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ORIGINAL PAPER

Poly(lactic acid) blends with desired end-use properties by addition of thermoplastic polyester elastomer and MDI

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Abstract The disadvantages of the poor mechanical properties of polylactic acid (PLA) limit its ability to be used in a wide number of applications. Melt blending of PLA and thermoplastic polyester elastomer (TPEE) has been performed in an effort to toughen the PLA without significant losses in modulus and ultimate tensile strength. In order to enhance the compatibility of PLA and TPEE, a diisocyanate compound was used as a reactive modifier. The thermal and mechanical properties, miscibility and phase morphologies of the blends were investigated. A blend of PLA and TPEE with a modifier does not lead to an important drop in tensile strength and modulus whereas the elongation at break is characterized by a significant increase (above 300%), compared with that of neat PLA and PLA/TPEE. The blends of PLA/TPEE/Modifier were found by thermal and fractured surface analysis to be an immiscible system with the addition of a modifier. However, the relative ductility of PLA/TPEE/Modifier is 34 times higher than that of neat PLA. The brittle fracture of neat PLA was transformed into a ductile fracture by the addition of a modifier.

Keywords Poly(lactic acid) · Thermoplastic polyester elastomer · Ductility · Toughening · Melt blending

Introduction

Poly(lactic acid) (PLA) is an attractive candidate for replacing petrochemical polymers because it is biodegradable and can be produced from annually renewable

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resources [1]. The needs for biodegradable polymers are growing every year and important demands can be expected for their many applications such as cast, blown, oriented films, and injection molded rigid products, etc. [2, 3]. In addition, PLA is suitable for its use in the household and packing fields. However, PLA has an inherent brittleness and thermal instability and the low elongation at break limits its applications [4]. There is a general interest to formulate new grades with improved flexibility, ductility, and high impact properties, while maintaining the tensile strength performances at the optimal level required by a given application. The brittleness of PLA can be modified by the copolymerization of lactides with other monomers such as ε-caprolactone [5, 6]. Because none of the aforementioned PLA copolymers are commercially available at this time, blending PLA with other polymers presents a more practical and economic method to obtain products with properties not currently attainable. Blending PLA with other polymers can substantially modify the mechanical and thermal properties, degradation rate and permeability. A large number of investigations have been performed on the blending of PLA with various polymers, for example, poly(ethylene glycol), poly(hydroxy butyrate), poly(hexamethylene succinate) [7–9]. Most of these studies are improved elongation at break and impact properties of PLA, but unfortunately, the tensile strength and thermal properties were dramatically diminished.

In this study, PLA was blended with a thermoplastic elastomer (TPE). TPEs are growing in importance as a new material which covers the boundary between rubber and plastic. Specifically, thermoplastic polyester elastomers (TPEE) among TPEs have high performance with respect to thermal and mechanical properties. TPEE is a flexible thermoplastic designed for film extrusion. In view of its high toughness, TPEE was considered good candidate for the toughening of PLA. However, blending PLA/TPEE has never studied. In order to enhance the compatibility of PLA and TPEE, diisocyanate compound was used as a reactive modifier. Diisocyanate is highly reactive with both hydroxyl and carboxyl groups and forms a urethane linkage [10].

Therefore, the objectives of this study were to produce blends of PLA and TPEE with increasing toughness while maintaining the thermal and tensile properties. The work presented here was undertaken is efforts to investigate the morphology, thermal and mechanical behavior of PLA/TPEE blends. The influence of MDI content on physical properties was also studied.

Experimental

Materials

PLA (Naturewarks PLA 4032D, $M_w = 200{,}000$ g/mol) was supplied by Naturewarks and TPEE (Samyang Corp., Korea) with a nominal I.V. 3.3 dL/g and measured carboxyl content of 33 eq./10^6g were used. Both polymers were supplied in pellet form and were used ad received. 4,4′-Methylenebis(phenylisocyanate) (MDI, Aldrich, USA) used in order to enhance adhesion between PLA and TPEE as a modifier.

Melt blends and sample preparation

Melt modification of the PLA was carried out in an intensive batch mixer (Brabender Plasticorder PL2000) on predried materials under a nitrogen blanket to minimize the possibility of hydrolytic and/or thermo-oxidative degradation. The mixing composition of the blends were 95/5, 90/10, 85/15, 80/20 and 70/30 wt/wt. Blending of PLA and TPEE was conducted at 50 rpm and 210 °C for 5 min. MDI was added to a PLA/TPEE blend in order to enhance the interfacial interactions between PLA and TPEE at same conditions. Also, the neat PLA was subjected to the same mixing treatment so as to obtain a reference material.

