

The effect of poly(ethylene glycol) as plasticizer in blends of poly(lactic acid) and poly(butylene succinate)

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ABSTRACT: The effect of polyethylene glycol (PEG) on the mechanical and thermal properties of poly(lactic acid) (PLA)/poly(butylene succinate) (PBS) blends was examined. Overall, it was found that PEG acted as an effective plasticizer for the PLA phase in these microphase-separated blends, increasing the elongation at break in all blends and decreasing the T_g of the PLA phase. Significant effects on other properties were also observed. The tensile strength and Young's modulus both decreased with increasing PEG content in the blends. In contrast, the elongation at break increased with the addition of PEG, suggesting that PEG acted as a plasticizer in the polymer blends. Scanning electron microscope images showed that the fracture mode of PLA changed from brittle to ductile with the addition of PEG in the polymer blends. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43044.

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INTRODUCTION

In recent years, the development of biodegradable polymers has attracted a great deal of interest. Aliphatic polyesters are among the most promising materials as high-performance environmentally friendly biodegradable plastics.^{1–3} Biodegradable polyesters have received considerable attention in recent decades. Owing to their biodegradability and biocompatibility, they were first intensively developed for biomedical applications. Poly(lactic acid) (PLA) is one of the most studied polymers of this family because it can be produced via the fermentation of renewable resources, such as cassava or corn starch.^{4–6} It also has good physical properties, such as high strength, thermoplasticity, and spinnability. However, the low deformation at break and high modulus limits the application of PLA as packaging materials. Attempts to improve the mechanical properties have focused on biocompatible plasticizers.^{7–9} To improve the thermal properties and processability of PLA, one approach is to blend PLA with biodegradable polymers with good mechanical and thermal properties. One of the biodegradable polymers with the potential to improve the PLA properties is poly(butylene succinate) (PBS).^{10–14} PBS is a biodegradable semicrystalline polymer synthesized from butanediol and succinic acid, which are both available from biobased renewable resources. PBS has excellent biodegradability, mechanical properties, good thermal properties, and processing capabilities.^{15–20}

However, the PLA and PBS blends (PLA/PBS blends) still have some limitations, such as poor ductility or stiffness. To improve the ductility of PLA-based materials, many investigations have attempted to modify the PLA properties via plasticization.¹⁷ Blending with low-molecular-weight poly(ethylene glycol) (PEG) improves the elongation at break and softness.^{8,9,18–21} The amount of PEG introduced into PLA has to be lower than or equal to 20 wt % to avoid phase separation. This limitation reduces the potential impact of PEG on the glass transition temperature (T_g) of PLA.^{21,22} However, the effect of PEG on the PLA/PBS blends has not yet been reported, i.e., thermal and mechanical properties and whether the PEG in PLA/PBS blends acts the same in PLA and PBS.

In this study, we investigated various aspects of the thermal, rheological, and mechanical properties of the PLA/PBS blends by adding PEG. Furthermore, the properties of the products, such as the compression and injection of molded parts, were also evaluated.

EXPERIMENTAL

Materials

Poly(lactic acid) (3052D, Natureworks LLC, MN, USA) with M_n and M_w of 1.4×10^5 and 2.1×10^5 g/mol, respectively, and poly(butylene succinate) (FZ91PD, Mitsubishi Chemical Co. Tokyo, Japan) with M_n and M_w of 3.6×10^4 and 6.4×10^4 g/

