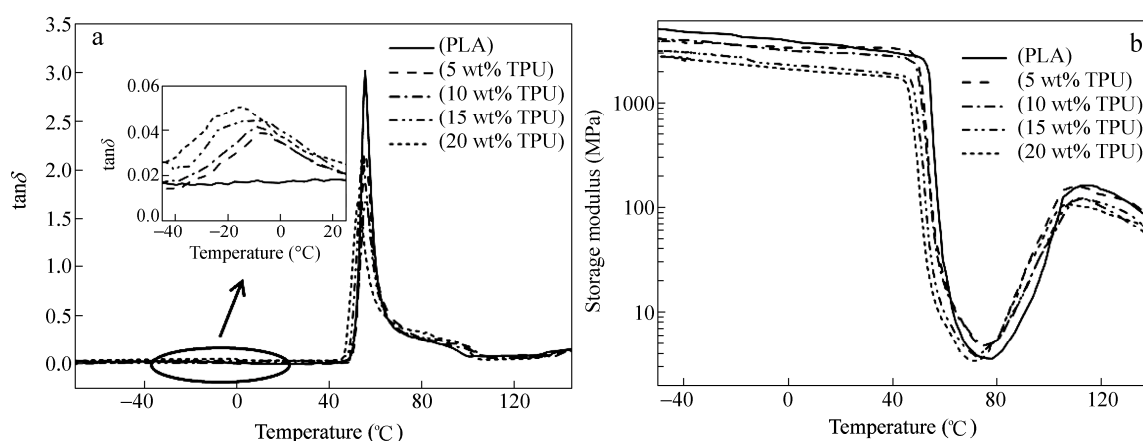


Fig. 4 Dynamic viscoelastic curves of PLA/TPU blends: (a) $\tan\delta$ versus temperature and (b) storage modulus versus temperature

In our bio-based TPU, on one hand, the soft segments of polyester, which contain large amount of ester bonds, play an important role in enhancing the compatibility between the PLA and TPU molecules^[25, 26]. While, on the other hand, the hard segments of IPDI and BDO contain a lot of carbamate groups which can form hydrogen bonds with the PLA molecules, and the hydrogen bond is well known to enhance interfacial adhesion and improve the compatibility. With both the effect of soft and hard segments, the compatibility between bio-based TPU and PLA was indeed improved and would improve the mechanical properties as will be shown below.

Figure 4(b) shows the temperature dependence of the tensile storage modulus (E') for pure PLA and the other four blends. The five samples shared a similar temperature dependence behavior. As the temperature increased, the storage modulus of PLA sharply dropped at 55–70 °C due to the glass-elastomer transition and then gradually rose up as the cold crystallization started. Finally, E' decreased rapidly again at temperatures over 115 °C owing to the continuous softening of the amorphous part in the blends. However, there was slight difference among these samples as shown in Fig. 4. Due to the addition of TPU, the $\tan\delta$ peaks of glass transition moved to lower temperatures and such trend coincided well with what we saw in DSC results. When TPU content increased in the blends, the glass transition temperatures of PLA/TPU became lower and lower. Besides, except for the cold crystallization regions, the storage modulus of pure PLA was always larger than PLA/TPU blends. It is quite understandable, because the linear addition of PLA and TPU storage modulus will be lower than pure PLA and the accelerated cold crystallization will promote the mechanical properties of PLA/TPU blends temporarily. Here, again, we see the weak miscibility worked, and the PLA chain mobility was improved and at the same time the glass transition temperatures were depressed. It is interesting that the bio-based TPU is not only functioned like filler but also played a role of plasticizer.

