

PLA/Chain-Extended PEG Blends with Improved Ductility

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ABSTRACT: Melt blending of polylactic acid (PLA) and a chain-extended polyethylene glycol (CE-PEG) have been performed in an effort to toughen the PLA without significant loss of modulus and ultimate tensile strength. The chain-extended PEG was prepared with melt condensation of a low molecular weight PEG and 4,4'-methylenebis(phenylisocyanate) (MDI) for enhancement of the molecular weight of PEG. The thermal and mechanical properties, miscibility and phase morphologies of blends were investigated. By using thermal and fracture surface analysis, the blends were found to be a partially miscible system with shifted glass transition temperatures. The addition of CE-

PEG leads to slight decrease in tensile strength and modulus, while the elongation at break is characterized by an important increase (540%), compared with neat PLA and PLA/PEG (low molecular weight PEG, $M_n = 35,000$). The relative ductility of PLA/CE-PEG is 40 times higher than that of neat PLA. The brittle fracture of neat PLA was transformed into a ductile fracture by the addition of CE-PEG. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2360–2367, 2012

Key words: polylactic acid; chain-extended polyethylene glycol; ductility; melt blending

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable thermo-plastic polyester that has been extensively investigated due to its biocompatibility and also because its mechanical properties outperform those of both polyethylene and polystyrene.¹

PLA has recently been considered as an alternative in the placing of petroleum plastics and renewable materials for disposable applications is becoming popular. PLA is characterized by its excellent optical properties and high tensile strength, however it is very rigid and brittle, through its rigidity and low ductility limit its utilization. There is a general interest to formulate new grades of PLA with improved flexibility, ductility, and higher elongation properties, while retaining tensile strength performances at the optimal level required for a given application. A large number of investigations have been made to improve PLA properties via plasticization, copolymerization, and blending with elastomers.^{2–7}

Many researchers have been performed on the blending PLA with various polymers and low molecular weight compounds have been used as plasticizers for PLA.^{8–12} However, it was observed that after aging the plasticized materials, the plasticizers had a tendency to migrate to the surface. Although a higher

molecular weight plasticizer would decrease migration, increasing the molecular weight too much would eventually decrease the solubility cause phase separation as well as formation of a two-phase system.^{13,14}

The plasticizer should not be prone to migration as this would cause contamination of the materials in contact with the plasticized PLA. It would also cause the blended materials to regain the brittleness of pure PLA.¹⁵

PEG have been known for quite some time as efficient plasticizers for PLA as they have good miscibility with PLA; even with a molecular weight of $M_n = 20,000$. Blending PLA with PEG can drastically lower the T_g of PLA and create homogeneous and flexible materials. However, the promising mechanical properties of PLA/PEG blends disappeared with time because of their slowly phase separation and the crystallization of PEG at the room temperature.¹⁶

In this study, investigation was made on the influence of the molecular weight of PEG on the physical properties of PLA. The chain-extended PEG (CE-PEG) was prepared by treating PEG with 4,4'-methylenebis(phenylisocyanate) (MDI). The molecular weight of PEG could be enhanced by creating a reaction on PEG with MDI as a direct chain extender. It is quite reasonable to expect that the coupling of PEG with chain extending reagents may cause either increased molecular weight and strength or improved flexibility in comparison to unreacted low molecular weight PEG.

The properties of PLA/CE-PEG blends were characterized through tensile testing, thermal analysis,

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and microscopy. The efficiency of the toughening materials as well as the compatibility of the PLA/CE-PEG blends was discussed.

EXPERIMENTAL

Materials

PLA (PLA 4032D, $M_w = 200,000$ g/mol) was supplied by Naturewarks and PEG ($M_n = 35,000$, Aldrich) was used as received. 4,4'-Methylenebis(phenylisocyanate) (MDI, Aldrich) was used for the enhancement of molecular weight of PEG as a chain extender.

Melt blends and sample preparation

Blending was carried out in a corotating twin-screw mixer (Brabender Plasticoder, 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. Before blending, the melt reaction of PEG and MDI was conducted on the same apparatus at 50 rpm and 120°C for 2 min. In addition, 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 180°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 (1 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 200°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 and 200°C.

The melt flow index was measured by using the melt indexer (Daveport) at 190°C for 5 min at a constant load (2.16 kg). Tensile testing was performed on a universal testing machine (UTM, Instron 4466) equipped with a 10 kN 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 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

Preparation of chain-extended PEG

A large number of investigations have been performed on the blending of PLA with low molecular weight PEG so as to produce plasticizers for PLA.² However, it was observed that after the aging of the plasticized materials, the plasticizers had a tendency to migrate to the surface.

