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Letter

Effect of Amorphous Region on Magnetic Orientation of Poly(lactic acid) Blend Films with Different Molecular Weight

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The magnetic-field-induced blend films, poly(L-lactide)(PLLA10) (M_n = 1.0 × 10^5) and poly(DL-lactide) (M_w = 1.0 × 10^4 (PDLLA1) and 1.0 × 10^5 (PDLLA10)) were prepared in isothermal process under the magnetic-field 10 T. The effects of amorphous region, i.e., molecular weight of PDLLA effect on crystallization and orientation of PLLA in the films were investigated using wide-angle X-ray diffraction and polarizing microscopy. The crystallinity of each films showed 60% at crystallization growth time t_c = 30 hrs irrespective of PDLLA molecular weight. The degree of orientation of PLLA10/PDLLA10 film increased with increasing t_c. We concluded that the blending with amorphous high-molecular-weigh PDLLA and crystallization in an applied high magnetic field is effective to achieve the PLLA film that has higher crystallinity and orientation.

Key words: magnetic-induced-orientation film, poly(L-lactide), poly(DL-lactide), amorphous, blend film, high magnetic field

1. Introduction

Recently, biomass plastics are interest for saving petroleum resources and reduction of carbon dioxide. It is especially expected that the biomass plastics produced from plant-derived raw materials. For example, poly(lactic acid)(PLA) is well-known biomass plastic which are produced from renewable resources and used in many field such as biomedical, packaging and ecological fields.

There has been an extensive effort to investigate for PLA such as crystal structure, crystal growth, melting behavior, and applications.[1] Many researchers have studied stereocomplex consist of blend of PLLA and poly(D-lactic acid)(PDLA) as a solution to improve the thermal and physical properties of PLLA.[2) 3)] However, PDLA is the high cost as industrial raw material. Another approach such as the orientation control is proposed to improve the properties of PLLA. Orientation control of PLLA is an important subject because the physical properties of PLLA are strongly affected by the orientation. By using mechanical orientation, one obtains materials with ordered polymer crystals. This method is often used in industry, however there is a fear of deformation. PLLA is known to be miscible with PDLLA and develop PLLA crystal in PDLLA.[4) 5)] We previously reported that the magnetic-induced oriented films of PLLA/PDLLA, which PDLLA has lower molecular weight than that of PLLA.[6)]

Crystallization of PLLA has been developed in PDLLA and shown the high degree of orientation.

In this work, the influence of molecular weight of amorphous PDLLA in the PLLA/PDLLA blend films on the crystallization and orientation behaviors of PLLA was investigated.

2. Experimental

2.1 Materials

PLLA of M_n = 1.0 × 10^5 (PLLA10), and PDLLA of M_w = 1.0 × 10^4 (PDLLA1) and M_w = 1.0 × 10^5 (PDLLA10) were purchased from Sigma-Aldrich Co. The optical purity was determined by the specific optical rotation measurement of PLA sample $[\alpha]_{sample}$ using P-2300 polarimeter (JASCO Corporation, Japan) with a wavelength of 589.3 nm (D-line of the sodium lamp) at 25 °C.

$$OP\% = \frac{[\alpha]_{sample}}{[\alpha]_{PLLA}} \times 100 \qquad (1)$$

where $[\alpha]_{PLLA}$ is the specific rotation of PLLA with 100% of L stereoisomer and value of -156° was used.[7)] The percentage optical purity of PLLA10, PDLLA1 and PDLLA10 were 98.3, 0.4 and 0.5%, respectively. This result shows both PDLLA10 and PDLLA1 are consisting of racemic lactate units and are completely noncrystallizable polymers.

2.2 Preparation of PLLA/PDLLA solution-cast films

Two kinds of solution-cast blend films, PLLA10/PDLLA1 film and PLLA10/PDLLA10 film, were prepared. Concentration of 10 wt% of PLLA10 chloroform solution and 10 wt% of PDLLA1 or PDLLA10 chloroform solution were mixed and stirred for 2 hrs, and the solution was put in petri dish and was

stood for 24 hrs. PLLA/PDLLA films were dried at 70 °C for 2 hrs in vacuum oven. The thickness of each films was 100 ± 20μm.

