

## Effects of Loading Amount of Plasticizers on Improved Crystallization of Poly(L-lactic acid)

Pham Thi Ngoc DIEP<sup>1</sup>, Hideaki TAKAGI<sup>2</sup>, Nobutaka SHIMIZU<sup>2</sup>, Noriyuki IGARASHI<sup>2</sup>,  
Sono SASAKI<sup>1</sup> and Shinichi SAKURAI<sup>1,\*</sup>

<sup>1</sup>Department of Biobased Materials Science, Kyoto Institute of Technology, Matsugasaki, Kyoto,  
606-8585, Japan

<sup>2</sup>Photon Factory, Institute of Materials Structure Science,  
High Energy Research Organization, 1-1 Oho, Tsukuba, 305-0801, Japan

### 1 Introduction

Poly(L-lactic acid) (PLLA) is one of the most popularly utilized biobased polymers, as it is derived from renewable sources (sugar, carbohydrate, etc). Although PLLA bears environmentally benign characteristics, there are crucial faults of PLLA such as slow crystallization and insufficient crystallinity which can be finally attained even after the fully thermal annealing. To improve crystallizability of PLLA, nucleation agents have been utilized. Although typical nucleation agents work at the solid state, we have reported that a special plasticizer (organic acid monoglyceride; OMG) can partly improve the crystallizability of PLLA [1,2]. The results are significant because plasticizers are believed to delay crystallization of polymers by reducing the thermodynamical driving force of crystallization. We speculated that the lowering of the activation energy for the PLLA crystallization may be the main effect of the plasticizer [3]. In this study, we confirmed that the enhanced crystallization of PLLA can be also attained by using a general plasticizer which is dioctyl phthalate (DOP). To identify the effects of loading amount of plasticizers on improved crystallization of PLLA, we conducted time-resolved small- and wide-angle X-ray scattering (SWAXS) to follow the isothermal crystallization of PLLA/plasticizer specimens.

### 2 Experimental

The PLLA samples used in this study are obtained from NatureWorks LLC. As shown in Table 1, one of them bears 1.4% D content (PLLA4032D) and the other 0.5% D content (PLLA2500HP), which enabled us to study the effects of the optical impurity on the crystallization of PLLA with or without the presence of plasticizers. The other characteristics and code names are listed together in Table 1.

Two kinds of plasticizers were used; OMG and DOP. The OMG contains an organic acid as a succinic acid and a saturated fatty acid as a stearic acid, and it is a product of Taiyo Kagaku Co., Ltd. with the commercial name of Chirabazol D which is a "100% plant-derived" fatty acid ester surfactant developed based on technology of the Taiyo Kagaku Co., Ltd. The OMG has a molecular weight of 500 and the melting temperature of  $T_m = 67$  °C (measured by DSC). DOP (purity: 99%) was purchased

Table 1: Sample characteristics

Sample	Code name	D content	$M_n$ (GPC)	$M_w$ (GPC)	$M_w/M_n$ (GPC)
PLLA2500HP	D0.5	0.5%	$1.74 \times 10^5$	$3.86 \times 10^5$	2.22
PLLA4032D	D1.4	1.4%	$1.66 \times 10^5$	$3.40 \times 10^5$	2.05

from Nacalai Tesque, Kyoto, Japan. The specimen code names are PLLA neat and PLLA/plasticizer(x) with "x" corresponding to the weight % of plasticizer amount loaded in the specimen of PLLA (D0.5 or D1.4).

All the specimens were prepared by a solution casting method. PLLA pellets were dried in a vacuum oven at 50 °C for 24 h before preparation of a solution. A given amount of PLLA and plasticizer were weighed and dissolved in chloroform (purchased from Nacalai Tesque) with the PLLA concentration of 5% (w/v). Then, the solution was poured in the Petri dish for the solvent evaporation under ambient condition at room temperature. The amount of PLLA solution was calculated so as to have the film thickness of 200  $\mu\text{m}$  after complete evaporation of the solvent. The films were further dried in a vacuum oven at 50 °C for 24 h for further measurements.

