Isothermal Crystallization Kinetics and Crystal Structure of Poly(lactic acid): Effect of Triphenyl Phosphate and Talc

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ABSTRACT: In this article, kinetics of neat poly(lactic acid) (PLA) and its blends with triphenyl phosphate (TPP) and/or talc crystallized isothermally in the temperature range of 113–128°C was analyzed by differential scanning calorimetry (DSC) and described by the Avrami equation. The results showed that the average value of Avrami exponents n is around 2.0 for neat PLA and the PLA/15TPP blend, and around 3.0 for the PLA/1.2Talc blend and the PLA/15TPP/1.2Talc blend. The crystallization rate constants k for neat PLA and its blends were increased in the following order: the PLA/15TPP blend, neat PLA, the PLA/15TPP/1.2Talc blend, and PLA/1.2Talc blend. The half-time of crystallization $t_{1/2}$ was increased with an increase of crystallization temperature T_c and the presence of TPP, and was decreased sharply with the incorporation of talc. Further investigation into crystallization activation energy ΔE_a of neat PLA and its blends with 15 wt % TPP and/or 1.2 wt % talc showed that the values of ΔE_a were increased with the incorporation of TPP and/or talc compared to that of neat PLA. It was verified by wide angle X-ray diffraction (WAXD) that neat PLA and its blends with TPP and/or talc crystallized isothermally in the temperature range of 113–128°C, and all formed the α-form crystal after enough annealing time. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3558–3569, 2010

Key words: biodegradable polymer; plasticizer; nucleating agent; crystallization kinetics; crystal structure

INTRODUCTION

Poly(lactic acid) (PLA) is an aliphatic biodegradable polymer which can be produced from annually renewable resources. This fact is responsible for a growing interest in many applications for PLA, as it is expected to reduce an impact on the environment caused by the production and utilization of petrochemical polymers. Although expensive in the past, PLA becomes more competitive due to a recent development in polymerization technology.[1] Moreover, the expected rise in the cost of petroleum based commodities in the next decades opens a bright perspective for this material.

PLA has high mechanical properties, thermoplasticity and biocompatibility, and is readily fabricated, thus being a promising polymer for various end-use applications.[2-6] However, PLA is a slowly crystallizing material, similar to poly(ethylene terephthalate) (PET), so PLA has poor processability. In many applications, increasing the crystallization rate of PLA is desired since in its amorphous form, the range of application of PLA is severely limited by its low glass transition temperature (T_g). Many attempts have been made to increase the crystallization rate of PLA. The extent and the rate of PLA crystallization is related to its microstructure.[7,8] Improvement of crystallization rate of PLA can also be obtained by adding nucleating agent, such as talc, organically treated montmorillonite (MMT) clay and poly(D-lactide) (PDLA), which increases the nucleation density and decrease the half-time of crystallization and the time to complete crystallization of PLA.[7-10] Research has shown that PDLA is more effective nucleating agent for PLA than talc.[9] However, a high production cost of PDLA is the bottleneck of the materials. Clay is less effective than talc as nucleating agents for PLA.[11] Recently, research efforts have shown that organic compounds, such as a series of organic compounds having hydrazide end-groups and an

aliphatic amide (AA), namely *N,N*-ethylenebis(12-hydroxystearamide) can greatly increase nucleation density and overall crystallization rate of PLA.[12,13] Unfortunately, these compounds are not readily available as they have only been synthesized at the laboratory scale.

Another shortcoming of PLA was low flexibility and impact resistance. Therefore, considerable efforts have been made to improve the properties of PLA. One of these attempts was carried out by means of plasticization. Various types of plasticizers, such as poly(ethylene glycol) (PEG),[14-19] poly(propylene glycol) (PPG),[20,21] oligomeric lactic acid (OLA),[15] glycerol,[15] and triphenyl phosphate (TPP)[22] were used to improve the flexibility and impact resistance of PLA. PEG is the most studied plasticizer for PLA, and the efficiency of plasticization was increased with decreasing molecular weight of PEG. Glycerol was the least efficient plasticizer, and OLA and the lower molecular weight PEG (PEG 400) gave the best result.[23] In our previous article,[22] for the first time, the plasticizing effect of TPP on PLA had been published. The T_gs of PLA were decreased from 60.7°C for neat PLA to 46.9, 34.2, and 21.5°C for PLA/TPP blends with 10, 20, and 30 wt % TPP, respectively.

Crystallization kinetics of plasticized PLA has been reported, and results showed that the addition of plasticizer into PLA accelerates the growth rate of spherulite.[23,24] Galeski et al. investigated the effect of two platicizers including PPG and PEG on the spherulite growth rate of PLA, and found that two plasticizers used all increased the spherulite growth rate at 90°C by the factor of 3–24, but enhancement of the growth rate by PPG is smaller than PEG.[25] In our study, the results showed that the maximum growth rate of spherulite of plasticized PLA was increased compared with that of neat PLA, but the temperature corresponding to the maximum growth rates was shifted to lower one with increasing TPP content.[22] Huneault et al.[26] investigated the effect of nucleation and plasticization on the crystalline content developed in nonisothermal conditions systematically. The nucleating agents including talc, sodium stearate, and calcium lactate and plasticizer such as acetyl triethyl citrate (ATC) and PEG were applied, respectively. The results showed that the combination of nucleating agent and plasticizer is necessary to develop significant crystallinity at high cooling rate.

PLA can crystallize in α, β, γ-forms, depending on the processing conditions.[27-34] The most common and stable polymorph can be developed from the melt or solution under normal conditions.[27] The α form grows upon the normal conditions such as the melt, cold, or solution crystallization.[28] Several research groups[35-38] investigated by means of infrared spectroscopy (IR) and wide-angle X-ray scattering (WAXS) the crystal structure of PLA crystallized at different temperatures, and found a new crystal, namely, α'-form, which is a "disordered crystal" having the same conformation as that in α form but a loose packing manner compared to the α form (order crystal). The transformation from α' to α takes place possibly via a solid-phase transition, without the melting-recrystallization process.[35,38] The α'-form crystal was formed when T_c was below 110°C, the α-form crystal was formed when T_c was above 120°C, and the mixture of α' and α-form crystal was formed when 110°C $\leq T_c \leq$ 120°C. The α'-to-α transition can occur, which depends on the annealing period and temperature.[35,38]

In this article, TPP and talc are used as plasticizer and nucleating agent for PLA, respectively, the addition of both 15 wt % TPP and 1.2 wt % talc not only improves flexibility and impact resistance of PLA, but accelerates its crystallization. Up to now, less work has been done to examine the combination effect of nucleation and plasticization on the isothermal crystallization kinetics. Our study is focused mainly on the isothermal crystallization kinetics and crystal structure of neat PLA and its blends with plasticizer and/or nucleating agent. It is well known that the crystallinity and crystal structure play an important role in the physical properties. It is expected that these results will be helpful for a better understanding the combined effect of plasticizer and/or nucleating agent on crystallization behavior of PLA.

EXPERIMENTAL

Materials

The commercial PLA in pellet form (NatureWorks PLA 4032D) exhibits a density of 1.25 g/cm^3, a weight-average molecular weight of 207 kDa, polydispersity of 1.74 (gel permeation chromatography analysis), and a glass transition temperature and melting point of 60°C and 168°C [differential scanning calorimeter (DSC) analysis], respectively. TPP (C.P. grade; Kelong Chemical Reagent Factory, Chengdu, China) was used as plasticizer for PLA, which has a molecular weight of 326.3 g/mol and a melting point of 48°C. Talc (Shanghai CNPC Power Material, Shanghai, China) with the average size of 400 meshes was used as nucleating agent for PLA.

