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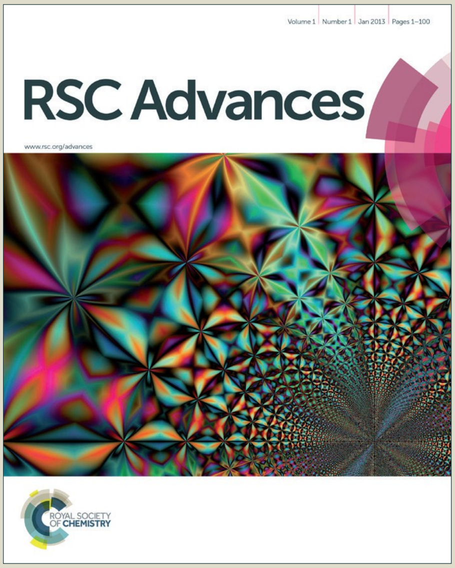

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Composites of Poly(lactic) acid/Thermoplastic Polyurethane/Mica with Compatibilizer: Morphology, Miscibility and Interphase

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ABSTRACT

Composites of poly(lactic) acid (PLA)/thermoplastic polyurethane (TPU)/mica were prepared by using a twin-screw extruder (TSE). Mica modified by a silicate coupling agent and/or a titanate coupling agent was incorporated into the PLA/TPU blends to investigate the influences of compatibilizers on nanophase morphology and interphase behaviors. The microstructure morphology of the composites was examined by high-resolution scanning electronic microscopy (SEM) and transmission electron microscopy (TEM). The observation indicates that the dispersed phase was homogeneously dispersed, and mica particles could effectively cut off PLA and/or TPU dispersion phase by melt-compounding. The dynamic mechanical properties of the composites were analyzed by using dynamic mechanical analysis (DMA), which confirms that the addition of modified mica strongly influences the miscibility of the multiphase composites. Effective modification in the surface of mica was detected by using Fourier transform infrared spectroscopy (FTIR). Slight reduction in the cold-crystallization temperature and crystallinity of the composites was observed with the modified mica addition under differential scanning calorimetry (DSC).

Keywords: Twin-screw extruder, Modification, Polymer-matrix composites， Interphase, Morphology

1. INTRODUCTION

Poly(lactic acid) (PLA), a polycondensation material of lactic acid, is a special biomaterial that can be broken down by hydrolytic scission into its monomeric form, lactic acid, which can be eliminated from the body by incorporation into the tricarboxylic acid cycle [1−3]. Because of its high strength and stiffness, excellent transparency, and biodegradability, PLA is a promising alternative to some petroleum-based polymers and has been applied in various medical applications, including biodegradable composites, drug delivery systems and tissue engineering, and so on [4-9]. Unfortunately, the inherent brittleness of PLA is a major weakness that has restricted its wide application [10−12]. Blending PLA with flexible polymers is a practical and economical way to toughen PLA products. Various biodegradable or nonbiodegradable polymers, which serve as toughening components, have been blended with PLA [13−17]. However, often, PLA might not be miscible with some of these polymers, with their blends resulting in phase-separated morphologies that eventually lead to the deterioration of properties. Therefore, various studies have aimed at modifying the morphology and increasing the compatibility between the two phases [6, 7, 13−17].

Thermoplastic polyurethane (TPU) is an ideal material for medical devices because of its flexibility and biocompatibility [18]. TPU elastomer is usually added to PLA to obtain PLA/TPU blends [19]. Generally, the high interaction parameter (χ) between TPU and PLA blends is responsible for the immiscibility. Thus insufficiency interaction in the interface between the PLA and the TPU must be improved for the

PLATPU blend application. Phase morphologies and interface properties can be enhanced to achieve strong and ductile PLA composites with the introduction of compatibilizers. And the fine comprehensive properties of PLA/TPU blends are usually used to prepare shape memory polymers. At presently, almost all of the reported PLA/TPU systems have not achieved a fine phase structure with good interfacial compatibility [20, 21].

Mica is an interesting kind of layered aluminosilicate with many good properties and its formula is $K_2Al_4(Al_2Si_6O_{20})(OH)_4$ [22]. As mica has a lot of interesting characteristics, such as the high heat stability, the high aspect ratio (ratio of diameter to thickness), the effect of two-dimensional reinforcing, the high swelling capacity, the high water-absorbing properties, the outstanding corona resistance and insulation properties, the low overall cost, the easiness in production, and the friendliness to the environment, many authors have studied composites with the addition of mica [23-31]. Okamoto et al. [32, 33] had blended PLA with synthetic fluorine mica, and they found that the mechanical properties of the composites were also improved greatly. Thus, the blending of PLA and mica has attracted significant attention to reduce cost and obtain unique properties for practical application.

Obviously it is very interesting to make researches on blending of biodegradable polymeric materials with mica from both academic and industrial perspectives of view, because of the possibilities for enhancing mechanical properties and thermal stability of biodegradable polymers, and reducing the material cost as well as extending their practical application. Therefore, to obtain better mechanical properties and lower cost of PLA/TPU/mica composite, the microstructure and interface morphologies should be studied. In the work, we exhibit the feasibility to create microsized dispersed particles in the PLA/TPU/mica composites, for the first time, by introducing appropriate coupling agent during the melt-compounding. The study main aims to investigate the effects of different types of coupling agent on phase morphology and interphase behavior of the PLA/TPU/mica multi-component materials in a TSE. Therefore, Evolution and comparison of the macrostructure and interphase of PLA/TPU/mica composites was executed by direct SEM observation, miscibility analysis and interphase behavior measurements. The PLA/TPU blends with treated mica addition showed microsized dispersed particles, outstanding surface and /or interphase properties, featuring a well-tailored balance by altering the PLA/TPU component ratio. The unprecedented method can be used for the design of morphologies and mechanical properties of multiphase composites and processing of low-cost commercial and/or excellent shape memory polymers .

2. EXPERIMENTAL

2.1 Materials

PLA (grade 4032D, density = 1.24 g/cm^3, Natureworks) was used. The melt flow index of the PLA is 28 g/10min (2.16 kg load, 210 °C). TPU (grade WHT1195; density = 1.2 g/cm^3) was supplied by Yantai Wanhua Polyurethanes Co., Ltd. Mica (grade GA-4, average particle size = 5±2 um) was obtained in form of trips from Grea minerals Co. Ltd. (Chuzhou, Anhui, China).

Silicone coupling agent (grade KH-550) and Titanate coupling agent (grade

TC-114) were provided by Longkai Co. Ltd. (Guangzhou, Guangdong, China). The density at the room temperature was 1.045 g/cm^3 and1.05 g/cm^3, respectively.

Ethyl alcohol was provided by Fuyu fine chemicals Co. Ltd. (Tianjin, China). Acetic acid was purchased from Zhouyuan chemicals Co. Ltd. (Nanhai, Guangzhou, China). Chloroform was purchased from Juda Co. Ltd. (Shandong, China).

2.2 Mica particles modification

The molecular structure of PLA, TPU and coupling agent (KH-550 and TC-114) is shown in Fig. 1. The amino and ethoxylated terminal of KH-550 can generate chemical interaction with matrix (PLA and TPU) and mica after hydrolyzation, respectively. However, only the isopropyl terminal of TC-114 can come up chemical interaction with mica after hydrolyzation, and its long-chain alkane terminal has good compatibility (physical crosslinking) with PLA/TPU blends.

