

Crystallization Behavior and Morphology of Poly(lactic acid) with a Novel Nucleating Agent

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ABSTRACT: To improve the crystallization ability of poly(lactic acid) (PLA), a novel nucleating agent with a benzoyl hydrazine compound was used in this study. The crystallization behaviors of PLA/talc and PLA/bibenzoylhydrazinepropane (BBP) with or without poly(ethylene glycol) (PEG) were investigated with differential scanning calorimetry (DSC) and polarized optical microscopy. The DSC curves showed that the crystallization temperature and crystallinity of PLA/BBP (PBBP) was higher than that of PLA/talc. With the addition of PEG, a synergistic effect was found. According to the results of nonisothermal crystallization kinetics, the values of $F(T)$ of PBBP_{0.5}PEG₅ were usually smaller than those of PTa₃PEG₅, so the nucleation efficiency of BBP was much better than that of talc. From a polarized optical microscopy photo, it was easy to determine that the nucleation density of BBP was higher than that of PTa₃PEG₅, and the spherulitic diameter increased linearly with the crystallization time no matter the impingements. The spherulitic growth rate of PBBP_{0.5}PEG₅ was faster than that of PTa₃PEG₅, and the induction time of PBBP_{0.5}PEG₅ was the shortest among all of the samples. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41367.

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INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable thermoplastic polyester from renewable agricultural resources. In the past decade, the application of PLA has widened from the initial biomedical applications to packaging and molded articles.^{1,2} Despite its good mechanical properties and processability, PLA has a lower heat resistance for its low glass-transition temperature and low crystallinity.^{3,4} The solution for this problem has attracted more attention in recent years.^{5–7} Many attempts have been made to accelerate the crystallization rate of PLA and increase the crystallinity of PLA by the addition of nucleating agents^{8–10} or plasticizers.^{11–13} It is well known that the addition of a plasticizer to increase the chain mobility of PLA tends to increase crystallization rate and extend the crystallization temperature (T_c) window. The most popular plasticizers of PLA in the past decade have been poly(ethylene glycol) (PEG)¹³ and triphenyl phosphate.^{11,12} However, the prevailing approach for improving the crystallization ability of PLA has been the addition of a nucleating agent.

In fact, there have been many publications reporting different nucleating agents in the past decade. These nucleating agents can be classified into three categories, including inorganic particles, organic compounds, and macromolecular agents.

The inorganic particles used in PLA as a nucleating agent include talc, Montmorillonite (MMT), and so on. The most recommendable inorganic nucleating agent is talc, which has been widely used as a nucleating agent. Unquestionably, the nucleation density in PLA sharply increases with the addition of talc or other inorganic particles, and this elevates T_c . However, the dispersability of inorganic particles in the PLA matrix is not very good, and this affects the mechanical properties. Another point to be considered is that the T_c of PLA/talc is not very high, although it is higher than that of PLA/PEG or PLA.

Compared to inorganic nucleating agents, organic nucleating agents have better compatibility with polymers and tend to disperse finely in the matrix.^{14,15} Okamoto et al.¹⁶ used a low-molecular-weight aliphatic amide, namely, *N,N*-ethylene bis(12-hydroxystearamide), as nucleating agents for PLA and found that the nucleation density and overall crystallization rate of PLA greatly increased. Zhaobin et al.¹⁷ used ethylene bishydroxystearamide as a nucleating agent and found that ethylene bishydroxystearamide reduced the crystallization half-time of PLA. Recently, phthalimide and orotic acid have also been proven to be an effective nucleating agent of PLA.^{18,19}

Another active topic of research about PLA nucleating agents is stereocomplex (SC) crystallites.^{20,21} It is well known that low-content poly(D-lactic acid) (PDLA) blending with poly(L-lactic

Table I. Sample IDs and Components

Sample ID	PLA (%)	PEG (%)	Sample ID	PLA (%)	Talc (%)	Sample ID	PLA (%)	BBP (%)
PLA	100	0	PTa ₁	99	1	PBBP _{0.1}	99.9	0.1
PPEG _{2.5}	97.5	2.5	PTa ₂	98	2	PBBP _{0.2}	99.8	0.2
PPEG ₅	95	5	PTa ₃	97	3	PBBP _{0.3}	99.7	0.3
PPEG _{7.5}	92.5	7.5	PTa ₄	96	4	PBBP _{0.4}	99.6	0.4
PPEG ₁₀	90	10				PBBP _{0.5}	99.5	0.5
PPEG _{12.5}	87.5	12.5				PBBP ₁	99	1
Sample ID	PLA (%)	PEG (%)	Talc (%)	BBP (%)		PLA	PEG (%)	BBP (%)
				PBBP _{0.1} PEG ₅		94.9	5	0.1
				PBBP _{0.2} PEG ₅		94.8	5	0.2
PTa ₃ PEG ₅	92	5	3	PBBP _{0.3} PEG ₅		94.7	5	0.3
				PBBP _{0.5} PEG ₅		94.5	5	0.5

acid) (PLLA) will format SC crystallites, which have a much higher melting temperature. So, it has been thought to be a promising nucleating agent.²² Although the SC crystallite is an excellent nucleating agent for PLA, the cost is higher than that of other nucleating agents. In this study, a new nucleating agent with a benzoyl hydrazine compound was prepared, and we present the crystallization kinetics and crystallization morphology of PLA with the new nucleating agent [bibenzoylhydrazinepropane (BBP)]. We focus on the effect of the BBP and talc on the crystallization kinetics of PLA.

