

A Novel Composite Coupled Hardness with Flexibility—Polylactic Acid Toughened with Thermoplastic Polyurethane

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ABSTRACT: With the aim to modify the brittleness of polylactic acid (PLA), it was firstly melt blended with thermoplastic polyurethane (TPU) at six different PLA wt % of 100, 90, 80, 70, 60, and 50 compositions. The properties of PLA/TPU composite were characterized by means of electron microscopy, rheological, mechanical and thermal methods. The results showed that the brittle fracture of pure PLA was gradually transformed into ductile fracture with the addition of the TPU elastomer. The notched impact strength of the composite at 10 wt % TPU was

over three times higher than that of pure PLA. The composite was found to be a partially miscible system with shifted glass transition temperatures. The molten blend was shear-thinning fluid and it could be processed by conventional thermoplastic processes such as extrusion and injection molding. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 855–861, 2011

Key words: polylactic acid; thermoplastic polyurethane; brittle; mechanical properties; rheology

INTRODUCTION

Loss of function of the knees can severely impact mobility and thus the patient's quality of life. Articular cartilage is composed of hyaline cartilage, which has unique properties, such as viscoelastic deformation, that allow it to absorb shock, distribute loads, and facilitate stable motion.^{1,2} The scaffold material of articular cartilage is one important part of tissue engineering. The material should be easily processed into desired shapes with good mechanical strength. Hydrogels have been extensively employed as carrier matrix for cartilage repair. The main disadvantage of hydrogel for articular cartilage repair is their deficiency of mechanical strength until sufficient tissue remodeling and regeneration occur.^{3–7}

Polymer blends is an important branch in polymer technology to obtain desired performance instead of

synthesizing a new material. The improvement of toughness or notch resistance and processability is the important objectives of many commercial blends/alloys' study. The development of elastomer toughening thermoplastics is a significant contribution to the commercial polymer industry. As for elastomer/thermoplastic composite, there is a very few literature report on it.^{8,9}

Both thermoplastic polyurethane (TPU) and polylactic acid (PLA) have good biocompatibility and various human clinical applications. PLA is widely used for many biomedical applications like surgical sutures, inner-fix material of bone fracture due to its degradability, high rigidity, and biocompatibility. Lactic acid is made by converting sugar or starch obtained from vegetable sources using a fermentation process. There are four unique groups attached to the central carbon atom; lactic acid is a chiral molecule. There are two major routes to produce polylactic acid from the lactic acid monomer: direct condensation polymerization of lactic acid and ring-opening polymerization through the lactide intermediate. Both polylactic acid and polylactide have similar mechanical properties and are commonly designated by the same acronym, PLA. One deficiency inherent to PLA is the brittle nature of the parent material under impact and

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tensile testing. PLA is fairly rigid material that shows little to none elastic behavior, and its inherent brittleness and low toughness restricts its application in which good flexible properties are required.^{10–12} On account of an immense consumption of PLA, considerable efforts would be required to overcome its mechanical brittleness. As for the melt blending of PLA with biodegradable materials like poly (ϵ -caprolactone) and polyethane glycol (PEG), there was no obvious toughness effective and PLA could not be in common use. TPU is a linear segmented block copolymer derived from the reaction of diisocyanates, oligomeric diols, and low molecular weight diols (called chain extenders). TPU morphology can be visualized as a coherent soft segments (SS) matrix with a dispersed phase of separated hard segment (HS) domains. At room temperature, low T_g SS sequences are quite mobile and mostly they present in an amorphous conformation. In contrast, high T_m HS sequences are quite polar and fixed by intermolecular bonding. Consequently, HS domains act as fillers as well as “physical crosslinks” for the soft segment matrix, giving high elasticity and strength to the resulting TPU. They are tough, biocompatible, and hemocompatible. They can be strong elastomer or rigid plastic, and they can be processed by using extrusion, injection molding, film blowing, solution dipping, and two-part liquid molding.^{13–15} Polyurethanes can be used in certain conditions where other materials do not work. Polyurethane is one of the most versatile construction materials that can be formulated for medical device. PLA and TPU are both FDA approved. If PLA was blended successfully with a polymer such as polyurethane, which has soft and elastic properties, then a new composite can be formed that exhibits much greater mechanical properties than pure PLA. In addition, by replacing the bulk of other plasticizer, the usage of TPU as a modifier to PLA will eliminate the concern about the migration of plasticizers.

