

Thermal, Morphological, Mechanical and Aging Properties of Polylactide Blends with Poly(ether urethane) Based on Chain-extension Reaction of Poly(ethylene glycol) Using Diisocyanate*

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Abstract Poly(ether urethane)s (PEU), including PEUI15 and PEUH15, were prepared through chain-extension reaction of poly(ethylene glycol) (PEG-1500) using diisocyanate as a chain extender, including isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI). These PEUs were used to toughen polylactide (PLA) by physical and reactive blending. Thermal, morphological, mechanical and aging properties of the blends were investigated in detail. These PEUs were partially compatible with PLA. The elongation at break of the reactive blends in the presence of triphenyl phosphate (TPP) for PLA with PEUH15 or PEUI15 was much higher than that of the physical blends. The aging test was carried out at $-20\text{ }^{\circ}\text{C}$ for 50 h in order to accelerate the crystallization of PEUs. The PEUs in the PLA/PEU blends produced crystallization and formed new phase separation with PLA, resulting in the declined toughness of blends. Fortunately, under the aging condition, although PEUH15 in blends could also form crystallization, the reactive blend of PLA/PEUH15/TPP(80/20/2) had higher toughness than the other blends. The elongation at break of PLA/PEUH15/TPP(80/20/2) dropped to 287% for the aging blend from 350% for the original blend. The tensile strength and modulus of PLA/PEUH15/TPP blend did not change obviously because of the crystallization of PEUH15.

Keywords: Polylactide; Poly(ethylene glycol); Poly(ether urethane); Toughness; Aging.

INTRODUCTION

Poly(lactic acid) (PLA), or polylactide, is a synthetic thermoplastic aliphatic polyester derived from renewable agricultural resources, such as starches, sugars and celluloses. PLA has wide applications in the fields of biomedical and environmentally-friendly polymer materials owing to its excellent biodegradability and biocompatibility. Over more than half a century, PLA as a new eco-friendly material has been developed into common plastics areas in the 1990s. Many performances of PLA are similar to general plastics, such as polyethylene, polypropylene and polystyrene, and thus can be widely used in the fields of electronic, automotive and environmentally-friendly packing materials^[1–4]. PLA has many good mechanical properties with a high strength and high modulus material, but compared to other general plastics, the toughness of PLA is poor, the elongation at break and impact strength are both very low. The inherent brittleness of PLA severely limits its more widespread implementation.

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PLA has good compatibility with poly(ethylene glycol) (PEG)^[5, 6]. PEGs with different molecular weights could be used as good plasticizers for PLA^[6–9]. PEGs could largely improve the flexibility of PLA and do not affect the transparency of PLA materials. Unfortunately, the PLA/PEG blends are not stable. The lower molecular weight PEG tends to slowly penetrate onto the surface of materials with time. The higher molecular weight PEGs can overcome the shortcoming of small molecules and cannot migrate onto the surface of materials, but the crystallization of PEGs with higher molecular weight in the blends could occur gradually at room temperature, thus leading to the phase separation between PEG and PLA, and finally the PLA blending materials regain the embrittlement and lose the attractive toughness^[8–11]. Our group^[12] synthesized two linear copolymers, including poly(ethylene glycol)-succinate copolymer (PES) and poly(ethylene glycol)-succinate-L-lactide copolymer (PESL). The copolymers were successfully used to improve the toughness of PLA materials. PESL is amorphous, and thus has good phase morphological stability in PLA blends. Polyurethane (PU) elastomers based on polyester and polyether have been used to toughen PLA^[13–17]. The backbone of PU includes soft and hard segments, which contribute to the performance of PU, including toughness, flexibility, biocompatibility, biological stability and compatibility with other polymeric materials and their ratios can be adjusted in a wide range. The soft segments of PU are usually composed of polyester or polyether. In our precious work, poly(L-lactide) (PLLA) was toughened with PEU based on low molecular weight poly(ethylene glycol) (PEG-400) through chain-extension reaction by isophorone diisocyanate as a chain extender^[17]. The PEU showed poor compatibility with PLLA so that the PLLA/PEU blends by physical blending gave a low elongation at break. In order to improve the compatibility between PLLA and PEU, and to improve the toughness of PLA composite, a PLLA-b-PEU block copolymer formed was necessary by reactive blending in the presence of triphenyl phosphite (TPP) which acted as a catalyst for transesterification or a chain-extender.