Films were prepared using a hot press at 210 °C, a hold pressure of 7 MPa and a hold time of 2 min. This was followed by cooling to room temperature between two thick-metal blocks kept at room temperature. A template frame was used to ensure a constant film thickness (0.5 mm) and care was taken to ensure the same thermal history of all films. The specimens were then sealed in plastic bags as they waited the processing and analysis.

Characterization

Differential scanning calorimetry (DSC) was carried out under nitrogen flow at a heating and cooling rate of 10 °C/min with TA Q100. The specimens were crimp sealed in aluminum crucibles. All specimens were heated to 240 °C at 20 °C/min and kept isothermal for 2 min to erase previous thermal history. Then they were cooled to −20 °C at 10 °C/min and subsequently scanned between −20 °C and 240 °C.

Tensile testing was performed on a screw-driven universal testing machine (Instron 4466) equipped with a 10 kN electronic load cell and mechanical grips. The tests were conducted at a crosshead speed of 30 mm/min and data was acquired by a computer. All tests were carried out according to the ASTM standards, and five replicates were tested for each sample to get an average value.

The morphology of the blends was observed by field emission scanning electron microscopy (FE-SEM), using a Hitachi S-4100 at an accelerating voltage of 10 kV. All of the samples were fractured after immersion in liquid nitrogen for about 5 min. The different zones of the specimens after tensile tests were also observed using the same SEM apparatus.

Results and discussion

PLA/TPEE blends

Thermal properties

The thermal properties of PLA and PLA/TPEE blends were investigated by DSC. The second heating curves for melt-quenched samples were chosen in order to remove previous thermal history and to make T_g more clear and obvious. The results are summarized at Table 1 and thermograms are shown in Fig. 1.

Table 1 Thermal properties of PLA/TPEE blends

Contents (PLA/TPEE)	T_g (°C)	T_c (°C)	ΔH_c^a (PLA) (J/g)	T_m (°C)	ΔH_m^b (PLA) (J/g)	X_c (PLA) (%)
100/0	59.7	131.5	0.8	154.0	1.6	1.7
95/5	59.6	125.0	19.6	151.9	20.9	23.5
90/10	60.0	129.5	11.0	152.9	12.3	14.6
85/15	59.9	130.4	14.4	153.1	16.4	18.4
80/20	59.7	130.0	17.4	153.2	19.0.	21.3
70/30	60.2	127.4	20.6	152.6	21.6	33.0

