Effects of organoclay to miscibility, mechanical and thermal properties of poly(lactic acid) and propylene-ethylene copolymer blends

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Abstract. The effects of propylene-ethylene copolymer (PEC or PEC3300) and clay surface modified with 25-30 wt% of trimethylstearyl ammonium (Clay-TSA) on morphology, thermal and mechanical properties of poly(lactic acid) (PLA) were investigated. The morphology analysis showed PLA/PEC3300 blends clearly demonstrated a two-phase separation of dispersed phase and the matrix phase and the addition of Clay-TSA could improve the miscibility of PLA and PEC3300 blends due to the decreased of the domain sizes of dispersed PEC3300 phase in the polymer matrix. From X-ray diffraction analysis showed the intercalation of PLA chains inside the Clay-TSA and this result implied that Clay-TSA platelets acted as an effective compatibilizer. The tensile properties showed the strain at break of PLA was improved after adding PEC3300 while Young's modulus, tensile strength and storage modulus decreased. The addition of Clay-TSA could improve Young's modulus of PLA/PEC3300 blends. The addition of Clay-TSA 7 phr showed the maximum of Young's modulus of PLA/PEC3300/Clay-TSA composites. The thermal properties found that the addition of PEC3300 and Clay-TSA did not change significantly on the glass transition temperature and melting point temperature of PLA. The percent of crystallinity of PLA decreased with increasing PEC content. The thermal stability of PLA improved after adding PEC3300.

1. Introduction

Poly(lactic acid) (PLA) is biodegradable polymer, an eco-friendly and biocompatible bioplastic. PLA can be processed by conventional processing methods such as extrusion, tubular blown film, injection molding, and thermoforming [1]. Another feature that makes PLA interesting is the fact that it can be processed similarly to polyolefins, and PLA has high strength, high modulus and transparency. However, the main drawbacks with PLA properties are too brittle for many applications, low heat distortion temperature (HDT) and low thermal stability compared to commercial polymers [2-5]. To extend the application field the improvement of mechanical and thermal properties is required. Therefore, it is interesting to study if the incorporation of reinforcements can improve the mechanical properties and thermal stability of PLA. Thus, some researchers have studied to improvethe toughness, mechanical and thermal properties, barrier properties, and degradation behavior of PLA by blending with plasticizers, rubber, thermoplastic starch (TPS) and other thermoplastic polymers [6-11]. For instance, Ferrarezi *et al.,* (2013) [9] prepared PLA/TPS blends by using poly(ethylene glycol) (PEG), a non-toxic polymer, as a compatibilizer. They found that the addition of

PEG resulted in the increase of PLA crystallization, due to its plasticizing effect, and improvement of the interfacial interaction between TPS and PLA matrix.

Nevertheless, the main problems with PLA toughening through plasticizers or rubber is the reduction in strength and modulus properties [6,8,11-12]. In the PLA/rubber blends, for example, reduction in stiffness mainly occurs due to the low modulus of the rubber component itself [12] and PLA/TPS showed the lower elastic modulus than pure PLA [9]. However, most of these polymers that are blended with PLA are partially immiscible and occur phase separation with poor mechanical performance because of a negligible entropy of mixing [13]. Thus, some authors have studied organoclay to improve the properties of polymer blendsand found that organoclay plays the role of both structural reinforcement and compatibilizer [14-16]. From some researchers have studied using the rubber and flexible polymer to improve the mechanical properties of PLA, and using organoclay to improve the miscibility and properties of PLA blends for more applications [12,17-18]. In stance, Baouz *et al.* (2013) [18] improved the toughening PLA with an ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) rubber by reactive blending in a twin screw extruder. The addition of E-MA-GMA rubber changed the brittle behavior of PLA to ductile and the E-MA-GMA rubber domain size increased with increasing rubber content in both the blends and nanocomposites.

The compatibilizing action of organoclay results in a decrease in interfacial tension and particle size and in a remarkable increase in mechanical and thermal properties of the immiscible blends. Thus, this work studied the influence of clay surface modified with 25-30 wt% of trimethylstearyl ammonium (Clay-TSA) on miscibility, mechanical and thermal properties of PLA/ propylene-ethylene copolymer (PEC) blends. PEC was used to improving the toughness of PLA and the Clay-TSA was used to improving the miscibility and modulus of PLA blends. The blends and composites with varying concentration of PEC3300 and Clay-TSA were prepared by a melt mixing technique in an internal mixer and molded by compression molding.