According to interaction mechanism between PLA, TPU matrix and coupling agent. Briefly, 2.0 ml acetic acid was dropped in 300.0 ml of absolute ethyl alcohol, and oscillated slightly. 1.0 ml of KH-550 and 50.0 g of mica powder were successively put in the above solution kept in ultrasonic bath for 45 min under maintaining the temperature at 85 °C. Then a sticky mixture was obtained and dried on a vacuum oven at 90 °C for 8 h. And, the mica powder was modified by TC-114 using super-speed mixture method. 300.0 g of mica powder and 10.0 ml of pitch were put in mechanical mixture device (SHR-50A, Dongguan, China) and mixed at 80 °C under 1000 rpm for 5 min. Then, 5.0 ml of TC-114 was splashed on the mica. The super-speed mixture was sustained for 10 min. The mixture was then dried at 90 °C for 6 h in a vacuum oven.

2.3 Samples preparation

The PLA/TPU blends with weight ratio of 10/90, 50/50, 90/10 and mica which was fixed 7.5 phr (approximate 7.0 wt.%) were manually premixed by tumbling in a plastic zip–lock bag before melt-compounding. The designation and composition for PLA/TPU/mica composites are shown in Table 1.

Table 1. Different formulations of PLA/TPU blends as a function of 7.5 phr mica

Sample	PLA (wt%)	TPU (wt%)	Mica	(KH-550/TC-114)
A	90	10	Unfilled	Unfilled
B	50	50	Unfilled	Unfilled
C	10	90	Unfilled	Unfilled
D	90	10	Filled	Unfilled
E	50	50	Filled	Unfilled
F	10	90	Filled	Unfilled
G	90	10	Filled	KH-550
H	50	50	Filled	KH-550
I	10	90	Filled	KH-550
J	90	10	Filled	TC-114
K	50	50	Filled	TC-114
L	10	90	Filled	TC-114

Then, the mixture supplies were fed into the TSE for melt processing, with an L/D ratio of 13.7 for die (D = 3 mm), at a rotation speed of 120 rpm. The TSE was operated using the temperature profile set at 180, 185, 185, 190, 190, 195, 195, 200 °C (for the different zones from hopper to die). The TSE-extruded composites was cooled in the air and subsequently granulated by a pelletizer.

The samples for SEM and AFM observation were prepared from the fresh extruder at the exit of die. The samples for TEM and DMA were compression-molded in a hydraulic press at 200 °C and 10 MPa for 30 min, which were in the form of 150 × 80 × 4 mm^3. All the specimens were conditioned at 50% relative humidity and 25 °C for at least 48 h before testing.

2.4 Characterizations

2.4.1 Scanning electron microscopy (SEM)

A JSM-6390LV NanoSEM instrument (JEOL Company, Japan) was used to investigate phase morphology. The PLA/TPU/mica specimens (untreated and treated mica) with dimensions of 40×10×4 mm^3 were immersed in liquid nitrogen for approximately 45 min and fractured to expose the internal structure for SEM investigation. To better clarify the dispersion particles morphologies of the specimens under different component ratio and modified mica in this research, the cryo-fracture surface was immersed in chloroform for nearly 30 second to dissolve the PLA. Then, the cryo-fracture surface morphologies of the composites etched by chloroform were also investigated by high-resolution SEM. Before testing, all the specimens were gold sputtered to provide enhanced conductivity.

2.4.2 Transmission electron microscopy (TEM)

A TECNAL 10 (Philips, Netherlands, accelerating voltage 120 KV) was used for TEM analysis. The dispersion of mica in the PLA/TPU blend was evaluated by TEM. TEM ultrathin sections from the compression-molded tensile samples were prepared by a Powertome X (Boeckeler Instrument) cryo-ultramicrotome. Freshly sharpened diamond knives were used to obtain cryo-sections of 70–100 nm thickness specimens at an ambient temperature of -70 °C.

2.4.3 Dynamic mechanical analysis (DMA)

Dynamic mechanical thermal properties of the PLA/TPU/mica (untreated and treated mica) composites were investigated using a DMA 242 (Netzsch, Germany). The three point bending method was used at a frequency of 1 Hz and a heating rate of 3 °C/min. All the specimens were rectangular trips with dimensions of 60×10×4 mm^3. The storage modulus (E′), loss modulus (E") and loss factor (tan δ) were measured as a function of temperature (-50 to 120 °C).

2.4.4 Fourier transform infrared spectroscopy (FTIR)

A FT-IR (Nexus 670, Nicolet Company, USA) was used to obtain spectra of the mica (untreated and treated) with a resolution of 4 cm^{-1} and 16 scans. The KBr disk sample preparation method was used before taking infrared spectra. Mica particles with KBr were dried and mixed with particles to KBr weight ratio of 1:90 nearly. Then, the mixture was pressed to form disk with thickness of 0.01-0.1 mm. FT-IR spectra were recorded in a range of 4000–400 cm^{-1}.

*2.4.5 D*ifferential scanning calorimetry *(DSC)*

The crystallinity of the PLA matrix phase can affect the mechanical properties of composites; thus, thermal analysis was executed using a Mettler Toledo instrument (DSC, Q100, Switzerland) under a nitrogen atmosphere. Approximately 5 mg samples were heated from -60 °C to 220 °C at a heating rate of 10 °C/min.

The crystallinity of PLA (X_c) was estimated according to the equation

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{w_f \Delta H_m^0} 100\% \tag{1}$$

Where $\triangle H_m$ and $\triangle H_{cc}$ are the enthalpies of melting and cold crystallization during the heating, respectively; ΔH_{m}^0 is the enthalpy assuming 100% crystalline PLA homopolymers (93.7 J/g); and W_f is the weight fraction of PLA component in the blend[34].

2.4.6 Mechanical Properties

A type MTS CMT5105 universal testing machine with a tensile speed of 20 mm/min was used, according to the GB/T 1447-2005 standard. The dimensions of elongation samples were 130×10×4 mm^3. All tests were performed at ambient temperature (25 °C), and five specimens were used in each test to obtain the average value.

3. RESULTS AND DISCUSSION

3.1 Morphology of composites

Figure 2 shows the SEM images of PLA/TPU blends (PLA phase etched by chloroform) in various component ratios with untreated and treated mica. For the untreated mica composites, the phase morphology of the short fibers and droplets when TPU was in the dispersed phase (10 wt.%) is shown in Fig. 2(D). The morphology of interlinked holes with the increase of TPU content was clearly exhibited, as shown in Fig. 2(E). These results suggest that the TSE can generate strong shear deformation, which induced the microfiber morphology of PLA/TPU blends during the melt compounding process. Fine and uniform particles were dispersed, whereas the TPU content further increased (90 wt.%), as shown in Fig. 2(F). Furthermore, compared with the PLA/TPU blends without mica after etching, as shown in Figs. 2(A-C), dispersion particles size of the PLA/TPU/mica composites were distinctly decreased with the introduction of untreated and/or treated mica. The phenomenon suggests that the rigid mica platelets played a cutting role under melt-compounding.

The dispersion morphology of PLA/TPU blends with the addition of mica treated by KH-550 exhibited a small particle size and fine size distribution in various component ratios, as shown in Figs. 2(G–I) which indicates that the surface tension of the PLA/TPU/mica composites was slightly decreased by the introduction of a silicone coupling agent; thus, the composites could be broken easily to form uniform and fine dispersed particles under the strong shear deformation. Some researchers reported a similar result [35, 36]. In the case of mica treated by TC-114, fine and uniformly dispersed phase morphology was also obtained as shown in Figs. 2(J–L), which indicates improved miscibility of the multiphase composites with the addition of treated mica during melt compounding. The abovementioned observations indicate that the collaborative effect of strong shear deformation and coupling agent could significantly improve dispersed particle morphologies.