Sample preparation

The neat PLA was predried in vacuum oven at 80°C for 24 h before using. Neat PLA, PLA blends with 15 wt % TPP, 1.2 wt % talc, and both 15 wt % TPP and 1.2 wt % talc were mixed together in Haake internal mixer (Rheomix600P, Germany) with Roller-Rotors R600 for 3 min. The mixing rollers were maintained at 90 rpm, and the temperature was set

at 185°C. The prepared samples were marked as PLA, PLA/15TPP, PLA/1.2Talc, and PLA/15TPP/1.2Talc, respectively. The melts were compressed to films with a thickness of around 0.2 mm for 3 min at 185°C and 10 MPa for neat PLA and its blends, respectively.

Thermal analysis

The thermal characteristics of the neat PLA and its blends was determined using a differential scanning calorimeter (DSC Q100, TA instrument) in nitrogen atmosphere (circulation). Samples (ca. 10 mg) were placed in sealed aluminum pans. For each sample, the following thermal cycles were applied: a first scan was made from room temperature to 185°C and maintained at this temperature for 3 min to destroy any thermal history. Then samples were cooled to different crystallization temperatures (113, 116, 119, 122, 125, and 128°C) at a rate of 50°C/min, and remained isothermal until the crystallization was completed. Finally, the samples were heated from the given crystallization temperature (T_c) to 200°C at a heating rate of 10°C/min. A nitrogen gas flow at a rate of 50 mL/min was maintained throughout the test. The melting temperature (T_m) was determined in the second heating scan.

The equilibrium melting temperature (T_m^0) of neat and plasticized PLA are determined by extrapolation to the lines of $T_m = T_c$ according to the Hoffman–Weeks equation.[39] Samples were heated to 185°C, maintained for 3 min, cooled down at a rate of 50°C/min and then crystallized in the temperature range of 115–150°C. At each temperature, annealing lasted 10 h in nitrogen atmosphere, the samples were cooled down to room temperature at a rate of 40°C/min and then were heated to 200°C at a rate of 10°C/min for the determination of the melting point.

Polarized optical microscopy

A polarizing optical microscope (Olympus BX51) equipped with a Linkam THMSE 600 hot stage was used to investigate the spherulitic morphology and the size of PLA. The samples were first placed between glass slides and melt on a hot stage at 185°C for 3 min and then rapidly cooled down to a preset crystallization temperature (T_c). The annealing lasted the given time.

Wide-angle X-ray diffraction

Before measurement isothermal crystallization of the thin film samples was performed on a hot stage in polarizing optical microscope, and crystallization time and sample-preparing procedure were in good

agreement with that in DSC measurement. X-ray scattering was used to probe the crystal structure of neat PLA and its blends. Thin film samples were analyzed using a WAXD apparatus (Shimadu XRD-6000) by Cu Kα (λ = 0.154 nm) radiation under a voltage of 35 kV and a current of 25 mA. Diffraction intensities were counted at 0.02° steps, and the scanning speed was 5°/min. The spectra are recorded in an angular range 5° < 2θ <40° at room temperature.

RESULTS AND DISCUSSION

Equilibrium melting point

Figure 1 shows the Hoffman–Weeks plots of neat PLA and its blends. The equilibrium melting point (T_m^0) was obtained from the intersection of this line with the $T_m = T_c$ equation. The T_m^0 for neat PLA was about 192.8°C, which was lower than previously reported values in the range from 198 to 212°C by Tsuji with different procedures.[40] The T_m^0 decreased with the presence of TPP and/or talc, and the maximum extent of this melting point depression was about 8.6°C in the PLA/15TPP blend, where T_m^0 was 184.2°C. The T_m^0 of neat PLA was higher than that of PLA in blends containing 15 wt % TPP and/or 1.2 wt % talc, the T_m^0 of neat PLA and its blends was decreased in the following order: neat PLA, the PLA/15TPP/1.2Talc blend, the PLA/1.2Talc blend, and the PLA/15TPP blend. Generally, melting point depression of PLA in blends is a result of kinetic, morphology, and dynamic. Thermodynamic factor is due to thermodynamics of mixing, and the addition of the TPP and/or talc decreases the chemical potential of the crystallizable polymer, resulting in melting point depression. The morphological contribution arises from the degree of perfection and finite size of the crystallites, and the incorporation of TPP
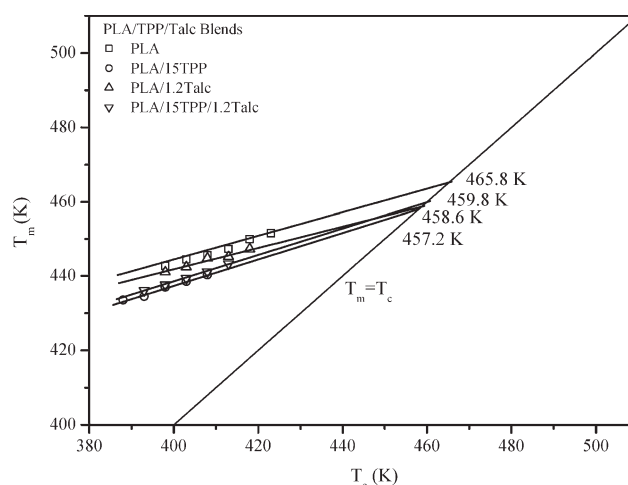

