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Controlled crystal nucleation in the melt-crystallization of poly(L-lactide) and poly(L-lactide)/poly(D-lactide) stereocomplex

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Abstract

Among the various inorganic nucleators examined, Talc and an aluminum complex of a phosphoric ester combined with hydrotalcite (NA) were found to be effective for the melt-crystallization of poly(L-lactide) (PLLA) and PLLA/poly(D-lactide) (PDLA) stereo mixture, respectively. NA (1.0 phr (per one hundred resin)) can exclusively nucleate the stereocomplex crystals, while Talc cannot suppress the homo crystallization of PLLA and PDLA in the stereo mixture. Double use of Talc and NA (in 1.0 phr each) is highly effective for enhancing the crystallization temperature of the stereo complex without forming the homo crystals. The stereocomplex crystals nucleated by NA show a significantly lower melting temperature (207 °C) than the single crystal of the stereocomplex (230 °C) in spite of recording a large heat of crystallization ΔH_c (54 J/g). Photomicrographic study suggests that the spherulites with a symmetric morphology are formed in the stereo mixture added with NA while the spherulites do not grow in size in the mixture added with Talc. The exclusive growth of the stereocomplex crystals by the melt-crystallization process will open a processing window for the PLLA/PDLA.

Keywords: Poly(L-lactide); Stereocomplex; Nucleator

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1. Introduction

Recently, various aliphatic polyesters, e.g. poly(L-lactide) (PLLA), poly(butylene succinate), poly(3-hydroxybutyrate), and poly(ε-caprolactone) have been developed as biodegradable polymers and manufactured on a commercial scale. Among them PLLA is now attracting the largest attention because it can be derived from renewable natural resources such as cornstarch, sugar cane, and sugar beet and is proven to be superior to the conventional petrochemical polymers in regard to the total energy consumption and CO_2 emission in the life cycle assessment [1]. PLLA is also superior to other biodegradable polyesters in terms of thermal and mechanical properties and transparency of the processed materials [2]. Since lactic acid is enantiomeric, its polymers (generally called polylactides: PLA) involve PLLA, poly(D-lactide) (PDLA), poly(DL-lactide) (PDLLA), poly(*meso*-lactide), and their copolymers having different enantiomeric structure and/or optical purity of the monomeric units [3–5]. While both PDLLA and poly(*meso*-lactide) are amorphous, the enantiomeric PLLA and PDLA are crystalline, showing a melting temperature (T_m) around 180 °C. Simple injection molding of the crystalline PLLA, however, generally gives amorphous products whose modulus greatly drops above the glass transition temperature (T_g) [2]. This behavior has limited the utility of PLLA in the general plastic use, and much effort has been paid to make the injection-molded PLLA to crystallize and attain increased heat resistance [6].

It has been known that an enantiomeric mixture of PLLA and PDLA forms a stereocomplex whose T_m is ca. 50 °C higher than that of PLLA or PDLA [7]. Although this stereocomplex is convinced to have high potential as a high-performance biodegradable polymer, its formation cannot easily be controlled because both the PLLA and PDLA chains should be aligned alternatingly in the crystal lattice of the complex. Accordingly, ordinary melt-crystallization of a PLLA and PDLA stereo mixture is always followed by the homo-crystallization of PLLA and PDLA along with the

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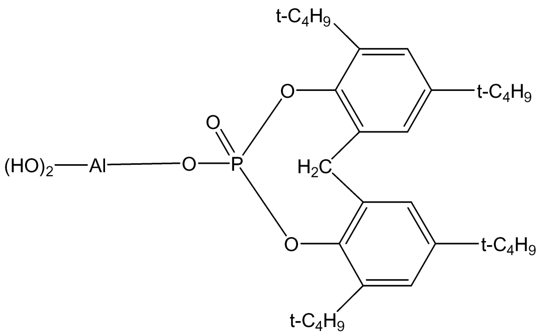
crystallization of the stereocomplex. We have, therefore, begun to analyze the crystallization behavior of PLLA and the PLLA/PDLA stereo mixture in the presence of various crystal nucleators with the aim of controlling their crystallization. In the present study, we disclose an enhanced stereocomplex formation by utilizing an aluminum complex of a phosphoric ester combined with hydrotalcite as the crystal nucleator and discuss its effect on the crystallization behavior of both PLLA and the stereocomplex in comparison with that of Talc which is known as an effective crystal nucleator of PLLA. The improved processability of the stereocomplex with the present crystal nucleator may lead fast expansion of the commodity applications of the PLA products.