To overcome the above problems, PLA was blended with a high molecular weight PEG to enhance the ductility of PLA. The low molecular weight PEG ($M_n = 35,000$) was melt reacted with various contents of MDI in preparation for the high molecular weight of PEG.

The introduction of hydroxyl groups in the PEG provides chain extension sites with diisocyanate. The melt reaction of PEG with MDI is an especially attractive method for the preparation for the high molecular weight of PEG. Hydroxyl groups and isocyanate groups can react under mild conditions, and as such, the reaction leads directly to the formation of urethane bonds, which are thermally and hydrolytically stable.¹⁷

To confirm the formation of high molecular weight PEG containing urethane bonds by melt reaction, its FT-IR measurement was studied. The disappearance of the characteristic peaks of -NCO groups at 2280 cm^{-1} was obvious and the urethane bond formed by the reaction between -OH and -NCO groups were observed in the region between 1880 and 1440 cm^{-1} .¹⁷

The intrinsic viscosity of chain-extended PEG(CE-PEG) could not be measured due to the fact that CE-PEG obtained with a high amount of MDI, could not dissolve the common organic solvents. So, the molecular weight of the CE-PEG was determined by melt index (M.I.). Results show that the M.I. dramatically decreased as the MDI content increase, reaches a bottom at MDI content of 3.5 phr and remains constant thereafter, as shown in Figure 1. However, the M.I. of CE-PEG could not be measured in the presence of a low content of MDI, because the molecular weight was too low. This might indicate that most of the hydroxyl groups in the PEG were consumed in the urethane formation reaction.

The reaction of the low molecular weight PEG and MDI led to chain extension. The rheological properties of the CE-PEG were investigated to confirm that phenomenon. The complex viscosity (η^*) of

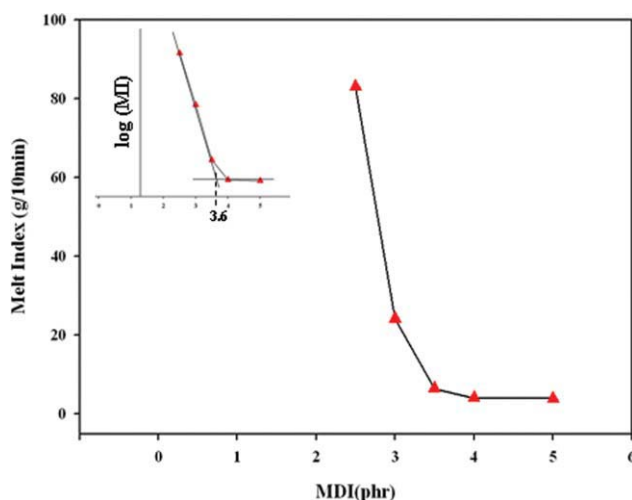


Figure 1 Melt Index of the chain-extended PEGs. (Measurement condition: 190°C, 5 min; Insertion: plot by log transform of MI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the CE-PEG was analyzed by rheometric mechanical spectrometer using frequency sweeps within the range 1 – 100 rad/s. The effect of MDI contents on η^* of the CE-PEG and unreacted PEG was examined and the results are shown in Figure 2.

The unreacted PEG and CE-PEG-1 showed very low complex viscosity in the experimental range, around 20 and 50 Pa s at 1 rad/s, respectively. The Newtonian plateau could be observed in the investigated frequency range. Increasing MDI content led to a continuous rise of complex viscosity and to an accentuation of the shear-thinning behaviors. The rheological curves obtained with 5.0 wt % MDI show the highest complex viscosity at low shear rates and high shear sensitivity as a result of increment of molecular weight and chain entanglement. The chain-extended PEG exhibited enhanced shear thinning behaviors at a lower shear rate region. That is in agreement with the long-time-relaxation mechanism, such as entanglement couplings between the high molecular weight and long chain branches.

The thermal properties of CE-PEG were shown in Table I. The T_m slightly decreased with the increasing of MDI content. However, the heat of fusion and crystallinity dramatically decreased. A decrease in crystallinity of PEG also indicates that most of the hydroxyl groups in the PEG reacted with the isocyanate. It is considered that the formation of urethane linkage hampered the growth of PEG crystals.

