Morphologies and Mechanical Properties of Polylactide/Thermoplastic Polyurethane Elastomer Blends

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ABSTRACT: To explore a potential method for improving the toughness of a polylactide (PLA), we used a thermoplastic polyurethane (TPU) elastomer with a high strength and toughness and biocompatibility to prepare PLA/TPU blends suitable for a wide range of applications of PLA as general-purpose plastics. The structure and properties of the PLA/TPU blends were studied in terms of the mechanical and morphological properties. The results indicate that an obvious yield and neck formation was observed for the PLA/TPU blends; this indicated the transition of PLA from brittle fracture to ductile fracture. The elongation at break and notched impact strength for the PLA/20 wt %TPU blend reached 350% and 25 KJ/m^2, respectively, without an obvious drop in the tensile strength. The blends were partially miscible systems because of the hydrogen bonding between the molecules of PLA and TPU. Spherical particles of TPU dispersed homogeneously in the PLA matrix, and the fracture surface presented much roughness. With increasing TPU content, the blends exhibited increasing tough failure. The *J*-integral value of the PLA/TPU blend was much higher than that of the neat PLA; this indicated that the toughened blends had increasing crack initiation resistance and crack propagation resistance. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2778–2783, 2011

Key words: mechanical properties; phase behavior; polymer blends; polyurethanes; structure–property relations

INTRODUCTION

Polylactide (PLA), as a well-known biopolymer, has received much attention recently from both industry and academia for its medical and pharmaceutical applications. Its monomer is derived from renewable resources instead of petroleum, and it possesses a high biocompatibility and a good biodegradability and physical properties.[1] If PLA can be substituted for some general-purpose plastics and a wider range of applications can be realized, this will help to overcome the problem of the increasing scarcity of petroleum.

Generally, PLA has a high strength, but its brittleness, with a very low impact resistance and flexibility, restricts its application as a general-purpose plastic. Considerable efforts have been made to improve the toughness of PLA. The blending of PLA with various polymers is efficient way, and most studies have focused on blends of PLA with aliphatic polyesters, poly(ethylene oxide), polycaprolactone, poly(butyrene succinate), cellulose, poly(3-hydroxyoctanoate), polyethylene, and so on.[2–8] Some of these blends were found to be immiscible, with fairly poor mechanical properties, and some toughening blends led to a noticeable reduction in the strength and modulus. A delicate balance among the modulus, yield/brittle stress, yield/brittle strain, and toughness has to be reached to achieve a system with improved toughness, strength, and modulus.[9]

Thermoplastic polyurethane (TPU) elastomers are widely used in the areas of automobile, electrical, and electronic applications; architecture; and medicine because of their unique combination of high strength, high toughness, durability, flexibility, biocompatibility, and biostability.[10,11] TPUs consist of thermodynamically incompatible hard and soft segments. The soft segments are usually high-molecular-weight (600–4000) polyether or polyester macroglycols with a high flexibility at room temperature; these largely controls the low-temperature properties of TPUs, whereas the hard segments consist of diisocyanate and a low-molecular-weight (60–400) diol (chain extender), which particularly provides the high modulus, hardness, and tear strength of the elastomer.[12]

In this study, TPU was blended with PLA, and the structure and properties of the PLA/TPU blends were studied to improve the toughness and balanced strength of the blends.