[a] Normalized heat of crystallization for PLA contents

[b] Normalized heat of fusion for PLA contents

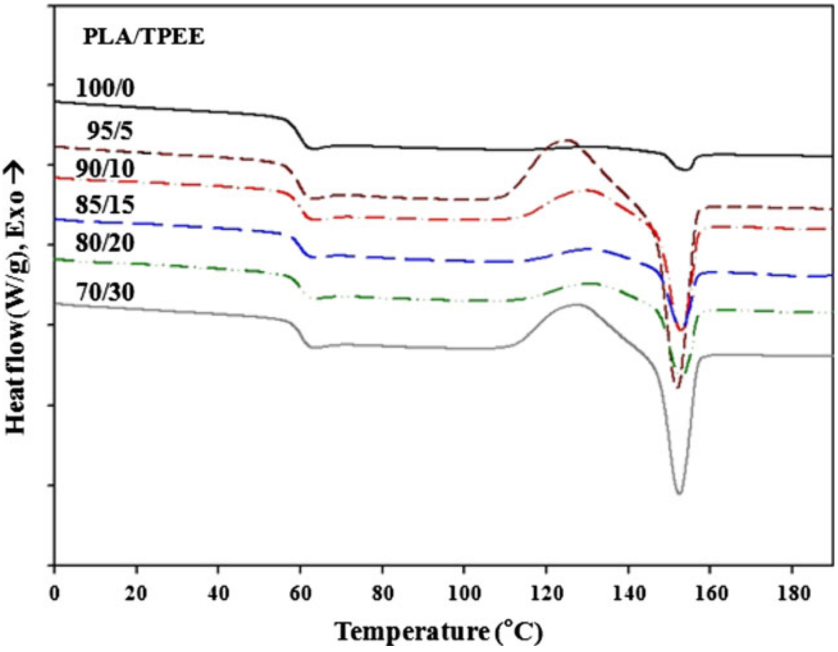

Fig. 1 DSC thermograms of PLA/TPEE blends

There are glass transition platforms at 60 °C corresponding to the T_g of PLA component on all blends. (DSC thermograms are not presented for the T_g of TPEE component at −30 °C.) The T_g of blends did not change with the TPEE contents added to the blends. This trend suggests that the PLA and TPEE are not thermodynamically compatible. The addition of TPEE to the PLA matrix resulted in weaker and wider crystallization peaks (about 130 °C), which were presented at a slightly lower temperature. Moreover, the T_ms of the blends were the same with the T_m of neat PLA. This is an indication that the addition of TPEE into PLA has no effect on the T_m of the PLA. The heat of fusion of blends increased with increasing TPEE contents. Therefore, the thermal properties of PLA are slightly affected by the addition of TPEE.

Mechanical properties and morphologies

The tensile properties of PLA/TPEE blends are shown in Table 2 and the stress–strain curves are presented in Fig. 2.

The tensile strength and modulus of PLA/aliphatic polyester blends closely follow the rule of mixtures over the whole of the composition range [11].

The tensile strength and modulus of the blends slightly decreased with the addition of TPEE, but the elongation at break increased with increasing amounts of TPEE. Neat PLA is very rigid and brittle. The tensile strength is 52 MPa, whereas the elongation at break is only about 2.0%. The tensile strength and modulus did not change when the TPEE contents were less than 5% but decreased with TPEE contents above 5%.

Neat PLA and PLA/TPEE (95/5 and 90/10) blends showed a distinct yield point with subsequent failure immediately upon introducing the introduction of the tensile load. In contrast, PLA/TPEE (70/30) blends showed clear yielding behavior upon stretching. After yielding occurred, the strain developed continuously, the samples finally broke at a significantly increased elongation, compared with that for the neat PLA. The blend with 30% TPEE had a very high elongation at break of 245%, while the tensile strength remained as high as 29 MPa.

To investigate the mechanism of the markedly increased elongation caused by the addition of TPEE (30 wt%), the morphology of fractured surfaces and necking regions of the tensile tested specimens were investigated using an SEM and the micrographs are shown in Fig. 3.

The fractured surface of neat PLA was very smooth. However, with the addition of TPEE into PLA, two phases can clearly be observed in the fractured surfaces. All of the blends show a clear, phase-separated morphology with TPEE dispersed in the PLA matrix. These phase-separated structures of the blends are in agreement with the constant T_g obtained for DSC measurements.

Neat PLA which had no necking in the tensile test showed a smooth longitudinal fracture surface without visible plastic deformation. Gaps between a PLA matrix and TPEE particles were visible. These findings indicated that the interaction between

Table 2 Mechanical properties of PLA/TPEE blends

TPEE contents (wt%)	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
None	1020	52 ± 2	2
5	1120	41 ± 2	15 ± 3
10	880	40 ± 2	35 ± 5
15	890	39 ± 2	65 ± 10
20	850	32 ± 2	80 ± 10
30	840	29 ± 2	245 ± 50