Figure 1 Hoffman–Weeks plots for neat PLA and its blends.
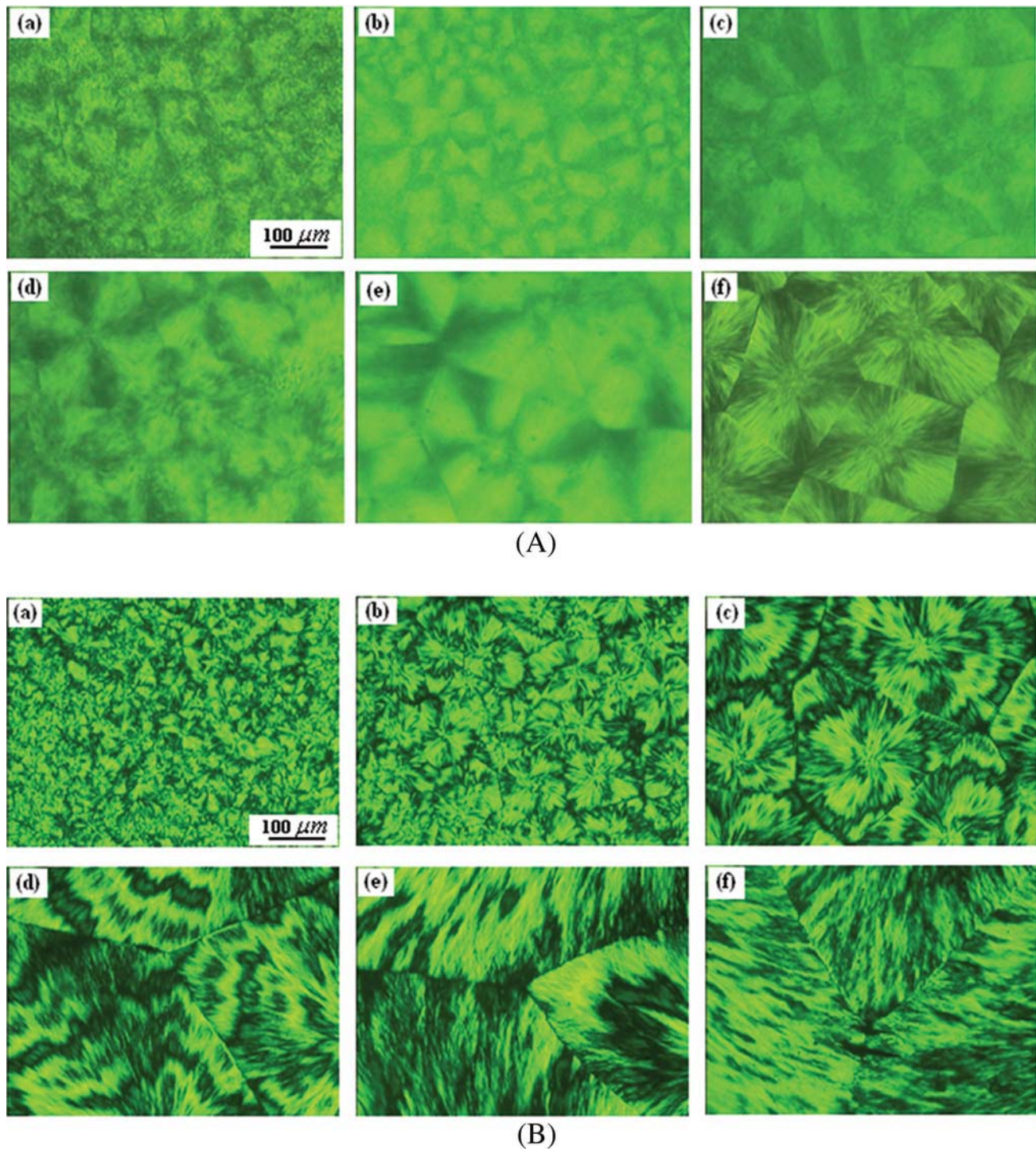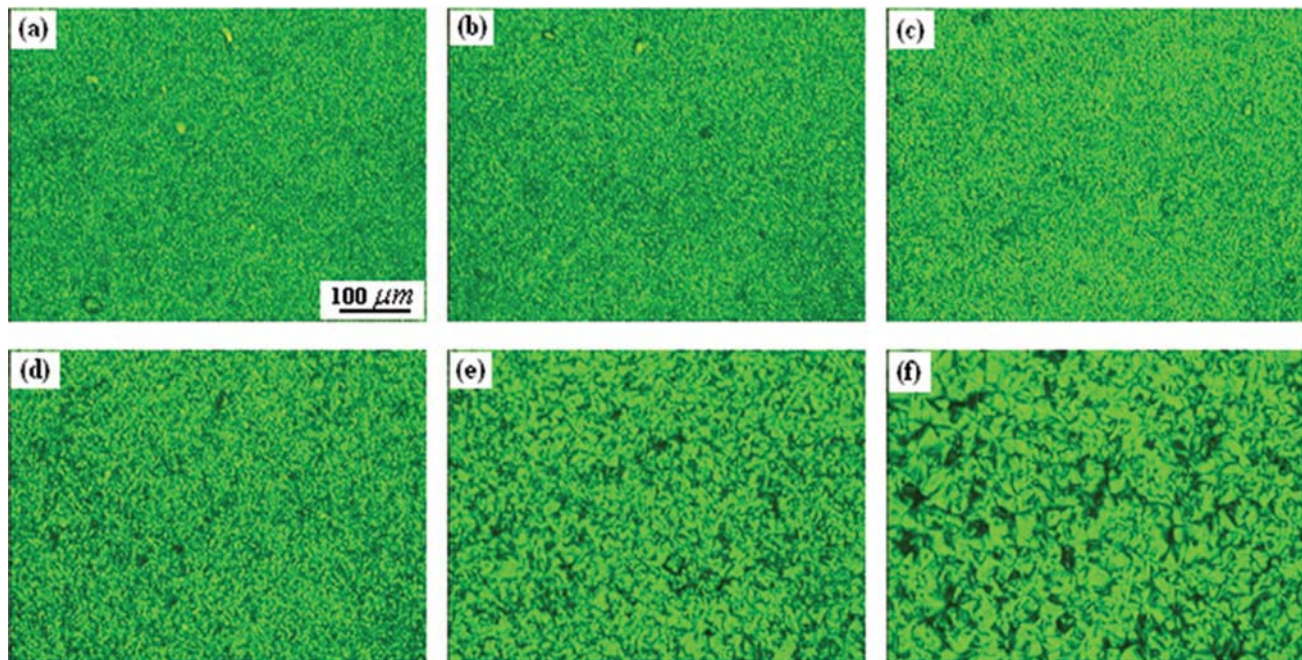
Figure 2 Polarizing optical micrographs of neat PLA (A), the PLA/15TPP blend (B), the PLA/1.2Talc blend (C), and PLA/15TPP/1.2Talc blend (D) crystallized isothermally at different temperatures: (a) 113°C; (b) 116°C; (c) 119°C; (d) 122°C; (e) 125°C, and (f) 128°C, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
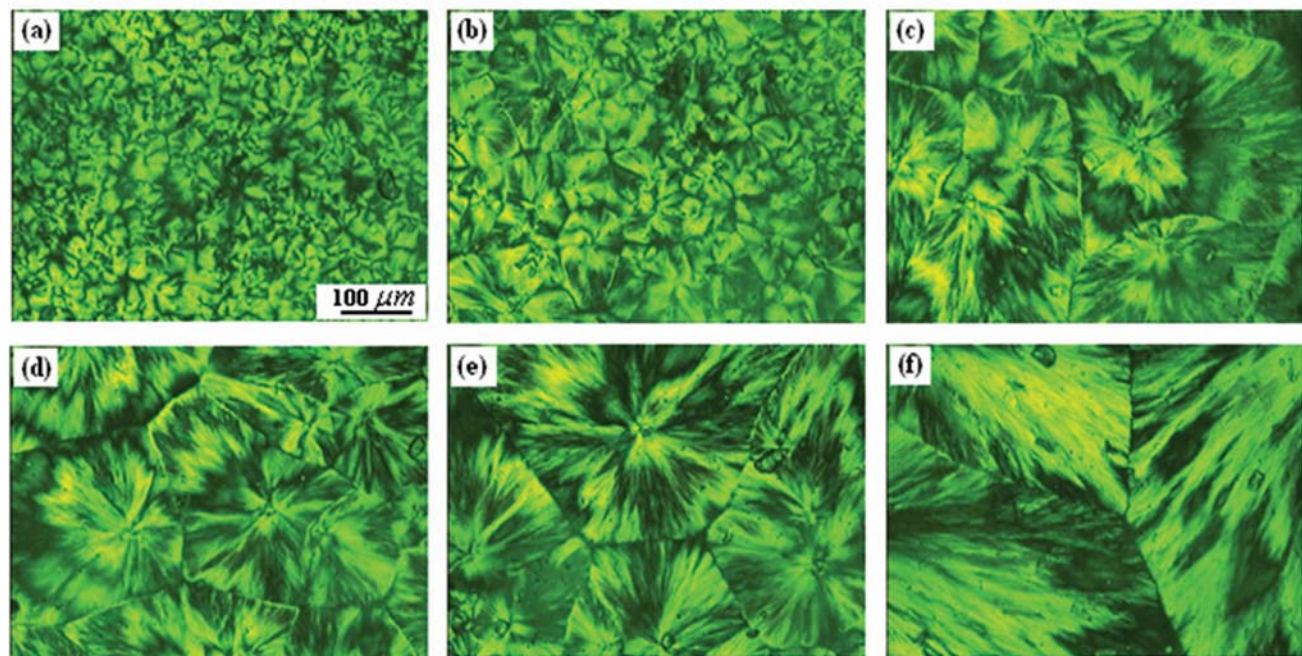
and talc decreases the perfection and the size of PLA crystallites, respectively, which depresses the melting point of PLA. Additionally, the melting point depression of PLA in blends might be related to the molecular weight of PLA used and experimental parameters.

