Kinetics and Crystal Structure of Isothermal Crystallization of Poly(lactic acid) Plasticized with Triphenyl Phosphate

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ABSTRACT: In this article, the spherulitic growth rate of neat and plasticized poly(lactic acid) (PLA) with triphenyl phosphate (TPP) was measured and analyzed in the temperature range of 104–142°C by polarizing optical microscopy. Neat PLA had the maximum value of 0.28 μm/s at 132°C, whereas plasticized PLA had higher value than that of neat PLA, but the temperature corresponding to the maximum value was shifted toward lower one with increasing TPP content. The isothermal crystallization kinetics of neat and plasticized PLA was also analyzed by differential scanning calorimetry and described by the Avrami equation. The results showed for neat PLA and its blends with various TPP contents, the average value of Avrami exponents n were close to around 2.5 at two crystallization temperatures of 113 and 128°C, the crystallization rate constant k was decreased, and the half-life crystallization time $t_{1/2}$ was increased with TPP content. For neat PLA and its blend with 15 wt % TPP content, the average value of n was 2.0 and 2.3, respectively, the value of k was decreased, and the value of $t_{1/2}$ was increased with crystallization temperature (T_c). Further investigation into crystallization activation energy ΔE_a of neat PLA and its blend with 15 wt % TPP showed that ΔE_a of plasticized PLA was increased compared to neat PLA. It was verified by wide-angle X-ray diffraction that neat PLA and its blends containing various TPP contents crystallized isothermally in the temperature range of 113–128°C all form the α-form crystal. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2980–2992, 2010

Key words: biodegradable polymer; blends; crystallization kinetics; crystal structures

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable crystalline polymer produced from renewable biomass such as corn, and it exhibits the biocompatibility and high mechanical performances comparable to those of petroleum-based traditional polymers.[1,2] In the past decades, PLA has been applied to products such as clothes, cups, packaging, and many other everyday products. Nowadays, more advantageous applications of this environmentally friendly polymer are under development for car and computer parts, which bring forward the demand on improving the thermal, crystallization, and mechanical properties of the PLA-based product.

One of these attempts was carried out by means of plasticization. Varying types of plasticizers, such as poly(ethylene glycol) (PEG),[3–9] poly(propylene glycol) (PPG),[10,11] oligomeric lactic acid (OLA),[4] glycerol,[4] citrate ester,[12,13] triacetine,[13] tributyl citrate,[14] acetyltriethyl citrate,[15] and TPP,[16] 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. The T_g was shown to be depressed from 58°C for neat PLA to 41°C and 30°C, respectively, at 10 and 20 wt % PEG loading levels for PEG molecular weight of 1500.[4] The T_g can be further depressed using a lower PEG molecular weight of 400 g/mol to 30 and 12°C, respectively, and the elongations at break were 26 and 160%, respectively, at those same PEG loading levels. When using high PEG concentration (e.g., 30 wt %), blends of PLA and PEG could undergo phase separation, depending on PEG molecular weight. One of the reasons of instability of PLA/PEG blends is crystallization of PEG that depletes the amorphous

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phase of the plasticizer.[5] Martin and Avérous studied plasticization and properties of PLA plasticized with OLA and glycerol[4] and compared OLA and glycerol with other plasticizer, such as citrate ester and PEG with different average molecular weight. Conclusions were drawn that glycerol was the least efficient plasticizer, and OLA and the lower molecular weight PEG (PEG 400) gave the best result.[4] In our previous article,[16] for the first time, the plasticizing effect of triphenyl phosphate (TPP) on PLA had been published. The T_gs of PLA were decreased from 60.7°C for neat PLA to 46.9°C, 34.2°C, and 21.5°C, respectively, at 10, 20, and 30 wt % TPP loading levels.

Crystallization kinetics from the melt of PLA has also been analyzed by a number of research groups.[17–23] Isothermal bulk crystallization rates were determined in a wide temperature range of 70–165°C.[17,18] The maximum in crystallization rate was observed around 100°C, and the most peculiar behavior was a discontinuity in phase change kinetics around 110–120°C. This discontinuity has been correlated to a transition in regimes II–III growth of spherulite that was observed in the same temperature range.[18,22]

Crystallization kinetics of plasticized PLA has been reported, and results all showed that the addition of plasticizer into PLA accelerate the growth rate of spherulite.[9,11,16] For PLA/PEG blends, the growth rate of spherulite was 0.46 μm/min at 130°C for neat PLA, 1.2 and 0.96 μm/min, and 1.7 and 1.6 μm/min for PLA containing 5 and 10 wt % PEG with molecular weight of 600 and 750 g/mol.[8] Galeski and coworkers investigated the effect of two platicizers including PPG and PEG on the spherulite growth rate of PLA and found that both plasticizers all increased the spherulite growth rate at 90°C by the factor of 3–24, but PPG enhanced the growth rate less than PEG.[11] The results of our study showed that the maximum spherulite growth rate of plasticized PLA with 10, 20, and 30 wt % TPP was increased when compared to that of neat PLA, but the temperature corresponding to the maximum growth rate was shifted to lower one with increasing TPP content.[16]

PLA can crystallize in α, β, γ-forms, depending on the processing conditions.[24–31] The most common and stable polymorph can be developed from the melt or solution under normal conditions.[24] The α form grows upon melt or cold crystallization and from solution-spinning processes at low drawing temperatures and/or low hot draw ratios.[25] The β modification, that was first observed by Eling et al.,[27] develops upon mechanical stretching of the more stable α form, or from solution-spinning processes conducted at high temperatures and/or high hot-draw ratios.[25,27] Another crystal modification of

PLA, α-form, has been obtained by Lotz and coworkers[28] via epitaxial crystallization on the hexamethylbenzene substrate. Zhang et al.[32–35] investigated by means of infrared spectroscopy and wide-angle X-ray scattering, 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 in α form but a loose packing manner compared to the α form (order crystal). The α′-to-α transition, which is mainly involved by the slight rearrangement of the chain conformation, is solid–solid phase transition, does not involve the melting-recrystallization process, and depends on the annealing period and temperature. The α′-form crystal was formed when the crystallization temperature (T_c) was below 110°C, the α-form crystal was formed when T_c was above 120°C,[32] and the mixture of α′ and α-form crystal was formed when $110°C \leq T_c \leq 120°C$.[33]

In this article, the study was mainly focused on the isothermal crystallization kinetics and the crystal structure of neat and plasticized PLA. It is well known that the crystallinity and crystal structure plays an important role in the physical properties. It is expected that the results will be helpful for a better understanding of crystallization behavior of the neat and plasticized PLA.

EXPERIMENTAL

Materials

The commercial PLA with 98.7 mol % L-isomeric content 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 and 168°C [differential scanning calorimeter (DSC) analysis], respectively. TPP (C.P. grade; Kelong Chemical Reagent Factory, Chengdu, China) was used as PLA plasticizer, which had a molecular weight of 326.3 g/mol and a melting point of 48°C.

Sample preparation

The neat PLA was predried in vacuum oven at 80°C for 24 h before use. PLA and TPP were mixed together with different weight ratios of 100/0, 95/5, 90/10, 85/15, and 80/20 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. Then, the melts were compressed to films with a thickness of around 0.2 mm for 3 min at 185°C and 10 MPa for both the neat and plasticized PLA.