PLA/PEG blends

Thermal properties

The blends of PLA and a low molecular weight PEG ($M_n = 35,000$) were prepared using a corotating

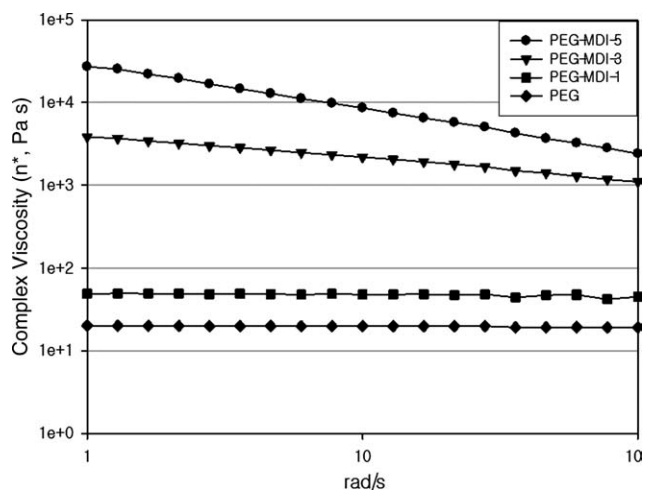


Figure 2 Effect of MDI contents on η^* of CE-PEG and unreacted PEG.

mixer for comparison with the chain-extended PEG. The thermal, mechanical properties and morphology of the PLA/PEG blends were investigated.

The glass transition temperature is an excellent indicator of polymer structure and chain mobility. The plasticizing efficiency was evaluated by the decrease in T_g as a function of plasticizer concentration.¹⁹

Thermal properties of PLA/PEG blends are shown in Table II and DSC thermograms are shown in Figure 3. The pure PLA shows a clear glass transition at 59.7°C and a very small melting endotherm at 154.0°C, corresponding to residual crystallinity. Compared to pure PLA, which solely shows a sharp T_g , the addition of PEG to the PLA induces crystallization (T_c) and thus fusion (T_m). This behavior is typical of plasticized thermoplastics, where plasticizers may promote crystallinity due to enhanced chain mobility. The T_c of PLA/PEG blends slightly decreased with increasing PEG content, however, the melting temperature was almost constant. Interestingly, most melting endotherms show two distinct peaks. This is true barring the exception of the PLA/PEG(70/30) blend, as shown in Figure 3.

This behavior, as a result of lamella rearrangement during the crystallization of PLA, demonstrates a

TABLE I
Thermal Properties of the CE-PEGs and PEG

Sample Name	MDI Contents (phr)	T_m (°C)	ΔH_m (J/g)	X_c^a (%)
PEG ^b	None	66.2	182.9	92.8
CE-PEG-1	1	63.5	164.8	82.8
CE-PEG-3	3	62.9	144.8	71.4
CE-PEG-5	5	62.0	121.9	58.9

^a Crystallinity, $X_c = \Delta H_m / \Delta H_m^\circ \times 100$, ΔH_m° of PEG = 197 J/g¹⁸.

^b Unreacted PEG : $M_n = 35,000$.

TABLE II
Thermal Properties of the PLA/PEG Blends

Contents (PLA/PEG)	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m^a (J/g)	X_c (%)
100/0	59.7	131.5	154.0	1.6	1.7
95/5	52.6	115.9	154.2	28.6	32.2
90/10	43.2	99.0	154.3	29.7	35.3
85/15	35.0	95.6	154.4	30.6	38.5
80/20	26.7	86.9	154.3	30.5	40.7
70/30	7.9	84.4	154.9	34.0	51.9

^a Normalized heat of fusion for PLA contents.

shoulder or low-temperature peak formed on the melting endotherm of the original crystallites. In the meantime, the degree of crystallinity was seen to increase.^{1,20,21}

The T_c was seen to decrease with increasing PEG content, which is consistent with the fact that PLA crystallizes more at ease at lower temperatures due to enhanced chain mobility as the plasticizer level increases. As far as T_g is concerned, and as is observed in Table II, the addition of 5, 10, 20, or 30 wt % PEG leads to PLA compositions characterized by only one T_g , the value of which is significantly decreased by comparison to the neat PLA matrix ($T_g = 59.7^\circ\text{C}$). It should be noted that the decrease in T_g is closely related to plasticizer efficiency. The T_g value of PLA is dependent on the blend composition, indicating that this blend is quite miscible.