2. Experimental

2.1. Materials

PLLA (Lacty 5400®) was supplied in pellet form by Shimadzu Corp. (Kyoto, Japan). Its number average molecular weight (M_n) and polydispersity index in weight/number average molecular weight ratio (M_w/M_n) were 52,000 Da and 2.3, respectively. PDLA was synthesized by the ring-opening polymerization of D-lactide supplied by Purac Biochem Gorinchem Ltd (Holland). The polymerization was performed in bulk at 140 °C for 8 h using tin octoate (0.3 wt%) as the catalyst [8]. PDLA was purified by reprecipitation using a solvent combination of chloroform (solvent)/methanol (precipitant). Reprecipitated PDLA was dried at 120 °C for 5 h under vacuum. Its M_n and M_w/M_n were 55,000 Da and 2.1, respectively. Talc ($Mg_3Si_4O_{10}(OH)_2$; Micro Ace P-6®) was supplied by Nippon Talc Co. Ltd (Tokyo). The nucleator (NA) comprising an aluminum complex of a phosphoric ester (Fig. 1) and hydrotalcite ($Li_{1.8}Mg_{0.6}Al_4(OH)_{18}CO_3\cdot 3.6H_2O$) was supplied by Asahi Denka Co. Ltd (Tokyo). This compound has been used as a crystal nucleator of polyolefins for making their products transparent.

Each of PLLA and PDLA was dissolved in chloroform in a polymer concentration of 10 g/dl, and a predetermined amount of a nucleator was added and well dispersed in it. Both of the resultant solutions were mixed in a volume ratio of 1:1, cast onto a flat glass plate, and evaporated at room temperature. The film resulting after one day was pealed off the plate to obtain a PLLA/PDLA stereo mixture containing the nucleator. A PLLA film added with the nucleator was also prepared likewise.



(1)

Fig. 1. Chemical structure of the aluminum complex of phosphoric ester used as a component of NA.

2.2. Measurements

2.2.1. Thermal analysis

Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-60 thermal analyzer under a nitrogen atmosphere for a sample weight of 9-11 mg with α-alumina as the reference sample. A four-step non-isothermal temperature program was used to evaluate the crystallization behavior of the samples. In the analysis of the PLLA/PDLA mixtures, the samples were heated from room temperature to 250 °C at a heating rate of 50 °C/min, held at 250 °C for 5 min, then cooled from 250 to 30 °C at a cooling rate of − 5 °C/min, and finally heated from 30 to 250 °C at a heating rate of 5 °C/min. In the measurement of the PLLA samples, the program was almost identical except that the final heating and holding temperatures were as high as 200 °C. The crystallization temperature (T_c) and the heat of crystallization (ΔH_c) were measured for the exothermic peak observed in the third cooling process, while T_m and the heat of fusion (ΔH_m) were measured in the fourth heating process. Both T_c and T_m were determined at the top and bottom temperatures of the peaks, respectively.

2.2.2. Photomicrography

Optical microscopy was performed on an Olympus BX50 polarizing microscope equipped with a Japan High-tech hot-stage RH-350. The PLLA/PDLA sample was heated on the hot-stage from room temperature to 250 °C at a heating rate of 50 °C/min, held at 250 °C for 5 min for completion of the polymer melting, and cooled from 250 °C at a heating rate of − 5 °C/min to a temperature where the growing of spherulites started. In the measurement of the PLLA samples the heating and cooling were set in the range from room temperature to 200 °C.

