

# Poly(ethylene glycol-co-propylene glycol) as a Macromolecular Plasticizing Agent for Polylactide: Thermomechanical Properties and Aging

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Received 5 January 2009; accepted 24 April 2009

DOI 10.1002/app.30638

Published online 16 June 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Finding a suitable plasticizer for polylactide (PLA) is necessary to overcome its brittleness and enlarge its range of applications. In this study, commercial PLA was melt-blended with a new plasticizer, an ethylene glycol/propylene glycol random copolymer [poly(ethylene glycol-co-propylene glycol) (PEPG)] with a typical number-average molecular weight of 12 kDa and an ethylene glycol content of 78.7 mol %. The thermal properties, crystallization behavior, and mechanical properties of the quenched blends and the properties of the blends after storage for 2 months under the ambient conditions were investigated in detail. The advantage of using PEPG is that it does not crystallize at room temperature and has good compatibility with PLA. The quenched PLA/PEPG blends were homogeneous and amorphous systems. With an increase in the PEPG content (5–20%), the glass-transi-

tion temperature, tensile strength, and modulus of the blends decreased, whereas the elongation at break and crystallizability increased dramatically. The cold crystallization of PLA resulted in phase separation of the PLA/PEPG blends by annealing of the blends at the crystallization temperature. After storage under the ambient conditions for 2 months, the PLA/PEPG blends retained good toughness but still lost some flexibility. The reasons for the aging of the blends were the enthalpy relaxation and cold crystallization of PLA and the induced phase separation. Poly(ethylene glycol) with a typical number-average molecular weight of 10 kDa was also blended with PLA for comparison. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1105–1117, 2009

**Key words:** polylactide; plasticizer; aging

## INTRODUCTION

Great attention has been focused on polylactides (PLAs), which are biocompatible and biodegradable polyesters derived from renewable resources, because of the rapid growth of intense interest in the global environment.<sup>1–3</sup>

Generally, commercial PLA is a copolymer of L-lactide and D-lactide that is either amorphous or semicrystalline at room temperature, depending on the amount of L-lactide in its structure. PLA resins containing more than 93% L-lactide can be semicrystalline, whereas PLA with 50–93% L-lactide is strictly amorphous.<sup>4,5</sup> Melt-quenched PLA can be completely amorphous and crystallized during heating.

PLA displays mechanical performance comparable to that of petroleum-based polymers; in particular, it shows high elastic modulus and high stiffness, ther-

moplastic behavior, biocompatibility, and good shaping capability.<sup>6</sup> However, PLA is not suitable for packaging applications in comparison with conventional packaging materials because of its inherent brittleness and low toughness. Several modifications have been proposed to improve the flexibility of PLA, such as copolymerization, polymer blending, and plasticization. By the copolymerization of PLA with other monomers,<sup>7,8</sup> the mechanical properties can vary over a wide range. However, none of the copolymerization approaches is economically practical for packaging applications. Various degrees of modification of PLA have been achieved via blending with other polymers, including poly( $\epsilon$ -caprolactone),<sup>9,10</sup> poly(vinyl acetate),<sup>11</sup> poly(ethylene oxide),<sup>12</sup> and poly(hydroxyl butyrate).<sup>13</sup> However, many of these blends are immiscible or partially miscible and have only poor mechanical properties and low transparency. Blending PLA with a biocompatible plasticizer may be an economical method for its modification. Plasticized PLA has good flexibility and high transparency. Triacetate,<sup>14</sup> citrate esters,<sup>14–16</sup> poly(ethylene glycol) (PEG),<sup>17–20</sup> and low-molecular-weight poly(propylene glycol) (PPGs)<sup>21</sup>

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Contract grant sponsor: National Science Foundation of China; contract grant number: 50703042.

have been found to be efficient plasticizers for PLA. However, considerable efforts would be required to overcome the embrittlement of plasticized PLA.

Plasticizers are mainly dispersed in the amorphous phase under the pressure of spherulites.<sup>22</sup> Any factor influencing the 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. As a result, the mechanical properties and morphology of the plasticized PLA can be degraded.<sup>23</sup> The low molecular weight of the plasticizers facilitates their migration from the bulk material to the film surface, ultimately leading to the blend regaining the inherent brittle properties of neat PLA. Plasticizers with high molecular weights are always desirable because of their higher stability.<sup>16</sup>

PEG, long known as an efficient plasticizer for PLA, has been intensively studied; it has good miscibility with PLA, even with a molecular weight of 20 kDa.<sup>17</sup> However, the promising mechanical properties of PLA/PEG blends disappear with time because of the slow phase separation and crystallization of PEG from homogeneous blends. Hu et al. reported that blends of PLA with a low L-lactide content and 30 wt % PEG with a molecular weight of 8 kDa were unstable because of the slow crystallization of PEG, which depleted the plasticizer,<sup>24</sup> whereas blends with PLA with a high L-lactide content first underwent phase separation before the crystallization of PEG.<sup>20</sup> In addition, the cold crystallization of PLA was also found to reduce the elongation at break of plasticized PLA.<sup>25</sup>

To avoid the disadvantages of PLA/PEG blends, PPG was proposed as a new plasticizer for PLA. PPGs with low molecular weights of 400–1000 Da were considered good candidates for PEGs<sup>21</sup> because they could be supercooled to the glassy state without crystallization. PPGs had a good plasticizing effect on PLA and less influence on the crystallization behavior of PLA than PEG. Phase separation occurred in quenched PLA/PPG blends when the content of PPG was 12.5 wt %, but this did not reduce the drawability of the material because of local plasticization.<sup>26</sup> The PLA/PPG blends should be stable at room temperature and under static conditions, but the aging of the promised materials was unknown. Moreover, there was difficulty in the process of blending PLA and PPG because of their weak compatibility. Normally, the higher the molecular weight is, the lower the compatibility is of the plasticizer. When the molecular weight of PPG was higher than 2000, it was very difficult to extrude the blend; in that case, PPG either stayed behind in the hopper or dropped out of the die as a liquid.<sup>27</sup> Modification of the structure of PPG may be necessary for its application.

In this study, a random copolymer of ethylene glycol and propylene glycol, poly(ethylene glycol-co-propylene glycol) (PEPG), was selected as a potential macromolecular plasticizer for PLA. It is also a viscous liquid at room temperature but obviously has better compatibility with PLA than PPG because of the existence of an ethylene glycol unit. The thermal properties, mechanical properties, crystallization behavior, and aging of PLA/PEPG and PLA/PEG blends were investigated and compared in detail.

## EXPERIMENTAL

### Materials

PLA (4032D), purchased from NatureWorks LLC (USA) and being around 98% L-lactide, had a density of 1.25 g/cm<sup>3</sup>, a weight-average molecular weight of 207 kDa, a polydispersity of 1.73 (gel permeation chromatography analysis), and a glass-transition temperature ( $T_g$ ) and a melting temperature ( $T_m$ ) of 59 and 167°C [differential scanning calorimetry (DSC) analysis], respectively. PEPEG with a typical number-average molecular weight of 12 kDa and PEG with a typical number-average molecular weight of 10 kDa were obtained from Sigma-Aldrich and used as received. The ethylene glycol content of PEPEG was 78.7 mol % (H-NMR analysis).

### Blend preparation

Before blending, all the polymers were dried *in vacuo* at 50°C for 24 h. PLA/PEG and PLA/PEPEG blends were prepared by melt mixing with a Haake Reomix 600 (Karlsruhe, Germany) with a twin screw 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 w/w. The addition of the modifier at a concentration greater than 20 wt % would not be reasonable with respect to applications. After blending, all the samples were cooled to room temperature under an air atmosphere. Also, the neat PLA was subjected to the same mixing treatment to obtain a reference material.

Films were prepared with a hot press at 180°C with a hold pressure of 6 MPa and a hold time of 3 min, and this was followed by quenching to room temperature between two thick metal blocks. The blocks were cooled on a large metal plate in 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 for all the films. The specimens were then sealed in plastic bags and stored in desiccators while awaiting the processing and analysis.

