Favorable Formation of Stereocomplex Crystals in a Blend of Poly (L-Lactic Acid)/ Poly (D-Lactic Acid) Promoted by Silk Nanocrystal

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Introduction

The blending of poly (L-lactic acid) (PLLA) and poly (D-lactic acid) (PDLA) results in the formation of stereocomplex crystallites (SC) with denser chain packing. The stereocomplex PLA (SC-PLA) has a higher melting temperature, better thermal stability than that of corresponding homocrysallites (HC). However, the formation of HC and SC are competing in the crystallization of PLLA/PDLA blends. Crystallization behavior of PLLA/PDLA blends are strongly influenced by the molecular weight of each components. In the case of high molecular weight PLLA/PDLA blends, it is well known that the formation of HC is predominant than SC [1]. In view of this, the current work has been focused on the inclusion of silk fibroin β-sheet nanocrystal (SNC) in the PLLA/PDLA blend with the aim of improving the formation of SC in the blend.

Experimental

PLLA was obtained from Nature Works (grade 2500HP) and PDLA was obtained from Purac (grade D130). The sample characterization is summarized in Table 1. The SNC is a nanoparticle having the disc like shape. The average diameter and thickness of SNC is ~ 45 nm and ~ 3 nm, respectively. The detailed information about the SNC is reported in ref. [2]. The equimolar PLLA/PDLA (neat) and PLLA/PDLA (1% SNC) specimens were prepared by the solution casting method using dichloromethane as a solvent. Differential scanning calorimetry (DSC) measurements were performed by NETZSCH DSC214 *Polyma*. For the isothermal crystallization experiment, the specimens were first melted at 260˚C for 5 min and immediately cooled to 110˚C (the cooling rate of 302˚C/min) and kept isothermally for 40 min. After isothermal crystallization the samples were heated to 250 ˚C with the heating rate of 20˚C/min. The time-resolved small- and wide-angle X-ray scattering (SWAXS) simultaneous measurements for the isothermal crystallization were performed at the BL-6A of Photon Factory, Tsukuba, Japan.

Table 1 Sample Characterization

Polymers	Optical impurity	No. average molecular weight, M_n (a)	Melting point, T_m (b)
PLLA	0.5 %	1.79×10^5	175 ˚C
PDLA	< 1%	1.41×10^5	175 ˚C

(a) Calculated from GPC (b) Calculated from DSC

Results and Discussion

Fig. 1 shows DSC results of PLLA/PDLA (neat) and PLLA/PDLA (1% SNC) specimens. The degree of crystallinity (ϕ) is calculated as $\Delta H_m/\Delta H_m^0$. ΔH_m^0 values of HC and SC are taken as 93 and 142 J/g, respectively, following the ref. [1]. The fraction of SC is calculated by the following equation:

$$f_{SC} = \frac{\phi_{SC}}{\phi_{SC} + \phi_{HC}}$$

Here, ϕ_{HC} and ϕ_{SC} are the degrees of crystallinity for the HC and SC, respectively.

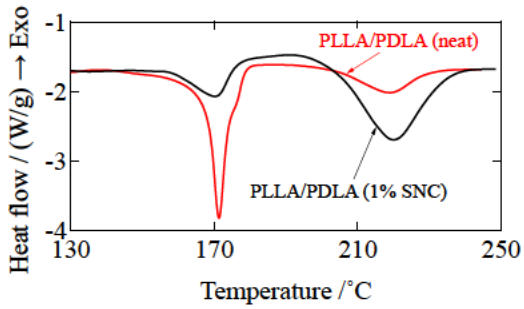

Table 2 ϕ_{HC}, ϕ_{SC}, f_{SC}

Specimens	ϕ_{HC} (%)	ϕ_{SC} (%)	f_{SC}
PLLA/PDLA (neat)	51.9	13.7	0.21
PLLA/PDLA (1 % SNC)	17	47.4	0.74

Figure 1: DSC curves in the heating scan after the isothermal crystallization at 110˚C

From Fig. 1 and Table 2, it is clear that the SNC can enhance the formation of SC by suppressing the formation of HC. The results of time-resolved SWAXS measurements with the plausible mechanism will be discussed in detail in the presentation.

References

1. Tsuji *et al, Macromolecules* **1991**, 24, 9651
2. Patwa *et al*, *Journal of Applied Polymer Science* **2018**, 135 (33), 46590.