In the present work, to toughen PLA, stable flexible blends of PLA/PEU were prepared. The PEUs, including PEUI15 and PEUH15, were prepared through chain-extension reaction of PEG-1500 using IPDI and HDI as chain extenders. The PEUs were used to toughen PLA through physical and reactive blending. The thermal, morphological, mechanical and aging properties of PLA/PEU blends were investigated in detail.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG-1500), isophorone diisocyanate (IPDI, > 99.0%), hexamethylene diisocyanate (HDI, > 99.0%) and triphenyl phosphite (TPP, CP, 97%) were purchased from Aladdin Chemistry Co., Ltd. Polylactide (PLA) was manufactured by Zhejiang Hisun Biomaterials Co., Ltd., Taizhou, Zhejiang, China. The number-average and weight-average molecular weights (M_n and M_w) and polydispersity index ($PDI = M_w/M_n$) of PLA were evaluated by gel permeation chromatography (GPC). The M_n , M_w , PDI and D-lactate unit content ($D\%$) of PLA are $M_n = 99$ kg/mol, $M_w = 153$ kg/mol, $PDI = 1.54$, and $D\% = 10.5\%$. ADR (JONCRYL® ADR-4370-S) was bought from BASF. M_w and epoxy equivalent weight of ADR are 6800 g/mol and 285 g/mol, respectively. PEUH15 and PEUI15 were prepared in our laboratory through chain-extension reaction of PEG-1500 using IPDI and HDI as chain extenders at 60–80 °C for 16 h, and then 100 °C for 2 h. The equivalent ratio of PEG-1500 to IPDI and HDI was 100/99.5–99.9. The obtained PEUs were sealed in polyethylene-aluminum composite bags in order to prevent moisture absorption. The M_n , M_w , PDI and glass transition temperature (T_g) of PEUI15 are $M_n = 69$ kg/mol, $M_w = 116$ kg/mol, $PDI = 1.7$ and $T_g = -48.8$ °C, respectively. The M_n , M_w , PDI and T_g of PEUH15 are $M_n = 32$ kg/mol, $M_w = 65$ kg/mol, $PDI = 2.0$ and $T_g = -50.2$ °C, respectively.

Sample Preparation

Solution blending

PLA blends with PEG-1500, PEUI15 or PEUH15 at various mass ratios, 95/5, 90/10, 80/20 and 70/30, were dissolved into dichloromethane, then the sample solutions were slowly evaporated at 30–40 °C in order to obtain the blending films, and finally the films were dried under high vacuum at 70 °C for 2 h for DSC measurements.

Melt blending

PLA and PEUs were melt mixed together in a mass ratio of 80 to 20 by physical blending in the presence of ADR as a processing stabilizer and by reactive blending in the presence of TPP as a coupling agent or a catalyst for transesterification. The amount of ADR and TPP used in the blends was 0.4 parts per hundred of resin (phr) and 2.0 phr, respectively. The process of sample preparation was carried out according to literature^[12].

Aging for blends

PLA/PEU blends were treated by aging at $-20\text{ }^{\circ}\text{C}$ for 50 h in order to accelerate the crystallization of PEUs in the blends, and then the blends were used for DSC and tensile mechanical tests.

Measurements

Differential scanning calorimetry (DSC) analysis was carried out on a TA Instrument DSC-Q10 under a nitrogen atmosphere. The mass of samples was 5–10 mg in an aluminum pan.

