

Compatibility improvement of poly(lactic acid)/thermoplastic polyurethane blends with 3-aminopropyl triethoxysilane

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ABSTRACT: Poly(lactic acid) (PLA)/thermoplastic polyurethane (TPU) blends were prepared via a melt-blending process with or without the addition of a 3-aminopropyl triethoxysilane (APTES) compatibilizer at different dosages. The addition of the compatibilizer showed improved compatibility between TPU and PLA; this led to an enhanced dispersion of TPU within the PLA matrix. With the addition of 1-phr APTES, the crystallization behavior did not vary much, but this exacerbated the formation of a second melting temperature for PLA at higher temperature. However, the addition of 5-phr APTES into the PLA/TPU blends depressed the crystallization temperature and resulted in a melting temperature depression phenomena with the disappearance of the second melting peak because of the lubricated effect of low-molecular-weight species of APTES. The addition of a low dosage of APTES improved the impact strength further from 29.2 ± 1.4 to 40.7 ± 2.7 J/m but with a limited improvement in the tensile properties; this indicated that a higher dispersion of the dispersed phase did not always improve all of the mechanical properties because of the low-molecular-weight nature of the compatibilizer used. The physical properties of the added modifier needed to be considered as well. A low dosage of APTES (1 phr) also increased the viscosity because of the improved interaction between TPU and PLA at all of the investigated shear rate regions, but a higher dosage of compatibilizer induced another plasticizing effect to reduce the viscosity. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42322.

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INTRODUCTION

Because of the growing concern about sustainable development and the environment, green processes with biobased materials as raw material sources have received much attention. In particular, a green manufacturing process, such as a melt-blending process, is in general considered an environmentally friendly process without the use of too much solvent, and it has a cost-competitive advantage. As for biobased materials, to reduce the environmental impact, poly(lactic acid) (PLA), obtained from lactide polymerization via the fermentation of the sugar feedstock, such as corn, has been widely used in some biomedical and environmental applications, such as bone screws, because of its biocompatibility, nontoxicity, and biodegradability.¹ However, because of its inherent low extensibility, many attempts to alleviate this problem through the preparation of derived blends have been on the rise to further expand the applications of PLA.^{2–10}

It is generally recognized that a small particle size is required to effectively promote toughness. Liu and Zhang¹¹ conducted an

extensive review on the recent research progress in the toughening modification of PLA. Choudhary *et al.*¹² included a maleic-grafted polypropylene compatibilizer to improve the compatibility between PLA and polypropylene and enhance their mechanical properties. Several researchers^{13,14} have used functionalized polyethylene–octene elastomer to increase the impact strength of PLA. Recently, we¹⁵ also reported the use of an ethylene–glycidyl methacrylate random copolymer as a compatibilizer via a melt-blending process to enhance the interfacial interaction for PLA/polyethylene–octene elastomer blends. Takayama and Todo¹⁶ pointed out that the addition of lysine triisocyanate improved the miscibility between PLA and polycaprolactone and the size reduction of spherulites to improve their impact strength. Zhang *et al.*¹⁷ used glycidyl methacrylate as a reactive processing agent to improve the compatibility between PLA and poly(butylene adipate-co-terephthalate). Feng and Ye,¹⁸ Hong *et al.*,¹⁹ and Li and Shimizu²⁰ independently indicated that thermoplastic polyurethane (TPU) showed good compatibility with PLA because of its hydrogen bonding without using a compatibilizer.

There have been numerous studies focusing on the applications of compatibilizers in compatibilized blends or composites. However, there has been limited work noting that this compatibilizer may also be detrimental to the final properties, even though it improves the interfacial interaction between the matrix and dispersed phase. For example, Szazdi *et al.*²¹ pointed out that high exfoliation did not guarantee high strength in layered silicate nanocomposites if polypropylene-*g*-maleic anhydride with a low molecular weight was used as a compatibilizer in the PP/clay nanocomposites. Our recent work on styrene-ethylene-butylene-styrene block copolymer/clay nanocomposites, with styrene-ethylene-butylene-styrene block copolymer grafted maleic anhydride and polypropylene-*g*-maleic anhydride to improve clay dispersion, also justified that interesting finding.^{22,23} It was suggested that the compatibilizer properties attributed to this unexpected decrement in the mechanical properties, even for the attained highly dispersed phases within the matrix through the help of a compatibilizer. In this study, we mainly attempted to further address the importance of the matrix properties and/or interfacial interaction through the addition of aminosilane compatibilizer into PLA/TPU blends. The amine group on silane was expected to interact with the urethane group of TPU, and the silanol group on partially hydrolyzed silane would interact with the carboxyl/hydroxyl group on PLA. Of course, other specific interactions, such as the amine group with the carboxyl/hydroxyl groups, were also plausible. To our best knowledge, there is no available literature that discusses this compatibilizer contribution for PLA/TPU blends, even though some studies have suggested a good interaction between PLA and TPU without the use of a compatibilizer.^{18–20} In particular, few studies have reported that a small molecule, such as diisocyanate, could serve as a compatibilizer to improve the compatibility between TPU and PLA.⁹ In this study, low-molecular-weight 3-aminopropyl triethoxysilane (APTES) at 1 and 5 phr was used to further improve the dispersion of TPU within the PLA matrix, and the effects of aminosilane on the thermal, mechanical, and flow properties are discussed. However, we found that at a higher dosage, this enhancement in the mechanical properties did not further improve because of the low-molecular-weight nature of APTES. This is generally considered to be detrimental to some properties in some cases. Thus, even the good dispersion of TPU within the PLA matrix was still observed at high dosage of APTES (5 phr); however, its role in improving the mechanical properties was not feasible. This study further justified the significance of the compatibilizer properties and a suitable dosage of low-molecular-weight compatibilizer for this biobased PLA/TPU blend.