For the analysis of the influence of the cold crystallization on the phase structures of the blends, the

quenched samples were put in the oven at 100°C for annealing for 4 h to obtain crystallized samples.

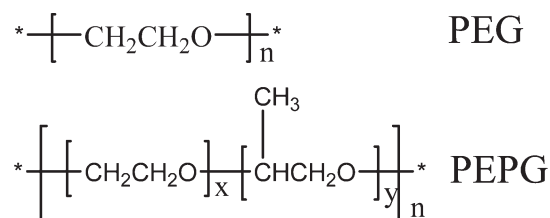
To study the effect of storage on the materials, samples of the blends were aged under the ambient conditions for 2 months. The samples were then characterized to investigate the stability of the blends.

### Sample characterization

DSC measurements were performed on a Perkin-Elmer Diamond DSC instrument under an N<sub>2</sub> atmosphere; it was calibrated with indium as the standard. Neat PEPG and PEG were first equilibrated at -90°C and then heated from -90 to 100°C at 10°C/min. The quenched blends and neat PLA were preliminarily heated to 190°C for 3 min to erase previous aging effects, then quenched to -50°C at a fast cooling rate of -70°C/min to prevent the crystallization of PLA, and finally heated at 10°C/min from -50 to 190°C. The aged and crystallized samples were cooled to -50°C from room temperature directly and then heated at 10°C/min from -50 to 190°C. The  $T_g$  values of all samples were measured as the temperature corresponding to the midpoint of the heat capacity increment. The  $T_m$  and heat of fusion values were taken from the last heating curve to minimize different thermal history effects. The degree of crystallinity of the blends was calculated from the melting enthalpy with a heat of fusion of 93 J/g<sup>28</sup> for complete PLA crystallization. Isothermal crystallization behaviors of the PLA/PEPG blends were also detected with DSC through the premelting of blends at 190°C for 5 min to completely eliminate any possible crystallinity or residual stresses in the samples; then, they were quenched to the designed temperature and held there for 30 min to allow crystallization from the quiescent melt. The exothermic curves of the heat flow as a function of time were recorded, and the relative crystallinity was expressed as the ratio of the peak areas at that time and at the end of crystallization.

Dynamic mechanical thermal analysis (DMTA) was performed on molded films with a DMA/SDTA861<sup>o</sup> apparatus (Mettler-Toledo, Switzerland) in the tensile mode. The relaxation spectrum was scanned from -80 to 120°C at a frequency of 1 Hz and a heating rate of 2°C/min. The shape of the film samples was rectangular (ca. 3.9 × 9.0 × 1.0 mm<sup>3</sup>). The storage modulus, loss modulus, and tan δ were recorded as a function of temperature.

Wide-angle X-ray diffraction (WAXD) experiments were carried out with a Rigaku (Japan) D/Max-II B X-ray diffractometer with a copper anode (Cu Kα1 = 1.5406 Å). The measurements were taken at 40 kV and 200 mA from 5 to 40° at a 2θ scan rate of 4°/min.



Scheme 1 Chemical structures of PEG and PEPG.

Tensile tests were performed on an 8.9-kN screw-driven universal testing machine (1211, Instron, Canton, MA) equipped with a 10-kN electronic load cell and mechanical grips. The tests were conducted at room temperature with a crosshead rate of 10 mm/min. At least three specimens with a 20.0-mm gauge length and a width of 4.0 mm were tested for each condition.

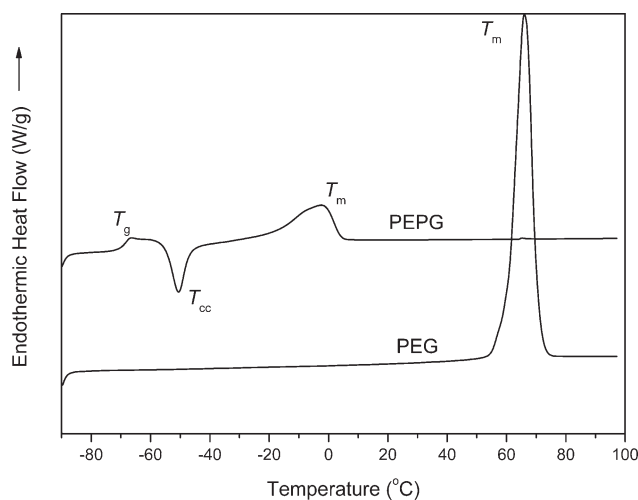
Fracture surfaces from the tensile tests were examined with field emission scanning electron microscopy (XL 30, Philips, The Netherlands). All specimens were sputter-coated with gold to provide enhanced conductivity before examination.

## RESULTS AND DISCUSSION

### Characteristics of PEPG and PEG

The chemical structures of PEG and PEPG are shown in Scheme 1. PEPG is a kind of random copolymer composed of ethylene glycol and propylene glycol units. Generally, PEG is a flaky, crystalline solid with a  $T_m$  value of 60–67°C and a crystallization temperature ( $T_c$ ) of 30–40°C. Because of the proximity of  $T_c$  of PEG to the ambient temperature, it is difficult to achieve stable PLA/PEG blends. It is well known that the thermal properties of random copolymers change greatly with the original polymers, especially the crystallization and melting behavior. Irregularities of the chain reduce  $T_m$  of a polymer because the formed crystal becomes less perfect. PEPG with 78.7 mol % PEG units changed into a kind of viscous liquid at room temperature.

Figure 1 shows typical DSC traces of the PEG and PEPG used in this study. The samples (ca. 10 mg) were first equilibrated at -90°C for 3 min and then heated to 100°C at a rate of 10°C/min to detect the glass-transition and melting behavior. The thermal properties of PEPG and PEG were very different. Neat PEG was a typical crystalline polymer. No clear  $T_g$  could be distinguished in the thermograms because of its high crystallinity. PEPG was a typical semicrystalline polymer and clearly showed the glass-transition, cold-crystallization, and melting behavior in its thermograms.  $T_g$  and the cold-crystallization temperature ( $T_{cc}$ ) of PEPG were detected at -68.0 and -50.6°C by DSC, respectively.  $T_m$

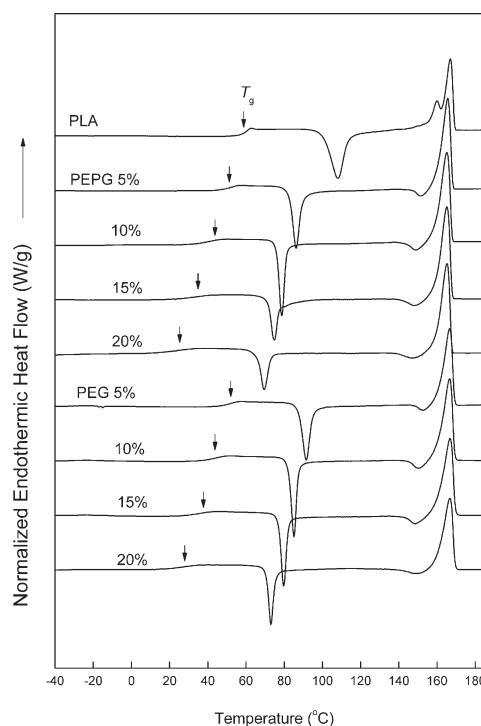


**Figure 1** DSC thermograms recorded for PEPG and PEG.

decreased from 66°C for neat PEG to -2°C for PEPG. Also, the melting enthalpy drastically decreased, changing from 187.0 J/g for neat PEG to 39.3 J/g for PEPG. These results indicated that the crystallization behavior of PEG was suppressed by the random introduction of propylene glycol units into its macromolecular chains.