As for PEG-1500, PEUH15 and PEUI15, (a) samples were heated to $120\text{ }^{\circ}\text{C}$ and held for 3 min to eliminate any thermal history, then annealed to $-80\text{ }^{\circ}\text{C}$ at a cooling rate of 10 K/min, and finally reheated to $120\text{ }^{\circ}\text{C}$ at a heating rate of 10 K/min. The melting temperature (T_m) and melting enthalpy (ΔH_m) for samples were obtained from the reheating scans. (b) Samples were heated to $120\text{ }^{\circ}\text{C}$ and held for 3 min to eliminate any thermal history, then quenched to $-80\text{ }^{\circ}\text{C}$, and finally reheated to $120\text{ }^{\circ}\text{C}$ at a heating rate of 10 K/min. T_g for samples was obtained from the reheating scans.

As for PLA blends with PEG-1500, PEUI15 and PEUH15, (a) samples were heated to $190\text{ }^{\circ}\text{C}$ and held for 3 min to eliminate any thermal history, then annealed to $-80\text{ }^{\circ}\text{C}$ at a cooling rate of 10 K/min, and finally reheated to $190\text{ }^{\circ}\text{C}$ at a heating rate of 10 K/min. The crystallinity of samples was obtained from the cooling and reheating scans. (b) Samples were heated to $190\text{ }^{\circ}\text{C}$ and held for 3 min to eliminate any thermal history, then quenched to $-80\text{ }^{\circ}\text{C}$, and finally reheated to $190\text{ }^{\circ}\text{C}$ at a heating rate of 10 K/min. T_g of PLA for the blends was obtained from the reheating scans.

Morphological observation and tensile mechanical tests were carried out according to standard procedure^[12].

RESULTS AND DISCUSSION

Crystallinity of PEU

The lower molecular weight PEG-1500 was incorporated into the higher molecular weight PEUs, PEUH15 and PEUI15, by chain-extension reaction using diisocyanate, IPDI and HDI, as chain extenders. The thermal properties of PEUs had many differences with PEG-1500. Figure 1 shows the DSC thermograms of PEG-1500, PEUH15 and PEUI15 for reheating at 10 K/min after cooling at 10 K/min from the molten state. The crystallization for PEUs attributed to the crystallization of PEG segments in the PEU molecules. PEG-1500 was a highly crystalline material, while the crystallinity of PEUs was greatly reduced. T_m and ΔH_m were $51.2\text{ }^{\circ}\text{C}$ and 147.9 J/g for PEG-1500. T_m was 44.7 and $33.4\text{ }^{\circ}\text{C}$ for the PEG segments in PEUH15 and PEUI15, while ΔH_m was 86.6 and 61.9 J/g for the PEG segments in PEUH15 and PEUI15, respectively. The lower melting point and crystallinity for PEUs might have a significant effect on the performance of PLA materials blending with PEUs.

Thermal Properties of PLA/PEU Blend

PLA is fully compatible with PEGs^[5, 18, 19], but the compatibility declined for PLA with the PEUs derived from PEG-1500. Figure 2 shows the relationship between T_g for PLA and the PEU content in PLA/PEU blends. The two curves were almost overlapped, thus the effect of PEUH15 and PEUI15 on T_g for PLA was coincident completely. T_g for PLA firstly decreased with increasing PEU content (0 wt%–10 wt%), and then changed little with the PEU content (10 wt%–30 wt%). As for the content of 20 wt%, PEUH15 and PEUI15 lowered T_g for PLA with values of 48.9 and 48.6 from $58.3\text{ }^{\circ}\text{C}$ for neat PLA, respectively. Therefore, PEUH15 and PEUI15 were partially compatible with PLA, and the compatibility of PEUH15 with PLA was identical to that of PEUI15.