To clearly distinguish dispersed particles size and particles size distribution of the PLA/TPU blends with untreated and treated mica addition, the PLA/TPU/mica (10/90/7.5) composites were selected and their mean droplet dispersion meter *d* was calculated by the following equation [37]: $\ln d = \frac{\sum_{i=1}^{n} n_i \ln d_i}{\sum_{i=1}^{n} n_i}$. Figs. 3(F1, I1 and L1) clearly demonstrates the presence of nanosized holes by etching the PLA matrix, yielding the quantitative analyses regarding the distribution of the droplet size as a function of Figs. 2(F, I and L). The average diameter (D) dramatically decreases from 335 nm for PLA/TPU blend with untreated Mica to around a 0.65 times value for the blends adding treated Mica by KH-550 and /or TC-114 (207 and 218 nm), and corresponding to particles size distribution was narrowed significantly (as shown in Fig. 3). The enhanced broken possibility of PLA melt droplets should be responsible for the decrease of particle size and distribution index, resulting from the decreased surface tension of the multi-phase composites by introducing the compatibilizers. Owing to the coupling agent, the size of dispersed phase can be refined, interaction of interphase can be also improved and solidified for the immiscible blends under the melt-compounding.

TEM observation can clearly distinguish the inner phase morphology and nanosized dispersed phase of multiphase materials. The dispersion of mica in the PLA/TPU blends and the morphology of the PLA and/or TPU dispersed particles as a function of different component ratio are shown in Fig. 4. The dark thread-like objects were identified as mica platelets, as shown in Fig. 4. An irregular scale of mica platelets (approximately 4 um) was dispersed in the PLA matrix under shear deformation. Interestingly, compared to the PLA/TPU blends without mica platelets, as shown in Figs. 4(A-C), PLA and/or TPU dispersion particles of the PLA/TPU/mica composites (untreated and/or treated mica addition) were evidently cut off by mica platelets and refined as short nanofibers, as shown in Fig. 4(D-L). The result suggested that rigid mica could effectively refine dispersed particles of multiphase composites in polymer processing. Moreover, owing to the modification, the mica platelet was embedded in PLA/TPU blends, as shown in Figs. 4(G - L), which suggests that interaction of the interphase between the treated mica and the PLA/TPU matrix improved effectively. Furthermore, the hundred of ordered microfibers are shown in Figs. 4(G-L), which indicates that surface tension of PLA/TPU blends were decreased with addition of coupling agent and orderly drawn morphologies were presented under strong shear deformation. The interface between PLA and TPU became indistinct, but ordered deformation never disappeared. These phenomena further demonstrated that the interaction of PLA/TPU blend was enhanced by introducing the coupling agent (KH-550 and/or TC-114).

3.2 Miscibility of composites

Dynamic mechanical analysis (DMA) was performed to study chain motion at the glassy/rubbery state of the polymer. Fig. 5 presents the storage modulus (E′) of PLA/TPU (90/10), (10/90) blends with untreated and treated mica addition. Compared with PLA/TPU blends (either 90/10 or 10/90) without mica, E′ of the PLA/TPU blends were increased with introduction of mica. The result indicates that the mica addition could effectively enhance stiffness of PLA/TPU blends. Moreover, For E′ of PLA/TPU/mica composites, E′ of the composites with the addition of treated mica slightly decreased ranging from -60 to 140 °C, compared to the untreated mica composite, as shown in Fig. 5. The result is contributed to the external plasticization of small amount of free coupling agent in the PLA/TPU matrix, resulting in the decrease of storage modulus. By contrast, Importantly, E′ of the composites with mica (either treated or untreated) showed a noticeable increase at a specific temperature (95 °C), indicating of the increase of strength of the PLA/TPU/mica composites. This is due to cold crystallization behavior of PLA under the periodic oscillation as the increase of temperature. With comparison, E′ of the composites exhibited enormous decrease with the increase of TPU addition (90 wt.%) in Fig. 5, which suggests that the mobility of the PLA chains clearly improved by adding the amount of thermoplastic elastomer. Owing to the modification, E′ of the composites with treated mica was lower than that of untreated composites ranging from -60 to -30 °C. The phenomenon implies that the coupling agent addition can effectively enhance ductile of PLA, which produces a broader industrial application.

The loss factor (tan δ) of the PLA/TPU/mica composites is shown in Fig. 6. Compared with the glass transition temperature (at 66 °C) of the PLA/TPU (90/10, 10/90) blends with untreated mica, PLA/TPU/mica composites showed a certain extent decrease when the mica powder was treated by the silicone coupling agent and/or titanate coupling agent. The modification evidently enhanced the miscibility of the PLA and TPU matrix, which decreased the glass transition temperature (T_g) of PLA. Noticeably, for either PLA/TPU (90/10) or PLA/TPU (10/90) blends, the D-value between T_g of PLA and T_g of TPU effectively decreased when mica was modified by using the KH-550 and TC-114 compared with that of the unmodified mica composites. This phenomenon indicates that the partial compatibility between the PLA matrix and TPU particles was better than that of the other specimens (untreated mica addition). This result is in agreement with the aforementioned analysis, including the SEM and TEM observation.

3.3 Interphase of composites

The FTIR absorption spectra of neat mica, and mica modified with silicone and titanate coupling agent were examined to verify the presence of surface modification, as shown in Fig. 7. The band at 3624 and 1630 cm^{-1} shows the most specific diffraction peaks for mica and represents asymmetrical stretching and bending vibrations of the -OH group, respectively. The band at 1078, 829, and 912 cm^{-1} represents asymmetrical stretching vibrations of the Si-O-Si and Si-OH group for the mica product [38]. By contrast, the inherent characteristic absorption peaks at 3624, 1630, 1078, 912, and 829 cm^{-1} for mica modified by the silicone and titanate coupling agent have not been changed. This phenomenon implies that the principal part of the mica product was not destroyed when the coupling agent was introduced. Owing to the modification, the decrease for the band at 3624 cm^{-1} contributed to the condensation reaction between Si-OH group of the coupling agent and –OH group of the mica product. Notably, the characteristic bands at 1720 cm^{-1} was exhibited for mica modified by KH-550 and represented the diffraction peak of C=O group. The phenomenon is due to insufficient hydrolysis of a small portion of silicone coupling agent. Moreover, the presence of this band at 2944 and 2840 cm^{-1} confirmed the asymmetrical stretching vibrations of the –CH_3 and -CH_2 group in the modified mica. The result indicates that the mica was successfully coated by using a coupling agent (KH-550 and TC-114).

Figure 8 shows SEM images of PLA/TPU blends with different component ratios and theirs composites with the addition of untreated and treated mica. Dispersed phase morphologies were clearly exhibited on a micrometer. In the case of PLA/TPU/mica (90/10/7.5) composites (Fig. 8D), a number of mica platelet–matrix debonding and mica platelet pull-outs were observed. Some pull-outs of mica and mica platelet–matrix debonding were also observed when the TPU content was 50 wt.% (Fig. 8E). In Fig. 8F, mica platelet pull-outs and mica–matrix debonding were not observed in the case of the PLA/TPU/mica (10/90/7.5) composites. Good mica–matrix adhesion was achieved because the TPU is the matrix of the composites, which indicates that the mica platelets were easily dispersed in the TPU. Some experts reported a similar result [39].