In this article, TPU was blended with PLA firstly to modify the impact toughness and maintain the high other mechanical strength of PLA for getting the wonderful PLA-based material. The properties of PLA/TPU composite were characterized by means of electron microscopy, rheological, mechanical and thermal methods. These obtained results will be important information on the material design for PLA/TPU blend system, the prediction of the mechanical properties between them and the choice of process method.

EXPERIMENTAL

Materials

With the molecular weight of 180,000 ($MI = 4.2$ g/10 min, 190°C), the PLA used in this study was

commercially available. The thermoplastic poly (ether) urethane (TPU, Shore hardness 65 A) was purchased from SK Chemicals, Korea.

Sample preparation

PLA and TPU pellets had been dried at 65°C for at least 12 h before processing to ensure the removal of any absorbed moisture. Using the Torque Rheometer (Rheocord 300P+Rheomin 600P, Thermo Hakke) at 170°C for 10 min, the composites were prepared by melt mixing of PLA and TPU pellets. All the obtained blends were compression-molded at 180°C under 15 MPa for 3 min into sheets with a thickness of 1-mm and 4-mm, respectively. Then the sample was subsequently cooled at 30°C in another compression-molding machine. The PLA/TPU compositions (w/w) were 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50, and coded as PLA₁₀₀, PLA₉₀, PLA₈₀, PLA₇₀, PLA₆₀, and PLA₅₀, respectively.

Tensile testing

Tensile analyses of PLA films and PLA/TPU composite films were performed by using a Microelectronic Universal Testing Machine (CMT 6104), according to the Chinese Standards GB/T 1040-1992. The specimen was clamped between static and moveable clamps of the CMT 6104. The upper clamp was raised at a 20 mm/min rate until fracture of the film occurred. The tensile strength at break, elongation at break, and Young's modulus were calculated from the load-extension plot. At least five specimens of each sample were tested.

Impact testing

Izod notched impact properties of the composite were measured on an Impact Tester (JJ-20 Memorial Impact Tester) according to the Chinese Standard GB/T 1043-1993 at ambient temperature. The specimens were notched up to prescribed depth, using a mechanical notcher. At least five specimens were tested for each sample material to get an average value.

Dynamic mechanical analysis

Dynamic mechanical properties of the samples were examined in tension mold by a TA instrument dynamic mechanical analyzer (DMA) 2980 on rectangular specimens. The temperature range used in the DMA measurement was from -80 to 150°C at a heating rate of 5°C/min and frequency of 1 Hz. Liquid nitrogen was used to generate low temperature and control temperature during heating.

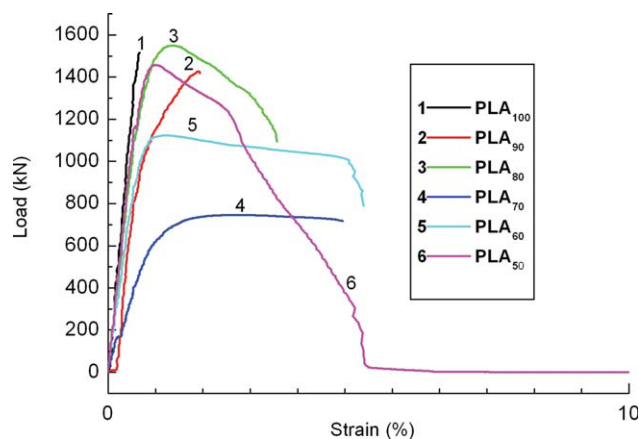


Figure 1 Load–strain plots of pure PLA and PLA/TPU composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal properties