### Properties of the quenched films

DSC and DMTA were employed to investigate the thermal properties of quenched PLA and the two kinds of blends. Exemplary heating thermograms of the quenched films are plotted in Figure 2. All the samples had similar heating thermograms. Above the glass transition, the films cold-crystallized, and as the temperature increased, they melted. Neat PLA exhibited a  $T_g$  of about 59°C, whereas the cold-crystallization peak was centered at 108°C. Both PEPG



**Figure 2** DSC thermograms recorded during heating at a rate of 10°C/min for the quenched PLA and the blends.

and PEG could efficiently decrease the  $T_g$  values of the blends, and the decrease was enhanced with a higher plasticizer content. PEPG reduced  $T_g$  from about 59.0°C for neat PLA to 50.9, 39.2, 33.7, and 23.4°C for the blends with 5, 10, 15, and 20 wt % plasticizer, respectively (Table I). Similar results were also obtained from the PLA/PEG blends. The correspondence of the enthalpies of cold crystallization and subsequent melting confirmed that the quenched PLA and blends were amorphous. However, the crystallizability of PLA increased because

**TABLE I**  
Thermal Properties of the Quenched PLA/PEPG and PLA/PEG Blends at a Heating Rate of 10°C/min

Plasticizer type	Plasticizer content (%)	Cold crystallization				Melting		
		$T_g$ (°C)	$T_c$ (°C)	$\Delta H$ (J/g)	$X_c$ (%) <sup>a</sup>	$T_m$ (°C)	$\Delta H$ (J/g)	$X_c$ (%) <sup>a</sup>
None	0	59.0	108.1	-36.4	39.2	166.9	36.5	39.2
PEPG	5	50.9	86.2	-35.0	39.6	165.7	35.6	40.3
	10	39.4	78.8	-38.7	46.2	165.2	38.5	45.9
	15	33.7	74.7	-36.0	45.5	165.2	37.6	47.6
	20	23.4	69.3	-33.9	45.6	165.2	36.4	48.9
	100	-68.0	-50.6	-24.2	—	-2.1	39.3	—
PEG	5	50.5	91.5	-37.1	42.0	166.6	37.4	42.3
	10	40.9	85.0	-39.6	47.3	166.6	40.2	48.0
	15	32.0	79.7	-38.9	49.2	166.8	39.7	50.2
	20	25.0	73.0	-37.9	50.9	166.7	39.1	52.5
	100	—	—	—	—	66.6	189.0	95.9

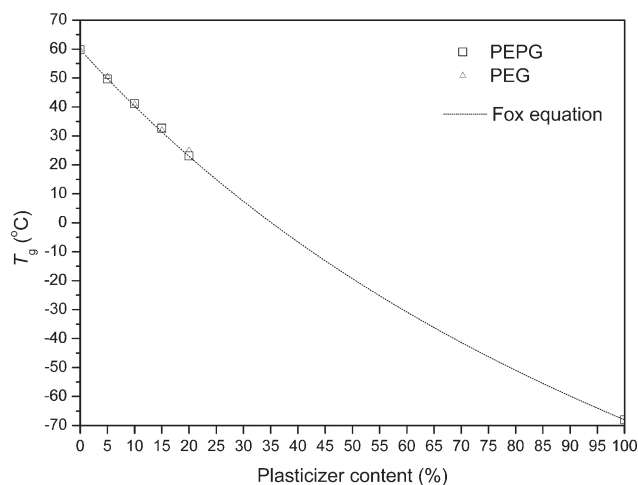
<sup>a</sup>  $X_c$  was the PLA crystallinity relative to total PLA.  $\Delta H$  was the enthalpy of cold crystallization or subsequent melting of PLA.

of the enhanced chain mobility due to the plasticizers. Cold crystallization shifted to a lower temperature as the PEPG or PEG content increased in parallel with the shift in  $T_g$ . Also, the crystallinity of PLA also increased with the increase in the plasticizer content, as shown in Table I. The incorporation of the plasticizer resulted in a larger free volume of PLA chains in comparison with neat PLA. Actually, there were almost no differences between the heating thermograms of PLA/PEPG blends and PLA/PEG blends with the same composition. This indicated that PEPG and PEG had similar plasticization efficiencies, and the thermal properties of quenched PLA/PEPG blends and PLA/PEG blends were the same.

The  $T_m$  value of the PLA component in the blends was essentially unaffected by the blend composition. Interestingly, the melting peak had two separate peaks corresponding to the neat PLA but a single peak corresponding to the blends. Also, there was a weak exothermic peak before the melting of PLA in the blends. The bimodal peak of neat PLA may be a result of melt recrystallization, which has been reported in the literature.<sup>18,29,30</sup> However, a new viewpoint has been proposed recently. Researchers<sup>31,32</sup> have shown that PLA with an L-lactide content of 100% displays two kinds of crystal modifications with different thermodynamic stability dependent on  $T_c$ : an  $\alpha$  form (high thermodynamic stability) when  $T_c$  is over 120°C and an  $\alpha'$  form (low thermodynamic stability) when  $T_c$  is lower than 100°C. Only PLA that crystallized at a temperature between 100 and 120°C showed the double melting peaks in the DSC curves. PLA that crystallized below 100°C demonstrated a peculiar small exothermal peak just before  $T_m$ . It was confirmed that the small exothermal peak corresponded to the  $\alpha'$ -to- $\alpha$  phase transition, in which the chain packing of the crystal lattice became more compacted. The transformation from the  $\alpha'$  form to the  $\alpha$  form was not via a simple melt-recrystallization process but was a solid–solid phase transition.<sup>31</sup> In this study, neat PLA had a  $T_{cc}$  value of 108°C, whereas all the blends had a  $T_{cc}$  value lower than 100°C. This may be the reason for the single peak for all the blends. Also, the weak exothermic peak near the melting peak should be considered the symbol of the reported  $\alpha'$ -to- $\alpha$  phase transition.

All the quenched samples exhibited only a single  $T_g$ , which might suggest that both PEG and PEPG were miscible with PLA in the investigated compositions. Different equations have been proposed to predict changes in  $T_g$  for polymer blends as a function of the composition. The most popular equation is the Fox equation:<sup>33</sup>

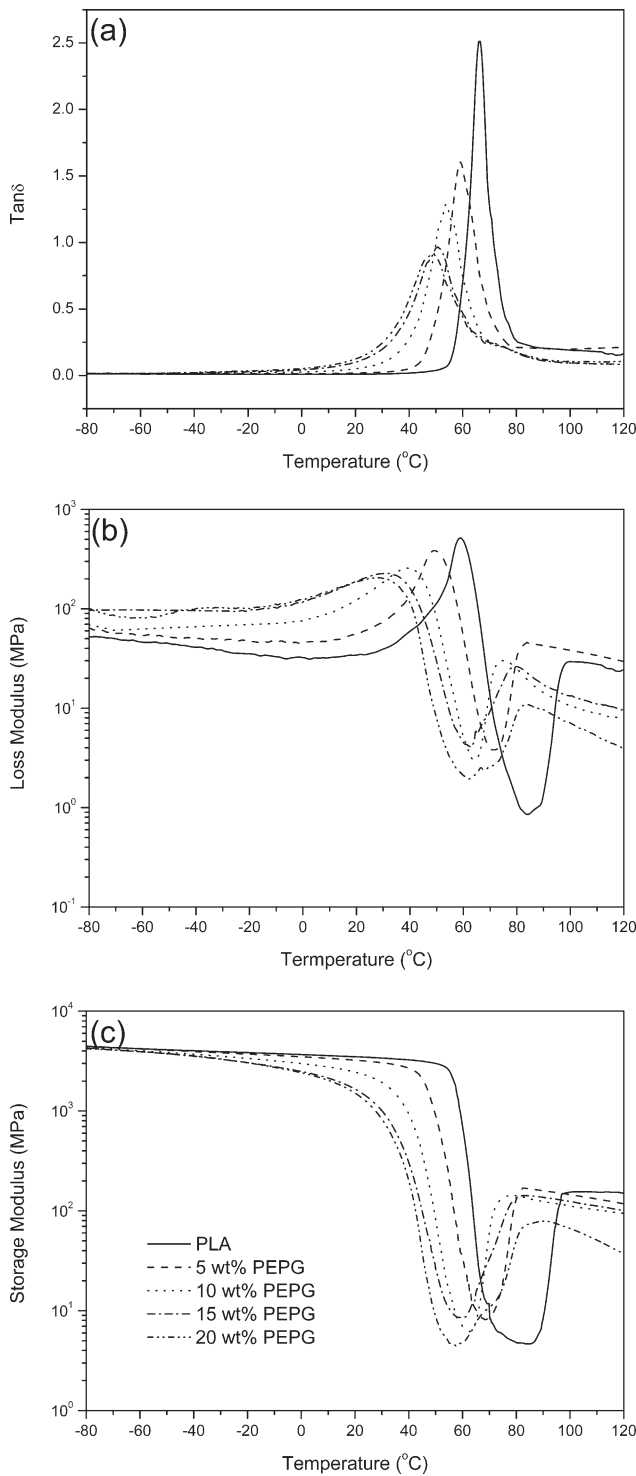
$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (1)$$