EXPERIMENTAL

Materials

The PLA used in this study was a commercial-grade granular product without any additives and was
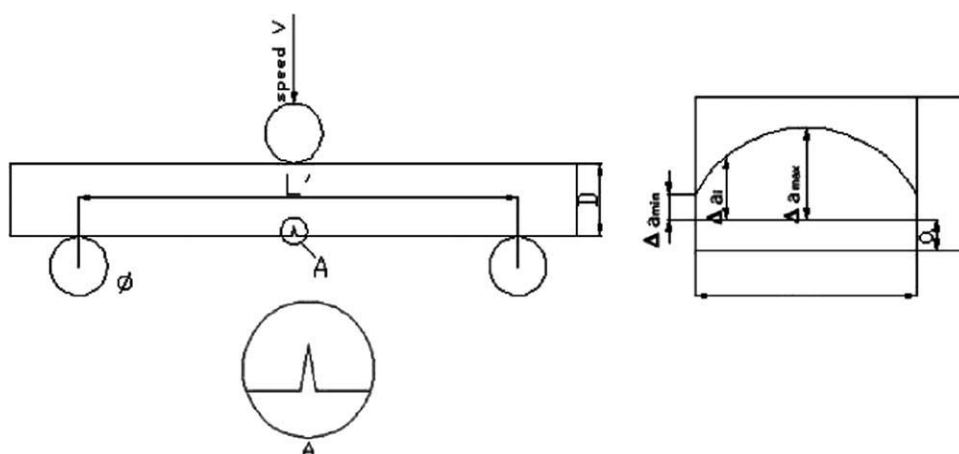
Figure 1 Schematic diagram of the *J* integral test.

supplied by Cargill Dow Co., New York, USA. The number-average molecular weight was about 1×10^5, and the weight ratio of PLA-l to PLA-d was 90/10. TPU, with a number-average molecular weight of 4.7×10^4, was purchased from Wanhua Polyurethane Co., Ltd. (Yantai, China).

Preparation of the PLA/TPU blends

The granules of PLA and TPU were compounded at appropriate proportions by a RC-90 Haake torque rheometer (Karlsruhe, Germany) at a rotational speed of 30 rpm for 5 min. The temperature of the barrel was 170°C. Then, the mixtures were hot-press-molded to form impact and tensile specimens and cooled to room temperature under pressure before they were taken out. The pressing temperature was 175°C, and the pressure was 10 MPa.

Measurement

Mechanical properties

The tensile performance of the samples of the PLA/TPU blends (five samples for each composition) was measured with a 4302 material testing machine from Instron Co., Massachusetts, USA according to ISO527/1-1993. The tensile speed was 5 mm/min, and the sample length between bench marks was 25 mm. The tensile strength for all of the samples was the maximum stress of the tensile stress–strain curves before they were broken.

The *J* integral was measured according to ASTM 1737. The schematic of the three-point bending test samples is shown in Figure 1. The Instron mechanical testing machine was used to perform the measurements at a speed of 2 mm/min.

Dynamic mechanical analysis (DMA)

DMA was performed with a Q800 instrument from TA Co., Delaware (DE), USA. The samples of the PLA/TPU blends with various contents of TPU were measured with a dual-cantilever mode over the temperature range −30 to 150°C at a heating rate of 3°C/min and a frequency of 1 Hz. The sample size was 35 $\times$ 3 $\times$ 0.8 mm³.

Scanning electron microscopy (SEM) analysis

The surface morphology observation of the cryogenically fractured and tensile fracture samples of the PLA/TPU blends was done with a JEOL JSM-5900LV scanning electron microscope (Tokyo, Japan) after the samples were sputter-coated with a thin gold layer. The operating voltage was 20 kV.

RESULTS AND DISCUSSION

Tensile properties of the PLA/TPU blends

In general, the mechanical properties of a polymer can be roughly classified into two categories:
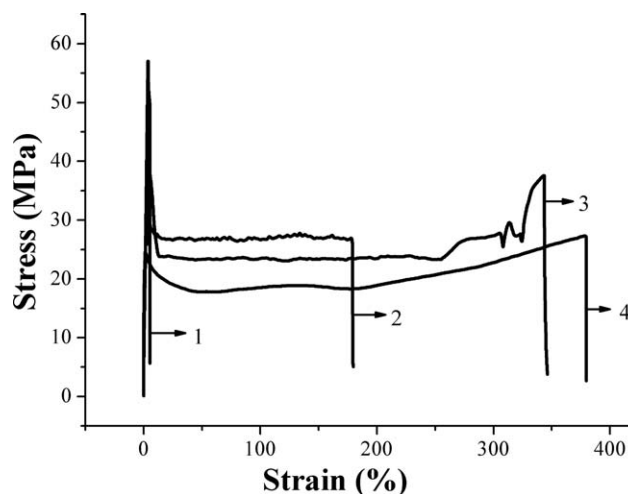

