

Plasticized Properties of Poly (lactic acid) and Triacetine Blends

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ABSTRACT: Systematically investigations of the plasticizing effects of triacetine (TAC) on crystallization, chain mobility, microstructure, and tensile properties of the Poly (lactic acid)/triacetine (PLA/TAC) blends are reported. A new transition hump was observed on the $\tan \delta$ curve of PLA_xTAC_y specimens at temperatures ranging from -80 to -20°C . Thermal, wide angle X-ray diffraction (WAXD) and dynamic mechanical analysis properties of PLA and PLA_xTAC_y series specimens suggest that PLA and PLA_xTAC_y series specimens can hardly crystallize by cooling the melt in room temperature. However, significant recrystallization of α form PLA crystals was found during the annealing processes of PLA_xTAC_y series specimens. Some

“less perfect” β form PLA crystals were found as the TAC contents of PLA_xTAC_y specimens reach 30 wt %. Further morphological analysis show that the inherent brittle deformation behavior of the PLA specimen was successfully transformed into relatively ductile fracture behavior after blending sufficient but optimum amounts of TAC in PLA resins. Possible reasons accounting for this interesting recrystallization, thermal, microstructure and tensile properties of PLA_xTAC_y specimens are proposed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2757–2763, 2009

Key words: poly (lactic acid); triacetine; plasticizing effect; recrystallization

INTRODUCTION

Poly (lactic acid) (PLA) is well known as a biodegradable thermoplastic, which can be produced from renewable resources. It can be used as packaging materials¹ and hygienic products because of its good biocompatibility, biodegradability and environmentally friendly character.² However, PLA is a relatively brittle material, and difficult for film-blowing or extrusion. To improve the processability of the film-blowing and/or extrusion of PLA resins, copolymerization^{3–12} or blending PLA with other polymers or compounds (e.g., plasticizers)^{5–38} were proved as feasible ways to improve their processability of film products.

In contrast to copolymerization technology, the capital investment of blending PLA with other polymers and/or plasticizers is much lower and appears as a more feasible technology. Possibly because of

these reasons, investigations on blending PLA with polymers and/or plasticizers appear to draw much attention than using copolymerization technology in the last decade. Investigations concern blending PLA with poly (ethylene oxide) (PEO),^{3–6,13} poly (ϵ -caprolactone) (PCL),^{7,8,14–16} poly (vinyl acetate) (PVA),¹⁷ poly (hydroxyl butyrate) (PHB)^{9–12,18,19} and poly (butylenes succinate) (PBS)^{20,21} have been intensively studied to improve mechanical and flexible properties of PLA blends. In fact, the flexibility and values of elongation at break (ϵ_f) of PLA resins were significantly improved after blending suitable amounts of polymers, such as, PEO,^{3–6,13} and PVA.¹⁷ For instance, ϵ_f values of PLA/PEO blends increase from 5% to more than 500%, as their PEO contents increase from 0 to 20 wt %. Similarly, the ϵ_f values of PLA/PVA blends reach 225% after blending only 5 wt % of PVA in PLA. In contrast, no significant improvement in ϵ_f values and flexibility was found, when PLA was blended with varying amounts of PCL, PHB, and PBS resins, respectively. The ϵ_f values of PLA/PHB blends reach merely about 28% even after adding 60 wt % of PHB in PLA. The ϵ_f values of PLA/PCL blends are always less than 10% when the PCL contents reach 30 wt %. Presumably, the poor flexibility of these PLA blends is attributed

