Preparation and Characterization of Biodegradable Polylactide/Thermoplastic Polyurethane Elastomer Blends

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Preparation and Characterization of Biodegradable Polylactide/Thermoplastic Polyurethane Elastomer Blends

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ABSTRACT: The melt blending of polylactide (PLA) and thermoplastic polyurethane (TPU) elastomer was performed in an effort to toughen the PLA. The phase morphology, mechanical properties, and toughening mechanism of the PLA/TPU blends were investigated. The results indicate that the spherical TPU particles dispersed in the PLA matrix, and the uniformity decreased with increasing TPU content. There existed long threads among some TPU droplets in blend with 30 wt % TPU. TPU improved the toughness of the PLA. With 30 wt % TPU, the elongation at break of the blend reached 602.5%, and samples could not be broken in the notched Izod impact tests at room temperature. The matrix ligament thickness of the PLA/TPU blends was below the critical value, and the blends deformed to a large extent because of shear yield caused by debonding, the formation of fibers upon impact; this dissipated a large amount of energy. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3217–3223, 2011

Key words: biodegradable; blends; elastomers; mechanical properties; morphology

INTRODUCTION

As a renewable resource derived from an aliphatic polyester with good biocompatibility and degradability, polylactide (PLA) has been used for biomedical products and is widely considered a potential alternative to conventional petroleum-based materials. However, its inherent brittleness and low toughness severely limit its range of applications. Several modifications, such as copolymerization, plasticization, and blending with other polymers,[1] have been proposed to improve the flexibility of PLA. However, the copolymerization of PLA with other monomers is not economically practical for packing applications. PLA toughened with plasticizers, such as low-molecular-weight poly(propylene glycol)[2] and poly(ethylene glycol) (PEG),[3] has good flexibility and high transparence. However, these plasticizers have a tendency to migrate from the bulk matrix to the surface, which causes the embrittlement of the blends. Hu et al.[4] reported that PLA/PEG blends exhibited aging under ambient conditions because of the slow crystallization of PEG. Therefore, the blending PLA with other polymers may be a more economical and more flexible technique for the property improvement of PLA. Simoes et al.[5] showed that the addition of poly(ε-caprolactone) effectively improved the strain at break but lowered the initial yield stress of PLA at the same time. Zhang et al.[6] succeeded in preparing PLA/poly(butylene adipate-*co*-terephthalate) blends with increased tensile toughness without a severe loss in tensile strength by adding 2 or 5 wt % glycidyl methacrylate. Also, numerous nondegradable polymers, such as polyethylene[7,8] and rubber,[9] have been blended with PLA to improve its toughness. However, among these blends, many had poor comprehensive mechanical properties, reduced biodegradability, or no biocompatibility; these disadvantages limit the applications of these blends.

Thermoplastic polyurethane (TPU) elastomer is an ideal material for medical devices because of its flexibility, abrasion resistance, biocompatibility, and biological stability.[10] TPU is made up of soft segments and hard segments, and the content of the hard segments can be regulated to obtain optimal mechanical properties. On the other hand, TPU has the ability to be compatible with PLA because the soft segment of TPU is mainly composed of polyester or polyether and PLA has been reported to be miscible with some polyesters or polyethers.[11,12] In addition, the hard segment of carbamate in TPU may form hydrogen bonds with PLA; thus, interactions between different phases can be strengthened. Therefore, in this study, PLA was blended with TPU to improve its toughness, and the toughening mechanism of the TPU in the PLA/TPU blends was investigated further.

EXPERIMENTAL

Materials and sample preparation

PLA (grade 2002D, density = 1.24 g/cm^3) was manufactured by Natureworks, Inc. (Burgess, Virginia).

