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ORIGINAL PAPER

Crystallization morphology and crystallization kinetics of poly(lactic acid): effect of *N*-Aminophthalimide as nucleating agent

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Abstract The effect of *N*-Aminophthalimide compound (NA-S) as nucleating agent on crystallization behavior and morphology of poly(lactic acid) was studied. With polarized optical microscope (POM), the unique phenomena of nucleation and epitaxial crystallization of PLA/NA-S system were observed. Dynamic morphology of crystallization was also studied by POM to investigate the relationship between growth behavior of PLA and nucleating agent. Isothermal and non-isothermal crystallization behavior of PLA were studied by differential scan calorimeter (DSC). When nucleating agent was added, a new peak appeared in wide angle X-ray diffraction (WAXD) compared with pure PLA, indicating the nucleating effect of NA-S on crystallization of PLA. All the results indicate that the nucleating agent of NA-S shows obvious nucleating effect on isothermal crystallization above 120 °C and in non-isothermal crystallization after it is added in PLA, that is, the induction crystallization time is reduced, the crystallization rate and nucleation density of PLA are increased.

Keywords *N*-Aminophthalimide · Poly(lactic acid) · Nucleating agent · Crystallization

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Introduction

Poly(lactic acid) (PLA), a kind of linear aliphatic thermoplastic polyester produced from renewable resources, has attracted much attention due to its distinct properties comparable to many petroleum-based plastics and other biodegradable materials [1]. However, the slow crystallization rate and low crystallinity of PLA make it difficult to be processed by some processing methods such as injection molding which has a short cooling cycle and limited orientation. To improve crystallization behavior of PLA, many studies have been carried out nowadays [2, 3]. One important way is to add nucleating agent to lower the surface-free energy barrier towards nucleation and initiate crystallization at higher temperature upon cooling [4]. There are many kinds of nucleating agents, and studies are focused on finding new effective nucleating agents as well as their nucleation mechanism.

Talc is a widely used nucleating agent for polymer. Haubruge et al. [5] studied the nucleation effect of talc on polymers with the epitaxial mechanism. Kolstad found that talc was an effective nucleating agent for PLA. When 2–21 wt% of talc was added to poly (91% L-lactide-*co*-9% meso-lactide), it was found that the best effect was achieved at 6 wt% talc, resulting in the 500-fold increase in nucleation density [6]. Ke and Sun [7] compared the increase in crystallization rate of PLA/starch with that of PLA/talc using Avrami kinetics, and concluded that talc was more effective to increase the crystallization rate of PLA than starch.

Stereocomplex PLA (SC-PLA) that is obtained by mixing PDLA and PLLA in solution for the two different helical polymers has been studied for a long time. It is regarded as a potential nucleating agent for PLA [8]. According to Tsuji and Tezuka [9], at the ratio of 50/50, the melting point of SC-PLA was 230 °C, 50 °C higher than that of pure PLLA or PDLA. Tsuji et al. [10] revealed that the addition of small amounts of PDLA could effectively accelerate overall PLLA crystallization when the PDLA content and crystallization conditions were scrupulously selected. With POM, the spherulite growth (G), density, and initiation time (t_i) were studied, and G_0, K_g for Hoffman–Laurizen theory were calculated which indicated that the crystallization was in Regime II. Also the Kinetics was studied from light intensity transmitted through the specimens by POM with photometer, and the starting, half, and ending times of overall crystallization were studied at various crystallization temperatures and stereocomplex contents. According to Schmidt and Hillmyer [11], a comparison between stereocomplex and talc as nucleating agents at 140 °C for isothermal crystallization showed that stereocomplex had almost two times higher nucleation efficiency (NE) than talc at 6 wt% of use level. And they also found that the thermal treatment and blend ratio strongly affected the ability of stereocomplex to nucleate the excess PLLA homopolymer.

Layered silicate nanocomposites have attracted much attention as well. Ray et al. [12, 13] reported the thermal and mechanical properties of PLA with C18-MMT and mica added, the change of crystalline structure of composites was observed by WAXD, which indicated that the polymer chains intercalated the silicate galleries and the coherent order of the silicate layers was very high with increasing clay content. From POM, decreasing ordering of PLA with MMT was observed, and with LS, the effects of MMT on reducing the spherulites radius and inducing time as well as increasing the overall crystallization rate were investigated [14]. Li et al. [15] studied the crystallization behavior of PLA with substituted aromatic phosphate salts, knowing that the univalent and trivalent substituted aromatic phosphate salts had effects on crystallizability, especially with lithium salt. In another article of Pluta [16], the presence of inorganic clay particles was reported to reduce the crystallinity of PLA from the glassy amorphous state, and this effect was more pronounced in nanocomposites due to the intercalated nanostructure.

In addition, many inorganic compounds have been used as nucleating agents. Liao et al. [17] studied nano-$CaCO_3$, $BaCO_3$, TiO_2 as nucleating agents in PLA with DSC, and found that nano-TiO_2 performed better than the other two because of the different nucleating agent shape. They also studied the crystallization kinetics with Avrami theory. Pluta et al. confirmed that β-calcium sulfate hemihydrate could enhance the crystallizability both during melt cooling and during heating from the amorphous glassy state. However, strictly speaking, β-calcium sulfate hemihydrate could not be called as the nucleating agent for PLA because its use level was as high as 40 wt% [18].

