Thermal and Mechanical Properties of Blends of Polylactide and Poly(ethylene glycol-*co*-propylene glycol): Influence of Annealing

Xianghai Ran, Zhiyuan Jia, Changyu Han, Yuming Yang, Lisong Dong

Polymer Engineering Laboratory and Graduate School of the Chinese Academy of Sciences, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

ABSTRACT: Two kinds of polylactide (PLA) which was named PLA1 with L-lactide content of 98% and PLA2 with L-lactide content of 88% were blended with poly(ethylene glycol-*co*-propylene glycol) (PEPG) in a batchwise mixer and pressed into films. The effect of annealing on the thermal properties, crystallization behavior, and mechanical properties of the quenched blends were studied by means of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), polar optical microscopy (POM), and tensile tests. PEPG was miscible with the two kinds of PLA in the blend composition range of 5–20 wt % and can effectively decrease the glass transition temperature of PLA. Neat PLA2 lost the ability to crystallize in the DSC and DMA measurements; however, it could crystallize after annealing for long time and crystallize more easily due to the improved crystallizability with the addition of PEPG. Both of the PLAs underwent cold crystallization when annealing at 90°C, and there were signs of phase separation occurring in the blends at the same time. The crystallization morphology and tensile properties of the annealed blends were different and dependent of the optical purity of PLA. The blends with PLA2 after annealing regained the brittleness with maximum of elongation at break about 20% and showed larger spherulites in the POM images, whereas the blends with PLA1 after annealing still kept some flexibility with maximum of elongation at break about 65% and showed fine spherulites. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2050–2057, 2010

Key words: polylactide; cold crystallization; thermal properties; blends

INTRODUCTION

Polylactide (PLA), a kind of environmental friendly polyester, is produced from renewable biomass, such as, corn, has been intensively studied due to its comparable mechanical performance to those petroleum-based polymers, especially high elasticity modulus and high stiffness, thermoplastic behavior, biocompatibility, and good shaping capability.[1,2]

Generally, commercial PLA grades are copolymers of L-lactide and D-lactide. The optical purity, defined as |L%-D%|, strongly influences the properties of PLA, such as, the melting temperature and degree of crystallinity. Both optically pure poly(L-lactide) and poly(D-lactide) is crystallizable polymer. Decreasing the optical purity can lower their crystallizability. It is well-known that PLA with optical purity lower than 76% is amorphous.[3]

The inherent brittleness and low toughness of PLA have been the major drawbacks for its practical application. Several modifications have been proposed to improve the flexibility of PLA, such as, copolymerization, polymer blending, and plasticization. Considering the economical reason a suitable plasticizer is a good choice. It has been known that citrate esters,[4,5] triactine,[5] poly(ethylene glycol)s (PEGs),[6,7] and poly(propylene glycol)s (PPGs) of low molecular weight[8] are efficient plasticizers for PLA. The limitation of plasticized PLA for application is its aging. Most of the plasticizers due to the low molecular weight tend to migrate from the bulk material to the film surface, ultimately leading to the blend regaining the inherent brittleness of neat PLA. High molecular weight plasticizers are always desirable because of the better stability of plasticized PLA.[9] PEGs long known as efficient plasticizers for PLA have good miscibility with PLA even with a molecular weight 20 kDa. Blending PLA with PEG can drastically lower the T_g of PLA and create homogeneous and flexible materials. However, the

promising mechanical properties of PLA/PEG blends disappeared with time because of their slowly phase separation and the crystallization of PEG at the room temperature.[10,11] In our previous study,[12] it has been known that poly(ethylene glycol-co-propylene glycol) (PEPG) was a good macromolecular plasticizer for PLA, which had good compatibility with PLA and kept a liquid state at room temperature. The PLA/PEPG blends had better stability than the PLA/PEG blends due to the uncrystallizability of the plasticizer at ambient condition. However, the PLA/PEPG blends still lost some flexibility after storing at ambient condition for 2 months due to physical aging and slow cold crystallization of PLA.

The plasticized PLA with high plasticizer content would undergo slow cold crystallization of PLA due to the increased crystallizability and the lowered glass transition temperature caused by the plasticizer. Generally, plasticizers are mainly dispersed in the amorphous phase under the pressure of spherulites.[13] Any factor influencing crystallinity or crystalline behaviors of PLA could disturb the distribution and compatibility of plasticizers with PLA and induce phase separation and segregation or migration of plasticizers.[14,15] As a result, the mechanical properties and morphology of the plasticized PLA can be degraded. Cold crystallization of PLA can reduce the ability of plasticized PLA to plastic deformation.

