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Effects of Blend Composition on Crystalline Behavior of Poly(L-lactic acid)/Poly(D-lactic acid) Blends as Revealed by Synchrotron Wide-Angle X-Ray Scattering

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1 Introduction

Polylactic acid (PLA), semicrystalline biocompatible polymer, which is an eco-friendly, renewable thermoplastic derived from sources like corn starch or sugarcane. Various factors, such as the rate of cooling, the molecular weights, optical purity, and the presence of certain additives, influence this crystallization. To enhance the PLA's crystallization is vital for improving its characteristics to suit diverse applications, including packaging, biomedical materials, and 3D printing. Stereocomplex crystal (SC) where PLA molecules with different enantiomer (L- and D-lactic acid units) come together to form a crystalline structure of which melting temperature (T_m) is higher than that of homocrystal (HC) due to the complementary helical structures [1,2]. This study focused on the effects of blend composition of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA), which resulted in a remarkably high amount formation of HC.

2 Experiment

PLLA sample obtained from Nature Works Co. (2500HP (D = 0.5%, weight-average molecular weight (M_w) = 1.74 × 10^5, and the index of polydispersity of molecular weight (M_w/M_n) = 2.22)), where M_n is the number-average molecular weight) and PDLA from PURAC Co. (D130 (L < 0.5%, M_w = 1.41 × 10^5, Mw/Mn = 2.03)). Specimens were prepared by solution casting method using dichloromethane (DCM) as solvent with biased blend compositions as ratio 20/80 and 80/20 by weight. The differential scanning calorimetry (DSC) measurement was performed using DSC214 polyma (NETZSCH, Germany) for isothermal crystallization for 5 h. at 170°C. The wide-angle X-ray scattering was conducted at BL-6A of Photon Factory (PF), Tsukuba, Japan. Home-made heater block and sample holder designed to conduct T-jump experiments from the melting temperatures (250°C) to the crystallization temperatures (170°C). The isothermal crystallization for 5 hrs. at 170°C was performed.

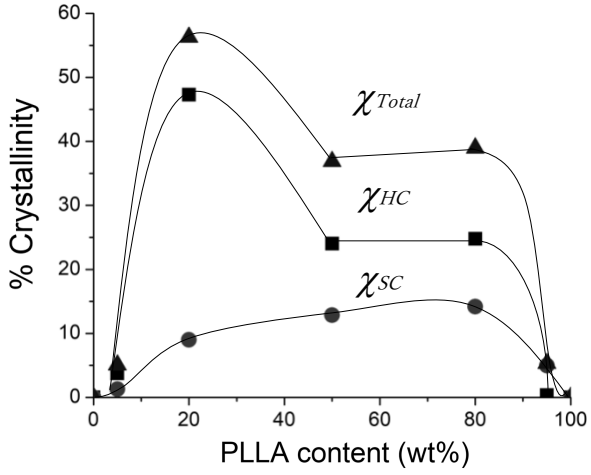

Fig. 1: Plot of %crystallinity obtained from the DSC measurement for each blend after 5h isothermal crystallization at 170°C.

3 Results and Discussion

Fig. 1 shows the degree of crystallinity obtained from the DSC measurement. PLLA/PDLA blend composition of 20/80 provided the highest amount of HC formation as 47% of the crystallinity, which led total crystallinity to 56%, while its counterpart blend (80/20) has only 25%. This shows great potential of this blend sample (20/80) for maintaining its shape when exposed to high temperatures (around 100°C).

The process of SC and HC formation was also studied by time-resolved WAXS. Peak assignment was conducted according to the previous work (Pandey, et al.)[3]. The q value refers to the magnitude of the scattering vector, as defined by

$$q = (4\pi/\lambda)\sin\theta \quad \text{---(1)}$$

Here, λ is the wavelength of the X-ray radiation, and θ is half the scattering angle.

Fig. 2 demonstrates the formation of $SC_{300/030}$ and SC_{220} reflection peaks apparently observed at 750 s. While $SC_{300/030}$ and SC_{220} reflection peaks abundantly evident at 2610 s, appearance of $HC_{110/220}$ reflection peak was less pronounced. At the later stage as 6000 s and later, appearance of HC_{203} reflection peak was pronounced along with the remarkable growth of the $HC_{110/220}$ reflection peak.

Fig. 3 compares 1D WAXS profiles for both blend specimens at 9000s time elapsed. While PLLA20 (20/80) has reflection peaks of HC pronounced obviously, the PLLA80 specimen still have no sign of HC reflection peaks, indicating that the isothermal crystallization at

170°C with 2.5 h time is not sufficient for formation of HC in the specimen that contains PLLA (lower optical purity compared to PDLA) as major part of the blend.

4 Conclusion

We have examined the crystallization behavior, concurrent formation of HC and SC, in a biased blend specimen of PLLA and PDLA (20/80) and (80/20) using DSC and WAXS measurements. The formation of HC in the 80/20 blend is much slower than that in the 20/80 blend, as detected by time-resolved WAXS measurements.

References

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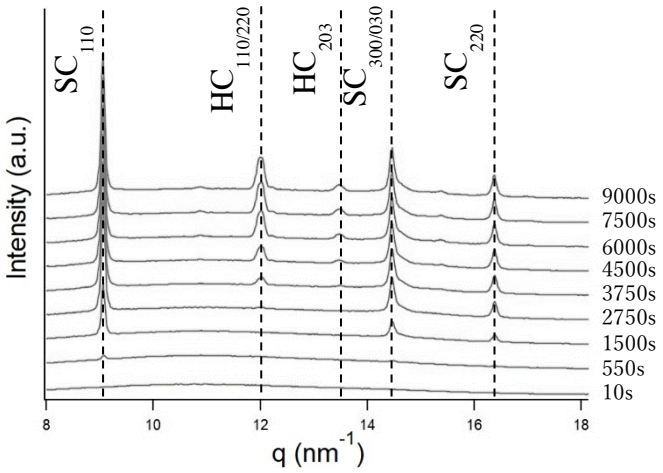

Fig. 2: Time evolution of the 1D WAXS profiles of isothermally crystallized PLLA20 (20/80 blend) at 170°C.

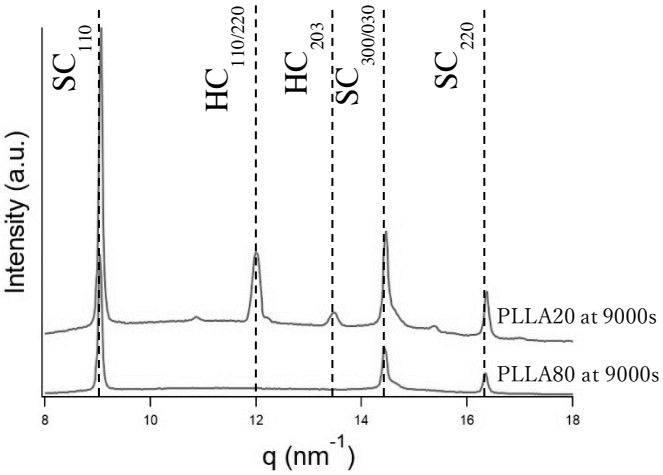

Fig. 3: 1D WAXS profiles of isothermally crystallized PLLA20 (20/80 blend) and PLLA80 (80/20 blend) isothermally crystallized at 170°C for 5 h.

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