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to the poor compatibility and phase separation of PLA phases with those of PCL⁹, PHB^{10-12,18} and PBS¹⁹⁻²¹ resins, respectively. Later investigations²²⁻³⁵ found that the flexibility of PLA resins can be efficiently improved by the addition of relatively small amounts of plasticizers, such as, lactic acid monomers, glucose monoesters, partial fatty acid esters,²² poly (ethylene glycol) (PEG),²²⁻²⁷ triacetine (TAc)³⁰ and low molecular weight citrates.²⁹⁻³⁶ For example, ϵ_f values of 200 and 235% were obtained when 20 wt % of lactic acid monomers and PEG were added in PLA resin, respectively.^{22,27} After blending 30 wt % of triethyl citrate, a maximum ϵ_f value of 610% was obtained for PLA/triethyl citrate resins.²⁹ In contrast, the flexibility of PLA can be significantly enhanced after addition of relatively small amounts of TAc.^{30,32} For instance, Ljungberg and Wesslen³² reported that the ϵ_f values of PLA/TAc resins can reach more than 350% after blending merely 15 wt % of TAc in PLA. In fact, significant reduction in glass transition temperature (T_g) of the PLA resin was found after adding suitable amounts of the plasticizers mentioned above. This reduction of T_g is generally attributed to the significant increase in the free volume and molecular mobility of the PLA resin after adding compatible plasticizers with the PLA molecules. It is, therefore, a significant improvement in the flexibility of the PLA/plasticizer is observed. On the other hand, the microstructures present in the crystalline and amorphous regions of the PLA/plasticizer resins are also expected to have a great effect on their flexibility. However, barely any investigation has ever been reported on the plasticizing effect on chain mobility and microstructure present in crystalline and amorphous phases of the PLA/plasticizer resins.

Varying compositions of PLA/TAc resins were prepared by melt-blending to enhance their flexibility and ability for film-blowing. A systematically investigation of TAc on the crystallization, chain mobility, microstructure and tensile properties of the Poly (lactic acid)/(PLA/TAc) blends are reported in this study.

EXPERIMENTAL

Materials and sample preparation

The PLA resin used in this study was obtained from Cargill-Dow, with a trade name of Nature green 2002D. The TAc was purchased from Yixing Chemical company, Jiangsu, China, which was used as the plasticizer for PLA. Before melt-blending, PLA was vacuum dried at 80°C for 3 h to remove the residual water, and then blended with varying compositions of plasticizer using a HAAKE Rheocord 600P instrument. During each compounding process, the

TABLE I
The Compositions of the PLA/TAc Specimens

Sample code	PLA content (wt %)	TAc content (wt %)
PLA	100	0
PLA95TAc5	95	5
PLA90TAc10	90	10
PLA85TAc15	85	15
PLA80TAc20	80	20
PLA75TAc25	75	25
PLA70TAc30	70	30

HAAKE instrument was operated at 180°C and a screw speed of 120 rpm for 3 min. The prepared PLA/TAc resins were then hot-pressed at 190°C and 10 MPa for 2 min and then cooled in air at about 25°C. The thickness of the hot-pressed PLA and PLA/TAc specimens is about 0.2 mm. The compositions of the PLA/TAc specimens prepared in this study are summarized in Table I. For comparison purposes, the annealed PLA and PLA/TAc specimens were also prepared by heating the hot-pressed specimens from 25 to 90°C at a heating rate of 3°C/min on a Linkam TMS-94 hot stage.

Thermal properties

Thermal properties of PLA and PLA/TAc resins were determined using a Du Pont 2010 differential scanning calorimetry (DSC) instrument. The PLA specimens were scanned at 3, 10, 20, 40, and 60°C/min and under flowing nitrogen at a flow rate of 25 mL/min to decide the optimal heating rate for testing. The DSC scans were then carried out at a heating rate of 40°C/min to minimize the re-crystallization exotherms of PLA molecules during their DSC scanning processes. The instrument was calibrated using the pure indium. Samples weighing of about 15 and 0.5 mg were placed in standard aluminum sample pans for T_g and T_m determination of each specimen, respectively.

Wide X-ray diffraction properties

The wide angle X-ray diffraction (WAXD) properties of hot-pressed and annealed hot-pressed PLA and PLA/TAc specimens were determined using a Rigaku Analytical X-ray (D/MAX-III) diffractometer equipped with a Ni-filtered CuK α radiation operated at 3 kV. The specimen with 1 mm thickness was maintained stationary at 25°C and scanned in the reflection mode from 2 to 50° at a scanning rate of 5° min⁻¹.

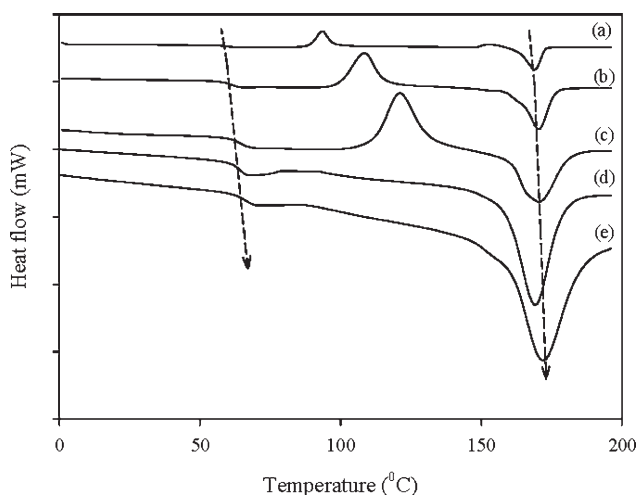


Figure 1 DSC thermograms of PLA specimens scanned at a heating rate of (a) 3°C/min; (b) 10°C/min; (c) 20°C/min; (d) 40°C/min, and (e) 60°C/min.