EXPERIMENTAL

Material Preparation

A commercial PLA, grade 3051D, was used in this study. It was a semicrystalline grade and was supplied by NatureWorks LLC that has a weight-average molecular weight of 160 kDa and is composed of about 3.3% β units. PEG was used as a PLA plasticizer and was supplied by GuoYao Group Chemical Reagent Co., Ltd. PEG had a molecular weight of 2000 g/mol and a melting point of 43°C. Talc was kindly supplied by KingPont Industry (Shanghai, China). BBP, a new nucleating agent, was prepared in our laboratory and consisted of a benzoyl hydrazine compound.

Sample Preparation

Preparation of BBP. An amount of 5.44 g of benzhydrazide was dissolved by 60 mL of dimethylformamide in a three-mouthed flask. An amount of 4.03 g of 1,3-dibromopropane was dissolved in 60 mL of dimethylformamide. The solution was mixed by a constant-voltage funnel with the temperature set at 70°C for a reaction time of 4 h. Then, BBP was obtained after five recrystallization times.

Preparation of the PLA Composites. Mixtures of PLA with various contents of PEG and nucleating agents were prepared on a 25-mm corotating twin-screw extruder. PLA was dried at 75°C for 4 h before extrusion. The temperature of the extruder was 140, 165, 170, 175, and 175°C in sequence. The die temperature was 170°C. The components of the samples are listed in Table I.

Measurements

Nonisothermal crystallization behavior of the samples was analyzed with a differential scanning calorimeter (DSC), Perki-

nElmer Diamond DSC, which was calibrated by the melting of indium and tin. The DSC scans were carried out in a flowing-nitrogen atmosphere.

The spherulitic growth in the films (thickness $\approx 3 \mu\text{m}$) was observed with an Olympus (Tokyo, Japan) polarization microscope (BX50) equipped with a heating-cooling stage and a temperature controller (Linkam LK-600PM) under a constant nitrogen gas flow. The crystallization of the films was performed as follows. The films were first heated to 200°C at 100°C/min, held at these temperatures for 3 min to destroy their thermal history, cooled at 100°C/min to an arbitrary T_c in the range 100–130°C, and then held at the T_c for 60 min.

Wide-angle X-ray diffraction (WAXD) measurement was carried out at room temperature with a Rigaku RINT-2000 diffractometer for all of the samples quenched from 200°C at a cooling rate of 2.5°C/min. Monochromatized Cu K α radiation ($\lambda = 0.154 \text{ nm}$) was transmitted through the sample.

RESULTS AND DISCUSSION

Nonisothermal Crystallization of PLA with Nucleating Agents and PEG

The nonisothermal crystallization thermograms of PLA/PEG 5% (PPEG₅) and PLA/Talc 3% (PTa₃) at various cooling rates are shown in Figure 1. As expected, with the increase of the cooling rate, the peak crystallization temperature upon cooling (T_p) shifted gradually to a low temperature; this is a common phenomenon for semicrystallization polymers because the polymer chains have enough time to arrange regularly at lower cooling rates, and the delay of response becomes apparent at high cooling rates. It was also found that the crystallization enthalpy upon cooling shrank with the cooling rate. As the cooling rate increased to 10°C/min, the exothermic peaks died down significantly, were hard find, and even disappeared. Evidently, the amorphous PLA chain did not have enough time to transfer to the crystallization sites with the higher cooling rate; this resulted in a decrease in the crystallization enthalpy upon cooling. The results also indicate that the crystallization rate of PLA was very slow, even with talc or PEG. This slowness could be attributed to two reasons: tardy nucleation and relatively low crystallization rates.¹³ According to Figure 1, the crystallinity of PLA/talc