Some organic molecules are regarded as more effective nucleating agents. Nam et al. [19] used *N*,*N*-ethylenebis (12-hydroxystearamide) (WX1) as nucleating agent, and found that it evidently enhanced the velocity of crystallization. Meanwhile, they investigated the mechanism of nucleation and concluded that WX1 presented no nucleation effect when WX1 was in its molten state, which implied that organic molecules must crystallize to promote the crystallization ability. Kawamoto et al. [20, 21] synthesized a series of hydrazide compounds and proved its effectiveness for the nucleation of PLA. In their articles, how the structures influence the effect on nucleation for crystallization of PLA was studied by changing the structures of nucleating agents, and the data regarding thermal, kinetic, and mechanical properties were obtained.

Among most of the nucleating agents that have been reported, many kinds of test methods were used for their evaluation. DSC as a thermal test method was used to analyze the exothermic and endothermic reaction involved in crystallization; WAXD was used to study the change of crystalline structure; LS and POM were used to determine the morphology and the growth rate. POM as a kind of powerful tool can be used to investigate the crystallization behavior and morphology of PLA.

In this article, NA-S was used as a new nucleating agent to enhance the crystallization properties of PLA, and unique phenomena of nucleation, epitaxial crystallization, and dynamic morphology of PLA/NA-S system were studied.

Experimental part

Materials and sample preparation

The PLA was provided by Nature Works. It is a semi-crystalline grade (PLA 4032D) containing around 2% D-LA. The number and weight average molecular

Table 1 Codes and composition of the samples

Samples codes	Content of NA-S/wt%	Content of pure PLA/wt%
S-00	0	100
S-05	0.5	99.5
S-10	1.0	99
S-15	1.5	98.5

weight are 112,389 and 194,660 g/mol, respectively. PLA was dried under vacuum at 70 °C for 24 h before use. Nucleating agent NA-S, an *N*-Aminophthalimide compound was obtained from Tong-Jie-Liang Biomaterial Co., Ltd (China). With melting point of 238.8 °C, about 80 °C higher than that of PLA, NA-S was potentially a nucleating agent for PLA. Methenyl trichloride as a solvent was bought from Sinopharm Chemical Reagent Co., Ltd.

The film of PLA/NA-S was prepared as follows. Nucleating agent was dispersed in methenyl trichloride by ultrasound for 30 min, and then PLA was added into the turbid liquid formed and the liquid was stirred for 24 h. The nucleating agent was dispersed into polymer solution. The solution was cast onto Petri dishes placed horizontally, and the solvent was evaporated at room temperature for about 24 h. The obtained film was dried in vacuum oven for 48 h, and then the sample was ready for test. The sample numbers with different concentrations of NA-S are shown in Table 1.

Characterization

Polarized optical microscope

The film (thickness ≈ 30 μm) was prepared by pressing the film between two cover glasses for 5 min at 185 or 195 °C using a hot stage to eliminate the thermal history. Then, it was quickly transferred onto a hot stage (Linkam TMS 600) with the particular T_c, and then crystallized isothermally for desired time and other requirements. The morphology of crystallite of NA-S and PLA/NA-S was observed by polarized optical microscope (POM) (Germany LEICA, DMLP) equipped with hot stage (Linkam TMS 600). The processes for each heating requirements are shown in Table 2.

Differential scanning calorimeter

The overall crystallization behaviors were monitored by DSC Q100 (USA) differential scanning calorimeter under nitrogen protection. By considering the melt enthalpy of 100% crystalline PLA as 93 J/g [22], the values of the crystallinities of PLA/NA-S were estimated in percentages.

Table 2 Isothermal crystallization kinetics data for PLA/NA-S

Temp (°C)	Samples	K ($\times 10^{-2}$)	n	$t_{1/2}$	X_c (%)
135	S-00	–	–	–	–
	S-05	–	–	–	–
	S-10	2.747	1.88	5.57	23.31
	S-15	5.511	2.76	2.50	42.85
130	S-00	0.3044	2.33	10.3	39.34
	S-05	1.015	2.75	4.64	40.68
	S-10	4.607	1.92	4.10	46.30
	S-15	17.42	2.25	1.84	42.86
125	S-00	0.211	2.11	15.5	24.64
	S-05	1.300	2.78	4.18	35.63
	S-10	5.343	2.19	3.22	38.22
	S-15	21.67	2.13	1.73	42.07
120	S-00	0.713	2.32	7.19	35.07
	S-05	2.162	2.54	3.91	38.08
	S-10	6.648	2.13	3.01	39.31
	S-15	22.68	2.06	1.72	40.77
110	S-00	2.182	1.85	6.48	36.76
	S-05	1.407	2.30	5.44	38.74
	S-10[a]	4.179	2.34	3.32	19.22
	S-15[a]	21.29	1.94	1.83	28.03

[a] Owing to the lack of liquid-nitrogen, the sample crystallized during cooling with the setting rate of 40 °C/min

Wide angle X-Ray diffraction

Wide angle X-Ray diffraction analyses were performed for PLA/NA-S on a Rigaku D/max diffractometer (Cu radiation, operated at 40 kV and 150 mA). Samples were scanned under diffraction angle 2° per min in the range of 5°–60° after melted at 185 °C for 5 min and crystallized at particular temperature (110 and 135 °C) for 30 min.