Dynamic mechanical analysis

The film specimens used for dynamic mechanical analysis (DMA) were prepared by hot-pressing the vacuum dried PLA and PLA/TAc resins prepared above at 190°C and 10 MPa for 2 min and then cooled in air at about 25°C. The hot-pressed specimens with 0.2 mm thickness were then sectioned into a rectangular strip with a dimension of 9 × 22 mm. All DMA experiments were operated at a frequency of 1 Hz, a heating rate of 3°C/min and in a temperature range from -100 to 180°C under N₂ atmosphere in the tensile mode.

Morphology analysis

The morphology of the PLA and PLA/TAc resins were observed using a Hitachi S-3000N scanning electron microscope (SEM). The hot-pressed specimens prepared in the previous section were fractured in liquid nitrogen and then gold-coated at 15 keV for 15 s before SEM examinations.

Tensile properties analysis

The tensile properties of the hot-pressed PLA specimens were determined using a Shimadzu tensile testing machine model AG-10KNA at 25°C and a crosshead speed of 50 mm/min. A 35 mm gauge length was used during each tensile experiment. The dimensions of the dog-bone shaped specimens were prepared according to ASTM D638 type IV standard. The values of tensile strength and elongation at break were obtained based on the average tensile results of at least five tensile specimens.

RESULTS AND DISCUSSION

Thermal properties

Figure 1 shows the DSC thermograms of PLA specimen scanned at varying heating rates. As expected, the T_g and T_m values of the PLA specimen increase significantly as the scanning rates increase, which are generalized attributed to the delayed heat-response of the PLA molecules at high scanning rates. On the other hand, it is interesting to note that a broad exotherm reflecting the recrystallization of PLA molecules was found on the DSC thermograms of PLA specimens scanned at heating rates lower than 40°C/min. However, as shown in Figures 1(d,e), the magnitudes of the recrystallization exotherms reduce and almost vanish at heating rates equal to or higher than 40°C/min. For convenient purposes, the scanning rate used for the following studies of PLA and PLA_xTAc_y specimens (see Table I) was chosen as 40°C/min to inhibit the recrystallization of PLA molecules during the DSC scanning processes.

Typical DSC thermograms of PLA and PLA_xTAc_y specimens scanned at 40°C/min are shown in Figure 2. In addition to the T_g at 62.3°C, the melting endotherm with an onset temperature at 158.8°C was found on the thermogram of PLA specimen. After blending TAc with PLA, the T_g and T_m values of PLA_xTAc_y specimens reduce significantly as their TAc contents increase (see Table II). For example, the glass transition and onset melting temperatures reduce from 62.3 to 29.2°C and 158.8 to 151.9°C, respectively, as the TAc contents of PLA_xTAc_y specimens increase from 0 to 30 wt %. On the other hand, as shown in Figures 2(b-g), another

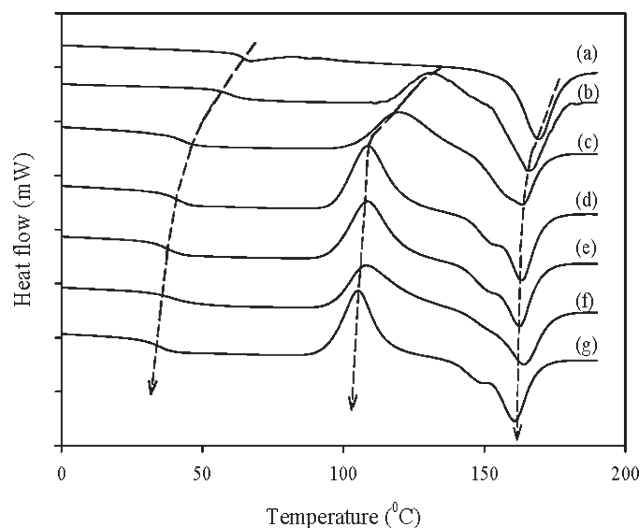


Figure 2 DSC thermograms of (a) PLA; (b) PLA₉₅TAc₅; (c) PLA₉₀TAc₁₀; (d) PLA₈₅TAc₁₅; (e) PLA₈₀TAc₂₀; (f) PLA₇₅TAc₂₅ and (g) PLA₇₀TAc₃₀ specimens scanned at 40°C/min.