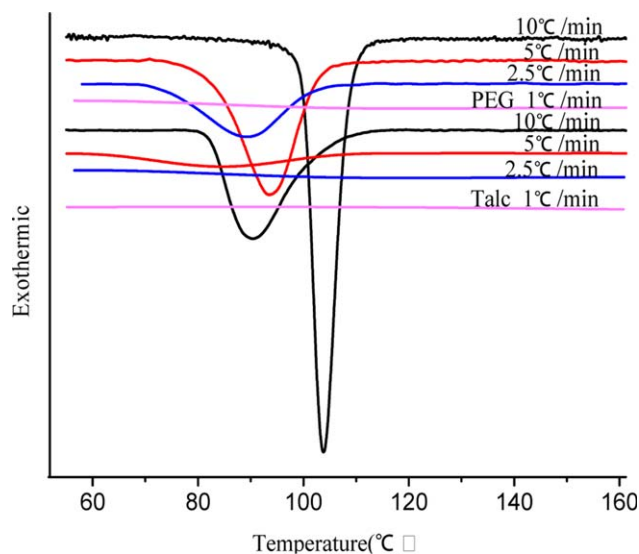


Figure 1. DSC thermograms of PPEG5 and PTa3 at different cooling rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was obviously larger than that of PLA/PEG. That is, the nucleation process was the rate-determining step; this was the primary hindrance during crystallization. So the important solution for accelerating the crystallization of PLA was the reduction of the induction time and the increase of its nucleation density by the addition of an effective nucleating agent. In this study, a new nucleating agent was prepared in our laboratory, and its basic structure is shown in Figure 2.

The effect of talc and BBP on the nonisothermal crystallization behavior of PLA was investigated. The DSC thermograms obtained for the cooling rate of 2.5°C/min with various composites are shown in Figure 3, and the parameters are listed in Table II. With the addition of talc, all of the samples exhibited an exothermal peak around 93.9–97.4°C; this peak should have been the T_p . T_p shifted to higher temperature, and the peak became stronger when the talc was increased. These results imply that the talc was an effective nucleating agent, and this agreed the results of previous authors.¹³ As expected, the pure PLA exhibited no T_p for the poor crystallization ability upon cooling. As the talc content increased up to 4 wt %, T_p was equal to 97.4°C, and the crystallinity was up to 20.8%. The effect of BBP on the nonisothermal crystallization kinetics of PLA are also shown in Figure 3. Compared with PLA/talc, the PLA/BBP composites showed a higher T_p , which was around 113°C. The BBP was more attractive for the PLA molecular chain, and surface nucleation occurred at a higher temperature than for PLA/talc. The crystallinity of PBBP_{0.2} was up to 31.5%. The data listed in Table II intimated that the nucleation efficiency of BBP was higher than that of talc. Another thing that

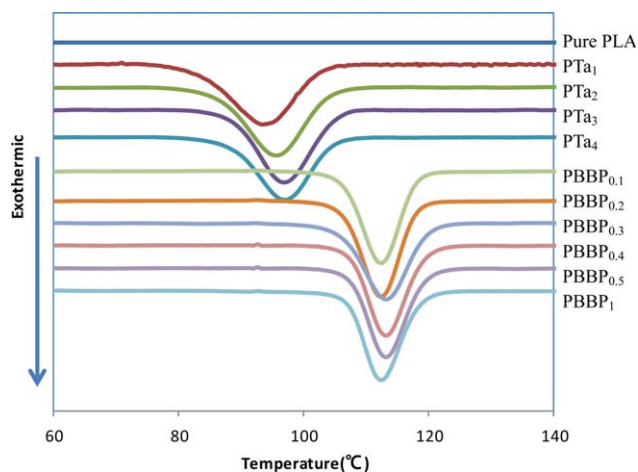


Figure 3. DSC thermograms of the PLA/talc and PLA/BBP composites at a cooling rate of 2.5°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

should be pointed out is that the content of talc shifted the T_p to a slightly higher temperature, whereas the content of BBP showed no significant impact on T_p . The exact T_p of the PLA composites are shown in Table II.

Figure 4 shows the DSC curve of PLA with or without PEG and nucleating agent; the cooling rate was 1°C/min. An abnormal phenomenon should be clarified in that PTa₃PEG₅ and PBBP_{0.5}PEG₅ exhibited better crystallization abilities than PTa₃ and PBBP_{0.5}. Usually, PEG acted as a plasticizer in the polymer and almost impaired the crystallization ability. However, the result shown in Figure 4 led us to the opposite conclusion. As shown in Figure 4, a very sharp T_p upon cooling was observed, and this peak shifted up to 110.0°C with 3 wt % talc and 5 wt % PEG concentrations. The crystallinity of PTa₃PEG₅ was up to 27.6%; this was higher than that of PPEG₅ (2.84%) and PTa₃ (23.6%), and the crystallization rate of PTa₃PEG₅ was the fastest among the samples. Talc generally nucleates the crystallization of polymers through an epitaxial mechanism.²³ The presence of PEG enhanced the segmental mobility of PLA and promoted the chain segments of PLA to transfer to the surface of the talc; this stimulated nuclei to be formed in the higher temperature range and faster spherulitic growth rate (G). The same trends could be found in the DSC curve of PLA/BBP/PEG, and the crystallinity of PBBP_{0.5}PEG₅ was very high, about 39.4%; this was higher than that of PPEG₅ or PBBP_{0.5} (33.4%) These results indicate a synergistic effect occurred to some extent by the combination of the plasticizer and the effective nucleating agent; this significantly broadened the crystallization window by increasing the nucleation rate in the upper temperature window and increasing the chain mobility in the lower temperature range. It was easy to find that the synergistic effect



Figure 2. Preparation of BBP.