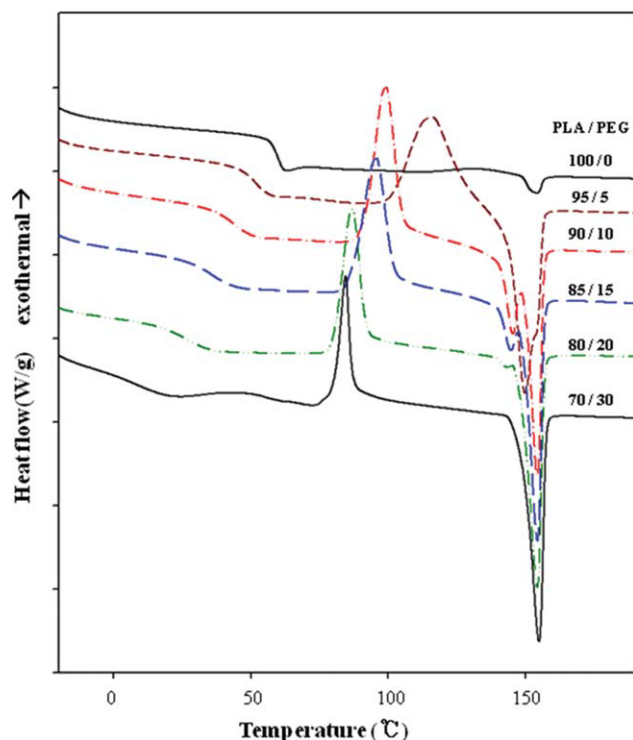


Figure 3 DSC thermograms of neat PLA and PLA/PEG blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical properties and morphologies

The major function of a plasticizer is to improve the elongation at break and increase the toughness of a polymeric material. The tradeoffs include reduced tensile strength and modulus.²²

The tensile strength, modulus, and elongation at break of PLA/PEG blends, as well as those of pure components, are shown in Table III and the stress-strain curves of PLA/PEG blends are given in Figure 4.

As expected, the addition of PEG significantly changed the tensile behavior of the PLA, as is shown in Figure 4. The brittle fracture of the neat PLA transformed into the ductile fracture of the PLA/PEG blends, after they were subjected to tensile testing. 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 decreased slowly at PEG contents of <10% but decreased dramatically at PEG contents above 10%. The blend with 30% PEG had a very high elongation at break of 405%, while the tensile strength had 13 MPa.

To investigate the mechanism of the markedly increased elongation caused by the addition of PEG, the morphology of fractured surface and necking region of the tensile tested specimen was investigated using a SEM and the micrographs are shown in Figure 5.

The fractured surfaces of neat PLA and PLA/PEG blends were very smooth. The addition of PEG into PLA leads to compositions in which the plasticizer tends to be rather homogeneously dispersed without phase separation.

Neat PLA, which had no necking in the tensile test showed a smooth longitudinal fracture surface without visible plastic deformation. The fracture surface

TABLE III
Mechanical Properties of PLA/PEG Blends

PEG contents (wt %)	Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
None	1020	52	2
5	1010	48	5
10	820	40	10
15	815	36	95
20	420	16	390
30	130	13	405

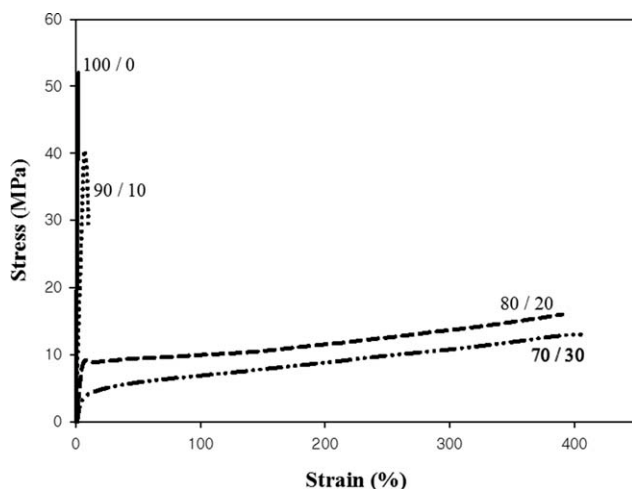


Figure 4 Stress-Strain curves of PLA/PEG blends.

in the tensile-tested specimens was almost the same as those for neat PLA. Moreover, no plastic deformation in the stress direction could be observed. In addition, the PLA/PEG blends could not be observed to show plastic deformation after tensile tests. From the micrographs of the fracture surfaces of PLA compared to PLA/PEG compositions it can be seen that is in agreement with the phenomenon of plasticizer efficiency.²

From the above results of thermal, mechanical properties and morphologies of PLA/PEG blends, the low molecular weight of PEG play a role as a plasticizer.