The thermal behavior of the pure PLA and PLA/TPU composites were determined by differential scanning calorimetry (DSC, modulated DSC2910, TA) under nitrogen atmosphere. Five to 10 mg of each of samples were heated from -60 to 180°C at a rate of $10^{\circ}\text{C}/\text{min}$ to eliminate the influence of thermal history at the first run and cooled to -60°C at a rate of $20^{\circ}\text{C}/\text{min}$. The DSC trace from -60 to 200°C was recorded at a rate of $10^{\circ}\text{C}/\text{min}$ during the second run.

Rheological properties

Dynamic melt rheological measurements were carried out using a Rheometer (Haake RS600, Thermo Electron, USA) with parallel plate geometry (diameter of 20 mm and a gap of 1 mm). All measurements were performed at 180°C under nitrogen atmosphere to avoid thermal degradation. The linear viscoelasticity regime was determined with a stress sweep test. Measurements were performed through a frequency sweep test from 0.01 to 650 rad/s.

Scanning electron microscopy

The morphology of the composite was observed by scanning electron microscopy (SEM, JEOL model

JSM-840) at an accelerating voltage of 10 kV. All of the samples were fractured after immersion in liquid nitrogen for about 10 min. The different zones of the specimens after tensile tests, and the fracture surface after impact tests, were also observed using the same SEM apparatus.

RESULTS AND DISCUSSION

Mechanical properties

The load–strain curve of PLA/TPU was shown in Figure 1. The tensile behavior of the PLA matrix was changed significantly with the adding of TPU. Pure PLA was very rigid and brittle with no yielding point and subsequently failed immediately upon the tensile load. The PLA/TPU composites yielded with obvious necking and rugged and irregular surface when the TPU content was over 10%. The load–strain curve presents the yielding point and stress platform of elastic deformation. Fracture behavior of the specimen changed from brittle fracture of pure PLA to ductile fracture of PLA/TPU composites.

The mechanical properties of PLA/TPU composites with different TPU content were shown in Table I. Pure PLA was hard and brittle. The tensile strength was about 37.9 MPa, and the elongation at break was 1%. With the 20% TPU content, the elongation at break was 2.5% and the tensile strength was maintained at 33.9 MPa. The toughness of PLA was increased without sacrificing too much of its original mechanical properties.

With the adding of TPU, the impact strength increased obviously. The impact strength of the pure PLA was $5 \text{ kJ}/\text{m}^2$. As for the 10% TPU content, the impact strength of composite was $15.25 \text{ kJ}/\text{m}^2$. The composite with 10% TPU content had triple the impact strength the pure PLA had. The results from Figure 2 and Table I indicated that TPU could not only improve the toughness of PLA but also keep the tensile strength of PLA. The PLA/TPU composites were possessed of preferable general mechanical properties.

The dynamic mechanical properties of PLA/TPU blend system were also studied. The glass transition

TABLE I
Mechanical Properties of Pure PLA and PLA/TPU Composites

Properties samples	Load at maximum (kN)	Strain at yielding (mm)	Tensile strength (MPa)	Elongation at break (%)	Load at breaking (kN)	Elastic modulus (MPa)
PLA ₁₀₀	1515 ± 78	0	37.9 ± 3.41	1.04 ± 0.15	1515 ± 78	3834 ± 263
PLA ₉₀	1549 ± 102	1.12 ± 0.07	38.7 ± 2.92	1.28 ± 0.22	1532 ± 99	2398 ± 184
PLA ₈₀	1354 ± 53	1.76 ± 0.13	33.8 ± 2.58	2.48 ± 0.20	$1342. \pm 56$	2202 ± 239
PLA ₇₀	1050 ± 35	2.08 ± 0.11	26.2 ± 1.98	3.12 ± 0.18	988 ± 26	1765 ± 126
PLA ₆₀	745 ± 41	3.16 ± 0.09	18.6 ± 1.92	4.60 ± 0.13	717 ± 38	1081 ± 117
PLA ₅₀	574 ± 25	3.40 ± 0.15	14.3 ± 2.02	9.04 ± 0.17	533 ± 23	838 ± 98