2. Experimental

2.1. Materials

PLA with the melt flow index (210°C, 2.16 kg) of 6.0 g/10 min and specific gravity of 1.24 g/mL was produced by NatureWorks LLC, USA, under the trade name of "Ingeo™ Biopolymer 2003D". The PEC was purchased from Chemical Innovation Co., Ltd, under the trade name of "VERSIFY™ 3300 Elastomer". After that this PEC was called PEC3300. The PEC3300 has the melt flow rate of 8 g/10 min, density of 0.867 g/mL and the ethylene content of 12 wt%, this work used the clay was surface

modified by 25-30 wt% of trimethylstearyl ammonium (Clay-TSA), was produced by Aldrich Company.

2.2. Sample Preparation

Before blending, PLA was dried at 80°C for 4 h and Clay-TSA was dried at 80°C 24 h in an oven. PEC3300 was not dried before blending process. PLA/PEC3300 blends were prepared by melt blending in an internal mixer at 180°C and a rotor speed of 50 rpm for 15 min. The PEC3300 contents were 5, 10, 15 and 20 wt%. While PLA/PEC blends with Clay-TSA content 3, 5, and 7 phr were prepared in the same condition, and Clay-TSA was added after 5 min of mixing of the blends. After compounding, polymer blends without and with Clay-TSA were dried in an oven at 80°C for 1 h for reject moisture. Afterward the blends and composites were compression molded for testing.

2.3. Sample Characterization

The morphology of tensile fractured surfaces of PLA/PEC3300 blends without and with Clay-TSA was investigated by scanning electron microscope (SEM) instruments (JSM-6400 Scanning electron microscope, JEOL) at 15 kV accelerating voltage after gold coating. The tensile test was conducted according to ASTM D 638 with a universal tensile testing machine (LR 50k from Lloyd instruments, UK) at a crosshead speed of 50 mm/min. Each value obtained represented the average of five samples.

The thermomechanical properties (storage modulus) of PLA/PEC3300 blends without and with Clay-TSA was measured in bending film mode at a constant vibration frequency of 1 Hz, a temperature ranges from 30-140°C, and a heating rate of 5°C/min in a nitrogen atmosphere with a DMA (Pyris Diamond DMA, Perkin Elmer, USA). The glass transition temperature was detected by using the peak of tan δ from DMA test. DSC characterization (Pyris I, Perkin EImer, USA) was performed to investigate the melting temperature of the blends and composites. The temperature was in the range of 50-200°C at a heating rate of 10°C/min in a nitrogen atmosphere for the heating scan then the analysis performed from the heating scan. The degradation temperature of PLA/PEC3300 blends without and with Clay-TSA was measured by TGA (SDT Q600, TA Instruments, UK). The temperature was in the range of 30-600°C at a heating rate of 10°C/min under nitrogen atmosphere.

3. Results and Discussion

3.1. Morphology

Figure 1 shows the SEM micrographs of the tensile fractured surfaces of pure PLA and PLA/Clay-TSA composites at various Clay-TSA contents. The tensile fractured surface of pure PLA was quite smooth which characteristic of a brittle semicrystalline polymer (Figure 1a). While tensile fractured surfaces of PLA/Clay-TSA composites in Figure 1b-d were relatively rough to the more ductile after adding Clay-TSA. Figure 2 shows the SEM micrographs of the tensile fractured surfaces of

PLA/PEC3300 blends at various PEC3300 contents. From PLA/PEC3300 blends clearly demonstrated a two-phase matrix-particle morphology and observed the minor phase of PEC3300 dispersed as spherical domains in PLA matrix. Moreover, the domain size of dispersed PEC3300 phase increased with increasing PEC3300 content. Additionally, it observes the microvoids surrounding the PEC3300 droplets indicates weak interfacial adhesion between PLA and PEC3300 due to the immiscible nature of the polymers. Because of the high interfacial tension between the two polymers, the spherical morphology is anticipated because of the minimization of the interfacial area [19].

