

Effect of Zinc Phenylphosphonate on the Crystallization Behavior of Poly(L-lactide)

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ABSTRACT: The effect of zinc phenylphosphonate (PPZn) on the crystallization behavior of poly(L-lactide) (PLLA) was investigated using differential scanning calorimetry (DSC) and Polarized Optical Microscopy (POM) measurements. The non-isothermal cold crystallization results showed that the addition of PPZn obviously decreased the cold crystallization temperature of PLLA and increased the degree of crystallinity of PLLA. The isothermal crystallization kinetics results showed that the crystallization rate of PLLA with small amount of PPZn was much higher than that of neat PLLA, and the half-time ($t_{1/2}$) of PLLA/PPZn sample is far less than that of neat PLLA. As an effective nucleating agent, PPZn particles had also some influence on nucleation mechanism and crystal growth of PLLA. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2744–2752, 2013

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INTRODUCTION

Poly(L-lactic acid) (PLLA) is a renewable, biodegradable, and biocompatible thermoplastic semicrystalline polymer with high tensile strength and high modulus, which has been widely used in the biomedical, agricultural, and package fields.^{1–10} However, its slow crystallization rate, relatively poor toughness, and low heat deflection temperature have restricted its further large-scale commercial application. In order to overcome these disadvantages, plasticization,¹¹ copolymerization,¹² blending with a variety of other polymers including poly(ϵ -caprolactone),¹³ poly(ethylene glycol),¹⁴ poly(*R,S*-3-hydroxybutyrate),¹⁵ poly(ethylene oxide),¹⁶ and reinforced composite^{17,18} have been developed to improve the mechanical properties of PLLA. In general, the addition of nucleating agents (NA) was an effective approach to enhance the crystallization rate and heat deflection temperature of PLLA matrix. In recent years, several kinds of nucleating agents have been developed and their effects on the crystallization behavior of PLLA have been widely studied.^{19–23} Talc has been widely used as NA for PLLA and other polymers, which was found that it dramatically decreased the crystallization half-time of PLLA.¹⁹ A kind of aliphatic amide, named as *N,N*-ethylenebis(12-hydroxysteramide) could be greatly increase the nucleation density and crystallization rate of PLLA.²⁰ Some hydrazide compounds²¹ and montmorillonite,²² and nanostructured carbon²³ could accelerate the crystallization rate.

In addition of the use of organic nucleation agents, a series of biodegradable polyesters including polyethylene glycol (PEG),¹¹ poly[(*R*)-3-hydroxybutyrate] (PHB),²⁴ poly(ϵ -caprolactone) (PCL),²⁴ and polyglycolide (PGA)²⁴ were used to be crystallization-accelerating agents, and the stereocomplexation between PLLA and PDLA [poly(*D*-lactic acid)] was also found to be one of effective nucleating agent.²⁵ Due to the extremely high radius growth rate and density of stereocomplex spherulites and a very short induction period compared to PLLA or PDLA spherulites, the overall crystallization rate of PLLA stereocomplexes was much higher than that of pure PLLA or PDLA.²⁶ However, the high production cost of PDLA greatly limits the widespread application of stereocomplexed PLLA material.

Recently, PLLA nanocomposites have received considerable attention, consisting of layered silicate,²⁷ polyhedral oligomeric silsesquioxanes (POSS),^{28,29} acrylic rubber nanoparticles (ACR),³⁰ and layered metal phosphonates.^{31,32} Specially, PLLA/layered metal phenylphosphonate composites could be prepared using a simple melt-blending, and zinc phenylphosphonate (PPZn) showed excellent nucleating efficiency on the crystallization of PLLA. In general, the mechanical properties, optics property, biodegradability, and processing of PLLA composites are closely related with the crystallization behavior. However, few studies have been conducted on the PLLA crystallization

behavior using PPZn as a kind of nucleating agent. In this study, the cold crystallization and melt crystallization process of PLLA in the presence of PPZn below 5.0 wt % was investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The principle aim of this work is to study the effect of PPZn on the crystallization behavior and polymorphism of PLLA.

