Flexible plasticized PLA with high crystallinity obtained by controlling the annealing temperature

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Abstract: In this study, plasticized polylactide (PLA) was prepared by blending PLA with high stereoregularity and poly(ethylene glycol-co-propylene glycol) (PEPG) in a batch wise mixer and pressed into films. The influence of annealing temperature on the thermal properties and tensile properties of quenched plasticized PLA was investigated by DSC, DMA and tensile tests. It was found that plasticized PLA after cold crystallization can keep its high flexibility with an elongation at break over 300% by choosing a proper annealing temperature. The difference of crystallization morphology formed at the different annealing temperature was thought as a possible reason for this result.

Introduction

Polylactide (PLA) has received wide attention in the fields of medicine and environmental science because of its high biocompatibility and good biodegradability in the human body as well as in the earth’s environment [1-3]. Many methods have been applied to overcome the brittleness of PLA for increasing its application fields [4-8]. Blending with a plasticizer might offer a cost-effective way of modifying the properties of hard and brittle PLA by decreasing the glass transition temperature of PLA. However, the soften point of amorphous plasticized PLA is near the room temperature which is too low for a kind of plastic and the mechanical properties of plasticized PLA are not stable due to the slow cold crystallization of PLA [9, 10].

If the plasticized PLA complete its cold crystallization, the soften point and the stability will apparently increase. But it is thought that the crystallization of PLA would embrittle the plasticized PLA, especially with high crystallinity level, because the crystallization of PLA induced phase separation of PLA and plasticizer. Research indicated that PLA blended with uncrystralized plasticizer of high molecular weight can keep some toughness after cold crystallization [11]. Blends of PLA and poly(propylene glycol) (PPG) after annealing at 90 °C had an elongation at break about 8%-105% dependence of the composition [11]. But the effect of different annealing temperature on the thermal and mechanical properties of plasticized PLA was still not investigated. It is well known that the crystallization temperature has also large influence on the thermal and mechanical properties of polymer. Not only the crystallinity but also the spherulite sizes can influence the mechanical properties of semi-crystalline polymer. The aggregate state of same polymer may be different after different crystallization temperature.

Recently, Jia et al. reported plasticization of semi-crystalline PLA with poly(ethylene glycol-co-propylene glycol) (PEPG) [12]. PEGP was viscous liquid with molecular
weight about 12 kDa and $T_g$ of -68 °C. PEPG had better compatibility with PLA than PPG and the plasticized PLA using PEPG had good stability after long time storing.

Here we report some astonishing effect of different cold-crystallization temperature on the properties of plasticized PLA. Poly(ethylene glycol-co-propylene glycol) (PEPG) was used as the plasticizer for PLA and its content in the blend was 15 wt%. The plasticized PLA after cold crystallization can be a brittle material by annealing at the high temperature or be a tough material by annealing at the low temperature.

**Results and discussion**

Fig. 1(a,b) shows the POM images at crossed polaroids for the samples prepared from two types of process, the crystallization temperature being reached (a) via cooling from the melt and (b) via heating from the quenched, amorphous state. The spherulite sizes of sample cooling from the melt are significantly larger than that of the sample heating from the amorphous state. This result is consisted with the work of Pluta et al [13]. Cold crystallization leads to more intense spherulite nucleation resulting in smaller spherulite sizes. The defect formed in crystallization process increased with the spherulite size. Generally, larger spherulite makes the polymer more brittle. So the cold crystallization process was chosen in many articles [10, 11] because large spherulite was not helpful for the toughness and embrittled the material.

![Polarizing light micrographs of plasticized PLA crystallized isothermally via cooling from the melt (a) and via heating from the quenched, amorphous state (b) at 130 °C.](image)

**Fig. 1.** Polarizing light micrographs of plasticized PLA crystallized isothermally via cooling from the melt (a) and via heating from the quenched, amorphous state (b) at 130 °C.
In this study quenched samples were put in the oven annealing at 50 and 90 °C for 24 h to obtain the completely crystallized samples, respectively. Neat PLA cannot crystallize at 50 °C because this temperature is lower than its glass transition temperature. But blending with 15 wt% PEPG, the glass transition temperature of plasticized PLA had changed from 59 °C to about 30 °C and the crystallizability of PLA significantly increased [12]. Fig. 2 shows the tensile properties of the quenched and crystallized samples. Quenched plasticized PLA was a kind of flexible material with a yield stress about 21 MPa and elongation at break about 420%. The crystallized sample obtained at 90 °C had lost the flexibility with an elongation at break of only about 26% due to the phase separation induced by cold crystallization of PLA, though the spherulite sizes was very small. However it was interesting that the crystallized sample obtained at 50 °C still kept a high elongation at break about 310%. Perhaps the crystallinity of the two types of samples was very different which caused this phenomenon. DSC was performed to investigate the thermal properties of quenched and annealed samples. Fig. 3 appeared the typical heat thermograms of samples with different thermal history. Quenched plasticized PLA showed apparently glass transition, cold crystallization and melting peak, while the crystallized samples showed only the melting behavior. The disappearance of $T_g$ was attributed to the decrease of amorphous region resulted in the crystallization of PLA. There was almost no difference between the two types of samples annealed at different temperature in their DSC traces. Both of the two type samples finished the crystallization of PLA so the cold crystallization peak vanished in the heating thermograms.