**Figure 3** Dependence of  $T_g$  on the blend composition from the DSC thermogram.

where  $W$  is the weight fraction and subscripts 1 and 2 indicate polymers 1 and 2, respectively. This equation is applicable to polymer/diluent mixtures and binary polymer blends that are completely miscible. The  $T_g$  values of the quenched PLA/PEPG blends followed the empirical Fox equation, with a  $T_g$  value of  $-68.0^\circ\text{C}$  for PEPG, and are plotted in Figure 3. Then, it was confirmed that the melt-quenched PLA/PEPG blends formed a single amorphous phase and that PLA and PEPG were completely miscible in these compositions. Many studies have shown that PEG is completely miscible with PLA below the concentration of 20 wt %. The  $T_g$  values of the PLA/PEG blends are also plotted in Figure 3 and almost followed the same Fox equation as the PLA/PEPG blends. Therefore, it can be inferred that PEG and PEPG should have similar  $T_g$  values according to the Fox equation.

The dynamic mechanical relaxation behavior of the quenched PLA and PLA/PEPG blends is presented as the temperature dependence of the loss modulus, storage modulus, and  $\tan \delta$  in Figure 4. The peak temperature of  $\tan \delta$  is commonly taken as  $T_g$ . As in the DSC thermograms, a single glass transition was observed that gradually shifted to a lower temperature as the PEPG concentration increased; this indicated that PEPG and PLA were completely miscible in the investigated composition. The  $T_g$  values obtained from DMTA exceeded those determined by DSC; it is known that 1-Hz DMTA data may corresponded to a DSC heating rate in the 20–40°C/min range. The peak temperature of the loss modulus can also be taken as  $T_g$ , and this correlates closely with the value obtained from DSC. A large drop in the storage modulus accompanied  $T_g$ . The increase in the storage modulus and loss modulus at a higher temperature corresponded to the onset of PLA cold crystallization. The material could not

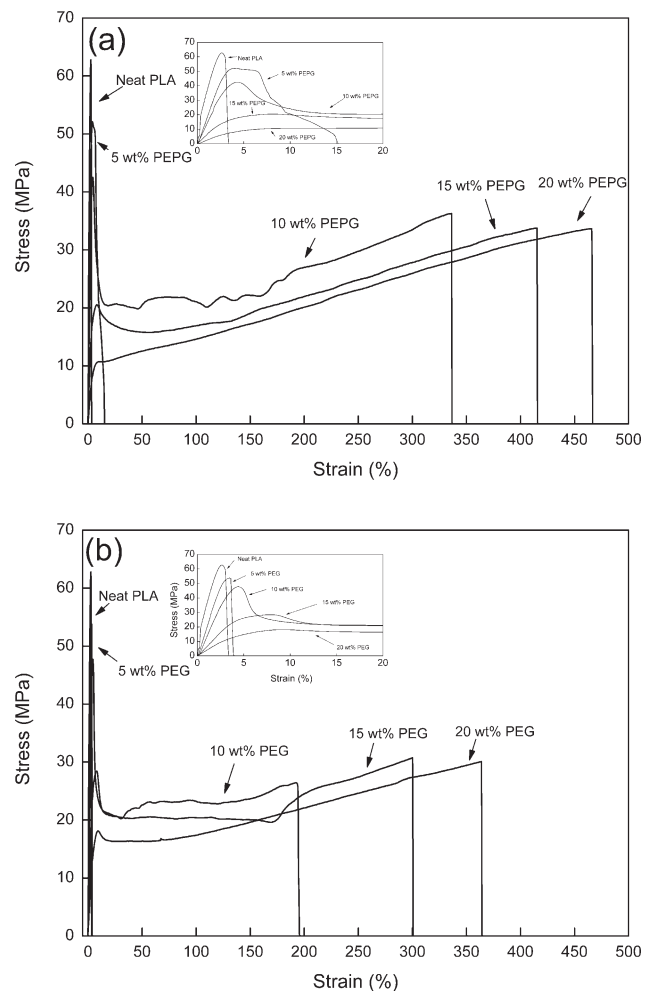


**Figure 4** Dynamic mechanical relaxation behavior of the quenched PLA and PLA/PEPG blends: (a)  $\tan \delta$ , (b) loss modulus, and (c) storage modulus.

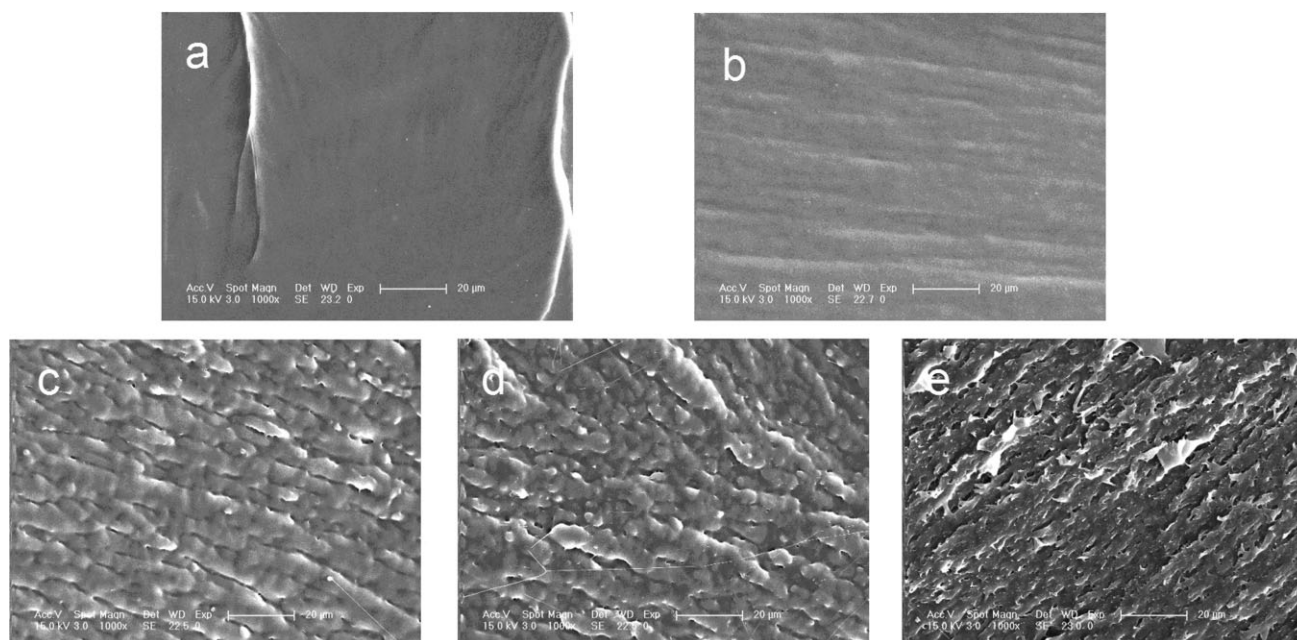
crystallize in the quenching process because of the slow crystallization rate of PLA, whereas the crystallization occurred beyond  $T_g$  during the heating process of the measurement. That the storage modulus of PLA/PEPG blends at room temperature

decreased with an increase in the PEPG content indicated the good plasticization of PEPG on PLA.