Results and discussion

Crystallite morphology of PLA/NA-S

Figure 1a shows the spherulite crystal morphology of NA-S. After melted for 5 min at 250 °C, the sample of NA-S was crystallized, and spherulites were formed during rapid cooling. The spherulites exhibit the negative birefringence. The NA-S crystallites having the spherulitic texture similar to that of the polymer may easily act as a nucleating agent for PLA crystallization [18]. Figure 1b shows the PLA/

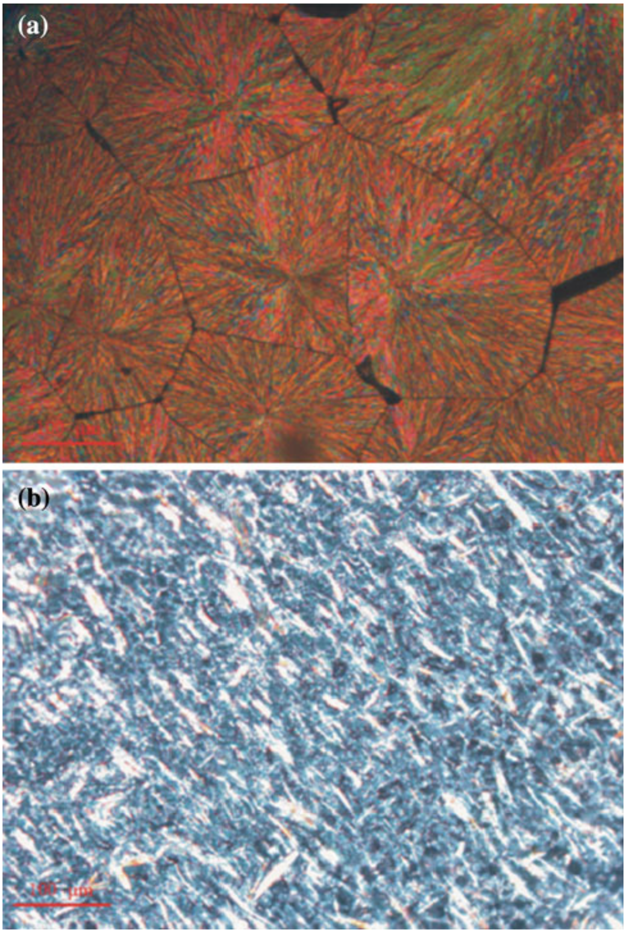

Fig. 1 **a** Spherulite of NA-S by POM. **b** Film of S-10 by POM

NA-S film at room temperature, and the bright needles are the crystals of NA-S indicating the uniform dispersion of NA-S.

Morphology of PLA with not melted NA-S

First, the isothermal crystallization of PLA without NA-S at different temperatures was investigated to compare with that of S-00 as shown in Fig. 2. The samples were tested by P1: the samples were first heated to 185 °C at 100 °C/min and held for 5 min to eliminate thermal history, then cooled at 40 °C/min to crystallization temperature. At the temperatures of 140, 130, and 120 °C, the spherulite density of S-10 is much higher than that of S-00, especially at 140 and 130 °C. However, at 110 and 100 °C, no manifest increase of spherulite density was observed. In Fig. 3, the overall crystallization times of the two samples are compared, and the effect of

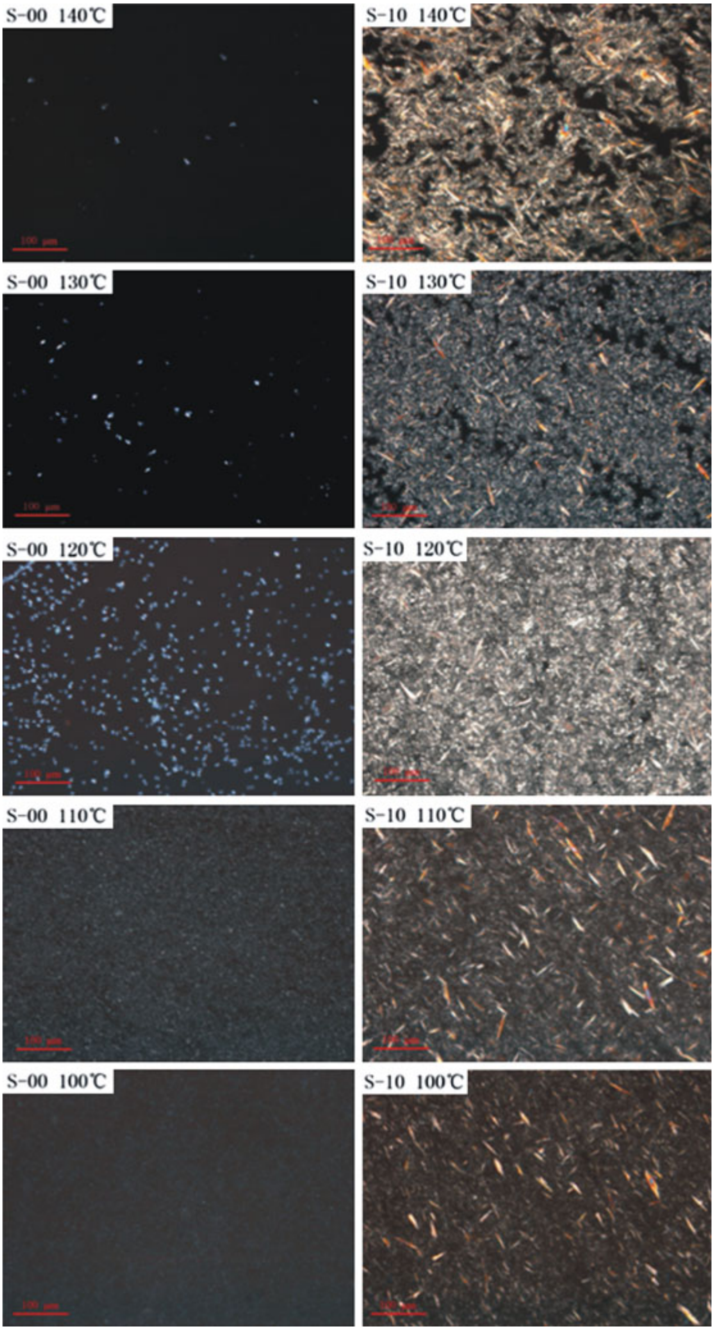

Fig. 2 Isothermal crystallization behavior comparison between S-00 and S-10 at a melting temperature of 185 °C for 180 s