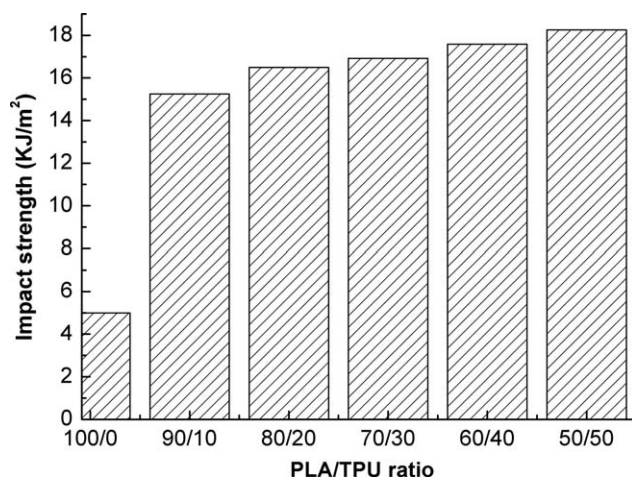


Figure 2 Effect of TPU contents in the composites on the impact strength.

temperature of PLA/TPU blends was determined by DMA, and the loss factor ($\tan \delta$) versus temperature was plotted in Figure 3. There was a glass transition at -48.61°C and -39.50°C . It is clear that this glass transition arises from motions of the soft segments of TPU, because the T_g of PLA is usually around 50 – 60°C and the T_g of TPU hard segments is usually around 100 – 110°C . The blend with a content of 10%

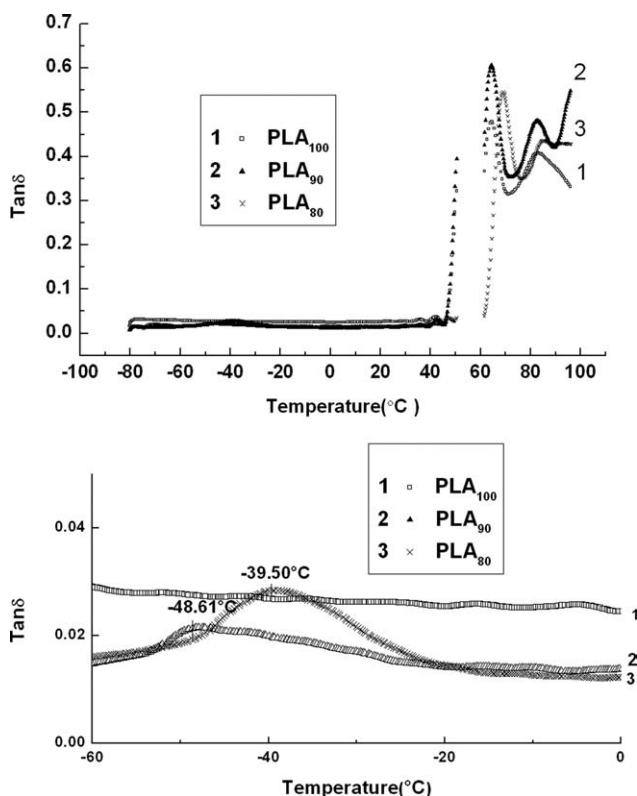


Figure 3 Plot of $\tan \delta$ versus temperature of pure PLA and PLA/TPU composites.