Figures 3-4 show the SEM micrographs of the tensile fractured surfaces of PLA/PEC3300 blends with Clay-TSA content of 3 and 5 phr, respectively. Moreover, PLA/PEC3300 blends with Clay-TSA content of 7 phr showed similar morphology as Clay-TSA 5 phr. It is clear that the addition of Clay-TSA in PLA/PEC3300 blends, the blends morphology shows a significant reduction in domain size of dispersed PEC3300 phase that means a high level of mixing between two polymer matrices [20]. Moreover, as the amount of the Clay-TSA increased, domain size of the dispersed PEC33000 phase in the blend gradually decreased. This indicated that the compatibility between PLA and PEC3300 improved with the presence of Clay-TSA when compared with PLA/PEC3300 blends, and showed a good dispersion uniformly at the content of Clay-TAS 3, 5 and 7 phr. Thus, Clay-TSA played an important role in reducing domain size of the dispersed PEC3300 phase PLA/PEC3300 blends, and Clay-TSA acted as an effective compatibilizer and the obtained morphology affected on the mechanical properties of the composites.
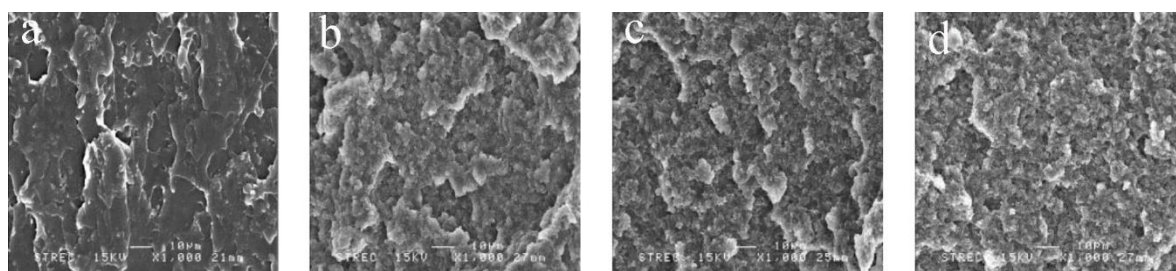

Figure 1. SEM Micrographs of the Tensile Fractured Surfaces of (a) Pure PLA, (b) PLA/Clay-TSA (100/3), (c) PLA/Clay-TSA (100/5) and (d) PLA/Clay-TSA (100/7)

3.2. XRD Analysis

The results from XRD patterns of Clay-TSA, PLA/PEC3300 (80/20) blends and PLA/PEC3300 blends with Clay-TSA showed that the Clay-TSA itself exhibited the characteristic peak at a 2θ of 3.67° correspond to the d-spacing of 2.41 nm. The peak position of clay-TSA was shifted to a lower 2θ region in the PLA/PEC3300/Clay-TSA composites indicated the intercalation of PLA chains inside the Clay-TSA. The relatively higher extent of intercalation in the PLA/PEC3300/Clay-TSA due to the different PEC3300 content (5, 10, 15 and 20 wt% of PEC3300 content). Interestingly, the

characteristic peak of Clay-TSA in PLA/PEC3300 blends at PEC3300 content 5, 10, 15 and 20 wt% with Clay-TSA 5 phr were found at 2θ =2.44°, 2.48°, 2.41° and 2.48°, which corresponds to d-spacing of 3.61, 3.55, 3.65 and 3.55 nm, respectively. In the same time PLA/PEC3300 blends with Clay-TSA 3 and phr showed the same trend XRD results. This result indicated the dispersed clay was intercalated due to the intercalation of polymer chains usually increases the d-spacing of the clay platelets [17]. From this result implied that Clay-TSA platelets acted as an effective compatibilizer that improved the miscibility of PLA/PEC3300 blends, due to the location of intercalated clay silicate layers at the interface decreased the interfacial tension and dispersed-phase particle sizes in immiscible blends [21].
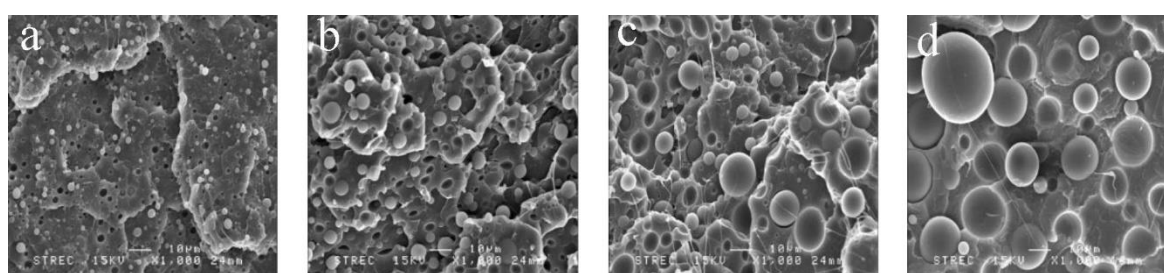