Morphology

Figure 5 shows the SEM micrographs of the cryofractured surfaces. Every blend exhibited sea-island morphology, which clearly was the evidence of phase separation. This phase-separated structure of the blends was also consistent with the two T_g s obtained from the DMTA measurements. The histograms in Fig. 6 present the statistical results of the diameters of TPU particles, and the analysis process is interpreted above in experimental section. The particle size went up with the TPU content increased. The average dispersed diameters d , calculated from Eq. (2), were 1.3, 1.5, 1.7, and 3.1 μm for PLA/TPU blends with 5 wt%, 10 wt%, 15 wt%, and

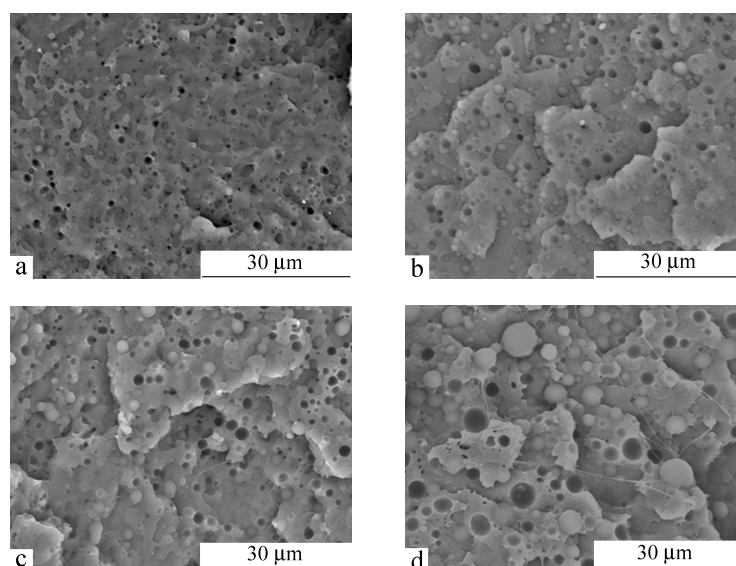


Fig. 5 Morphology of freeze-fractured surfaces of blends with (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, and (d) 20 wt% TPU (The holes on the surfaces of blends are left by the detached TPU particles.)

20 wt% TPU, respectively. If we take these averaged size to calculate the polydispersity σ of TPU in PLA matrix, we can find that the specific surface ration is 1.3, 1.4, 1.3, and 1.7 for TPU5, TPU10, TPU15 and TPU20 respectively.

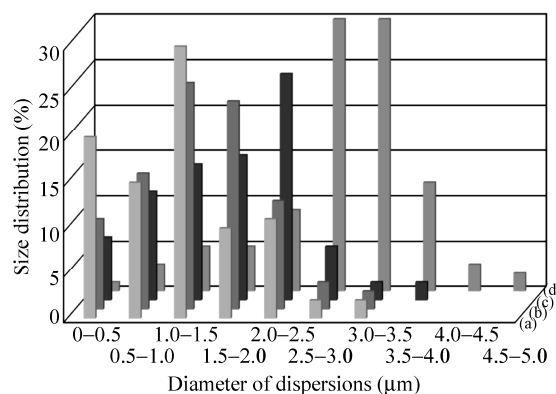


Fig. 6 Distribution of rubber droplet size in PLA/TPU blends with (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, and (d) 20 wt% TPU

Mechanical Properties

Figure 7 shows the stress-strain curves of neat PLA and PLA/TPU blends. Neat PLA fractures at 7% strain without yielding and its tensile yield strength was 70 MPa. By adding TPU, all of the blends showed distinct yielding with necking and were fractured at significantly increased elongation at break in comparison with neat PLA. Elongation at break was largely enhanced with the increasing TPU content until 15%, and then it decreased significantly. TPU15 shows the highest elongation at break of 230% among these five samples, as shown in Fig. 7.