EXPERIMENTAL

Materials

The materials used in this study were PLA and TPU. PLA (4032D) was supplied from NatureWorks LLC. The density was 1.24 g/cm³. TPU (Desmopan, KU2-8785) was supplied from Bayer Taiwan Co., Ltd. The silane coupling agent (APTES) obtained from Acros was used as a compatibilizer.

Sample Preparation

All pristine resins were predried at 80°C for 4 h in a vacuum oven before mixing. The mixing of PLA and TPU at a composi-

tion ratio of 70/30 was conducted in a Brabender internal mixer (815605, Plastograph) under 50 rpm at 170°C for 10 min. The processing conditions were based on the process temperature above the melting temperature of TPU in a general mixing condition to reach an equilibrium torque in a mixer for a typical toughened blend with compromised stiffness. Of course, other compositions and different processing conditions would be worth studying to meet different applications. Furthermore, 1- or 5-phr APTES compatibilizer was added to the PLA/TPU blends to form compatibilized blends. The prepared PLA/TPU batch was hot-pressed to form a specimen about 1 mm thick at 180°C for about 3 min.

Measurements

Structural Characterization. An X-ray diffractometer (Rigaku Corp., Ultima IV) operating at 40 kV and 20 mA was used to observe the crystalline behaviors of the prepared blends. Cu K α radiation at a wavelength of 1.54 Å was used for the scanned range from 10 to 50° at a rate of 2°/min.

Morphological Characterization. A scanning electron microscope (Tescan, 5136 MM) was used to observe the cryofractured surfaces morphology of the samples, which were sputtered with gold before characterization. Transmission electron microscopy (TEM) was used to evaluate the dispersion of the neat TPU within the PLA matrix. TEM observations were performed on ultrathin sections of cryomicrotomed thin films with a Hitachi H-7100 with an acceleration voltage of 75 kV.

Thermal Characterization. The thermal behaviors of the samples were characterized with a differential scanning calorimeter (TA Instrument, Q10). First, all of the test samples were heated to 250°C at a heating rate of 20°C/min to eliminate the thermal history and were then cooled to 0°C at a cooling rate of 10°C/min to record the crystallization temperatures; this was followed by a second heating to 250°C at the same heating rate of 20°C/min to record the melting temperatures and cold crystallization temperatures. The crystallinity (X_c) of PLA was determined by the following equation:

$$X_c = (\text{Melting enthalpy} - \text{Enthalpy of cold crystallization}) / \text{Weight fraction of PLA in the blend}$$

The specific melting enthalpy of 100% crystalline PLA was taken as 93 J/g.^{24,25} The glass-transition temperature (T_g) values and dynamic properties were determined with a dynamic mechanical analyzer (PerkinElmer) under three-point bending mode with a deformation amplitude of 20 μ m at a frequency of 1 Hz at a heating rate of 3°C/min from -80 to 160°C.

Mechanical and Rheological Properties. Tensile measurements were conducted on the basis of ASTM D 638 with a gauge length of 25 mm at a crosshead speed of 10 mm/min with a universal tensile tester (Instron 4469). The tensile strength, elongation at break, and Young's modulus were recorded. The impact test was conducted with an impact tester (Gotech, GT-7045-1). Rheological measurements were carried out at 180°C with a TA AR2000 instrument to determine the dynamic storage modulus against the strain with angular frequencies from 0.1 to 100 rad/s at a linear strain of 2%. The viscosity against shear rates ranging from 0.1 to 10 s⁻¹ was determined.

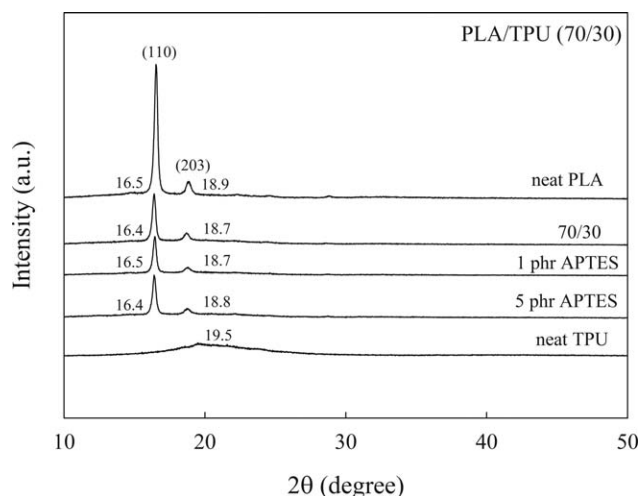


Figure 1. X-ray diffraction patterns of the PLA/TPU (70/30) blends.