Figure 2. SEM micrographs of the Tensile Fractured Surfaces of PLA/PEC3300 Blends (a) 95/5, (b) 90/10, (c) 85/15 and (d) 80/20
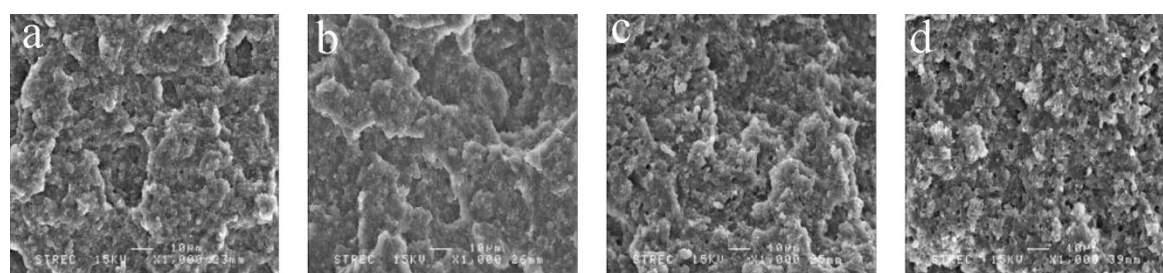

Figure 3. SEM micrographs of the Tensile Fractured Surfaces of PLA/PEC3300/Clay-TSA Composites (a) 95/5/3, (b) 90/10/3, (c) 85/15/3 and (d) 80/20/3
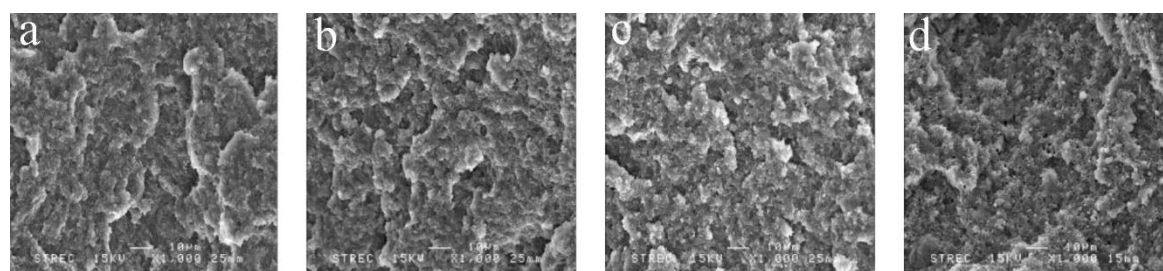

Figure 4. SEM micrographs of the Tensile Fractured Surfaces of PLA/PEC3300/Clay-TSA Composites (a) 95/5/5, (b) 90/10/5, (c) 85/15/5 and (d) 80/20/5.

3.3. Mechanical Properties

Figure 5 presents Young's modulus PLA/PEC3300 blends without and with Clay-TSA. The result found that Young's Modulus of PLA was 1,098.59 MPa and most of Young's modulus of PLA/PEC3300 blends was lower than pure PLA, and Young's modulus of PLA/PEC3300 blends

decreased with increasing PEC3300 content because the polymer blends increased flexibility after adding PEC3300. The result found that Young's modulus of PLA/PEC3300/Clay-TSA composites was higher than that of PLA/PEC3300 blends, and most Young's modulus of PLA/PEC3300/Clay-TSA composites increasing PEC3300 content. So the incorporation of Clay-TSA significant improved Young's modulus of PLA/PEC3300 blends. The addition of Clay-TSA could improve Young's modulus of PLA/PEC3300 blends due to the reinforcement effect of the rigid inorganic Clay-TSA induced a substantial increase in the modulus of the composites owing to the stiffening effect of the Clay-TSA that induced chain immobilization [18].

The tensile strength of PLA/PEC3300 blends without and with Clay-TSA is presented in Figure 6. The result found that tensile strength of PLA was 53.11 MPa and tensile strength of PLA/PEC3300 blends was lower than pure PLA, and tensile strength of PLA/PEC3300 blends decreased with increasing PEC3300 content. The tensile strength of PLA/PEC3300 blends after adding Clay-TSA decreased with increasing Clay-TSA content. So, the addition of PEC3300 and Clay-TSA did not improve the tensile strength of PLA and PLA/PEC3300 blends.