Figures. 8(G-L) represent the SEM images of the interface morphology of PLA/TPU blends with the addition of treated mica. Compared with untreated mica composites, the interfaces between the PLA and TPU matrix were vague. Moreover, according to the PLA/TPU/mica (90/10/7.5) composites (Figs. 8G and 8J), a considerable degree of mica platelet–matrix adhesion was detected, but mica platelet pull-outs were not observed. Relatively better mica–matrix adhesion was observed in the case of modified Mica PLA/TPU composites with the increase of TPU (Figs. 8H, I, K, L). Mica platelets were impregnated in the PLA/TPU matrix. The modification ensured that good mica–matrix adhesion was achieved in the melt-compounding. Therefore, the modification can significantly improve adhesion for multiphase composites.

3.4 Thermal properties of composites

PLA is a semicrystalline polymer, and its mechanical properties strongly depend on its crystallization behavior[40]. Only the DSC data from the first heat scan are shown because the mechanical properties of the blends and theirs composites can only be influenced by the crystalline state of the PLA in the molded samples. Fig. 9

represents the melting behavior of the different component ratios of PLA/TPU blends with untreated and/or treated mica. To clearly observe the influences of untreated and treated mica on crystallization behaviors of PLA/TPU blends, theirs thermal properties were calculated and listed, as shown in Table 2.

Table 2. Thermal properties of PLA/TPU blends and theirs composites.

Composites	A	B	C	D	E	F	G	H	I	J	K	L
$T_{m,PLA}$(°C)	170.0	170.1	168.7	169.4	169.8	168.2	170.1	169.8	168.3	169.7	169.9	171.3
$T_{cc,PLA}$(C)	**108.9**	**109.1**	**110.2**	**104.4**	**105.4**	**103.4**	**105.2**	**108.3**	**107.7**	**102.5**	**107.3**	**105.5**
$\Delta H_{m,PLA}$(J/g)	32.48	21.52	4.17	31.63	15.86	4.67	30.99	19.23	5.19	31.86	20.31	4.02
$\Delta H_{cc,PLA}$(J/g)	22.90	16.46	0.505	20.36	10.54	0.35	22.56	15.19	3.36	22.34	15.80	0.05
Xc(%)	**11.36**	**11.74**	**43.46**	**14.67**	**12.62**	**51.23**	**10.97**	**9.58**	**21.70**	**12.39**	**10.69**	**47.07**

$T_{cc,PLA}$(C) and $\Delta H_{cc,PLA}$(J/g) represent cold-crystallization temperature and enthalpy, respectively.

In comparison, the cold-crystallization temperature (T_{cc}) of the PLA/TPU blends without the mica was slightly higher than those the PLA/TPU blends incorporated in untreated mica. The result is contributed to the nucleation of mica particles, resulting in a lower nucleation free energy of PLA component. Notably, compared with PLA/TPU blends with untreated mica, a slight increase in the T_{cc} of the PLA/TPU/mica composites (mica modified by KHT-550 and/or TC-114) was observed. The phenomenon indicates that the modification of mica particles can effectively enhance interface interaction with PLA/TPU blends and give rise to the decreasing of motion capacity of macromolecular chain. Moreover, comparison of the crystallinity (X_c) of PLA/TPU blends with mica, the X_c of PLA/TPU/mica composites was reduced when the coupling agent was incorporated. Owing to the modification, strong mica platelet–matrix adhesion occurred because of a strong interaction between the PLA/TPU blends and the mica platelets, as shown in Fig. 8, which prevented the macromolecule chains from packing to form perfect crystals. This behavior resulted in decreased T_{cc} and X_c values.

3.5 Mechanical properties of composites

Figure 10 gives the tensile properties curves (tensile strength, tensile modulus and elongation at break) of PLA/TPU blends as a function of component ratio with untreated and treated mica addition. Figs. 10 (a, b and c) represent tensile strength and modulus of the PLA/TPU blends and theirs composites with different component ratio (90/10, 50/50 and 10/90), respectively. Compared to the PLA/TPU blends without mica, the tensile strength of the PLA/TPU/mica composites (with untreated mica) was evidently reduced. A slight improvement in tensile strength of the PLA/TPU/mica composites was achieved with introduction of the coupling agent (KH-550 and TC-114). The results suggest that the modified mica platelets were uniformly dispersed in PLA/TPU blends and the coupling agent could enhance interface interaction between the PLA/TPU matrix and mica platelets. Moreover, the tensile modulus of PLA/TPU blends with addition of mica was effectively superior to that of the blends without mica. The result demonstrates that the rigidity of mica platelets and increased crystallization of the PLA matrix play a significant role in reinforcing.

In addition, Figs. 10 (a_1, b_1 and c_1) show elongation at break of the PLA/TPU blends and theirs composites with different component ratio (90/10, 50/50 and 10/90), respectively. We can see that elongation at break of the PLA/TPU/mica composites (mica modified by KH-550 and/or TC-114) was higher than that of the PLA/TPU blends with untreated mica. Therefore, on the basis of the above results, the significantly increased strength and toughness of the PLA/TPU/mica composites can be attributed to the good interfacial compatibilization between PLA/TPU blends and mica platelets, rather than the reduction of crystallinity of PLA. The good comprehensive mechanical properties of PLA/TPU/mica composite (mica modified by KH-550) will provide a possibility for excellent shape memory polymer.

4. CONCLUSIONS

Silicone and titanate coupling agent successfully modified the mica surface. The phase morphology of the samples influenced by the melt-compounding and coupling agent exhibited fine microfibers and/or particles. For comparison, the dispersion phase of the PLA/TPU blended with treated mica showed a smaller particle size than that of the untreated mica composite. The TEM observation indicates that the treated mica and the PLA/TPU matrix exhibited vague surface morphology because of the modification. By contrast, owing to the modification, the interphase property was slightly enhanced for PLA/TPU/mica composites on the basis of SEM observations. Owing to the modification, PLA and TPU are partially miscible and have strong interlocking according to the DMA curves of the PLA/TPU blends with the introduction of untreated and/or treated mica. Additional, the low-cost and good comprehensive performance of PLA/TPU/mica composites are achieved. Particularly, the PLA/TPU blends with introduction of treated mica (KH-550) can be used to prepare excellent shape memory polymers.

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Figure Captions

Fig. 1. Molecular structure of PLA, TPU and coupling agent (KH-550 and TC-114).

Fig. 2. SEM images of cryofracture surfaces of the PLA/TPU blends with untreated and treated mica as a funcation of different component ratio after etching PLA phase.

Fig. 3. The quantitative analyses in terms of the distribution of PLA phase size of untreated and treated PLA/TPU/mica (10/90/7.5) composites as shown in F(1), I(1), and L(1), respectively. And the average diameter (D) is marked in the right up corner of these figures.

Fig. 4. TEM images of PLA/TPU blends and theirs composites under the melt-compounding. (A-C): PLA/TPU blends (90/10, 50/50 and 10/90) without mica, (D-F): PLA/TPU blends (90/10, 50/50 and 10/90) with untreated mica, (G-I): PLA/TPU blends (90/10, 50/50 and 10/90) with mica treated by KH-550, (J-L): PLA/TPU blends (90/10, 50/50 and 10/90) with mica treated by TC-114.

Fig. 5. Storage modulus of the PLA/TPU blends with untreated and /or treated mica as a function of different component ratio.

Fig. 6. Loss factor of the PLA/TPU blends with untreated and /or treated mica as a function of different component ratio.