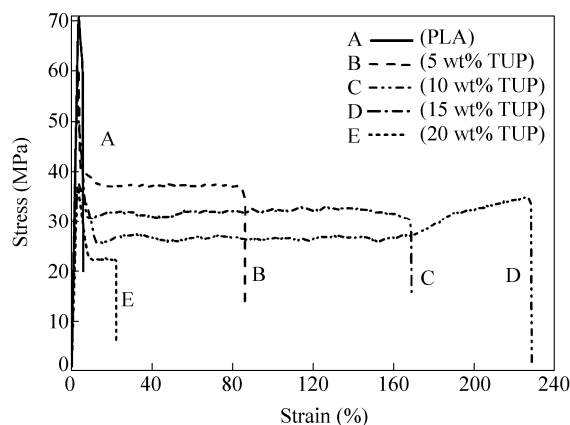


Fig. 7 Tensile stress-strain curves of the blends with different TPU contents

On the other side, the tensile strength and modulus of the PLA/TPU blends decreased after adding TPUs, as shown in Fig. 8. This was expected since TPU has a lower modulus and tensile strength than PLA. When the TPU content was 10%, it was very surprising to note that the elongation at break reached 168.9% while the yield strength of blend was up to 54.3 MPa, only decreased by 22.4% when compared to neat PLA. That is to say, the blending of PLA with proper amount of TPUs could increase the elongation at break significantly while little deterioration was found on the tensile strength and modulus. The high content of hydrogen bonding between PLA and TPU may explain such excellent mechanical behaviors.

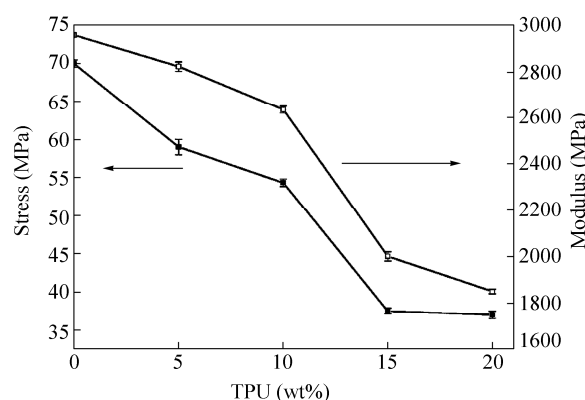


Fig. 8 Tensile strength and modulus of blends with different TPU contents

To explain the mechanism of the distinctly increased elongation caused by the addition of TPU elastomer, the tensile-fractured surfaces along the tensile direction were investigated by SEM as shown in Fig. 9. Neat PLA broke at very low elongation and the surface was flat and mirror-like. However, the blend with 15 wt% TPU content showed different behaviors under the same tensile testing, as shown in Fig. 9(b). The tensile-fractured surface of the TPU15 exhibited fibril-like morphology, which is the evidence of large scale deformation caused matrix shear yielding. These results proved that the addition of the TPU rubber led to large amount of plastic deformation with the formation of necklace. The stress-strain curves in Fig. 7 can be qualitatively explained by the stress concentration effect.

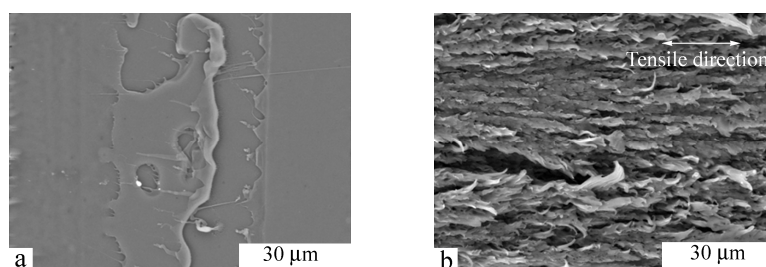


Fig. 9 Fractured surface of stretched materials: (a) PLA and (b) PLA/TPU = 85/15

The elastic TPU particles could behave as stress concentrator during the initial stretch, and with the increase of stress, the TPU particles deformed and debonded from the PLA matrix due to the insufficient interfacial adhesion. When the debonding occurred, the yield point in stress-strain curves formed at which stable plastic deformation took place. After the yielding point, obvious neck was observed and then extended in a “cold drawing” process.