TABLE II
Thermal Properties Obtained from DSC and DMA^a

Sample code	DSC		
	T_g (°C)	T_m (°C) ^b	T_g (°C)
PLA	62.3	158.8	73.7
PLA ₉₀ TAc ₁₀	39.4	156.7	52.0
PLA ₈₅ TAc ₁₅	36.9	154.7	44.6
PLA ₈₀ TAc ₂₀	33.4	153.2	42.3
PLA ₇₅ TAc ₂₅	33.6	152.5	38.3
PLA ₇₀ TAc ₃₀	29.2	151.9	34.9

^a Scans presented in Figures 2 and 5.

^b T_m was determined from the onset temperature of DSC thermograms of PLA and PLA_xTAc_y specimens.

recrystallization exotherms were found on the DSC thermograms of the PLA_xTAc_y specimens with TAc contents equal to or more than 10 wt %. Presumably, the reduction of T_g and appearance of the recrystallization exotherms is attributed to the expected increase in the free volume and molecular mobility of the PLA molecules as the TAc contents of PLA_xTAc_y specimens increase, since TAc is well known as the effective plasticizer for PLA resins. The reduced onset melting temperatures observed for PLA_xTAc_y specimens can be due to the fact that recrystallized PLA crystals are less perfect and with lower T_m values, since the plasticized and relatively mobile PLA molecules can recrystallize at relatively low temperatures during the heat-scanning processes.

Wide angle X-ray diffraction

Typical WAXD patterns and peak diffraction angles of hot-pressed PLA and PLA_xTAc_y specimens are shown in Figure 3. Only a diffuse amorphous hump centered at $2\theta = 16.98^\circ$ was found on the WAXD patterns of the PLA and PLA_xTAc_y specimens. Similar characteristics of the WAXD patterns were found on the annealed PLA specimen [see Fig. 4(a)]. In

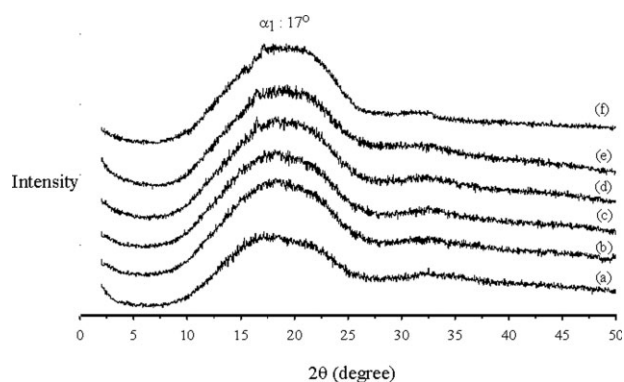


Figure 3 Wide angle X-ray diffraction patterns of hot-pressed (a) PLA; (b) PLA₉₀TAc₁₀; (c) PLA₈₅TAc₁₅; (d) PLA₈₀TAc₂₀; (e) PLA₇₅TAc₂₅ and (f) PLA₇₀TAc₃₀ specimens.

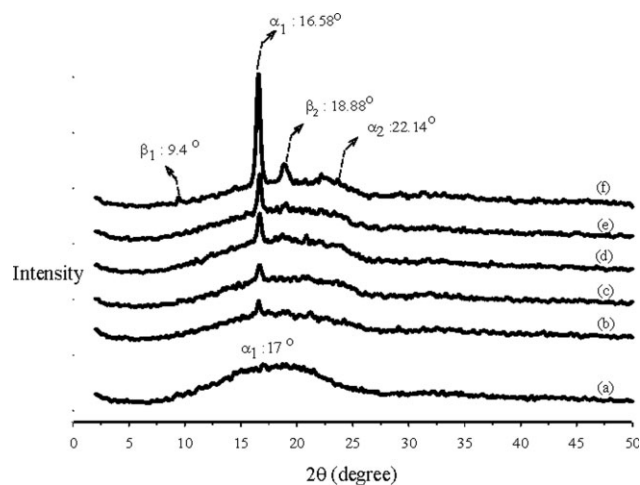


Figure 4 Wide angle X-ray diffraction patterns of annealed (a) PLA; (b) PLA₉₀TAc₁₀; (c) PLA₈₅TAc₁₅; (d) PLA₈₀TAc₂₀; (e) PLA₇₅TAc₂₅ and (f) PLA₇₀TAc₃₀ specimens.