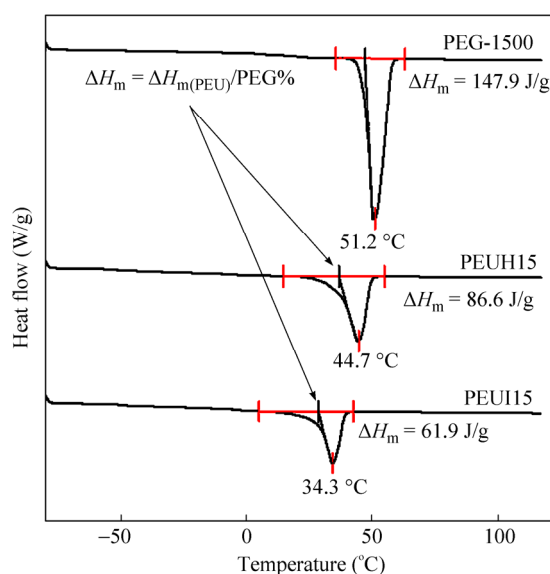


Fig. 1 DSC thermograms of PEG-1500 and PEUs for reheating at 10 K/min after cooling at 10 K/min from the molten state

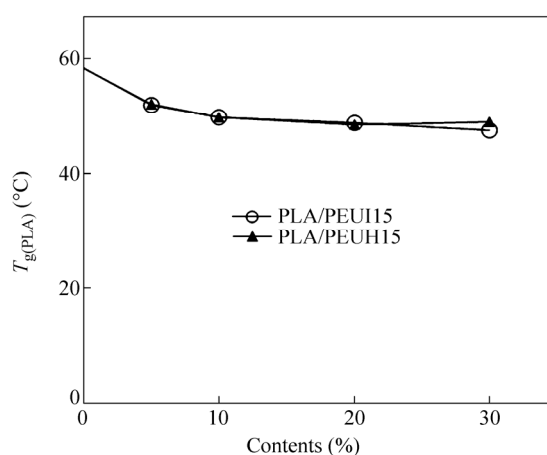


Fig. 2 Relationship between T_g for PLA and PEU contents in PLA/PEU blends

Figure 3 shows the DSC thermograms of PLA blends with PEG-1500 and PEUs through cooling from molten state and reheating. The crystallization and melting behaviors for PEG-1500 and PEUs were observed from the DSC cooling and reheating curves. When the PEG-1500 content was not more than 20 wt%, the cold crystallization and melting peak of PEG-1500 in the blends could not be observed at the cooling and reheating DSC curves. When the PEG-1500 content was 30 wt%, the cold crystallization peak of PEG-1500 did not appeared in the cooling DSC curves, but appeared in the reheating DSC curves and its melting peak was obvious. When the PEU content was 5 wt%–30 wt%, the crystallization peaks of PEUH15 and PEUI15 both appeared at the temperature between -20 and -30 °C for the cooling DSC curves, and the melting peaks of PEUH15 and PEUI15 were observed in the reheating DSC curves. These phenomena showed that the PEUs as plasticizers for PLA were more prone to crystallization, compared to PEG-1500. The crystallizations of PEUs and PEG-1500 were both derived from the PEG segments. PLA had complete compatibility with PEG-1500, thus PEG molecules could uniformly disperse in the PLA matrix. The PEG molecules were not conducive to agglomerate together and form crystal structure due to the limitation of PLA. The PEUs were obtained from

PEG-1500 by coupling reaction using diisocyanate, and the PEUs dispersed in the PLA matrix were conducive to agglomerate and form crystal structure due to their lower compatibility.