Crystallization can drastically influence the mechanical properties of semicrystalline polymers. It is well-known that a low crystallinity level and fine spherulitic structure is advantageous for development of crazes in the semicrystalline polymers. At the same crystallinity, the fine sperulite will have a positive effect on the toughness of polymer. The crystalline structure of PLA is in relation to the crystallization method. It has been known that PLA cooling form the melt would form a larger spheulite than that via heating from the amorphous state.[16] Recent studies indicated that plasticized PLA with uncrystallized PPG of low molecular weight could keep some flexibility after cold crystallization of PLA due to the fine spherulite and local plasticization.[17] The utilized PLA in their studies had an optical purity of 87.6%. The crystallization behavior of PLA is significantly influenced by its optical purity. The crystallinity and crystallization rate decreased with the decrease of optical purity. Blending PEPG with PLA of low optical purity may be a method to overcome the cold crystallization of plasticized PLA.

In this study, the influence of annealing on the thermal, crystallization, and mechanical properties of PLA/PEPG blends were investigated. The aim of the study is to identify whether blending PEPG with PLA of low optical purity can hinder the cold crystallization or keep the flexibility after annealing.

EXPERIMENTAL SECTION

Materials

There are two commercial grades PLA (Natureworks 4032D, 4060D) utilized in this study. PLA1 (4032D) exhibits a weight-average molecular weight of 207 kDa, polydispersity of 1.73, and L-lactide content about 98% (optical purity about 96%). PLA2 (4060D) exhibits a weight-average molecular weight of 320 kDa, polydispersity of 1.77, and L-lactide content about 88% (optical purity about 76%). The PLA1 exhibited 40% crystallinity after annealing at 90°C for 24 h with melting temperature of 167°C, whereas the PLA2 exhibited 18% crystallinity after the same processing with melting temperature of 120°C. PEPG with a typical number-average molecular weight of 12 kDa and ethylene glycol content of 78.7 mol % was obtained from Sigma-Aldrich and used as received. The glass transition temperature and melting point of PEPG is −68°C and −2°C [differential scanning calorimetry (DSC) analysis], respectively.

Sample preparation

Before blending, all polymers were dried in vacuum at 50°C for 24 h. Blends of PLA1/PEPG and PLA2/PEPG were prepared by melt mixing using a twin-screw Haake Reomix 600 at 60 rpm and 180°C for 5 min. The mixing compositions of the blends were 95/5, 90/10, 85/15, and 80/20 wt/wt. Addition of more than 20 wt % plasticizer is not reasonable considering application aspects. After blending, all the samples were cooled to room temperature under atmosphere air. Also, the neat PLA was subjected to the same mixing treatment so as to obtain a reference material.

Films were prepared using a hot press at 180°C, a hold pressure of 6 MPa and a hold time of 3 min, followed by quenching to room temperature between two thick-metal blocks kept at room temperature. The blocks were cooled on a large metal plate in the air for about 10 min between each quenching round to keep the same processing temperature. A template frame was used to ensure a constant film thickness (1.0 mm), and care was taken to ensure the same thermal history of all films. The specimens were then sealed in plastic bags awaiting the processing and analysis.

To obtain the annealed samples, the entirely amorphous films were laid on a hot stage (Linkam LTS 350) covered with a metal block as soon as the sample had been prepared to avoid some possible aging. The PLA1/PEPG blends and PLA2/PEPG blends

were annealed at 90°C for 4 h and 24 h, respectively. The hot stage enabled holding steady temperature with accuracy of 0.1 K. Time required for processing depended on optical purity: 4 h was enough for PLA1/PEPG blends to complete the crystallization, whereas PLA2/PEPG needed more time to consummate the potential crystallization.

Characterizations

DSC measurements were performed on a Perkin-Elmer Diamond DSC instrument under a N_2 atmosphere, which was calibrated using indium as standard. The quenched blends and neat PLA were preliminarily heated to 190°C for 3 min to erase previous thermal history, then quenched to −50°C at a cooling rate −70°C/min so as to prevent PLA crystallization, and finally heated from −50°C to 190°C at a heating rate 10°C/min. The blends after annealing were cooled to −50°C from room temperature directly and then heated from −50°C to 190°C at a heating rate 10°C/min. T_g of all materials were measured as the temperature corresponding to the midpoint of the heat capacity increment. The T_m and the value of fusion heat (ΔH_m) were taken from the latest heating curve. The degree of crystallinity of the blends was calculated from the melting or crystallization enthalpy using heats of fusion of 93 J/g[18] for complete PLA crystallization.