Thermal analysis

The thermal characteristics of the neat and plasticized PLA were determined using a differential scanning calorimeter (DSC Q100, TA instrument, USA) in nitrogen atmosphere (circulation). Samples (ca. 10 mg) were cut from a sample and 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 for 3 min to destroy any thermal history. Then, samples were cooled to the given crystallization temperature (T_c) at a rate of 50°C/min to crystallize neat and plasticized PLA in the time range of 4–600 min. The samples were heated from the given crystallization temperature (T_c) to 200°C at a heating rate of 10°C/min after the isothermal crystallization finished. A nitrogen flow was maintained throughout the test. The degree of crystallinity (x_c) and the melting temperature (T_m) were determined in the second heating scan. Based on the heat of fusion of 100% crystallinity of PLA (93 J/g),[36] the degree of crystallinity of PLA was calculated from the melting endotherms of the samples and normalized with respect to the composition of PLA in the plasticized PLA.

The equilibrium melting temperatures (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.[37] Samples were heated to 185°C and maintained for 3 min and then cooled at 50°C/min and crystallized in the temperature range of 120–142°C for neat PLA sample and 115–140°C for plasticized PLA samples, respectively. At each temperature, annealing lasts 10 h in nitrogen atmosphere, and then the samples were cooled to room temperature at 40°C/min and heated to 200°C at 10°C/min for the determination of the melting points.

Polarized optical microscopy

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

Wide-angle X-ray diffraction

Prior to measurement, isothermal crystallization of the thin film samples was performed on hot stage in polarizing optical microscope, and isothermal crystallization procedure was in accordance with DSC measurement. X-ray scattering was used to probe the crystal structure of neat and plasticized PLA.
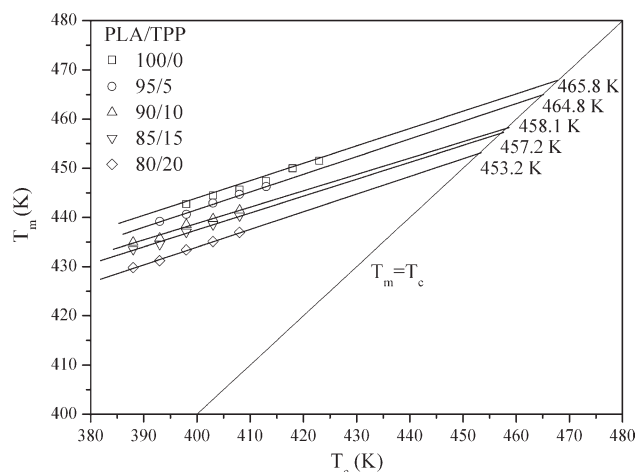
Figure 1 Hoffman–Weeks plots for neat PLA and its blends.

Thin film samples were analyzed using a wide-angle X-ray diffraction (WAXD) apparatus (Shimadu XRD-6000) by Cu Kα (λ = 0.154 nm) under a voltage of 35 kV and a current of 25 mA radiation. Diffraction intensities were counted at 0.02° increments, and the scanning speed was 5°/min. The spectra are recorded in an angular range of 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 with various TPP contents. 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 of 198–212°C by Tsuji with different procedures.[38] The deviation might be related to the molecular weight, the % L or D content of PLA and the DSC scanning rate. The T_m^0 decreased with increasing TPP content and the maximum extent of this melting point depression was about 12.6°C in PLA with 20 wt % TPP content, where T_m^0 was 180.2°C. The T_m^0 of neat PLA was higher than that of plasticized PLA, indicating that the crystalline phase of neat PLA was more perfect than that of plasticized PLA.

Spherulite growth rate

Spherulitic morphology of the neat PLA and its blends with various TPP contents crystallized isothermally in the temperature range of 113–128°C were examined, and impinged spherulitic morphology was shown in Figure 2. As shown in Figure 2(A–E), it was apparent that for the neat PLA and its blends, the spherulite's size was increased with
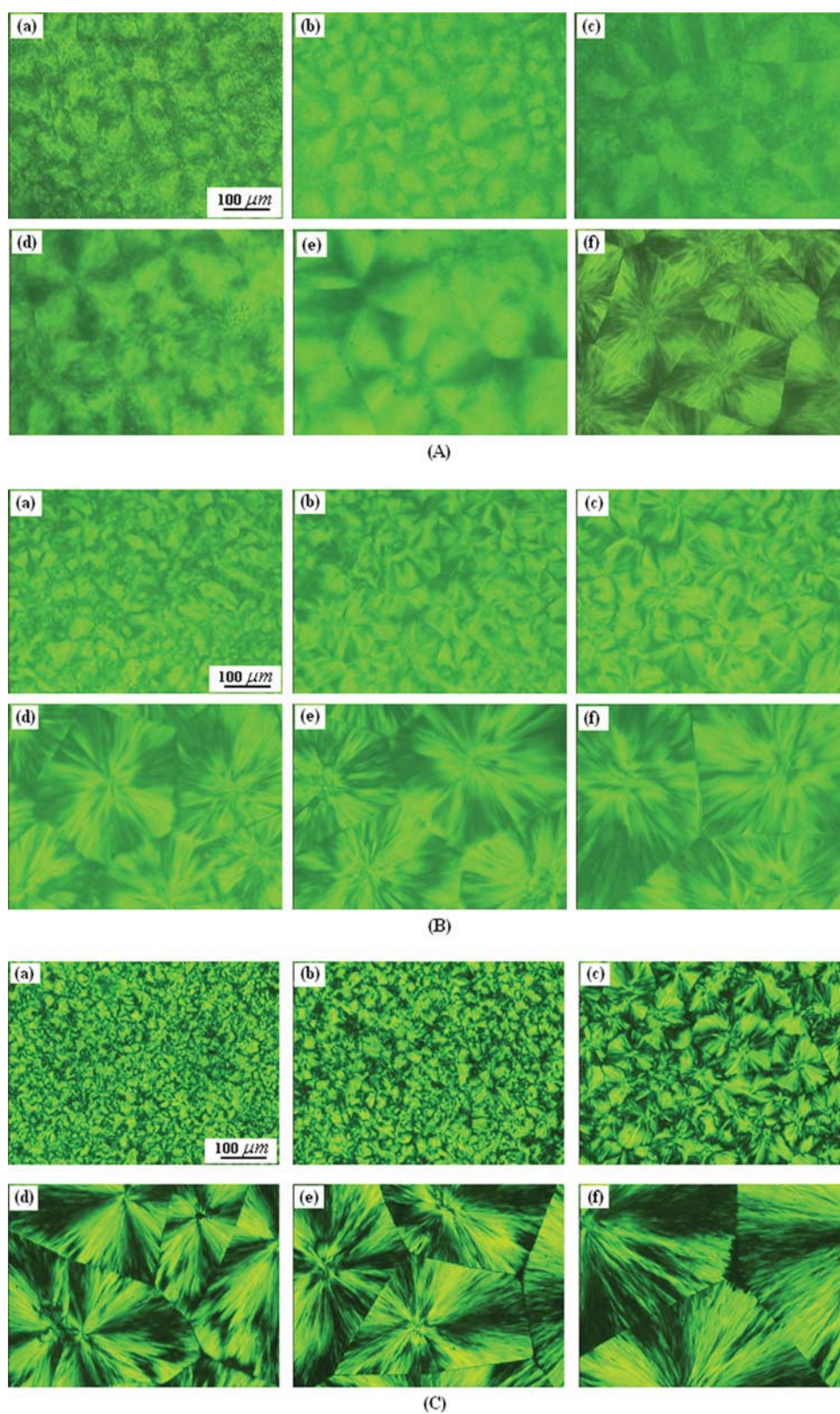
Figure 2 Polarizing optical micrographs of neat PLA (A) and its blends containing 5 (B), 10 (C), 15 (D), and 20 wt % TPP (E) crystallized isothermally at different temperatures: (a) 113; (b) 116; (c) 119; (d) 122; (e) 125, and (f) 128°C, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the increase of crystallization temperatures as the growing spherulites impinged with each other, indicating that the nucleation density was decreased.