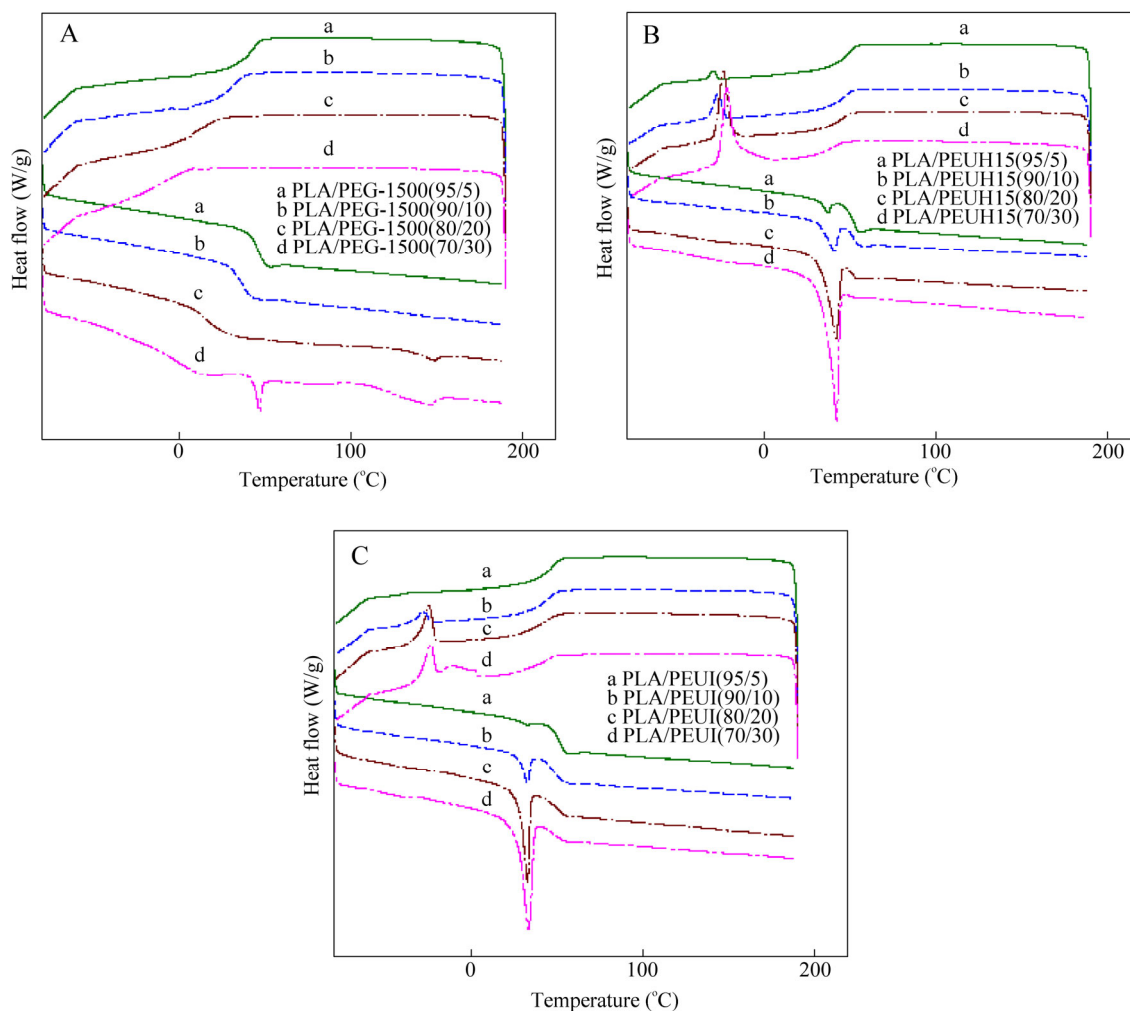


Fig. 3 DSC thermograms of PLA blends with PEG-1500 and PEUs through cooling from molten state and reheating: (A) PLA/PEG-1500, (B) PLA/PEUH15 and (C) PLA/PEUI