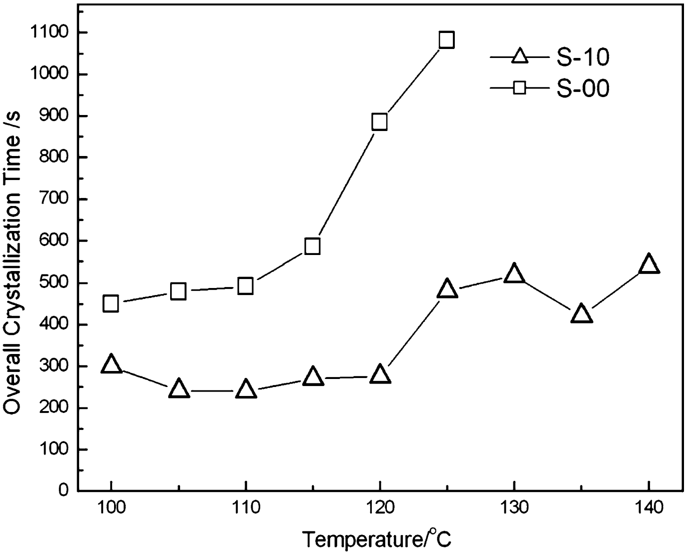

Fig. 3 Overall crystallization time of S-00 and S-10 (the data of S-00 at 140, 135, and 130 °C could not be obtained because of extremely long overall crystallization time)

NA-S can be seen when the temperature is high (above 120 °C). The reason might be related to the second-nucleation theory. The transition temperature from Regime II to Regime III kinetics is at about 120 °C [23]. At Regime II, secondary nuclei formation rate *i* approximates the lateral growth rate *g*, but at regime III, *i* is higher than *g* [24]. So at the temperature below 120 °C, nucleation is so effective that the influence of nucleating agent is not evident enough. NA-S is proved to be an effective nucleating agent that can be used to reduce at least half of the overall crystallization time and enhance the spherulite density.

Morphology of PLA with partially melted NA-S

The samples were tested by P2: the samples were first heated to 195 °C at 100 °C/min, and held for 5 min to eliminate thermal history, then cooled at 40 °C/min to 130 °C. In Fig. 4a, the bright needles in the dark area are the crystals of NA-S that cannot be melted completely at this temperature. After 5 min, tiny branch crystal of NA-S begins to grow from the root of NA-S crystal; meanwhile, spherulite of PLA starts to form separately. After 10 min, on the crystal branches of NA-S, PLA crystal grows epitaxially while the spherulites of PLA grow. In Fig. 4c–e, the NA-S grows with the PLA just like an agglomeration, and the spherulites of PLA are much smaller than the ones that are growing separately, and also the nucleation density is much higher. It takes only 24 min to grow to full screen, much shorter than that for the pure PLA. Figure 5 shows the spherulite radius growth rate of S-00 and the separate spherulite in S-10. The growing rate for S-10 is lower than that for S-00, which implies that NA-S not only increases the density of nuclei by making PLA crystal generated epitaxially, but also reduces the spherulite growth. To prove that