Dynamic mechanical analysis (DMA) was performed on molded films with a Mettler DMTA analysis (DMA/SDTA861e) in the tensile mode. The relaxation spectrum was scanned from −100°C to 150°C with a frequency of 1 Hz and a heating rate of 3°C/min. The shape of the film samples was rectangular: ∼ 9.0 mm × 4.0 mm × 1.0 mm. The max value of amplitude was 5 μm and the max dynamic force was 5N. Storage modulus, loss modulus, and tan δ were recorded as a function of sample temperature.

Polar optical microscopy studies (POM) were carried out with a Leica polarized light microscope (DM 2500P) in conjunction with a hot stage (Linkam LTS 350). The samples of PLA/PEPG blends were prepared by cutting small pieces from the quenched films. Samples weighing 5 mg were melted on glass slides with coverslips to form thin films 20–50 μm thick. To obtain quenched sample, the specimens were heated to 190°C on the hot stage and held at that temperature for 3 min and then quenched in the liquid nitrogen. The quenched specimens were also laid on the hot stage at 90°C annealing for 4 h or 24 h. Then the photographs were taken at room temperature by a digital camera.

Wide-angle X-ray diffraction (WAXD) experiments were carried out by the use of Rigaku D/Max-II B X-ray diffractometer with a Cu anode (Cu Kα1 =

1.5406 Å). The measurements were operated at 40 kV and 200 mA from 5° to 40° at a 2θ scan rate of 4°/min.

Tensile tests were performed on an 8.9 kN, screw-driven universal testing machine (Instron 1211, Canton, MA) equipped with a 10 kN electronic load cell and mechanical grips. The tests were conducted at room temperature using a cross-head rate of 10 mm/min. At least three specimens with 20.0 mm gauge length and width of 3.9 mm were tested for each condition.

RESULTS AND DISCUSSION

Properties of quenched PLA2/PEPG blends

The thermal properties of quenched PLA2/PEPG blends were studied by DSC and shown in Figure 1. All the thermograms were obtained at a heating rate of 10°C/min. Not as the DSC traces of blends of PLA1 and PEPG from our previous study,[12] the blends of PLA2 and PEPG showed only the glass transition behavior in the thermograms. Neat PLA1 had good crystallizability due to the high optical purity showing an intensive cold crystallization peak and subsequent melting peak. With the increase of PEPG content, the cold crystallization peak shifted to the lower temperature indicating that PEPG enhanced the crystallization ability of PLA1, whereas neat PLA2 could not appear the cold crystallization behavior due to its low optical purity. The addition of PEPG should also improve the crystallizability of PLA2, but the crystallization behavior of PLA was still not observed. This phenomenon suggested that plasticized PLA2 had very slow crystallization rate and cannot show the cold crystallization ability in the DSC runs. The glass transition temperatures of PLA1/PEPG blends and PLA2/PEPG blends were almost same at the same composition indicating that the plasticization efficiency of PEPG for PLA with different optical purity had no difference. Through our previous study,[12] we have known that PLA1 and PEPG have good compatibility and form the homogeneous system. It can also be concluded that PLA2 and PEPG were completely miscible according to the well-known Fox equation.[19]

The dynamic mechanical relaxation behavior of the quenched PLA2/PEPG blends is presented by the temperature dependence of loss modulus in Figure 2. All data were obtained at a frequency of 1 Hz and a heating rate of 3°C/min. As in the DSC thermograms, a single glass transition was observed which gradually shifted to the lower temperature as PEPG concentration increased. The PLA2/PEPG blends did not show the modulus increase after the
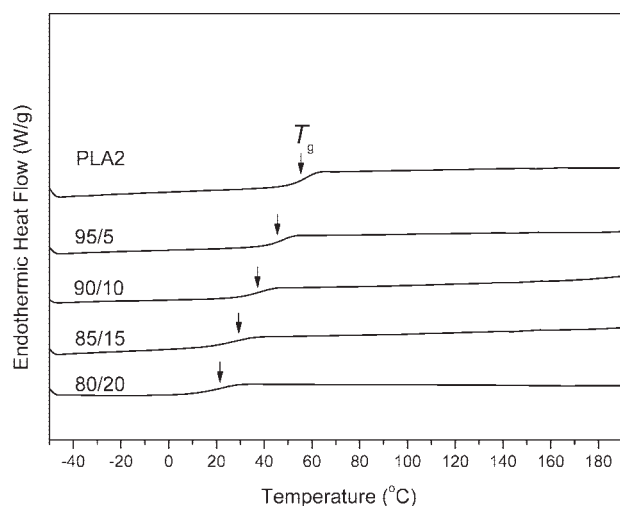
Figure 1 Thermograms of quenched PLA2 and PLA2/PEPG blends with a heating rate of 10°C/min.

glass transition but only a flatten curve indicating no cold crystallization existence.