Phase Separation Behavior

Effect of PEU crystallization on T_g for PLA

The crystallization of a toughening agent or a plasticizer in polymer blends will directly lead to a phase separation between the toughening agent or the plasticizer and polymer matrix, thus potentially losing the toughening effect that had obtained. In this work, the PLA/PEU blends were treated by aging at low temperature of $-20\text{ }^{\circ}\text{C}$ for 50 h, in order to promote the crystallization of PEUs in the blends and to investigate the performance change of blending materials. Table 1 shows glass transition temperatures of PLA in PLA/PEU(80/20) blends for original and aging at $-20\text{ }^{\circ}\text{C}$ for 50 h. As for the original physical and reactive blends, T_g s of PLA in the blends had no significant difference, indicating that the reactive blends did little improvement in the compatibility between PLA and PEUs. Compared to the original blends, T_g s of PLA in physical and reactive blends treated through aging increased significantly. Under the aging condition, the PEU crystallization could occur, as seen in Fig. 3, leading to the new micro phase separation of PEUs dissolved into the PLA matrix. In the DSC testing process, PLA/PEU blends were heated to molten state firstly and the melting

PLA was a high viscosity fluid. The new PEUs phase formed due to the PEU crystallization could not mix rapidly with the PLA phase because of large mass transfer resistance from PEUs to PLA, so that T_g of PLA obtained increased. The phenomenon also showed that the phase separation occurred further between PEUs and PLA under the aging condition for the crystallization of PEUs.

Table 1. T_g of PLA for PLA/PEU(80/20) blends for original and aging samples

Samples	T_g for PLA ($^{\circ}\text{C}$)	
	Original	Aging
PLA/PEUI15/ADR	48.9	54.8
PLA/PEUH15/ADR	48.6	54.2
PLA/PEUI15/TPP	48.5	54.9
PLA/PEUH15/TPP	48.3	52.9

ADR: 0.4 phr or TPP: 2 phr

Effect of PEU crystallization on morphology

Figure 4 shows SEM images of cryo-fracture surfaces of PLA/PEUI15 blends. PEUI15 as a dispersion dispersed in PLA as a continuous phase, and thus formed a "sea-island" structure. In the original physical and reactive blends, the phase size of PEUI15 in the blends had no significant difference, indicating that the reactive blends marginally improved the compatibility between PLA and PEUI15. After treated by aging at the low temperature of -20°C , the phase size of PEUI15 did not change for the physical and reactive blends, but the amount of PEUI15 phase increased obviously, thus indicating the occurrence of new phase separation between PEUI15 and PLA. The new phase separation was mainly due to PEUI15 crystallization at -20°C . These results indicate that the phase separation occurred further between PLA and PEUI15 due to the crystallization of PEUI15, which was consistent with the results of DSC.

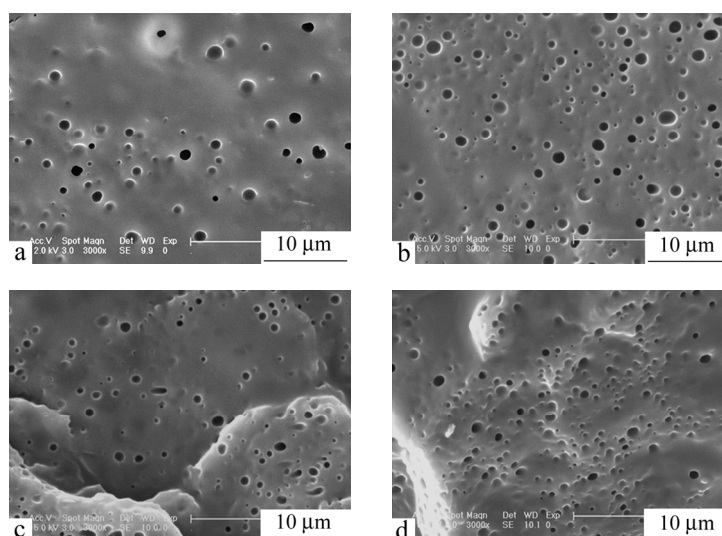


Fig. 4 SEM images of cryo-fracture surfaces of PLA/PEUI15/ADR(80/20/0.4): (a) original sample and (b) aging at -20°C for 50 h, and PLA/PEUI15/TPP(80/20/2): (c) original sample and (d) aging at -20°C for 50 h