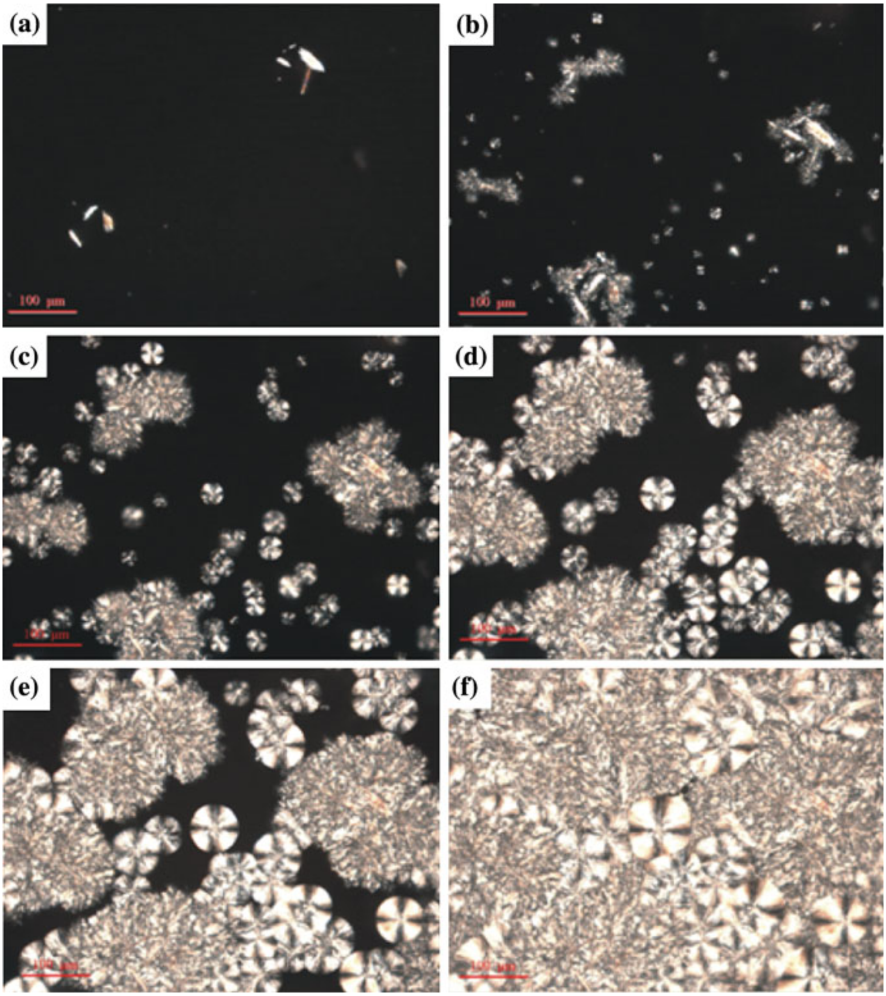

Fig. 4 **a** Beginning of S-10 at 130 °C. **b** S-10 isothermal crystallization for 5 min, **c** 10 min, **d** 15 min, **e** 20 min, **f** end of crystallization (24 min)

the agglomeration (Fig. 4c–e) is the crystal of NA-S with PLA epitaxial spherulite on it instead of only on the crystal of NA-S, another experiment was made by P3, and the result is shown in Fig. 6. First, the crystal agglomeration and PLA spherulites grow by the same way as shown in Fig. 4 till the crystals grow completely. When heated to above 165 °C, part of the crystal is melted. In Fig. 6c, some holes are observed where the PLA spherulites exist as seen in Fig. 6b. The venation shape emerges at which the agglomeration can be seen in Fig. 6b, which proves that the disappearing crystal is PLA. In Fig. 6d, PLA epitaxially crystallizes on NA-S again, and because the NA-S is fully bestrewed and grown, the overall crystallization time is 8.5 min, 21.5 min shorter than the first crystallization process.

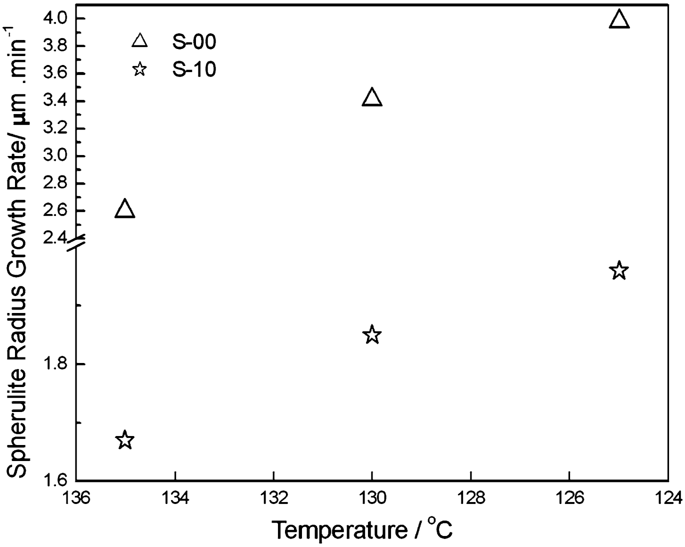

Fig. 5 Spherulite radius growth rate comparison between S-00 and S-10

Morphology of NA-S and PLA crystal epitaxially crystallized on NA-S

To show the NA-S morphology in molten PLA clearly, S-10 was tested by P3: the samples were first heated to 195 °C at 100 °C/min and held for 5 min, and cooled at 40 °C/min to 130 °C, then heated to 185 °C at 10 °C/min and held for 5 min, and cooled at 40 °C/min to 130 °C. Figure 7a shows a more clear morphology of NA-S when PLA is molten at 170 °C. It can be discovered that new branches grow successively on the original needles regarded as stem that are not melted. Pure NA-S and NA-S in PLA have the same growth direction, but as organic molecules, NA-S crystallites tend to search for any spaces to grow with molten PLA instead of making ordered arrangement. Comparing Figs. 4 and 6, there is no phenomenon that two kinds of spherulites coexist. The reason for that is that the crystallization rate of NA-S may be a positive function of temperature. Therefore, at 140 °C, crystals of NA-S grow faster than that of PLA; hence there is no separate PLA spherulite. The samples shown in Fig. 7a are heated to 185 °C and kept for 5 min, then cooled down to 140 °C rapidly and crystallized for 3 min; the results are shown in Fig. 7b. The epitaxial PLA spherulites on the NA-S branches are observed, which means that the mechanism of NA-S to nucleate is epitaxial crystallization.

