

Crystallization of press-drawn poly(L-lactic acid)

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Introduction

Poly(L-lactic acid) (PLLA) is one of the most attractive plant origin polymers. Amorphous PLLA shows high transparency, however, heat resistance is low because glass transition temperature (T_g) is about 60°C. The heat resistance can be improved by crystallization of PLLA, though the crystallized PLLA is opaque by light scattering. In order to satisfy both of the high crystallinity and the excellent transparency, we have investigated the press-drawn and crystallized PLLA. Press-drawing method is the method to draw a specimen by compressive force at just above the T_g . When a polymer is drawn just above T_g , relaxation of molecular chain during the press drawing process hardly takes place and then very high orientation of molecular chain can be realized. It was reported that press-drawn high molecular weight poly(methyl methacrylate) sheet shows high impact strength and high solvent resistance[1]. When the press-drawn amorphous polymer is annealed above the T_g , the shape of press-drawn polymer almost returns to the original one just before press-drawing, because the polymer deformed elastically during the press-drawing process.

In our previous study, we tried to induce micro-crystal formation in the PLLA by press-drawing method. PLLA is not crystallized by the press-drawing. However, we found that the following annealing process bring about the transparent and crystallized PLLA. By the measurements of both small angle X-ray scattering and wide angle X-ray diffraction, it was suggested that the molecular chains in the PLLA crystal orientate in the press-drawn plane and the suppression of molecular chain movement may induce the crystal formation smaller than the wavelength of visible light.

In this study, we focus on the crystallization of press-drawn uncrystallized PLLA by the annealing and compare with the cold-crystallized PLLA.

Experimentals

PLLA was supplied from Mitsui Chemicals Inc. (LACEA, H100). The press-drawn PLLA sheet was made by the following procedures: i) PLLA pellets were melted at 210°C, and molded to disc-like shape with 20 mm of diameter and 7 mm thick, and then the uncrystallized 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 T_g of the PLLA, to 1.5 mm thick and cooled to the room temperature. iii) The specimen was crystallized by

annealing at 110°C between two metal plates to prevent the expansion of the specimen.

The crystallization process was analyzed by using the differential scanning calorimeter (DSC) and the synchrotron radiation small-angle X-ray scattering (SR-SAXS).

Results and Discussion

Crystallization process of the press-drawn PLLA was measured by DSC during annealing process at 110°C. Both the press-drawn and unpress-drawn PLLAs showed exothermic peaks about 500s. However, peak height of the former is much higher than that of the latter. This indicates that the crystallization progresses more rapidly in the press-drawn PLLA. The crystallinities of them after the annealing show almost same values. To confirm the phenomenon more clearly, SR-SAXS measurement of the uncrystallized press-drawn PLLA was performed during the annealing process at 110°C. When the thickening during the annealing process is not suppressed, scattering peak originates in the long period of crystal lamellae can be observed and the intensity increased with the annealing time. Invariants of them during the annealing process are plotted in Fig. 1. From the figure, it is obvious that the crystallization of press-drawn PLLA is faster than the unpress-drawn one. It is considered that the fast crystallization is brought about by the sudden relaxation of elongated polymer chains in the press-drawn PLLA when the temperature becomes above T_g during temperature jump from the room temperature to the annealing temperature.

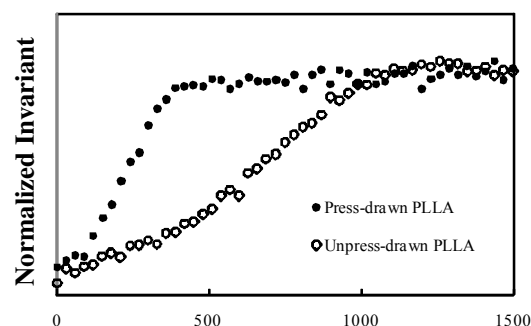


Figure 1. Invariants of press-drawn and unpress-drawn PLLAs during annealing process at 110°C

References

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