Spherulitic size

Neat PLA and its blends with TPP and/or talc crystallized isothermally at the temperature ranging from 113°C to 128°C, and the impinged spherulitic morphology and size of PLA are shown in Figure 2(a–d).

Figure 2 (*Continued from the previous page*)

As shown in Figure 2(A–D), for neat PLA and its blends, the size of spherulite was all increased with the increase of crystallization temperature, indicating that the nucleation density was decreased. At the same crystallization temperature, in comparison with the neat PLA, the size of spherulite was increased with the incorporation of TPP, while decreased with the addition of talc. It can be concluded that on the one hand, the incorporation of TPP can increase the spherulitic growth rate of PLA,[22,25] on the other hand, decreased the nucleation density. The latter might play a dominant role. In the case of the PLA/1.2Talc blend, talc was acted as nucleating site for PLA crystallization, increased the number of crystal nuclei, and spherulites impinge into each other easily due to more crystal nuclei and space confinement, leading to smaller and denser spherulites. For the PLA/15TPP/1.2Talc blend, the size of spherulite
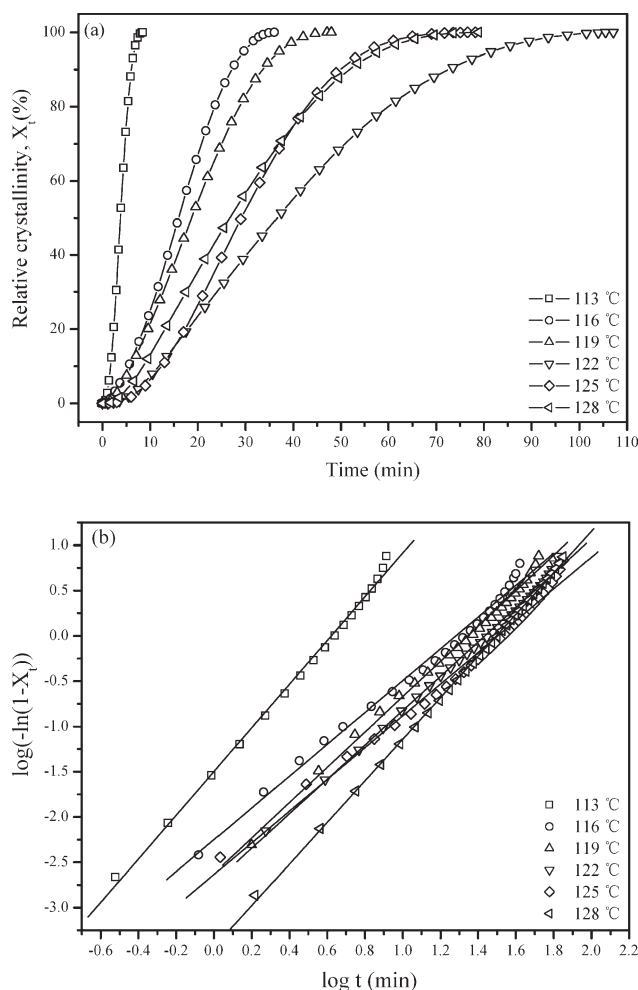
Figure 3 (a) Plots of relative crystallinity as a function of crystallization time for neat PLA at 113°C–128°C and (b) Avrami plots for neat PLA at 113–128°C.

mainly depends on two facts: the incorporation of TPP accelerates the spherulitic growth rate, and decreases the nucleation density; while talc increase the nucleation density significantly. The size of spherulite is the combination effect of above factors. For the PLA/15TPP/1.2Talc blend, the effect in the former might play a dominant role for the size of spherulite, so the size of spherulite is larger than that in the neat PLA and the PLA/1.2Talc blend. In comparison with the PLA/TPP blend, the size of PLA spherulite in the PLA/15TPP/1.2Talc blend decreases slightly due to the result in the latter.

Crystallization kinetics

The melting neat PLA and its blends with 15 TPP and/or 1.2 wt % talc were cooled down to a predetermined crystallization temperature (T_c) at a rate of 50°C/min, and the isothermal crystallization was performed in the temperature range of 113–128°C for various crystallization times. The plots of the rel-

ative crystallinity X_t versus the crystallization time t are shown in Figures 3(a), 4(a), 5(a), and 6(a). As expected, the crystallization time of neat PLA and its blends at high crystallization temperature was longer than that at low one. In comparison with neat PLA, it was found that the crystallization time of PLA was lengthened due to the addition of TPP, while the incorporation of talc shortened crystallization time. The crystallization time of neat PLA and its blends was increased in the following order: the PLA/1.2Talc blend, the PLA/15TPP/1.2Talc blend, neat PLA, and the PLA/15TPP blend. The variation of the crystallization time indicates that talc accelerates the crystallization rate of PLA, while TPP decreases the crystallization rate of PLA, which might be related to four factors: first, the addition of TPP decreased T_g of PLA, and therefore increased the chain mobility of PLA. Second, the addition of talc greatly increases the nucleating site for PLA crystallization, so increases the nucleation density and the rate of crystal nuclei formation. Third, the
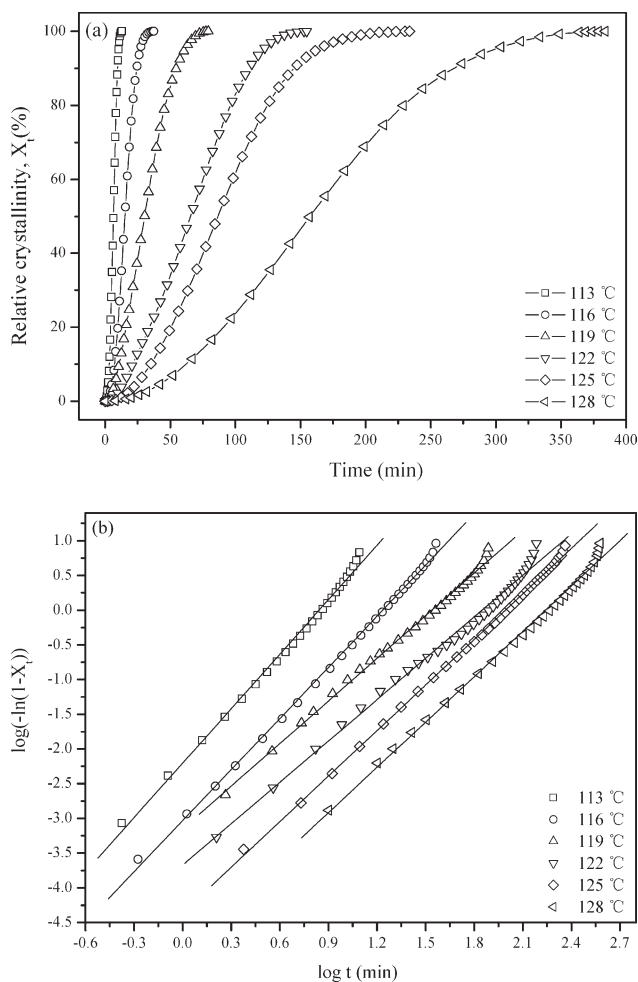