Figure 2 Tensile stress–strain curves of the PLA/TPU blends: (1) PLA/TPU (100/0), (2) PLA/TPU (90/10), (3) PLA/TPU (80/20), and (4) PLA/TPU (70/30).
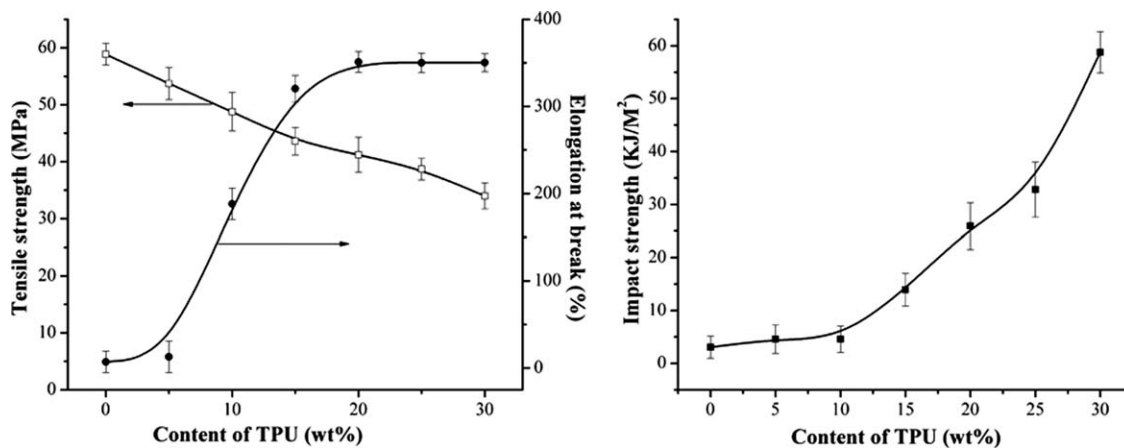
Figure 3 Mechanical properties of the PLA/TPU blends as a function of the TPU content.

strength and toughness. The tensile strength and modulus can be considered material strength, whereas the tensile toughness and impact strength are the material toughness.[9] The tensile stress–strain curves of the PLA blends are shown in Figure 2. The stress–strain behavior of PLA varied dramatically with the addition of TPU. No obvious yield occurred for the neat PLA, which presented a high tensile strength and very poor toughness. However, an obvious yield and neck formation were observed for the PLA/TPU blends. The stress–strain curves of the blends exhibited an elastic deformation stress plateau even in the presence of 10 wt % TPU; this indicated the transition of PLA from brittle fracture to ductile fracture.

The mechanical properties of the PLA/PA blends as a function of TPU content are shown in Figure 3. In the whole range of TPU content, the tensile strength declined slowly with increasing TPU content, and the elongation at break increased rapidly above 5 wt % TPU, which was improved from 5% for neat PLA to 350% for PLA/20 wt %TPU, whereas the tensile strength was still maintained above 40 MPa. The impact strength reached 25 kJ/m^2 for the PLA/20 wt %TPU blend and 58 kJ/m^2 for the PLA/30 wt %TPU blend; this indicated that TPU improved the toughness of the blend without a