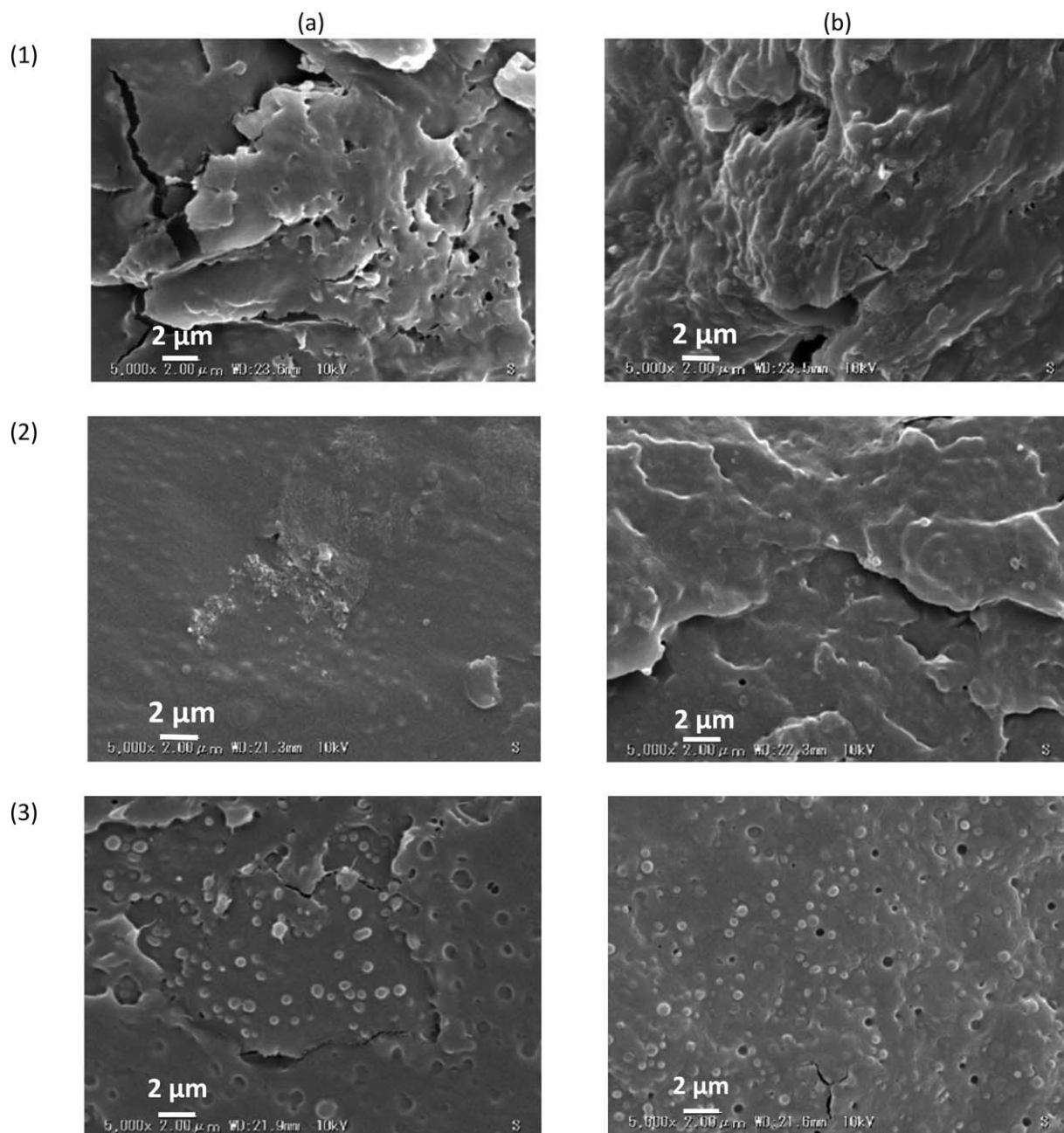


Figure 1. Phase morphology of PLA and PBS blends with PEG. The ratio of PLA:PBS are (1) 100:0, (2) 90:10, (3) 80:20, (4) 70:30, (5) 60:40, and (6) 0:100. PEG was (a) not added and (b) added at 10 phr.

mol, respectively, were used in this study. Poly(ethylene glycol) (Merck Co., NJ, USA) has an M_w about 4,000 g/mol.

Compounding

The pellets of PLA and PBS were dried in an oven at 80°C *in vacuo* for 8 h prior to the melt processing. The blending weight ratios of each component (PLA:PBS) were 90:10, 80:20, 70:30 and 60:40. 2, 6, and 10 parts per hundred resin (phr) of PEG were mixed into the blends in a twin-screw extruder (CTE-D20L800, $L/D = 40$, $D = 48$ mm, $h = 20$ mm, CHAREON TUT

Co., Samutprakarn, Thailand). The extruder was operated at 200°C and 60 rpm screw speed for the compounding.

Injection Molding

Blend pellets were dried again as the same condition above before injection molding (SM120, model AP 120T, Asian Plastic Machinery Co., Taoyuan, Taiwan) into dumbbells. The temperature setting of the injection molding machine was 220°C. The dumbbell of test specimens are as per ASTM D638 ($25 \times 197 \times 3$ mm) for tensile testing, and ASTM D256 ($63.5 \times 12.7 \times 3.2$ mm) with a V-notch cut for Izot impact testing. Test

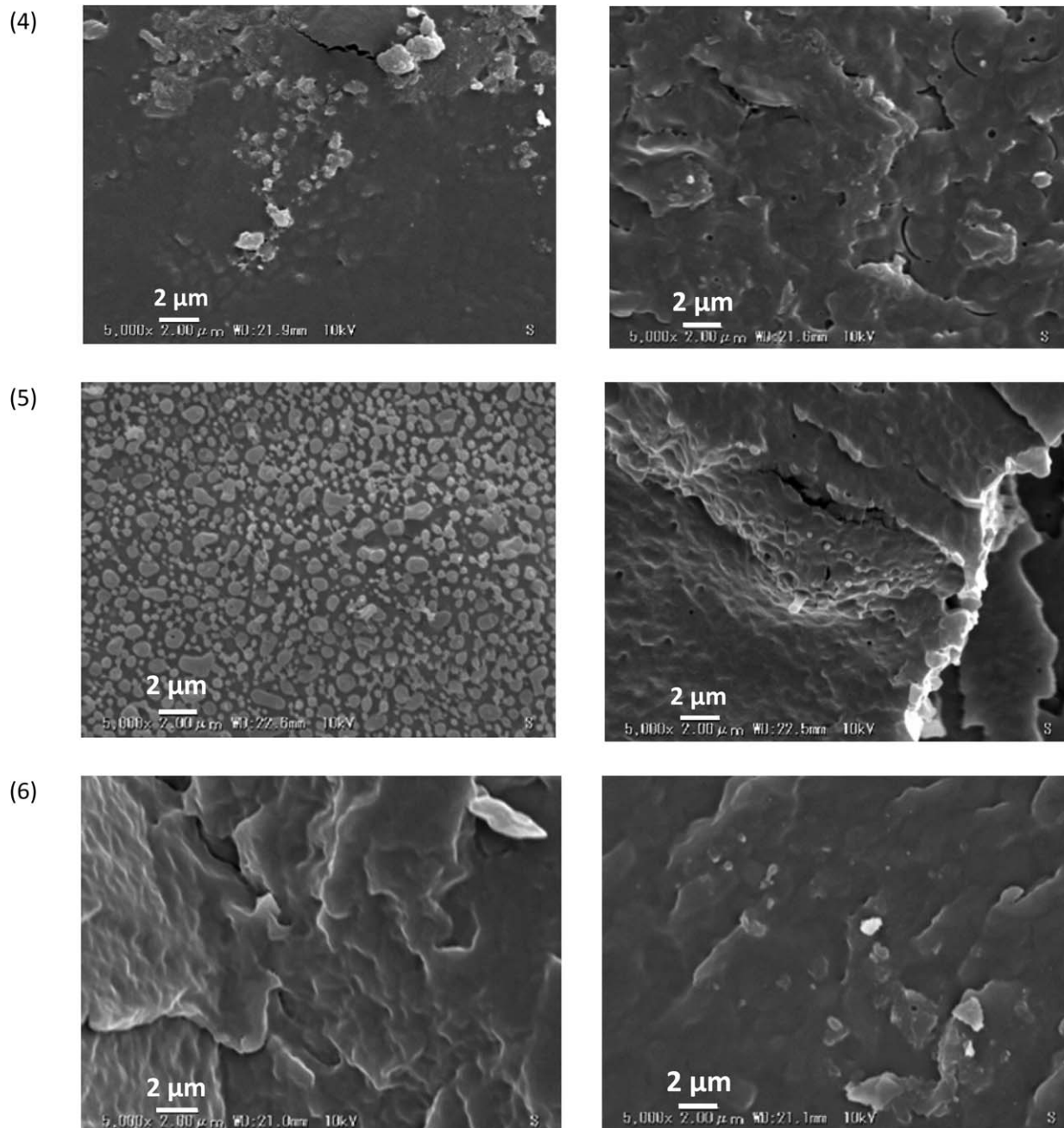


Figure 1. Continued.

specimens were conditioned for 48 h at 25°C before the measurement. PBS would be crystallized while PLA kept amorphous state in this condition.