PLA/CE-PEG blends

Thermal properties

The blends of PLA and chain-extended PEG were prepared in the same manner. The thermal

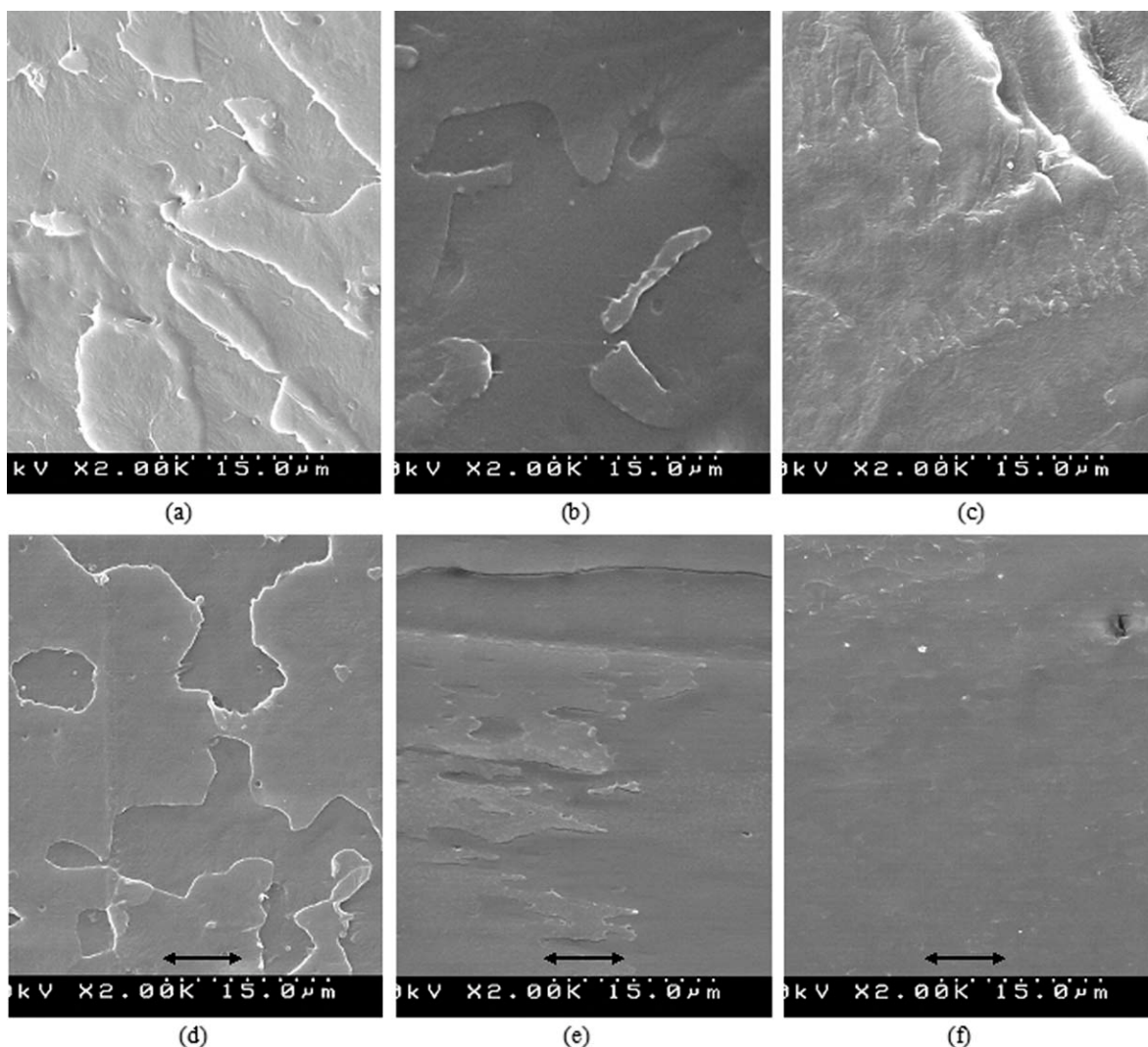


Figure 5 SEM micrographs of fractured surfaces of PLA/PEG blend before and after tensile tested specimen. Before stretching: (a) Neat PLA, (b) PLA/PEG (85/15), and (c) PLA/PEG (70/30). After stretching: (d) Neat PLA, (e) PLA/PEG (85/15), and (f) PLA/PEG (70/30).