significant drop in the tensile strength. For comparison, for the PLA/20 wt % PEO blend, the elongation at break was not more than 200%, whereas its tensile strength was reduced by half to 22 MPa.[13]
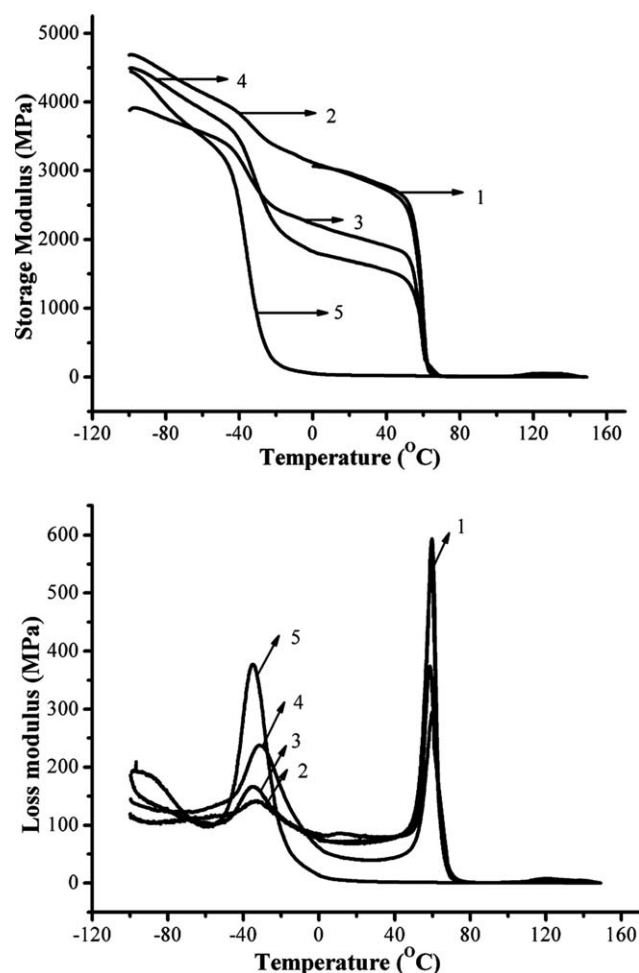

Figure 5 DMA of the PLA/TPU blends as a function of the TPU content: (1) PLA/TPU = 100/0, (2) PLA/TPU = 90/10, (3) PLA/TPU = 80/20, (4) PLA/TPU = 70/30, and (5) PLA/TPU = 0/100.
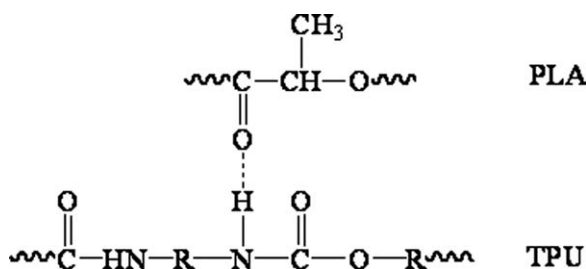

Figure 4 Schematic illustration of hydrogen bonding between the molecules of PLA and TPU.

TABLE I
T_g **Values of the PLA/TPU Blends**

PLA/TPU (wt %)	$T_{g(PLA)}$ (°C)	$T_{g(TPU)}$ (°C)	ΔT_g [$T_{g(PLA)} - T_{g(TPU)}$]
100/0	59.78		
0/100		−35.00	94.78
90/10	59.60	−32.50	92.1
80/20	58.61	−34.03	92.64
70/30	60.04	−31.17	91.21

Dynamic mechanical properties of the PLA/TPU blends

PLA as an aliphatic polyester was compatible with TPU, which was composed of diisocyanate hard segments and polyester macroglycol soft segments, and hydrogen bonding formed between the molecules of the blend, as shown in Figure 4.

Figure 5 displays the storage modulus and loss modulus of the blends as a function of temperature. The storage modulus of the blend decreased with temperature and also decreased with the addition of TPU. E'' is the loss modulus. In principle, E'' can be used to measure the characteristic temperatures matched with various relaxation processes, although a very small quantitative difference is frequently found between the temperature values determined by E'' and the loss factor.[14] In this case, the plots of neat PLA and neat TPU each showed one relaxation peak at 59.78 and −35.0°C, respectively; these were ascribed to the α-relaxation arising from the chain segmental motion of the molecules in the amorphous regions and corresponded to the glass-transition temperature (T_g).[15] In the case of the blends, the DMA plots showed two detectable peaks; these indicated the presence of significant phase separation in the blends at a microscopic level. However, the fact that the two T_g's of the PLA-rich phase and TPU-rich phase in the blends shifted to the inside of their respective original T_g suggested that although the two components were not completely miscible, there existed marked interactions between the molecules of PA and PLA that resulted in a partial miscibility of the two components.