The strain at break of PLA/PEC3300 blends without and with Clay-TSA is illustrated in Figure 7. It can be seen that the strain at break of PLA was 8.59% and strain at break of PLA/PEC3300 blends increased with increasing PEC3300 content. This implied that PEC3300 could improve the elongation and flexibility of PLA due to the nature elastomer characteristic of PEC3300. While the addition of Clay-TSA decreased strain at break of PLA/PEC3300 blends and decreased when the increase of Clay-TSA content. This result indicated that Clay-TSA decreased the movement of the polymer chain and reduced the elongation of PLA/PEC3300 blends.
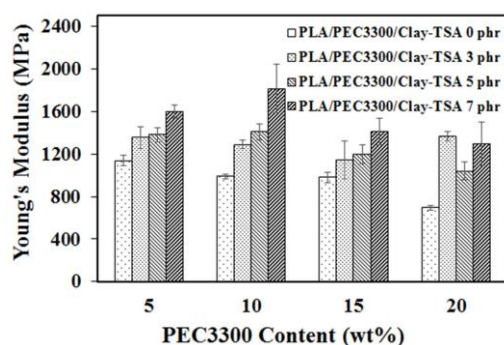

Figure 5. Young's Modulus of PLA/PEC3300 Blends without and with Clay-TSA.
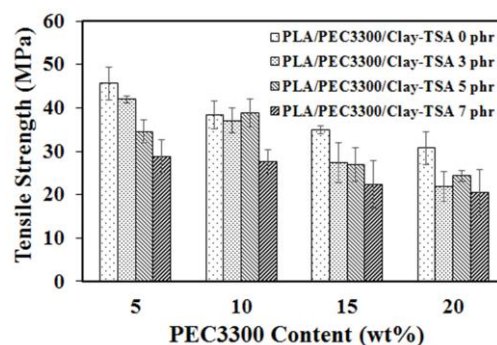
Figure 6. Tensile Strength of PLA/PEC3300 Blends without and with Clay-TSA.
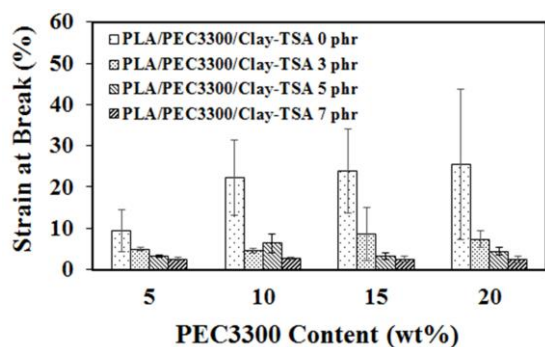
Figure 7. Strain at Break of PLA/PEC3300 Blends without and with Clay-TSA.
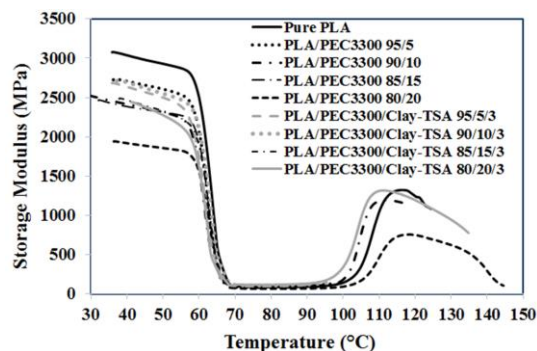
Figure 8. Storage Modulus of PLA/PEC3300 Blends without and with Clay-TSA 3 phr.

3.4. Thermomechanical Properties

The variation of storage modulus of PLA, PLA/PEC3300 blends and composites with Clay-TSA 3 phr is presented in Figure 8. The results found that the both the PLA/PEC3300 blends and pure PLA exhibited lower storage modulus as temperature increased. The sharply decrease was observed at the temperature higher than 63°C. The storage modulus of PLA/PEC3300 blends showed a similar trend to the pure PLA. The results found that the PLA/PEC3300 blends with Clay-TSA exhibited a higher storage modulus than the blends without Clay-TSA at a temperature lower than 63°C. The storage modulus sharply decreased was observed at the temperature higher than 63°C.