The stress–strain behavior of melt-quenched PLA and blends was examined at the ambient temperature with a crosshead rate of 10 mm/min, as shown in Figure 5. Neat PLA as a kind of stiff and brittle polymer displayed no yield point, and its elongation at break was only about 3.7%. On the contrary, the blends with more than 10 wt % plasticizers showed distinct yielding and stable neck growth through cold drawing. The stress–strain curves indicated that the fracture behavior of the specimen displayed a transition from brittle fracture to ductile fracture. For example, in the blend with 10 wt % PEPG, the elongation at break reached 340%, increasing 90 times over that of neat PLA, whereas the yield stress was 42.4 MPa lower than that of neat PLA. This result indicated that PEPG had a good plasticizing effect on PLA. The tensile properties of the PLA/



**Figure 5** Tensile stress–strain behavior of the quenched PLA and plasticized PLA at ambient temperature. The inset shows the modulus and yielding regions on an expanded strain scale.



**Figure 6** SEM photographs of the fracture surfaces of the PLA/PEPG blends after tensile tests: (a) neat PLA, (b) 5 wt % PEPG, (c) 10 wt % PEPG, (d) 15 wt % PEPG, and (e) 20 wt % PEPG.

PEPG and PLA/PEG blends were similar. In both cases, the increase in the PEPG or PEG content from 5 to 10 wt % resulted in a significant change in the stress–strain dependence. Both of the blends with 10 wt % PEPG and PEG showed a pronounced yield. Increasing the content of PEPG or PEG decreased the yield stress and increased the elongation at break of the blends. The elongation at break almost remained constant with the increase in the PEPG or PEG content from 15 to 20%. However, the PLA/PEPG blends had slightly lower stress and higher strain than the PLA/PEG blends with the same composition. This indicated that the plasticization of PEPG was as good as that of PEG.

The fracture surfaces of quenched PLA and PLA/PEPG blends after tensile tests were observed by SEM, as shown in Figure 6. Neat PLA and the blend with 5 wt % PEPG, which had no necking in the tensile test, showed a smooth fracture surface with a small amount of plastic deformation in the microphotographs. On the contrary, a large amount of plastically deformed material was visible on the fracture surfaces of the samples of PLA with over 10 wt % PEPG. PEPG, enhancing the mobility of PLA chains, increased the ability of amorphous PLA to plastically deform.  $T_g$  of the blends was crucial for the tensile properties. In PLA and in the blend with 5 wt % PEPG, for which  $T_g$  was still well above room temperature, the specimens appeared brittle. With the PEPG content increasing,  $T_g$  was near room temperature, and then the blend with over 10 wt % PEPG became flexible.

#### Isothermal crystallization kinetics and phase structure analysis

It was addressed previously that PEPG and PEG enhanced the crystallizability of PLA. To further demonstrate this, the crystallization rate of neat PLA and the blends was investigated with isothermal crystallization kinetics. To describe this, the classic Avrami equation was used:<sup>34</sup>

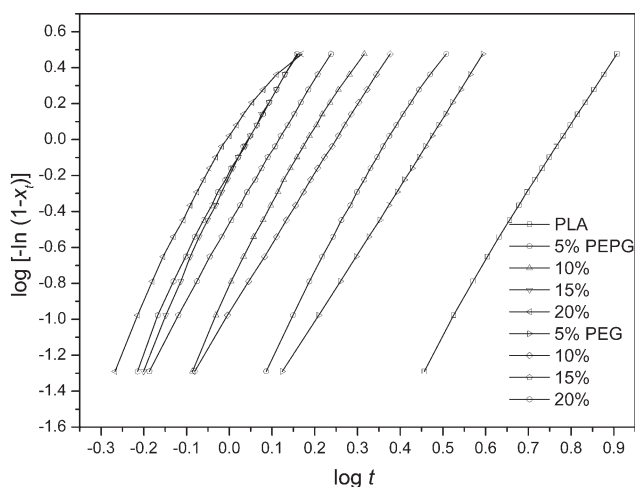
$$1 - X_t = \exp(-kt^n) \quad (2)$$

where  $X_t$  is the amount of crystallized material or the degree of conversion to the crystalline phase;  $k$  is the rate constant of crystallization;  $t$  is the crystallization time; and  $n$  is the Avrami exponent, which can be related to the type of nucleation and to the geometry of the growing crystalline phase. In this model, it is assumed that the material reaches 100% crystallinity. Taking the double logarithm of eq. (2) gives

$$\log[-\ln(1 - X_t)] = \log k + n \log t \quad (3)$$

This suggests that  $\log[-\ln(1 - X_t)]$  versus  $\log t$  should be linear, and  $k$  and  $n$  can be calculated by the fitting of a line to the experimental data.  $n$  is equal to the growth dimensionality plus 1, and  $k$  is a function of the growth geometry.

Plots of  $\log[-\ln(1 - X_t)]$  versus  $\log t$  of PLA in blends with different PEPG and PEG contents at 100°C are presented in Figure 7. Each curve in Figure 7 exhibits a good linear relationship, suggesting



**Figure 7** Effect of the plasticizer content on the isothermal crystallization of PLA at 100°C.

that the isothermal crystallization kinetics was in good agreement with the Avrami equation, and the secondary crystallization was not obvious. The  $n$ ,  $k$ , and crystallization half-life ( $t_{1/2}$ ) values calculated from the lines are summarized in Table II.  $n$  varied between 3.77 and 4.82, indicating that the crystallization mode was three-dimensional growth.<sup>35</sup> PEPG and PEG had similar influences on the crystallization behavior of PLA in the blends.  $t_{1/2}$  is defined as the time at which 50% of the normalized crystallinity is reached. The larger  $k$  was and the smaller  $t_{1/2}$  was, the higher the crystallization rate was. The data listed in Table II demonstrate that the incorporation of both PEPG and PEG increased the crystallization rate of PLA, and this was consistent with the depression of  $T_{cc}$  and  $T_g$ . In general, the crystallization kinetics of a semicrystalline polymer depends on effects of intermolecular interactions of the diluent amorphous phase and  $T_g$ , which is related to its chain mobility. High chain mobility is favorable for a high crystallization rate.

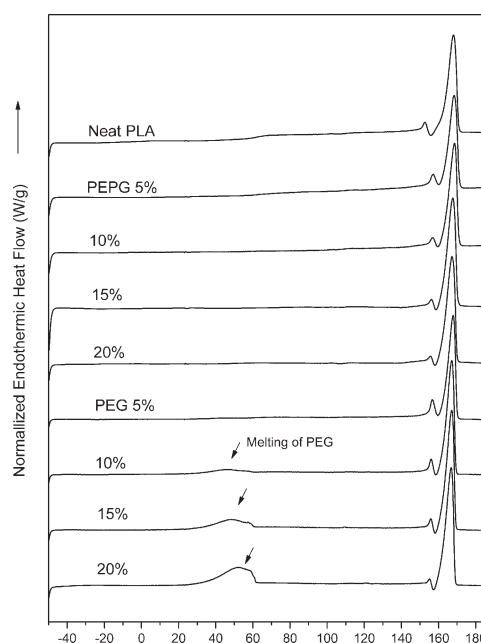
Plasticizers are mainly dispersed in the amorphous phase under the pressure of spherulites.<sup>22</sup> Therefore, the crystallization of PLA could disturb

**TABLE II**  
Crystallization Kinetic Parameters of PLA at 100°C in the PLA/PEPG and PLA/PEG Blends

Blend composition	$n$	$k$ (min <sup>-n</sup> )	$t_{1/2}$ (min)
0 wt %	3.84	0.00103	5.44
5 wt % PEPG	4.20	0.0265	2.17
10 wt % PEPG	4.34	0.154	1.41
15 wt % PEPG	4.82	0.586	1.03
20 wt % PEPG	4.10	0.935	0.93
5 wt % PEG	3.77	0.0169	2.67
10 wt % PEG	3.86	0.108	1.62
15 wt % PEG	4.12	0.332	1.19
20 wt % PEG	4.56	0.623	1.02