3. Results and discussion

3.1. Effect of the crystal nucleators on the crystallization of PLLA and stereo mixture

Many reports have been published thus far on the effect of crystallization on the properties and morphology of PLLA specimen [9–14]. For example, Tsuji and Ikada showed that the thermal and mechanical properties of PLLA are affected by the crystalline morphology that is changed by the annealing conditions [9]. Baratian et al. reported that the crystallinity and spherulite growth rate decrease substantially with increasing D-lactide content in PLLA [11], while Mijovic and Sy indicated that the spherulite size of PLLA is larger in the melt-crystallized specimen than in the cold crystallized [13]. On the other hand, Miyata and Masuko reported that the overall crystallization rate increases with decreasing molecular weight of PLLA [15]. Ogata et al. reported the crystal morphology of PLLA heat-treated below its T_g [16]. Kolstad [17] and Schmidt et al. [18] showed the effectiveness of Talc and the PLLA/PDLA stereocomplex as the crystal nucleators of PLLA, respectively. However, little has been known about the crystal nucleation for the stereocomplex, particularly, in the process of its melt-crystallization in the presence of crystal nucleators.

We made a simple screening test by utilizing DSC for the crystal nucleators that can promote crystallization of PLLA (or PDLA) and the PLLA/PDLA stereocomplex. Among the various inorganic nucleators examined, Talc and NA were found to give the most interesting results in the crystallization of the both polymer systems. Figs. 2 and 3 show the DSC curves measured at the third cooling stage after the first heating and the second melting processes for the PLLA and stereo mixture samples added with NA and Talc in 1.0 phr (per one hundred resin). Each trace in Fig. 2 shows an exothermic peak due to the crystallization of PLLA. It is known that the addition of Talc is the most effective in regard to the enhanced T_c and also the increased ΔH_c (30 J/g) of PLLA. NA is not effective at all for the T_c enhancement in spite of giving a moderately increased ΔH_c (28.3 J/g) as compared with that of PLLA alone (22.0 J/g).

The DSC traces recorded for the stereo mixtures (Fig. 3) are quite different from those of PLLA. The mixture added with NA shows a single large exothermic crystallization peak around 143 °C, while the traces of the stereo mixture alone and the one added with Talc show bimodal exothermic peaks. The peak tops appearing at the high (138 °C for the stereo mixture alone and 175 °C for the Talc-containing mixture) and low temperatures (119 °C for the stereo mixture alone and 134 °C for the Talc-containing mixture) are attributed to the crystallizations of the stereocomplex and the PLLA or PDLA homo-crystals, respectively.

It is therefore known that Talc, being a good crystal nucleator of PLLA homo-crystals, cannot suppress the homo-crystallization although it can nucleate the stereocomplex crystals at high temperature. Since the T_c for the homo-crystals becomes much higher in the stereo mixtures than in the single PLLA samples, the good nucleating ability of the pre-formed stereocomplex crystals is supported in the homo-crystallization of PLLA or PDLA [18].

Table 1 summarizes the numerical data extracted from the above DSC measurements and those obtained at different conditions. Judging from the ΔH_c values, a higher crystallinity is given with 1.0 phr of Talc and NA than with 2.0 phr relative to the stereo mixture. The fourth heating of the stereo mixture alone and the one with Talc show both the endothermic peaks around 170 and 215 °C due to the melting (T_m) of the homo-crystals and the stereocomplex crystals, respectively, to support the formation of the mixed crystals. The fourth heating of the sample containing NA, on the other hand, shows only one endothermic peak (T_m) at 207 °C, which is slightly lower than that shown by the formers (215–217 °C). The ΔH_c of the stereocomplex crystals observed with NA (53 J/g) is much higher than that observed with Talc (33 J/g). Although the double use of Talc and NA (1.0 phr for each) is not so effective for increasing T_c of PLLA, their double use for the stereo mixture is highly effective for the crystal nucleation of the stereocomplex. Particularly, T_c is enhanced up to 170 °C with a small increase in ΔH_c. These results reveal that NA can be a good crystal nucleator of the stereocomplex though the T_m of the resultant crystals is slightly lower than that of its single crystal (230 °C).