3.5. Thermal Properties

Table 1 shows the glass transition temperature, melting temperatures and percent crystallinity of pure PLA, PLA/Clay-TSA, PLA/PEC3300 blends and composites. The results revealed that the glass transition temperature of PLA was 65.5°C and glass transition temperatures of PLA/Clay-TSA at 3, 5 and 7 phr were 65.0, 64.7 and 61.1°C, respectively. Thus, that addition of Clay-TSA decreased the glass transition temperature of PLA at high Clay-TSA loading. The glass transition temperatures of PLA/PEC3300 blends at various PEC3300 content were in between 65.3 ± 1.0°C. Thus, the addition of PEC3300 had no effect on the glass transition temperature of PLA. The glass transition temperature of PLA/PEC3300/Clay-TSA composites at various PEC3300 and Clay-TSA contents were in between 64.7 ± 2.2°C. Therefore, the glass transition temperatures of the PLA/PEC3300 blends were slight changed when Clay-TSA was incorporated.

The melting temperatures of pure PLA, PLA/Clay-TSA, PLA/PEC3300 blends and composites are presented in Table 1. The melting temperature of PLA was 153.0°C and glass transition temperatures of PLA/Clay-TSA at 3, 5 and 7 phr were 154.2, 155.3 and 154.7°C, respectively. Thus, the incorporation of Clay-TSA slight increased the melting temperature of PLA. The melting temperatures of PLA/PEC3300 blends at various PEC3300 content were 152.8 ± 0.4°C. Thus, the addition of PEC3300 had no effect on the melting temperature of PLA. The melting temperatures of

PLA/PEC3300/Clay-TSA composites at various PEC3300 and Clay-TSA contents were $153.5 \pm 0.4°C$. This indicated that the addition of Clay-TSA had no effect on the melting temperature of the blends.

Table 1 shows the percent crystallinity of pure PLA, PLA/Clay-TSA, PLA/PEC3300 blends and composites, it was found that percent crystallinity of PLA was 25.2 and percent crystallinity of PLA dramatically decreased when added Clay-TSA. Moreover, PLA/PEC3300 blends showed the decrease of percent crystallinity with increasing PEC3300 content due to PEC3300 behaved as the amorphous polymer. However, the presence of Clay-TSA had a slight effect on the percent crystallinity of PLA/PEC3300/Clay-TSA composites.

The thermal stability of the PLA/PEC3300 blends without and with Clay-TSA was investigated by TGA. The degradation temperatures corresponding to the 10% weight loss (Td_{10}) were calculated and are shown in Table 1. The degradation temperatures of PLA and Clay-TSA were 320 and 294°C, respectively. The result showed the incorporation of Clay-TSA and PEC3300 improved the degradation temperature of PLA. This indicates that an improvement in the thermal stability in the PLA/PEC3300 blends due to PEC3300 had the higher degradation temperature. The degradation temperatures of PLA/PEC3300/Clay-TSA composites are illustrated in Table 1. The result showed that the addition of Clay-TSA did not improve the degradation temperature of PLA/PEC3300 blends and they had a slight influence on the thermal stability of the blends.

Table 1. Glass Transition Temperature (T_g), Melting Temperature (T_m), Percent Crystallinity and Degradation Temperature (T_d) of PLA/PEC3300 Blends without and with Clay-TSA

Sample	T_g (°C)	T_m (°C)	%Crystallinity of PLA	T_d (°C)
Pure PLA	65.5	153.0	25.2	320
PLA/PEC3300 (95/5)	66.1	152.6	23.8	334
PLA/PEC3300 (90/10)	64.0	152.8	22.2	334
PLA/PEC3300 (85/15)	65.3	152.4	24.0	326
PLA/PEC3300 (80/20)	66.1	153.4	19.0	332
PLA/Clay-TSA (100/3)	65.0	154.2	15.2	330
PLA/PEC3300/Clay-TSA (95/5/3)	66.3	154.1	24.1	332
PLA/PEC3300/Clay-TSA (90/10/3)	65.2	153.5	23.2	333
PLA/PEC3300/Clay-TSA (85/15/3)	65.2	153.5	20.3	330
PLA/PEC3300/Clay-TSA (80/20/3)	63.7	152.9	19.2	335
PLA/Clay-TSA (100/5)	64.7	155.3	7.9	328
PLA/PEC3300/Clay-TSA (95/5/5)	63.6	154.2	23.5	331
PLA/PEC3300/Clay-TSA (90/10/5)	65.0	153.4	21.8	334
PLA/PEC3300/Clay-TSA (85/15/5)	64.1	153.2	20.9	332
PLA/PEC3300/Clay-TSA (80/20/5)	64.4	153.2	19.4	320
PLA/Clay-TSA (100/7)	61.1	154.7	7.9	329
PLA/PEC3300/Clay-TSA (95/5/7)	68.4	153.9	22.2	332
PLA/PEC3300/Clay-TSA (90/10/7)	66.4	153.8	22.5	329
PLA/PEC3300/Clay-TSA (85/15/7)	59.2	152.9	20.5	329
PLA/PEC3300/Clay-TSA (80/20/7)	64.8	153.8	18.5	328