Morphology of PLA crystal with totally melted NA-S

If NA-S is melted during heating, then there will be no effect, which can be seen from the experiment P4: the samples were first heated to 195 °C at 100 °C/min and held for 5 min, and cooled at 40 °C/min to crystallization temperature, then heated to 185 °C at 10 °C/min and held for 5 min, and cooled at 40 °C/min to 140 °C. As shown in Fig. 8, after 10 min, NA-S in PLA has little nucleation effect in

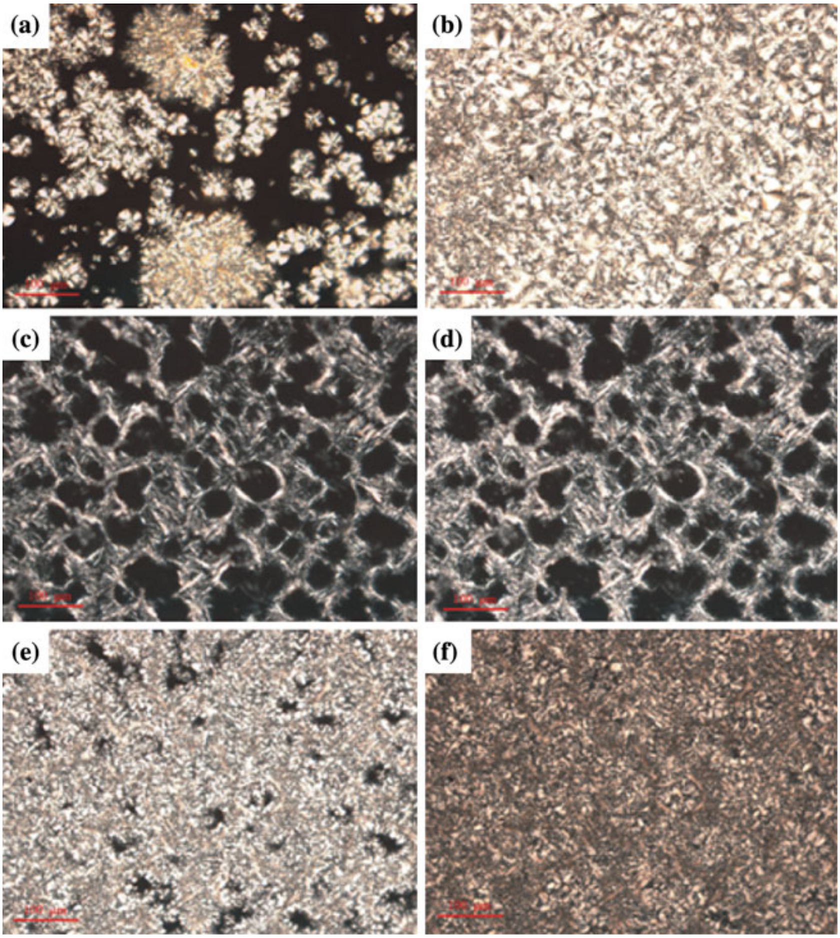

Fig. 6 **a** Isothermally crystallized for 10 min; **b** for 28 min (fully crystallized); **c** heated to 176 °C; **d** isothermally crystallized at 130 °C; **e** at 130 °C for 5 min; **f** at 130 °C for 8.5 min

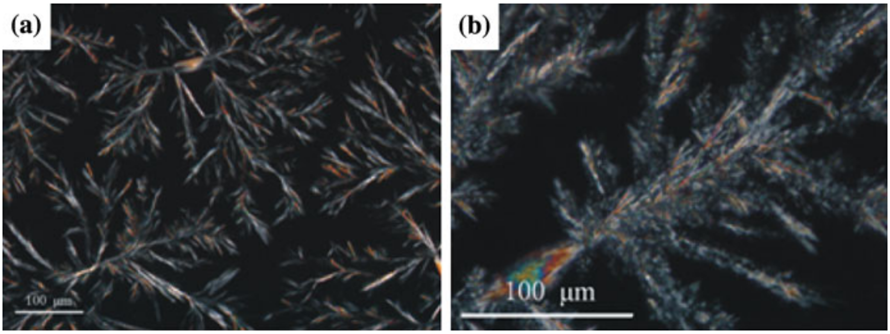

Fig. 7 **a** Morphology of NA-S with Molten PLA. **b** Morphology of PLA epitaxial on NA-S

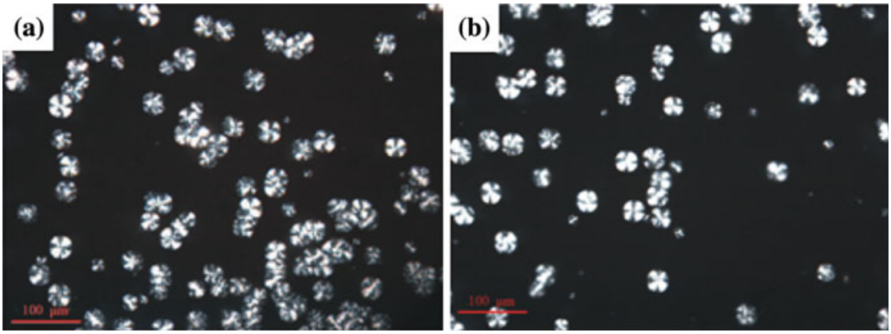

Fig. 8 **a** S-10 isothermally crystallized for 10 min. **b** S-00 isothermally crystallized for 10 min

comparison with pure PLA. The spherulite radius is almost the same when isothermally crystallized for 10 min, which implies that NA-S has no effect on decreasing the spherulite radius, and indicates that organic molecules must crystallize to promote the crystallization ability, this is in agreement with the conclusion made by Nam et al. [19]. NA-S has a high melt point of 238.8 °C in DSC. However, its melting point in PLA is only about 210 °C when it is well dispersed in PLA, which may be attributed to the destruction of PLA to the lattice structure of NA-S.