Exemplary stress-strain dependencies for the quenched blends studied are plotted in Figure 3. Neat PLA2 yielded at the deformation of about 6% and the stress above 53 MPa, which was lower than that of PLA1 according to Ref. [12]. It is well-known that the mechanical properties of PLA are influenced by the molecular weight and optical purity. PLA with high molecular weight shows poor tensile properties with the decrease of optical purity. In this study, the existence of PEPG caused a decrease of the yield stress in all blends and an increase of the elongation at break. When the plasticizer content was over 10 wt %, the brittle to ductile transition of PLA2/PEPG blends occurred as shown in Figure 3. At the same composition, PLA1/PEPG blends showed a higher yield stress than PLA2/PEPG blends. PLA1/PEPG 85/15 had a yield stress of about 20 MPa and an elongation at break of about 410%, whereas PLA2/PEPG 85/15 showed a lower yield stress of about 14 MPa and a larger elongation at break of about 470%. The PLA2/PEPG blends were softer than the PLA1/PEPG blends.

It should be noted that both PLA1/PEPG blends and PLA2/PEPG blends were amorphous at room temperature after the normal melt-quench processing. Although PLA1 had better crystallizability than PLA2 due to the difference of optical purity, there was no substantial difference between them. Both of the two kinds blends were transparent and soft and had not the crystallization of PLA. Both the two kinds of blends existed at a metastable state, physical aging and cold crystallization may occur.[12] Only PLA2 had a very slow cold crystallization rate which may have a positive effect on the stability of material.

Properties of PLA/PEPG blends after annealing

It was addressed earlier that the PLA2/PEPG blends did not indicate the cold crystallization behavior in the DSC thermograms and the DMA runs. PLA2 was able to crystallize but needed long time at its crystallization temperature. It was necessary to
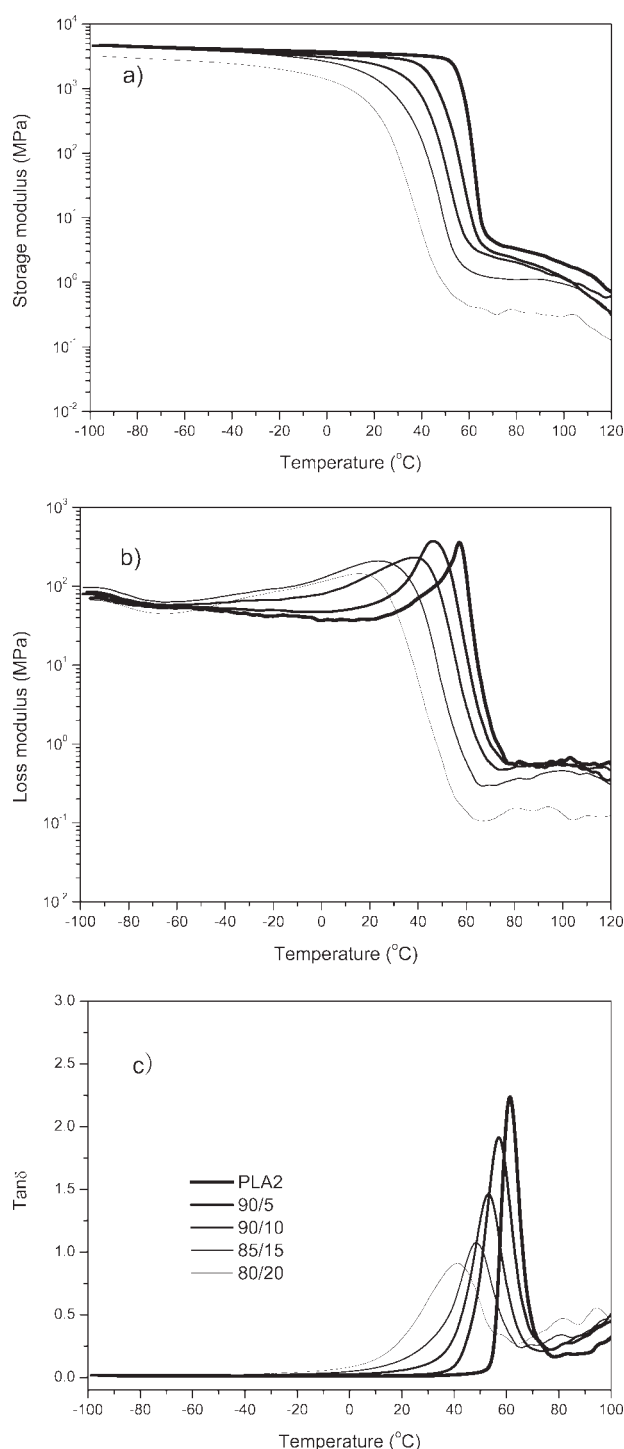