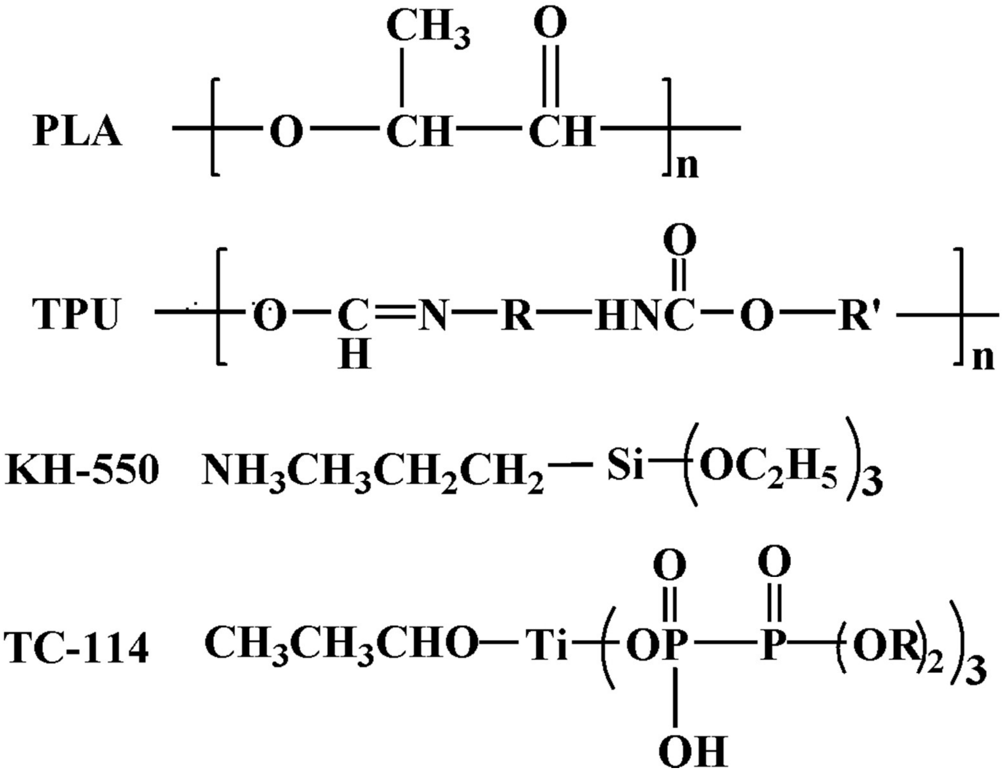
Fig. 7. FT-IR spectrum of untreated and /or treated Mica.

Fig. 8. SEM observations for PLA/TPU blends as a function of different ratio and theirs composites with untreated and/or treated mica (KH-550 and TC-114)

respectively.

Fig. 9. DSC curves for PLA/TPU blends and theirs composites with untreated, treated mica using KH-550 and TC-114, respectively.

Fig. 10. The tensile strength, tensile modulus and elongation at break curves of PLA/TPU blends as a function of component ratio with untreated and treated mica addition.



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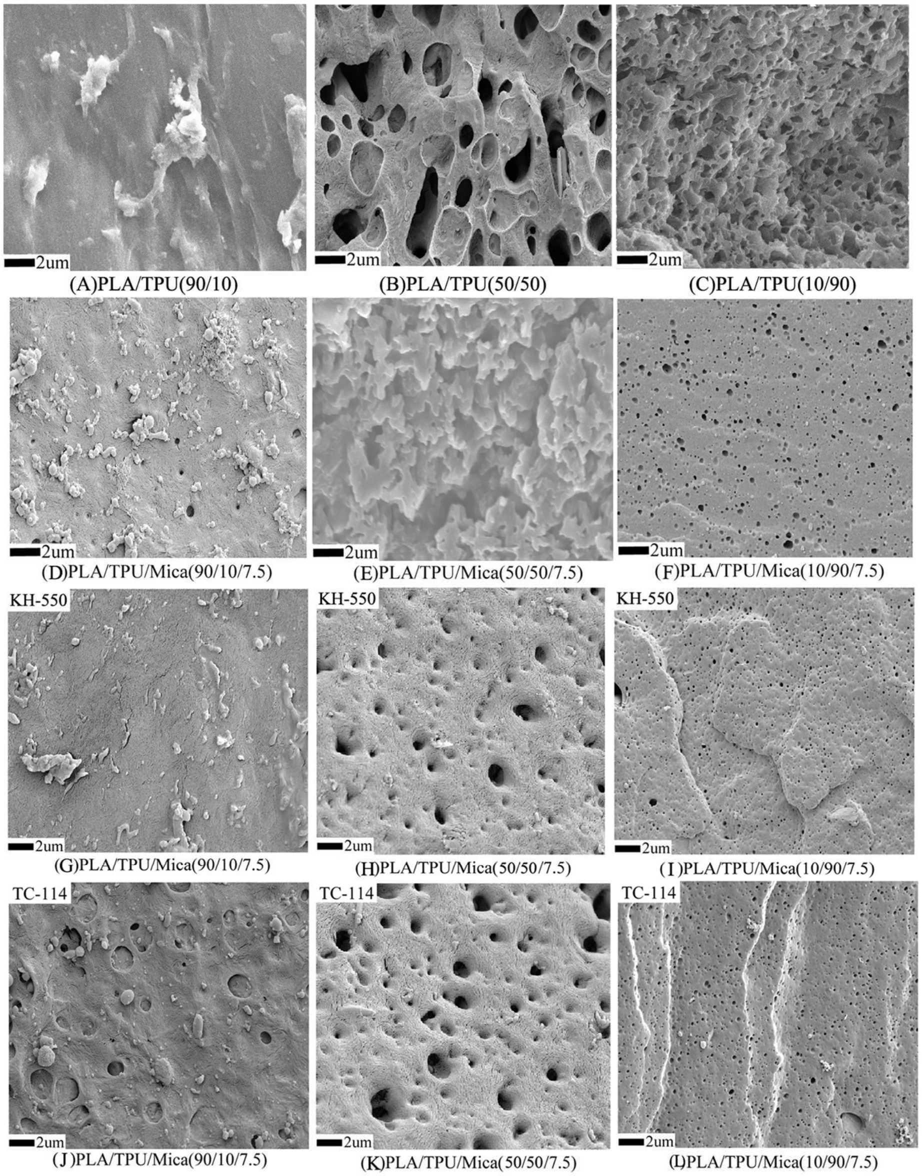

(A)PLA/TPU(90/10) (B)PLA/TPU(50/50) (C)PLA/TPU(10/90)

(D)PLA/TPU/Mica(90/10/7.5) (E)PLA/TPU/Mica(50/50/7.5) (F)PLA/TPU/Mica(10/90/7.5)

(G)PLA/TPU/Mica(90/10/7.5) (H)PLA/TPU/Mica(50/50/7.5) (I)PLA/TPU/Mica(10/90/7.5)

(J)PLA/TPU/Mica(90/10/7.5) (K)PLA/TPU/Mica(50/50/7.5) (L)PLA/TPU/Mica(10/90/7.5)