TABLE IV
Thermal Properties of the PLA/CE-PEG (80/20) Blends

Sample Name	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m^a (J/g)	X_c (%)
PLA	59.7	131.5	154.0	1.6	1.7
PLA/PEG	26.7	86.9	154.3	30.5	40.7
PLA/CE-PEG-1	27.6	83.7	154.5	28.1	37.9
PLA/CE-PEG-3	–	72.0	153.5	28.6	39.3
PLA/CE-PEG-5	–	80.2	153.0	27.9	39.1

^a Normalized heat of fusion for PLA contents.

properties of PLA/CE-PEG (80/20) blends are shown in Table IV.

It should be noted that all the curves show three transitions upon heating: a PLA glass transition, a cold-crystallization exothermic peak, and a melting endothermic peak. The PEG melting endothermic peak was also observed.

The T_g decreased with the addition of a low molecular weight PEG such as CE-PEG-1, whereas high molecular weight PEGs (CE-PEG-3 and CE-PEG-5) lead to a PLA composition that could not be observed.

The addition of low molecular weight PEG to the PLA resulted in a clear crystallization peak. This suggests that the low molecular weight of PEG has an influence on crystallizability of PLA like plasticizers. With the addition of high molecular weight PEG, the T_m of blends are same with the T_m of pure PLA and the T_m of PEG was also observed, indicating that the PLA and high molecular weight of PEG are not thermodynamically compatible.

Mechanical properties and morphologies

The addition of PEG significantly changed the tensile behavior of the PLA as described previously. Although elongation at break increased up to 405%, tensile strength dramatically decreased. The low molecular weight of PEG plays the role of a plasticizer. In fact, the main goal of a high molecular weight PEG addition into PLA matrix is to decrease its stiffness while polymer strength properties are maintained at the optimum level. In this study, the high molecular weight of PEG was used to achieve PLA toughening without significant modulus and ultimate tensile strength losses.

TABLE V
Mechanical Properties of PLA/CE-PEG (80/20) Blends

	Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
PLA	1020	52	2
PLA/PEG	420	16	390
PLA/CE-PEG-1	520	18	470
PLA/CE-PEG-3	830	31	505
PLA/CE-PEG-5	880	38	540

PLA was blended with the different molecular weights of chain-extended PEG at constant contents. The tensile strength, modulus and elongation at break of PLA/CE-PEG blends, as well as those of pure components and PLA/PEG blends, are shown in Table V. Stress-strain curves of PLA/CE-PEG blends are given in Figure 6.

The modulus and tensile strength of PLA/CE-PEG blends increased after increasing the molecular weight of PEG. The values of PLA/CE-PEG-5 were 880 MPa and 38 MPa, respectively. The studied neat PLA has a maximum tensile strength of 52 MPa, while the low molecular weight of the PEG added composition (PLA/PEG) is characterized by an important reduction of tensile strength performance (16 MPa).

Interestingly enough, the maximum tensile strength values of PLA composition containing 20% chain-extended PEG(CE-PEG-5) are slightly lower than the value recorded for neat PLA. Neat PLA shows a distinct yield point with subsequent failure immediately upon introducing the tensile load. In contrast, PLA/CE-PEG blends show clear yielding behavior upon stretching. After yielding occurred, the strain developed continuously. As a result, the samples were finally broken at a significantly increased elongation, compared with that for the neat PLA. It was interesting to find that the blend with 20% chain-extended PEG had a very high

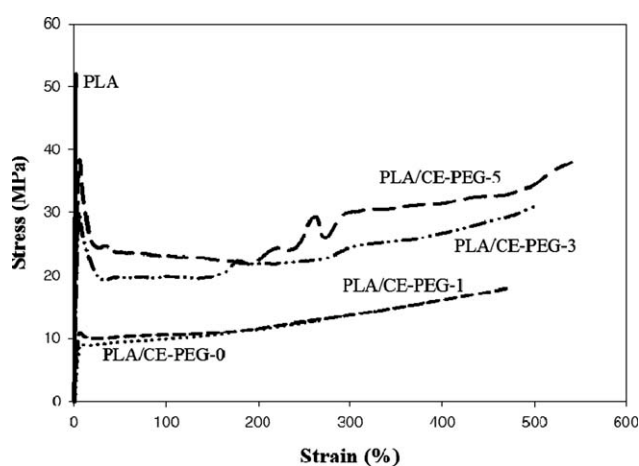


Figure 6 Stress-Strain curves of PLA/CE-PEG blends.