However, at the same crystallization temperature, the pattern of the change of spherulite's size cannot be observed for the neat PLA and its blends
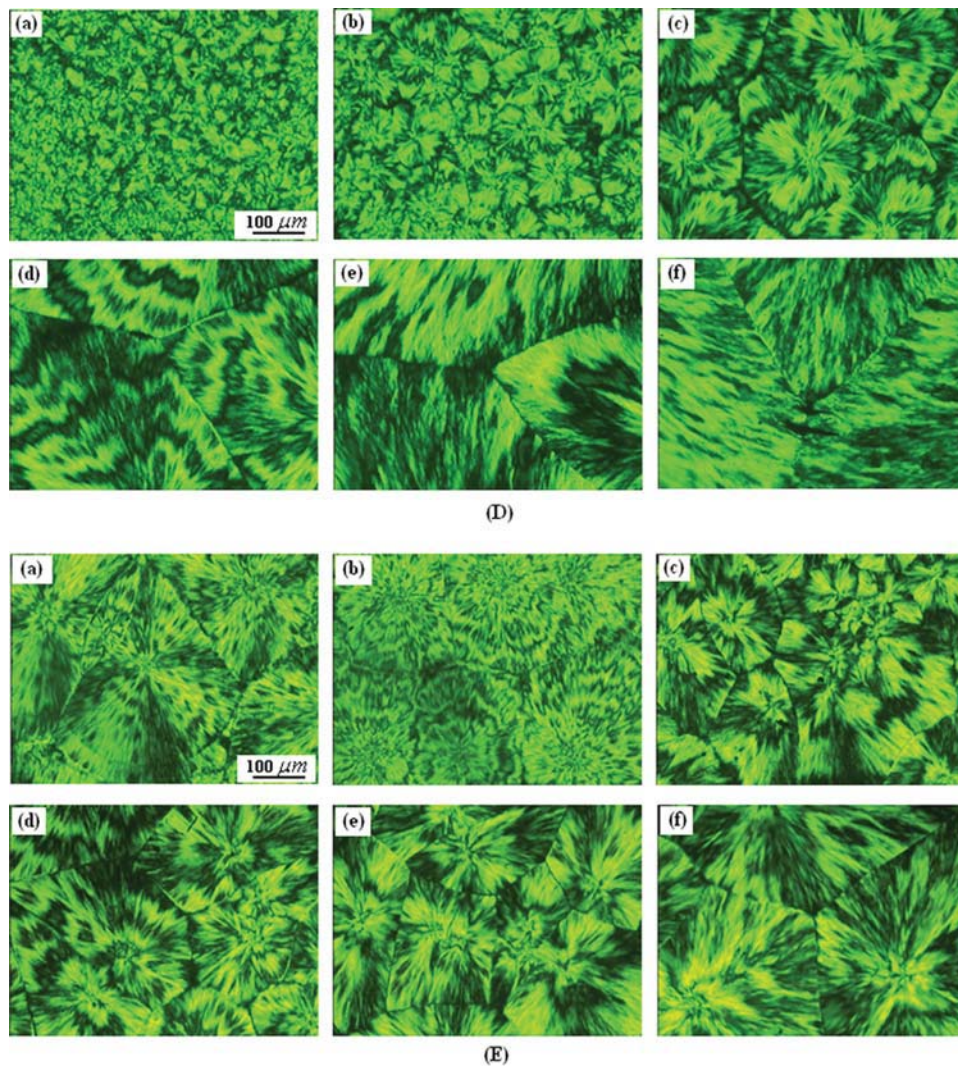
Figure 2 (*Continued*)

containing various contents of 5, 10, 15, and 20 wt % TPP, respectively. It was because that the spherulite's size mainly depends on two factors before the growing spherulites impinged with each other: one is the growth rate of spherulite, another is the density of the crystal nuclei. Generally speaking, the incorporation of plasticizer can accelerate the growth rate of spherulite, yet decrease the density of the crystal nuclei. Moreover, two factors aforementioned will change with the temperature. The variation of spherulite's size was the combined effect of aforementioned two factors.

The spherulitic growth rates of neat and plasticized PLA were measured by following the development of radius with time. PLA spherulites showed a linear growth until impingement takes place during the crystallization process. Figure 3 shows the temperature and component dependence of the spherulitic growth rates of neat and plasticized PLA in the crystallization temperature range of 104–142 °C. In

fact, in the case of neat and plasticized PLA, the separate spherulite was hardly detectable because of the high nucleation density when the isothermal temperatures were low. Meanwhile, the spherulites were distorted seriously so that the size of spherulites did not define easily when the isothermal temperatures were high. The spherulitic growth rates of neat and plasticized PLA exhibited different maximum values, which corresponded to the different temperatures, and maximum values of the spherulitic growth rate were shifted to lower temperature with the increase of TPP content. As shown in Figure 3, the neat PLA showed a maximum value of 0.28 μm/s for the growth rate at 132°C, and maximum values of 0.41, 0.51, 0.55, and 0.88 μm/s for PLA blends with 5, 10, 15 and 20 wt % TPP content at 122, 122, 116, and 110°C, respectively. For neat PLA, initially, the spherulitic growth rate increases, then reaches a maximum value, and finally decreases in the temperature range of 123–142°C. The spherulitic growth
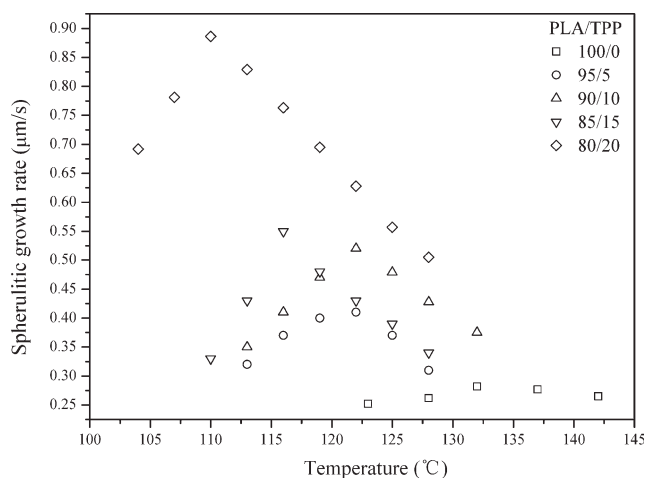
Figure 3 Temperature and component dependence of the spherulitic growth rates of neat and plasticized PLA.