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TPU (grade WHT2190, density = 1.2 g/cm^3) was manufactured by Yantai Polyurethanes Co., Ltd. (Yantai, China). Both PLA and TPU were dried in a vacuum oven at 80°C for 24 h. Dried PLA and TPU were dry-mixed thoroughly and then directly fed into a corotating twin-screw extruder (Ruiya Company, Nanjing, China) with a diameter of 20 mm at a feed rate of 3 kg/h. The screw speed was set at 60 rpm, and the barrel temperatures were set at 160, 175, 180, 180, 180, 180, and 175°C in order. Four PLA/TPU blends with 10, 20, 25, and 30 wt % TPU were prepared. The extruded blend strand was then pelletized after solidification in air. The samples for rheological testing and scanning electron microscopy (SEM) observation were prepared from the melt at the exit of die; this was followed by quenching in ice water. The samples for the former were in the form of 25-mm diameter disks 1.5 mm in thickness. The pellets were dried in a vacuum oven at 80°C for 6 h and then molded into samples for mechanical property testing with an injection-molding machine (KM80SP180CX, Krauss-Maffei GmbH, Munchen, Germany) at a screw speed of 110 rpm. The temperature along the barrel of the injection-molding machine was set at 190, 195, 200, and 200°C. The samples for rheological measurements were dried in a vacuum oven at 80°C for 6 h before use.

Characterization

Rheological measurements were performed on a rotational rheometer (Bohlin Gemini 200HR, Bohlin Ltd., Worcestershire, UK) with 25-mm parallel-plate geometry. All of the data were determined at a frequency range of 0.01–100 rad/s at 180°C. During testing, the given strain was set at 1%, and the plate gap was set at 1 mm.

Tensile tests were carried out according to ISO 527-2:1996 with a tensiTECH electronic tensile tester (Tech Pro Inc., Roseville, Minnesota). The notched impact properties were determined according to ISO 180:2000 with a a pendulum impact tester (Zwick 5113.300, Zwick GmbH, Ulmer, Germany). All of the data are the average from five determinations.

The phase morphology was observed on a Quanta 200 scanning electron microscope (FEI, Eindhoven, Holland). The samples were immersed in liquid nitrogen for 15 min and freeze-fractured into pieces along the extrusion direction. All of the fracture surfaces were sputtered with gold before examination. The droplet diameters of the dispersed phase were measured with Image Pro image analysis software (Media Cybernetics Inc., Silver Spring, Maryland). The mean diameter of a single droplet was calculated by averaging all of the diameters obtained from a rotation of 5° one time with the droplet centroid as the center. The mean droplet diameter (d) and its distribution (σ) were calculated by the following equations:[13,14]

$$\ln d = \frac{\sum_{i=1}^{N} n_i \ln d_i}{\sum_{i=1}^{N} n_i} \quad (1)$$

$$\ln \sigma = \sqrt{\frac{\sum_{i=1}^{N} n_i (\ln d_i - \ln d)^2}{\sum_{i=1}^{N} n_i}} \quad (2)$$

where n_i is the number of droplets whose diameter is d_i in the SEM micrographs, N is the number of all of the droplets in the SEM micrographs, and $\sigma = 1$ for monodispersity and $\sigma > 1$ for polydispersity.

To study the toughening mechanism of the PLA/TPU blends, the Izod-fractured surface of the blend samples was also observed in SEM.

RESULTS AND DISCUSSION

Morphology

Figure 1 represents the SEM micrographs of the fractured surfaces of the PLA/TPU blends with various TPU contents. We observed easily that TPU was dispersed spherically in PLA matrix on a micrometer scale with clear interfaces; this indicated that the PLA was incompatible with TPU. There were not only TPU droplets but also threads between some TPU droplets when the TPU content was 30 wt %, as shown in Figure 1(d). These threads may act as bridges, translating stress from one droplet to another when they were subjected to external force.

The histograms in Figure 2 present the statistical results of the d and σ values in Figure 1. As shown, the mean diameter of TPU particles increased, and its distribution widened gradually with increasing TPU content. The particle size σ values, calculated from eq. (2), were 1.390, 1.486, 1.677, and 1.701 for PLA/TPU blends with 10, 20, 25, and 30 wt % TPU, respectively; this demonstrated the reduced uniformity of TPU particles with increasing TPU content.