Figure 2 Temperature dependence of DMA curves from PLA2/PEPG blends: (a) Storage modulus; (b) loss modulus; (c) tan δ.
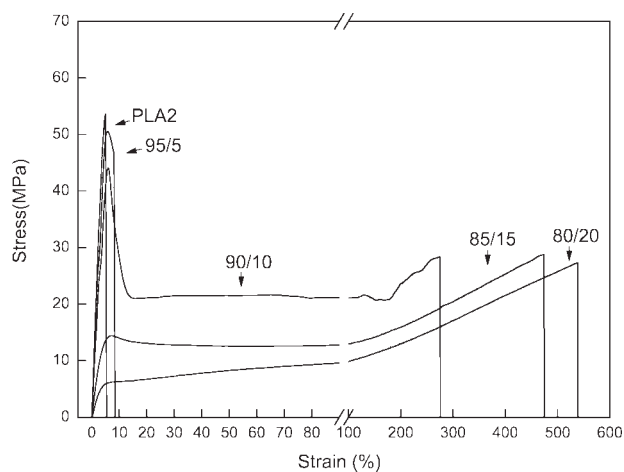
Figure 3 Exemplary stress/strain curves of quenched PLA2/PEPG blends.

Figure 5 X-ray diffractograms of neat PLA and PLA/PEPG 85/15 blend after annealing at 90°C for 2 h.

investigate the properties of PLA/PEPG blends after completing its crystallization to identify the stability of plasticized PLA. For further identify and investigate, both of the two kinds of blends were annealed
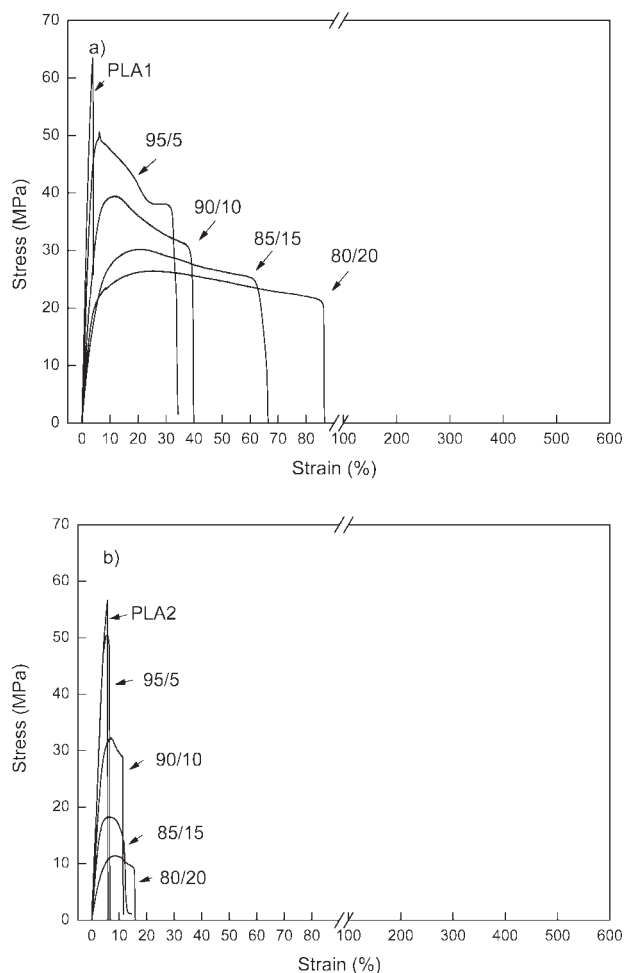