Morphology

Observations of the phase morphology of the compounded strand and the fracture surface of the tensile specimens were carried out by scanning electron microscope (SEM) (JSM-S410LV, JEOL Ltd., Tokyo, Japan) operated at 15 kV. The strands extruded through a die of the twin-screw extruder were fractured at liquid nitrogen temperature. The samples were fixed on supports and coated with gold.

Thermal Properties

The thermal properties of the samples were studied by use of a differential scanning calorimetry (DSC 8000, Perkin Elmer, MA, USA) under N₂ atmosphere at heating and cooling rates of 10°C min⁻¹. The samples (10 mg) were placed into alumina crucibles. After the first heating from -50 to 200°C, the sample was held at that temperature for 5 min, then cooled to hold at -50°C before a second heating step. The melting temperature (T_m), the heat of fusion (ΔH_m), and the cold crystallization temperature (T_c) were determined from the second heating scans.

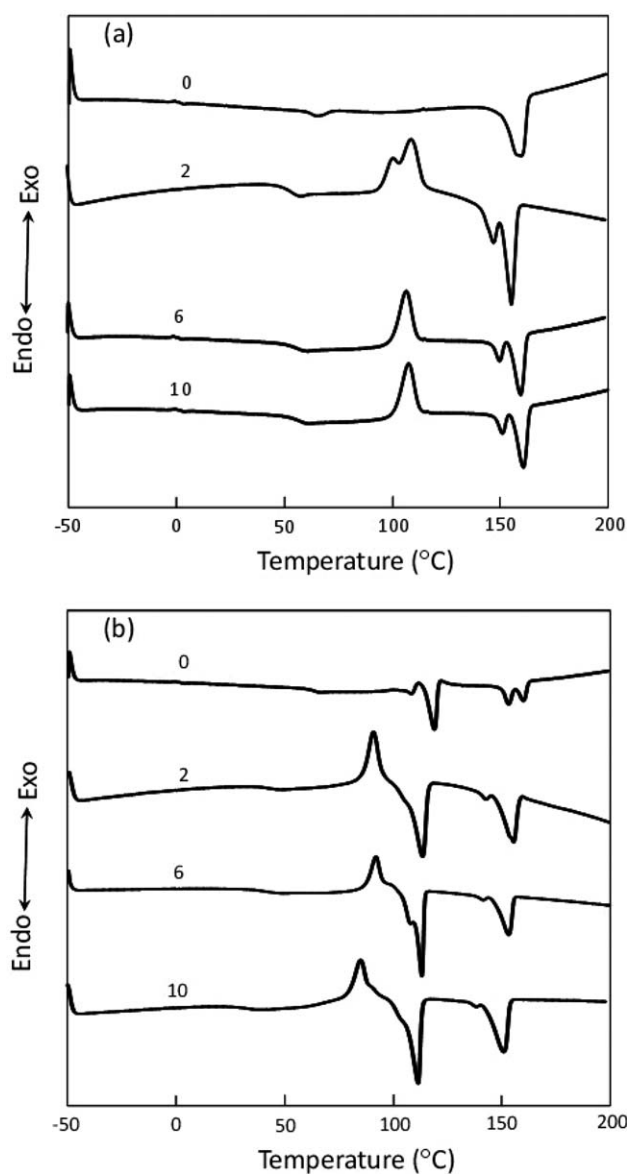


Figure 2. DSC trace of second heating scan of (a) neat PLA and (b) blends of PLA and PBS at a ratio of 60:40. The parts per hundred resin of PEG are shown above each curve.

Rheological Properties

Dynamic mechanical analyses (DMA) were performed using a rheometer (Reogel-E4000, UBM Co., Kyoto, Japan) in a tensile mode over a temperature ranging from -50 to 200°C . Data acquisition and analysis of the storage modulus (E'), loss modulus (E''), and loss $\tan \delta$ were recorded. The heating rate and frequency were fixed at $3^{\circ}\text{C min}^{-1}$ and 32 Hz, respectively. Compression molded film samples of $100\ \mu\text{m}$ thickness quenched from 200°C were prepared for DMA experiments.

Mechanical Properties

Tensile strength, Young's modulus, and elongation at break were determined according to ASTM method D638 under ambient conditions, using a tensile testing machine (LR10K Plus series, LLOYD Instrument, West Sussex, UK) at a cross-head speed of

Table I. Thermal Data of Neat PLA, Neat PBS, and Blends of PLA and PBS with PEG

PLA:PBS	PEG (phr) ^a	PLA				PBS				
		T_m ($^{\circ}\text{C}$)	ΔH_m (J g^{-1})	$\Delta H_m/\phi_{\text{PLA}}^b$ (J g^{-1})	T_c ($^{\circ}\text{C}$)	ΔH_c (J g^{-1})	$\Delta H_c/\phi_{\text{PLA}}^b$ (J g^{-1})	T_m ($^{\circ}\text{C}$)	ΔH_m (J g^{-1})	$\Delta H_m/\phi_{\text{PBS}}^c$ (J g^{-1})
60:40	0	153.3	11.2	18.7	-	-	-	119.1	15.8	39.5
	2	155.3	16.5	28.1	90.5	-15.7	-26.7	113.2	27.0	68.9
	6	152.3	15.5	27.4	91.6	-12.8	-22.6	112.7	27.0	71.6
	10	152.2	17.2	31.5	86.8	-13.1	-24.0	112.5	22.2	61.1
100:0	6	155.8	24.6	26.1	107.2	-19.1	-20.2	-	-	-
90:10	6	152.1	22.8	26.9	82.8	-13.2	-15.5	109.3	3.5	37.1
80:20	6	153.6	25.0	33.1	84.1	-13.7	-18.1	110.4	9.1	48.2
70:30	6	153.4	18.3	27.7	87.7	-13.1	-19.8	113.0	20.3	71.7
60:40	6	152.3	15.5	27.4	91.6	-12.8	-22.6	112.7	27.0	71.6
0:100	6	-	-	-	-	-	-	113.4	64.7	68.6

The data were measured by DSC during the second heating at $10^{\circ}\text{C min}^{-1}$.