Mechanical properties

The stress–strain curves of the PLA/TPU blends are shown in Figure 3. As shown, neat PLA was rigid and brittle, its tensile yield strength was 67.2 MPa, and the elongation at break was only 13%. Moreover, neat PLA showed a distinct yield point, beyond which failure occurred immediately with the tensile load. It was found by some researchers, including Grijpma and Pennings,[15] that cracks are induced and developed in PLA, and these cracks fracture under a relatively high level of stress. The addition of TPU changed the tensile behaviors of

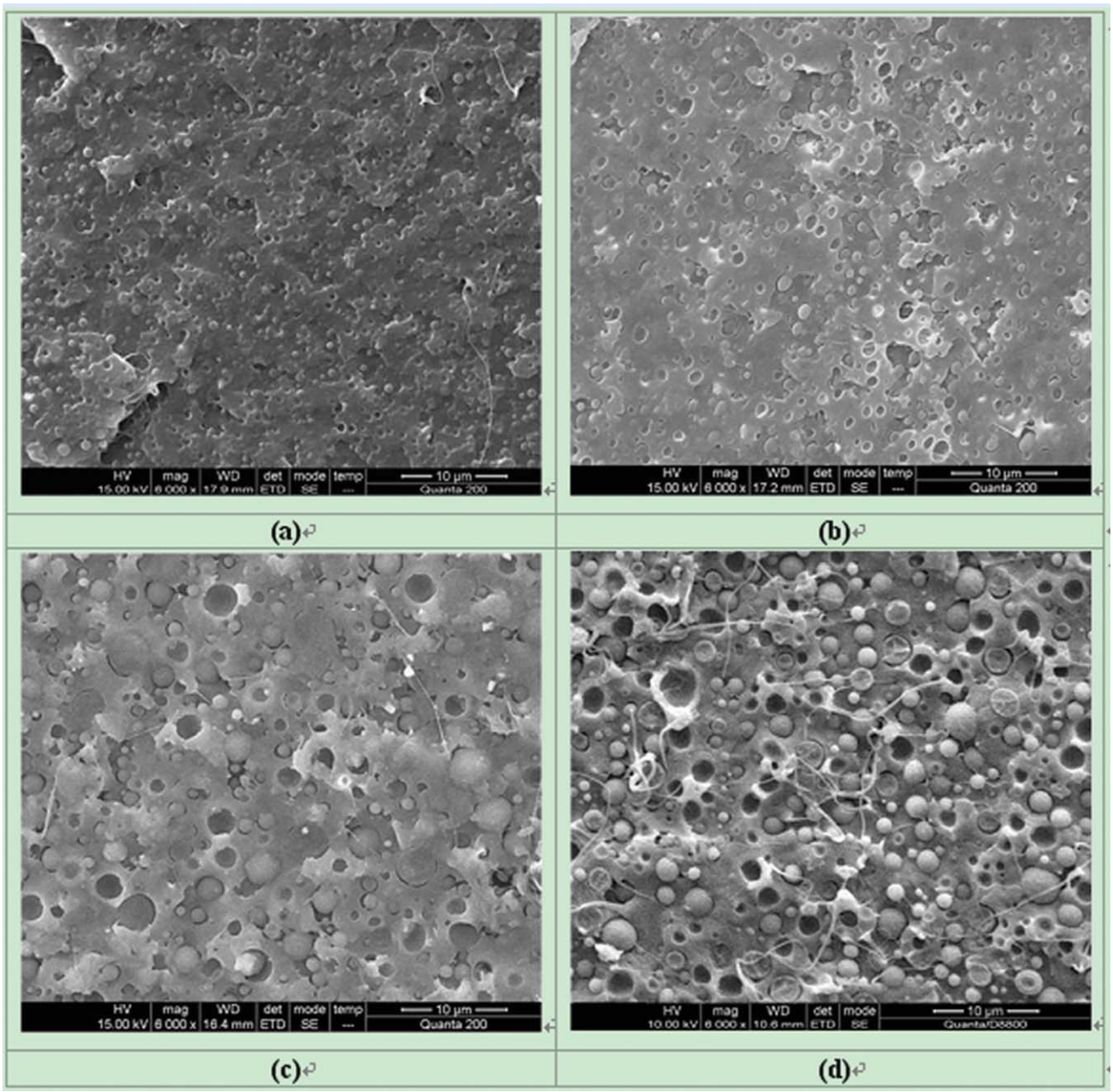

Figure 1 SEM micrographs of the cryofractured surfaces of PLA/TPU blends with (a) 10, (b) 20, (c) 25, and (d) 30 wt % TPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PLA. The continuous development of deformation appeared after yield in all of the blends. The stress–strain curve showed an elastic stress plateau, and the samples eventually showed failure at a larger elongation. As shown in Figure 4(a), the elongation at break of the blends exhibited a small increase upon the addition of 10 wt % TPU and a remarkable increase when the TPU content was further increased to 30 wt %, whereas the yield strength of the blends decreased with increasing TPU content in a nearly linear manner. When the TPU content was 20 wt %, the elongation at break reached 211.7%, and the yield strength was 45.8 MPa; when the TPU content increased to 30 wt %, the elongation at break presented a much greater enhancement, up to 602.5%, whereas the yield strength was 36.8 MPa. The decrease in the yield strength of blends, on the one hand, was caused by the lower yield strength of TPU; on the other hand, the decrease resulted from the absence of strong interactions between the PLA matrix and the TPU droplets; this resulted in interfacial debonding at low tensile stress and subsequent premature yielding.[16] At the same time, as shown in Figure 4(b), the impact strength of the blends was improved with increasing TPU content, especially when the TPU content was 30 wt %. A region