As shown in Table I, the composition ratio of PLA to TPU affected the miscibility of the blends. The T_g peak of TPU shifted toward a higher temperature for the blend with increasing TPU content, and there was a relatively low value of ΔT_g ($T_{g(PLA)} - T_{g(TPU)}$). This suggested that each component of the blend had increasing miscibility.

Morphology and toughening mechanism of the PLA/TPU blends

It is well known that the mechanical properties of blends are strongly dependent on their morphology
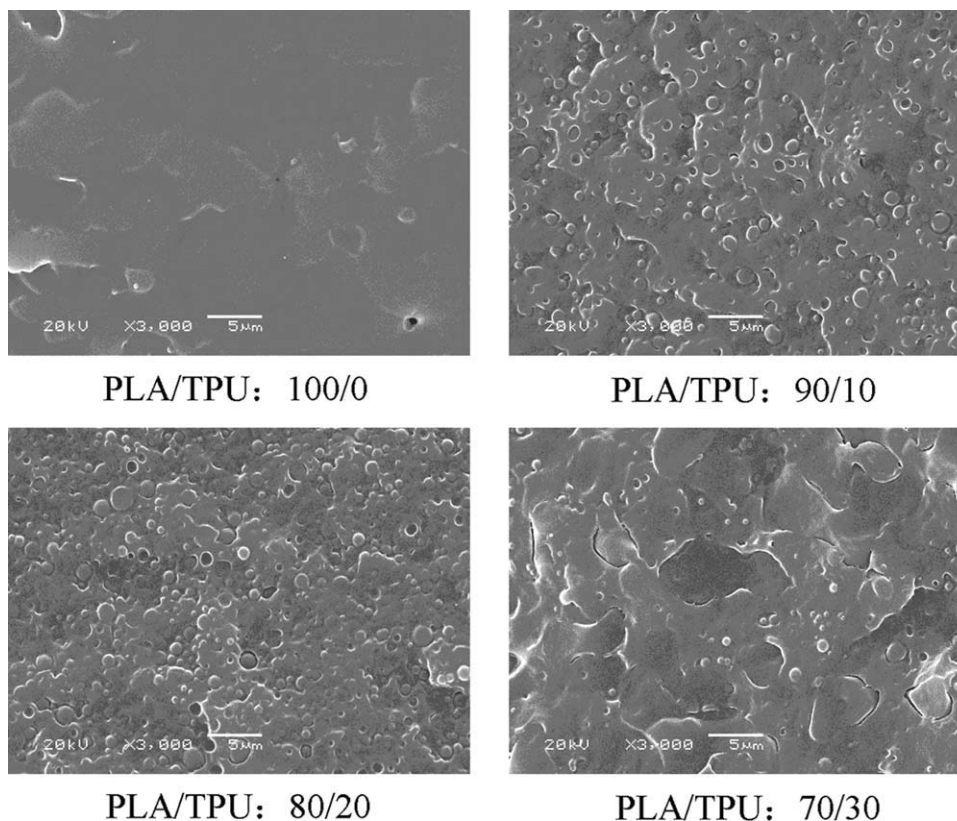