contrast, additional diffraction peaks centered at $2\theta = 16.58^\circ$ and 22.14° were found on the X-ray diffraction patterns after the PLA_xTAc_y specimens were annealed at 25 to 90°C at a heating rate of 3°C/min. These diffraction peaks are very similar to the diffraction patterns of α form PLA crystals reported in the literatures,^{37,39–42} and hence, are ascribed to the α form PLA crystals formed during the annealing processes of the PLA_xTAc_y specimens. The stable α form PLA crystals is classified as pseudo-orthorhombic,^{24–26,37,43} pseudo-hexagonal⁴⁴ or orthorhombic modification,⁴⁵ which is generally formed on crystallization from PLA melts or dilute solutions.⁴⁶ The magnitudes of the diffraction peaks of the α form PLA crystals grow as the TAc contents of annealed PLA_xTAc_y specimens increase. Somewhat interesting, diffraction peaks at $2\theta = 9.4^\circ$ and 18.88° corresponding to β form PLA crystals appear on the X-ray diffractograms of the annealed PLA_xTAc_y specimens, as their TAc contents are more than 25 wt %. As reported by Zhong and coauthors,⁴¹ the β form crystals can hardly crystallize by cooling PLA melts in air environment, but can be obtained by annealing the PLA specimens for certain amounts of time at a specific temperature. In contrast to α form crystals, β form PLA crystals are normally recognized present as frustrated structures with lower melting temperatures.^{47,48}

Dynamic mechanical analysis

Figures 5 and 6 summarized the temperature dependence of the $\tan \delta$ and the storage modulus of PLA and PLA_xTAc_y specimens, respectively. As shown in Figure 5, a distinct transition is observed at temperatures near 74°C in the $\tan \delta$ curve of PLA

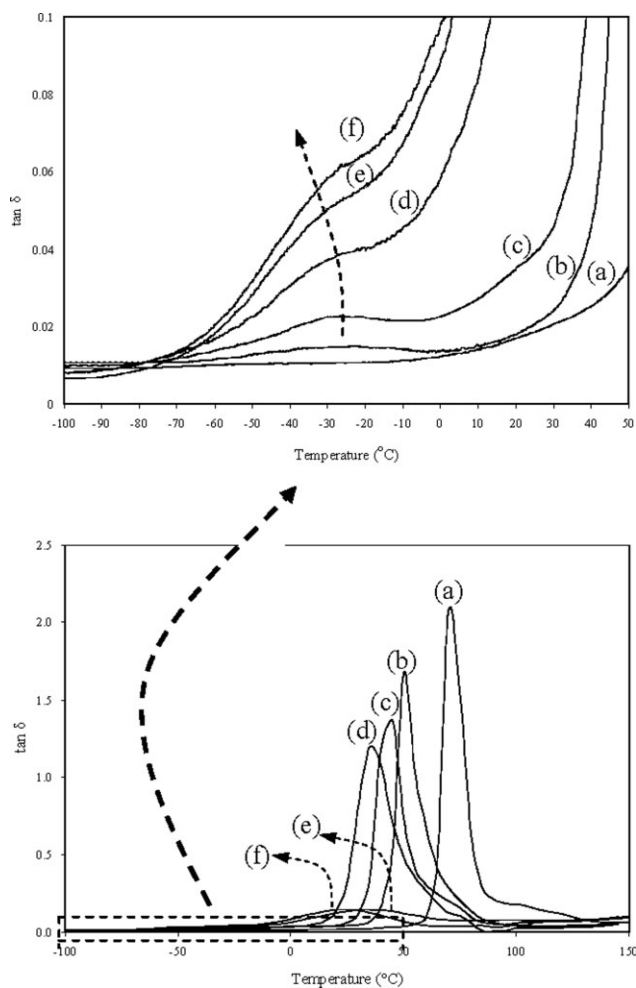


Figure 5 $\tan \delta$ curves of (a) PLA; (b) $\text{PLA}_{90}\text{TAC}_{10}$; (c) $\text{PLA}_{85}\text{TAC}_{15}$; (d) $\text{PLA}_{80}\text{TAC}_{20}$; (e) $\text{PLA}_{75}\text{TAC}_{25}$ and (f) $\text{PLA}_{70}\text{TAC}_{30}$ specimens scanned at $3^\circ\text{C}/\text{min}$.