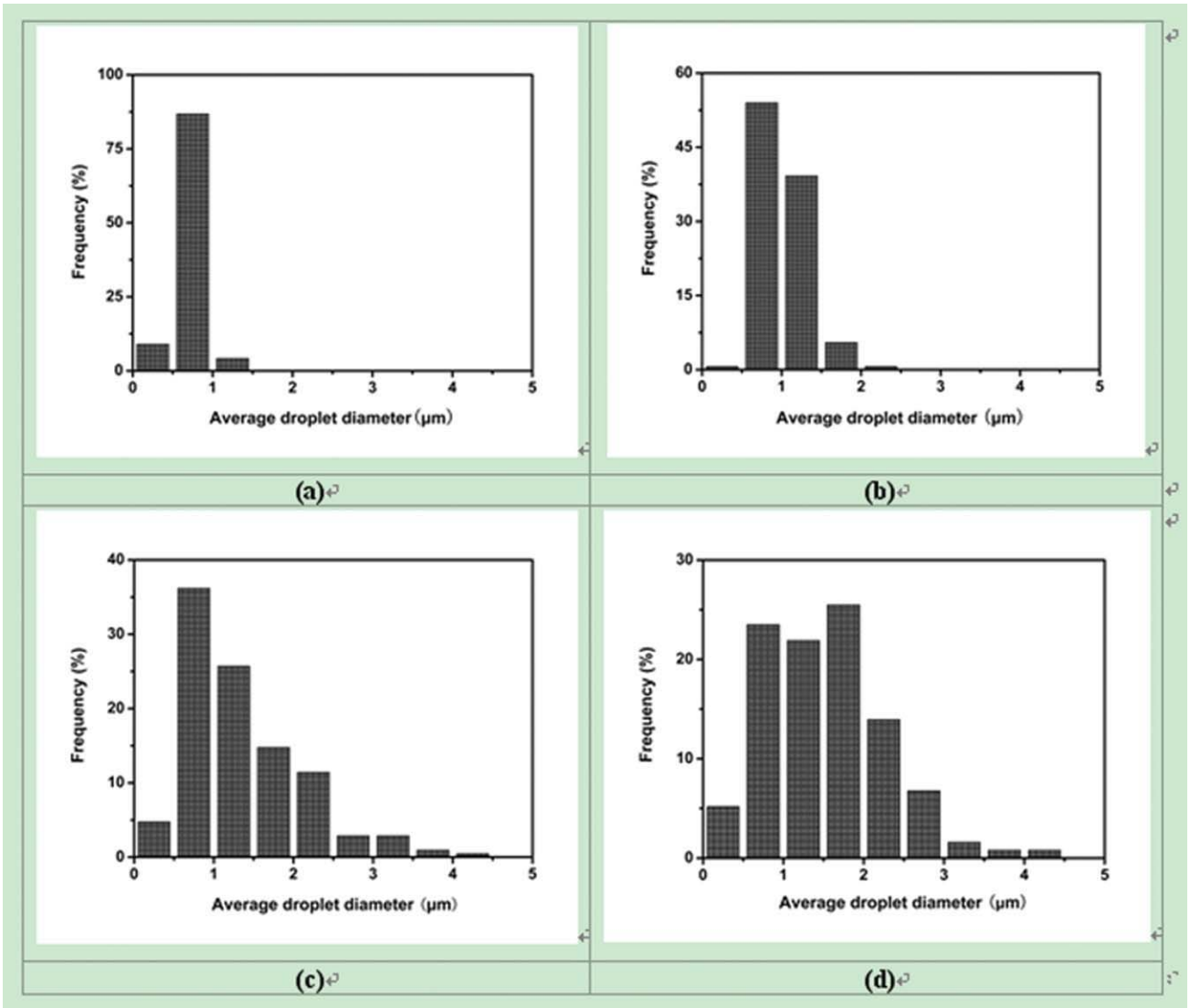

Figure 2 σ values of the PLA/TPU blends with (a) 10, (b) 20, (c) 25, and (d) 30 wt % TPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

approximately 1–2 mm in width was still retained in the sample not broken after impact testing, even with a larger pendulum bob. This phenomenon suggested that the actual fracture impact strength of the blend with 30 wt % TPU would be larger than 40.7 kJ/m^2.

Toughening mechanism

