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Enhancement of Spherulite Growth of Poly (L-lactic acid) by Liquid-Type Additive

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1 Introduction

Poly (lactic acid) (PLA) is one of the most famous biobased polymers. PLA can greatly contribute to the achievements of SDGs (Sustainable Development Goals) and Decarbonized Society because of its biobased and biodegradable characters. But, PLA has low mechanical property and poor crystallizability. It is significant to improve the properties of PLA to meet the demand for PLA. In this study, poly (L-1actic acid) (PLLA) with a small amount of the organic acid monoglyceride (OMG) as an additive to accelerate the growth of spherulite. Based on the Hoffman-Lauritzen theory, the value of the surface free energy of the crystalline lamella (plane including the polymer chain folding) was evaluated, and the reason why the OMG can accelerate the PLLA crystallization was tried to be accounted for even when the OMG was a molecularly dispersed in the polymer matrix phase.

PLLA samples, D0.5 and D1.4 (D0.5 is containing 0.5wt% D-body, D1.4 is containing 1.4% D-body), were mixed with a small amount of the OMG, and dissolved in dichloromethane. Then, the dichloromethane was evaporated to form films. These films were heated to 200ºC to melt and subsequently was rapidly cooled down to 100ºC~135ºC to observe isothermal crystallization by using polarized optical microscope and the wide-angle X-ray scattering (WAXS).

2 Experiment

The WAXS measurements were carried out by using the synchrotron radiation as an X-ray source at the beamline BL-6A of Photon Factory at KEK (High-Energy Accelerator Research Organization) in Tsukuba, Japan. The wavelength of the incident X-ray beam was 0.150 nm. The scattering vector q was calibrated by using polyethylene for WAXS. Here, the magnitude of q is defined as, $|\boldsymbol{q}| = q = (4\pi/\lambda)\sin(\theta/2)$ with λ and θ being the wavelength of X-ray and the scattering angle, respectively. The background scattering was subtracted. The one-dimensional WAXS profiles was obtained by taking the sector average of the 2d-WAXS pattern.

3 Results and Discussion

The time-resolved 1d-WAXS profile for the isothermal crystallization at 100ºC~135ºC showed evolution of the crystalline peaks as a function of the crystallization time. The linear growth rate of the spherulite was evaluated from the POM observation results and is show in Figure 1. Although there was some variation, the growth rate of spherulite increased with the OMG content at all crystallization temperatures. The linear growth rate of D0.5 was clearly higher than that of D1.4. From the data in Figure 1, the nucleation constant Kg was obtained based on the Hoffman-Lauritzen theory. The surface free energy of the interface σe including the folded molecular chains of the crystalline lamella was eventually obtained from the value of Kg. The OMG content dependency of σe is plotted in Figure 2, showing that the value of σe for both D0.5 and D1.4 decreases as the OMG content increases. This means that the molecularly dispersed OMG contributes to more regular chain folding of the PLLA.

The results of this study clearly show that the addition of OMG promotes PLLA spherulite growth (crystal growth). The overall surface free energy of D0.5 was higher than that of D1.4. Since the surface free energy decreases as the chain folding becomes more regular, we expected that the surface free energy would be lower for D0.5, which has a higher L-body fraction than D1.4. But in fact, the result is opposite, and the explanation for this is currently under consideration.

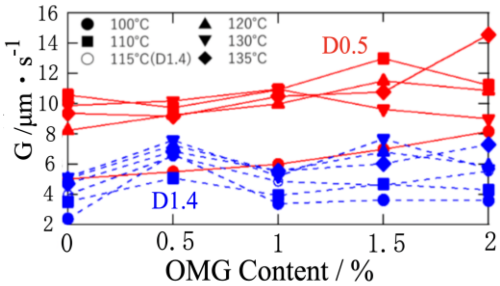

Fig. 1: Plots of the linear growth rate of spherulite against the OMG content for all of the specimens examined in this study.

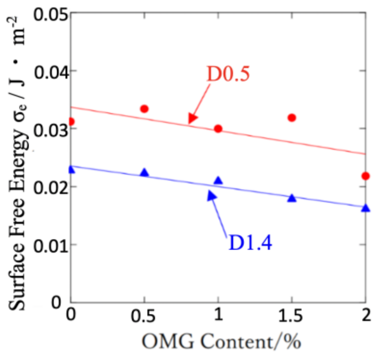

Fig. 2: P Plots of the surface free energy of the PLLA crystalline lamella against the OMG content.

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