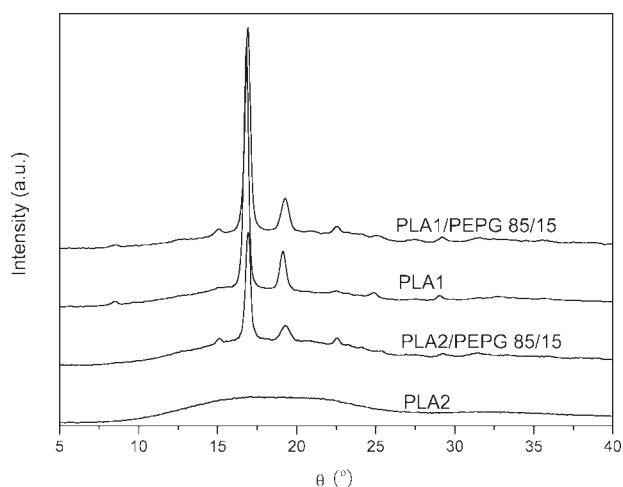**Figure 4** Exemplary stress/strain curves of annealed PLA/PEPG blends: (a) PLA1/PEPG; (b) PLA2/PEPG.

at 90°C for different time to obtain the crystallized samples. PLA1/PEPG blends were annealed for 4 h to finish the cold crystallization, whereas PLA2/PEPG blends were annealed for 24 h due to the very slow crystallization rate. An astonishing result was obtained that PLA2/PEPG blends crystallized after the long time annealing and regained the brittleness, whereas the PLA1/PEPG blends still kept some flexibility after the cold crystallization had finished.

Figure 4 shows the exemplary stress-strain curves of annealed PLA/PEPG blends. Neat PLA after annealing almost kept the same tensile properties as the quenched one. However, quenched plasticized PLA lost their good drawability after annealing. The elongation at break of PLA1/PEPG 85/15 decreased from 410% to 65%, whereas PLA2/PEPG 85/15 changed from 470% to 10%. Not as imagined, the PLA2/PEPG blends were more brittle than the PLA1/PEPG blends though the PLA2 had a poor crystallizability. Elongation at break of all the PLA2/PEPG blends was below 20% indicating a rather brittleness. It was interesting that the PLA1/PEPG 95/5 blends increased the elongation at break from 15% to 35% after annealing. To analysis the reason for these results, WAXD, DSC, DMA, and POM were continued.

Exemplary 2θ scans for neat PLA and PLA/PEPG 85/15 blends after annealing at 90°C for 2 h are plotted in Figure 5. Neat PLA2 did not show any peak about the cold crystallization due to the poor crystallizability caused by the low optical purity. The scans of neat PLA1 and the blends revealed peaks typical of α-crystallographic form described as pseudo-orthorhombic[20] or orthorhombic.[21] The peak intensity of PLA2/PEPG 85/15 blend was apparent lower than that of PLA1/PEPG 85/15 blend indicated that its crystallinity was low. As we have known, the crystallizability of PLA increased with the increase
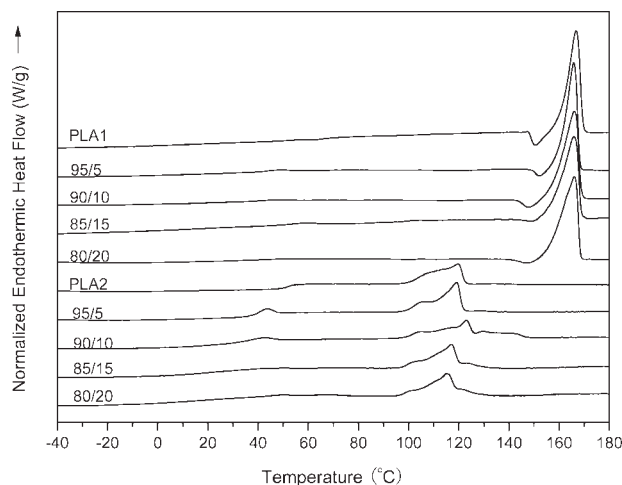
Figure 6 Thermograms of annealed PLA and PLA/PEPG blends with a heating rate of 10°C/min.

of plasticizer content. PLA2 of low optical purity showed visible crystallizability with the existence of PEPG. Its crystallization rate was so slow that we could not observe its crystallization behavior in the general measurements. The plasticizers improve the chain mobility of PLA and enhance its crystallization rate and crystallinity. We still need anneal them for a long time to observe its crystallization behavior, which cannot observe in the DSC and DMA measurements.