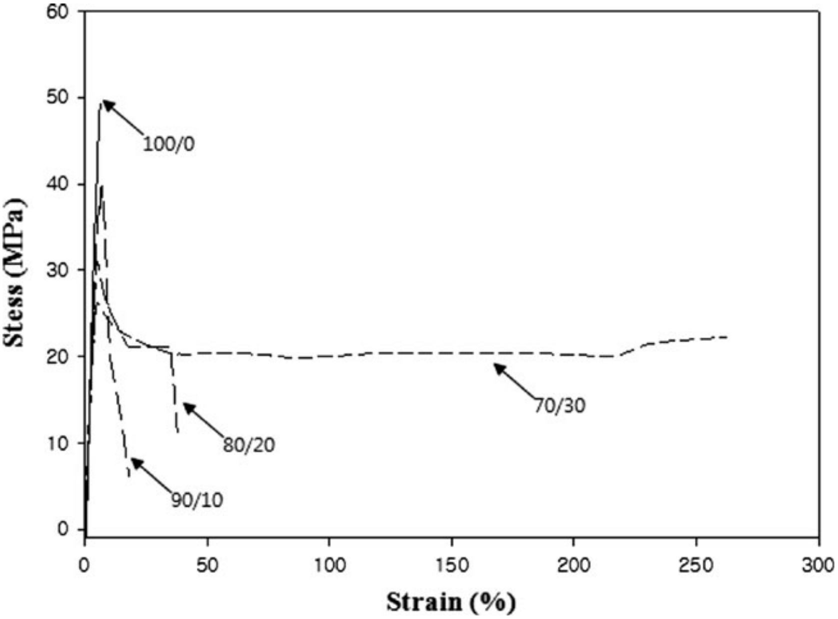

Fig. 2 Stress–strain curves of PLA/TPEE blends

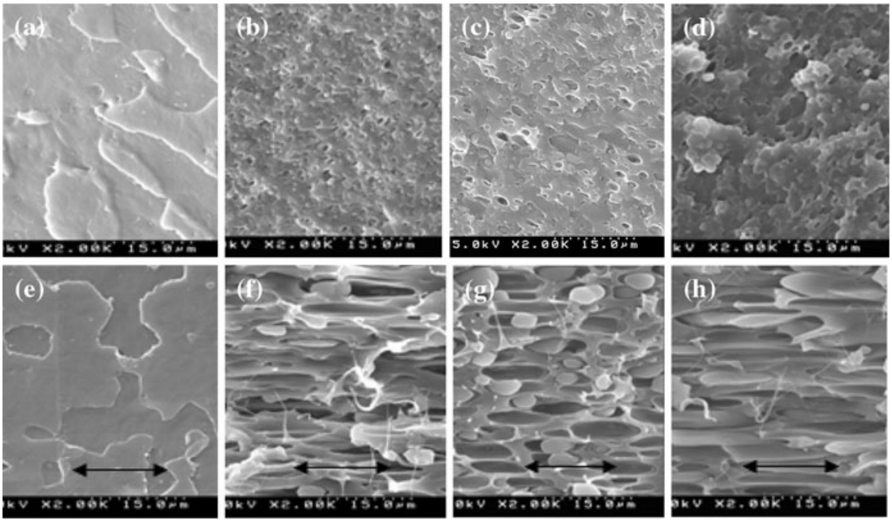

Fig. 3 SEM micrographs of fractured surfaces of PLA/TPEE blends before and after tensile tested specimens. Before stretching: **a** Neat PLA, **b** 90/10, **c** 80/20, and **d** 70/30. After stretching: **e** Neat PLA, **f** 90/10, **g** 80/20, and **h** 70/30

PLA and TPEE was quite weak, resulting in less interfacial adhesion. These features suggested that these polymer blends behaved like typical incompatible blends. PLA/TPEE (70/30) had the highest elongation at break, and its matrix experienced tremendous plastic deformation in the stress direction (Fig. 3h). For 90/10 and 80/20 PLA/TPEE samples whose elongations were lower than 100%, their SEM micrographs (Fig. 3f, g) evidently suggest a toughening mechanism was present. Debonding of the round TPEE particles from the PLA matrix under tensile stress was clearly observed. The oval cavities and enclosure round the TPEE particles were visible. These oval cavities were formed during tension when the stress was higher than the bonding strength at the interface between the PLA matrix and TPEE inclusions. These cavities were enlarged in the direction of the stress along with the deformation of the matrix. Because there was not sufficient interfacial adhesion between the TPEE and PLA, instead of cavitation within the TPEE core under the triaxial stress, interfacial debonding took place. The voids caused by the debonding altered the stressed state in the PLA matrix surrounding the voids. A triaxial tension was locally released and shear yielding was allowed.

PLA/TPEE blends with MDI

PLA/TPEE blends show poor interfacial adhesion between the PLA matrix and TPEE particles as described previously. 4,4′-Methylenebis(phenylisocyanate) (MDI) is highly reactive with both hydroxyl and carboxyl groups and forms a urethane and amide linkage, respectively [10]. Ke et al. [12] found that triethyl citrate was added as a plasticizer to a blend of PLA and starch in the presence of MDI. The tensile strength of the blend with MDI was much greater than the tensile strength without MDI.

In this study, MDI was added to a PLA/TPEE (80/20) system in order to enhance the interfacial interactions between PLA and TPEE.