The results of aforementioned tensile and impact tests show that TPU not only maintained a relatively high tensile yield strength of PLA but also effectively improved its toughness, especially for the PLA/TPU blend with 30 wt % TPU. The toughening mechanism of TPU in the PLA/TPU blends was analyzed from the following three aspects. First, stress whitening through cold drawing was observed for all of the PLA/TPU blends. A stress-whitening

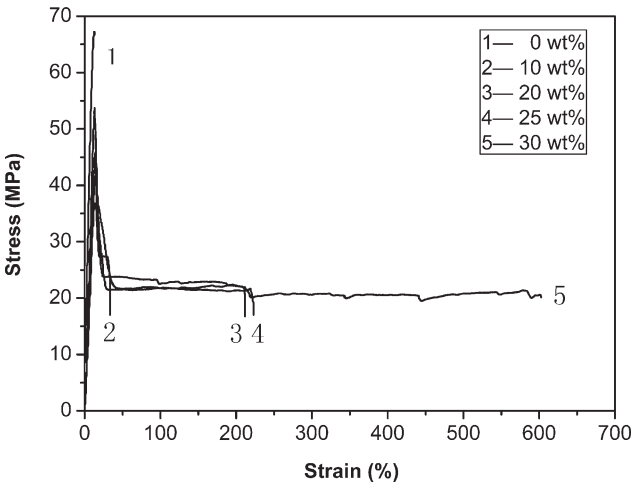

Figure 3 Stress–strain curves of PLA/TPU blends with different TPU contents.