Table II. T_p and X_t Values of the PLA/Talc and PLA/BBP Composites at a Cooling Rate 2.5°C/min

Sample	T_p (°C)	X_t (%)	$t_{1/2}$ (s)	Sample	T_p (°C)	X_t (%)	$t_{1/2}$ (s)
PTa ₁	93.9	17.2	362	PBBP _{0.1}	112.3	31.2	304
PTa ₂	96.3	19.8	349	PBBP _{0.2}	113.2	31.5	296
PTa ₃	96.9	20.5	346	PBBP _{0.3}	113.2	31.6	293
PTa ₄	97.4	20.8	344	PBBP _{0.4}	112.8	31.2	294
				PBBP _{0.5}	113.8	31.1	289
				PBBP ₁	112.5	33.0	286

$t_{1/2}$ half crystallization time.

in PBBP_{0.3}PEG₅ was stronger than that of PTa₃PEG₅; this was associated with the fact that the T_p of PBBP_{0.5} was very high for PLA. All of the crystallization parameters at different cooling rates are listed in Table III.

Nonisothermal Crystallization Kinetics of PLA with Nucleating Agents and PEG

To further analyze the crystallization kinetics of PLA/talc and PLA/BBP, different approaches were carried out for the analysis of the DSC curve. The relative degree of crystallinity (X_t) as a function of T_c was estimated according to the following equation:²⁴

$$X_t = \frac{\int_{T_0}^T (dH/dT) dT}{\int_{T_0}^{T_\infty} (dH/dT) dT} \quad (1)$$

where T_0 is the initial crystallization temperature; T and T_∞ are the crystallization temperature at time t and the ultimate crystallization temperature, respectively; and dH/dT is the heat flow rate. With eq. (2),²⁴ the temperature could be related to the crystallization timescale in nonisothermal crystallization:

$$t = \frac{T_0 - T_t}{\beta} \quad (2)$$

where β is the cooling rate, T_t is the instantaneous temperature.

Figure 5 shows the crystallization time dependence on the relative crystallinity of PBBP_{0.5}PEG₅ and PTa₃PEG₅ at different cooling rates. As expected, the crystallization time decreased and the crystallization rate increased with increasing cooling rate. It was easy to observe that higher cooling rate resulted in a higher relative crystallization rate.

Although the most common approach used to describe the overall isothermal crystallization is the Avrami equation, the Avrami exponent (n) has different physical meanings because of the instantaneous temperature changes over the course of nonisothermal crystallization. In this study, the Avrami equation was considered to be inapplicable and is not discussed. A previous publication reported the combination of Avrami equation and Ozawa equation on the basis of a mathematical method:²⁵

Table III. Crystallization Parameters of the PLA/Talc and PLA/BBP at Different Cooling Rates

Sample	β (°C/min)	T_p (°C)	ΔH_c (J/g)	X_t (%)
PTa ₃	1	106.2	21.3	23.6
	2.5	97.9	18.5	20.5
	5	91.3	6.8	7.5
	10	—	—	—
PBBP _{0.5}	1	121.1	30.9	33.4
	2.5	113.2	28.8	31.1
	5	107.3	25.9	28.0
	10	102.7	11.8	12.8
PTa ₃ PEG ₅	1	110.3	23.7	27.6
	2.5	102.6	21.5	25.1
	5	93.6	20.6	24.1
	10	86.2	14.4	16.8
PBBP _{0.5} PEG ₅	1	123.2	34.7	39.4
	2.5	116.7	31.3	35.6
	5	112.1	31.1	35.4
	10	105.3	30.8	35.0

β , cooling rate. A dash indicates that there was no peak. ΔH_c is the heat flow, X_t is the degree of crystallization.

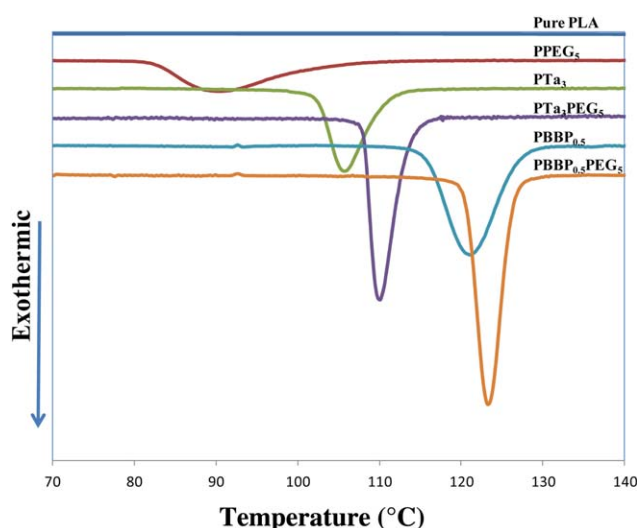


Figure 4. DSC thermograms of PLA, PPEG₅, PTa₃, PTa₃PEG₅, PBBP_{0.5}, and PBBP_{0.5}PEG₅ at a cooling rate of 1°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