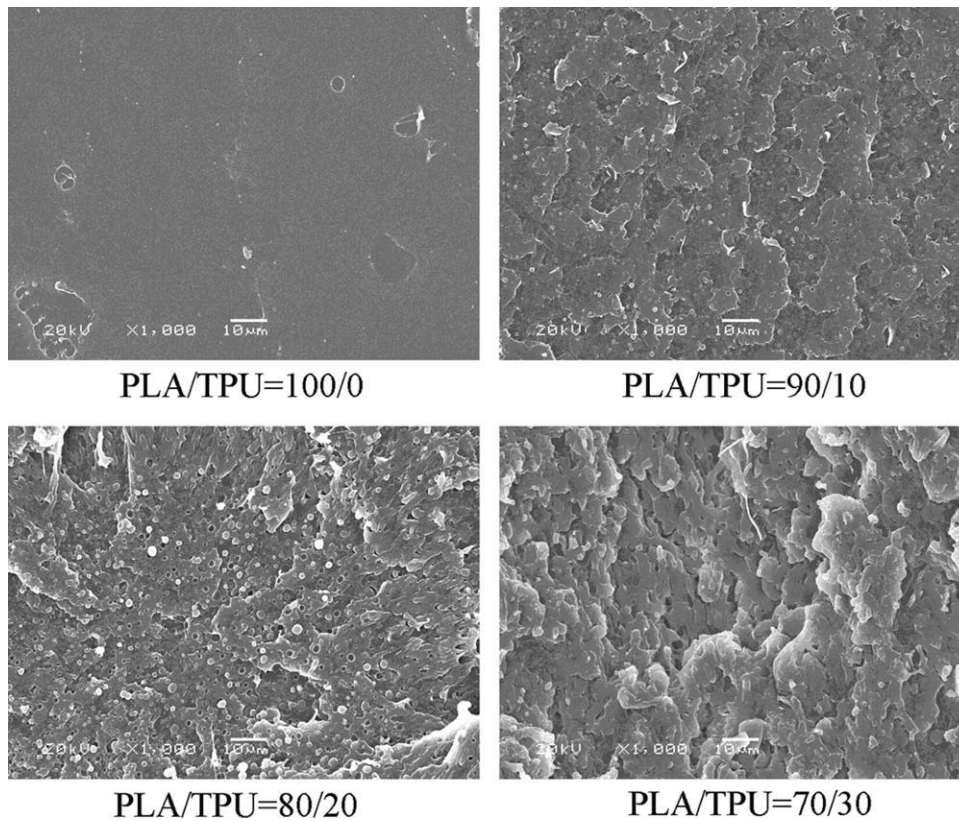**Figure 6** SEM image of the cryogenically fractured surfaces of the PLA/TPU blends (magnification: 3000×).

Figure 7 SEM image of the impact fractured surfaces of the PLA/TPU blends (magnification: 1000×).

and the control of the morphology is of vital importance for the final properties of the product.[16,17]

SEM images of the cryofractured surfaces of the PLA/TPU blends with various content of TPU are shown in Figure 6. Spherical particles of TPU dispersed homogeneously in the PLA matrix. With increasing TPU content, the TPU dispersed particles were more dense. For the blend with 30 wt % TPU, a bicontinuous phase structure was formed; this indicated a good compatibility of the two phase in the blend.