rate of neat PLA mainly depends on the crystallization temperature (T_c). On one hand, the chain mobility of PLA increases with increasing T_c, which accelerates the spherulitic growth. On the other hand, the degree of supercooling, i.e., the difference between the equilibrium melting point, T_m^0, and the crystallization temperature, T_c, decreases with the increase of T_c, which decreases the thermodynamic driving force required for the growth of PLA spherulites. The variation of the spherulitic growth rates can be assigned to the combined effects of the chain mobility and the degree of supercooling. Two effects might be counteracted at lower and higher temperature, so the spherulitic growth rates were low. On the contrary, the synergic effect of the chain mobility and the degree of supercooling resulted in the maximum spherulitic growth rate of PLA at a moderate temperature. For the plasticized PLA, the variation of the spherulite growth rate against the temperature had the same tendency as the neat PLA, but the maximum values of the spherulitic growth rates were shifted to lower temperature. It might be related to the following two facts: first, the addition of low T_g-component TPP decreases the T_g of PLA, resulting in the increase of the chain mobility of PLA. Second, the addition of TPP decreases the equilibrium melting point of PLA, which decreases the degree of supercooling at the same crystallization temperature. As shown in Figure 3, the spherulite growth rates of plasticized PLA increased when compared with neat PLA. It can be attributed to the first effect. For PLA with various TPP contents, the maximum values of the spherulites growth rates were shifted to lower temperature with the increase of TPP content, which mainly arises from the depression of PLA's T_g, leading to the increasing of the chain mobility at lower temperature. From Figure 3, it can be found that the spherulitic growth

rates of PLA with various TPP contents did not increase simply at the same temperature as TPP content increased. It might be caused by the combined effect of two factors mentioned earlier.

Crystallization kinetics

The melting neat PLA and its blends containing 5, 10, 15, and 20 wt % TPP were cooled to a predetermined crystallization temperature (T_c) at a rate of 50°C/min, and the isothermal crystallization was performed at two T_cs of 113 and 128°C during various crystallization times. The plots of the relative crystallinity X_t versus the crystallization time t are shown in Figures 4(a) and 5(a) for the isothermal crystallization at 113 and 128°C of neat PLA and its blends. It was found that in comparison to neat PLA, crystallization time of plasticized PLA crystallized at 113 and 128°C lengthened except for PLA blend containing 15 and 10 wt % TPP, respectively. Moreover, for neat PLA and its blends crystallized
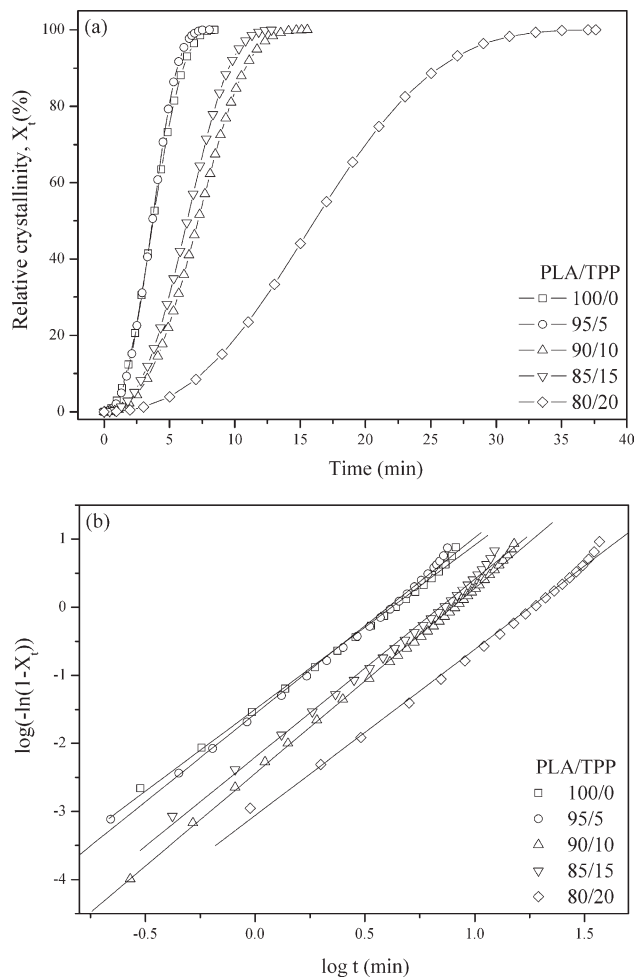

Figure 4 (a) Plots of relative crystallinity as a function of crystallization time for neat and plasticized PLA at the different temperatures of 113°C and (b) Avrami plots for the neat and plasticized PLA at 113°C.
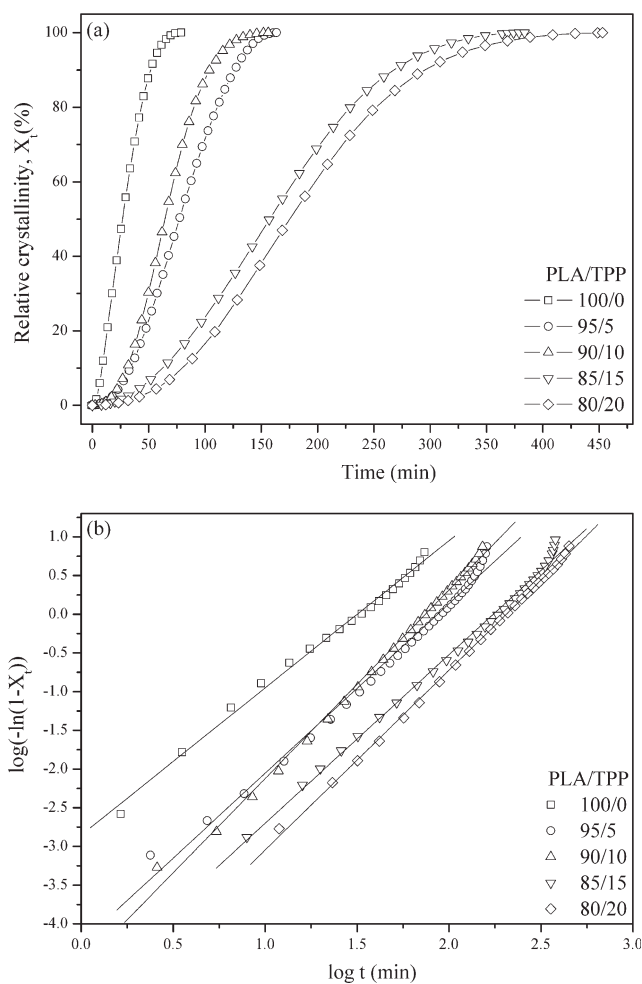
Figure 5 (a) Plots of relative crystallinity as a function of crystallization time for neat PLA and its blends containing 5, 10, 15, and 20 wt % TPP at 128°C and (b) Avrami plots for the neat PLA and its blends containing 5, 10, 15, and 20 wt % TPP at 128°C.

at the same crystallization temperature, the crystallization time at 128°C was longer than that at 113°C. These results might be related to three factors: first, the addition of TPP decreased T_g of PLA, therefore, increased the chain mobility of PLA. Second, the added TPP was a diluent to PLA, resulting in the dilution of PLA chains at the spherulites growth front. Third, the decrease of the degree of supercooling depressed at the same crystallization temperature. The crystallization time lengthened when TPP content was increased, indicating that the latter two factors were dominant. The well-known Avrami equation has often been used to analyze the isothermal crystallization kinetics.[39–41] It was assumed that the relative degree of crystallinity develops with crystallization time t as follows:

$$1-X_t=\exp(-kt^n) \tag{1}$$

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 parameters.[42] The plots of log $(-\ln(1 - X_t))$ vs. log t according to eq. (1) are shown in Figures 4(b) and 5(b). As shown in Figures 4(b) and 5(b), all curves were divided into two sections: the primary crystallization stage and the secondary crystallization stage. At the primary stage, the value of n was in the ranges of 2.4–2.7 and 2.2–2.4 at the isothermal crystallization temperatures of 113 and 128°C, indicating that the value of n was decreased with increasing crystallization temperature. At the secondary stage, the values of n were larger than those of the primary crystallization. The secondary crystallization became more obvious with increasing TPP content. 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.[43–46] As shown in Figures 4(b) and 5(b), the occurring time of the secondary crystallization of the neat and plasticized PLA was different. Generally, the secondary crystallization of the neat PLA was much shorter than that of the plasticized PLA. This fact indicated that without the incorporation of TPP, the nucleus in neat PLA grew rapidly into spherulites before they impinge against each other. TPP caused crystallization of PLA to be completed later. It can be explained that although the incorporation of TPP increased the growth rate of spherulite, yet more importantly, decreased the density of PLA crystal nuclei, as a result, slowed impinging against each other.