Figure 4 (a) Plots of relative crystallinity as a function of crystallization time for the PLA/15TPP blend at 113–128°C and (b) Avrami plots for the PLA/15TPP blend at 113–128°C.
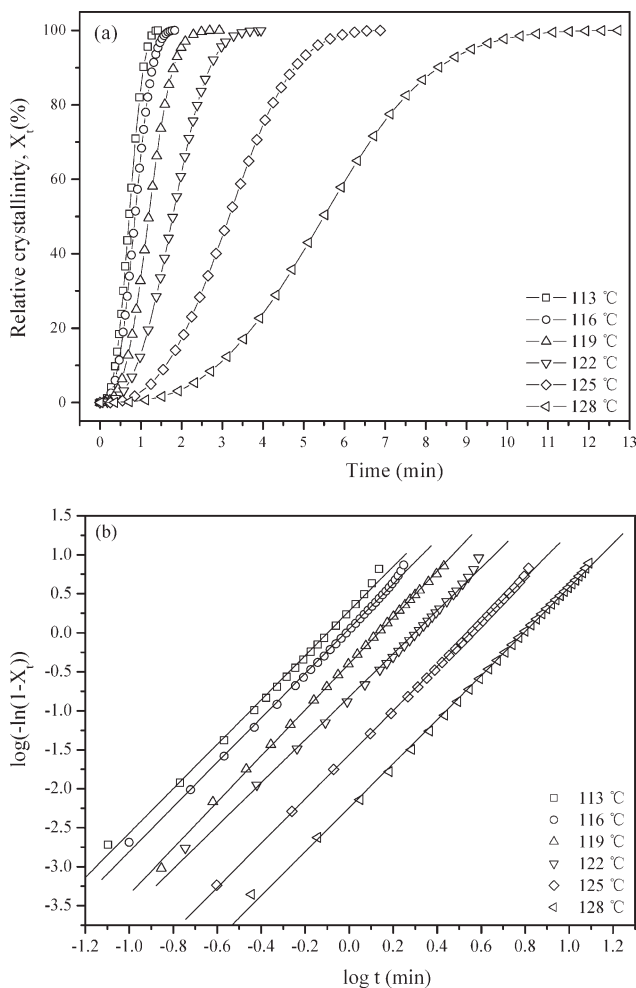
Figure 5 (a) Plots of relative crystallinity as a function of crystallization time for the PLA/1.2Talc blend at 113–128°C and (b) Avrami plots for the PLA/1.2Talc blend at 113–128°C.

added TPP is a diluent to PLA, resulting in the dilution of PLA chains at the spherulite growth front. Fourth, the decrease of the degree of supercooling, i.e., the difference between equilibrium melting point T_m^0 and crystallization temperature T_c, depressed at the same crystallization temperature due to the incorporation of TPP and/or talc, which decreases the growth rate of spherulite. The crystallization time for PLA blend containing TPP was lengthened, indicating that two factors in the latter were dominant. The crystallization time for the PLA/15TPP/1.2Talc blend or the PLA/1.2Talc blend was shortened significantly, indicating that talc increases the crystallization rate of PLA.

The well-known Avrami equation was often used to analyze the isothermal crystallization kinetics.[41-43] It was assumed that the relative degree of crystallinity develops with crystallization time t as follows:

$$1 - X_t = \exp(-kt^n) \qquad (1)$$

where X_t is the relative degree of crystallinity at time t, the exponent n is a mechanism constant with a value depending on the type of nucleation and the growth dimension, and the parameter k is a growth rate constant involving both nucleation and the growth rate parameter.[44] The plots of $\log(-\ln(1 - X_t))$ vs. $\log t$ according to eq. (1) are shown in Figures 3(b), 4(b), 5(b), and 6(b). As can be shown in Figures 3(b), 4(b), 5(b), and 6(b), in the crystallization temperature range of 113–128 °C, all curves are divided into two sections: the primary crystallization stage and the secondary crystallization stage. At the secondary stage, the values of n are larger than those of the primary crystallization. The occurring time of the secondary crystallization for all samples is increased with the T_c. It was generally believed that the secondary crystallization was caused by the spherulite impingement in the later stage of crystallization process at longer crystallization time.[45-48] It can be expected that the occurring time of secondary
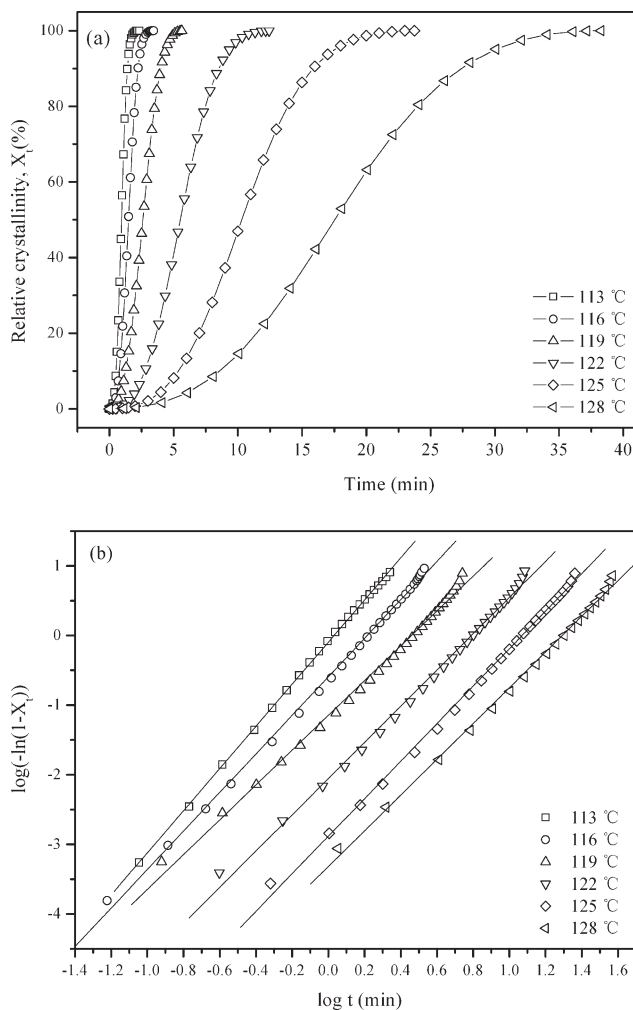

Figure 6 (a) Plots of relative crystallinity as a function of crystallization time for the PLA/15TPP/1.2Talc blend at 113–128°C and (b) Avrami plots for the PLA/15TPP/1.2Talc blend at 113–128°C.