The morphology of the tensile fracture surfaces of the PLA/TPU blends, shown in Figure 7, provided a better understanding of the toughening effect of TPU on PLA. The neat PLA showed a typical brittle fracture, and the fracture surface was very smooth. With the addition of TPU to the PLA matrix, the fracture surface presented much roughness. With increasing TPU content, the blends exhibited increasing tough failure. The dispersed TPU particles, as a large number of stress concentration points in the PLA matrix, initiated crazing and shear banding
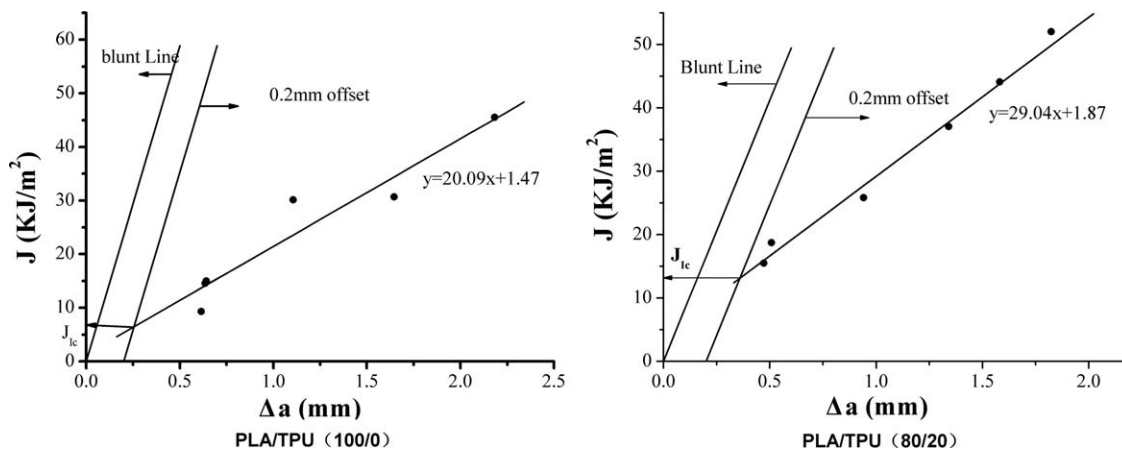

Figure 8 *J* values versus Δα for the PLA/TPU blends.

TABLE II
J_C **Values of the PLA/TPU Blends**

Sample	σ_y (MPa)	E (MPa)	J_C (kJ/m^2)
PLA	58.87	2302.49	6.40
PLA/TPU (80/20 wt %)	41.22	2547.64	13.20

E, elastic modulus

and, thus, absorbed a lot of energy and hindered crack growth under a strong external shock. For 30 wt %TPU, the blend system exhibited a bicontinuous phase structure, better absorbed the impact energy, and delayed the development of crazing and access to more prominent toughness.

The J integral was used to characterize the fracture toughness of the materials and was calculated with the following equation:[17]

$$J = -\frac{2U}{B(W - \alpha)}$$

where U is the input energy to the sample given by the area under the load–displacement curve, B is the thickness of the sample, W is the width of the sample, and α is the crack length.

The calculated J values were plotted against the advanced crack length ($\Delta\alpha$) to obtain a J–$\Delta\alpha$ curve, and the J_C values were determined at the point of intersection between the J–$\Delta\alpha$ curve and the blunting line ($J = 2\sigma_y \times \Delta a$, where σ_y is the yield stress). If $J \geq J_C$, the sample would experience unstable crack growth.

The J–$\Delta\alpha$ curves with a blunting line for the PLA blend system are shown in Figure 8, and the J_C values for all of the samples are listed in Table II. J_C of the PLA/TPU blend was twice that of the neat PLA; this indicated that the toughened blends had a much higher crack initiation resistance and crack propagation resistance. It was evident that the utilization of TPU greatly improved the fracture toughness of PLA.[17]

CONCLUSIONS

To improve the toughness of PLA, PLA/TPU blends were prepared, and their structure and properties were studied in terms of their mechanical and morphological properties. The results indicate that no obvious yield occurred for the neat PLA, and an obvious yield and neck formation was observed for the PLA/TPU blends. The stress–strain curves of the blends exhibited an elastic deformation stress plateau; this indicated the transition of PLA from brittle fracture to ductile fracture. The two T_g's of PLA and TPU in the blends shifted to the inside of their respective original T_g's; this was suggestive of a partially miscible system because of the hydrogen bonding between the molecules of PA and PLA. Spherical particles of TPU dispersed homogeneously in the PLA matrix, and the fracture surface presented much roughness. With increasing TPU content, the blends exhibited increasing tough failure. J_C of the PLA/TPU blend was much higher than that of the neat PLA; this indicated that the toughened blends had an improved crack initiation resistance and crack propagation resistance. It was evident that the use of TPU greatly improved the fracture toughness of PLA.

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