RESULTS AND DISCUSSION

The effects of added APTES compatibilizer was compared between 1- and 5-phr-loaded cases, including those on the structural characterization, morphology observation, thermal properties, mechanical properties, and rheological analyses.

Crystal Structure Characterization (X-ray Diffraction)

The X-ray diffraction technique was used to evaluate the effect of TPU blending with PLA with or without the addition of compatibilizer on the formation of PLA crystalline forms. The results are shown in Figure 1. Major diffraction peaks around 2θ at 16.5 and 18.9° were observed for α -form crystal planes at (110) and (203), respectively, for PLA.²⁶ Neat TPU showed a broad amorphous halo around 2θ at 19.5°. The diffraction patterns of the PLA/TPU blends did not vary much with the addition of TPU and the added compatibilizer; this indicated a limited change in the crystalline structure. A more elaborate evaluation of the variation of crystalline structures were examined with differential scanning calorimetry analysis.

Morphological Observations

Figure 2 shows the scanning electron microscopy (SEM) micrographs of the noncompatibilized and compatibilized PLA/TPU blends. Figure 2(a) displays the cryofractured surface of the neat PLA/TPU blend; this revealed visible TPU domains dispersed in the PLA matrix in a few micrometer dimensions. This suggested a limited interaction between PLA and TPU, even though some studies have suggested a good interaction between PLA and TPU without the use of a compatibilizer.^{18–20} Perhaps, the various types of PLA and TPU are essential for their specific interaction as well. In particular, few studies have reported that a small molecule, such as diisocyanate, could serve as a compatibilizer to improve the compatibility between TPU and PLA.⁹ In this study, with the addition of APTES compatibilizer (1 and 5 phr), as shown in Figure 2(b,c), the interphase between the TPU domains and PLA matrix boundary became vague; this suggested an improved compatibility between TPU and PLA and led to an enhanced dispersion of TPU within the PLA matrix. Apparently, the interaction of APTES with TPU and PLA was quite helpful in reducing the surface energy and stabilizing the

TPU domains within the PLA matrix. The amine group on silane was expected to interact with the urethane group of TPU, and the silanol group on the partially hydrolyzed silane interacted with the carboxyl/hydroxyl group on PLA. To our best knowledge, there is no available literature that discusses this compatibilizer contribution for PLA/TPU blends. In addition to SEM investigations, TEM observation was performed further to reveal the phase morphology of the dispersed TPU within the PLA matrix with or without compatibilizer, as shown in Figure 3. The low and high magnifications of the representative images are displayed for ease of comparison. Interestingly, Figure 3(a–d) clearly shows the phase separation of the PLA/TPU blend (adapted from our other recent work on shape-memory blends²⁷). Although PLA and TPU elastomers are organic materials in nature, the incompatibility due to the chemical structure and viscosity difference resulted in this observed phase contrast in the TEM morphology as seen for polypropylene/polyethylene elastomer blends.²⁸ An increased compatibility between PLA and TPU was found with the addition of the APTES compatibilizer (1 and 5 phr) on a significant decrease in the TPU domain sizes to a few hundred nanometers, as shown Figure 3(b,c,e,f). The results were in line with previous observations from SEM morphology. Figure 4 illustrates the possible molecular mechanism for the compatibilization effect of the aminosilane. The amine group on silane was expected to interact with the urethane group of TPU, and the silanol group on the partially hydrolyzed silane interacted with the carboxyl/hydroxyl groups on PLA. Of course, other specific interactions, such as the amine group with the carboxyl/hydroxyl groups, were also plausible. However, the detailed mechanism requires a further in-depth study. In addition, the later discussion on the 5-phr-loaded compatibilized showed a deterioration in some mechanical properties; thus, a 1-phr-loaded compatibilized case was suggested as a suitable dosage to contrast the significance of the dispersion of TPU.

Thermal Characterization

The crystallization behaviors for PLA and its TPU blends with or without compatibilizer under cooling conditions are shown in Figure 5(a). The T_g value of PLA was about 62.4°C, and it remained largely unchanged with the addition of TPU. In addition, the PLA/TPU blend exhibited a crystallization temperature (T_c) at 80.6°C. However, the crystallization temperature of TPU was about 82.2°C. Thus, the crystallization peak of the PLA/TPU blend was attributed to the contribution of the TPU component. With the addition of 1-phr APTES, the crystallization behavior did not vary much. However, the addition of 5-phr APTES into the PLA/TPU blend depressed the crystallization temperature because of the lubricated molecular motion of the PLA/TPU blend with the help of a high dosage of APTES. Most likely, for higher amounts of APTES, the tendency to take part in the PLA matrix was expected because of the higher amount of PLA as a matrix to encapsulate the TPU domains. In addition, the low-molecular-weight species normally tended to be in the continuous phase because of large difference in the viscosity ratio for the molten polymer and low-molecular-weight molecules.²⁹