TABLE I
Crystallization Kinetic Parameters and Half-Time of Crystallization for Neat PLA and its Blends Crystallized at 113–128°C

PLA/TPP/Talc Blends	n, k (R)[a], and $t_{1/2}$	T_c (°C)					
		113	116	119	122	125	128
PLA	n	2.4	1.8	1.9	1.9	1.8	2.3
	k (10^{-4} min^{-n}) (R)	316.23	56.23	23.99	7.35	3.06	0.26
		(0.998)	(0.995)	(0.998)	(0.998)	(0.994)	(1.000)
	$t_{1/2}$ (min)	3.6	14.5	19.7	36.8	73.1	84.0
PLA/15TPP	n	2.6	2.5	2.0	2.0	2.2	2.2
	k (10^{-4} min^{-n}) (R)	63.10	22.06	7.08	2.14	0.44	0.13
		(0.998)	(0.999)	(0.998)	(0.996)	(0.999)	(0.997)
	$t_{1/2}$ (min)	6.1	10.0	31.3	56.9	81.1	139.8
PLA/1.2Talc	n	2.8	2.9	3.0	2.8	2.8	2.8
	k (10^{-3} min^{-n}) (R)	1905.46	1122.02	407.38	151.36	27.54	1.74
		(0.998)	(0.999)	(1.000)	(0.999)	(1.000)	(0.999)
	$t_{1/2}$ (min)	0.7	0.8	1.2	1.7	3.2	8.5
PLA/15TPP/1.2Talc	n	3.0	2.8	2.5	2.6	2.7	2.6
	k (10^{-3} min^{-n}) (R)	812.83	257.04	70.79	8.71	1.32	0.48
		(1.000)	(0.999)	(0.998)	(0.998)	(0.999)	(0.998)
	$t_{1/2}$ (min)	0.9	1.4	2.5	5.4	10.2	16.4

[a] Correlation coefficients.

crystallization at low temperature was much shorter than that at high temperature due to both high nucleation density and rapid growth rate of spherulite. Comparing Figure 3(b) with Figures 4(b), 5(b), and 6(b), it was found that the occurring time of the secondary crystallization is increased in the following order: the PLA/1.2Talc blend, neat PLA, the PLA/15TPP/1.2Talc blend, and the PLA/15TPP blend. The number of crystal nuclei and spherulite increases greatly with the incorporation of talc when PLA crystallizes isothermally, and the spherulite impinges into each other rapidly due to the space confinement. The incorporation of TPP increases the growth rate of PLA spherulite, but decreased the nucleation density of PLA, and thus lengthened occurring time of spherulite impingement.

The Avrami parameters n and k were obtained from the plots of log($-\ln(1 - X_t)$) vs. log t in Figures 3(b), 4(b), 5(b), and 6(b). The Avrami exponent n and crystallization rate constant k of neat PLA and its blends were listed in Table I. The average value of n was around 2.0 for neat PLA, and 2.3, 2.9, and 2.7 for the PLA/15TPP blend, the PLA/1.2Talc blend, and the PLA/15TPP/1.2Talc blend, respectively. It is an average value of various nucleation types, and the growth dimensions occurred simultaneously in a crystallization process. For neat PLA without almost heterogeneous nucleus, its nucleation type should predominantly be homogeneous nucleating and its growth dimensions should predominantly be a two-dimensional growth. For the plasticized PLA, its nucleation type should mostly be heterogeneous nucleating and its growth dimension should mostly be two-dimensional space extension. The value of n was close to 3.0 for the isothermal

crystallization of the PLA/15TPP/1.2Talc or the PLA/1.2Talc blend, indicating that the crystallization mechanism of PLA was affected in the presence of talc. On the other hand, the values of crystallization rate constant k were decreased with increasing T_c when neat PLA and its blends crystallized isothermally at 113–128°C. The results showed the fact that the experimental crystallization temperature is higher than that of the maximum crystallization rate. In comparison with neat PLA, the value of k has around 7-fold decrease at 125°C for the PLA/15TPP blend, has around 20.6-fold increase at 122°C for the PLA/1.2Talc blend, and around 4.6-fold increase at 116°C for the PLA/15TPP/1.2Talc blend, suggesting that talc can act as effective nucleating agent for PLA.

The half-time of crystallization $t_{1/2}$ of PLA is an important parameter for the discussion of crystallization kinetics. The value of $t_{1/2}$ is calculated by the following equation:[49]

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{\frac{1}{n}} \quad (2)$$

where k and n are the same as in the Avrami equation. The values of $t_{1/2}$ for neat PLA and its blends were calculated and listed in Table I. In comparison with the neat PLA, the values of $t_{1/2}$ of PLA were increased and decreased with the presence of TPP and talc, respectively, indicating that the incorporation of TPP slowed the crystallization rate of PLA, while the addition of talc accelerated the crystallization rate of PLA. Two possible reasons were proposed to explain the depression of the crystallization rate of PLA after the incorporation of TPP. One is
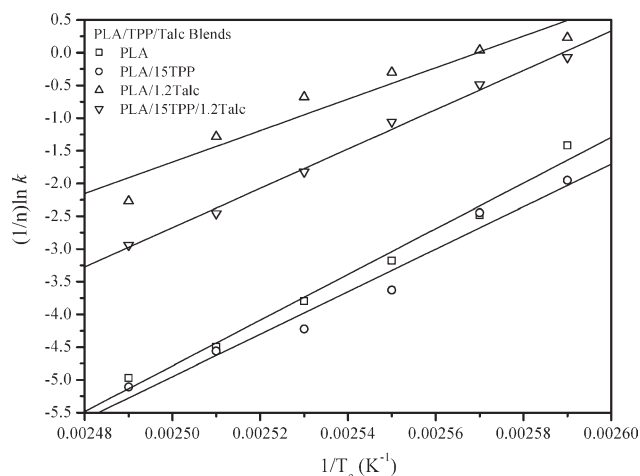
Figure 7 Activation energy (ΔE_a) from isothermal crystallization of neat PLA and its blends.

the presence of TPP prejudiced the nucleation of PLA. In other words, the presence of TPP has a negative effect on the primary nucleation of PLA. Another possible reason was from a physical restriction to the growth of PLA spherulites by TPP. Talc being acted as PLA nucleating agent mainly provided nucleating site for PLA, and decreased the nucleation activation energy significantly, leading to rapid crystallization rate.

The crystallization process is assumed to be thermally activated and the crystallization rate constant k can be approximately described as follows:

$$\left(\frac{1}{n}\right) \ln k = \ln k_0 - \frac{\Delta E_a}{RT_c} \qquad (3)$$

where k_0 is the temperature-dependent pre-exponential factor, R the gas constant, T the absolute crystallization temperature, and ΔE_a the effective energy barrier. The ΔE_a for the isothermal crystallization process can be obtained from the slope of a plot of $(1/n)\ln k$ versus $1/T_c$ as shown in Figure 7. ΔE_a values for the neat PLA, the PLA/15TPP blend, the PLA/1.2Talc blend, and the PLA/15TPP/1.2Talc blend were found to be −290.32, −270.09, −200.10, and −249.73 kJ/mol, respectively, suggesting that as the crystallization progressed, it was more difficult for PLA with TPP and/or talc to crystallize. As regards kinetics, the activation energy can be correlated to the crystallization rate. The above results suggest that it is more difficult for PLA to crystallize with the incorporation of TPP and/or talc. It is noteworthy that the important bulk or overall crystallization kinetic parameter is determined by the half-time of crystallization. As shown in Table I, TPP retards the PLA crystallization, while talc accelerates the PLA crystallization significantly.