Thermal properties

The thermal properties of PLA/TPEE (80/20) blends with MDI were investigated by DSC. The results for the transition temperatures of the blends with various MDI contents are summarized in Table 3 and the thermograms are shown in Fig. 4.

The second heating scan results were used so that any effects from their heating history would be avoided. All the transition temperatures of the blends, including the T_g, cold crystallization temperatures (T_c) and T_m were almost as constant as the

Table 3 Thermal properties of PLA/TPEE (80/20) blends with MDI

MDI contents (wt%)	T_g (°C)	T_c (°C)	ΔH_c^a (PLA) (J/g)	T_m (°C)	ΔH_m^b (PLA) (J/g)	X_c (PLA) (%)
0	59.7	130.0	7.4	153.2	9.0	12.0
1	60.6	130.4	7.6	152.9	8.5	11.5
3	59.3	130.8	5.6	152.5	6.9	9.5
5	57.5	129.3	4.4	151.7	6.0	8.4

[a] Normalized heat of crystallization for PLA contents

[b] Normalized heat of fusion for PLA contents

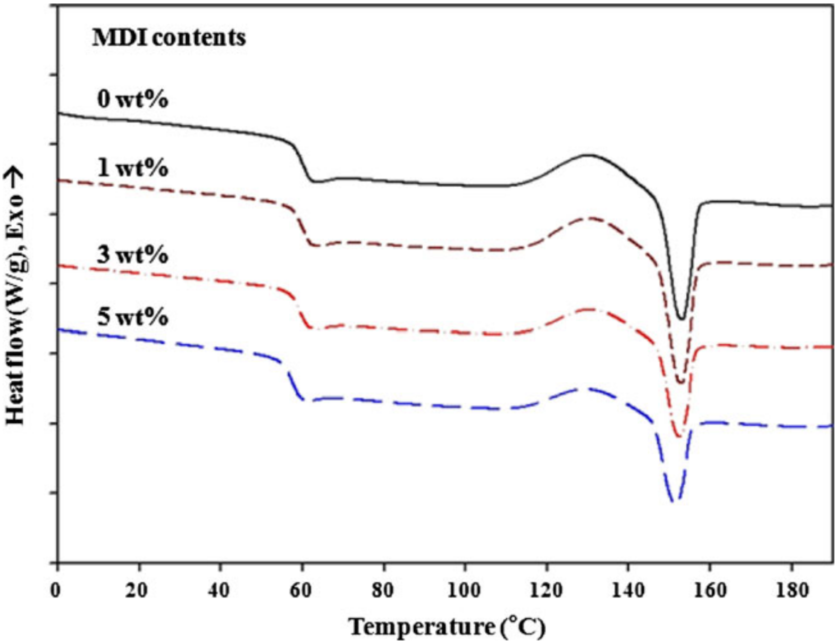

Fig. 4 DSC thermograms of PLA/TPEE (80/20) blends with MDI

MDI contents. Although the incorporation of MDI was achieved, PLA/TPEE blends with MDI are not thermodynamic compatible. The addition of MDI to the PLA/TPEE blends resulted in a weaker and wider melting peak (about 153 °C). Moreover, the heat of fusion of the blends decreased with increasing amounts MDI. This phenomenon suggests that a coupling reaction between the PLA and TPEE occurred with the addition with MDI. Therefore, the degree of crystallinity of the PLA decreased. The coupling reaction was confirmed by FT-IR. The disappearance of the characteristic peaks of –NCO groups at 2280 cm^{-1} was obvious and the amide bond formed by the reaction between –COOH and –NCO groups was observed in the region between 1705 and 1650 cm^{-1} [13].

Mechanical properties and morphologies

The tensile properties of PLA/TPEE (80/20) blends with MDI are shown in Table 4 and the stress–strain curves are presented in Fig. 5.

PLA/TPEE (80/20) blends showed a clear yielding with subsequent failure immediately introducing the introduction of the tensile load. In contrast, PLA/TPEE/MDI blends show clear yielding behavior upon stretching. After yielding occurred, the strain developed continuously. The samples finally broke at a significantly increased elongation, compared with that the compounds without MDI.