We conducted SWAXS measurements to study isothermal crystallization kinetics. The time-resolved SWAXS measurements were conducted upon T-jump from the melt (200 °C) and rapidly cooling down to  $T_c = 100$  °C for the D0.5/OMG and D1.4/OMG specimens or to  $T_c = 110$  °C for the D0.5/DOP and D1.4/DOP specimens, with an exposure time of 5s using PILATUS3 200K for WAXS and PILATUS3 2 M for SAXS (DECTRIS Ltd., Baden, Switzerland) as a two-dimensional detector at BL-10C of the Photon Factory in High Energy Accelerator Research Organization, Tsukuba, Japan. The sample to-WAXS and SAXS detector distances are 40 mm and 2 m, respectively. The X-ray wavelength was 0.150 nm.

### 3 Results and Discussion

Fig.1 shows temporal changes in the one-dimensional WAXS (1d-WAXS) profiles upon temperature jump (T-jump) from 200 °C to 110 °C for (a) D1.4 neat, (b) D1.4/DOP(1.0), and (c) D1.4/DOP(2.0) specimens. These profiles were obtained by conducting a sector average. Here,  $q$  denotes the magnitude of the scattering vector as defined by  $q = (4\pi/\lambda) \sin(\theta/2)$  with  $\lambda$  and  $\theta$

being the wavelength of the X-ray and the scattering angle, respectively. The 1d-WAXS profiles at  $t = 25$  s for all specimens show only amorphous halo peaks where  $t$  is the elapsed time from T-jump from 200 °C. As time goes on, the crystalline peak appears and the number of peaks also increases. At  $t = 100$  s, the (200/110) reflection peak is clearly observed for the D1.4/DOP(1.0) and D1.4/DOP(2.0) specimens while this peak is not clear for the D1.4 neat specimen, indicating that the DOP can enhance the crystallization of PLLA. In order to evaluate the crystallinity from the results of WAXS, the peak decomposition of the 1d-WAXS profiles was conducted to distinguish the crystalline peaks from the amorphous halo peak. The area of the crystalline peaks and the amorphous halo peak was used to calculate the apparent degree of crystallinity [ $\phi(t)$ ].  $\phi(t)$  is plotted as a function of  $t$  in Fig. 2 for the case of DOP loading (isothermal crystallization at 110 °C) as well as OMG loading (isothermal crystallization at 100 °C). Note here that the  $\phi(t)$  is just apparent crystallinity because the WAXS does not completely cover the whole  $q$  range of the crystalline peaks of PLLA. However, comparison of  $\phi(t)$  values between the different PLLA specimens with different plasticizer loading amounts is possible because of the same chemical structure of PLLA with the negligibly small amount of plasticizer and D moieties.

Overall, we may be able to recognize that OMG improved crystallization of PLLA from the plots of Fig. 2. As for the DOP loading, it is important to examine its ability as an agent for improved crystallization of PLLA. For this purpose, we evaluated the crystallization half time ( $t_{1/2}$ ), the induction period, and the ultimate degree of crystallinity (the degree of crystallinity finally attained) from the results shown in Fig. 2. Note that  $t_{1/2}$  was evaluated as the time when the 50% of the ultimate

crystallinity was attained. Thus-evaluated  $t_{1/2}$  is shown in Fig. 3(a) as a function of the OMG content for the OMG loading, and it is shown in Fig. 3(b) as a function of the DOP content for the DOP loading. Since the inverse of  $t_{1/2}$  can be a measure of the crystallization rate, it is clearly observed in Fig. 3 that the OMG and DOP accelerated the crystallization of PLLA. However, for the case of the 2% OMG loading is not so effective as expected. Although the crystallization temperature for the OMG loading is different from that for DOP loading, the results of the OMG loading may suggest that there is an appropriate amount of loading for the best effect of improved crystallization of PLLA. For the case of the DOP loading, the appropriate amount will be somewhat larger than that for the OMG loading (about 2% of DOP). This is due to the effect that too much amount of loading the plasticizer decreases  $T_m^\circ$  (the equilibrium melting temperature) which in turn decreases the thermodynamic driving force of crystallization. Anyhow, the fact that we can recognize the improved crystallization of PLLA in Fig. 3 by the very small amount of loading of plasticizers (0.5 ~ 1.0% with the negligibly small lowering of  $T_g$  (1.7 ~ 4.0 °C) is surprising because generally speaking the plasticizers are believed to depress the crystallizability of polymers. The depression of the thermodynamic driving force of crystallization is simply the case of the large amount loading (2%), of which improving effects of the crystallization behaviors of PLLA is not so clear as is shown in Fig. 3. The fact that only 1% or several % of loading plasticizers can improve crystallization is a very important and valuable finding, although the mechanism of the improved crystallization is still unknown at present [1,3]. It is needless to say that  $t_{1/2}$  always longer for the D1.4 specimens than those for the D0.5 specimens because of the larger D content which depresses the