2.3 Preparation of PLLA/PDLLA oriented films under high magnetic field

Preparation of PLLA/PDLLA oriented films in a magnetic field was carried out at Institute for Materials Research, Tohoku University. The temperature program for the crystallization of PLLA in the blend films was illustrated in Figure 1. The films were heated from room temperature to the annealing temperature 185°C at a rate of 3°C/min and held constant for 10 min. Then, films were cooled to 140°C (isothermal crystallization temperature) for isothermal crystallization time t_c = 0, 2, 15 and 30 hrs. The magnetic field of 10 T was applied throughout the whole thermal process.

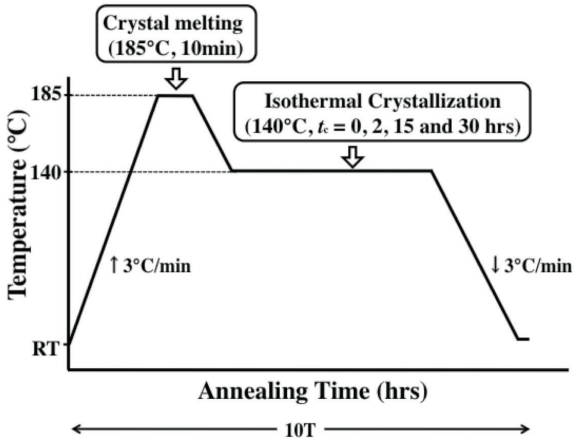

Fig.1 Thermal process for PLLA10/PDLLA1 and PLLA10/PDLLA10 films. Throughout the whole thermal process, the magnetic field of 10 T was applied.

2.4 Measurements

WAXD measurement was carried out using X'Pert PRO MPD(PANalytical, Japan) operated at 45 kV and 40 mA to generate Ni-filtered CuKα X-ray beam. Scanning speed was 0.01°/s and measurement range was 3 – 60° at room temperature. Crystals growth in the films was observed by polarization microscope (BX53-33P-OC-1, Olympus, Japan).

3. Results and discussion

3.1 Crystallization of oriented films

In Figures 2 and 3, WAXD pattern of PLLA10/PDLLA1 and PLLA10/PDLLA10 films after annealing at 140°C for different periods was shown. PLLA shows the two dominant diffraction peaks at 16.7° and 19.1° of α-form crystal. These diffraction peaks are assigned to the 110/200 and 203 reflections, respectively. [8) 9) 10)] The intensity of these diffraction peaks increased gradually with increasing crystallization time. However, refraction peaks of 110/200 and 203 of the PLLA10/PDLLA10 film for t_c = 2 hrs have been not detected.

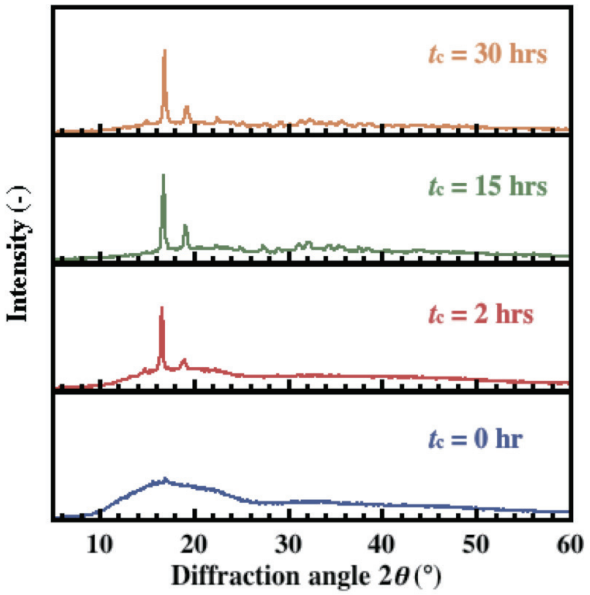

Fig.2 WAXD patterns of PLLA10/PDLLA1 films.

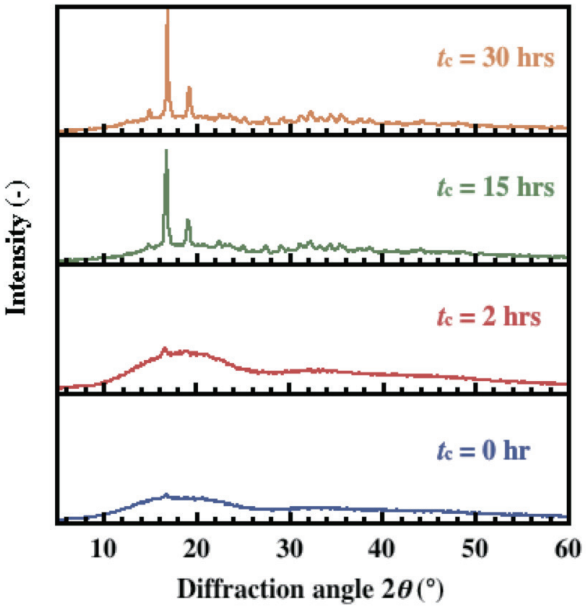

Fig.3 WAXD patterns of PLLA10/PDLLA10 films.