To further investigate the melting behaviors of the cooled samples, Figure 5(b) delineates a detailed comparison. For the neat

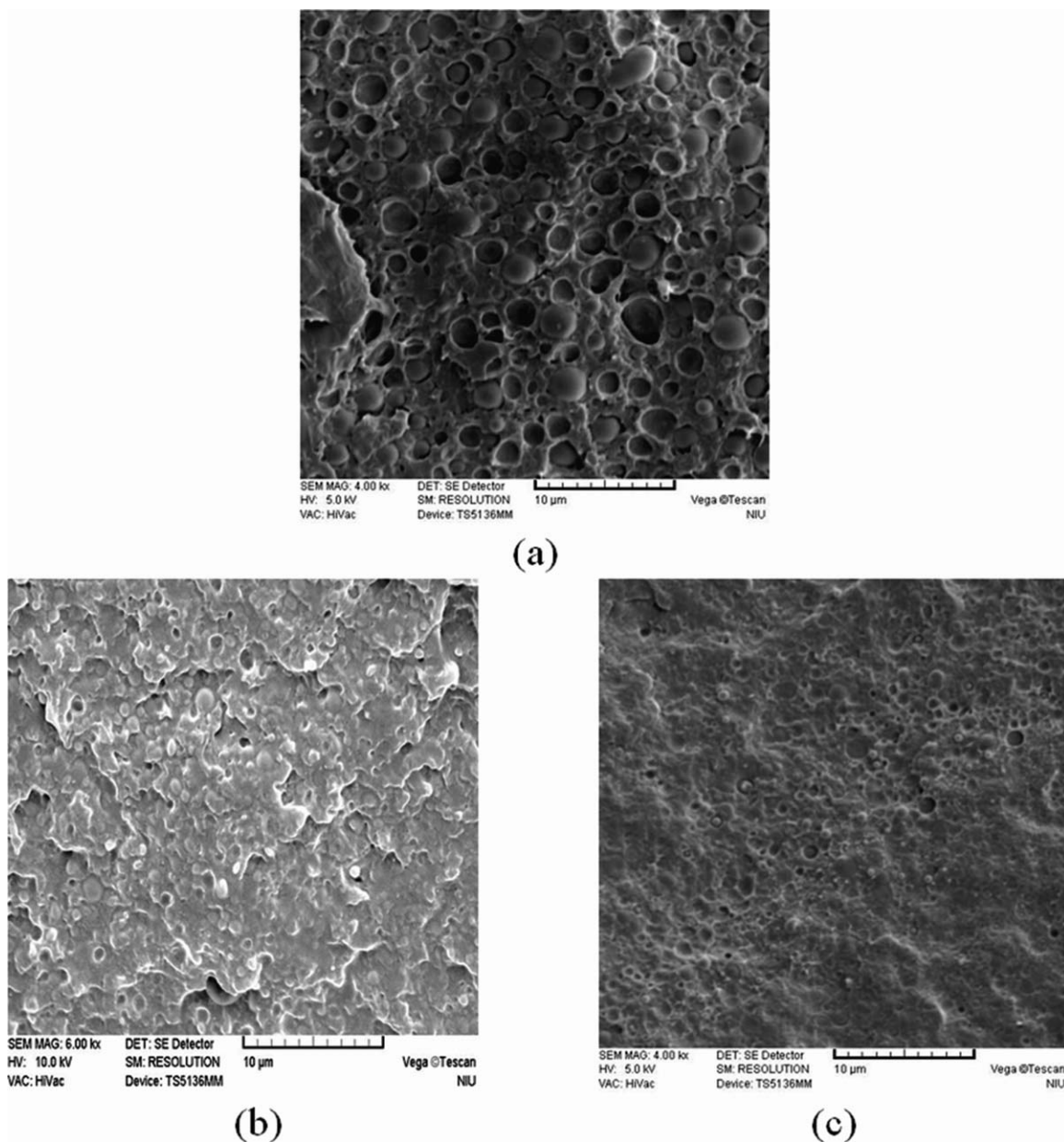


Figure 2. SEM micrographs of the PLA/TPU (70/30) blends: (a) 0-, (b) 1-, and (c) 5-phr APTES compatibilized blends (scale bar = 10 μm).

PLA sample, there was a cold crystallization peak around 120.5°C; this was followed by a major melting peak near 164.4°C (T_{m1}). With the addition of TPU, an additional minor shoulder peak at 167.7°C (T_{m2} ; second melting temperature) was observed. A similar cold crystallization phenomenon and two melting processes were also observed in the literature.³⁰ A lower dosage of APTES exacerbated the formation of T_{m2} . However, for the APTES compatibilized blend at high APTES content, the T_{m2} disappeared. This observed melting temperature depression phenomena with the disappearance of the T_{m2} was attributed to the lubricated effect of low-molecular-weight species of APTES. As for X_c of PLA, the neat PLA did not show much X_c (0.9%) under the prescribed cooling conditions. Only a small increase in X_c was observed for the PLA/TPU blend

(2.9%), 1-phr case (3.2%), and 5-phr case (1.9%), respectively. The variation was within the experimental error.