Crystal structure

DSC analysis

The heating DSC curves of neat PLA and its blends containing 15 wt % TPP and/or 1.2 wt % talc crystallized isothermally at six different temperatures of 113, 116, 119, 122, 125, and 128°C are shown in Figure 8(a–d). As shown in Figure 8(a–d), the thermal behavior of all these samples showed essentially the same T_c dependence. At T_c = 113°C, the melting endotherms of neat PLA and its blends all show two distinct peaks (T_{m1} and T_{m2}), but the higher melting peak disappears at higher T_c. The peak height of T_{m2} relative to T_{m1} decreases with increasing T_c. At 125°C or more, only a single melting peak (T_{m1}) appears for all samples. The crystal structure may be responsible for the unusual melting behavior of PLA. Research by Zhang et al.[36] showed that when 110°C ≤ T_c ≤ 120°C, PLA crystallized in the temperature range is the mixture of α′ and α-form crystal. The crystal transformation from α′ to α transition can occur during annealing, which depends on two key factors such as the time and temperature.[36-38] In our experiment, it can be expected that the α′-form may be completely transformed into α-form due to enough annealing time, which will be further verified by X-ray diffraction experiment in the next section. The endotherm at lower temperature arises from the α′-form crystal formed in annealing, while the endotherm at higher temperature results from the α-form crystal formed in its own melt-recrystallization during the reheating process. The endotherm at higher temperature disappears at 116°C or more for neat PLA, at 119°C or more for the PLA/15TPP blend, at 119°C or more for the PLA/1.2Talc blend, and at 125°C or more for the PLA/15TPP/1.2Talc blend. Two melting peaks at low and high temperature merge with each other, which depends on the T_c and the blend component. As shown in Figure 8, the lower melting point (T_{m1}) is shifted towards higher temperature with increasing the T_c for all samples. This result indicates that the crystal size and crystallinity of PLA increase with the T_c. It may be rational that when the T_c is increased, the supercooling is decreased, so crystallization time is prolonged, resulting in the increase of the melting point. In contrast, the higher melting point (T_{m2}) almost maintains unchangeable for all sample despite the variation of T_c. It is because the crystal size of the recrystallized crystal does not largely change in the heating process.[36]

WAXD analysis

To get further information of crystallization of neat PLA and its blends, the crystalline nature of neat PLA and its blends was checked by X-ray diffraction. Figure 9 demonstrates the X-ray diffraction
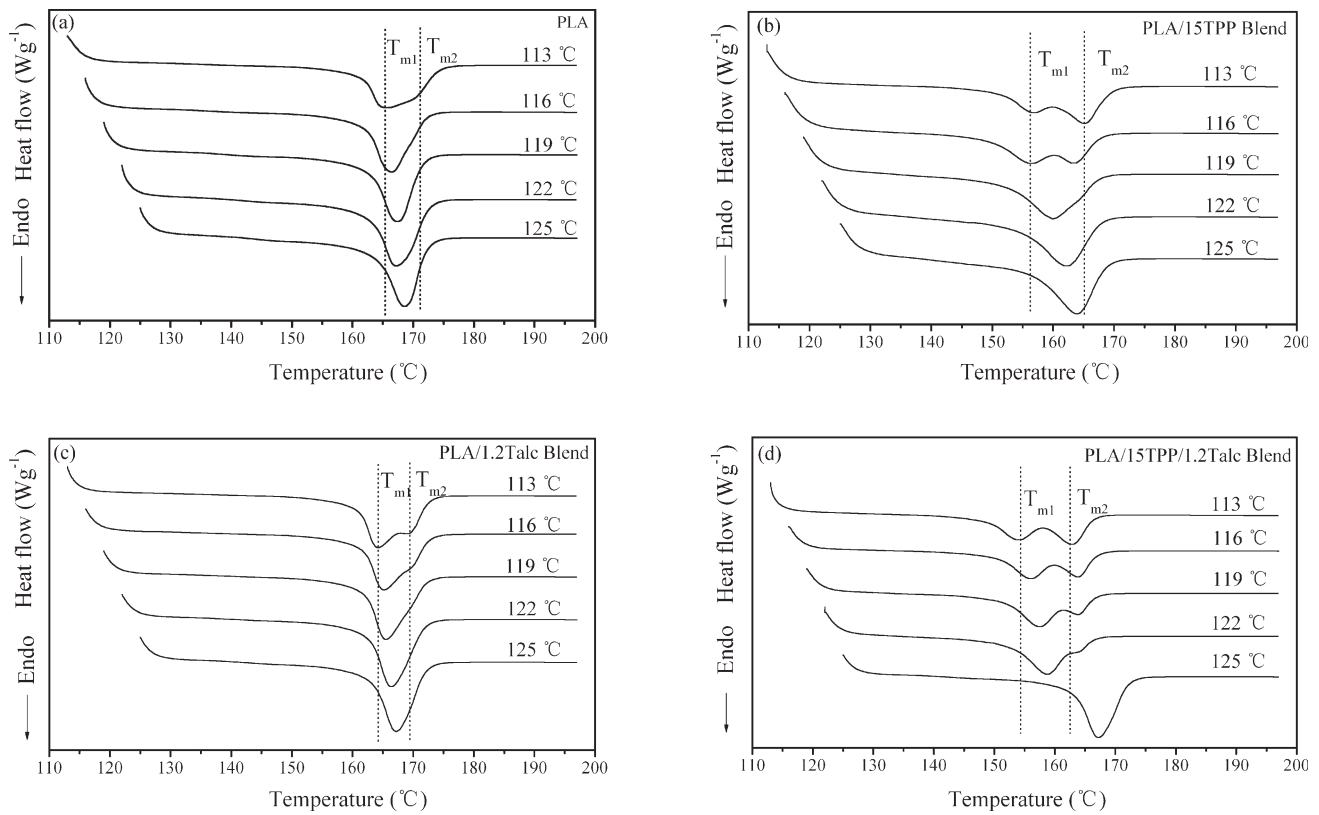
Figure 8 DSC heating curves of neat PLA (a), the PLA/15TPP blend (b), the PLA/1.2Talc blend (c), and the PLA/15TPP/1.2Talc blend, (d) crystallized isothermally at 113–125°C.
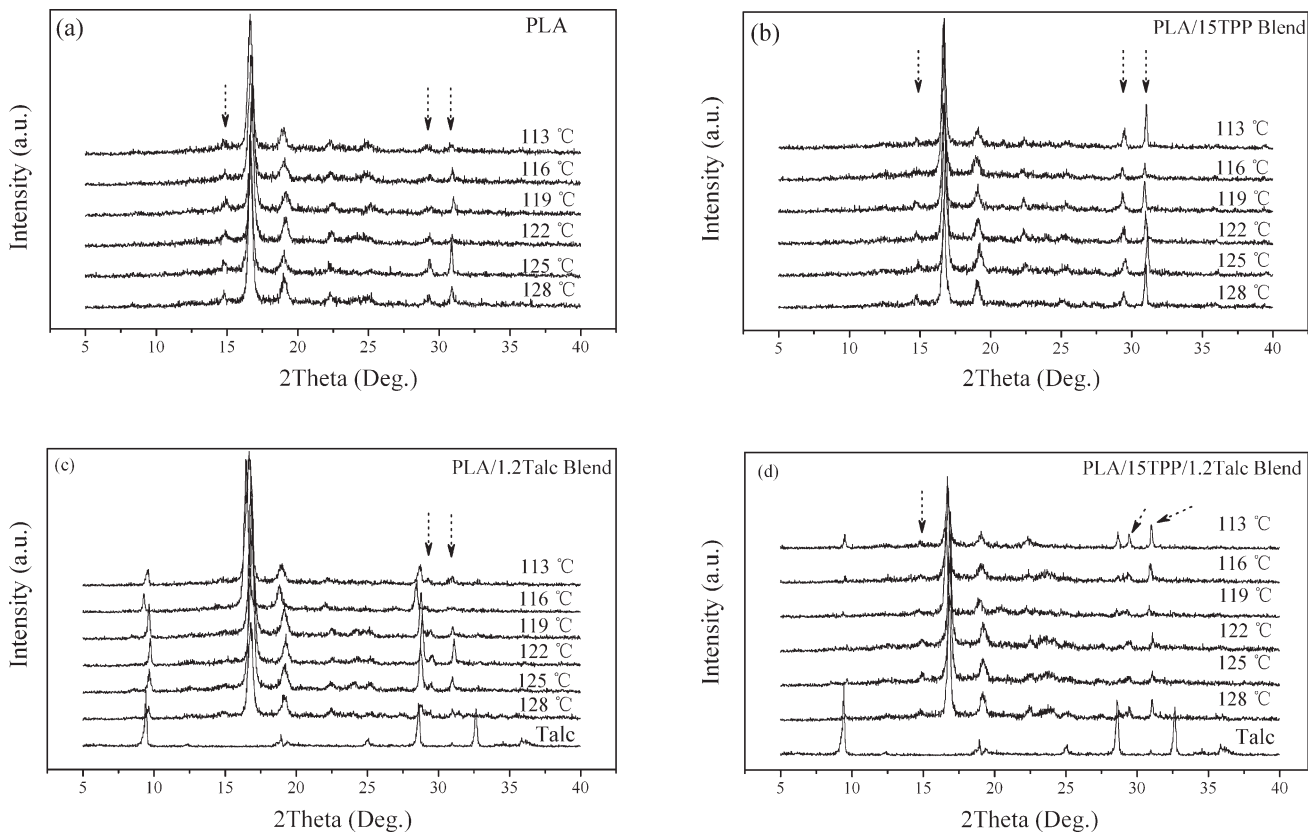