The relationship between t_c and the degree of crystallization X_c was shown in Figure 4. From the peak areas of WAXD patterns, X_c was calculated by the following equation,

$$X_C\% = \frac{S_{PLLA}}{S_{PLLA} + S_{PDLLA}} \times 100 \qquad (2)$$

where S_{PLLA} and S_{PDLLA} are PLLA and PDLLA

diffraction peaks areas.[11] X_c of neat PLLA film which prepared in the same condition also was shown for comparison. From the figure, it is clear that the induction period of PLLA crystallization of blend films are longer than that of neat PLLA10 film. The induction period of PLLA10/PDLLA1 is short in comparison with PLLA10/PDLLA10. This could be interpreted that the mobility of PLLA10 chains are large because the melt viscosity of low-molecular-weight PDLLA1 are lower than that of PDLLA10. The crystallization rate of both blend films is faster than that of neat PLLA after the induction period. The value of X_c of all films, however, attained about 60% for t_c = 30 hrs.

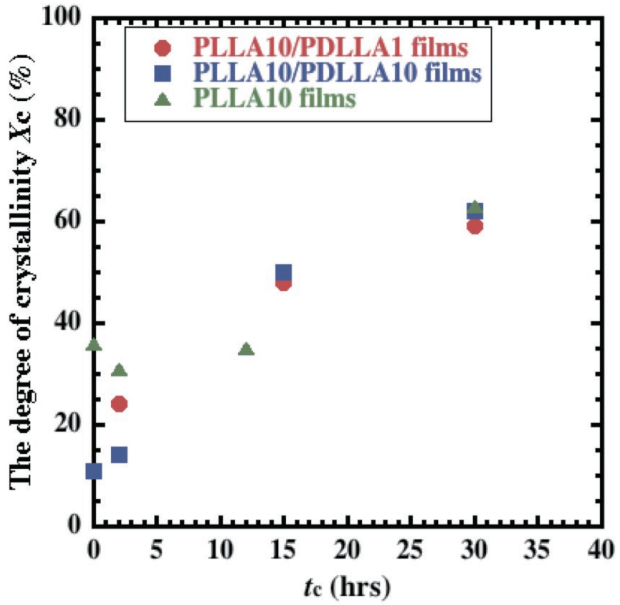

Fig. 4 The degree of crystallinity X_c by WAXD measurement of PLLA10/PDLLA1 and PLLA10/PDLLA10 films.

3.2 Magnetic orientation of oriented films

The c-axis of PLLA crystal in the PLLA/PDLLA film was oriented in the parallel direction to the magnetic field.[6] The degree of orientation was defined as the azimuthal angle of reflected intensity of 110/200 planes. The degree of the magnetic-field-induced orientation f_c was calculated by the following equations,

$$\langle \cos^2 \varphi \rangle = \frac{\int_0^{\frac{\pi}{2}} I(\varphi) \cos^2 \varphi \sin \varphi d\varphi}{\int_0^{\frac{\pi}{2}} I(\varphi) \sin \varphi d\varphi} \quad (3)$$

$$f_c = \frac{3\langle \cos^2 \varphi \rangle - 1}{2} \quad (4)$$

where φ is the azimuthal angle and I(φ) is the azimuthal intensity. Figure 5 shows f_c against t_c of blend films and neat PLLA film.

In the case of PLLA10/PDLLA10 film, f_c increased with increasing t_c. In contrast, a f_c of PLLA10/PDLLA1 and neat PLLA films are constant for all range of t_c, i.e., this shows that applied magnetic field has no effect on the orientation of these films.