The Avrami parameters n and k were obtained from the plots of log $(-\ln(1 - X_t))$ vs. log t as shown in Figures 4(b) and 5(b). The Avrami exponent n and crystallization rate constant k of neat and plasticized PLA are shown in Table I. The average value of n was around 2.5 at the isothermal crystallization temperature of 113°C and around 2.3 at 128°C. It is an average value of various nucleation types, and the growth dimensions occurred simultaneously in a crystallization process. For neat PLA without any 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 values of n were close to 2.5 for the isothermal crystallization of the neat and plasticized PLA, indicating that the crystallization mechanism of PLA was almost not affected in the presence of TPP. On the other hand, the value of crystallization rate constant k of plasticized PLA crystallized isothermally at 113 and 128°C was decreased when compared with the neat PLA.

TABLE I
Crystallization Kinetic Parameters of PLA and its Blends at 113 and 128 °C

PLA/TPP Blends	T_c (°C)	n	k (10^{-3} min^{-n})	$t_{1/2}$ (min)	PLA/TPP Blends	T_c (°C)	n	k (10^{-5} min^{-n})	$t_{1/2}$ (min)
100/0	113	2.4	31.62	3.6	100/0	128	2.3	8.64	26.1
95/5		2.6	27.51	3.5	95/5		2.2	5.62	72.4
90/10		2.7	3.63	7.0	90/10		2.4	2.75	68.2
85/15		2.6	6.31	6.1	85/15		2.2	1.32	139.8
80/20		2.4	0.87	16.2	80/20		2.3	0.43	183.7

Furthermore, the value of k was decreased with TPP content. For the PLA blend containing 20 wt % TPP, the value of k was decreased, at most, by two orders and one order of magnitude compared to neat PLA at 113 and 128°C, respectively. These results did not seem to be in accordance with those of the spherulitic growth rates at 113 and 128°C as shown in Figure 3. It should be emphasized that overall crystallization rates were not as easy to interpret as the spherulitic radial growth because of the combination of nucleation and growth phenomena. However, the nucleation process could not be observed directly by POM. The half-life crystallization time $t_{1/2}$, the time required to achieve 50% of the final crystallinity of the samples, is an important parameter for the discussion of crystallization kinetics. Usually, the crystallization rate is described as $t_{1/2}$. The value of $t_{1/2}$ is calculated by the following equation:[47]

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

where k and n are the same as in the Avrami equation. The values of $t_{1/2}$ for neat and plasticized PLA were calculated and listed in Table I. In comparison to the neat PLA, the values of $t_{1/2}$ of plasticized PLA were almost increased, which indicated that the addition of TPP slowed the crystallization rate of PLA. Two possible reason was that the presence of TPP suppressed the nucleation of the PLA. In other words, the presence of TPP has a negative effect on the primary nucleation of PLA.

In the above section, the crystallization kinetics of the neat PLA and its blends containing various TPP contents at the isothermal crystallization temperatures of 113 and 128°C were discussed in detail. In the following, the crystallization kinetics of neat

PLA and its blends containing 15 wt % TPP in the temperature range of 113–128°C will be discussed. The plots of the relative crystallinity X_t versus the crystallization time t are shown in Figures 6(a) and 7(a) for the isothermal crystallization of neat PLA and its blend containing 15 wt % TPP. It was found that for the neat PLA and its blend, the crystallization time all lengthened with increasing crystallization temperature. Moreover, at the same crystallization temperature, the crystallization time of plasticized PLA lengthened significantly when compared with neat PLA. These results were in agreement with values of $t_{1/2}$ as listed in Table II. It may be that for the isothermal crystallization of neat PLA and its blends at various temperatures, the decrease of the degree of supercooling depressed with increasing crystallization temperature, resulting in the increase of crystallization time. In the same isothermal crystallization temperature, the crystallization time of plasticized PLA was longer than that of neat PLA. It can be attributed to two factors: the nucleation density and the degree of supercooling of PLA were decreased when compared with those of neat PLA, due to the incorporation of TPP.

The Avrami parameters n and k were obtained from the plots of log $(-\ln(1 - X_t))$ vs. log t as shown in Figures 6(b) and 7(b). The Avrami exponent n and crystallization rate constant k of neat PLA and its blends containing 15 wt % TPP in the temperature range of 113–128°C are shown in Table II. At the primary crystallization stage, the average values of n were around 2.0 for the neat PLA at the isothermal crystallization of 113°C, around 2.3 for plasticized PLA with 15 wt % TPP at 128°C. These results indicated that the crystallization mechanism of the neat PLA and its blend was not affected significantly in various crystallization temperatures. At the

TABLE II
Crystallization Kinetic Parameters of PLA and its Blends in the Temperature Range of 113–128°C

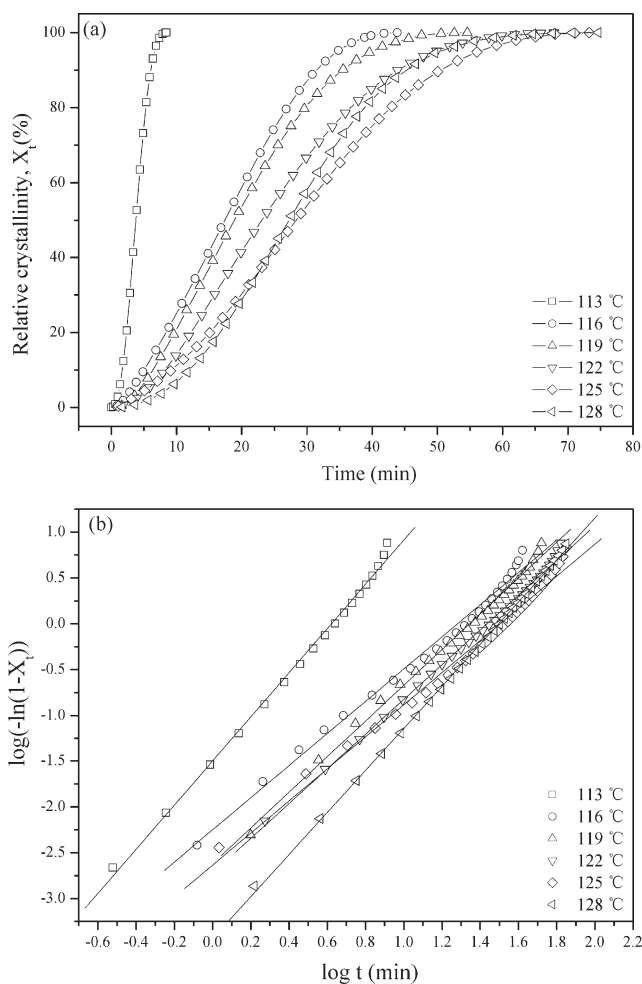| PLA	T_c (°C)	n	k (10^{-4} min^{-n})	$t_{1/2}$ (min)	PLA/TPP Blend	T_c (°C)	n	k (10^{-5} min^{-n})	$t_{1/2}$ (min)
100/0	113	2.4	316.23	3.6	85/15	113	2.6	630.96	6.1
	116	1.8	56.23	14.5		116	2.5	220.56	10.0
	119	1.9	23.99	19.7		119	2.0	70.79	31.3
	122	1.9	7.35	36.8		122	2.0	21.38	56.9
	125	1.8	3.06	73.1		125	2.2	4.37	81.1
	128	2.3	0.26	84.0		128	2.2	1.32	139.8

