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Transparent and crystallized poly(L-lactic acid) made by press-drawing

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Introduction

Plant-derived polymers have been developed and put into practical use, recently. Especially, poly(L-lactic acid) (PLLA) is one of the most promising biopolymers. It is known that amorphous PLLA shows excellent transparency, however, it has disadvantage such as low heat resistance caused by its low glass transition temperature (Tg) of about 60°C and brittleness. In order to improve the heat resistance, the PLLA should be crystallized and the crystallinity should be high. Crystallized polymer usually is opaque by light scattering. Therefore, to satisfy both of high crystallinity and the excellent transparency, it is necessary to suppress the growth of large crystal but to form microcrystals, which is sufficiently smaller than the wavelength of visible light. In the case of a stretched crystalline polymer film, transparent but crystallized specimen can be formed by orientation-induced crystallization during the stretching process.

In this study, by considering the analogy of stretching film, making a thicker sheet with a transparent but crystallized PLLA was examined by using press-drawing method [1] and the mechanism of forming the transparent crystalline PLLA sheet was discussed.

Experimentals

The press-drawn PLLA sheet was made by the following procedures: i) PLLA pellets were melted at 210°C, molded to disc-like shape with 20 mm of diameter and 12 mm thick, and then the amorphous PLLA specimen was prepared by quenching it to the room temperature. ii) The specimen was press-drawn by the hot-pressing machine at 60°C, which is just above the Tg of the PLLA), to 4 mm thick and cooled to the room temperature. iii) The specimen was crystallized by annealing at 130°C between two metal plates to prevent the expansion of the specimen.

Results and Discussion

The press-drawn and cooled PLLA sheet was transparent but the crystallinity was very low. It suggests that the orientation-induced crystallization did not occur during during the press-drawing process. To crystallize the sheet, the press-drawn sheet was annealed at 130°C between two metal plates not to expand during the annealing, because the press-drawn sheet recovers to the original shape when the sheet is annealed over Tg. After the annealing, the press-drawn PLLA sheet remained transparent. The crystallinity of the annealed sheet was about 40% and it was found that the transparent but crystallized PLLA sheet could be obtained by annealing the press-drawn sheet.

To clarify the mechanism that such a sheet was obtained, the structure of the sheet was measured by SR-SAXS. The SAXS profiles of the press-drawn and annealed specimen are shown in Figure 1. In the press-drawn plane of the sample, a peak, comes from the long period of crystal lamellae, was observed. On the contrary, in the cross-sectional plane of the press-drawn sheet, no peak was observed. The result indicates that the crystal lamellae form stacks in the press-drawn plane, while there is no lamella stack in the cross-sectional plane. From the result, it is suggested that the molecular chain took planer orientation along the press-drawn plane. Moreover, the no large crystal existence in the cross-sectional plane resulted in the transparent feature of crystallized press-drawn PLLA.

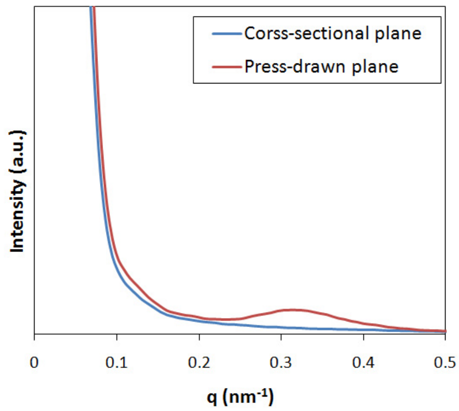

Figure 1. SAXS profiles of press-drawn at 60°C and annealed at 130°C for 3hours.

References

[1] H. Kataoka, K. Toyouchi, Kobunshi-Kako, No. 4, pp.306 (1997). (in Japanese)

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