specimen. This transition temperature is recognized as the T_g , since it is close to the T_g found above using DSC analysis and reported in the literatures.^{42,49} After blending TAC with PLA, the magnitudes and peak temperatures of the glass transition of PLA_xTAC_y specimens reduce significantly with increasing their TAC contents. For example, the T_g of PLA_xTAC_y specimens reduce from 73.7 to 34.9°C as their TAC contents increase from 0 to 30 wt % (see Table II). In particular, a significant drop and broadening of the $\tan \delta$ peak of PLA_xTAC_y specimens were found as their TAC contents are equal to or more than 20 wt %. Presumably, the significant drop and broadening of the $\tan \delta$ peak are attributed to the lack of uniform dispersion of TAC in PLA_xTAC_y specimens as their TAC contents increase. On the other hand, a new but minor transition hump was observed on the $\tan \delta$ curve of PLA_xTAC_y specimens at temperatures ranging from -80 to -20°C [see Figs. 5(b–f)]. In fact, the magnitudes and peak temperatures of the newly developed hump increase and reduce significantly as their TAC contents

increase, respectively. For instance, the peak temperatures of the new transition humps of PLA_xTAC_y specimens reduce from -30 to -55°C , as the TAC contents of PLA_xTAC_y specimens increase from 10 to 30 wt %, respectively. It is not completely clear what accounts for the newly developed hump observed above. Presumably, the new transition humps of PLA_xTAC_y specimens is originated from the rotation motion of $-\text{CH}_3$ group of PLA, which can be promoted as the TAC contents of PLA_xTAC_y specimens increase.

The storage moduli (E') of PLA and PLA_xTAC_y specimens were summarized in Figure 6. Similar to those found on their $\tan \delta$ curves, the values of glass transition accompanied by a sharp reduction of E' of PLA_xTAC_y specimens reduce significantly as their TAC contents increase. It is interesting to note that an additional rise on storage modulus (E') was found on the rubbery plateau of the PLA and PLA_xTAC_y specimens. As shown in Figure 6(a), the E' values of PLA specimen increase by almost fivefolds as the temperatures increase from 90 to 125°C . Similar increase in E' values on the rubbery plateau of PLA_xTAC_y specimens was observed after blending varying amounts of TAC in PLA. However, the onset temperatures corresponding to the increase in E' values shift to lower temperatures as the TAC contents of PLA_xTAC_y specimens increase. Moreover, the magnitudes of E' values arose on the rubbery plateau of PLA_xTAC_y specimens increase significantly as their TAC contents increase. For instance, the E' values of $\text{PLA}_{75}\text{TAC}_{25}$ specimen increase by almost three orders of magnitudes as the temperatures increase from 40 to 80°C . Apparently, these significant increases in E' values of PLA and PLA_xTAC_y specimens in their rubbery plateau regions is due to the recrystallized PLA crystals.

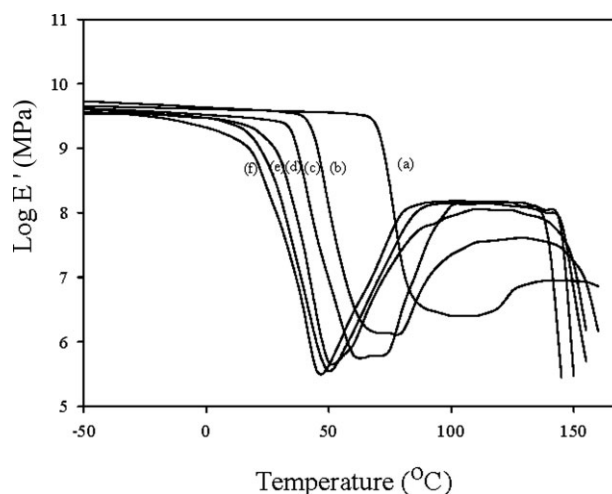


Figure 6 Storage modulus (E') curves of (a) PLA; (b) $\text{PLA}_{90}\text{TAC}_{10}$; (c) $\text{PLA}_{85}\text{TAC}_{15}$; (d) $\text{PLA}_{80}\text{TAC}_{20}$; (e) $\text{PLA}_{75}\text{TAC}_{25}$ and (f) $\text{PLA}_{70}\text{TAC}_{30}$ specimens scanned at $3^\circ\text{C}/\text{min}$.