The tensile strength, modulus, and elongation at break slightly increased with increasing amounts of MDI. All the blends showed distinct yielding and stable neck growth through cold drawing. Surprisingly, it was noticed that with even 1%

Table 4 Mechanical properties of PLA/TPEE (80/20) blends with MDI

MDI contents (wt%)	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Neat PLA	1020	52 ± 2	2
0	850	32 ± 3	80 ± 10
1	850	34 ± 2	210 ± 50
3	830	38 ± 2	280 ± 50
5	890	36 ± 2	340 ± 50

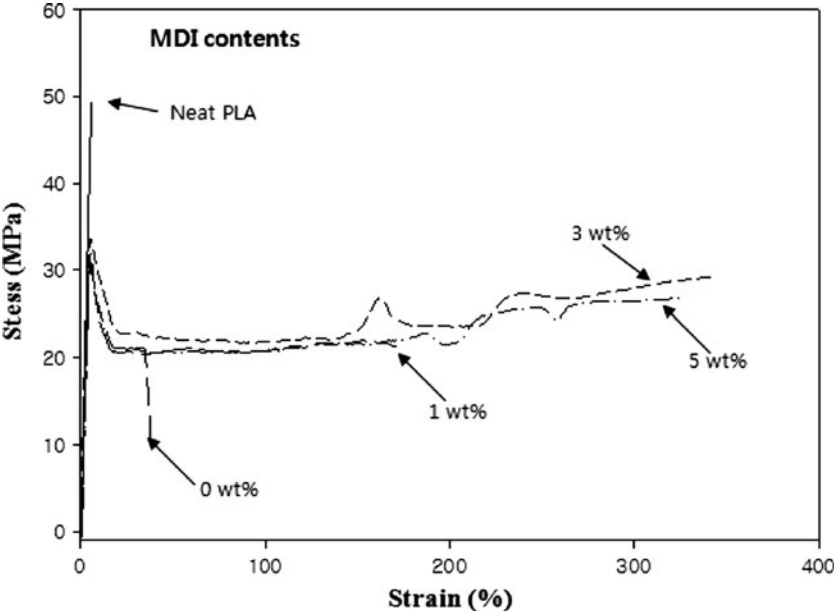

Fig. 5 Stress–strain curves of PLA/TPEE (80/20) blends with MDI

addition of MDI the elongation of the blend was tremendously increased (>200%), and the elongation continuously increased with increasing amounts of MDI. The blend with 5% MDI had a very high elongation at break (above 300%) without a diminishment of modulus and tensile strength.

To investigate the behavior of the markedly increased elongation without a decrease in the tensile strength and modulus caused by the addition of MDI, the morphology of the fractured surfaces and necking regions of the tensile tested specimens were investigated using SEM and the micrographs are shown in Fig. 6.

All the fractured surfaces showed a clear phase-separated morphologies with the TPEE dispersed in the PLA matrix. The addition of MDI into PLA/TPEE can clearly be observed in two phases; however, the particle size of the TPEE decreased with increasing amounts of MDI. These phase-separated structures are in agreement with the constant T_g and the PLA and TPEE blends are an immiscible system with the addition of MDI as a modifier. With a PLA/TPEE blend, its elongation is lower

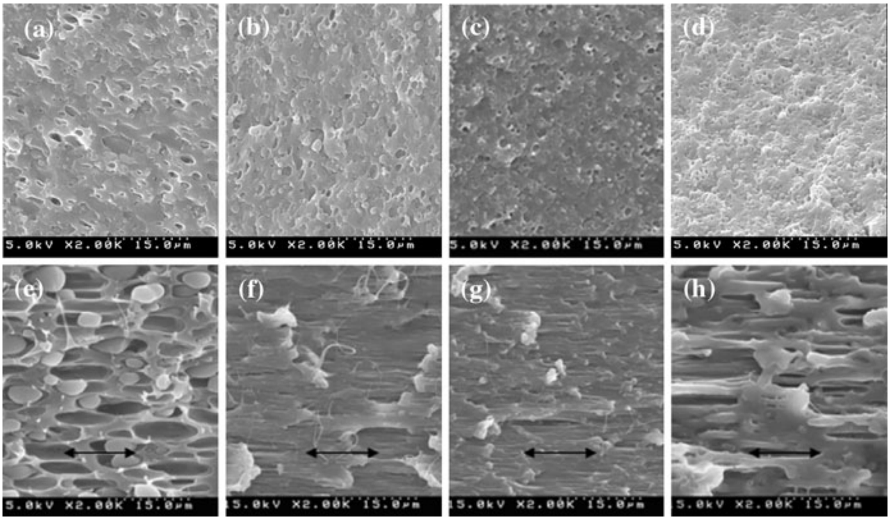

Fig. 6 SEM micrographs of fractured surfaces of PLA/TPEE (80/20) blends with MDI before and after tensile tested specimens. Before stretching: MDI contents **a** 0 wt%, **b** 1 wt%, **c** 3 wt%, and **d** 5 wt%. After stretching: MDI contents **e** 0 wt%, **f** 1 wt%, **g** 3 wt%, and **h** 5 wt%