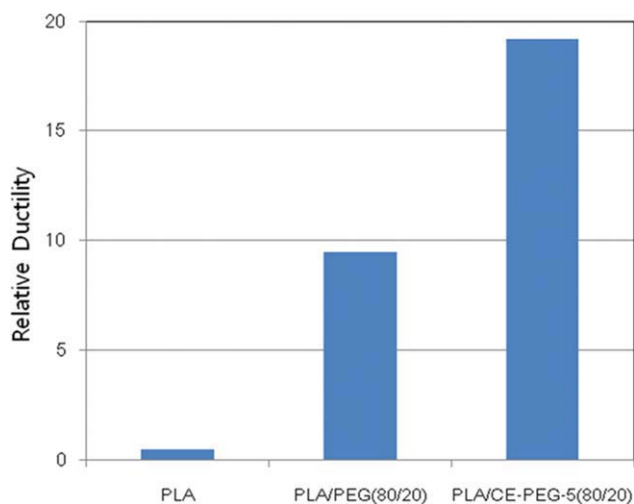


Figure 7 Relative ductility of PLA, PLA/PEG, and PLA/CE-PEG-5 blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

elongation at break of 540%, while the tensile strength remained as high as 38 MPa (Table IV).

As summarized in Table IV and Figure 6, the addition of a high molecular weight PEG leads to a slight decrease in tensile strength and modulus, while the elongation at break is characterized by an important increase. The blend of PLA and high molecular weight PEG achieved high ductile PLA without significant modulus and tensile strength losses.

The relative ductility was calculated from stress-strain curves and the values are shown in Figure 7. Ductility determined by measuring the area underneath the stress-strain curves. The relative ductility of PLA/CE-PEG-5 is 40 times and 20 times higher than that of neat PLA and PLA/PEG blend, respectively. This is because the modulus and tensile strength of PLA/CE-PEG are twice as higher as those of the PLA/PEG blend are. A low molecular weight PEG behaves like a plasticizer (reduction in tensile