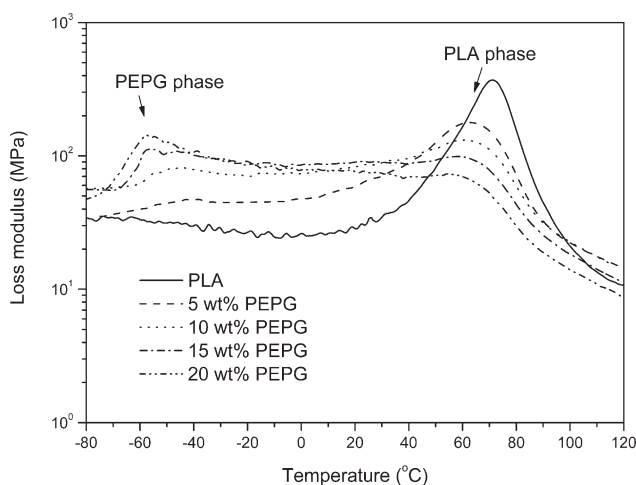
the distribution and compatibility of the plasticizer with PLA and induce phase separation. It is known that PEG can crystallize from PLA/PEG blends with a low PEG content (<30 wt %) following the crystallization of PLA.<sup>36</sup> Also, the crystallization of PEG is thought to be one of the main reasons for embrittlement of the material.<sup>20,24</sup> In this study, all the blends after isothermal crystallization were cooled to -50°C and then heated to 190°C at a heating rate of 10°C/min to investigate the thermal properties of crystallized samples. Figure 8 shows the DSC traces of all the blends after isothermal crystallization at 100°C for 30 min.  $T_g$  of all the samples was not apparent because of the reduction of the amorphous phase. The PLA/PEPG blends showed only the melting of PLA in the DSC traces. However, with over 5 wt % PEG content, the PLA/PEG blends showed the apparent melting peak of PEG, and the area of the melting peak increased with the increase in the PEG content in the DSC thermograms. Phase separation of PEG and PLA occurred during the crystallization of PLA, and PEG could crystallize during the cooling process. Whether the phase separation existed in the PLA/PEPG blends could not be determined from the DSC data. The isolated PEPG phase also could not crystallize during the cooling process because of the weak crystallizability of PLA.

To confirm the phase structure of the crystallized PLA/PEPG blends, the dynamic mechanical behavior of cold-crystallized samples was investigated. The temperature dependence of the loss modulus for the cold-crystallized PLA and PLA/PEPG blends is shown in Figure 9. There were two glass



**Figure 8** DSC traces of the neat PLA and plasticized PLA after isothermal crystallization.





**Figure 9** Loss modulus curves as a function of temperature from DMA runs of the annealed PLA/PEPG blends.

transitions in the crystallized blends, as shown in Figure 9, indicating that phase separation had taken place in the materials. The lower glass transition corresponded to the PEPG phase, whereas the higher glass transition corresponded to the PLA phase. Both of the glass transitions shifted to a lower temperature with the increase in the PEPG content. The transition in the loss modulus for the cold crystallization disappeared because of the complete crystallization of PLA. In comparison with the quenched samples,  $T_g$  of the neat PLA and PLA amorphous phase in the blends increased after the cold crystallization of PLA was finished. The crystallization was equal to physical crosslinking, which limited the mobility of PLA chains in the amorphous phase.

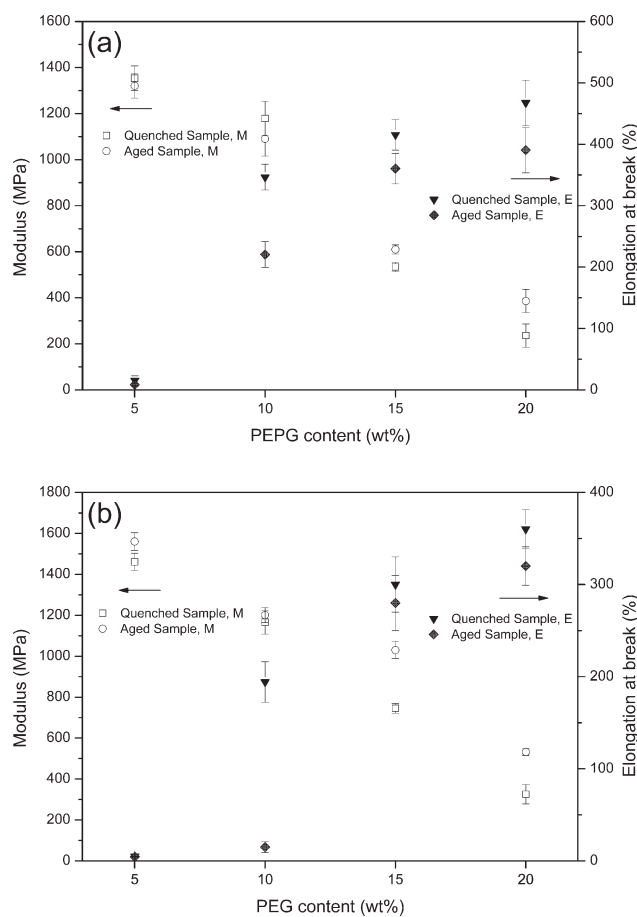
### Properties of the films after aging

In the packaging material industry, there is always an interval between the processing and shifting to the customer. That the packaging material remains stable under the ambient conditions is necessary for its application. In this study, samples of PLA/PEPG and PLA/PEG blends were naturally aged at the ambient temperature (ca. 20 to 30°C) in sealed plastic bags for 2 months to investigate their storage stability.

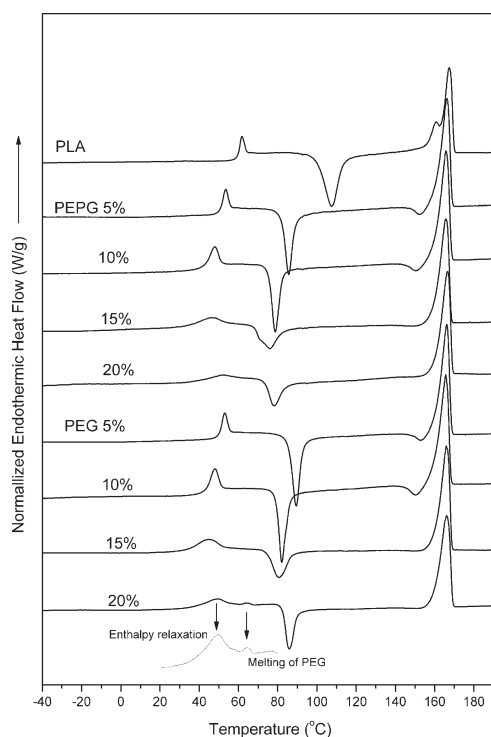
The generated changes in the tensile properties (modulus and elongation at break) after aging are shown in Figure 10. The modulus of the blends with 5 and 10 wt % plasticizer contents apparently did not change, whereas that of the blend with 15 and 20 wt % plasticizer contents increased significantly after aging; for example, the modulus of 80/20 PLA/PEG increased from 320 to 530 MPa, and that of 80/20 PLA/PEPG increased from 240 to 390 MPa. The elongation at break of the blends with 10, 15, and 20 wt % plasticizer contents decreased after

aging. In particular, the blend with 10 wt % PEG experienced a large change. The elongation at break of this blend changed from 240 to 14%, whereas that of the blend with 10 wt % PEPG varied from 340 to 220%. The blend with 10 wt % PEG regained its brittleness after aging. Under the same conditions, PLA/PEPG blends had good tensile properties in comparison with PLA/PEG blends. However, both the PLA/PEPG and PLA/PEG blends lost some flexibility after a long period of storage. A previous study of PLA/PEG blends by Hu et al.<sup>20</sup> demonstrated that slow crystallization of PEG from a homogeneous and amorphous blend in storage is the reason for its embrittlement. Compared with PEG, PEPG lost its crystallizability under the ambient conditions because of its low  $T_m$  value, so there should be other reasons for the aging.

