Effects of Methanol on Stereocomplexation of Solvent-Cast Poly (lactic acid)

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1. INTRODUCTION

Poly (lactic acid) (PLA), which is made from starch such as corns, sugar beets, or sugar canes, has been widely studied actively as biobased plastics1). PLA, as a chemical formula, (-C(CH)_3H-CO-O-)_n), has an asymmetric carbon atom in its monomer unit, so there exists optical isomers such as poly (L-lactic acid), (PLLA), and poly (D-lactic acid) (PDLA). Because of the strong affinities between these enantiomers, it is known that they are packed in pairs inside the racemic crystal to form stereocomplex. The existence of stereocomplex crystal has been confirmed by the crystalline structure different from homo-crystal and the melting temperature (= 230°C2) 50°C higher than the homo crystal. However, stereocomplexation of PLA occurs under very limited conditions. In most cases, homo crystallization is preferred to stereocomplex crystallization. It is interesting to prepare the PLA sample containing only stereocomplex-type crystals by simple solution casting method. In this paper, stereocomplex crystallization is studied by solvent casting from chloroform/methanol mixed solvent. Methanol and chloroform is usually used as poor and rich solvents of PLA, respectively.

2. EXPERIMENTS

2.1 Materials

PLLA (Lacty, medical grade, weight-average molecular weight, \(M_w = 220,000\) and polydispersity, DPI = 1.96) and PDLA (PURAC, \(M_w = 263,000\), DPI = 1.77) were used in this study.

2.2 Solvent-casting

The blend films of PLLA and PDLA were obtained by the following casting method. Solutions of PLLA and PDLA in chloroform were separately prepared in a polymer concentration of 5 g/dL and then admixed with each other in the ratio of 1:1 under vigorous stirring. Chloroform was chosen as it has a low boiling temperature (61°C) and thus can be readily removed from the cast film by drying. Then, 0, 0.5, 1, 5, or 10 mL methanol was added to 10 mL of the PLLA/PDLA solution. The mixed solutions were cast onto a flat glass plate, and the solvent was allowed to evaporate at room temperature for approximately 1 week. The resulting films were dried in vacuo for another week. The films cast from the solution containing 0, 0.5, 1, 5, and 10 mL methanol were denoted as PLA, PLA/Me0.5, PLA/Me1, PLA/Me5, and PLA/Me10, respectively.

2.3 X-ray analysis

Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature on a Rigaku RINT 2100-FSL system using a nickel-filtered CuK\(\alpha\) radiation with a wave-length of 0.1542 nm. The scans were recorded for the 2\(\theta\) range of 5 to 40° at a scan rate of 2° min\(^{-1}\) operating at 40 kV and 20 mA.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction

Fig. 1 shows the WAXD results for PLA, PLA/Me0.5, PLA/Me1, PLA/Me5, and PLA/Me10. Three different crystal structures (\(\alpha\)-, \(\beta\)- and \(\gamma\)-form) have been proposed for PLLA, based on X-ray diffraction patterns and conformational energy analysis. The \(\alpha\)-form of PLLA, as shown in Fig. 2a, is in a pseudo-orthorhombic system with parameters for \(a = 1.07\) nm, \(b = 0.595\) nm, and \(c_{(fiber\ axis)} = 2.78\) nm. Two chains with 10 helix conformation are contained in a unit cell. The \(\beta\)-form appears in solution spun and drawn fibers at higher drawing temperature and/or at higher draw ratios. An orthorhombic with \(a = 1.03\) nm, \(b = 1.82\) nm, and \(c_{(fiber\ axis)} = 0.900\) nm, containing six chains with 3 helix conformation, is proposed for this structure. In the stereocomplex crystal as depicted in Fig. 2b, the crystalline system is triclinic (P1) with cell dimensions: \(a = 0.916\) nm, \(b = 0.916\) nm, and \(c_{(fiber\ axis)} = 0.870\) nm, \(\alpha = 109.2°\), \(\beta = 109.2°\), and \(\gamma = 109.8°\). PLLA and PDLA segments are packed laterally in a parallel fashion as a pair in the unit cell. Stereocomplex takes a 3 helical conformation, which is extended a little from a 10 helix in the homo crystal with the \(\alpha\)-form.

In this study, the X-ray pattern of pure PLA film shows three
main peaks at 2θ = 11.8° and 20.5°, which corresponds to (100)/(010)/(-110) and (110)/(-120)/(-210) of the stereocomplex crystal, respectively, while 2θ = 17.0° corresponds to (110)/(200) of the α-form for homo crystal. By adding the methanol, the peaks at 2θ = 11.8° and 20.5° increases compared to the peak at 2θ = 17.0°, indicating that the stereocomplex crystal increases, while homo crystal decreases. Finally, the X-ray diffraction pattern of PLA/Me10 shows only stereocomplex crystalline reflection peaks.

3.2 Crystallinities

A typical X-ray diffraction pattern of crystalline PLA is shown in Fig. 3. The pattern was divided into a broad peak at 2θ = 9-30° from the amorphous phase and narrow peaks from the crystals. The crystallinity was estimated by dividing the crystalline peaks by the overall region. Among the reflection peaks of crystalline region, the peak corresponds to homo and stereocomplex crystals exist. From the ratio of these ranges, the crystallinities of homo and stereocomplex phases were estimated.

As shown in Fig. 4, the homo crystallinity slightly decreases with the increase of the amount of methanol, and finally no homo crystal was observed in 10 mL. On the other hand, the overall crystallinity increases slightly with the amount of methanol up to 5 mL, and then increases drastically to 90 % at 10 mL. The increment of the crystallinity was attributable to the increase of the stereocomplex crystallinity. As shown in Fig. 5 (a), the PLA film is completely transparent. But by adding methanol, the film became unclear. The PLA/Me10 film, formed only stereocomplex
crystal, looked white turbid (Fig. 5 (b)). This sample show relative high crystallinity, almost no amorphous phase. Therefore, it was confirmed that methanol is an effective agent for the stereocomplex crystallization of PLA.

In a rich solvent such as chloroform, the interaction between PLA and solvent is preferred to that between PLA chains. The crystallization of PLA proceeded based on the intramolecular interaction rather than the intermolecular interaction. As a result, homo crystallization must take advantage. The racemic crystallization, which requires the intermolecular interaction between PLLA and PDLA, is restricted. Thus, homo-crystallization proceeded when the solvent-polymer interaction is strong. The racemic crystallization must take place only in the limited region where PLLA and PDLA molecules overlap. On the other hand, by the addition of MeOH, which is a poor solvent for PLAs, the phase separation occurs between solvent and the polymer chains in the solution, leading to the aggregation of polymer chains. The interactions between PLLA and PDLA are strong compared to those between homo molecules. Because of the strong interaction between the enantiomers, the overlapping between PLLA and PDLA is preferred to that between homo chains in the aggregate. Therefore, stereocomplex crystallization occurred preferentially in a poor solvent.

4. CONCLUSIONS

Solvent cast films of the enantiomeric PLAs in chloroform were prepared. Homo crystalline reflections were observed in the X-ray diffraction patterns, but also small peaks of stereocomplex crystals were observed. But when methanol was added in the PLA solution, the stereocomplexation was enhanced. Only stereocomplex crystals were finally detected with the excess of methanol. These results indicate that homo-crystallization takes place with intermolecular crystallization, while stereocomplexation takes place by the intramolecular crystallization.

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REFERENCES


Fig. 5 Photographs of PLA films: (a) PLA and (b) PLA/Me10.