

Improvement of Crystallizability of Poly (L-lactic Acid) by Addition of Plasticizers

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Introduction:

Poly(L-lactic acid) (PLLA) is a biodegradable and biocompatible polymer. Moreover, PLLA can be synthesized from renewable sources such as sugar, carbohydrate, etc. In recent several decades, scientists are interested in PLLA because of environment-friendly characteristics. However, there existing some big problems of PLLA, which are low crystallization rate and low crystallinity. In order to overcome such drawbacks, nucleation agents have been incorporated into PLLA. On the contrary, we have reported that a special plasticizer (organic acid monoglyceride; OMG) can improve the crystallization of PLLA. The results are significant because plasticizers are believed to delay crystallization of polymers by reducing the thermodynamical driving force of crystallization. We now recognize that the lowering of the activation energy for the PLLA crystallization may be the main effect of the special plasticizer. In this study, we investigate the effect of another plasticizer (DOP: dioctyl phthalate) on the crystallization of PLLA. To identify the effect of the plasticizer, we conducted time-resolved small- and wide-angle X-ray scattering (SWAXS) simultaneous measurements and differential scanning calorimetric (DSC) measurements to follow isothermal crystallization of PLLA/plasticizer. Moreover, polarizing optical microscopic (POM) observation was also conducted to evaluate the growth rate of a spherulite and the number of nuclei formed as a function of time.

Experimental:

We used two types of neat PLLA samples from Nature Works. The characteristics of those samples are summarized in Table 1. The sample code names are D1.4 and D0.5. The "x" is for the specimens with x (%) loading of the plasticizer.

The time-resolved SWAXS measurements in each 5s step were conducted at BL-6A beamline in KEK, Tsukuba, Japan, upon temperature jump from 200°C to 110.2°C (cooling rate was approximately 385°C/min, T-jump was completed within 14s). The wavelength of the X-ray (λ) was 0.150 nm.

Results and discussion:

The apparent crystallinity was evaluated from the WAXS results by the following equation:

$$\phi = \sum A_c / (\sum A_c + A_a)$$

Here, $\sum A_c$ and A_a are the summation of the peak area of crystallization peaks and amorphous halo, respectively. The crystallization half time is defined as the time required for the material to complete 50% its crystallization process. The crystallization half time is plotted as a function of OMG content in Fig.1 for D0.5 and D1.4 specimens at 100°C and 110°C crystallization temperature. Fig.1 clearly shows that the crystallization was accelerated both at 100°C and 110°C crystallization temperature by the addition of OMG. Nevertheless, the effect became less pronounced when the OMG content was increased from 1.0% to 2.0%. It is considered from this result that too much amount of the OMG loading may decrease the viscosity of the specimen (PLLA/OMG), which results in turn in the counter effect of deceleration of the crystallization. The amount of D-content in PLLA also strongly affects the crystallization rate of PLLA. As shown in Fig. 1, the crystallization half time for the D1.4 specimens are very much longer than that for the D0.5 specimens. This result is reasonable because PLLA with a higher content of L-moiety can crystallize faster.

The crystallization half time at the crystallization temperature of 110°C is plotted as a function of the DOP content in Fig. 2. Fig. 2 confirms that DOP also can accelerate the crystallization of PLLA by the addition of DOP with 1.0 ~ 2.0 wt%. Note here that the data for the neat specimens were not coincident with those for the neat specimens as plotted in Fig. 1 for the case of OMG loading because the specimen preparation method is different. Namely, the series of the specimens used for the OMG loading were prepared with the melt blending by an extruder, while those for the DOP loading were prepared by the solution casting. In the former case, there would be unfavorable effects of the thermal degradation of PLLA due to the melt blending. As a matter of fact, the crystallization half time for the DOP loading shows somewhat lesser tendency as compared to those for the OMG loading. Furthermore, the crystallization half time was still decreased a bit by increasing the addition of DOP from 1.0% to 2.0%, which is a contrast to the result of the OMG loading. As compared to the special plasticizer OMG, DOP is not special but ordinary. Nevertheless, it was found that DOP can accelerate the crystallization rate for PLLA. This means that such accelerating effects of the plasticizers are common and the same mechanism of the acceleration (reduction of the activation energy with the reduction of the thickness of the critical nucleus) can be considered for both of OMG and DOP.

Table I. Sample characterization and specimen code

Product code	D content (%)	MFR (g/10min) at 210 °C	Neat PLLA specimens	Specimens with loading of OMG (x %)	Specimens with loading of DOP (x %)
2500HP	0.5	7	D0.5	D0.5/x	D0.5/x % DOP
4032D	1.4	8	D1.4	D1.4/x	D1.4/x % DOP

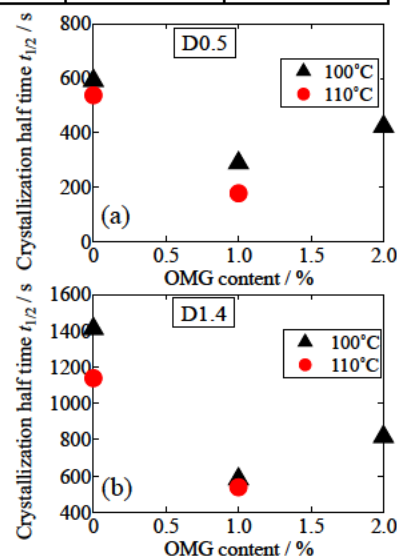


Fig. 1. Crystallization half time $t_{1/2}$ as a function of the OMG content.

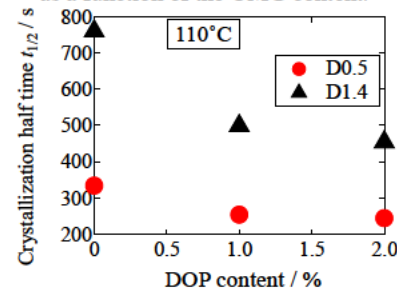


Fig. 2. Crystallization half time $t_{1/2}$ as a function of the DOP content.