To analyze possible reasons for the aging, the thermal properties of aged samples were investigated. Figure 11 displays the DSC traces of neat PLA and all blends after aging. The detailed data are shown in Table III. There was an obvious enthalpy relaxation in all the heating thermograms. Compared with



**Figure 10** Data for the modulus and elongation at break from tensile tests of the aged and unaged PLA/PEG and PLA/PEPG blends: (a) PLA/PEPG blends and (b) PLA/PEG blends.



**Figure 11** DSC traces of the neat PLA and the blends after storage under ambient conditions for 2 months.

thermograms of the quenched samples, the thermograms of the aged PLA and blends with 5 and 10 wt % plasticizer contents experienced almost no changes, except for the enthalpy relaxation, whereas those of the blends with 15 and 20 wt % PEPG showed not only enthalpy relaxation but also a reduction of the cold-crystallization peak area and increases in  $T_g$  and  $T_{cc}$ . Similar phenomena were observed in the thermograms of blends with 15 and 20 wt % PEG, except for the melting of the PEG crystal, which was found in the aged blend with 20 wt % PEG. It was noticed that  $T_g$  and  $T_{cc}$  of blends with 20 wt % plasticizer contents increased over

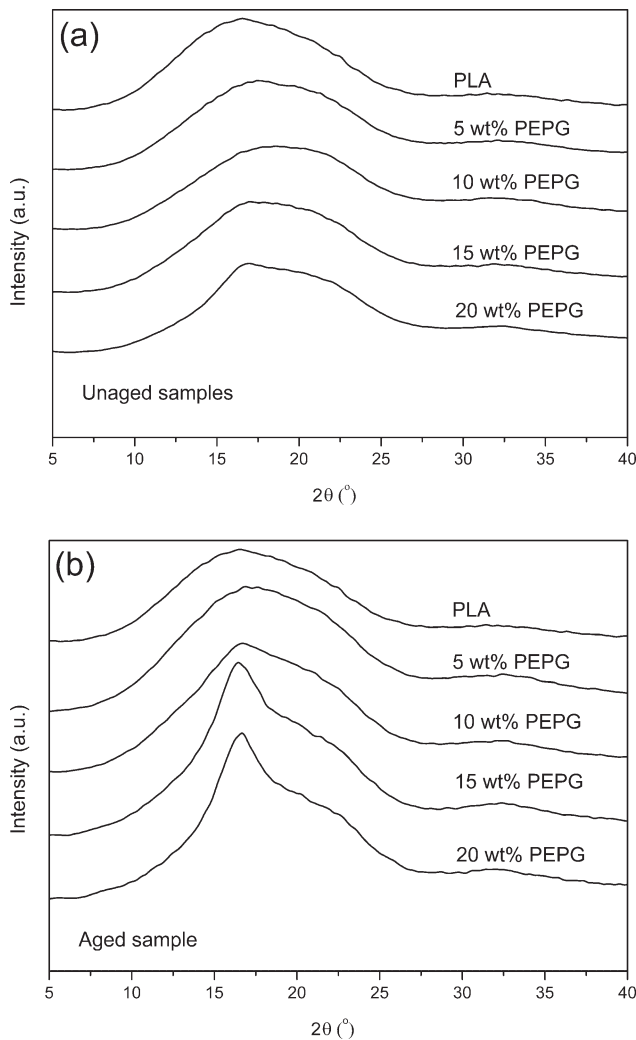
those of blends with 15 wt % plasticizer contents (Tables I and III). This indicated that the aging depended on the composition of the blends. With the increase in the plasticizer content, the thermal properties changed more and faster after aging. The correspondence of the enthalpies of cold crystallization and subsequent melting confirmed that blends with 15 and 20% plasticizer contents had partial PLA crystallization, whereas PLA and blends with 5 and 10 wt % plasticizer contents were still amorphous. These data showed that blends with high plasticizer contents experienced slow cold crystallization of PLA during aging.

The cold crystallization of PLA in the aged PLA/PEPG blends can also be confirmed by WAXD, as shown in Figure 12. The peak intensity of the blends with over 10 wt % PEPG increased at 16.7° after aging, and the diffraction peaks were extremely broad, indicating that the crystals were small and imperfect. It is interesting that the exothermic peak near the melting peak of PLA corresponding to the  $\alpha'$ -to- $\alpha$  phase transition disappeared in the thermograms of aged blends with 15 and 20 wt % plasticizer contents, as shown in Figure 11. The slow cold crystallization possibly induced the rearrangement of the polymer chains, which made the phase structure change from disorder to order during the aging. The melting of PEG corresponding to its crystallization after phase separation was observed only in the blends with 20 wt % PEG but was not apparent because of weakness near the enthalpy relaxation. According to these results, it can be concluded that the aging of PLA/PEPG and PLA/PEG blends was related to the enthalpy relaxation and cold crystallization of PLA. Figure 13 shows the loss modulus curves as a function of temperature obtained from dynamic mechanical analysis (DMA) runs for a comparison of the quenched and aged PLA/PEPG blends. Blends with 10 and 15 wt % PEPG did not show the signs of two relaxation peaks, and this

**TABLE III**  
Thermal Properties of the Aged PLA/PEPG and PLA/PEG Blends at a Heating Rate of 10°C/min

Plasticizer type	Plasticizer content (%)	$T_g$ (°C)	Cold crystallization			Melting		
			$T_c$ (°C)	$\Delta H$ (J/g)	$X_c$ (%) <sup>a</sup>	$T_m$ (°C)	$\Delta H$ (J/g)	$X_c$ (%) <sup>a</sup>
None	0	59.1	107.5	-36.4	39.2	167.4	37.0	39.8
PEPG	5	50.0	85.7	-35.8	40.5	166.2	37.9	42.9
	10	41.5	78.8	-37.6	44.9	165.7	39.4	47.0
	15	36.7	76.0	-27.2	34.4	165.7	38.0	48.1
	20	40.1	78.1	-26.2	35.2	166.7	36.7	49.3
PEG	5	49.8	88.5	-35.9	40.6	165.8	36.1	40.9
	10	42.8	82.0	-36.0	43.0	166.2	38.1	45.5
	15	37.5	80.8	-21.9	27.7	165.9	37.2	47.0
	20	42.2	85.8	-21.3	28.6	166.2	35.3	47.4

<sup>a</sup>  $X_c$  was the PLA crystallinity relative to total PLA.  $\Delta H$  was the enthalpy of cold crystallization or subsequent melting of PLA.