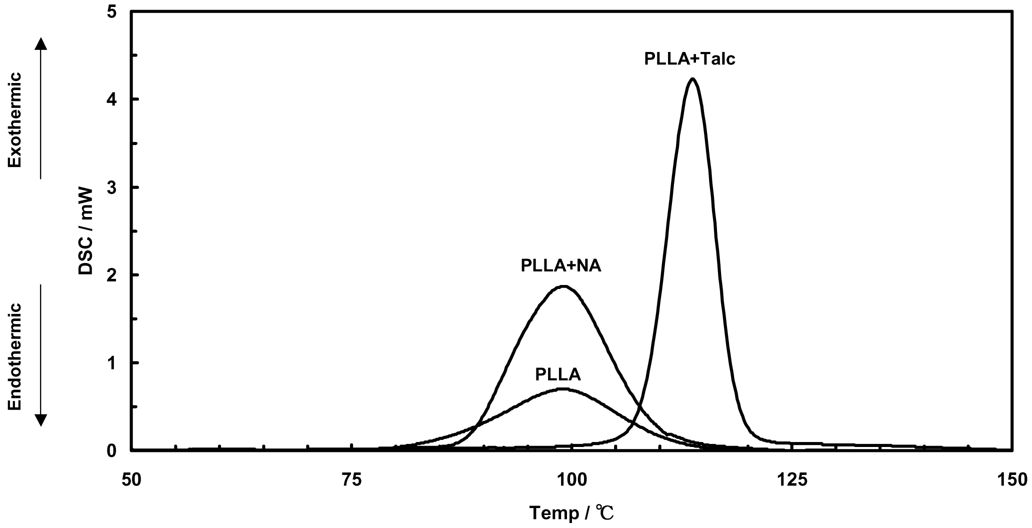


Fig. 2. DSC traces of the PLLA samples with and without nucleators (1.0 phr) at the 3rd cooling scan (from 200 to 30 °C at −5 °C/min).

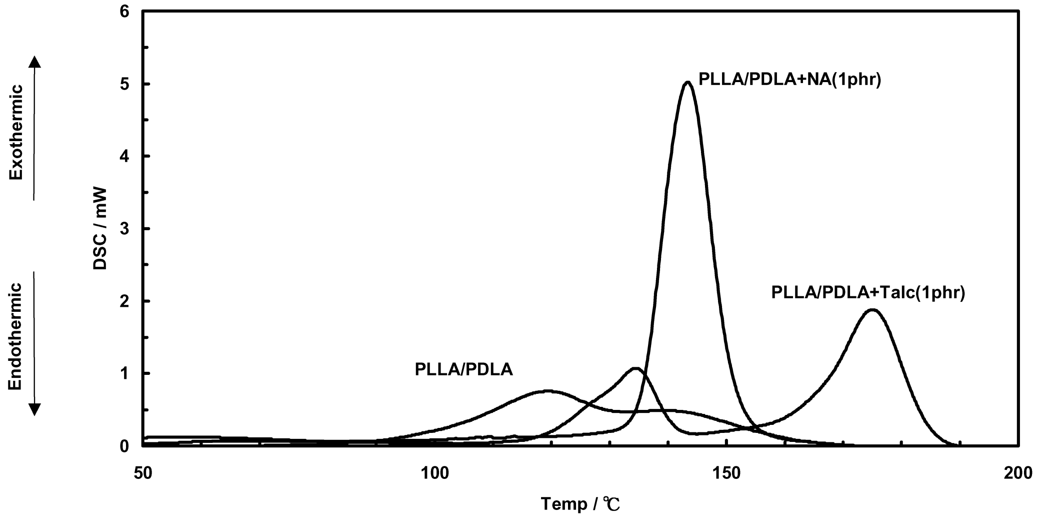


Fig. 3. DSC traces of the PLLA/PDLA stereo mixtures with and without nucleators (1.0 phr) at the 3rd cooling scan (from 200 to 30 °C at − 5 °C/min).