Figure 9 XRD for neat PLA (a), the PLA/15TPP blend (b), the PLA/1.2Talc blend (c), and the PLA/15TPP/1.2Talc blend (d) crystallized isothermally at 113–128°C.

profiles of neat PLA and its blends isothermally crystallized in the temperature range of 113–128°C from the melt. As shown in Figure 9(a–b), Neat and plasticized PLA all presented six peaks at around 2θ = 14.8°, 16.7°, 19.3°, 22.3°, 29.4°, and 30.9° three peaks of which at 2θ = 16.7°, 19.3°, and 22.3° are characteristic peaks of PLA, which agrees with the α-form. In the case of plasticized PLA, they involved all the diffraction peaks corresponding to neat PLA, suggesting that PLA blending with TPP doesn't modify the crystal structure in the blends.

X-ray diffraction profiles of the PLA/1.2Talc blend and the PLA/15TPP/1.2Talc blend crystallized isothermally at six different temperatures of 113, 116, 119, 122, 125, and 128°C are shown in Figure 9(c,d). Talc exhibited six diffraction peaks at around 2θ = 9.5°, 18.9°, 24.9°, 28.6°, 32.5°, and 35.9°. In Figure 9(c), the PLA/1.2Talc blend presented seven diffraction peaks at around 2θ = 9.5°, 16.7°, 19.3°, 22.3°, 28.6°, 29.4°, and 30.9° which is different from those of neat PLA and the PLA/15TPP blend, as shown in Figure 9(a,b). It can be speculated that two diffraction peaks at around 2θ = 9.5° and 28.6° in Figure 9(c) result from those of talc, while five diffraction peaks at around 2θ = 18.9°, 24.9°, 28.6°, 32.5°, and 35.9° didn't appear due to low talc content in the blend or peaks' overlapping, suggesting that crystal structure of PLA didn't change with the addition of talc. The PLA/15TPP/1.2Talc blend presents all diffraction peaks which are the same as those of the PLA/1.2Talc blend, additionally, a peak appears at around 2θ = 14.9°

It is noteworthy that Figure 9(a–d) all show three distinct peaks at 2θ = 14.8° [except for Fig. 9(c)], 29.4°, and 30.9° (indicated by the dotted arrow), respectively, which correspond to α-form crystal.[32,37,50] But three distinct peaks didn't appear for unannealing samples.[27] In Figure 9(a–d), it was observed that two peaks 2θ = 29.4° and 30.9° which correspond to α-form, are stronger for neat and plasticized PLA. The above results suggested that the formation of α-form may be related to blend component, annealing time and temperature employed.

CONCLUSIONS

The spherulitic size, the isothermal crystallization kinetics and the crystal structure of neat PLA and its blends with 15 wt % TPP and/or 1.2 wt % talc were investigated with polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD) in detail in this work. The spherulitic size was observed by POM with hot-stage in a wide crystallization temperature range of 113–128°C. The spherulitic size of PLA was influenced apparently by the T_c and the

incorporation of TPP and/or talc. The sizes of spherulite for all samples were increased with increasing the T_c. At the same T_c, the sizes of spherulite were decreased in the following order: the PLA/15TPP blend, the PLA/15TPP/1.2Talc blend, neat PLA, and the PLA/1.2Talc blend. The isothermal kinetics of neat PLA and its blends in the temperature range of 113–128°C was studied by DSC and analyzed by the Avrami equation. The results showed that the average value of Avrami exponents n for neat PLA and the PLA/15TPP blend is very close to 2.0, while around 3.0 for the PLA/15TPP/1.2Talc blend or the PLA/1.2Talc blend. The crystallization rate constant k was decreased with the incorporation of TPP and the increase of the T_c. In comparison with neat PLA, the value of k for PLA blend with 15 wt % TPP was decreased significantly, while the value of k for PLA blend with 1.2 wt % talc or with both 15 wt % TPP and 1.2 wt % talc was increased greatly, suggesting that talc is an effective nucleating agent for PLA, and dramatically accelerates the crystallization rate of PLA. Further analysis on crystallization activation energy ΔE_a of neat PLA and its blends showed that the value of ΔE_a was increased with the incorporation of TPP and/or talc. The half-time of crystallization implies that TPP favors the molecular mobility of PLA, while talc retards the process. The crystal structure of PLA crystallized isothermally in the temperature range of 113–128°C was not modified by the presence of TPP and/or talc, and still formed α-form. Moreover, the peaks at 2θ = 14.8°, 29.4°, and 30.9° which corresponds to α-form, appear after enough annealing time.

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