The viscoelastic behaviors of the PLA/TPU blends with or without compatibilizer were investigated with a dynamic mechanical analyzer. The storage modulus of the PLA/TPU blends is depicted in Figure 6(a). For better comparison, the results for the neat resins are also displayed, where PLA and TPU gave the highest and lowest values because of their plastic and elastomer natures, respectively. The dynamic storage modulus of the PLA/TPU blends with or without modification did not vary much and generally followed the general trend for viscoelastic polymers, except some unusual increase near 100°C due to the cold crystallization phenomena. Figure 6(b) shows the $\tan \delta$ values

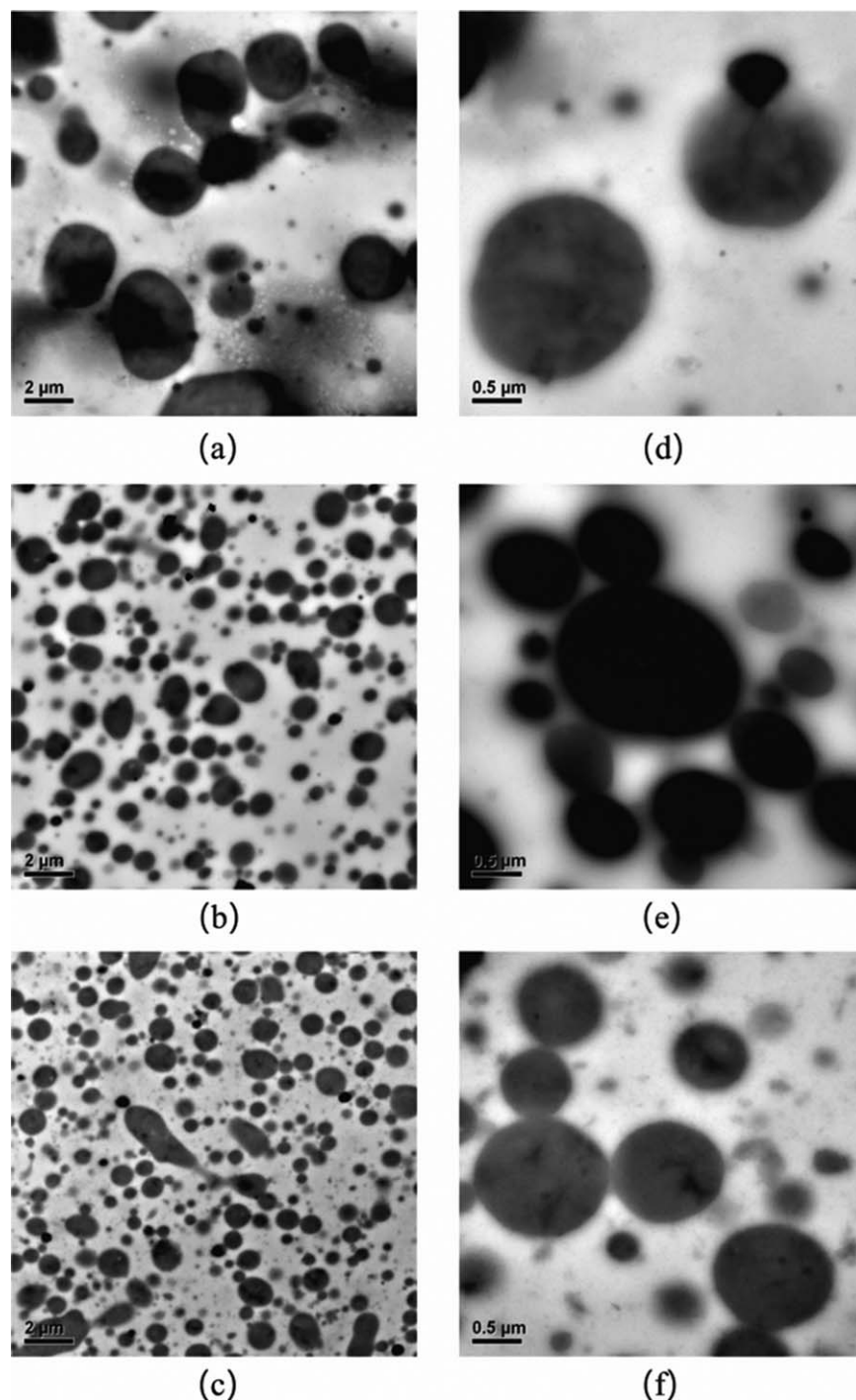


Figure 3. TEM micrographs of the compatibilized PLA/TPU (70/30) blends: (a) 0, (b) 1, and (c) 5 phr (scale bar = 2 μm) and (d) 0, (e) 1, and (f) 5 phr (scale bar = 0.5 μm).