^a Parts per hundred resin of PEG.

^b The values were converted to per gram of PLA by division of the weight ratio of PLA in PLA and PBS blends with PEG.

^c The values were converted to per gram of PBS by division of the weight ratio of PBS in PLA and PBS blends with PEG.

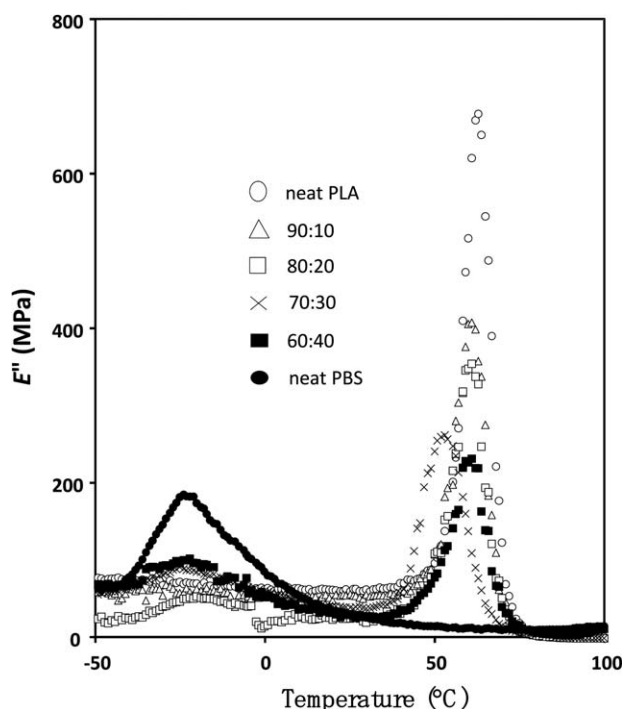


Figure 3. Temperature dependence of $\log E''$ for neat PLA, neat PBS, and their blends without PEG.

5 mm min⁻¹. The reported values were the average of at least 10 measurements.

Izod impact strength was determined according to ASTM method D256, using impact tester (Ceast 6545, Instron, Torino, Italy), and calculated by dividing impact energy in Joule by the thickness of the specimen. Measurements were done at 10 times for each point. The standard deviations were calculated and showed the error bar in the figures.

RESULTS AND DISCUSSION

Phase Morphology of the PLA/PBS Blends

Figure 1 shows the scanning electron microscope (SEM) images of the compounded strands with PLA:PBS ratios of up to 60:40. The fracture surfaces of neat PLA and neat PBS are fairly smooth and scale-like regardless of the PEG content. This is due to the brittleness of these materials at liquid nitrogen temperature. The blend PLA:PBS = 90:10 has many whitish spots <1 μm in size. The size of the white spots tended to increase with increasing PBS content indicating that they are likely a PBS-rich phase and most likely a phase-separate PBS. The dark and whitish phases are closely adhered. PLA seems to be a continuous phase up to 10–40 wt % of PBS content and the addition of 10 phr PEG changed the phase morphology of PBS on PLA matrix which resulted in smaller particles of PBS. PEG reduced the surface energy of PBS and decreased the particle size. The results confirmed the role of PEG as a compatibilizing agent between PLA and PBS. Figure 1(5a,5b) of PLA/PBS blend with a ratio of 60/40 clearly shows the reduced particle size of PBS with the addition of PEG. The results are in agreement with the reduction and shift of T_g of PLA close to that of PBS (Figure 4).

Thermal Properties

Figure 2(a) shows the second heating curves of neat PLA and of PLA blends that contain PEG. The first heating cycle to a temperature higher than the T_m of the component polymers removed the uncertain thermal history of the samples in the compounding process.²³ Neat PLA showed T_g around 60°C and a single melting peak around 160°C. Crystallization was not observed in the second heating cycle; thus, this single melting peak is due to the melting endotherm of the PLA that crystallized in the earlier cooling process. The addition of PEG slightly lowered the T_g of PLA, and the presence of PEG inhibited the crystallization of PLA as suggested by the appearance of a cold crystallization peak. This indicated that the PEG enhanced the mobility of PLA chains. Interestingly, the melting endotherm of PEG-containing PLA showed two distinct peaks. As the crystallization of PEG-containing PLA occurred in the cooling and second heating process, the crystalline phases formed under these different conditions resulted in two melting peaks.