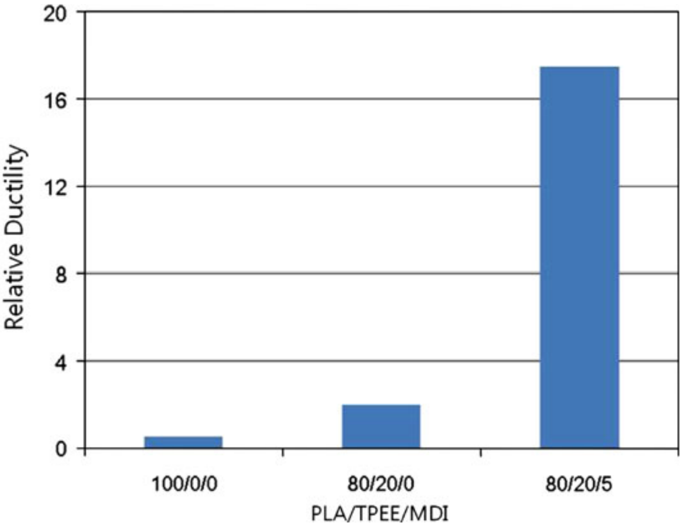

Fig. 7 Relative ductility of PLA, PLA/TPEE, and PLA/TPEE/MDI blends

than 100% and, the results from the SEM micrograph (Fig. 6e) evidently suggest that this structure is a debonding mechanism. The cavities were formed during tension when the stress was higher than the bonding strength at the interface between the PLA matrix and TPEE particles. However, the matrix experienced tremendous plastic deformation in the stress direction of PLA/TPEE/MDI blends.

Since TPEE has different elastic properties compared to the PLA matrix, its particles served as stress concentrators under tensile stress. The oval cavities could not be observed in PLA/TPEE/MDI blends, because the interfacial adhesion between PLA and TPEE increased by the coupling reaction with MDI [14, 15].

As summarized in Figs. 5 and 6, the addition of a modifier (MDI) leads to an increase in the elongation at break. The blend of PLA and TPEE achieved high ductile PLA without significant tensile properties losses by the coupling reaction with MDI.

The relative ductility was calculated from stress–strain curves and the values are shown in Fig. 7.

The relative ductility of PLA/TPEE/MDI is 34 times and 7 times higher than that of neat PLA and PLA/TPEE blend, respectively. Because the modulus, tensile strength, and elongation at break of PLA/TPEE/MDI were higher than those of PLA/TPEE blend, and the interfacial adhesion between the PLA and TPEE was enhanced by the coupling reaction with MDI.

Conclusion

To reduce the brittle behaviors of PLA and to improve its ductility, thermoplastic polyester elastomer (TPEE) has been mixed into a PLA matrix with a modifier. The effects of the modifier content on the PLA thermal, mechanical properties were evaluated. Melt blending of PLA and TPEE with MDI does not lead to an important drop in tensile strength and modulus. Whereas the elongation at break is characterized by a significant increase (340%) when compared with neat PLA and PLA/TPEE blend. The elongation at break and tensile properties of PLA/TPEE/MDI blends increased with increasing amounts of MDI. PLA/TPEE/MDI blends are an immiscible system with a two-phase morphology and the addition of MDI decreases PLA crystallinity. The relative ductility of PLA/TPEE blend with MDI is 34 times higher than that of neat PLA, because the elongation at break dramatically increased whereas the modulus and tensile strength were almost constant. The stress–strain curves showed that the blends changed from brittle to ductile failures with the addition of TPEE and MDI. The fractured surfaces and tensile tested fractured surfaces revealed that the debonding initiated shear yielding mechanism was involved in the toughening of the blend. The interfacial adhesion between the PLA and TPEE increased with the addition of MDI as a modifier.

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