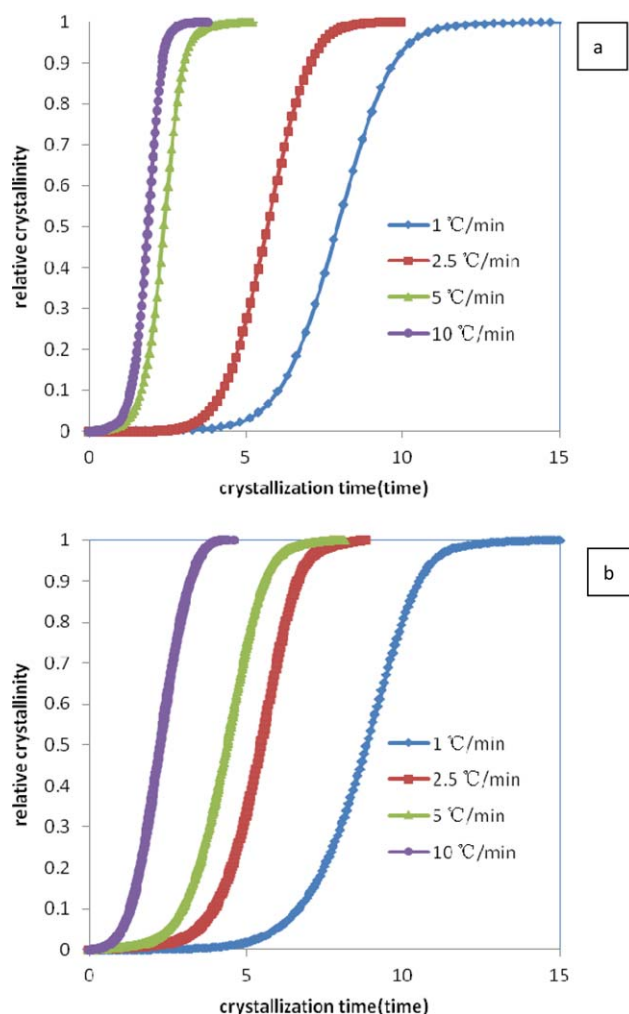


Figure 5. Variation of X_t with time for the nonisothermal crystallization of (a) PTa_3PEG_5 and (b) $\text{PBBP}_{0.5}\text{PEG}_5$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\log Z_t + n \log t = \log [K(T)] - m \log \beta \quad (3)$$

Z_t is a composite rate constant involving both nucleation and growth rate parameters. $K(T)$ is cooling or heating function.

$$\log \beta = \log [F(T)] - \alpha \log t \quad (4)$$

where the parameter $F(T) = [K(T)/k]^{1/m}$ refers to the cooling rate that needs to reach a defined relative crystallinity at unit crystallization time and $\alpha = n/m$ is the ratio between n and the Ozawa exponent (m). k is the crystallization rate constant. The

values of α and $F(T)$ are tabulated in Table IV. According to the physical meaning of $F(T)$, the value of $F(T)$ mainly reflects the crystallization facilitation effect of the nucleation agents on the matrix. So, the smaller value of $F(T)$ indicated a better nucleation efficiency. As shown in Table IV, it was easy to determine the value of $F(T)$, which monotonically increased with increasing relative crystallinity for PTa_3PEG_5 and $\text{PBBP}_{0.5}\text{PEG}_5$. The values of $F(T)$ of $\text{PBBP}_{0.5}\text{PEG}_5$ were usually smaller than those obtained for PTa_3PEG_5 ; this confirmed that the nucleating efficiency of BBP was better than that of talc. So, this result was the same as that from the previous conclusion.