Figure 2(b) shows the second heating curves of the PLA:PBS blend with a ratio of 60:40 containing between 0 and 10 phr of PEG. Similar to the phenomenon observed in Figure 2(a), the blends containing PEG clearly showed the crystallization peak of the PLA phase. All curves showed the melting endotherm of PBS around 110°C. In the absence of PEG, there is no cold crystallization. The PLA phase crystallized during the cooling

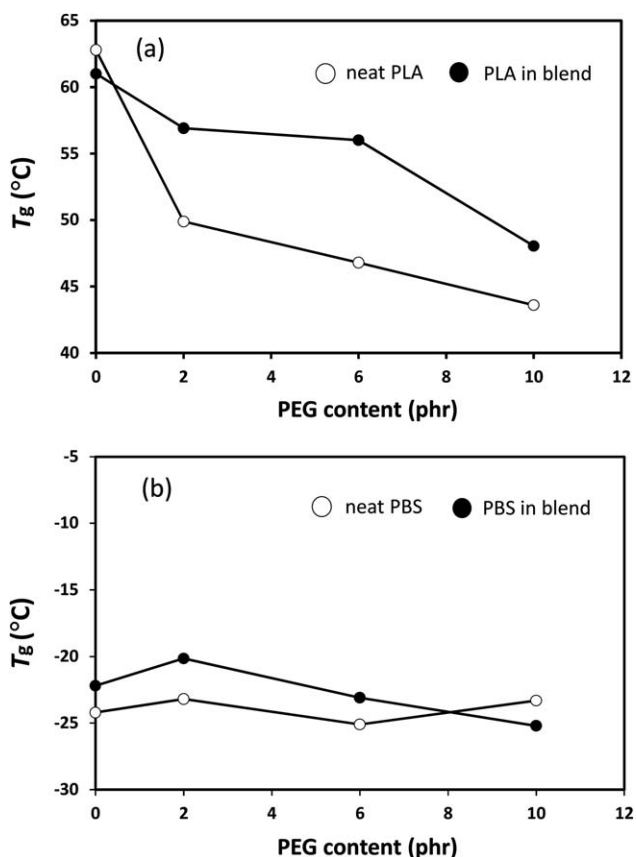


Figure 4. The effect of PEG content in PLA and PBS blends (60:40) on T_g . (a) Neat PLA and PLA phase in blends of PLA and PBS and (b) neat PBS and PBS phase in blends of PLA and PBS, as measured by DMA.

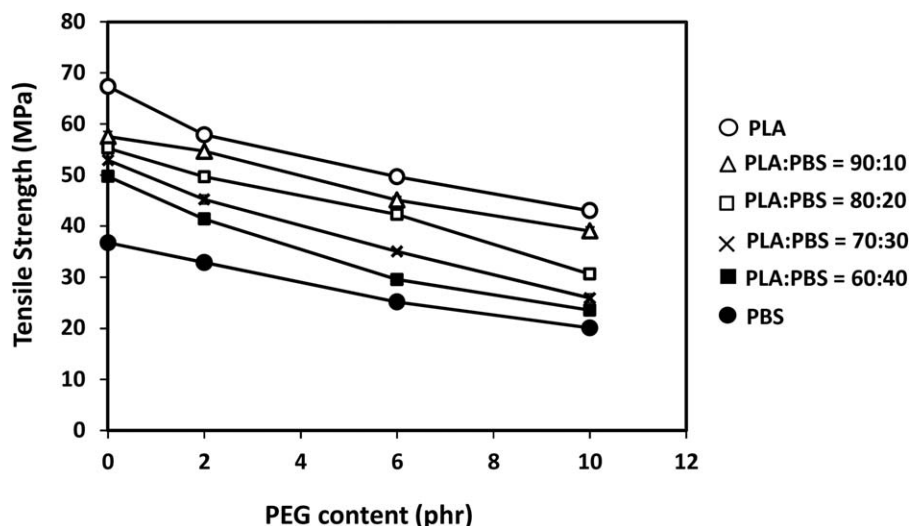


Figure 5. Tensile strength of blends of PLA and PBS with PEG. Measurements were done at 10 times for each point. The standard deviations were very small to show on the figure.

phase of the first heat-cool cycle. However, in the presence of PEG, cold crystallization peaks appear and are significant. This indicates that the presence of PEG significantly slows the crystallization rate of the PLA phase. The presence of separate melting and T_g peaks in the differential scanning calorimeter (DSC) scans of the PLA and PBS phases clearly suggest that these are phase-separated blends.

Table I summarizes the thermal properties of the PLA/PBS blends with and without PEG, as measured by DSC. The addition of PEG did not affect the melting point of the PLA phase in the blends PLA:PBS = 60:40. The enthalpy of fusion of the PLA phase increased with increasing PEG content. The crystallization temperature (T_c) of the PLA phase decreased with increasing PEG content. The blending of PBS and PLA did not affect the thermal properties of the PLA phase.

The enthalpy of melting of the PLA crystals increases in the presence of PEG although there is not much difference between samples with 2, 6, and 10 phr PEG. In the past, this has been attributed to the increase in the molecular mobility afforded by the plasticizer allowing for better chain packing. Moreover, this may be linked with the slower crystallization rate that affords time for chain reordering. Judging by the T_g values for neat PLA, neat PBS, and the 60:40 blends, there is a little difference in T_g with blending and, presumably, little miscibility between the phases. Likewise, there is a little effect of blend composition on the T_m values for both phases. However, the enthalpy of melting (crystallinity) of the PBS phase is affected (decreased) because of PLA when the PBS content in the blend is at or below 20 wt %. In contrast, the enthalpy of melting of the PLA phase is not affected by the presence of the PBS phase. The effect of PEG on the T_g of the PLA phase is significant, whereas

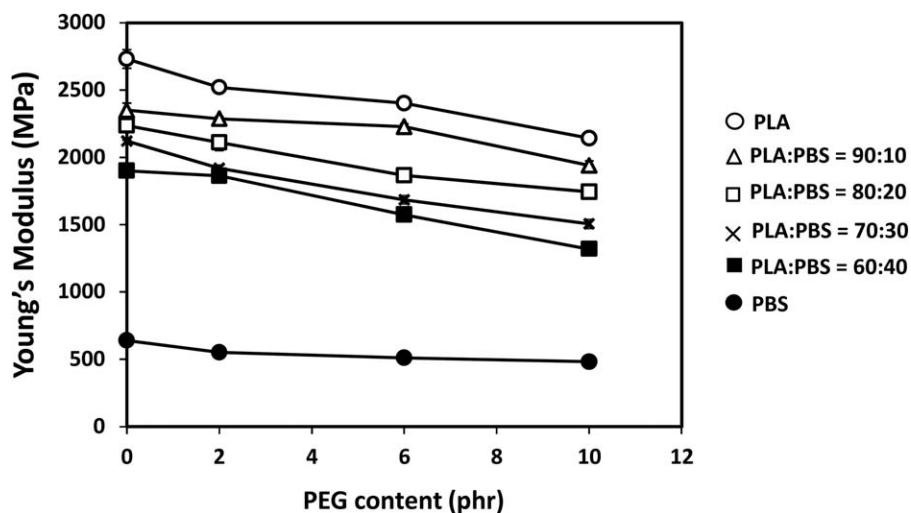


Figure 6. Young's Modulus of blends of PLA and PBS with PEG. Measurements were done at 10 times for each point. The standard deviations were very small to show on the figure.