of the PLA/TPU blends with or without compatibilizer. The difference in the T_g values for PLA and TPU was about 100.2°C. The value did not vary much at 98.7°C for the APTES (5 phr) compatibilized blend. Because of the small variation in T_g for dynamic mechanical analysis tests, the variation was considered to be within the experimental error. Even though the limited variation on the compatibility from the variation of T_g , the morphological section did indicate an improved compatibility,

which was helpful in supporting later discussion on the mechanical and rheological properties. In addition to the peak positions, it was worth noticing an increased peak intensity in the T_g range for the PLA/TPU blend; this indicated an increased dissipation process. This increment justified the higher impact strength of the PLA/TPU blend discussed later. In addition, the 1-phr-compatibilized case conferred the further increase in the peak intensity with a slightly broader peak width; this suggested

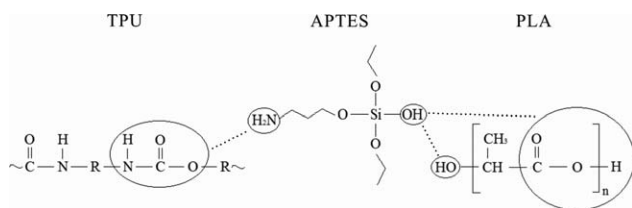


Figure 4. Possible molecular mechanism for the compatibilization effect of the aminosilane.

a higher dissipation as well. However, the further increase in the peak intensity was not found for the 5-phr-compatible case, and in fact, that was similar to the peak shape of the neat PLA. Interestingly, those observations were closely related to the impact strength discussed later. A similar correlation between the dissipation peak height and sample toughness was also reported in the literature for PLA modified with plasticized clay.³¹

Mechanical Properties

As discussed earlier in the SEM and TEM morphology, there was a certain degree of improved interfacial interaction between PLA and TPU for the APTES-compatible systems. It was worthwhile to see how the added modifier affected the mechanical properties of the investigated blends. The results of tensile and impact properties are shown in Table I. The addition of elastomeric TPU within the brittle PLA matrix significantly increased the impact strength of PLA by more than threefold. A corresponding decrement in the tensile strength and Young's modulus and an increase in the elongation at break were found for the tensile properties. To further elucidate the effect of the compatibilizer on the tensile properties of the blends, the Young's modulus of the PLA/TPU blend only slightly increased with the addition of 1-phr APTES, even though a dramatic difference in the morphological observation was observed. In addition, the tensile strength and elongation at break remained largely unchanged. However, the addition of APTES improved the impact strength further from 29.2 ± 1.4 to 40.7 ± 2.7 J/m; this was attributed to the higher dissipation process, as discussed

in the viscoelastic properties and the higher dispersion of elastomeric TPU. In balancing the impact strength and tensile properties, we noticed that a higher dispersion of the dispersed phase did not always improve all of the mechanical properties because of the low-molecular-weight nature of the compatibilizer used. The physical properties of the added modifiers needed to be considered as well. To confirm this finding in our case, a higher dosage at 5-phr compatibilizer was added to evaluate the mechanical properties again. Table I shows unexpected decreases in the elongation at break and impact strength. A small decrement in the tensile strength was also observed, especially with the consideration that high amounts of low-molecular-weight species as the defects or flaws were rather important in determining these mechanical properties. This was also manifested in the difference in the improvement of the impact strength of the PLA/TPU blends for a suitable dosage of compatibilizer in the 1-phr-loaded case over 5-phr-loaded case, as shown in Table I. This agreed with our previous findings on the importance of the compatibilizer properties for styrene-ethylene-butylene-styrene copolymer/clay nanocomposites^{22,23} and other literature work, which also indicated that a high exfoliation extent could not guarantee a high strength for layered silicate nanocomposites, as demonstrated by polypropylene (PP)/clay nanocomposites with polypropylene-*g*-maleic anhydride as a compatibilizer because of the deterioration in the physical properties of low-molecular-weight polypropylene-*g*-maleic anhydride.²¹ Apparently, the physical properties of the added modifiers should be considered as well. Later examination of the rheological properties also demonstrated this finding.

Rheological Properties

Basically, for a melt-blending process to prepare compatibilized blends, it is essential to generate enough shear stress to break up the dispersed domains. This is also facilitated by the addition of compatibilizer or coupling agent to improve dispersion. To gain further insight into this melt-blending process in terms of rheological behaviors, the rheological properties of the PLA/TPU blends, including the dynamic viscoelastic properties and steady shear viscosity, were determined (Figures 7 and 8). As