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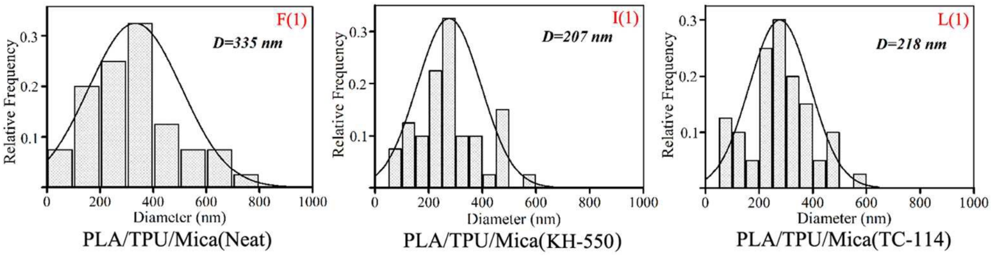

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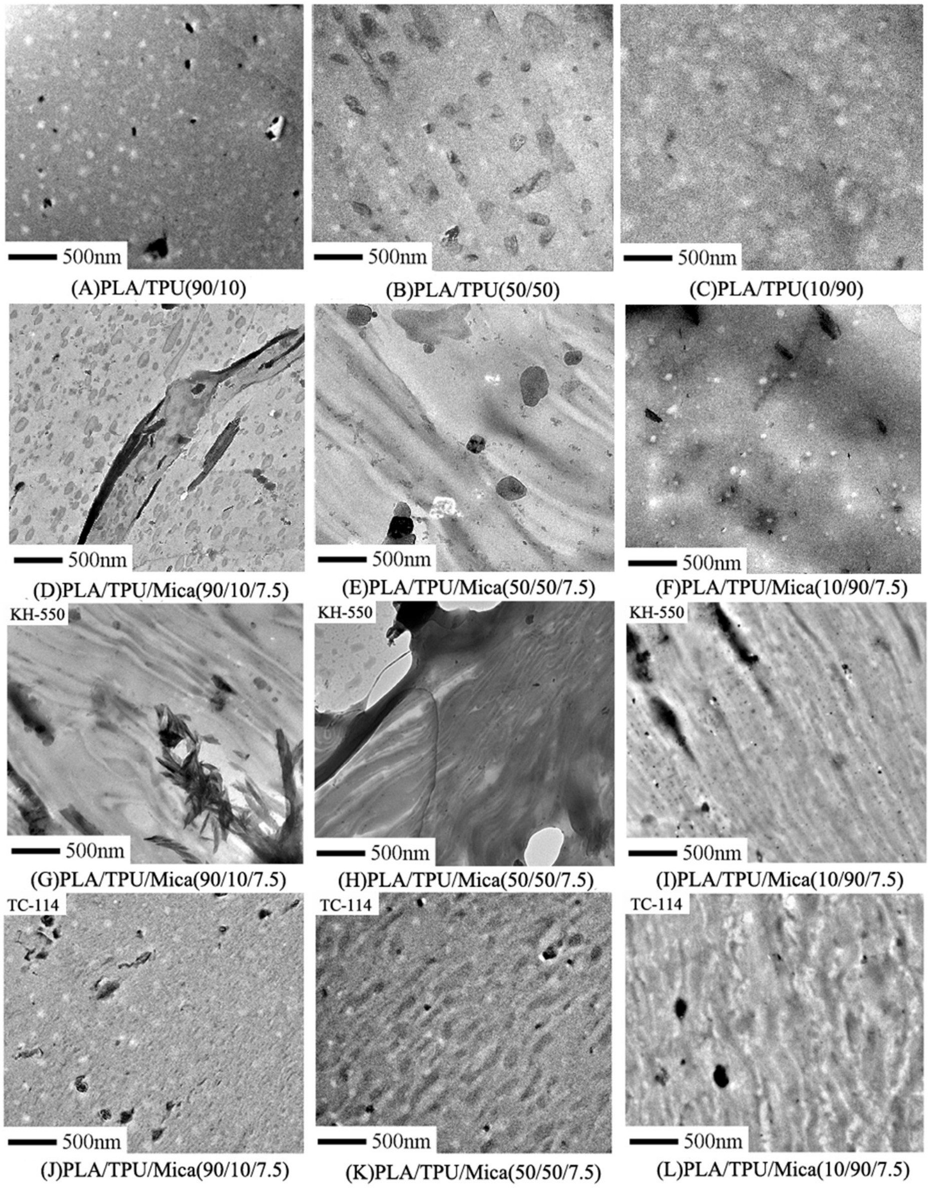

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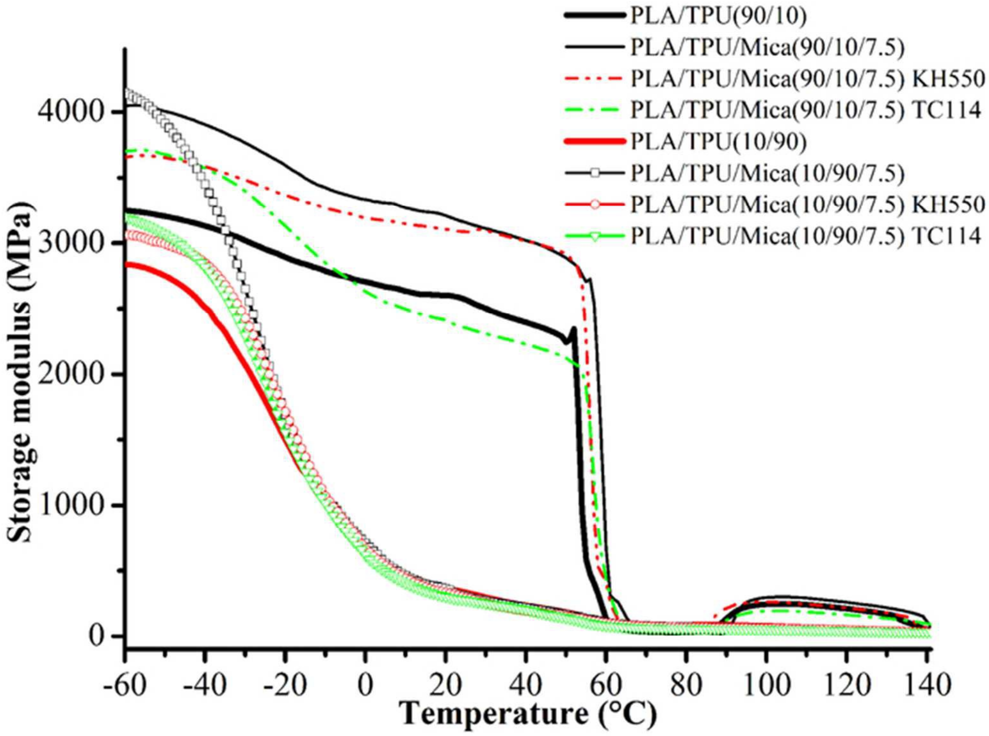