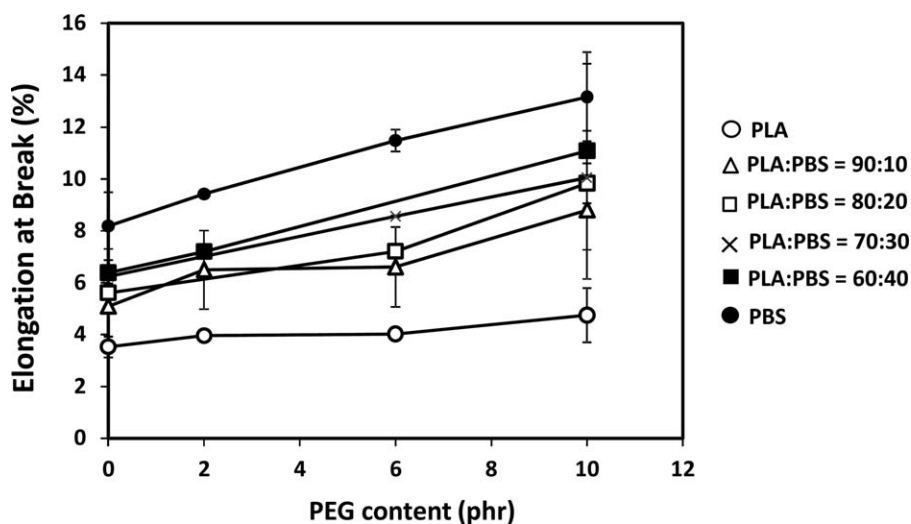


Figure 7. Elongation at break of blends of PLA and PBS with PEG. The error bars means standard deviations for 10 times measurement at each point.

it has marginal effect on the T_g of the PBS phase. The addition of PEG affects the melting temperature of the PBS phase but not that of the PLA phase.

DMA analysis gives clear information on the T_g of the component polymers; therefore, the plasticizing efficiency was evaluated by measuring the change in T_g as a function of PBS and PEG contents. Figure 3 shows the temperature dependence of the loss modulus (E'') of neat polymers and their blends without PEG. Neat PLA and PBS showed a very sharp E'' peak around 60°C and a rather broad and smaller peak around -20°C , respectively. The peaks of E'' may be ascribed to the movement of amorphous chains of PLA and PBS, and the peak temperature may be corresponding to T_g . Figure 3 shows that the T_g of PLA slightly shifts to a lower temperature and that of PBS shifts to a higher temperature with increasing PBS content, suggesting partial compatibility between PLA and PBS.

Figure 4(a,b) compares the effect of PEG content on T_g of PLA and PBS in neat component polymers and in PLA:PBS = 60:40 blends. Although T_g of PLA phase in both the neat PLA and

PLA/PBS blends decreased with the addition of PEG, the effect is stronger for neat PLA. The result indicates that PEG prefers to stay in PBS rather than PLA, which results in lower T_g for PLA and higher T_g for PBS when the PEG content is 10% in the PLA:PBS = 60:40 blend. In contrast, the effect of the addition of PEG on T_g of PBS is rather weak because T_g of PBS and PEG is in the same temperature range.

Mechanical Properties

The higher the PBS ratio in PLA:PBS blends, the lower the tensile strength (Figure 5). The addition of PEG to PLA/PBS blends caused the tensile strength to decrease. The effect was stronger with increased PEG content. Amita *et al.* reported that the tensile strength and modulus of the PLA/PBS blends decreased with increasing PBS content but followed approximately the mixing rule for 90:10 and 80:20 blends.²⁴ This means that some compatibility between PLA and PBS phases is possible when the PBS concentration is lower.

The Young's modulus of PLA/PBS blends with PEG also shows the same tendency to decrease with increasing PEG content

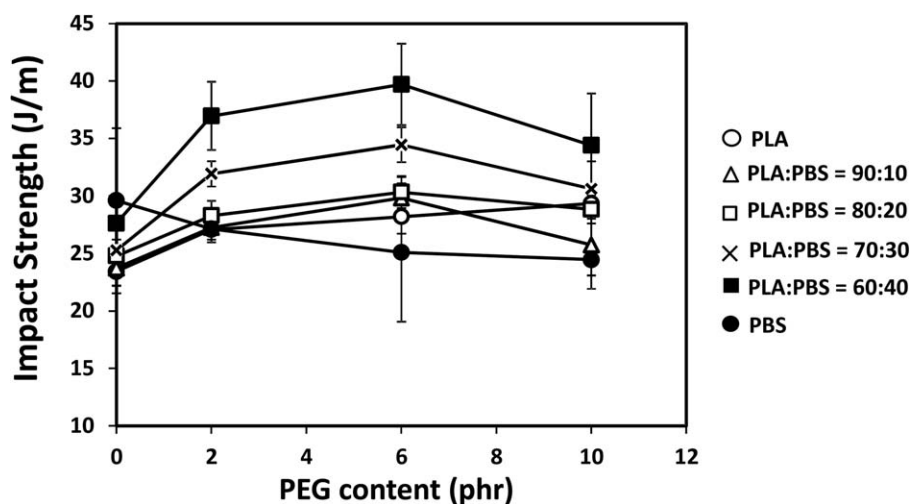


Figure 8. Impact strength of blends of PLA and PBS with PEG. The error bars means standard deviations for 10 times measurement at each point.