Isothermal Crystallization Morphology of PLA with Nucleating Agents and PEG

The isothermal crystallization morphology of the PLA/talc and PLA/BBP composites, especially the spherulitic radius, was studied in the temperature range from 90 to 125 °C by means of polarized optical microscopy. Figure 6 shows the spherulitic morphology of PLA, PPEG_5 , PTa_3PEG_5 , and $\text{PBBP}_{0.5}\text{PEG}_5$ during isothermal crystallization at different temperatures. Although all of the samples showed a Maltese cross pattern, the spherulitic size and spherulitic density were totally different each other.²⁶ At 90 °C and 17 min, some well-defined spherulites were observed in the PPEG_5 film, whereas few spherulites were formed in the pure PLA film, even at crystallization times up to 38 min. These results reoffer the evidence that the pure PLA was almost not crystallized; this was in agreement with the results of DSC. With the addition of talc and BBP, many small spherulites were observed in the early stages of crystallization. Large spherulites, sized about 100 μm in diameter, were seen in PPEG_5 , whereas the diameter of the spherulites in the PTa_3PEG_5 and $\text{PBBP}_{0.5}\text{PEG}_5$ composites were around 55 and 40 μm , respectively. Meanwhile, the nucleation density for $\text{PBBP}_{0.5}\text{PEG}_5$ was higher than that of PTa_3PEG_5 . This result confirmed the fact that both talc and BBP increased the nucleus number of the PLA spherulites and that the nucleation efficiency of BBP was better than that of talc. This supported the DSC results shown in Figure 2. Moreover, it was interesting to note that the spherulites of PTa_3PEG_5 were very unevenly distributed and many spherulites impinged on each other. However, the spherulitic distribution in $\text{PBBP}_{0.5}\text{PEG}_5$ was more uniform.

Figure 7 shows the dependence of the spherulitic diameter from Figure 6 on the crystallization time. As shown in Figure 7, we found that G in $\text{PBBP}_{0.5}\text{PEG}_5$ was the fastest among those of all of the samples; this was associated with the higher T_c and higher chain segment mobility. As expected, G of pure PLA was

Table IV. Nonisothermal Crystallization Kinetic Parameters for the PTa_3PEG_5 and $\text{PBBP}_{0.5}\text{PEG}_5$ Blends at Different X_t Values by a Combination of a Modified Avrami–Ozawa Equation

Sample	X_t (%)	α	$F(T)$	Sample	X_t (%)	α	$F(T)$
PTa_3PEG_5	0.02	0.94	7.16	$\text{PBBP}_{0.5}\text{PEG}_5$	0.02	0.80	5.36
	0.20	0.73	9.58		0.20	0.70	7.39
	0.40	0.67	10.47		0.40	0.70	8.38
	0.60	0.63	11.18		0.60	0.68	9.06
	0.80	0.59	11.82		0.80	0.68	9.99