The formation of bio-based TPU particles, which randomly distributed in the matrix, acted as stress concentrators and induced matrix shear yielding. Such mechanism could be identified as very important procedure for the dissipation of the breaking energy, and resulted in significant increase of the toughness of the material^[35, 36]. Similar behavior was observed by Kim and Michler^[37, 38].

The notched Izod impact strength of the pure PLA and PLA/TPU blends were also measured. The notched Izod impact strength was improved after adding the TPU as shown in Fig. 10. The increase of the TPU content could result in a gradual increase in toughness below 15 wt%, and then a decrease after that. At TPU content of 15%, the PLA/TPU blend showed the maximum impact strength of 9.5 kJ/m², a 2.5 fold increase over neat PLA (3.77 kJ/m²). Figure 11 contains SEM micrographs of the impact-fractured surfaces of neat PLA and other TPU blends. In Fig. 11, the neat PLA shows typical brittle fracture surface which was very flat. The fracture surfaces of the PLA/TPU blends exhibited some fibrils and shear damage at some level, consistent with ductile fracture.

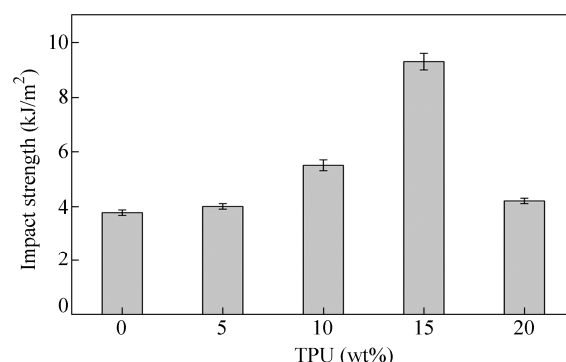


Fig. 10 The effect of TPU content on impact strength
Samples were measured for 5 times and an averaged number and error bar was then obtained.

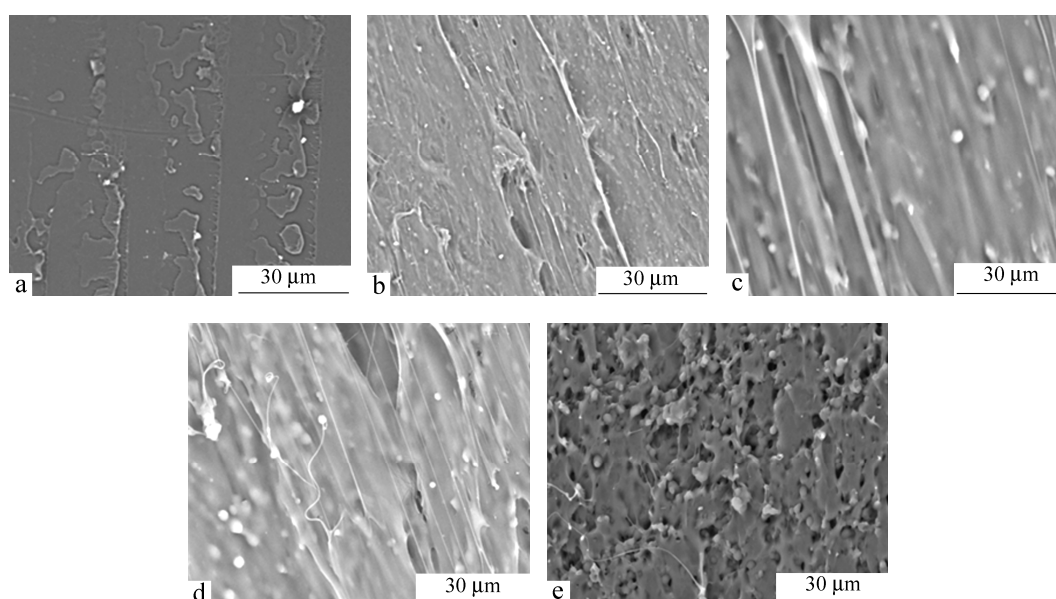


Fig. 11 Micrographs of impact-fractured surfaces of blends with different TPU contents: (a) neat PLA, (b) 5 wt% TPU, (c) 10 wt% TPU, (d) 15 wt% TPU and (e) 20 wt% TPU