Table 2 summarizes the crystallization data of the stereo mixtures with different PLLA/PDLA compositions when nucleated with 1.0 phr of NA. It is shown that only the stereocomplex crystallization is induced even in the samples having excess PLLA. Both T_c and ΔH_c recorded for the stereo mixtures with PLLA/PDLA = 50/30 and 50/40 are almost comparable with those recorded for the 50/50 stereo mixture (shown for a new experiment confirming that the data are similar to those of the run of NA (1.0) in Table 1). This result indicates that the presence of NA can suppress the homo-crystallization of PLLA to induce the stereocomplex crystallization quite effectively.

3.2. Changes in crystal morphology of PLLA and stereo mixture

Fig. 4 and 5 show the photomicrographs of the PLLA and stereo mixture, respectively, in the initial and final processes of crystallization when their melts were cooled. In the sample of PLLA alone (Fig. 4(a)), the crystallization starts around 110 °C with formation of small spherulites. When cooled to 60 °C, the first formed spherulites grow larger with formation of a number of small crystals in places. This result shows the crystal nucleation is quite slow without any crystal nucleator added. In the PLLA sample added with Talc (Fig. 4(b)), the crystal nucleation initiates around 125 °C in many parts of the observation area. At 110 °C small crystallites cover the whole area without formation of large spherulites. The PLLA sample added with NA starts the crystallization with formation of a small number of spherulites (Fig. 4(c)), as does the PLLA alone. With lowering temperature, further crystal nucleation is induced until the whole area is covered with large and small spherulites. Comparison of these results well supports the effectiveness of Talc as the crystal nucleator of PLLA.

On the other hand, the crystallization of the stereo mixture starts at a high temperature of 150 °C even in the absence of the nucleator (Fig. 5(a)). Many spherulites with

Table 1
Thermal data obtained by DSC for PLLA and PLLA/PDLA added with different nucleators

Polymer	Nucleator (phr)	T_c[a] (°C)	ΔH_c[a] (J/g)	T_m[b] (°C)	ΔH_f[b] (J/g)
PLLA	None	98.8	14.5	171.4	40.7
	Talc (1.0)	113.7	32.2	173.7	37.4
	NA (1.0)	99.0	28.3	171.6	36.8
	Talc (1.0) + NA (1.0)	112.4	41.5	164.7	51.1
PLLA/PDLA	None	119.1/138.4	37.3[c]	168.4/215.5	21.6/19.2
	Talc (1.0)	134.5/175.0	14.5/33.1	169.8/217.5	17.6/37.3
	Talc (2.0)	126.6/165.3	17.4/24.5	164.4/209.0	21.7/22.4
	NA (1.0)	143.3	53.0	206.9	53.9
	NA (2.0)	144.8	46.9	202.7	45.4
	Talc (1.0) + NA (1.0)	170.9	58.3	208.9	55.8

Scanning condition; 1st heating: room temperature → 250 °C at 50 °C/min, 2nd holding: 250 °C for 5 min, 3rd cooling: 250 °C → 30 °C at − 5 °C/min, 4th heating: 30 °C → 250 °C at 10 °C/min.

[a] Measured for the 3rd cooling.

[b] Measured for the 4th heating.

[c] For the whole exotherms.