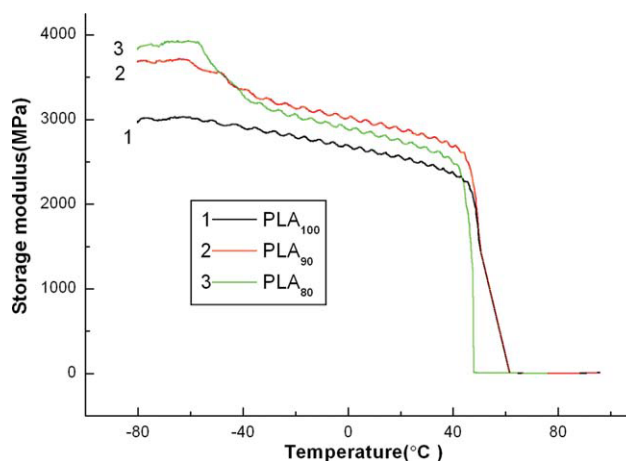


Figure 4 Dynamic mechanical properties of pure PLA and PLA/TPU composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TPU showed a $\tan \delta$ peak at -48.61°C , which was shifted to -39.50°C . As shown in Figure 4, the dynamic storage modulus of PLA/TPU composite or pure PLA decreased with the temperature increasing and increased with the TPU content. As for pure PLA, a peak at 56°C corresponding to the α changes could be observed. The binary blends exhibit two distinct glass transition temperatures corresponding to the PLA-rich and TPU-rich phases, respectively. These peaks approach each other with increasing TPU content, indicating that the PLA/TPU composite was a partially compatible composite. The result was corresponding with Table I. Aforementioned facts provided the evidence that PLA was thermodynamically partially miscible with the soft segments of TPU.

Thermal properties

Table II displayed the thermal properties of PLA/TPU composites. The samples were cooled to -65°C and heated up to 200°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere with a frequency of 1 Hz. All the binary composites exhibited two

TABLE II
Thermal Properties of Pure PLA and PLA/TPU Composites

Sample	T_g , TPU ($^\circ\text{C}$)	T_g , PLA ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH_c (J/g)	ΔH_m (J/g)
PLA ₁₀₀		57.5	128.4	154.3	10.81	21.63
PLA ₉₀	-50.5	57.4	103.9	152.5	15.54	20.42
PLA ₈₀	-48.96	51.9	99.5	151.8	11.98	19.23
PLA ₇₀	-48.91	50.6	115.5	150.8	18.27	19.44
PLA ₆₀	-46.59	49.3	99.2	149.7	12.12	13.79
PLA ₅₀	-45.28	47.7	108.6	148.8	14.12	14.8

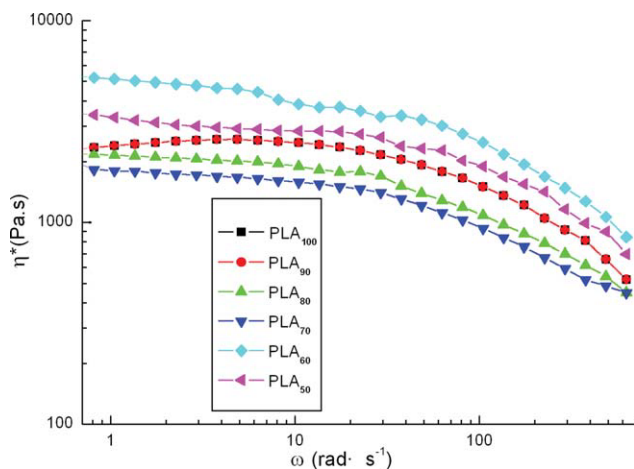


Figure 5 The complex viscosities of pure PLA and PLA/TPU composites versus frequency at the stress of 180 MPa and 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

distinct glass transition temperatures corresponding to the TPU-low and TPU-high phase, respectively. The decreased T_g of the PLA made the PLA molecular chain more flexible in the composite. It was beneficial to the improvement of PLA brittleness. The result was consistent with that of DMA. The heat of melting (ΔH_m) and temperature of melt (T_m) decreased continuously upon increasing TPU elastomer content in the composites, suggesting that the addition of TPU decreased the crystallinity of the PLA. The results could be attributed to the molecular interactions between the PLA and the soft segments of TPU.