Cold crystallization of PLA could disturb the distribution and compatibility of plasticizer with PLA and induce phase separation. In our previous study,[12] it has been observed that phase separation occurred following the cold crystallization of PLA. Similar results obtained from other plasticized PLA were also reported.[14,17] In this study, all the blends after annealing were directly cooled to −50°C from room temperature, and then heated to 190°C with a heating rate of 10°C/min, so that the thermal properties of the annealed samples can be observed. Figure 6 shows the DSC traces of both of the two kinds of blends after annealing at 90°C for 4 h and 24 h, respectively. All the PLA/PEPG blends showed only the melting behavior of PLA without the melting of PEPG. The melting point of PLA1 was at about 166°C, whereas PLA2 was at about 120°C. This result was consistent with their optical purity. The crystallinity of PLA2/PEPG blends was lower than that of PLA1/PEPG blends from the DSC data. Whether the phase separation existed or not in the PLA/PEPG blends cannot be determined from the only DSC data because the onset of thermograms was not low enough. To confirm the phase structure of the annealed PLA/PEPG blends, the dynamic mechanical behavior of crystallized samples was investigated. The temperature dependence of the loss modulus for the crystallized PLA and PLA/PEPG

blends are shown in Figure 7. A two-phase system was identified due to the existence of two glass transitions in the annealed blends indicating that phase separation had taken place in the materials. The lower glass transition corresponded to the PEPG rich phase, whereas the higher one corresponded to the PLA rich phase. The transition of the loss modulus corresponding for the cold crystallization disappeared due to the complete crystallization of PLA. The T_g of PLA compared with the quenched samples increased after the completion of PLA crystallization due to the limited chain mobility and decreased amorphous regions. The plasticization effect of PEPG to PLA decreased and the blends regained the brittleness. The blends had changed to a multiphase systems, there were many factors influencing the ultimate tensile properties of blends. The special phenomenon of blends of PLA1/PEPG 95/5 should be related to the crystalline structure and complicated aggregate state.

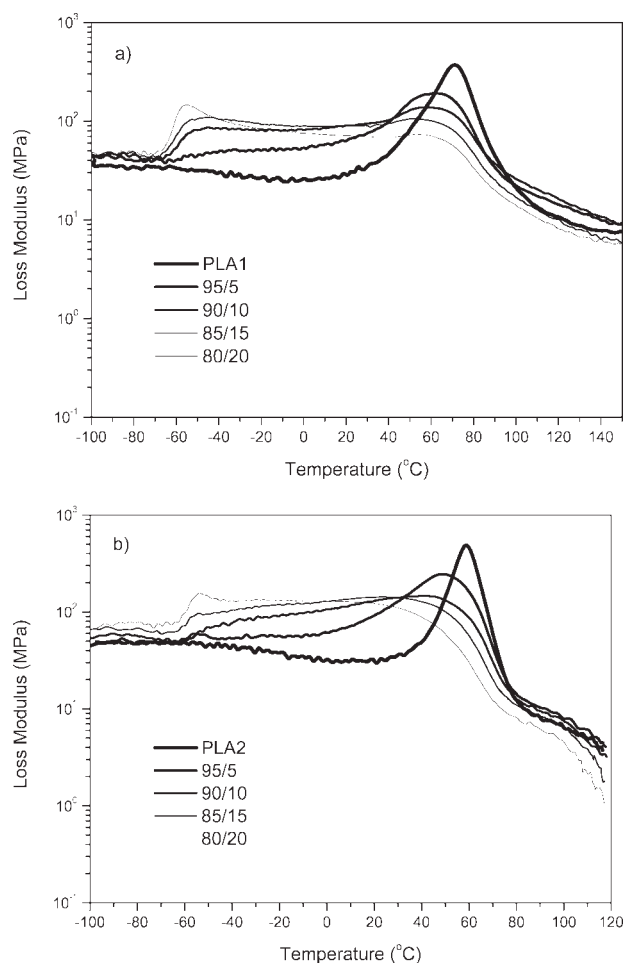All of the above data supported a phase separation in both two types of blends, which was caused

