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Magnetic Alignment of Poly(L-lactic acid) Containing a Nucleating Agent

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The magnetic alignment of poly(L-lactic acid) (PLA) containing octamethylenedicarboxylic dibenzoylhydrazide (OMBH) as a nucleating agent was studied. OMBH also affected PLA as a nucleating agent when about 5 wt % of d-type material was included. The magnetic alignment of PLA including OMBH was achieved. The *c* axis of the PLA was parallel to the magnetic field.

Since the mechanical strength of PLA is higher in biodegradable plastics, the application of PLA to the production of machine parts has been anticipated. However, the crystallization kinetics of PLA is slow, and it is known that crystallinity is lowered by the usual conditions used for molding, resulting in lower heat-resistance.[1] The addition of a nucleating agent has been used in order to increase the crystallinity of crystalline polymers. The development of a high-performance nucleating agent for PLA is an important theme in this field. Therefore, various materials that are effective as nucleating agents for PLA have been reported.[2–5]

Mechanical properties such as Young's modulus are not only dependent on crystallinity, but also on the orientation of a crystal. Mechanical drawing processes have been used to control the orientation in polymer materials that have been shaped into films or fibers. Although drawing is an excellent method for controlling the orientation of a polymer, there are some disadvantages. For instance, the direction of crystal orientation is limited to the drawing direction, in addition to restrictions in terms of shape. Therefore, drawing is not always suitable for orientation control in bulk materials.

Meanwhile, it is known that crystalline polymers such as poly(ethylene naphthalate),[6] isotactic polystyrene,[7–9] and poly(ethylene terephthalate)[10] can be orientated by the use of melt-crystallization in a magnetic field. Magnetic alignment could become a novel technique by which orientation can be controlled, even in a bulk material.[11] It is also known that isotactic polypropylene can be orientated by inducing a magnetic alignment in the nucleating agent.[12] Although the magnetic alignment of a neat polymer is very dependent on the heat treatment conditions,[8,9] this method can facilitate the magnetic alignment of a polymer.

Therefore, the magnetic alignment of PLA containing a nucleating agent was examined in order to achieve the orientation control of bulk PLA. In this study, we used OMBH, which is expected to become an effective nucleating agent for PLA.[5,13]

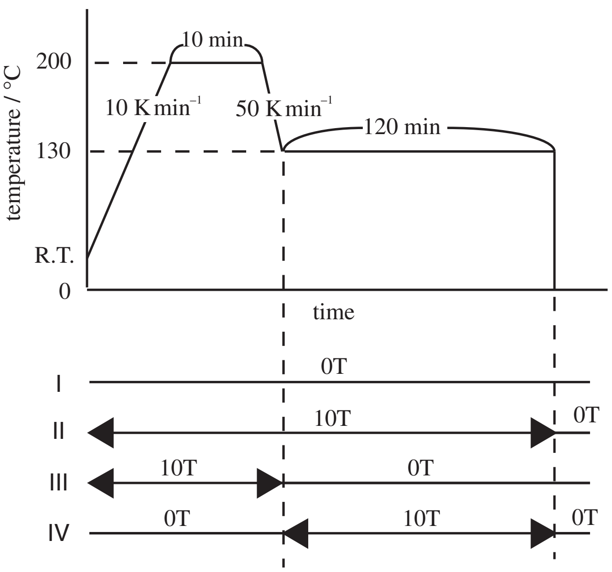
PLA ($M_w = 118100$; Daishin Pharma-Chem Co., Ltd.) with 4.67% of d-type content was used. The OMBH that was used as the nucleating agent was synthesized according to previous literature.[5] The crystal size of OMBH was about 7 µm in length and 500 nm in diameter and the melting point of OMBH was 210 °C. OMBH was dry-blended with PLA pellets, and the mixture was dried at a temperature of 70 °C for 5 h in vacuo. The dried mixture was extruded by using a single-screwed extruder (Imoto Machinery Co., Ltd.) at a temperature of 200 °C. The samples that were obtained were hot-pressed in order to fabricate films. The crystallization half-time ($t_{1/2}$) was determined by differential scanning calorimetry (DSC6200, Seiko Instrument Co., Ltd.) with the following temperature program. The sample was heated from room temperature to 200 °C at a heating rate of 10 K min^{-1}, held for 10 min, and then cooled to its crystallization temperature at a cooling rate of 50 K min^{-1}.

The film sample was annealed according to the following procedure. A superconducting magnet (HF10, Sumitomo Heavy Industries, Ltd.) was used to apply a magnetic field. This magnet has a 100-mm-diameter vertical bore tube, and a homebuilt heating system has been installed in the bore. The direction of the magnetic field was parallel to the film surface. The sample was heated from room temperature to 200 °C with a heating rate of 10 K min^{-1}, held for 10 min, and then cooled to a crystallization temperature of 130 °C at a cooling rate of 50 K min^{-1}. The sample was quenched in iced water outside the magnet after the heat treatment. We prepared samples with various applied magnetic field histories. The thermal and applied magnetic field histories are shown in Scheme 1.

2D-WAXD measurements were carried out using a Nano-Viewer (Rigaku Co., Ltd.) in order to observe the magnetic alignment of the PLA.

Figure 1 shows the crystallization half-time of neat PLA and nucleated PLA at various crystallization temperatures. We could not detect an exothermic signal originating from neat PLA when the crystallization temperature was over 120 °C, since the crystallization rate of neat PLA is very low. On the other hand, crystallization could be observed, even above 130 °C, in PLA containing 0.5 wt % OMBH. The addition of OMBH clearly promotes the crystallization of PLA. The value of $t_{1/2}$ in our work is longer than that published in a previous report.[13] It has been reported that the crystallization rate of PLA depends significantly on the content of d-type PLA.[14] This was the reason why the sample that we used had a high d-type PLA content.