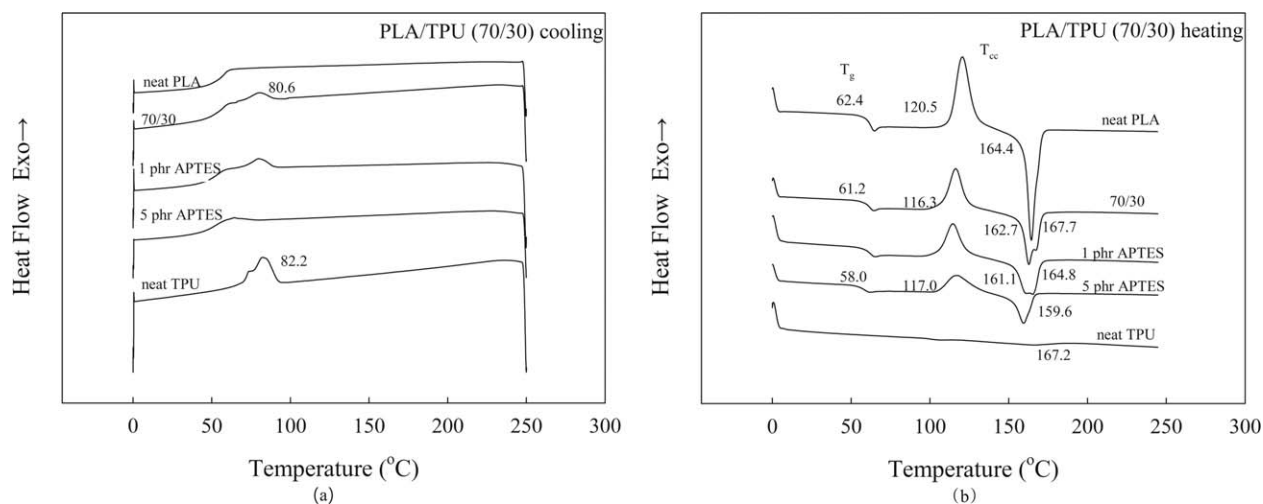


Figure 5. Differential scanning calorimetry curves of the PLA/TPU blends: (a) cooling and (b) heating. T_{cc} , cold crystallization temperature.

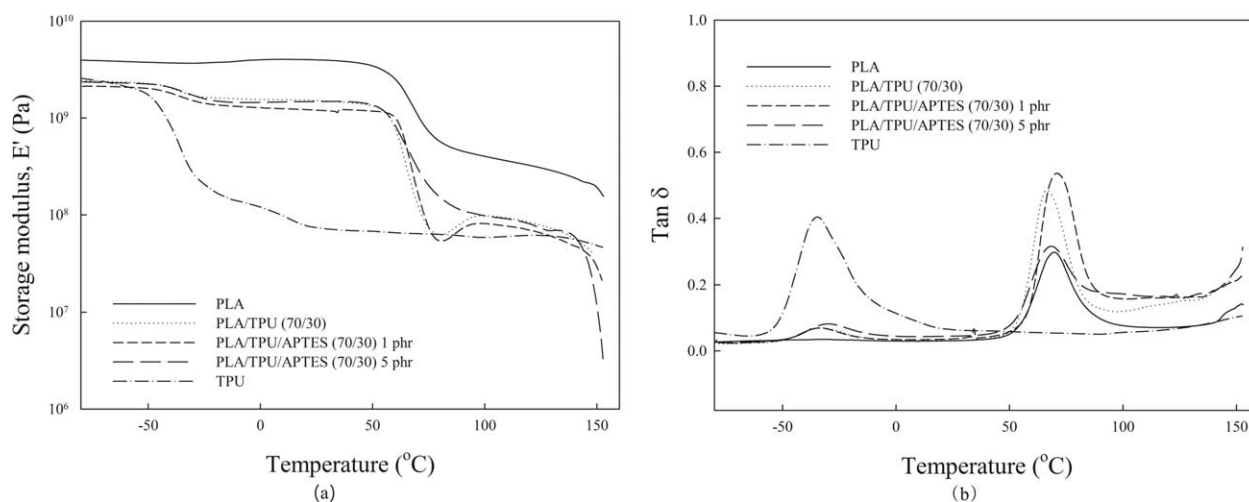


Figure 6. Viscoelastic properties of the PLA/TPU (70/30) blends: (a) storage modulus (E') and (b) $\tan \delta$.

shown in Figure 7, the dynamic storage modulus was plotted against the angular frequency. As normally observed in the viscoelastic behaviors of polymeric fluids, the dynamic storage modulus increased with increasing frequency in all of the investigated cases. TPU with the highest resistance of flow gave the highest dynamic storage modulus. For the PLA/TPU blends, the dynamic storage modulus decreased because of the contribution of the PLA matrix with lower dynamic storage modulus in the investigated frequencies. With the addition of APTES (1 phr), the enhanced dynamic storage modulus was observed; this indicated a higher compatibility, as shown in the morphology section. On the other hand, at high dosages of APTES, the compatibilized blend gave a slightly lower dynamic storage modulus than the neat blend. This peculiar observation was mainly due to the high amounts of APTES with low-molecular-weight nature to offset the positive improvement on the dynamic shear modulus, as shown in the 1-phr-compatibilized blend. However, because both 1- and 5-phr-loaded systems showed a similar morphology, the higher dosage of APTES appeared to be the dominant factor to this observed decrement in the dynamic storage modulus. Apparently, APTES played an important role in reducing the flow resistance, as discussed in the viscosity section later.