Crystallization kinetics and thermal analysis

The isothermal and non-isothermal crystallization behavior were also studied with DSC, and the kinetics data of isothermal crystallization using Avrami theory are shown in Table 2 [25–27]. The isothermal crystallization was investigated with a method as follows. The sample was heated from 20 to 185 °C at a rate of 10 °C/min, held for 5 min, and then cooled down to a particular crystallization temperature and held for 30 min, finally heated to 185 °C with the same heating rate. When the use level of NA-S is 1 and 0.5%, and at the temperature above 120 °C, the rates of crystallization at each temperature are increased compared with S-00, and the half crystallization times are shortened; However, at the temperature of 110 °C, there are no significant differences between pure PLA and PLA/NA-S system, this is in agreement with the conclusions made from POM studies. With the use level of 1.5%, the effects of reduction of half crystallization time is so evident in all the temperatures, so that this use level is considered as the most suitable one for PLA.

As for the kinetic parameters, the avrami exponent n is 1.85–2.78, which proves that the heterogeneous nucleation takes place. The rate constant K becomes higher when the use level is increased. K values at 110, 120, and 125 °C for S-15 are generally the same and much higher than that of others at the same temperatures (Fig. 9), which indicates that it has effect even in Regime III. This may be because so many nuclei are generated in the matrix with the use level of 1.5% that the

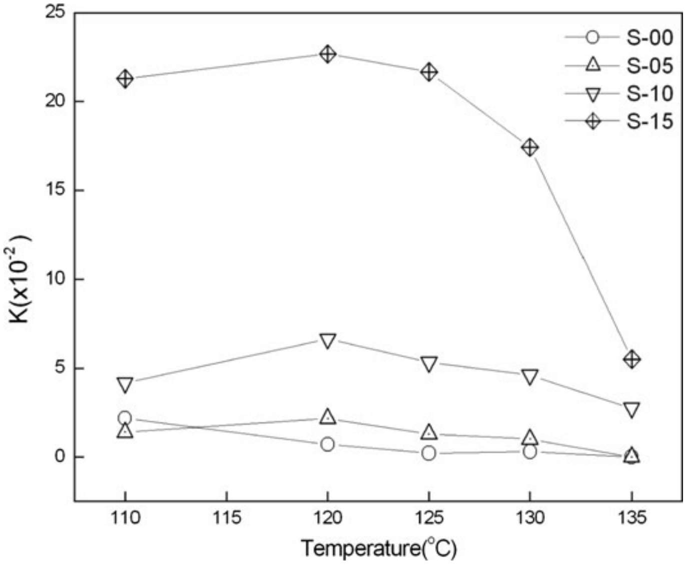

Fig. 9 Rate constant *K* for each sample in different temperatures

homogeneous nucleation that depends on temperatures is no longer necessary. The critical use level for the nuclei saturation was not studied.

Non-isothermal DSC crystallization and melting curves are shown in Figs. 10 and 11. Kinetic and thermodynamic parameter data are shown in Table 3. For non-

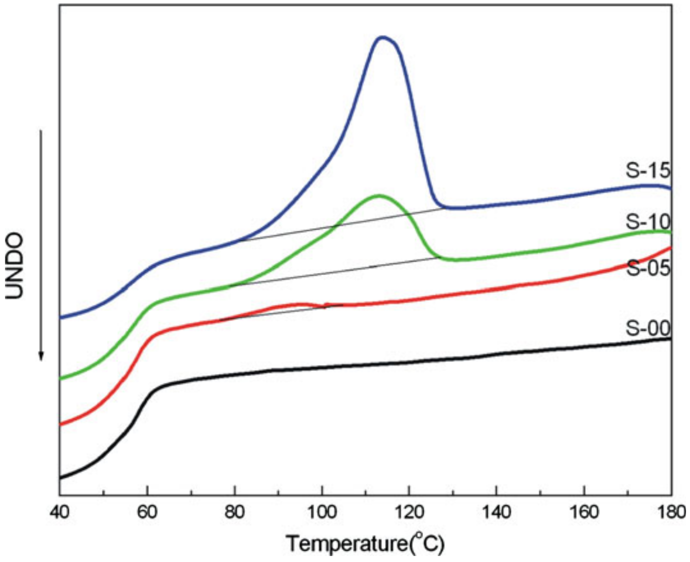

Fig. 10 Cooling curves of samples in non-isothermal crystallization (cycle 2)

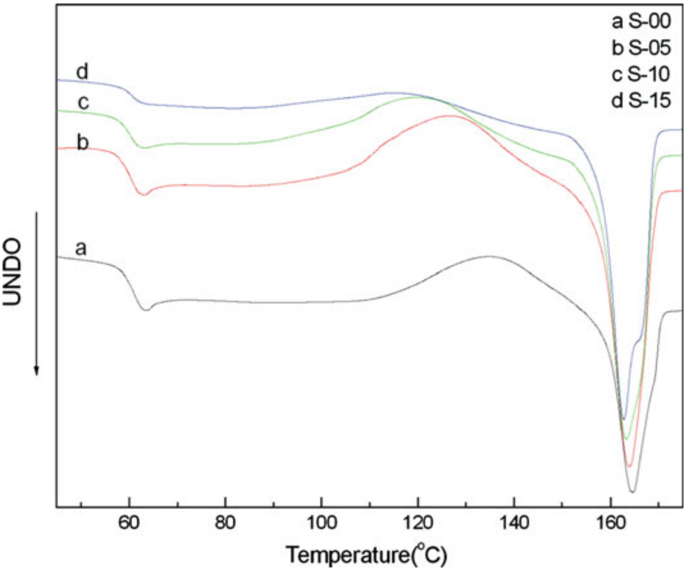

Fig. 11 Heating curves of samples in non-isothermal crystallization (cycle 3)

Table 3 Non-isothermal crystallization kinetics and thermodynamics data for samples

Sample	T_c^a (°C)	K_{c1}	n_1	K_{c2}	n_2	X_c (%)	T_m^b (°C)
S-00	–	–	–	–	–	–	164.50
S-05	93.05	1.12	2.12	1.01	2.78	2.96	163.90
S-10	112.28	1.47	2.52	1.04	3.15	12.75	163.31
S-15	113.40	1.56	2.08	1.19	3.87	26.09	162.74

[a] Measured in cycle 2

[b] Measured in cycle 3

isothermal crystallization, sample was tested by the method as follows. The sample was heated from 20 to 185 °C at a rate of 10 °C/min (cycle 1), held for 5 min, then cooled down to 20 °C (cycle 2) and reheated to 185 °C with the same rate (cycle 3).