![Fig. 2. Tensile properties of the quenched and crystallized plasticized PLA.](image)

The calculated crystallinity of crystallized sample obtained at 90 °C was 53.4%, whereas that value of the sample obtained at 50 °C was 48.7%. The crystallinity of the two types of samples was similar, so there must be some other reason for the difference of tensile properties. The POM images of the crystallized samples are shown in Fig. 4 and an apparent difference of the crystallization morphology was observed. The spherulite obtained at 50 °C was more fine and perfect than that
obtained at 90 °C. The spherulite sizes had changed to lower than 1 μm after annealing at 50 °C, only about 500~900 nm. Maybe this different crystallization morphology was the reason for the different tensile properties of crystallized samples.

![DSC data of quenched and crystallized plasticized PLA](image)

**Fig. 3.** DSC data of the quenched and crystallized plasticized PLA.

![Polarizing light micrographs](image)

**Fig. 4.** Polarizing light micrographs of plasticized PLA after annealing at different presetting temperature for 24 h, (a) at 90 °C and (b) at 50 °C.

The dynamic mechanical properties of quenched and crystallized samples were investigated by DMA. Fig. 5 shows the temperature dependencies of loss modulus, storage modulus and tan δ determined for these samples. Quenched sample showed a typical homogeneous system, only one glass transition as shown at Fig. 5(a,c). After annealing, phase separation took place and two glass transitions were observed, the lower one for the PEPG phase and the higher one for PLA phase. The detailed data obtained from the loss modulus is shown in the Table 1. The glass transition temperature of PLA increased after annealing and T_g of the sample obtained at 90 °C was higher than that of the sample obtained at 50 °C. This result corresponded to their different crystallinity. The crystallization limited the mobility of
the polymer chain and then the glass transition temperature increased. Because the crystallization had been finished at the annealing process, we did not observe the cold crystallization at the crystallized samples as shown in Fig. 5 (b). Both the two kinds of crystallized samples keeping a high value over 100 MPa until 80 °C indicated that the soften point of the plasticized PLA had a significant enhancement.

**Tab. 1.** The glass transition temperature obtained from the loss modulus.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$, PEPG (°C)</th>
<th>$T_g$, PLA (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quenched blends</td>
<td>-</td>
<td>32.3</td>
</tr>
<tr>
<td>After annealing at 50 °C</td>
<td>-46.7</td>
<td>49.6</td>
</tr>
<tr>
<td>After annealing at 90 °C</td>
<td>-50.1</td>
<td>58.7</td>
</tr>
</tbody>
</table>

**Fig. 5.** Dynamic mechanical relaxation behavior of the quenched and crystallized plasticized PLA: (a) loss Modulus; (b) storage modulus; and (c) tan δ.

**Conclusions**

Plasticized PLA can keep its high flexibility after complete crystallization by controlling the annealing temperature. The crystallizability of PLA increased with the existence of PEPG. Then plasticized PLA can crystallize at a lower temperature (50
°C) and formed a fine spherulite (<1μm) with high crystallinity over 40 wt%. This method will be helpful for obtaining stable plasticized PLA with good toughness and high soften point.

**Experimental**

**Materials**

The utilized PLA (Natureworks PLA 4032D, 98% L-lactide) exhibits a density of 1.25 g/cm3, a weight-average molecular weight of 207 kDa, polydispersity of 1.73 (GPC analysis), and a glass transition temperature and melting point of 59 and 167 °C (DSC analysis), respectively. PEPG with a typical number-average molecular weight of 12 kDa were obtained from Sigma-Aldrich and used as received. The ethylene glycol unit content of PEPG is 78.7 mol% (H-NMR analysis). The glass transition temperature and melting point of PEPG is -68 and -2 °C (DSC analysis), respectively.

**Binary blend preparation**

Prior to blending, all the polymers were dried in vacuum at 50 °C for 24 h. Blend of PLA/PEPG 85/15 w/w were prepared by melt mixing using a twin-screw Haake Reomix 600 at 60rpm and 180 °C for 5 min. After blending, the samples were cooled to room temperature under an air atmosphere.

Entirely amorphous films were prepared using a hot press at 180 °C, a hold pressure 6 MPa and a hold time of 3 min, followed by quenching to room temperature between two thick metal blocks kept at room temperature. A template frame was used to ensure a constant film thickness (1.0 mm). To obtain entirely crystallized samples, the quenched films were put in the oven annealing at 50 and 90 °C for 24 h, respectively. The oven held steady temperature with an accuracy of 0.5 K.

**DSC**

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer Diamond DSC instrument under a N2 atmosphere which was calibrated using indium as standard. All the specimens were first equilibrated at -50 °C and then heated from -50 °C to 190 °C at a rate of 10 °C/min. The degree of crystallinity of the blends was calculated from the melting enthalpy using heats of fusion of 93 J/g [14].

**Tensile test**

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 ambient condition using a cross-head rate of 10 mm/min. At least five specimens with 20.0 mm gauge length and width of 4.0 mm were tested for each condition.

**POM**

Polar optical microscopy studies 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 85/15 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 melt-crystallized sample, the specimens were heated to 180 °C on the hot stage and held at that temperature for 3 min and
then cooled to 130 °C at a rate of 30 °C/min and held at the temperature for 2 h. To obtain cold-crystallized sample, the specimens were quenched from 180 °C to room temperature and then heated to 130 °C at a rate of 30 °C/min and held at that temperature for 2 h. In addition, the quenched specimens were also put in the oven at 50 and 90 °C annealing for 24 h, respectively. Then the photographs were taken by a digital camera.

**DMA**

Dynamic mechanical thermal analysis (DMTA) was performed on molded films with DMA/SDTA861e (Mettler Toledo) in the tensile mode. The relaxation spectrum was scanned from -100 to 140 °C with a frequency of 1 Hz and a heating rate of 2 °C/min. The shape of the film samples was rectangular; approximately 3.9×9.0×1.0 mm. Storage modulus, loss modulus and tan δ were recorded as a function of temperature.

**References**