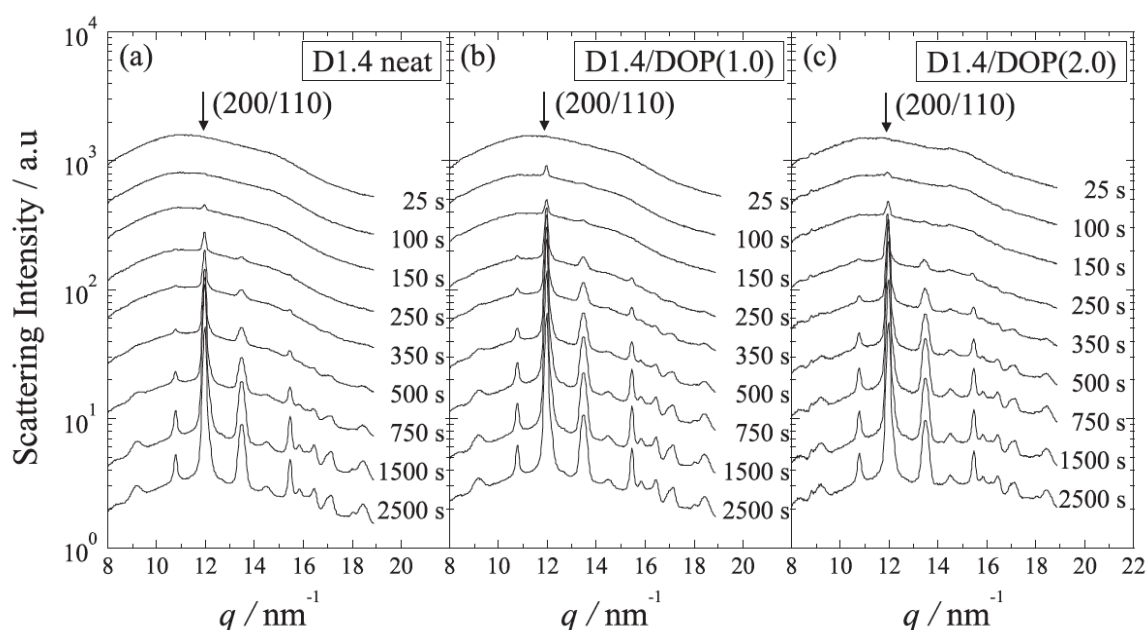


Fig. 1 Temporal changes in the 1d-WAXS profiles upon T-jump from 200 °C to 110 °C for (a) D1.4 neat, (b) D1.4/DOP(1.0), and (c) D1.4/DOP(2.0) specimens.

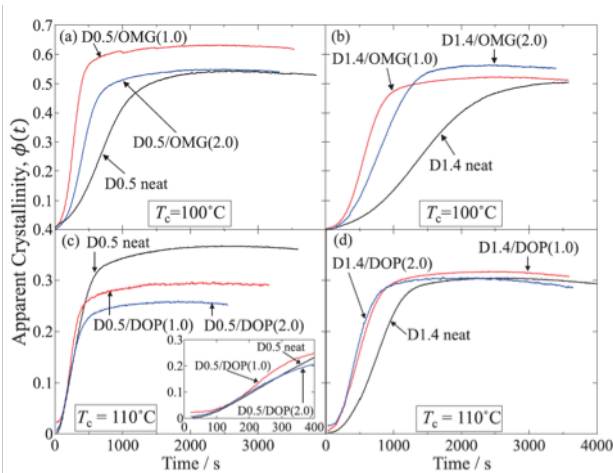


Fig. 2 Apparent crystallinity as a function of time, as evaluated from the results of the isothermal crystallization WAXS measurements at 100 °C for (a) D0.5/OMG, and (b) D1.4/OMG specimens and at 110 °C for (c) D0.5/DOP, and (d) D1.4/DOP specimens.