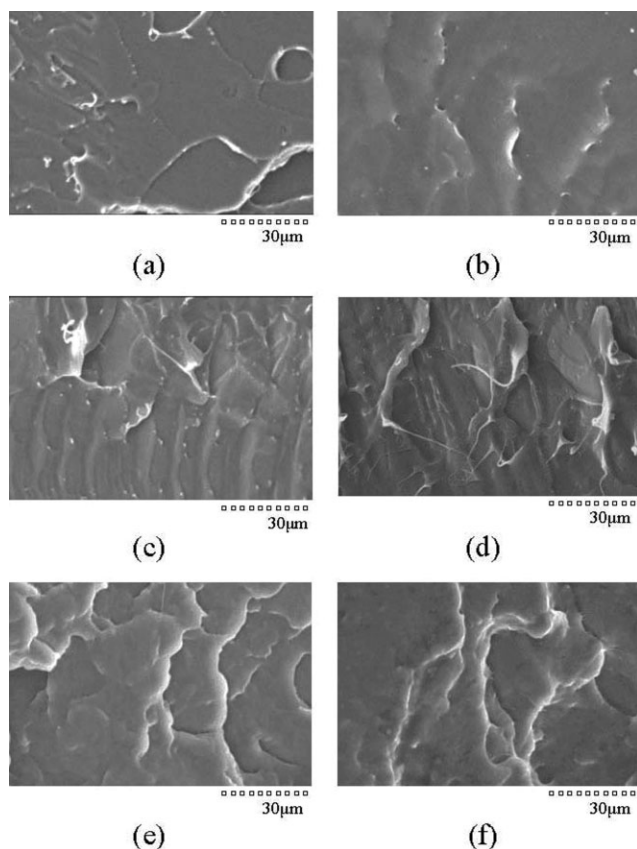


Figure 7 SEM micrographs of the fracture surfaces of (a) PLA; (b) PLA₉₀TAC₁₀; (c) PLA₈₅TAC₁₅; (d) PLA₈₀TAC₂₀; (e) PLA₇₅TAC₂₅ and (f) PLA₇₀TAC₃₀ specimens.

These interesting DSC, WAXD, and DMA properties of PLA and PLA_xTAC_y series specimens suggest that PLA and PLA_xTAC_y series specimens can hardly crystallize by cooling the melt in room temperature. However, as evidenced by WAXD analysis, significant recrystallization of α form PLA crystals was found during the DSC and DMA scanning or annealing processes of the PLA_xTAC_y series specimens. In fact, some "less perfect" β form PLA crystals were found as the TAc contents of PLA_xTAC_y specimens reach 30 wt %. Presumably, the appearance of the recrystallized α and β form PLA crystals is attributed to the expected increase in the free volume and molecular mobility of the PLA molecules as the TAc contents of PLA_xTAC_y specimens increase, since the plasticized and relatively mobile PLA molecules can recrystallize at relatively low temperatures during the heat-scanning processes.

Morphology analysis and tensile properties

Typical SEM micrographs of the fracture surfaces of PLA and PLA_xTAC_y specimens are shown in Figure 7. As shown in Figure 7(a), relatively brittle and smooth fracture surface morphology was found on the fracture surface of the PLA specimen. After

blending TAc in PLA resins, more demarcated plastic-deformed PLA debris or fibrils were found on the fracture surfaces of the PLA_xTAC_y specimens, as their TAc contents increase [see Figs. 7(b–f)].