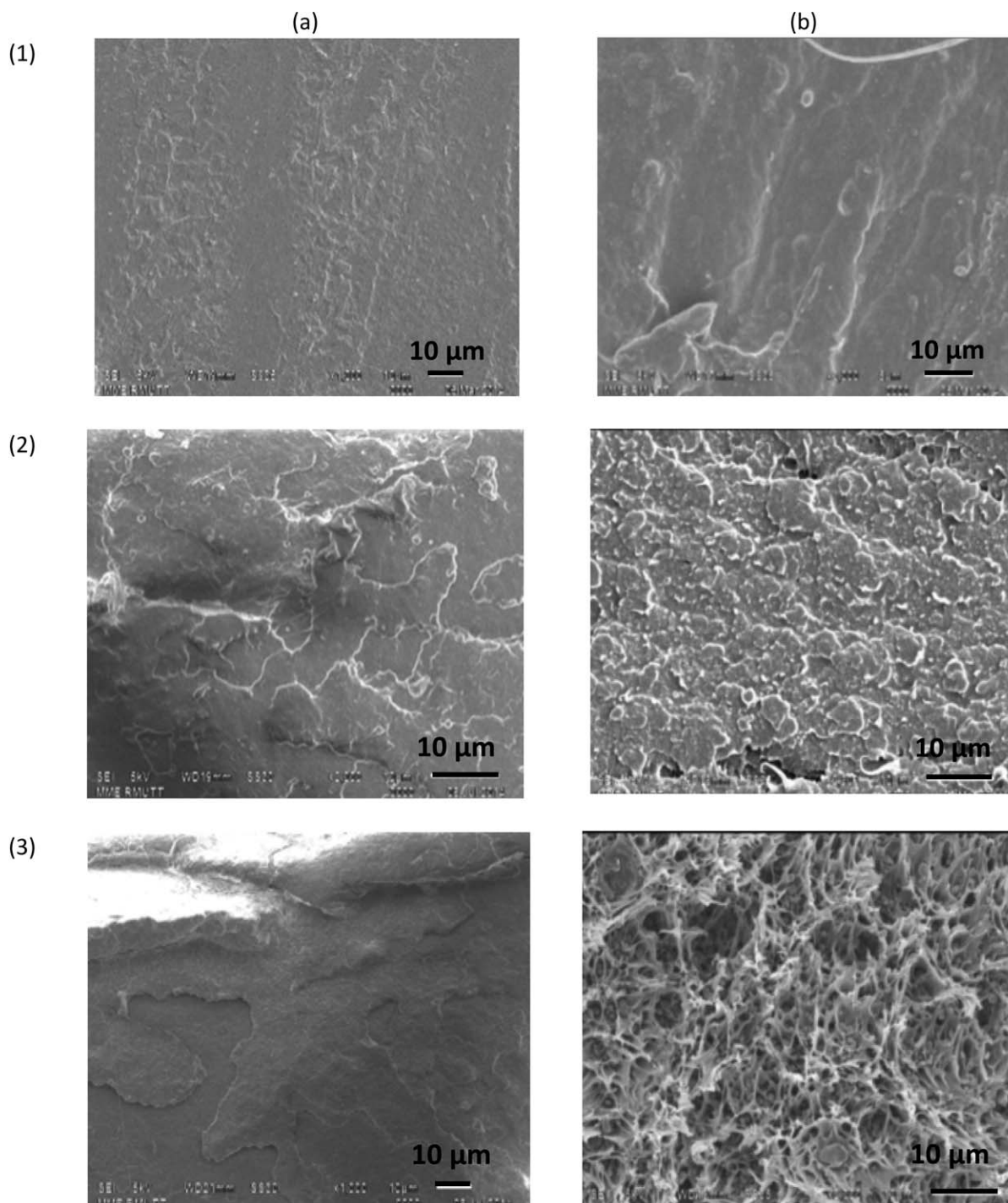


Figure 9. Morphology of fractured surface of tensile specimen of blends of PLA and PBS with PEG. The ratio of the PLA:PBS blends are (1) 100:0, (2) 90:10, (3) 80:20, (4) 70:30, (5) 60:40, and (6) 0:100. PEG was (a) not added and (b) added at 10 phr.

(Figure 6). With different results, the Young's modulus and tensile strength of PLA/PBS blends with PEG show the same tendency to decrease with increasing PEG content in all compositions of the blends from 90/10 to 60/40 (Figure 6). The tensile strength of the blends approaches the values for PBS but higher than neat PBS indicates compatibilizing effect on PEG addition in the blends.

The elongation at break of PLA/PBS blends with PEG is shown in Figure 7. Neat PLA shows an elongation at break lower than that of neat PBS owing to PLA being a low-deformation-at-break material,^{15–17} whereas PBS is a high-flexibility material.²⁵ The PLA:PBS blends with a ratio of 60:40 show higher elongation at break than other blend ratios at all PEG contents. The addition of PEG results in apparent plastic deformation