To further investigate the rheological behaviors of the PLA and TPU blends, the shear viscosity of the blends with or without APTES modifier is shown in Figure 8. The high viscosity of TPU tended to increase the viscosity of PLA at various shear rates. In addition, the viscosity of the PLA/TPU blends slightly decreased with increasing shear rate as a result of the combined effects from both neat PLA exhibiting polyester nature with Newtonian behavior and neat TPU possessing elastic nature with shear sensitive behavior. On the other hand, a low dosage of APTES (1 phr) increased the viscosity because of improved interaction between TPU and PLA at all of the investigated shear rate regions. With the addition of a higher amount of APTES compatibilizer (5 phr), the viscosity of the compatibilized blend surprisingly decreased because of the low molecular weight of APTES, as mentioned previously in the discussion of the dynamical storage modulus, even though it was originally thought that the improved compatibility between PLA and TPU via a specific interaction increased the viscosity of compatibilized blend further. This result indicates that the plasticizing effect at higher APTES dosages dominated the viscosity of the compatibilized blend in this study. Control tests on both the PLA/APTES (5 phr) and TPU/APTES (5 phr) blends also showed a decrement in the viscosity to justify the observed

Table I. Mechanical Properties of the PLA/TPU Blends

Sample code	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Impact strength (J/m)
PLA	57.8 ± 6.2	7 ± 2	1249.6 ± 139.3	8.1 ± 0.3
TPU	49.4 ± 7.1	1436 ± 172	11.4 ± 0.6	NB
PLA/TPU (70/30)	31.8 ± 1.6	134 ± 50	751.8 ± 152.2	29.2 ± 1.4
PLA/TPU/APTES (70/30) (1 phr)	32.9 ± 1.0	120 ± 57	838.7 ± 32.5	40.7 ± 2.7
PLA/TPU/APTES (70/30) (5 phr)	25.8 ± 1.2	6 ± 1	892.4 ± 4.9	9.5 ± 2.5

NB, no break.

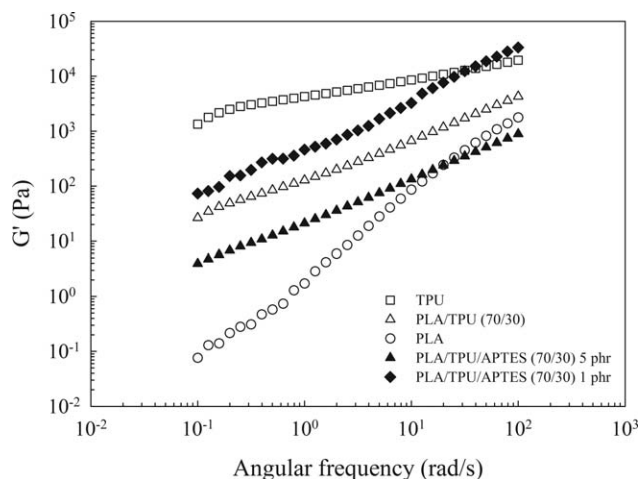


Figure 7. Dynamic storage modulus (G') of the PLA/TPU (70/30) blends in the melt state.

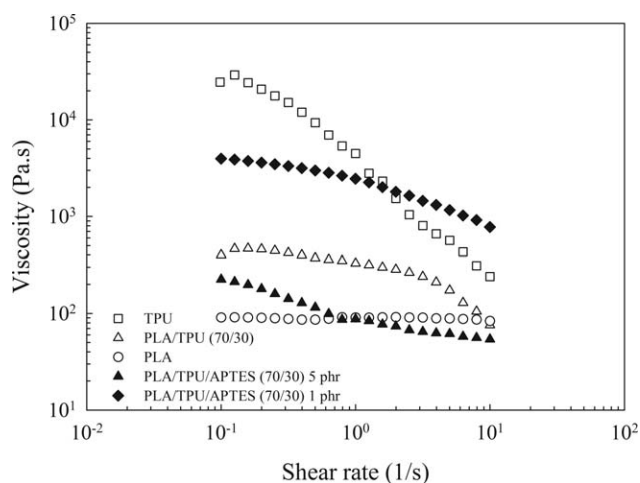


Figure 8. Viscosity of the PLA/TPU (70/30) blends.

viscosity decrement for the compatibilized blends (not shown here for brevity). Thus, higher amounts of compatibilizer, especially for the low-molecular-weight type, may have induced another plasticizing effect to reduce the viscosity. With the help of the rheological properties, a suitable dosage of compatibilizer could be elucidated to balance the required thermal and mechanical properties.

CONCLUSIONS

The physical and thermal properties of the PLA/TPU blends prepared through a melt-blending process were investigated with APTES as a compatibilizer to enhance their interfacial interaction. Recent literature has indicated a good compatibility between PLA and TPU without the need for a compatibilizer. Here, we used the novel compatibilizer to further improve their compatibility; this led to an enhanced dispersion of TPU with the PLA matrix. The addition of a high dosage of APTES into the PLA/TPU blends depressed the crystallization temperature because of the hindered molecular motion of PLA through the increased interaction between TPU and PLA and the melting temperature depres-

sion phenomena due to the plasticizing effect of low-molecular-weight species of APTES. A low dosage of APTES (1 phr) increased the viscosity because of the improved interaction between TPU and PLA at all of the investigated shear rate regions. A suitable dosage of compatibilizer was thus justified, and the physical properties of the added modifier should be carefully considered for different aspects of property requirements.

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