Table 2
Thermal data for the stereo mixtures with different PLLA/PDLA compositions as crystallized in the presence of NA (1.0 phr)

PLLA/PDLA	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_f (J/g)
50/50	144.2	55.7	209.1	51.8
50/40	146.4	56.0	212.7	56.7
50/30	143.6	50.7	210.1	51.9

By DSC at the same conditions as shown in Table 1.

detectable sizes are generated in places with a rapid rate. At 130 °C these spherulites are allowed to contact with each other to cover the whole area, while small crystallites are also detected in the dark amorphous region present among the large spherulites. The crystal formation is much more rapid in the stereo mixture added with Talc even at 170 °C (Fig. 5(b)), and many incomplete spherulites consisting only leaflets are quickly formed at 150 °C to cover the whole area. The stereo mixture added with NA, in return, shows a completely different crystal growth (Fig. 5(c)). At 140 °C, well-shaped spherulites with different sizes are formed in

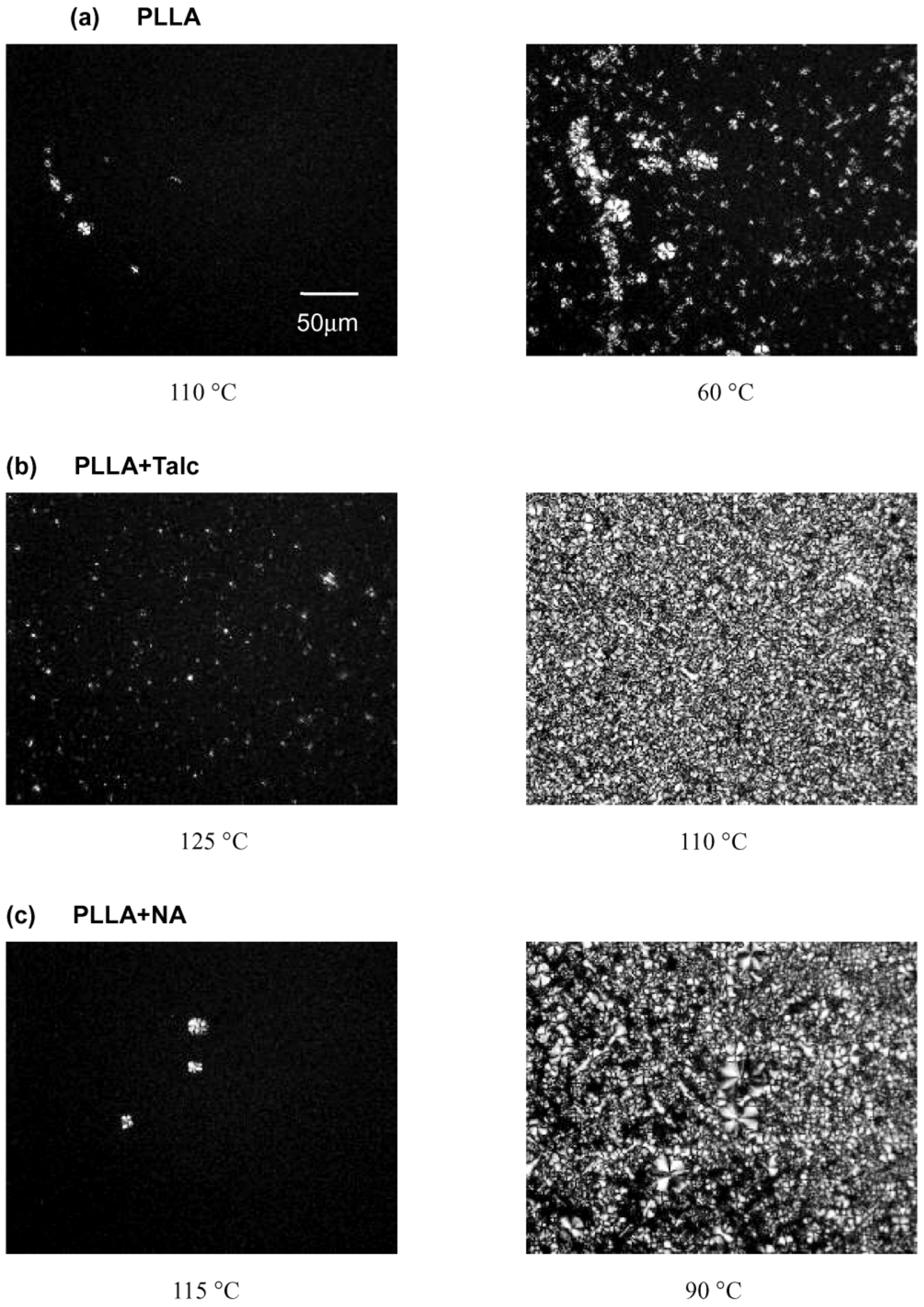
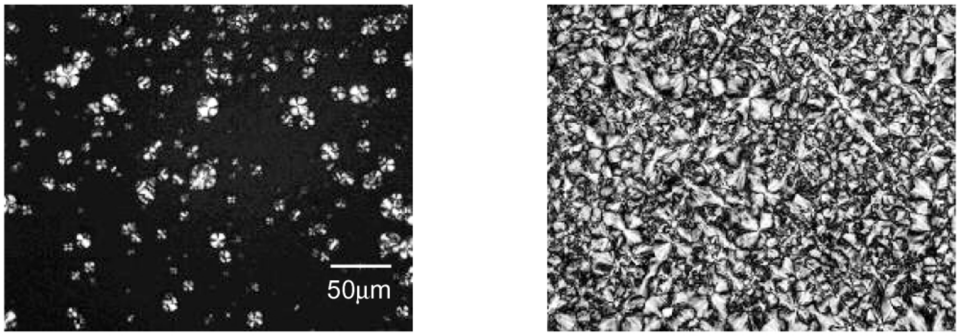