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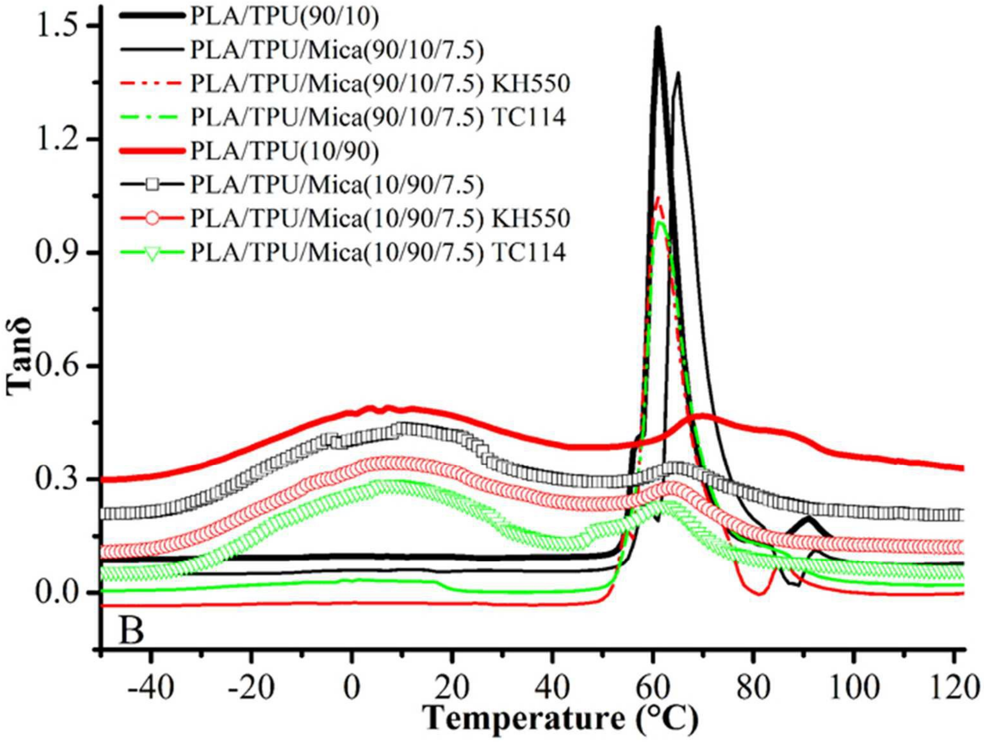

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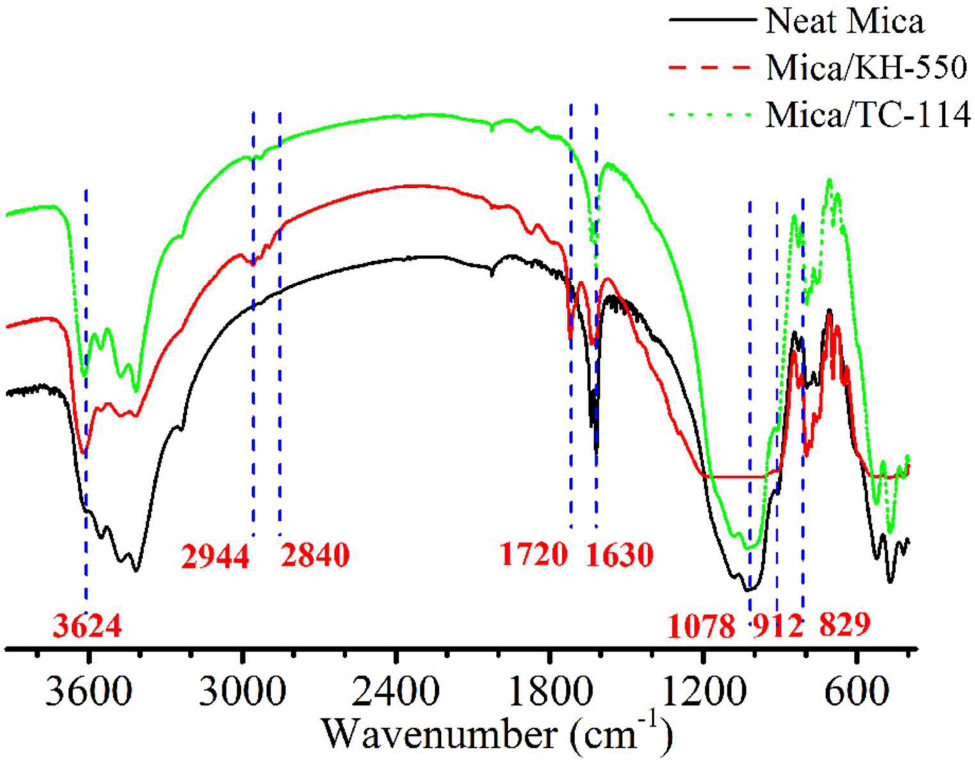

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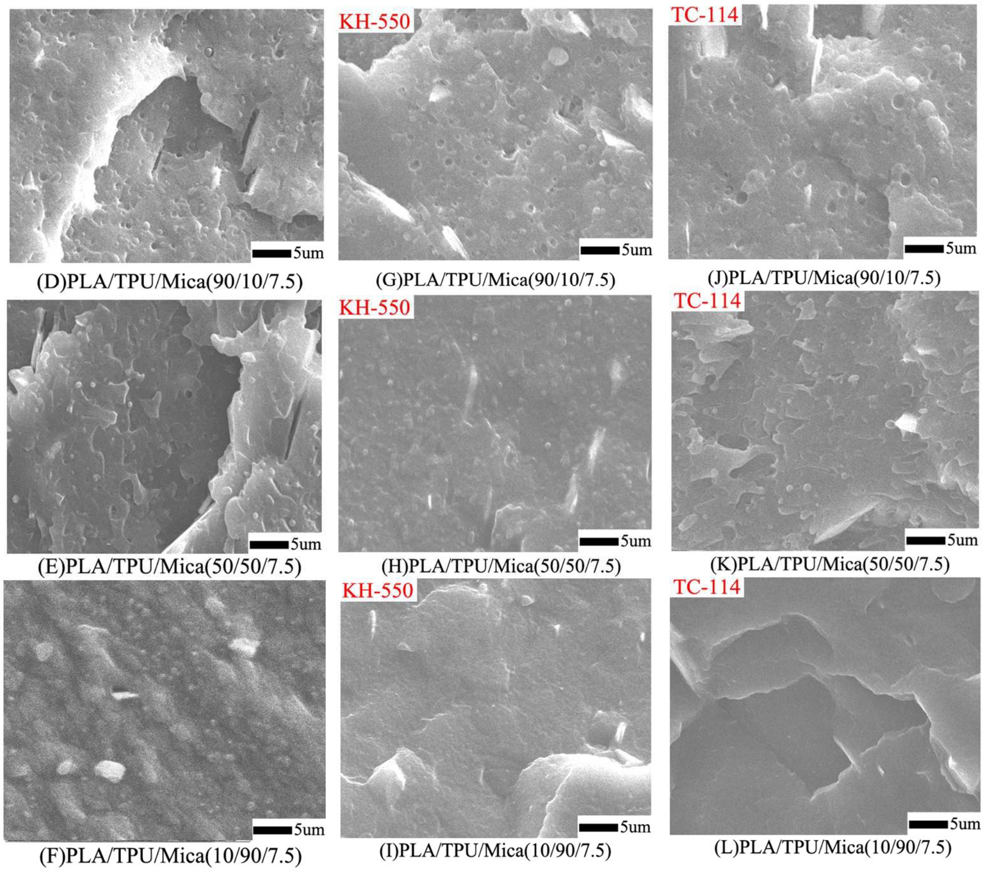

(D)PLA/TPU/Mica(90/10/7.5) (G)PLA/TPU/Mica(90/10/7.5) (J)PLA/TPU/Mica(90/10/7.5)

(E)PLA/TPU/Mica(50/50/7.5) (H)PLA/TPU/Mica(50/50/7.5) (K)PLA/TPU/Mica(50/50/7.5)

(F)PLA/TPU/Mica(10/90/7.5) (I)PLA/TPU/Mica(10/90/7.5) (L)PLA/TPU/Mica(10/90/7.5)