EXPERIMENTAL

Materials

PLLA pellets (Natureworks 2002D, $M_w = 38 \times 10^4 \text{ g mol}^{-1}$, $M_w/M_n = 1.59$) were purchased from America Natureworks Company. Phenylphosphonic acid (analytical grade) was provided from Shandong University of Science and Technology, China. ZnCl_2 and NaOH (analytical grade) were purchased from Beijing Chemical Co., China. PEG was provided by Tianjin Damao Chemical Agent Company China. ($M_w = 1000 \text{ g mol}^{-1}$, PCL was provided by Shenzhen Guanghua Weiye Co., China. ($M_w = 10.0 \times 10^4 \text{ g mol}^{-1}$, $M_w/M_n = 1.8$). Talc was purchased from Shanghai Chuangyu Chemical Engineering Co., China. The average size of Talc particles is about $2.6 \mu\text{m}$.

Synthesis of Zinc Phenylphosphonate (PPZn). PPZn was synthesized by aqueous solutions of phenylphosphonic acid and ZnCl_2 according to previous work.³³ One gram of phosphonic acid dissolved in 40 mL water. One equivalent of metal salt dissolved in 20 mL water was added to the stirred phosphonic acid solution, followed by sufficient 0.1 mol L^{-1} aqueous NaOH to adjust pH to 5–6. The Zinc phenylphosphonate precipitated as poorly crystalline. The crystalline of PPZn was increased by stirring filtered precipitates in water at 50°C for 3 days. The result was filtered, washed with water and dried at 200°C for 24 h. It was observed using SEM measurement that the PPZn particles were rod-like structure and the average size of PPZn was about $0.6 \mu\text{m} \times 0.1 \mu\text{m}$. The distribution of PPZn particles in PLLA matrix was shown in Figure 1.

Preparation of PLLA/PPZn blends. The PLLA and PLLA blend samples with different content of PPZn were mixed using HAAKE PolyLab OS (Thermo Fisher Scientific, Germany) at 180°C for 8 min, with a rotor speed of 50 rpm.

DSC Measurement

The non-isothermal and isothermal crystallization behavior of PLLA and PLLA blend samples were monitored during heating and cooling using DSC measurement (TA Company Q-20) under nitrogen gas. The samples were first heated at rate of $10^\circ\text{C min}^{-1}$ from room temperature to 190°C , and melt at 190°C for 2 min, rapidly quenched to 0°C at 100°C/min . In non-isothermal crystallization process, the samples were heated from 20 to 190°C at 10°C/min and melt at 190°C for 2 min, and then cooled from 190 to 20°C at 10°C/min . In the isothermal crystallization process, the samples were rapidly cooled from 190°C to the different set temperature from 80 to 125°C , and crystallized at set temperature for the set time, then heated from the set temperature to 190°C at 10°C/min .

Polarized Optical Microscopy (POM)

An optical microscope (OLYMPUS BX50, Japan) equipped with a Linkam temperature controller was used to observe the spherulitic morphology of PLLA and PLLA/PPZn blends. The samples were

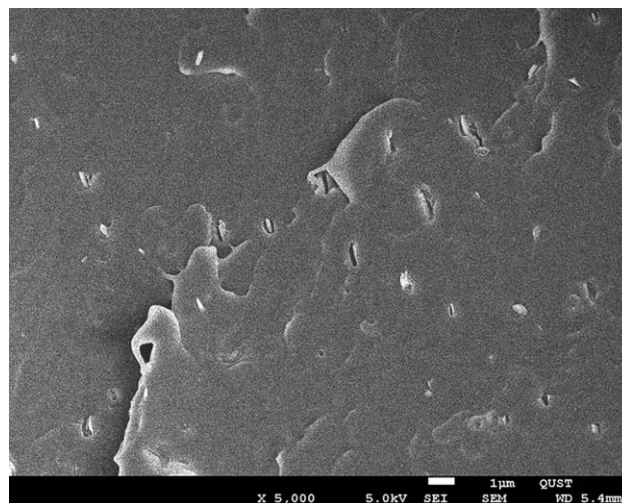


Figure 1. SEM photograph of surface fracture of PLLA/1.0 wt % PPZn sample.

first heated from room temperature to 190°C and kept at 190°C for 2 min to eliminate thermal history and then cooled to set temperature at a cooling rate of 50°C/min and isothermal crystallized at 110, 115, 120, 125°C for 120 min. The spherulite morphology was recorded during the isothermal crystallization process.