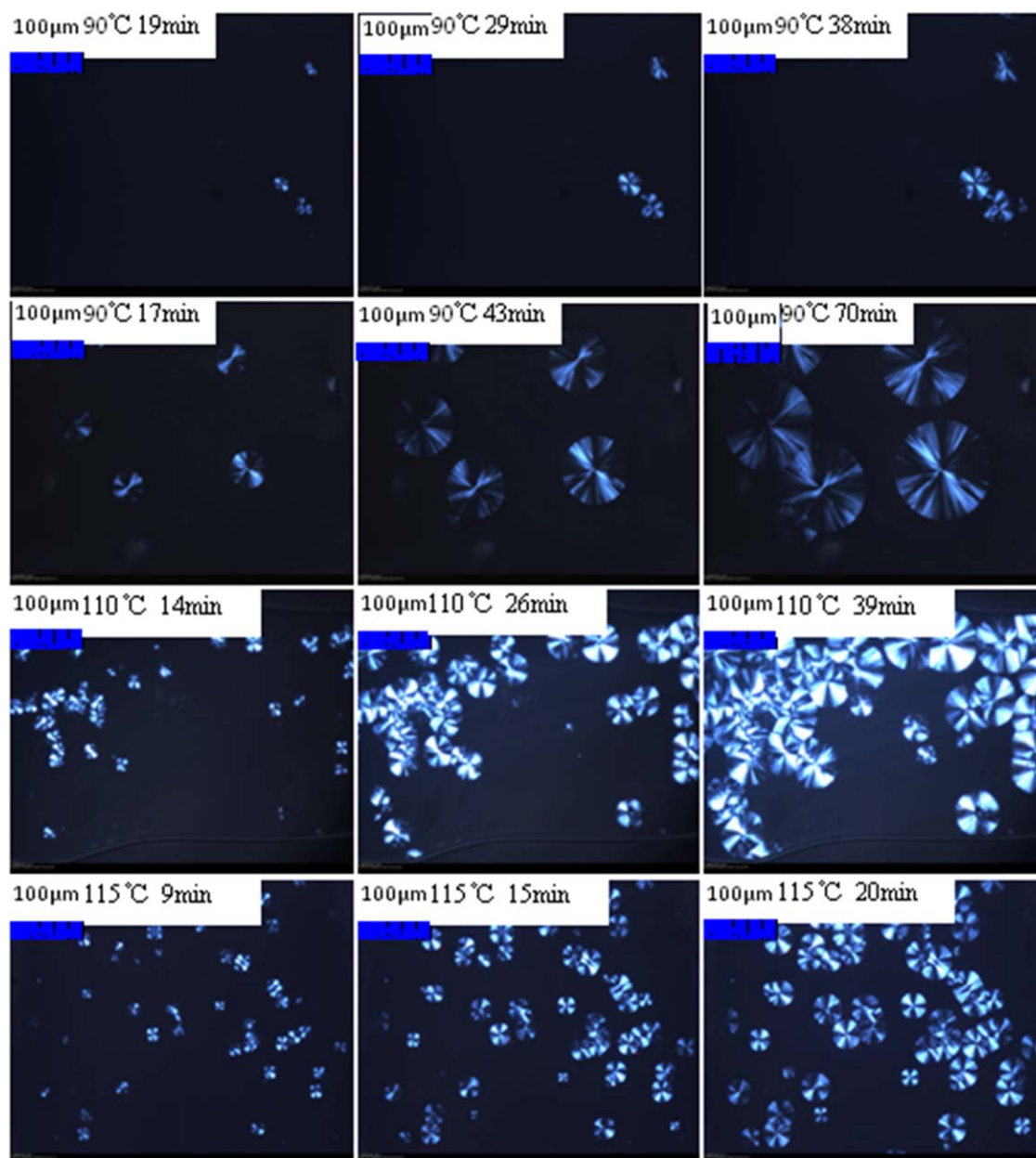


Figure 6. Polarization photomicrographs of the final morphologies of (a) PLA, (b) PPEG₅, (c) PTa₃PEG₅, and (d) PNA_{0.5}PEG₅. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the slowest. However, G in PPEG₅ was higher than that in PTa₃PEG₅; this may have been associated with the lower density of the spherulites in PPEG₅. The induction time of all of the samples were compared by extension of the tendency line to the opposite. The induction times of PBBP_{0.5}PEG₅ and PTa₃PEG₅ were very short, only 1–2 min, whereas the reduction of pure PLA was very long, over 17 min. These results confirmed the nucleation efficiencies of BBP and talc.

Figure 8 gives the spherulitic diameter of the PBBP_{0.5}PEG₅ films as a function of the crystallization time at different T_c 's. The spherulites of PBBP_{0.5}PEG₅ were observed at a temperature 100°C, but a too-high density and more rapid growth completion of the spherulites disturbed the evaluation of the time

change of the radii. It was easy to find that the spherulites for the PBBP_{0.5}PEG₅ films grew linearly with time, regardless of the T_c or impingements between the spherulites. In fact, impingements between spherulites were very common after 2000 s, but the impingements had a negligible effect on G , according to Figure 8. The G values were estimated from the slope of the spherulitic diameter in Figure 8, and the obtained G values were plotted in Figures 9 as a function of T_c . The G curves showed a well-known bell-shaped temperature dependence, as reported by previous authors.²⁷ However, the G values obviously deviated from the model when T_c was lower than 110°C; this was associated with the different nucleation densities at different temperatures. According to the chain sliding diffusion theory of

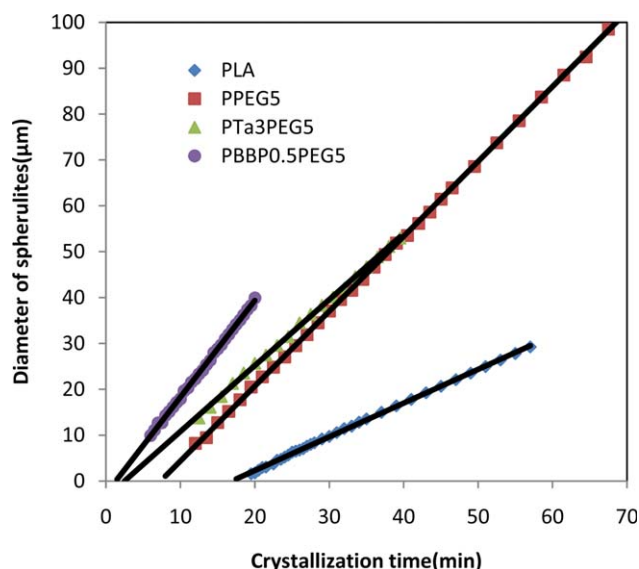


Figure 7. Changes in the spherulitic diameter as a function of the time for PLA, PPEG₅, PTa₃PEG₅, and PBBP_{0.5}PEG₅. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nucleation,²⁸ the nucleation rate is a function of the supercooling degree. According to Figure 9, the G of PBBP_{0.5}PEG₅ films had maximum values of 1.67 $\mu\text{m}/\text{min}$ around 120°C, whereas no spherulitic growth was observed at T_c 's exceeding 130°C.