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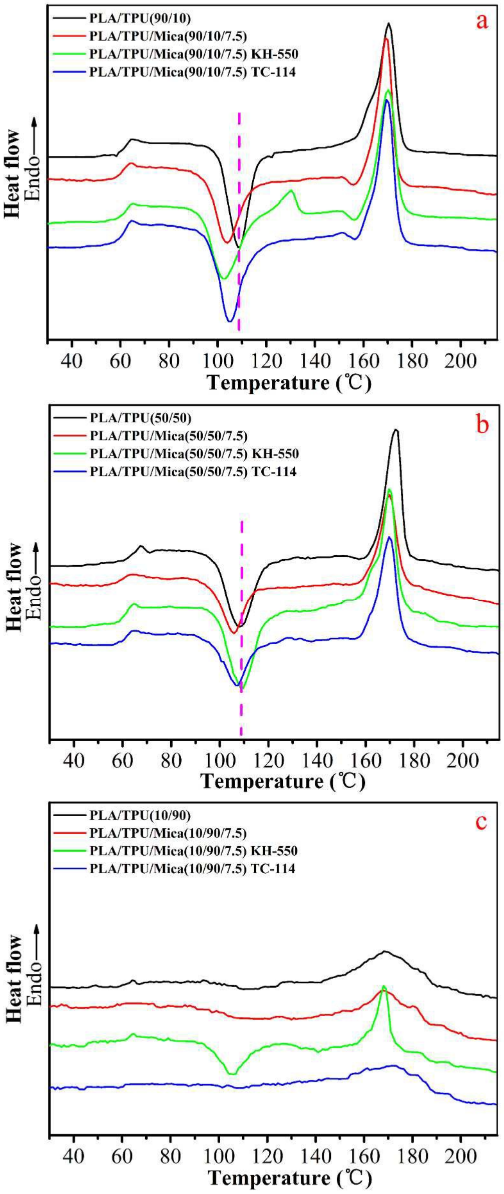

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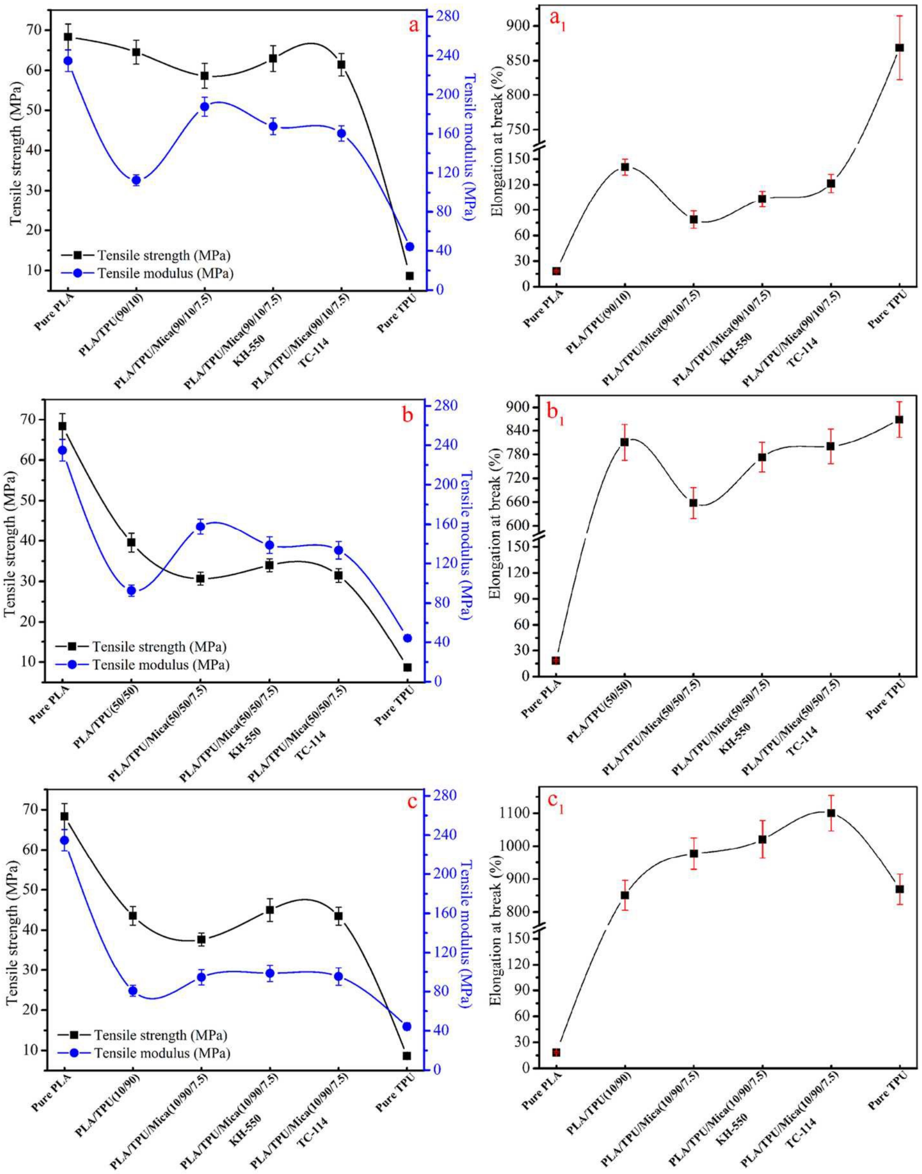

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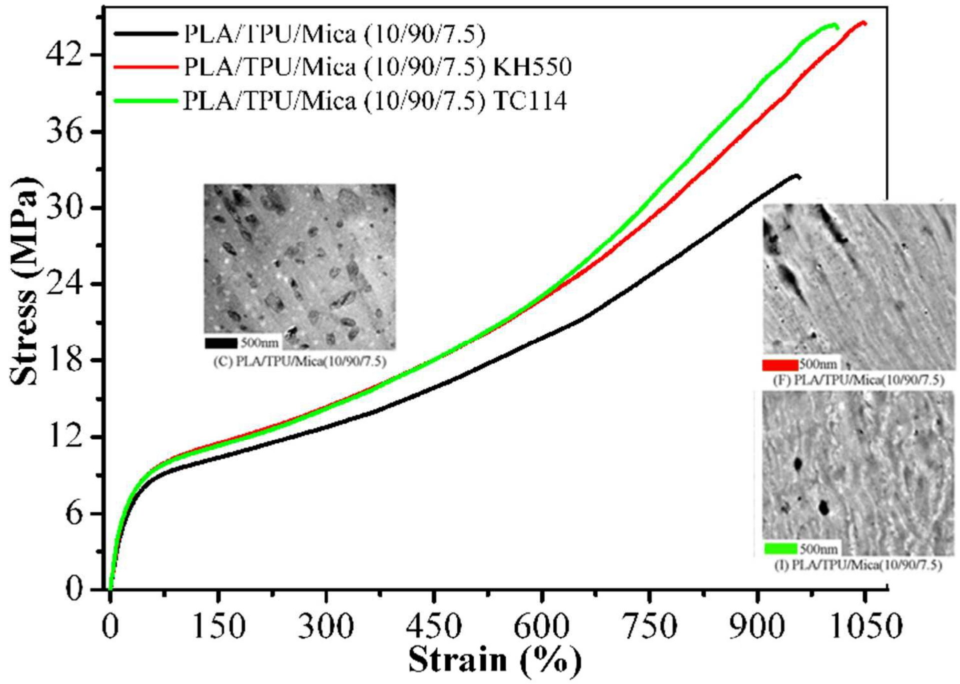

Graphical abstract
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