Mechanical Properties

The main purpose of PLA blending with PEUs is to improve its flexibility, to increase the elongation at break of PLA materials, with a hope to obtain long-term stable toughening PLA composites. Figure 5 shows the elongation at break of PLA/PEU blends for original and aging at -20°C for 50 h, including physical and reactive blends. Simple physical blending could not greatly improve the toughness of PLA materials. The elongation at break was only 41.6% for PLA/PEUI15/ADR(80/20/0.4) and 48.3% for PLA/PEUH15/ADR(80/20/0.4). The reactive blending catalyzed by TPP could greatly improve the toughness of PLA materials. The elongation at

break reached 170% for PLA/PEUI15/TPP(80/20/2) and 350% for PLA/PEUI15/TPP(80/20/2). Our previous work^[17] has reported the intermolecular reactions between PLA and poly(ether urethane) (PEU) in the presence of TPP as a transesterification catalyst or a coupling agent formed a microstructure of PLA-*b*-PEU copolymer. The microstructure was identical to intramolecular plasticity. Therefore, the elongation at break of the PLA/PEU blends by reactive blending was much higher than that by physical blending. PEUH15 was better than PEUI15 in improving toughness of PLA, because the flexibility of hexamethylene in PEUH15 derived from HDI molecules is higher than that of six-membered ring with side groups in PEUI15 derived from IPDI molecules.

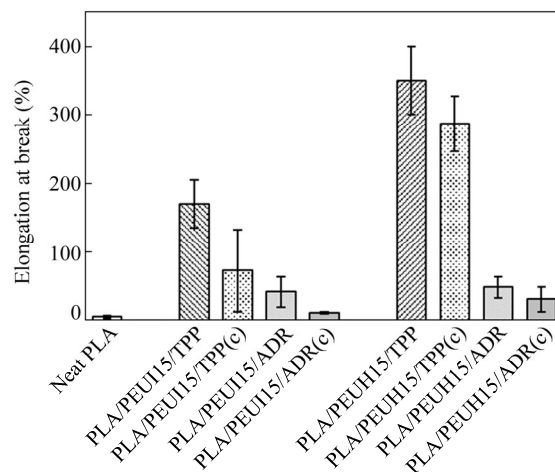


Fig. 5 Elongation at break of PLA/PEU blends for original, aging at -20°C for 50 h (PLA/PEU(80/20), ADR: 0.4 phr; TPP: 2 phr; c: for aging samples)

As already mentioned above, the crystallization of PEUs could lead to the phase separation with PLA. In order to know the effect of phase separation on the mechanical properties of PLA/PEU blends, the blends were treated by aging at low temperature of -20°C for 50 h to accelerate the crystallization of PEUs. The elongation at break of PLA/PEU blends before and after aging is shown in Fig. 5. The elongation at break of all the blends by aging at low temperature decreased to some degree. Through aging, PLA/PEUH15/TPP(80/20/2) still maintained its high toughness and its elongation at break still reached 287%, while the elongation at break decreased to 72.4% from 170% for PLA/PEUI15/TPP(80/20/2), to 30.8% from 48.3% for PLA/PEUH15/ADR(80/20/0.4), and to 22.7% from 41.6% for PLA/PEUI15/ADR(80/20/0.4). Under the aging condition, the elongation at break of the blends decreased, because the PEUs in blends formed a new micro-crystal structure, and thus intensifying the phase separation with PLA; while the elongation at break of PLA/PEUH15/TPP (80/20/2) decreased slightly, mainly due to the flexibility of hexamethylene in PEUH15 derived from HDI molecules. Therefore, the PLA composite toughened with PEUH15 through reactive blending in the presence of TPP has stable high toughness, since the elongation at break of the PLA does not decline obviously due to the crystallization of PEUH15.