With the cooling rate of 10 °C/min, there is no exothermic crystallization peak for S-00, whereas a small peak at the temperature of 93.05 °C is observed for S-05 while obvious peaks at the temperatures of 112.28 and 113.40 °C are observed for S-10 and S-15, respectively, which proves the presence of the nucleation effect. The melting points are lowered with the increase of NA-S use level in PLA from 164.50 to 162.74 °C. It can be explained by phase equilibrium theory of thermodynamics, which says that the impurities would reduce the melting point. For polymer, the equation is as follows:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}\left(\phi_1 - \chi_1\phi_1^2\right)$$

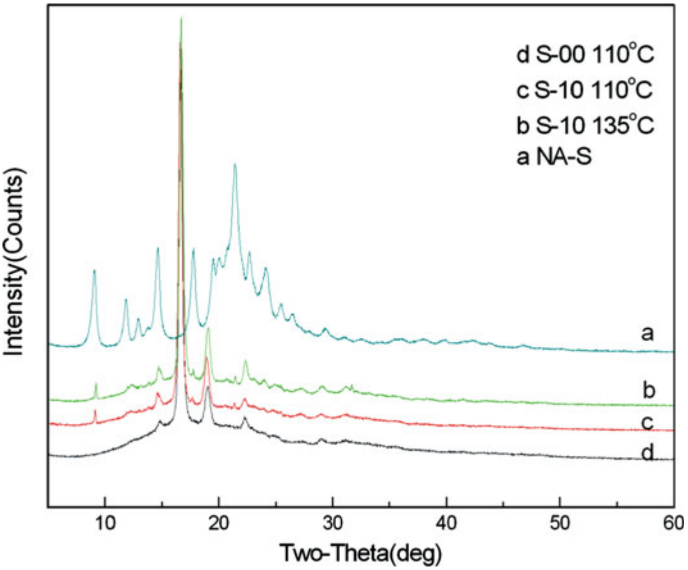

Fig. 12 WAXD of samples and NA-S

ϕ_1 is the volume fraction of the impurities such as plasticizers and monomers, and V_u and V_1 represent the molar factions of polymer and impurities. χ_1 is the interactional parameter between polymer and impurity, which is a constant for a particular polymer and impurity system. If the nucleating agent is treated as the impurity, the more it is in the PLA, the lower the melting point would be, which is in consistence with experiment results.

Crystalline structure analysis

In order to investigate or confirm the crystal structure of PLA with nucleating agent, WAXD was utilized. In addition to peak at $2\theta = 16.7°$ (S-00), 16.6° (S-10 110 °C) due to diffraction from (200) and/or (110) planes, another reflection peak at $2\theta = 19.0°$ (S-00), 18.9° (S-10 110 °C) from (203) plane appears. WAXD study indicates that pure PLA crystals are the typical orthorhombic crystal [8, 16], and its crystalline structure is not changed even when NA-S was added. In Fig. 12, a new peak at 9.1° (S-10 110 °C) appears, whereas no such peak is observed for pure PLA. However, there seems to have a peak for NA-S at $2\theta = 9.12°$. Besides, the peak of $2\theta = 19.0°$ (S-00) shifts toward lower diffraction angle of 18.9° (S-10, 110 °C). This may be attributed to the epitaxial crystallization. PLA/NA-S sample is crystallized to form defect ridden crystalline due to the nucleation accompanied with NA-S crystallites. As for layered silicate, there are some studies about the peak shifting and peaks ($2\theta = 2°–3°$) for clay existing in PLA/clay composites [12–14, 28, 29]. On low-molecular weight aliphatic amide [19], peak ($2\theta = 5.8°$) for WX1 appears in PLA/WX1. However, because NA-S is a new nucleating agent that has never been studied, there have been no articles relevant to it.

Conclusion

The detailed crystallization behavior and morphology of PLA/NA-S were studied in this study. The crystallization behavior and morphology of PLA were analyzed by POM, DSC, and WAXD. The possible mechanism of NA-S acting as a nucleating agent is explained and discussed as below. First, the melting point of NA-S is lower than that of pure PLA. Second, the PLA crystallizes epitaxially on NA-S because typical tans-crystallization occurs at the interface between PLA and NA-S. Third, only at crystal state could NA-S act as a nucleating agent for PLA. Fourth, its crystal shape in PLA is needle or branch, which grows around the branch although it grows spherulitically itself. Finally, the crystallization rate of NA-S may be a positive function of temperature. So at 130 °C, the spherulites and agglomerations co-exist, but at 140° there is no separate PLA spherulite. In a word, NA-S has a manifest epitaxial effect on PLA, it can make PLA crystallize on it quickly, which can significantly reduce the spherulite radius and shorten the crystallization time especially at high temperatures (above 120 °C).

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