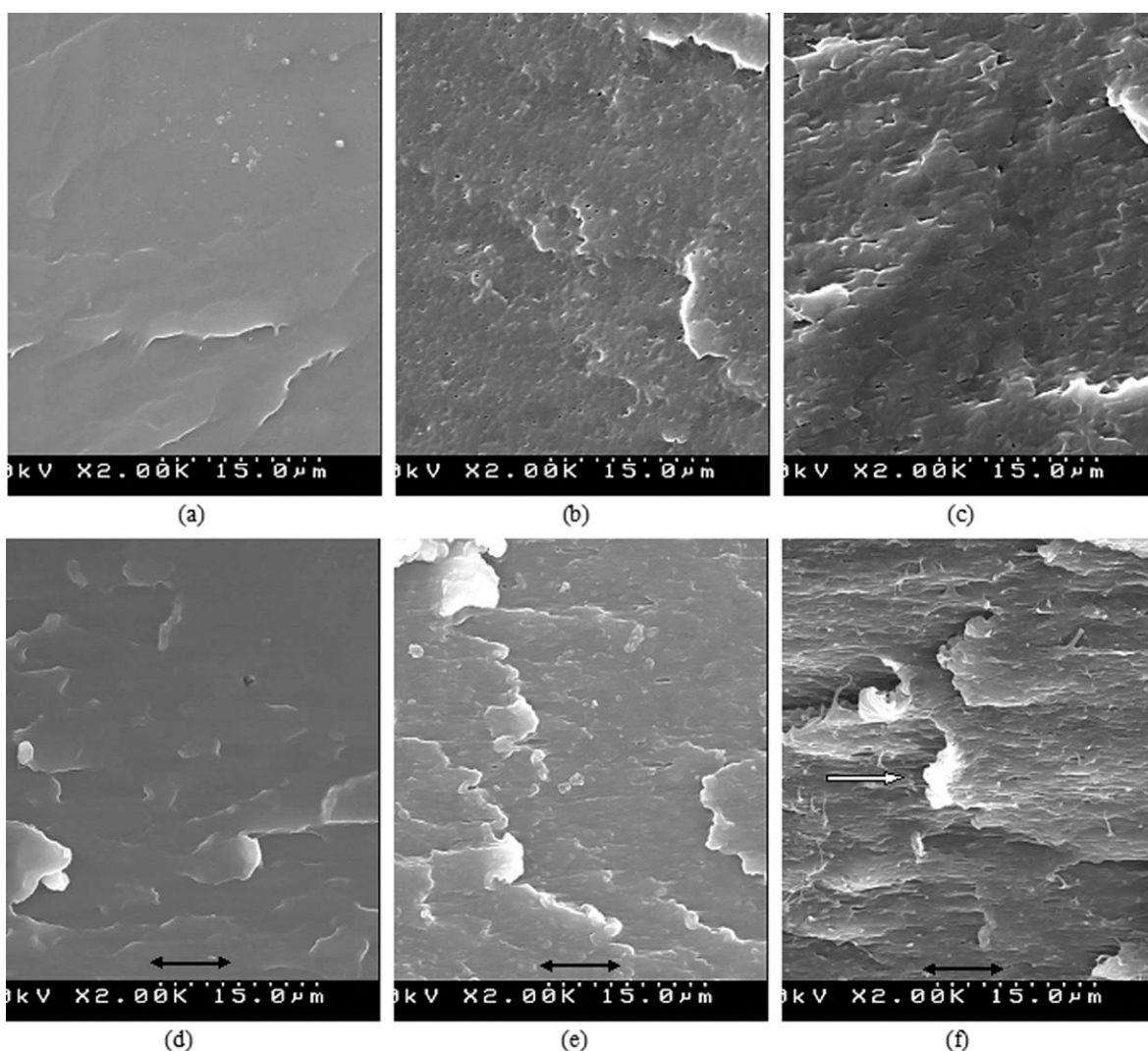


Figure 8 SEM micrographs of fractured surfaces of PLA/CE-PEG blend before and after tensile tested specimen. Before stretching: (a) Neat PLA, (b) PLA/CE-PEG-3 (80/20), and (c) PLA/CE-PEG-5 (80/20). After stretching: (d) Neat PLA, (e) PLA/CE-PEG-3 (80/20), and (f) PLA/CE-PEG-5 (80/20).

strength and increased elongation at break). However, a high molecular weight PEG behaves as ductile thermoplastics, it leads to maintain tensile strength properties and increase the elongation at break.

To investigate the mechanism of the markedly increased elongation caused by the addition of chain-extended PEG, the morphology of fractured surface and necking region of the tensile tested specimen were investigated using a SEM. The micrographs are shown in Figure 8.

The fracture surface of neat PLA was very smooth, whereas after the addition of the high molecular weight PEG to the PLA, PEG domains could be barely observed. As well, the fractured surface also shows a difference from that of neat PLA.

Neat PLA and PLA/PEG blends, which had no necking in the tensile test showed a smooth longitudinal fracture surface without visible plastic deformation (Fig. 4). However, the PLA/CE-PEG blends showed different behaviors under tensile testing, as shown in Figure 8.

For the rubber toughened plastic system, two types of cavitations induced by impact or tensile testing have been discriminated. The first of these were internal cavitations in the rubber domains for the blends with strong interfacial adhesion. The second were debonding cavitations between the interfaces, when the interfacial adhesion was not sufficient.^{23,24}

For the PLA/CE-PEG blend, the debonding of the CE-PEG domains from the PLA matrix under tensile stress was observed [Fig. 8(f)]. It is considered that the CE-PEG domains act as stress concentrators upon being subjected to the tensile test. This is because they have an elastic property that differs from the PLA matrix. The CE-PEG domains are elongated along the stress direction and their shape becomes an ellipsoid. As the debonding progresses, the PLA matrix between the CE-PEG domains deforms more easily and therefore shear yielding occurs. From the micrographs of the fracture surfaces of PLA compared with PLA/CE-PEG compositions, it can be observed that they are in agreement with the phenomenon of the partially miscible system.

CONCLUSIONS

To reduce the brittle behavior of PLA and to improve its ductility, the high molecular weight PEG has been mixed with a PLA. The effects of the molecular weight of PEG on the PLA thermal and mechanical properties have been evaluated. The chain-extended PEG (CE-PEG) was prepared by melt condensation with diisocyanate compound for the enhancement of molecular weight PEG. Accordingly, melt blending of PLA with CE-PEG does not

lead to an important drop in tensile strength and modulus whereas the elongation at break is characterized by a significant increase (540%), compared with neat PLA and PLA/PEG (low molecular weight PEG, $M_n = 35,000$). The elongation at break and tensile properties of PLA/CE-PEG blends grew because of increasing the molecular weight of PEG. A PLA/CE-PEG blend is a partially miscible system with a two-phase morphology and the addition of CE-PEG decreases the PLA crystallinity. The relative ductility of PLA/CE-PEG-5 is 40 times higher than that of neat PLA, because the modulus and tensile strength of PLA/CE-PEG slightly decreased whereas the elongation at break dramatically increased. The stress-strain curves show that the blend changed from being brittle to demonstrating ductile failure with the addition of the high chain entanglement PEG (CE-PEG). SEM micrographs revealed that a debonding initiated shear yielding mechanism was involved in the toughening of the blend.

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