Tables 2 and 3 present tensile strength and modulus of PLA/PEU blends for original and aging at -20°C for 50 h. The tensile strength and modulus for the blends of PLA/PEUI15/ADR and PLA/PEUI15/TPP increased obviously by aging at low temperature, due to the crystallization of PEUs. The tensile strength increased a little, and the modulus was unchanged obviously for PLA/PEUH15/ADR. The tensile strength and modulus were unchanged obviously for PLA/PEUH15/TPP. These results indicate that the tensile strength and modulus of PLA/PEUH15/TPP blend did not change because of the crystallization of PEUH15.

The blend of PLA/PEUH15/TPP has high toughness, consistent tensile strength and modulus even under aging conditions which lead to the crystallization of PEUH15 component.

Table 2. Tensile strength of PLA/PEU blends for original and aging at -20°C for 50 h

Samples	Tensile strength (MPa)	
	Original	Aging
Neat PLA	57.3 ± 3.7	
PLA/PEUI15/ADR	31.3 ± 2.0	44.0 ± 2.1
PLA/PEUH15/ADR	29.2 ± 0.8	32.4 ± 0.5
PLA/PEUI15/TPP	33.7 ± 1.7	38.8 ± 1.5
PLA/PEUH15/TPP	35.3 ± 2.0	34.2 ± 0.7

PLA/PEU(80/20), ADR: 0.4 phr; TPP: 2 phr

Table 3. Tensile modulus of PLA/PEU blends for original and aging at -20°C for 50 h

Samples	Tensile modulus (MPa)	
	Original	Aging
Neat PLA	1712 ± 196	–
PLA/PEUI15/ADR	1145 ± 158	1440 ± 212
PLA/PEUH15/ADR	1245 ± 139	1272 ± 132
PLA/PEUI15/TPP	1057 ± 171	1279 ± 244
PLA/PEUH15/TPP	1406 ± 102	1438 ± 141

PLA/PEU(80/20), ADR: 0.4 phr; TPP: 2 phr

CONCLUSIONS

PEUs, including PEUI15 and PEUH15, were prepared through chain-extension reaction of PEG-1500 using diisocyanate as a chain extender, including IPDI and HDI. These PEUs were used to toughen PLA by physical and reactive blending. The PEUs were partially compatible with PLA. The melting temperature and crystallinity for PEUs were much lower than those for PEG-1500. When blended with PLA, PEUs were more easily in crystallized form than PEG-1500.

The reactive blending with the PEUs catalyzed by TPP could greatly improve the toughness of PLA. The intermolecular reactions between PLA and PEU in the presence of TPP formed a microstructure of PLA-*b*-PEU copolymer, which was identical to intramolecular plasticity. Therefore, the elongation at break of the PLA/PEU blends by reactive blending was much higher than that by physical blending. The elongation at break reached up to 170% for PLA/PEUI15/TPP(80/20/2) and 350% for PLA/PEUH15/TPP(80/20/2). PEUH15 was better than PEUI15 in improving toughness of PLA, because the flexibility of hexamethylene in PEUH15 derived from HDI molecules is higher than that of six-membered ring with side groups in PEUI15 derived from IPDI molecules.

The crystallization of PEUs could lead to phase separation with PLA by aging at -20°C for 50 h, and resulting in the decrease of the elongation at break of all the blends to some extent. Fortunately, by aging, PLA/PEUH15/TPP(80/20/2) still maintained its high toughness and its elongation at break still reached 287%. Under the aging condition, the elongation at break of the blends decreased, because the PEUs in blends formed new micro-crystal and intensified the phase separation with PLA; while the elongation at break of PLA/PEUH15/TPP(80/20/2) decreased slightly, mainly due to the flexibility of hexamethylene in PEUH15. The tensile strength and modulus of PLA/PEUH15/TPP blend did not change because of the crystallization of PEUH15. Therefore, the blend of PLA/PEUH15/TPP has high toughness, consistent tensile strength and modulus even under aging conditions which lead to the crystallization of PEUH15 component.

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