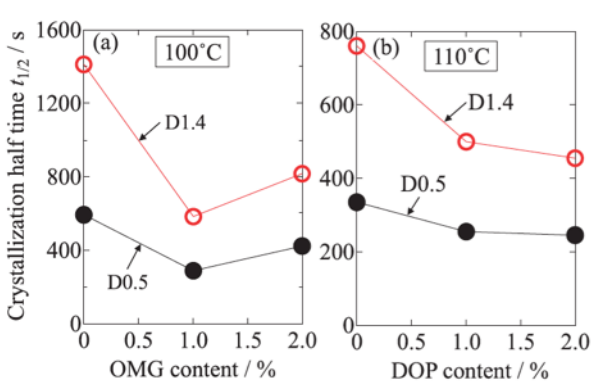


Fig. 3 Crystallization haft time  $t_{1/2}$  as a function of (a) OMG content for PLLA/OMG specimens isothermally crystallized at 100 °C and as a function of (b) DOP content for PLLA/DOP specimens isothermally crystallized at 110 °C.

crystallizability of PLLA due to the effect as an impurity.

Fig. 4 shows the plots of the ultimate crystallinity, which is the crystallinity value attained in the final stage of crystallization (from the plots shown in Fig. 2 showing a constant value in the final stage) against the content of plasticizer for PLLA/OMG specimens isothermally crystallized at 100 °C or for PLLA/DOP specimens isothermally crystallized at 110 °C. For the case of the OMG loading, the ultimate crystallinity is increased as a function of OMG content, although at 2% loading for D0.5 is decreased as compared to the case of 1% loading which is similar tendency as observed in Fig. 3(a). On the other hand, the ultimate crystallinity is almost constant for the D1.4/DOP specimens or it decreases as a function of the DOP content for the D0.5/DOP specimens. Thus, there are opposed effects of the plasticizers on the ultimate crystallinity as the effect of loading OMG on the improvement of the ultimate crystallinity is clear while

the effect of loading DOP is unclear or even negative. The reason may lie in a presumably attractive interaction between the phenylene ring in DOP and the lone pair of electrons existing at the oxygen atom in the main chain of PLLA. Such attraction (too much favorable interaction) may degrade the ultimate crystallinity even though the crystallization rate is enhanced by DOP.

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**Research Achievements**

1. Pham Thi Ngoc Diep, JFST Best Paper Awards of the Society of Fiber Science and Technology, Japan (*J. Fiber Sci. Technol.*, 75(8), 99-111 (2019).) \* shin@kit.ac.jp

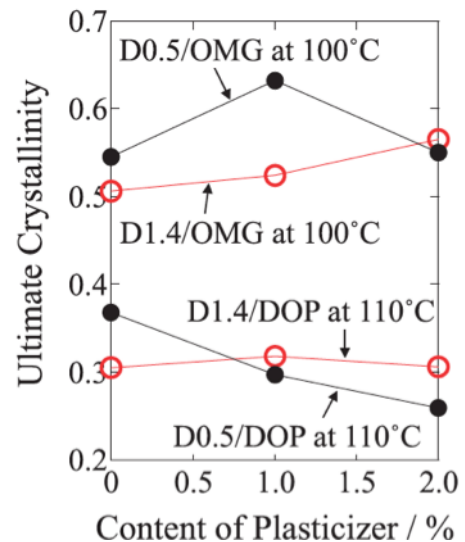


Fig. 4 Plots of the ultimate crystallinity, which is the crystallinity value attained in the final stage of crystallization (from the plots shown in Fig. 2 showing a constant value in the final stage) against the content of plasticizer for PLLA/OMG specimens isothermally crystallized at 100 °C or for PLLA/DOP specimens isothermally crystallized at 110 °C.