The effect of the TPU particle size and concentration on the impact strength can be explained by the thickness of the matrix ligament. The matrix ligament thickness was defined as the distance between the surfaces of two neighbouring rubber particles. Wu^[39, 40] suggested that the matrix ligament thickness was the primary controlling parameter which determines whether a rubber/polymer blend will be brittle or tough. When the average ligament thickness was below a critical value, the blend would be tough; when it was greater than the critical value, it would be brittle. In other words, a sharp brittle-tough transition would occur at the critical ligament thickness.

Wu also pointed out that the critical parameter was independent of particle size and rubber volume fraction, but is dependent on the inherent properties of the matrix. The matrix ligament thickness explains the effects of particle size, rubber volume fraction, particle flocculation, phase morphology and particle-size polydispersity on toughness. The large variability in the TPU particle size among the four PLA/TPU blends allowed us to examine this theory quantitatively. To calculate the single matrix parameter, we used the following equation^[41]:

$$T = d \left[\left(\frac{\pi}{6V} \right)^{1/3} \exp(1.5 \ln^2 \sigma) - \exp(0.5 \ln^2 \sigma) \right] \quad (4)$$

where T is the critical interparticle distance between the surfaces of two neighbouring particles as defined in Fig. 12, d is the average particle diameter, V is the volume fraction of rubber, and σ is the particle size distribution parameter, which were calculated on the basis of Eqs. (2) and (3).

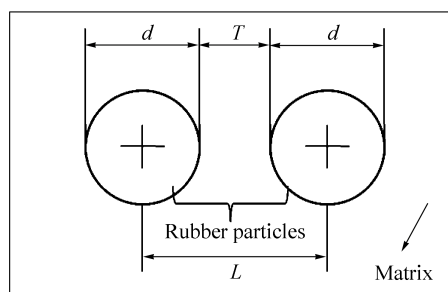


Fig. 12 Model for (surface-to-surface) interparticle distance T , (centre-to-centre) particle separation L , and rubber particle diameter d

In this study, the values of V were 0.058, 0.115, 0.171, and 0.226 for TPU5, TPU10, TPU15 and TPU20 respectively. When V were combined with the aforementioned values of d and σ , the values of matrix ligament thicknesses were obtained, which were 1.66, 1.36, 0.98, and 2.69 μm for TPU5, TPU10, TPU15 and TPU20, respectively. A critical matrix ligament thickness (1.0 μm) for PLA was reported by Anderson *et al.*^[42], and according to Wu's theory, the toughness will be continuously strengthened before the matrix ligament thickness reached the critical point. Thus we see the impact strength regularly changed with the matrix ligament thickness in Fig. 10. In this study, Wu's model for brittle-tough transition provides a very positive explanation for the toughening behavior of the PLA/TPU blends.

CONCLUSIONS

Bio-based TPU was synthesized by a two-step method and was used to toughen the polylactide (PLA). SEM pictures clearly showed a sea-island phase separated structure in PLA/TPU blends. However, both dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) manifested that PLA/TPU blend is also a partially miscible system. The plasticizing effect of TPU on PLA could be revealed by the accelerated cold crystallization and lower T_g . The PLA/TPU blends showed significantly increased elongation at break without severe loss in tensile strength and modulus. The impact strength of the blend with TPU was also significantly improved compared with neat PLA. Besides, with the addition of TPU, the SEM micrographs showed that a large scale shear yielding occurred in the PLA matrix instead of brittle break in pure PLA. The shear yielding was initiated by the stress concentrations and then TPU particles were deformed and debonded from the PLA matrix that caused the necking phenomenon. The matrix ligament thickness theory can quantitatively explain the toughening mechanism of TPU particles. Our further research will try to distinguish the effects of interrelated parameters and to investigate the biodegradability of the materials.

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