The azimuthal angle intensity distributions of (200)/(110) and (203) for nucleating PLA are shown in Figure 2. Figure 2a shows the intensity distribution of (200)/(110) for a sample prepared outside the magnetic field, which corresponds to the magnetic field history I in Scheme 1. No distribution in azimuthal angle intensity for any plane could be observed in



Scheme 1. Thermal and applied magnetic field histories used in sample preparation. The thermal history was the same for all samples. The applied magnetic field history was four-ways. The parts surrounded by arrows represent the period when a magnetic field of 10 T was applied.

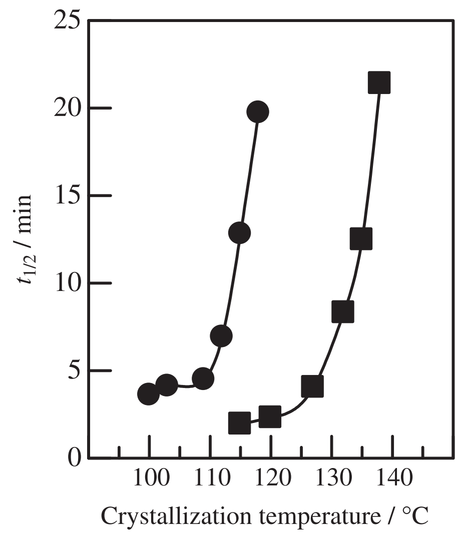


Figure 1. Change in crystallization half-time as a function of isothermal crystallization temperature. The solid circles and squares represent neat PLA and PLA containing 0.5 wt % OMBH respectively.

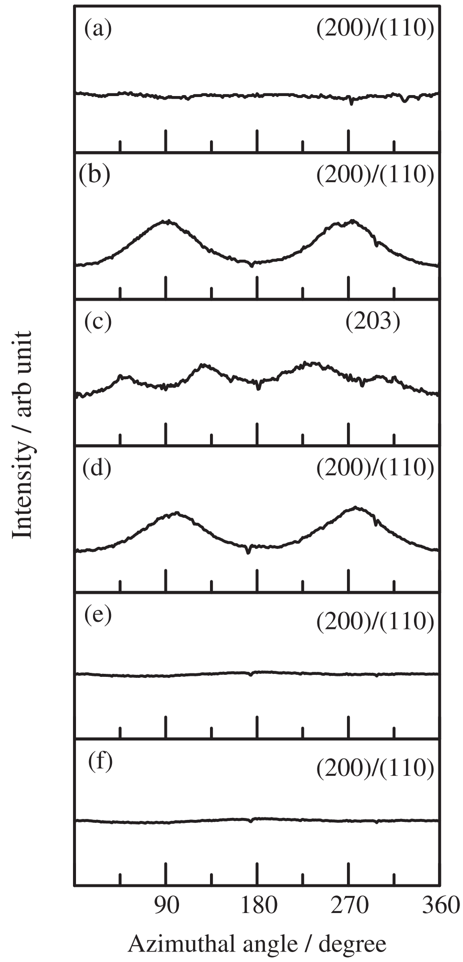


Figure 2. Azimuthal intensity distributions at (200)/(110) and (203) of PLA. The nucleated PLA samples were annealed using the magnetic field histories I (a), II (b, c), III (d), and IV (e). The neat PLA sample was annealed at 110 °C using the magnetic field histories II (f).

the sample prepared outside the magnetic field. Meanwhile, the intensity distribution of (200)/(110) for the sample prepared inside the magnetic field, which corresponds to the magnetic field history II, was also observed (Figure 2b). The direction of the magnetic field is represented by 0 and 180 degrees. The intensity of (200)/(110) is strong in the equatorial direction. This fact suggests that the *c* axis of PLA is aligned parallel to the magnetic field. Under the assumption that the *c* axis is parallel to the magnetic field, we can estimate that the azimuth angle of (203) is about 40 degrees. This value agrees with the experimental value shown in Figure 2c. These results strongly suggest that the *c* axis of PLA containing OMBH was aligned parallel to the magnetic field.

In order to confirm in which period the magnetic alignment occurs, a selection of samples was prepared using various applied magnetic field histories. Figures 2d and 2e show the azimuthal intensity distributions at (200)/(110) of nucleated PLA samples that were annealed using magnetic field histories III and IV in Scheme 1. In the sample produced in the magnetic field using history III, the presence of magnetic alignment was confirmed. However, alignment could not be confirmed in the sample annealed using magnetic field history IV. The viscosity increases when the temperature is lowered to the crystallization temperature, and magnetic alignment is difficult in a high-viscosity environment.[11] Therefore, we could not confirm that magnetic alignment was induced by applying a magnetic field only at the crystallization temperature, as for the magnetic field history IV. In addition, we could not confirm the magnetic alignment of the neat PLA (Figure 2f). These results show that the presence of OMBH crystals in melted PLA is important to achieve the magnetic alignment of PLA. It is suggested that the alignment of PLA was induced by the crystallization of PLA at the surfaces of the OMBH crystals, which were aligned along the magnetic field. In addition, we have supposed until now that this result was due to an epitaxial mechanism between PLA and OMBH. However, the crystal system of OMBH is not defined. A discussion of the epitaxial mechanism between PLA and OMBH will be reported in future work.

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