Formation of Homocrystal with Remarkably High Melting Temperature in PLLA/PDLA Blend Revealed by WAXD

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\textbf{1 Introduction}
Poly(lactic acid) (PLA) is an environment friendly material. It is biodegradable, non-toxic and highly transparent. However, PLA mechanical and thermal properties require significant enhancements. PLA exists in two enantiomeric forms, L-lactic acid (PLLA) and D-lactic acid (PDLA). Each on their own can form homo crystallites (HC). Moreover, these two enantiomers, together, can form stereocomplex crystallites (SC). The tightly packed SC has a melting temperature 50°C higher than HC.

\textbf{2 Experiment}
The isothermal crystallization of PLLA/PDLA (50/50) blend was examined, at different temperatures and for different durations, by means of differential scanning calorimetry (DSC), time-resolved wide-angle X-ray diffraction (WAXD) and polarized optical microscope (POM) observation. WAXD measurements were performed at BL-10C beamline of photon factory (PF) of high-energy research organization (KEK), Japan, with the wavelength of 0.10 nm and the size of the incident X-ray beam being 182\,\mu m (H) \times 346\,\mu m (V). The distance between the specimen and the 2-dimensional detector (PILATUS3 2M, DECTRIS, Switzerland) was set at 0.25 m. The exposure time was 30s.

\textbf{3 Results and Discussion}
Figure 1 shows the particular case of Tc = 170°C, where the isothermal crystallization duration plays a major role in the formed crystallites and their melting temperatures. For the 1- and 5-min durations, no endothermic peaks appeared, indicating the absence of crystallites formation. However, for the durations between 10 and 65 min, two endothermic peaks appeared, both ascribed to the melting of SC. The HC melting peak appeared after 100 min of isothermal crystallization with a significantly high melting temperature of 184°C. Moreover, the HC melting temperature increased with the longer isothermal crystallization durations, resulting in a remarkably high melting temperature of Tm (5 h) = 187.3°C. To the best of our knowledge, such high Tm has never been reported before.

The assignment of the melting peaks to HC and SC was confirmed by the time-resolved wide-angle X-ray diffraction experiments performed after quenching the sample from 250°C to 170°C. As shown in the inset in Figure 2, the first peak of HC emerged 70 min after the temperature stabilized at 170°C. While the second peak appeared after more than 2 h and 13 min. Furthermore, the POM observations carried out at the same Tc indicate that HC was formed within the already established SC spherulites, as the SC completely filled the observed space prior to the HC crystallization setting in.

As for the isothermal crystallization performed at different temperatures, the DSC results at Tc = 110°C and Tc = 150°C showed the appearance of HC (along with SC) melting peaks after 1- and 5-min durations, respectively, with its melting temperature increasing with the longer crystallization durations. For Tc = 110°C, Tm of HC increased from 173.5°C to 176°C after 1 min and 5 h durations, respectively. As for Tc = 150°C, Tm of HC increased from 176.3°C to 180.1°C after 5 min and 5 h durations, respectively. However, for Tc = 180°C only SC was formed after 5 h of isothermal crystallization.

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