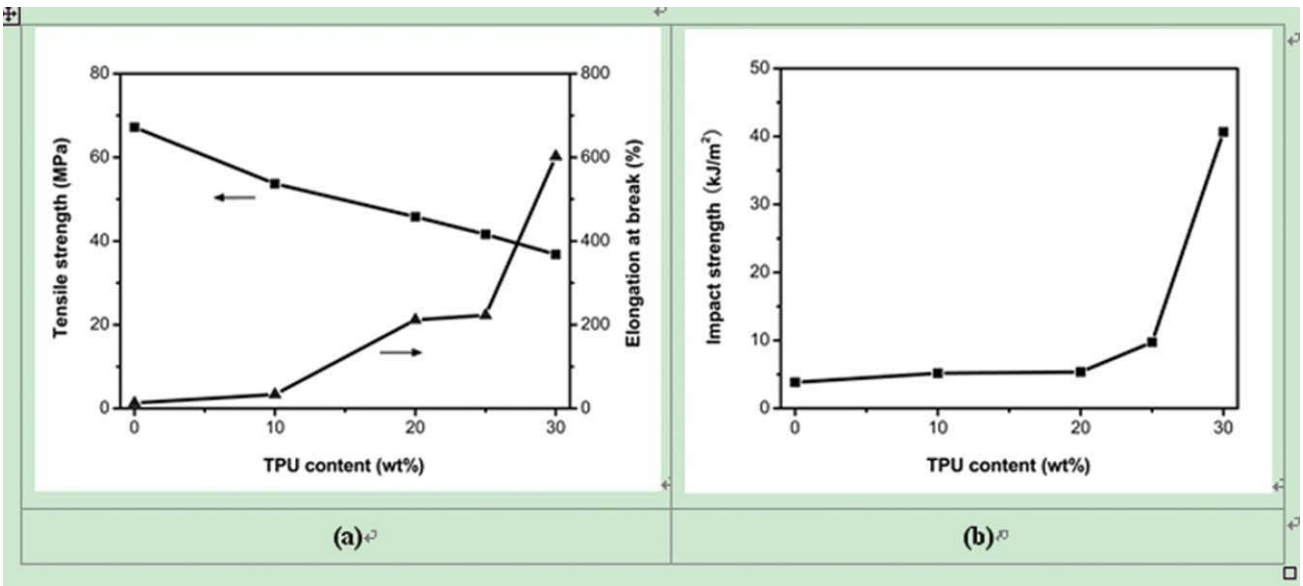

Figure 4 (a) Tensile properties and (b) impact strength of the PLA/TPU blends as a function of the TPU content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phenomenon is induced by a large amount of crazes in materials, and crazing is a dilative process and involves localized plastic deformation.[17] So the stress whitening of the PLA/TPU blends demonstrated that the toughness of PLA was improved. Second, the thickness of the matrix ligament was used to explain the improvement in toughness of PLA. Wu[18,19] suggested that the thickness of the matrix ligament is the primary controlling factor for rubber toughening in polymer blends. The *matrix ligament thickness* is defined as the surface-to-surface interparticle distance. Wu stated that if the average matrix ligament thickness is smaller than the critical value, the blend will be tough; if it is larger than the critical value, the blend will be brittle. Wu also stated that the critical matrix ligament thickness is independent of rubber volume fraction and particle size but is dependent on the intrinsic properties of the matrix. Anderson et al.[8] reported that the critical matrix ligament thickness was approximately 1.0 μm for PLA/linear low-density polyethylene blends. The following equation[13] was used to calculate the matrix ligament thickness for the PLA/TPU blends prepared in this study:

$$T = d\left[\left(\frac{\pi}{6\phi}\right)^{1/3}\exp(1.5\ln^2\sigma) - \exp(0.5\ln^2\sigma)\right] \quad (3)$$

where T is the matrix ligament thickness and ϕ is the volume fraction of the dispersed phase. In this study, the ϕ values were 0.103, 0.205, 0.256, and 0.307 and the d values were 0.480, 0.710, 1.172, and 1.351 μm for PLA/TPU blends with 10, 20, 25, and 30 wt % TPU. When both ϕ and d were combined with the aforementioned values of σ, the matrix ligament thicknesses for blends with 10, 20, 25, and 30 wt % TPU were 0.465, 0.460, 0.881, and 0.909 μm, respectively. The obvious increase in the matrix ligament thickness with 25 and 30 wt % TPU contents may have been caused by larger sizes of droplets and the increased distribution, as shown in Figure 1. Nevertheless, the values of the matrix ligament thickness for all of the blends were smaller than the critical matrix ligament thickness of PLA (1.0 μm), as reported by Anderson et al.[8] This provides a potential explanation for the tough behavior of the PLA/TPU blends prepared in this study. Because of the thinner PLA matrix ligament thickness, a plane-strain to plane-stress transition occurred; the ligament yielded because of shear, and the blends were tough during impact testing.[19]