Figure 6 (a) Plots of relative crystallinity as a function of crystallization time for neat PLA in the temperature range of 113–128°C and (b) Avrami plots for neat PLA in the temperature range of 113–128°C.

secondary crystallization stage, the values of Avrami exponent were greater than those of the primary crystallization. Moreover, for plasticized PLA, the temperature which corresponded to the secondary crystallization was shifted to higher one in comparison to the neat PLA, which mainly resulted from the decrease of growth rate of spherulite and the nucleation density of crystal nuclei. In the case of crystallization rate constant k, the value of the neat PLA and its blends was all decreased with the increase of crystallization temperature. The value of k was decreased, at most, by three orders of magnitude for the neat PLA, by two orders of magnitude for plasticized PLA when the crystallization temperature was increased from 113 to 128°C.

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

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

where k_0 is the temperature-dependent pre-exponential factor, R is the gas constant and ΔE_a is the activation energy for the primary crystallization process which consists of the transport activation energy and the nucleation activation energy.[48,49] The ΔE_a is estimated from the slopes of linear plots of $(1/n)\ln k$ against $1/T_c$ and shown in Figure 8. Because it has to release energy when the molten fluid transformed into the crystalline state, the value of ΔE_a is negative on the basis of the concept of the heat quantity in physical chemistry. In this study, the ΔE_a value for the neat PLA and its blend with 15 wt % TPP in primary crystallization stage is found to be −290.32 and −270.09 kJ/mol, respectively. This result suggests that the incorporation of plasticizer resulted in the increase of the crystallization activation energy, implying that the incorporation of TPP retarded crystallization of PLA.
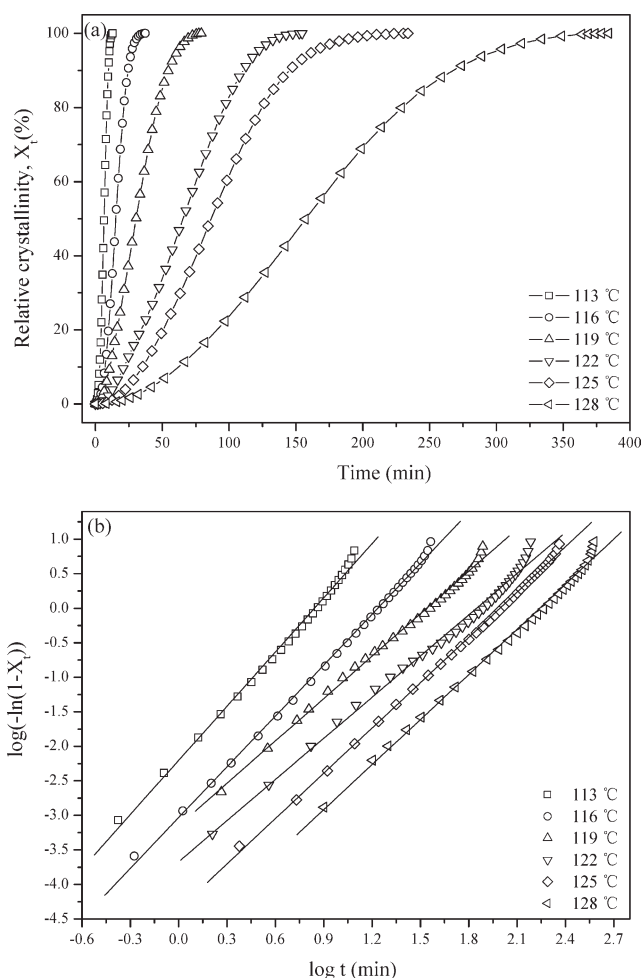

Figure 7 (a) Plots of relative crystallinity as a function of crystallization time for PLA containing 15 wt % TPP in the temperature range of 113–128°C and (b) Avrami plots for neat PLA and its blends containing 15 wt % TPP in the temperature range of 113–128°C.
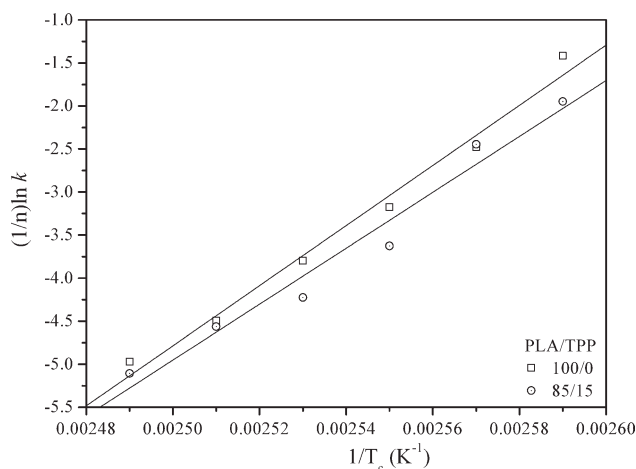
Figure 8 Activation energy (ΔE_a) from isothermal crystallization of neat and PLA blends containing 15 wt % TPP.

Crystal structure

DSC analysis

The heating DSC curves of neat PLA and its blends containing 5, 10, 15, and 20 wt % TPP crystallized isothermally at four different temperatures of 113, 116, 119, and 122°C were shown in Figure 9(a–d). As shown in Figure 9 (a–d), the thermal behaviors of all these samples show essentially the same T_c dependence. At $T_c = 113$°C, the melting endotherms of neat and plasticized PLA show two distinct peaks (T_{m1} and T_{m2}), but the higher melting peak disappears at more than 116°C for neat PLA, above 122°C for plasticized PLA. The peak height of T_{m2} relative to T_{m1} increases with increasing T_c from 113 to 116°C. Above 119°C, only a single melting peak appears for all samples. The crystal structure may be responsible for the unusual melting behavior of PLA. Research by Zhang et al.[33] showed that when the T_c was between 110 and 120°C, PLA formed the mixture of α' and α-form crystals. The crystal transformation from α' to α transition can occur during annealing, which depends on the two key factors such as the time and temperature.[33–35] In our experiment, it can

be expected that the α'-form crystal may completely be 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, whereas the endotherm at higher temperature results from the α-form crystal formed in its own melt-recrystallization in the heating process. The higher melting peak (T_{m2}) of neat PLA appears at lower T_c (i.e. 116°C), whereas the T_{m2} of plasticized PLA disappears at more than 119°C. The both T_{m1} and T_{m2} merge with each other, which depends on T_c and the blend component. As listed in Table III, the lower melting point (T_{m1}) is shifted toward higher temperature with increasing T_c for all samples. This result indicates that the crystal size and crystallinity of PLA increase with T_c. It may be that when the T_c is increased, the supercooling is decreased, so crystallization time is prolonged, and crystal becomes more perfect, resulting in the increase of the melting point. In contrast, the higher melting point (T_{m2}) almost maintains unchangeable for neat and plasticized PLA despite different T_c. It is because that the crystal size of the recrystallized crystal does not largely change in the heating process.[33]