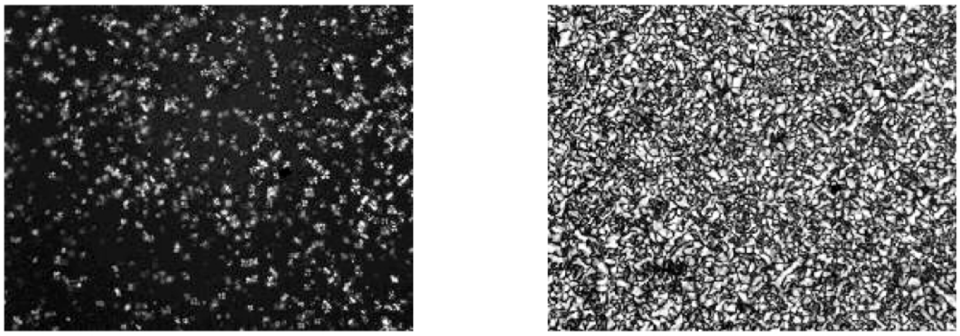
Fig. 4. Photomicrographs of (a) PLLA, (b) PLLA added with Talc (1.0 phr) and (c) NA (1.0 phr) in the crystallization processes.

(a) PLLA/PDLA



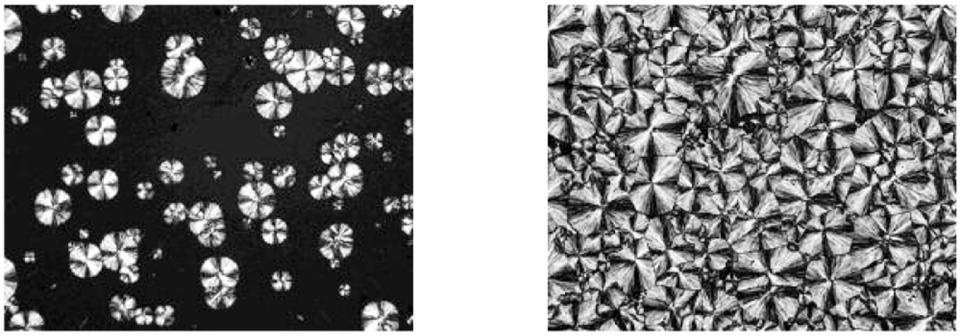
150 °C 130 °C

(b) PLLA/PDLA+Talc



170 °C 150 °C

(c) PLLA/PDLA+NA



140 °C 120 °C

Fig. 5. Photomicrographs of (a) PLLA/PDLA, (b) PLLA/PDLA stereo mixtures added with Talc (1.0 phr) and (c) NA (1.0 phr) in the crystallization processes.

many spots. They grow into larger ones at 120 °C to occupy the whole area by contacting with each other. Although the dark regions involve many smaller crystallites, they seem to keep the complete spherulite shape. This morphological uniformity is significantly different from the random shapes observed for the pure stereo mixture and the one added with Talc. It is therefore concluded that the crystallization of the stereocomplex is well controlled in the presence of NA.