Third, the phase morphology of different regions on the fractured surface of the impacted blend sample with 30 wt % TPU content was investigated with SEM. The zone that was not broken in impact testing was fractured along the impact direction in liquid nitrogen. The results are shown in Figure 5. Crazing and shear yielding are known to be two main mechanisms of impact toughening in rubber-modified polymer blends at ambient temperature. As shown in Figure 5, both the TPU domains and PLA matrix exhibited obvious deformation, so shear yielding was more predominant than crazing. The different locations in Figure 5 represent the different deformation states of the process of shear yield. During impact testing, cracks were easily induced because of the stress concentration near the notch where the sample started to fracture immediately without large yielding, as shown in Figure 5(a); this illustrated the

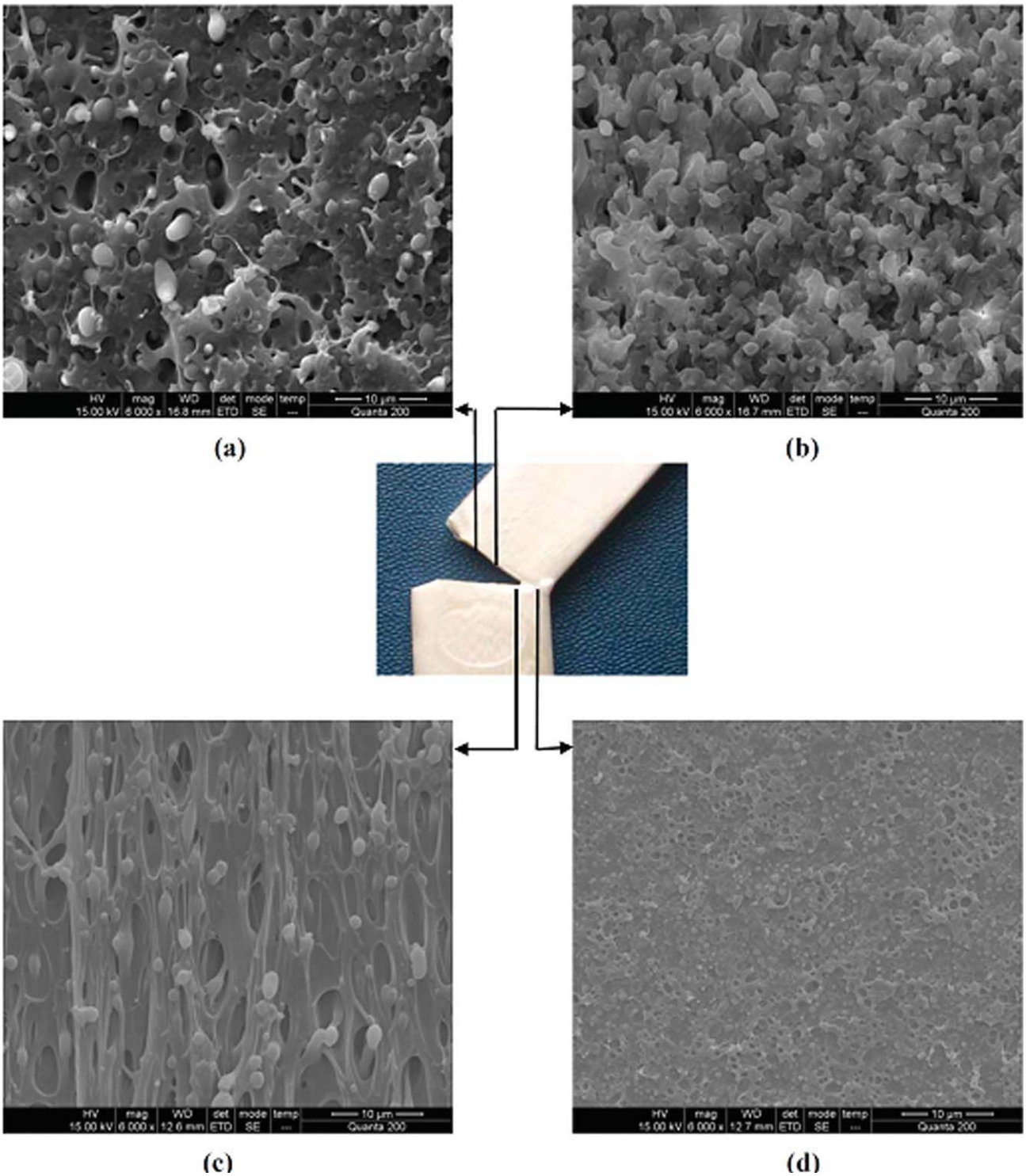

Figure 5 SEM micrographs taken from different regions on the Izod-fractured surface of the blend sample with 30 wt % TPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

morphology of the initial stage of shear yielding; that is, the voids around the TPU particles and some TPU particles exhibited small deformation and tended to be pulled out of the PLA matrix. This can be explained as follows. As a rubber-toughened polymer blend, the phase separation mentioned previously indicated insufficiently strong interactions between the TPU domains and PLA matrix. When the hydrostatic stresses were released, debonding was easily induced on the interfaces between the TPU domains and PLA matrix;[20–22] this resulted in voids around the TPU particles, as displayed in

Figure 5(a). When debonding took place, the triaxial stress in the TPU particles, which acted as stress concentrators, was locally released in the surrounding voids, and shear yielding of the matrix was allowed. Then, the stress was applied to the TPU particles, and it elongated them. As debonding continued, the PLA matrix between the TPU particles deformed more easily, and shear yielding occurred,[20] going with the further deformation of the TPU particles and the development and coalescence of some voids, as shown in Figure 