Rheological properties

The main processing methods for PLA products were based in melt processing. The melt rheological behavior of the polymer is critical to optimize the process and part quality. To determine the limits of linear viscoelastic properties of the melts, dynamic stress sweep were performed at 180°C and a frequency of 10 rad/s. The linear viscoelastic properties of PLA/TPU melts were conducted at a stress of 100 Pa.

The complex viscosities versus shear rate was plotted in Figure 5 at 180°C. The blend viscosities showed similar trends with the change of composition. Compared with pure PLA, pure TPU had rheological complex behavior, which was due to the phase separation of the soft and hard segments. Figure 5 showed that pure PLA and PLA/TPU composites exhibited pseudoplastic behavior, i.e., all were shear sensitive. The viscosity values among all samples approached each other at high frequencies.

With 10, 20, and 30% TPU blends, there were two phases, which were continuous phase and separation phase. The TPU particles were dispersed in the PLA matrix. The melt viscosity of composites was lower than that of pure PLA due to the functioning of TPU as a plasticizer. It made the large molecular disentanglement and slip. With the 40 and 50% content of TPU composites, both PLA-rich and TPU-rich were in continuous phase. It was interesting to note that the melt viscosity increased and appeared higher than that of PLA. TPU contained the hard segments with rigid and polar molecular chains while PLA was nonpolar polymer. The increase in viscosity was a result of increased interactions between the PLA/TPU molecular and TPU/TPU chains. It was understandable that a large quantity addition of TPU made the emergence of interaction of the hard segments of TPU both inside bulk and at the interface of TPU and PLA.

Between 30 and 40% TPU content composites, the complex viscosity shifted from lower than that of PLA to higher than PLA. Higher viscosities compared with pure component may be desirable in melt processing, e.g., extrusion and blow molding with less sagging.

Miscibility and morphology

As for the sense of touching, PLA scaffolds were hard and brittle while TPU scaffolds were soft and elastic. The SEM images of fracture surface for the pure PLA and PLA/TPU blends were shown in Figure 6. The pure PLA scaffolds possessed a smooth fracture surface as well as sheet-like structure. It was a typical brittle break. TPU was a linear segmented block copolymer composed of alternating hard and soft segments. The hard segments were held together by interchain hydrogen bonds to form physical crosslink. The thermodynamic immiscibility between hard and soft segments resulted in a microphase separation and consequently a multiphase structure. PLA was completely immiscible with the strongly polar hard segments of TPU, it may be partially miscible with the soft segment. For the 90% PLA, 80%, 70%, and 60% PLA composites, samples present two-phase structure. PLA forms a continuous phase and TPU a separated coarse phase, which the diameter of dispersed droplets ranges from 1 to 2 μm . Some of the dispersed phase showed an elongated structure and stress whiten, which could be ascribed to the interfacial tension between hydrophilic polymer and hydrophobic one. For the 50% PLA blends, cocontinuous structure of the binary polymer blend was formed. The increasing roughness of fracture surface and the toughness fracture occurred with