Influence of Talc and BBP on the Crystallization Form of PLA

WAXD was used to examine the crystal form in PLA/talc and PLA/BBP in this study. Figure 10 shows the WAXD patterns of PLA/talc, PLA/BBP, and neat PLA crystallized at a cooling rate of 2.5°C/min. The neat PLA sample showed a small peak with a maximum at 16.5°; this indicated that the sample was almost amorphous. The patterns of PLA/talc and PLA/BBP were similar

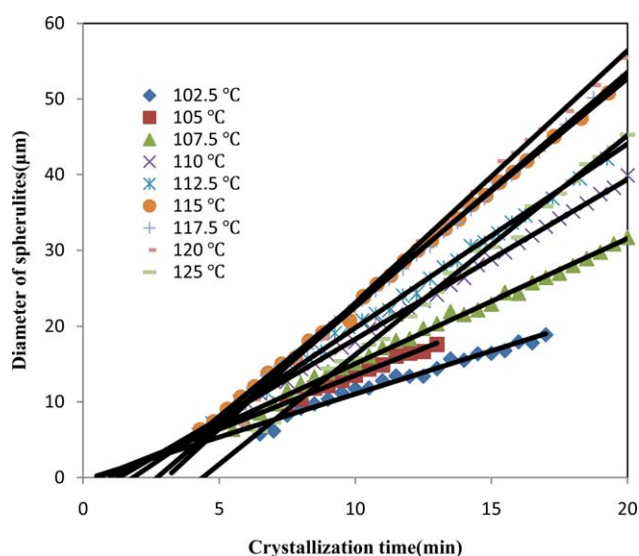


Figure 8. Changes in the spherulitic diameter as a function of the time for PBBP_{0.5}PEG₅ at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

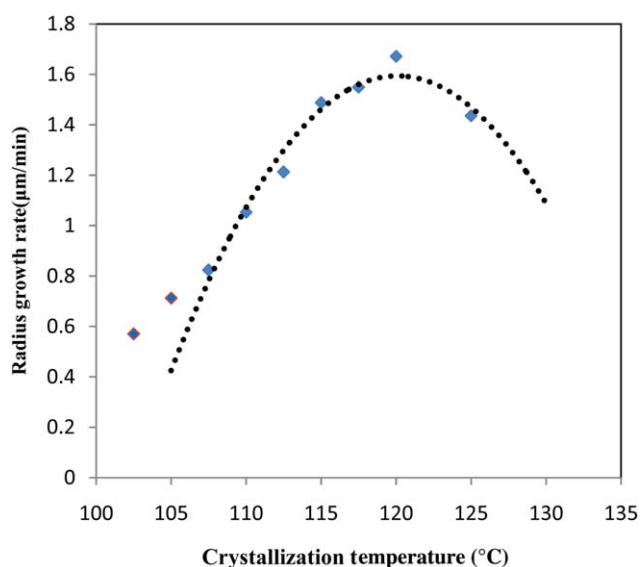


Figure 9. Changes in G as a function of the temperature for PBBP_{0.5}PEG₅. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and showed several strong diffraction peaks ($2\theta = 16.6, 18.9,$ and 22.2°); this revealed that they were both the α -form crystal of PLA,²⁹ and they crystallized well after cooling at a rate of 2.5°C/min. This indicated that the α -form crystallite of PLA did not change upon the addition of talc and BBP. However, one weak diffraction peak was observed around 28.5° in PTa₃PEG₅, and we could not explain why this peak appeared in this sample.

CONCLUSIONS

The effects of BBP and talc on the crystallization behavior of PLA were investigated extensively with DSC and polarized optical microscopy. As a nucleating agent, BBP was better than talc. PEG improved the crystallization ability of PLA/BBP and PLA/

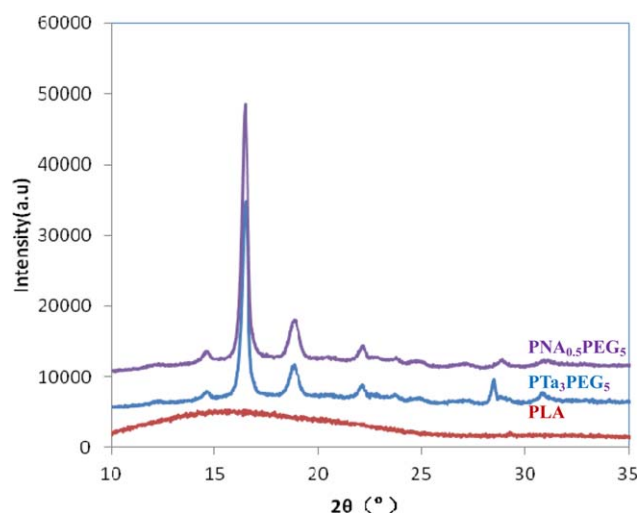


Figure 10. XRD patterns of PLA, PTa₃PEG₅, and PBBP_{0.5}PEG₅. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tal, although it was a plasticizer for PLA. The T_c and crystallinity of PLA/BBP/PEG was higher than that of PLA/talc/PEG. Meanwhile, the G of PBBP_{0.5}PEG₅ was higher than that of PTA₃-PEG₅; this was associated with the higher T_c . However, the G of PPEG₅ was also higher than that of PTA₃PEG₅, and this was associated with the lower density of the spherulites. The WAXD patterns confirmed that both BBP and talc did not change the crystal form in PLA.

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