Figure 9-10 show the thermogravimetric curves of thermal degradation of PLA/PEC3300 blends without and with Clay-TSA 5 phr. It is evident that the thermal degradation of PLA showed only single step of weight loss, while the thermal degradation of the blends and composites proceeded by two degradation steps. It was found that the first step showed a large mass loss starting at around 300°C, this main region was thermal degradation of PLA. The second step showed a small mass loss starting at around 370°C, this region was thermal degradation of PEC3300. Moreover, this region showed the mass loss of PLA/PEC3300 blends at high PEC3300 content was lower than the blends at low PEC3300 content. This indicated that the addition of PEC3300 could improve the thermal stability of PLA blends. The thermogravimetric curves of PLA/PEC3300 blends with Clay-TSA 3 and 5 phr displayed the same trend curves.
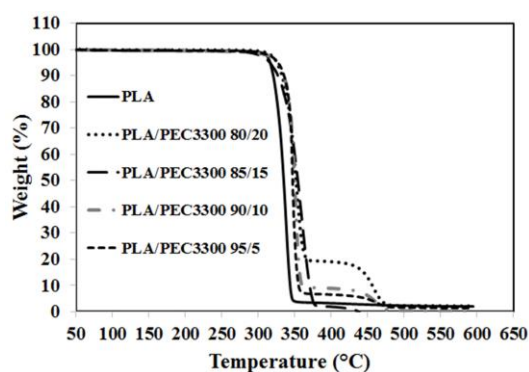

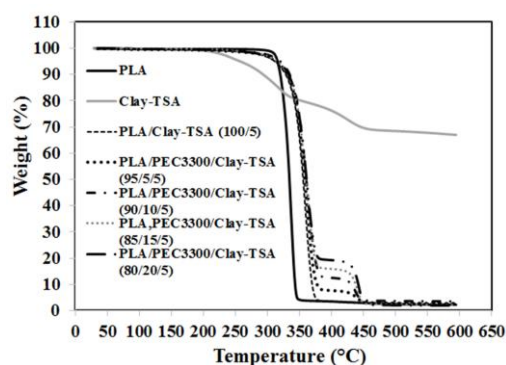**Figure 9.** TGA thermograms of PLA/PEC3300 blends.

Figure 10. TGA thermograms of Clay-TSA, PLA, PLA/Clay-TSA 5phr and PLA/PEC3300 blends with Clay-TSA 5 phr.

4. Conclusions

The effects of Clay-TSA on miscibility, mechanical and thermal properties of PLA/PEC3300 blends were investigated. The morphology analysis showed PLA/PEC3300 blends clearly demonstrated a two-phase separation of dispersed phase and the matrix phase, and the addition of Clay-TSA could improve the miscibility of PLA and PEC3300 blends due to the decrease in interfacial tension and domain size of dispersed PEC3300 phase in PLA matrix. From XRD analysis showed the peak position of clay-TSA shifted to a lower 2θ region in the PLA/PEC3300/Clay-TSA composites indicated the intercalation of PLA chains inside the Clay-TSA. This result implied that Clay-TSA platelets acted as an effective compatibilizer due to the location of intercalated clay silicate layers at the interface decreased the interfacial tension and dispersed-phase particle sizes in PLA/PEC3300 blends. The tensile properties showed the strain at break of PLA was improved after adding PEC3300.

The addition of Clay-TSA could improve Young's modulus and storage modulus of PLA/PEC3300 blends. The addition of PEC3300 could improve the thermal stability of PLA.

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