When the aluminium complex of a phosphoric ester (Fig. 1) was singly used as the crystal nucleator of the stereo mixture, mixed formation of the homo and stereocomplex crystals was observed. Their T_c were 117 and 147 °C with low ΔH_c (10.1 and 19.6 J/g), respectively. Therefore, the incorporation of hydrotalcite in NA is essential for the crystal nucleation of the stereocomplex. Although Talc and hydrotalcite have different compositions, the enhanced effect by the double use of Talc and NA may also be understood in relation with the role of hydrotalcite in NA, which is now under study.

3.3. General features in the crystal nucleation of the stereocomplex

When the 1:1 stereo complexation is induced in the zones having compositional fluctuation of PLLA/PDLA, PLLA and PDLA-rich regions are generated and their homo-crystallization is likely induced by the crystal-nucleating effect of the first-formed stereocomplex crystallites. Accordingly, the crystallization of stereocomplex is usually accompanied by the homo-crystallization as observed in the absence of nucleator or in the presence of Talc as the nucleator. In the presence of NA, however, the stereo-complex crystals are preferentially formed with efficient suppression of the homo-crystallization of PLLA and PDLA. This may be because the crystallization of the stereocomplex does not lead the chain segregation of PLLA or PDLA, allowing the uniform stereo-complexation to grow large symmetrical spherulites. These spherulites may have a large chance to involve non-crystalline PLLA and PDLA chains inside the spherulites or in the crystal-amorphous interface. In the absence of nucleator and in the presence of Talc, on the other hand, partial spherulites are formed with the compositional fluctuation occurring around the stereocomplex crystals. In this case, the spherulites should contain only a small amount of non-crystalline PLLA and PDLA chains inside. These crystallization features are consistent with the aforementioned fact that the T_m (207 °C) of the stereocomplex crystals nucleated by NA is significantly lower than that (215–217 °C) of the same crystals formed without nucleator and nucleated with Talc.

Schmidt and Hillmyer reported that in the crystal nucleation of PLLA with the stereocomplex the total crystallinity of PLLA becomes much lower than expected from the PLLA/PDLA blend ratio [18]. Therefore, the stereo-complexation should intrinsically retard the segmental arrangement of PLLA for crystallization. With this effect dominating in the presence of NA, the suppressed homo-crystallization of PLLA and PDLA and the concomitant growth of the large spherulites may be possible even in the systems with biased PLLA/PDLA compositions (Table 2). The poorer nucleation effect of NA on the homo-crystallization is also related with the least formation of the homo-crystals. On the other hand, in the absence of nucleator and in the presence of Talc, the partial spherulites are quickly formed without such suppression of the compositional fluctuation and segment arrangement for crystallization.

4. Conclusions

Among the various inorganic nucleators examined, Talc and NA were found to be effective for the crystallization of PLLA and PLLA/PDLA stereo mixture, respectively. The DSC analyses showed that NA induces the sole crystallization of the stereocomplex to show a single melting peak in the DSC traces, while Talc cannot prevent the homo crystallization of PLLA and PDLA to give a bimodal melting peak in DSC. Photomicrographic study revealed that the large spherulites with good shape are formed from the melt of the stereo mixture added with NA while a large number of small, incomplete crystallites are formed in the presence of Talc. The double use of NA and Talc enhanced T_c of the stereocomplex with the homo-crystallization of PLLA and PDLA excluded. The present controlled melt-crystallization of the stereocomplex will allow us to improve its processability and to expand its real applications.

Acknowledgements

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