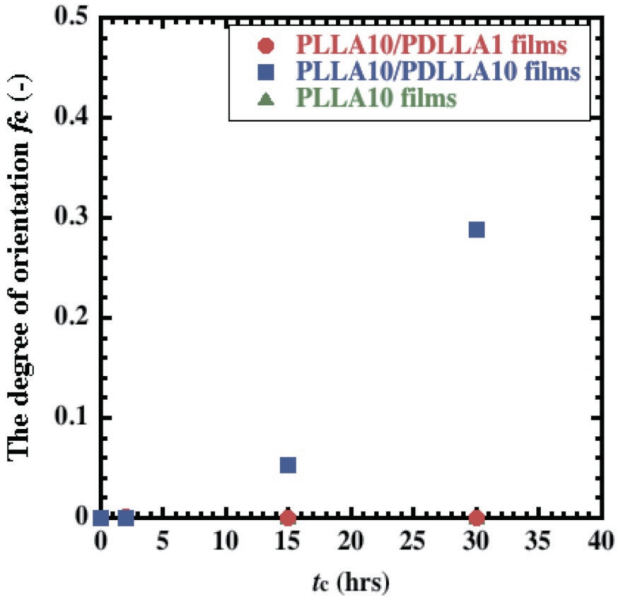

Fig. 5 The degree of orientation f_c by WAXD measurement of PLLA10/PDLLA1 and PLLA10/PDLLA10 films.

3.3 Isothermal crystalline behavior of oriented films

Figure 6 shows a polarizing optical micrograph of (A) PLLA10/PDLLA1, (B) PLLA10/PDLLA10, and (C) neat PLLA films. Optical micrographs were taken at different crystal growth time ranging from 0 to 30 hrs. These films show the formation of spherulite that was grown isothermally at 140°C, and its content increase with increasing t_c. As is seen in Figure 6(C), the spherulite radius of neat PLLA10 increased with

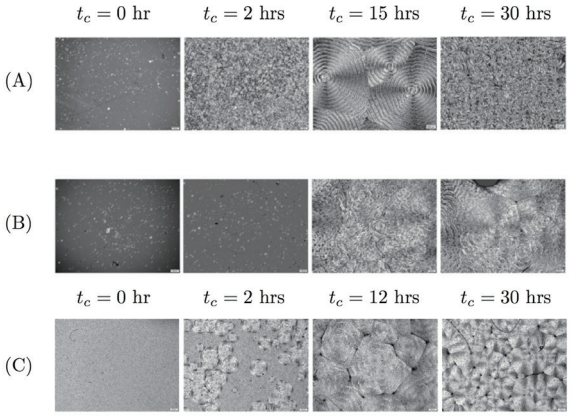

Fig.6 Polarized photomicrographs of films. (A): PLLA10/PDLLA1 and (B): PLLA10/PDLLA10 at t_c = 0, 2, 15 and 30 hrs. (C): neat PLLA10 at t_c = 0, 2, 12 and 30 hrs.

increasing t_c, and the behavior agrees with the literature.[12] On the other hand, the crystallization behavior of blend films could be explained by following.
Increasing of spherulites in both blend films is due to trapping amorphous PDLLA in the spherulite of PLLA.[5] [12] For t_c = 0 hr, the photomicrographs demonstrate small crystallites grew spherically from single nuclei. For t_c = 2 hrs, numbers of small crystallites increase in PLLA10/PDLLA1 film, but a faintly increase in PLLA10/PDLLA10 film. For t_c > 15 hrs, it is clear that the spherulites contents in each films increased with increasing crystal growth time. For t_c = 30 hrs, PLLA10/PDLLA1 film shows large optical textures in Figure 6(A).
Comparison with spherulite structure of PLLA10/PDLLA1 and PLLA10/PDLLA10, the latter is more disordered than the former. Formation of these large spherulites observed in PLLA10/PDLLA1 can be explained by the homogeneous crystallization. In contrast, PLLA10/PDLLA10 film shows small optical texture(Figure 6(B)). This is due to heterogeneous nucleation, i.e., the locally orientated domain.

4. Conclusions

We have investigated the magnetic-field-induced PLLA in amorphous PDLLA oriented films without nucleating agents in a 10 T magnetic field. The dependence of molecular weight of PDLLA on crystallization of PLLA in the blend films was not observed in the crystallization in the magnetic field. However, orientation behavior is quite different between PLLA10/PDLLA1 and PLLA10/PDLLA10 films. That is, trapping of low-molecular-weight PDLLA in the spherulite of PLLA10 show disturb the orientation of PLLA crystal. On the other hand, trapping high-molecular-weight PDLLA promote higher orientation film. Hence, the blending with amorphous high-molecular-weigh PDLLA and crystallization in an applied magnetic field is effective to achieve the PLLA film that has higher crystallinity and orientation.

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