The degree of crystallinity for neat and plasticized PLA crystallized isothermally at different T_c was listed in Table III. The degree of crystallinity was calculated based on the following eq.(4):

$$x_c = \frac{\Delta H_f}{w_{PLA} \times \Delta H_f^0} \times 100\% \qquad (4)$$

Where ΔH_f is the heat of fusion, ΔH_f^0 is the heat of fusion for 100% crystalline PLA, and w_{PLA} is the weight fraction of PLA in the PLA/TPP blends. The results showed that the degree of crystallinity was increased for all samples with T_c. As shown in Table III, for all samples the degree of crystallinity was increased with T_c. It can be ascribed to the annealing time and T_c, whereas for all samples the annealing

TABLE III
Results from the Thermal Analysis of Neat PLA and PLA/TPP Blends

| PLA/TPP Blends	T_c (°C)	ΔH_f (J g^{-1})	T_{m1} (°C)	T_{m2} (°C)	x_c (%)	PLA/TPP Blends	T_c (°C)	ΔH_f (J g^{-1})	T_{m1} (°C)	T_{m2} (°C)	x_c (%)
100/0	113	38.8	165.6	169.4	41.7		119	44.3	159.7	165.1	52.9
	116	39.6	166.4	–	42.6		122	47.9	161.3	–	57.2
	119	42.7	167.4	–	45.9	85/15	113	32.1	154.9	163.3	40.6
	122	47.2	167.4	–	50.8		116	33.2	156.4	163.4	42.0
95/5	113	32.8	162.7	168.8	31.1		119	37.4	158.1	–	47.3
	116	33.8	163.6	168.8	38.3		122	38.0	161.2	–	48.1
	119	36.1	164.6	168.3	40.9	80/20	113	33.0	153.7	161.5	44.4
	122	38.8	165.8	–	43.9		116	33.1	154.9	161.8	44.5
90/10	113	38.3	158.3	165.8	45.8		119	33.2	156.9	–	44.6
	116	42.9	159.0	165.2	51.3		122	33.2	159.2	–	44.6
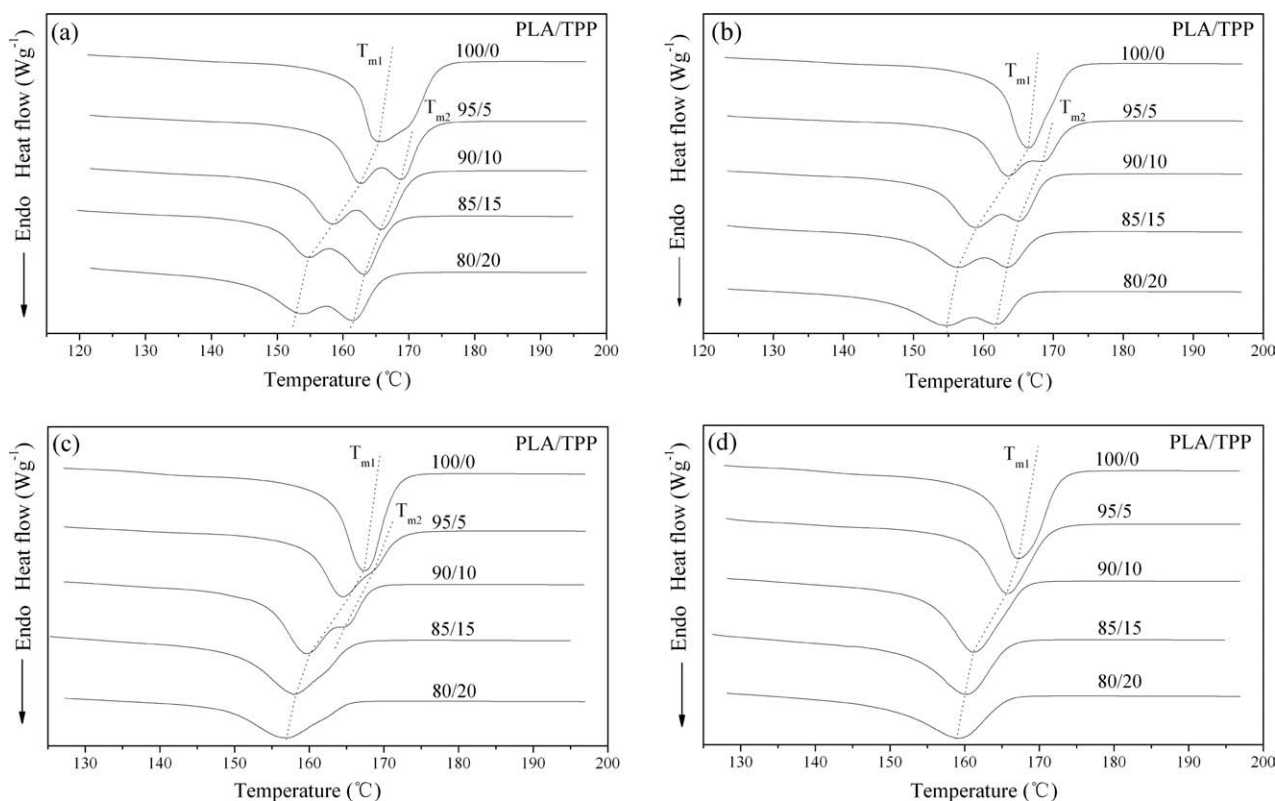
Figure 9 DSC heating curves of neat PLA and its blends containing 5, 10, 15 and 20 wt % TPP crystallized isothermally at different temperatures: (a) 113; (b) 116; (c) 119, and (d) 122°C.

time was prolonged with T_c. The mobility of PLA molecular segment becomes easier in higher T_c and has enough time to arrange in order, resulting in the increase of the degree of crystallinty. At the same T_c, the variation of the degree of crystallinity of PLA containing various TPP contents was discrete. It may mainly be related to the variation of the melting point (T_m), the glass transition temperature of PLA, even phase change kinetic during crystallization.[18] Both T_m and T_g depressed when TPP content in PLA/TPP blends increased, which in turn, influenced the range of PLA crystallization. For PLA/TPP blends with various TPP contents, the maximum of PLA crystallization rate was different at the same T_c due to the discontinuity in phase change kinetic. The above discrete result of the degree of crystallinity of PLA might be caused by the combination effects aforementioned.