Figure 7 Temperature dependence of loss modulus curves from DMA runs: (a) annealed PLA1/PEPG blends; (b) annealed PLA2/PEPG blends.
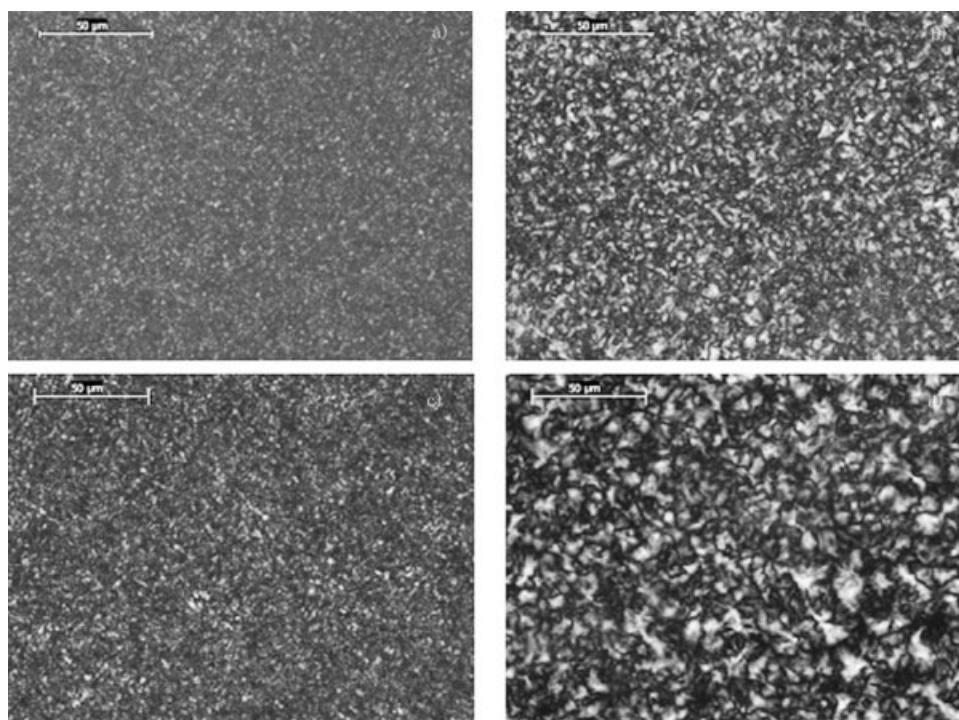
Figure 8 POM images of annealed PLA/PEPG blends: (a) PLA1/PEPG 85/15; (b) PLA2/PEPG 85/15; (c) PLA1/PEPG 80/20; (d) PLA2/PEPG 80/20.

by a redistribution of the plasticizer during cold crystallization of PLA. The phase separation can reduce the drawability of the material, but we still did not know why the PLA2/PEPG blends got more brittle than the PLA1/PEPG blends, especially with the lower crystallinity. It was demonstrated in the past that a low crystallinity level and fine spherulitic structure were advantageous for development of crazes in the semicrystalline polymers. PLA2/PEPG blends after annealing with a lower crystallinity level should show more flexible than PLA1/PEPG blends. Contrarily, annealed PLA1/PEPG blends had better flexibility. Further, we investigated the spherulite morphology by POM as shown in Figure 8. It was found that PLA2/PEPG blends after annealing formed a larger and scarce sperulite crystal compared with the PLA1/PEPG blends at the same composition. Possibly, this was the reason for the poor mechanical properties of annealed PLA2/PEPG blends. PLA of low optical purity had a very slow crystallization rate and the nucleus density of crystal was low, which was helpful for forming the large spherulite.

CONCLUSIONS

In this study, a macromolecular plasticizer-PEPG was added to two kinds of PLA with different optical purity for improving the flexibility of neat PLA. PEPG had good compatibility with both two types of PLA and formed homogeneous systems after melt-quench processing. Blends of PEPG with PLA of high optical purity showed good crystallizability in the DSC and DMA measurements, whereas blends of PEPG with PLA of low optical purity cannot crystallize at the same condition due to the very slow crystallization rate. Quenched PLA/PEPG blends are completely amorphous and PLA2/PEPG blends were softer than PLA1/PEPG blends.

After annealing, blends PEPG with PLA of low optical purity showed their crystallizability. PEPG significantly increased the crystallization rate of PLA as confirmed by WAXD. The cold crystallization of PLA induced phase separation of the homogeneous systems, and then the drawability of the quenched plasticized PLA was reduced. It was noted that PLA2/PEPG blends became more brittle than the PLA1/PEPG blends. Further analysis indicated that the latter had a larger crystallinity level, but fine spherulite. The fine spherulite had a positive effect on the tensile properties of material.

Blending PEPG with PLA of low optical purity cannot obtain crystallized plasticized PLA, which have good drawability. The optical purity of PLA had a significant influence on the properties of plasticized PLA, especially the crystallized one. It should be noted that quenched blends with PLA of low optical purity should had better stability due to the

slow crystallization rate. There is still an effort to find method obtaining stable plasticized PLA.

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