Remarkably high crystallinity in PLLA/PDLA (20/80) by prolonged isothermal crystallization at 170°C

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Polylactic acid (PLA) is a biodegradable polymer derived from natural plants. The study of homocrystal (HC) and stereocomplex (SC) formation makes it versatile and deserves further development of sustainable materials. The HC consists of either poly(L-lactic acid) (PLLA) or poly(D-lactic acid) (PDLA), and the SC, formed by intertwining PLLA and PDLA chains, possesses distinct material characteristics[1,2]. This study focused on the biased blend composition of PLLA and PDLA, which resulted in a remarkably high amount formation of HC.

Specimens with biased blend compositions as ratio 20/80 of PLLA/PDLA (defined as PLLA20) and 80/20 (defined as PLLA80) by weight were subjected to the differential scanning calorimetry (DSC) measurements for isothermal crystallization at 170°C for 5 h and the wide-angle X-ray scattering (WAXS) at BL-6A of Photon Factory (PF), Tsukuba, Japan. The characteristics of the PLLA and PDLA samples used in this study were summarized in Table 1.

Table 1 Characteristics of PLA samples.

Sample	code	Optical purity	M_n	PI
PLLA	2500HP (NatureWorks Co.)	99.5% (%D = 0.5)	1.74 x 10^5	2.22
PDLA	D130 (PURAC Co.)	> 99.5% (%L < 0.5)	1.41 x 10^5	2.03

Fig. 1 shows the degree of crystallinity obtained from the DSC measurements. Among the blends studied, PLLA20 exhibited the highest level of HC formation, reaching 47% of the total crystallinity, while PLLA80 achieved only 25%. This striking contrast emphasizes the exclusive potential of PLLA20 to prevent thermal shrinkage up to around 100°C. Fig. 2 demonstrates the evolution of SC reflection peaks in the WAXS profiles, started to be observed at 750 s after the T-jump, while HC peaks were observed at 2610 s. At the later stage at 6000 s and later, the remarkable growth of the HC reflection peaks were pronounced along with concurrent growth of the SC reflection peaks. The significant role played by the surplus of PDLA can be attributed to the HC formation in PLLA20, which boasts superior optical purity when compared to PLLA. Furthermore, the lower molecular weight of the excess PDLA can reduce the viscosity of the blended specimen in its molten state, facilitating greater mobility of the overall polymer chains within the matrix, making crystallization more accessible.

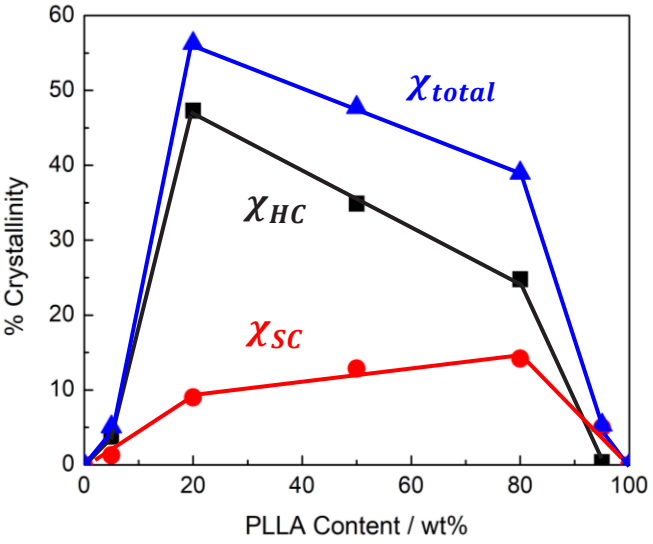

Fig. 1 Plot of %crystallinity obtained from the DSC measurements for blends after 5h isothermal crystallization at 170°C.

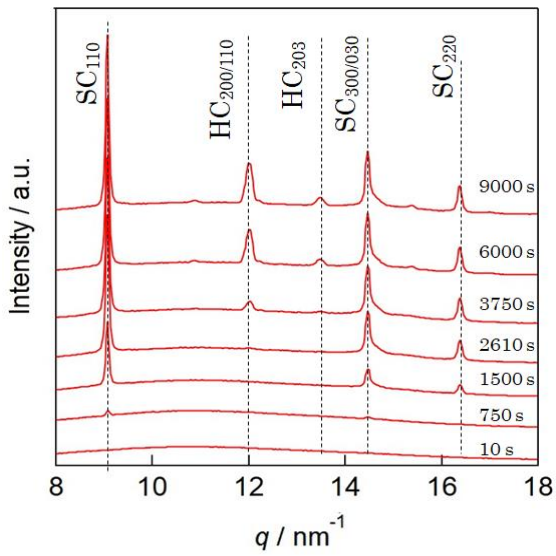

Fig. 2 Time evolution of the 1D WAXS profiles of isothermally-crystallized PLLA20 (20/80 blend) at 170°C.

References
[1] Kister, G., Cassanas, G. and Vert, M., Polymer, 39, 267-273 (1998).
[2] Furuhashi, Y., Kimura, Y. and Yoshie, N., Polym J, 38, 1061–1067 (2006).

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