WAXD analysis

To get further information of crystallization of neat and plasticized PLA, the crystalline nature of the neat and plasticized PLA was checked by X-ray diffraction. Figure 10 demonstrates the X-ray diffraction profiles of neat and plasticized PLA isothermally crystallized at 113 and 128°C. As shown in Figure 10(a,b), neat and plasticized PLA all present three

peaks at around $2\theta = 16.7°$, $19.3°$, and $22.3°$, which agrees with the α form of PLA. For the plasticized PLA, they involved all the diffraction peaks corresponding to neat PLA, and the intensity of the diffraction peaks of PLA decreased with increasing TPP content. Although the same position peaks suggest that plasticized PLA has the same unit cell structure as neat PLA, the intensity of plasticized PLA decreased with the increasing TPP content, suggesting that PLA blending with TPP doesn't modify the crystal structure in the blends.

X-ray diffraction profiles of neat PLA and its blend containing 15 wt % TPP crystallized isothermally at six different temperatures of 113, 116, 119, 122, 125, and 128°C are shown in Figure 11. Neat and plasticized PLA presented three strong diffraction peaks at around $2\theta = 16.7°$, $19.3°$, and $22.3°$, which are the same as in Figure 10, which suggests that crystal structure did not change in the crystallization temperature used.

It was noteworthy that Figures 10 and 11 all show three distinct peaks at $2\theta = 14.8°$, $29.4°$, and $30.9°$ (indicated by the dotted circle), respectively, which correspond to α-form crystal.[34,50] But three distinct peaks did not appear for samples that were not annealed.[16] From Figure 10(a,b), it was observed that two peaks, which correspond to α-form crystal, became stronger for neat and plasticized PLA with
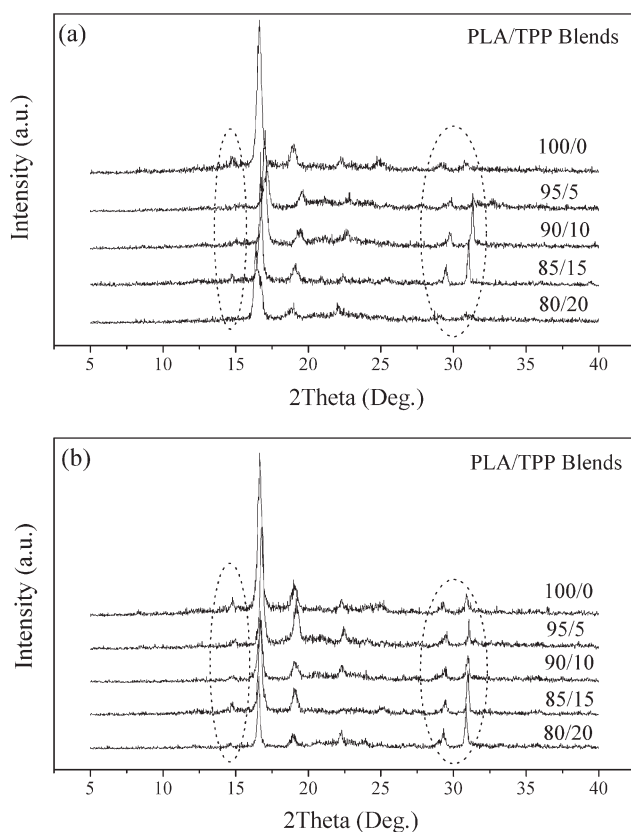
Figure 10 XRD for the neat and PLA blends containing 5, 10, 15, and 20 wt % TPP crystallized isothermally at two temperatures: (a) 113 and (b) 128°C.

various TPP contents when the crystallization temperature was increased. While at the same crystallization temperature, three peaks corresponding to α-form crystal got stronger with the introduction of TPP, as shown in Figure 10(a,b). Above results suggested that the formation of α-form crystal may have to do with the incorporation of plasticizer and annealing temperature used.

CONCLUSIONS

The spherulitic growth rate, the isothermal crystallization kinetics, and the crystal structure of neat and plasticized PLA were investigated with POM, DSC, and WAXD in detail in this work. The spherulitic growth rate was observed with hot-stage POM in a wide crystallization temperature range of 104–142 °C. The spherulitic growth rate of PLA was influenced apparently by the crystallization temperature and the TPP content in the PLA TPP blends. For the neat and plasticized PLA, the spherulitic growth rates of PLA depended on the temperature or TPP content. The maximum values of spherulitic growth rates of plasticized PLA increased when compared with neat PLA but shifted to lower temperature as TPP content was increased. For neat PLA and its blends

with 5, 10, 15, and 20 wt % TPP, the maximum growth rate of spherulite was 0.28, 0.41, 0.51, 0.55, and 0.88 μm/s, respectively, which correspond to the temperatures of 132, 122, 122, 116, and 110°C, respectively. It demonstrated that the incorporation of TPP favored the spherulitic growth. The isothermal crystallization kinetics of the neat and plasticized PLA was studied with DSC and analyzed by the Avrami equation. The results showed that for neat PLA and its blends with various TPP contents, the average value of Avrami exponents is very close to 2.5 at two crystallization temperatures of 113 and 128°C, the crystallization rate decreased with increasing TPP content. For neat PLA and its blend with 15 wt % TPP content, the average value of n was 2.0 and 2.3, respectively. The crystallization rate decreased with the increase of crystallization temperature. Further investigation into crystallization activation energy of neat PLA and its blend with 15 wt % TPP showed that the crystallization activation energy of plasticized PLA increased when compared with that of neat PLA, indicating that the incorporation of TPP retards crystallization of PLA. The crystal structure of PLA crystallized isothermally in the temperature range of 113–128°C was not modified by the plasticizer, and was still α-form.
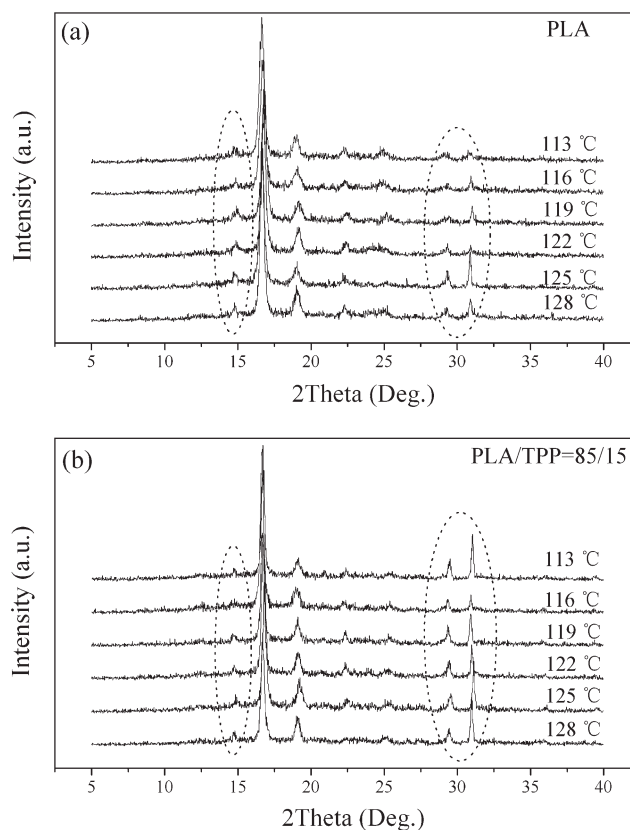

Figure 11 XRD for neat PLA (a) and its blends containing 15 wt % TPP (b) crystallized isothermally at various temperatures of 113, 116, 119, 122, 125, and 128°C.

But it is noteworthy that the peaks at $2\theta = 14.8°$, $29.4°$ and $30.9°$, which correspond to α-form crystal, cannot appear under the unannealing condition.

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