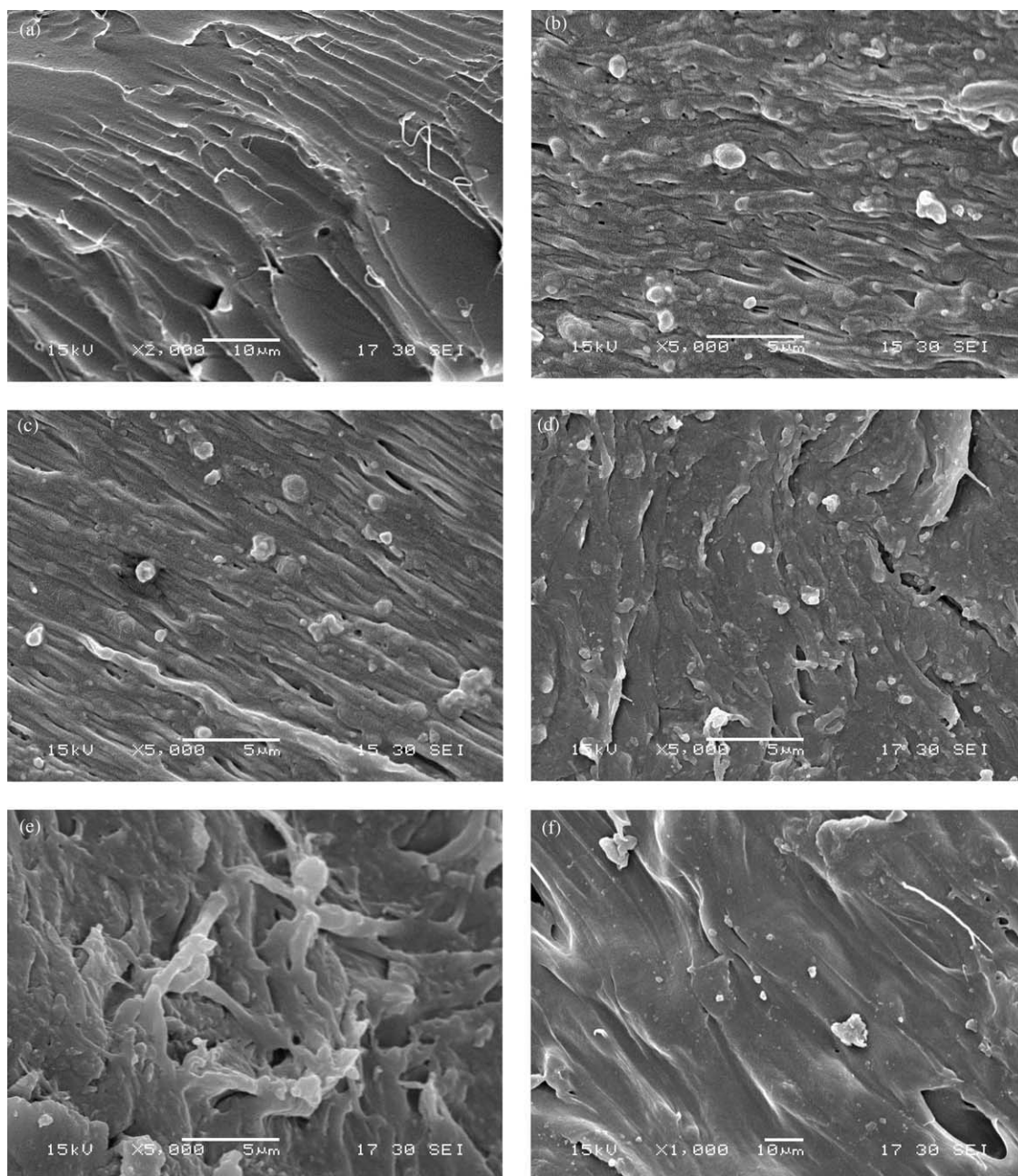


Figure 6 SEM micrographs of the fracture surfaces of pure PLA and PLA/TPU composites with different PLA content: (a) PLA₁₀₀, (b) PLA₉₀, (c) PLA₈₀, (d) PLA₇₀, (e) PLA₆₀, (f) PLA₅₀.

the addition of TPU to PLA revealed that the PLA/TPU composites were partially miscible.

CONCLUSIONS

There were three main conclusions of this study. First, the PLA/TPU composite was a partially miscible system. Second, the adding of TPU to PLA could enhance the impact strength and toughness of PLA without sacrifice necessary mechanical strength. Third, the composite melt was shear-thinning fluid

and it could be processed by conventional thermo-plastic processes such as extrusion and injection molding.

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