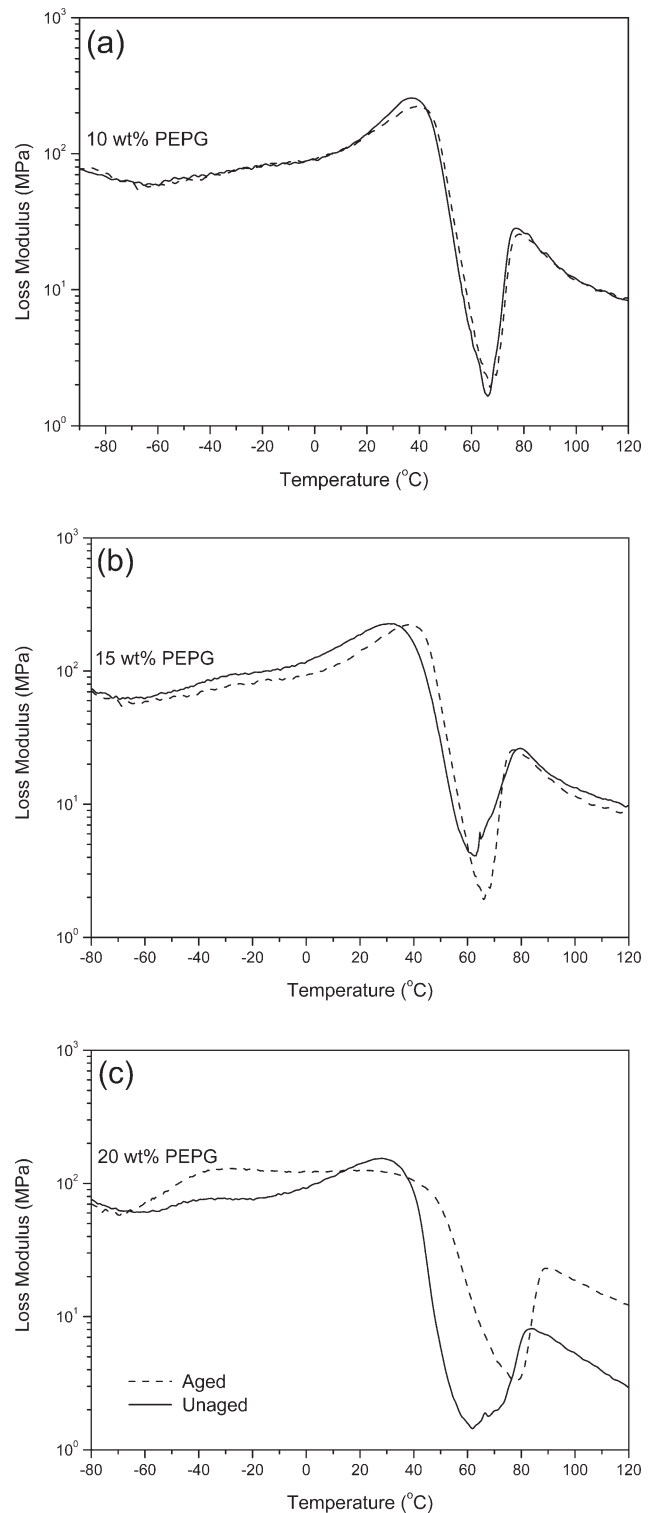


**Figure 12** WAXD patterns of the PLA/PEPG blends: (a) unaged samples and (b) aged samples.

indicated that phase separation did not occur in these systems, whereas the blend with 20 wt % PEPG apparently changed after aging, showing a typical two-phase system. These data showed that phase separation occurred only in the blend with a 20 wt % plasticizer content.

The aging of plasticized PLA has been investigated in many studies.<sup>14,16,24</sup> The cold crystallization of PLA, which exists in blends with high plasticizer contents, has been thought to be one main reason.<sup>14</sup> For the PLA/PEG blends, the crystallization of PEG is another important reason for the aging of the material.<sup>24</sup> However, there are few articles considering the influence of enthalpy relaxation on the properties of aged plasticized PLA. Enthalpy relaxation corresponds to the physical aging of materials. Physical aging<sup>37,38</sup> is a general phenomenon of the glassy state of all materials that has a dramatic influence on polymer properties, such as a reduction of the impact strength, because it increases the relaxation

times of the polymer. After rapid cooling processing of the polymer, the material becomes a thermodynamically unstable glass that tends to reach equilibrium through slow rearrangements. Also, this aging



**Figure 13** Temperature dependence of the loss modulus curves from DMA runs of aged and unaged PLA/PEPG blends: (a) 10, (b) 15, and (c) 20 wt % PEPG.

process develops at a faster rate as the aging temperature approaches  $T_g$ . Pan et al.<sup>39</sup> investigated the physical aging of neat PLLA in detail and reported that enthalpy relaxation made PLLA brittle.<sup>39</sup> For the PLA/PEPG and PLA/PEG blends, their  $T_g$  values were shifted almost to room temperature with the increase in the plasticizer content, so the physical aging should be more apparent. A quenched blend with 10 wt % PEPPG had no crystallization of PLA and PEPPG or phase separation under the ambient conditions, but the drawability was reduced after aging, which should be the influence of enthalpy relaxation.

Hu et al.<sup>20,24</sup> already investigated the aging of PLA/PEG blends in detail, but they did not report the influence of physical aging on the properties of plasticized PLA. A possible reason is that their main research object was the 70/30 PLA/PEG blend, which had a  $T_g$  lower than room temperature, so the enthalpy relaxation did not exist and was not observed. Quenched PLA/PEPPG blends exist in a thermodynamically unstable condition. Both the enthalpy relaxation and crystallization of PLA during aging are processes in which polymer chains vary from disorder to order, and  $T_g$  experiences a corresponding increase. In addition, in this aging, the phase structure of the blends may be influenced, and phase separation may take place. Blends with 15 and 20 wt % PEPPG showed the cold crystallization of PLA, but phase separation was observed only in the latter, perhaps because of the higher plasticizer content. Certainly with longer storage, phase separation may also occur in the other blends. It is interesting that cold crystallization and phase separation in the aged blend with 20 wt % PEPPG did not cause a drastic decrease in the drawability, and  $T_g$  shifted to 40.1°C at the same time. According to the work of Kulinski et al.,<sup>21</sup> phase separation that occurred in the blends of PLA with an uncrystallized plasticizer did not reduce the drawability of the material because of the reported local plasticization.<sup>26</sup> Also, the small and imperfect crystals formed during aging should have little influence on the drawability of the material.

The disorder-to-order transition of PLA chains due to cold crystallization or enthalpy relaxation should be a crucial reason for the aging of plasticized PLA, which induced the blends to phase-separate. PEG, because of its crystallizability, lost its plasticization after phase separation, whereas PEPPG, keeping its amorphous state, still had good plasticization for PLA.

## CONCLUSIONS

PEPPG was a good plasticizer for PLA. Blending PLA with PEPPG significantly lowered  $T_g$ . DMA and DSC

results indicated that both PEPPG and PEG were compatible with PLA at concentrations up to 20 wt %. Melt-quenched PLA/PEPPG and PLA/PEG blends were completely amorphous. Cold crystallization of the blends shifted to lower temperatures with increased plasticizer content in parallel with the shift in  $T_g$ . Tensile tests and SEM indicated that the material changed from brittleness to ductility with the addition of the plasticizer (10 wt %). Actually, no difference between the quenched PLA/PEPPG and PLA/PEG blends existed.

The addition of PEPPG or PEG was found to accelerate the crystallization rate of PLA and increase its final crystallinity. Isothermal crystallization kinetics indicated that the crystallization mode of PLA in the blends was three-dimensional growth, and PEPPG and PEG had similar effects on increasing the crystallization rate of PLA. The crystallization of PLA influenced the distribution of PEG and PEPPG in the blends and induced phase separation. DSC traces of crystallized samples showed clearly the melting peak of PEG but did not show the melting peak of PEPPG. DMA of the cold-crystallized PLA/PEPPG blends indicated a typical two-phase system.

The storage stability of PLA/PEG and PLA/PEPPG blends was investigated in detail. Although PEPPG had lost its crystallizability at room temperature, aged PLA/PEPPG blends still lost some flexibility. The enthalpy relaxation and cold crystallization of PLA were responsible for this aging. The crystallization of PEG was observed only in the blend with 20 wt % PEG. After 2 months of storage, the crystallization of PLA occurred in the blends with 15 and 20 wt % PEPPG, as shown by DSC and WAXD data; the enthalpy relaxation of PLA existed in all the blends, whereas phase separation occurred only in the blends with 20 wt % plasticizer contents. Under the same conditions, the aged PLA/PEPPG blends had better flexibility than the aged PLA/PEG blends. Phase separation should be induced by the cold crystallization and enthalpy relaxation of PLA, which make the disordered PLA chains vary to order. A PLA blend with an uncrystallized plasticizer of a high molecular weight was not enough to obtain completely stable plasticized PLA. However, compared with crystallized PEG, PEPPG, because of its amorphous state under the ambient conditions, could retain the properties of plasticized PLA for a longer time.

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