The tensile properties of PLA_xTAC_y specimens are summarized in Figure 8. The PLA specimen exhibits relatively high tensile strength (σ_f) at 52.6 MPa but low elongation at break (ϵ_f) of 2.8%. After blending TAc in PLA, the PLA_xTAC_y specimens revealed substantial reduction in σ_f values but increase in ϵ_f values as their TAc contents increase. For example, the σ_f and ϵ_f values of PLA_xTAC_y specimens reduce and increase from 52.6 to 30 MPa and from 2.8 to 267.2%, respectively, as their TAc contents increase from 0 to 25 wt %. However, both ϵ_f and σ_f values of PLA_xTAC_y specimens reduce abruptly from 30 MPa and 267.2% to 10.4 MPa and 126.9%, respectively, as their TAc contents increase from 25 to 30 wt %.

Apparently, the inherent brittle deformation behavior of the PLA specimen was successfully transformed into relatively ductile fracture behavior after blending sufficient amounts of TAc in PLA resins. However, PLA molecules may be over-plasticized by adding excess amounts of TAc, since the over-plasticized PLA molecules are too soft to hold as a ductile PLA_xTAC_y specimen during their tensile drawing processes. In fact, the PLA molecules may become relatively easy to slide and disentangle during early stages of the drawing processes. As a consequence, both ϵ_f and σ_f values of PLA_xTAC_y specimens reduce abruptly as their TAc contents increase from 25 to 30 wt %.

CONCLUSIONS

Distinct recrystallization exotherms were found as PLA specimens were scanned at heating rates lower than 40°C/min. The magnitudes of recrystallization

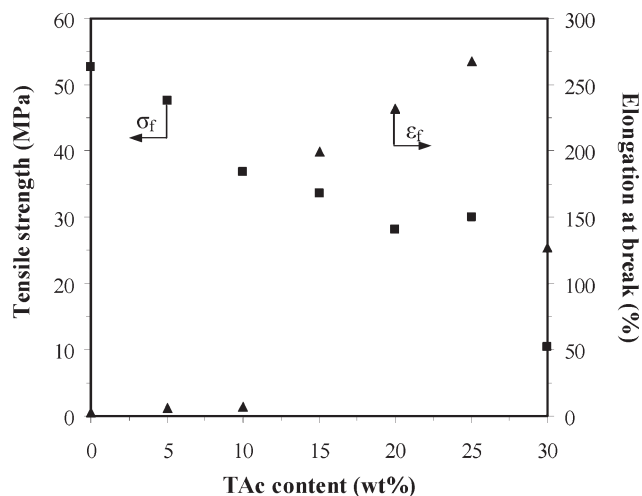


Figure 8 Tensile properties of PLA_xTAC_y specimens with varying TAc contents.

exotherms reduce and almost vanish at heating rates equal to or higher than 40°C/min. After blending TAC with PLA, the T_g and T_m values of PLA_xTAC_y specimens reduce significantly as their TAC contents increase. A new but minor transition hump was observed on the tan δ curve of PLA_xTAC_y specimens at temperatures ranging from -80 to -20°C. Presumably, the new transition humps of PLA_xTAC_y specimens is originated from the rotation motion of -CH₃ group of PLA, which can be promoted as the TAC contents of PLA_xTAC_y specimens increase. The thermal, WAXD and DMA properties of PLA and PLA_xTAC_y series specimens suggest that PLA and PLA_xTAC_y series specimens can hardly crystallize by cooling the melt in room temperature. However, as evidenced by WAXD analysis, significant recrystallization of α form PLA crystals was found during the annealing processes of the PLA_xTAC_y series specimens. In fact, some "less perfect" β form PLA crystals were found as the TAC contents of PLA_xTAC_y specimens reach 30 wt %. Presumably, the appearance of the recrystallized α and β form PLA crystals is attributed to the expected increase in the free volume and molecular mobility of the PLA molecules as the TAC contents of PLA_xTAC_y specimens increase, since the plasticized and relatively mobile PLA molecules can recrystallize at relatively low temperatures during the heat-scanning processes. The PLA specimen exhibits relatively high σ_f but low ε_f values. After blending TAC in PLA, the σ_f and ε_f values of PLA_xTAC_y specimens reduce and increase significantly from 52.6 to 30 MPa and from 2.8 to 267.2%, respectively, as their TAC contents increase from 0 to 25 wt %. However, both ε_f and σ_f values of PLA_xTAC_y specimens reduce abruptly as their TAC contents increase from 25 to 30 wt %. Apparently, the inherent brittle deformation behavior of the PLA specimen was successfully transformed into relatively ductile fracture behavior after blending sufficient but optimum amounts of TAC in PLA resins.

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