5(b). This process dissipated a great deal of energy. The fibers and elongated cavities shown in Figure 5(c) resulted from the large deformation of the PLA matrix, which was caused by the shear yielding of the matrix. This deformation was enlarged by the stretching effect of the upper region of the sample suffering impact to the fixed region; this was caused by the flexure of the sample along the impact direction. In addition, we believe that the separation of some particles from the matrix, shown in Figure 5(c), during the impact testing facilitated the plastic deformation of the matrix, which was reflected in a decreased yield stress.[23] Figure 5(d) shows the morphology of the freeze-fractured surface in the unfractured region of the impact tested sample. There may have been two reasons that the region was not fractured by impact energy. The first one was that most of applied impact energy was dissipated, and there was not enough impact energy to destroy the blend sample. The second one was that the structure of matrix shown in Figure 5(d) resulted from a slight yield deformation of the PLA matrix upon stress without the stretching effect of the region impacted by the pendulum, and this structure transferred stress and dissipated energy effectively, which induced a favorable toughening effect.

CONCLUSIONS

PLA/TPU blends with improved toughness were prepared by melt blending. The morphology of blends with different TPU contents showed that PLA was incompatible with TPU and the uniformity of the TPU particles dispersed in the PLA matrix decreased with increasing TPU content. The blend with 30 wt % TPU possessed unfractured bars after impact testing at room temperature and exhibited a much higher value of elongation at break in comparison with neat PLA. The toughening mechanism was analyzed through three aspects, including the stress whitening, matrix ligament thickness, and observation of the fracture surface of the impacted sample. The results reveal that a large-extent shear yielding occurred in the PLA matrix. The shear yielding was initiated by stress concentrations and interfacial debonding; these led to the formation of fibers in the both tensile and impact samples.

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