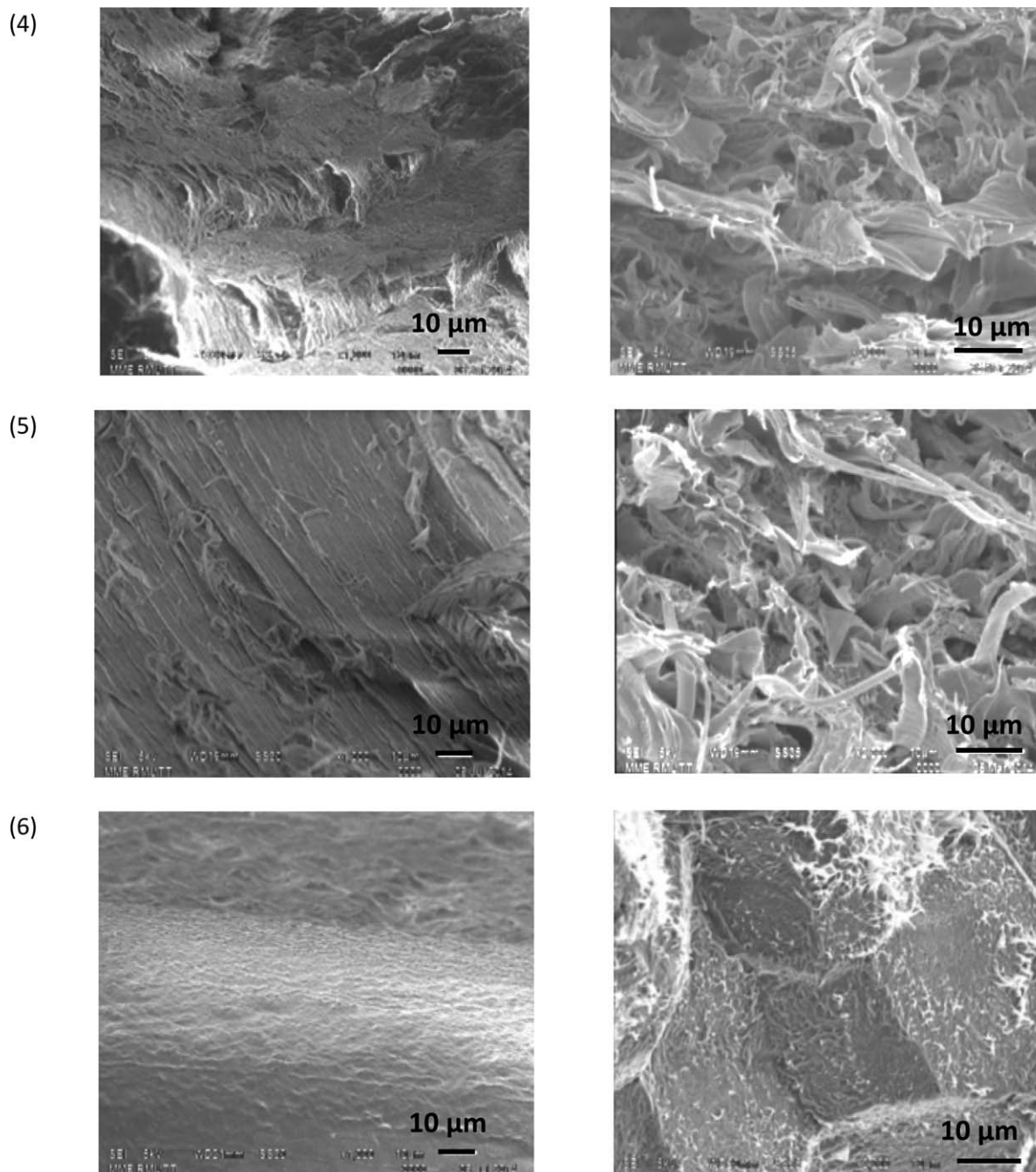


Figure 9. Continued.

behavior between the linear elastic deformation and necking region, indicating improved ductility.^{23,26} As mentioned above, PEG localized at the PLA phase in the PLA/PBS blends. Therefore, when comparing PLA:PBS blends with ratios of 90:10, 80:20, 70:30, and 60:40, the lower the PLA content is, the higher the concentration of PEG in the PLA phase is, which increases the toughness of the polymer.

The impact strengths of neat PLA and PBS and PLA/PBS blends with variable PEG contents are shown in Figure 8. The impact strengths of PLA/PBS blends with PEG slightly increased with

the addition of PEG up to 10 phr PEG. However, 10 phr PEG decreased the impact strength of the blends compared to the 5 phr PEG blends. The PLA : PBS blends with ratios of 90:10, 80:20, 70:30, and 60:40 all showed similar results. In contrast, the addition of PEG increased the impact strength of pure PLA at all levels, whereas it reduced the impact strength of pure PBS.

Fracture Surface

The morphology of the fractured surface of tensile specimens of PLA/PBS blends with and without PEG is shown in Figure 9(a,b), respectively. The most compatible ratio of PLA:PBS is

80:20 with and without PEG addition. The morphology shows less clear phase separation compared to other blend ratios without PEG. The fracture surface of the tensile specimen of PLA:PBS with ratio of 80:20 and 10 phr PEG shows ductile fracture behavior. For neat PLA, the addition of PEG [Figure 9(1-b)] changed the fracture mode of PLA from brittle to ductile. Although neat PBS without PEG is ductile, PBS with PEG at 10 phr [Figure 9(6-b)] showed rather brittle fracture probably because of the agglomeration of PEG in the PBS phase. The blends without PEG show brittle fracture behavior up to 20 wt % of PBS in the blends. At higher PBS content, stretching of the PBS phase was observed. A similar morphology was observed up to 10 wt % of PBS with PEG, and fibrous morphology was observed at higher PBS content. These results suggest that the transition from brittle to ductile behavior occurs at lower PBS content when the blends contain PEG.

CONCLUSIONS

The addition of PEG to PLA/PBS blends results in a significant decrease in the T_g of the PLA phase in these blends. Thermal analysis confirmed preferably migration of PEG to PLA phase than that of PBS. The PEG enhances mobility of PLA molecules. The mechanical property measurement of injection-molded samples shows a decrease in Young's modulus and tensile strength with an increase in PEG content. The mode of fracture of PLA in blends of PLA and PBS changes from brittle to ductile fracture following the addition of PEG as illustrated by SEM imaging. The addition of PEG to PLA/PBS blends decreases T_g of the PLA phase in these blends. Thermal analysis confirmed the migration of PEG to the PLA phase rather than PBS. PEG enhances the mobility of the PLA molecules. Injection molding samples show decreasing Young's modulus and tensile strength with increasing PEG content. The fracture mode of PLA in blends of PLA and PBS changes from brittle to ductile following the addition of PEG as shown in the SEM images. Morphological studies verified the phase separation of polymer components, while the addition of PEG affected the morphology of PBS phase on PLA matrix as a compatibilizing agent. At low PEG contents, a good distribution of polymer components and plasticizer resulted in high Izod impact strength.

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