RESULTS AND DISCUSSION

Non-isothermal Cold Crystallization and Melting Process of PLLA with Different Nucleating Agents

The non-isothermal cold crystallization behavior of PLLA with different kind of nucleating agents was investigated by DSC measurement. Talc is one of widely inorganic nucleating agent for semicrystalline polymers. PEG is one of plasticization agent, which is used to accelerate the crystallization rate of PLLA. PCL is a kind of comprising biomaterial, which also found to be an effective

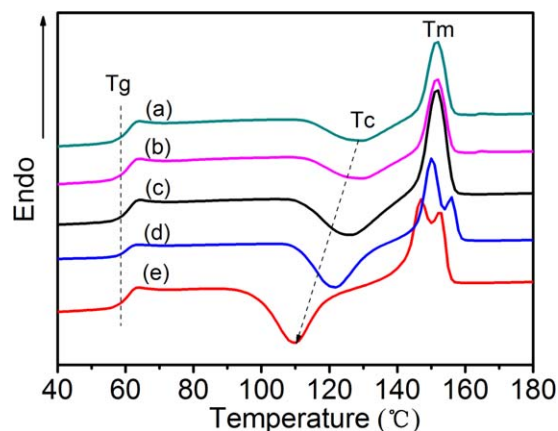


Figure 2. DSC curves of PLLA and PLLA blends with 1.0 wt % different nucleating agent at the heating rate of 10°C/min (a) neat PLLA, (b) PLLA/Talc (1.0 wt %), (c) PLLA/PCL (1.0 wt %), (d) PLLA/PEG (1.0 wt %), and (e) PLLA/PPZn (1.0 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Thermodynamic Parameters of PLLA and PLLA/NA Samples During Non-Isothermal Cold Crystallization at 10°C/min

Sample	T_g (°C)	T_{cs} (°C)	T_{cp} (°C)	T_{ce} (°C)	ΔH_c (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	X_c (%)
PLLA	61.4	113.7	128.3	142.0	9.16	-	151.6	12.17	13.08
PLLA/PCL (1.0 wt %)	61.3	112.1	126.6	141.5	15.43	-	151.6	16.99	18.26
PLLA/PEG (1.0 wt %)	60.9	110.8	122.0	140.0	14.83	150.2	156.2	15.46	16.77
PLLA/Talc (1.0 wt %)	61.0	109.3	124.3	135.5	17.86	-	151.8	22.36	24.04
PLLA/PPZn (1.0 wt %)	61.2	98.8	110.1	119.3	18.86	146.9	152.6	24.17	25.98

crystallization-accelerating agent for PLLA. Figure 2 shows the DSC curves of non-isothermal cold crystallization and subsequent melting process for neat PLLA and PLLA with 1.0 wt % PEG, PCL, Talc, and 1.0 wt % PPZn. T_{cs} , T_{cp} , T_{ce} represent the crystallization onset temperature, crystallization peak temperature, and crystallization end temperature of PLLA samples, respectively, which were obtained from DSC curves of PLLA and PLLA/NA samples during non-isothermal crystallization. The thermal properties of neat PLLA and PLLA/NA samples during non-isothermal cold crystallization are summarized in Table I. T_{cp} of neat PLLA is about 128.3°C and the whole cold crystallization peak of PLLA is very wide. With the addition of 1.0 wt % Talc, PCL, and PEG, T_{cp} of PLLA/NA samples appear at 126.6, 124.3, and 122.0°C in the DSC curves, respectively. For PLLA with 1.0 wt % PPZn, T_{cp} shifts to a lower temperature at about 110.1°C, and the melt enthalpy (ΔH_m) of PLLA is 18.86 J/g, which is twice times that of neat PLLA (9.16 J/g), and it is also larger than that of PLLA/1.0 wt % PEG, PLLA/1.0 wt % PCL, and PLLA/1.0 wt % Talc. It is shown that the addition of PPZn could greatly accelerate the cold crystallization process of PLLA, and its efficiency on PLLA crystallization is much better than that of the same amount of PEG, PCL, and Talc.

Figure 3(a) and (b) shows DSC curves of PLLA and PLLA blend samples with different content of PPZn during non-isothermal cold and melt crystallization at 10°C/min. The thermal properties of neat PLLA and PLLA/PPZn samples are summarized in Table II. The glass transition temperature of PLLA (T_g) is about 61.4°C, T_{cp} is at around 128.3°C with crystallization enthalpy (ΔH_c) about 9.16 J/g, and the melt temperature (T_m) is around 151.6°C with melt enthalpy (ΔH_m) about 12.17 J/g. For PLLA with the addition of 0.1 wt % PPZn, T_g of is about 61.4°C, which indicates that the variation of PPZn loading has little influence on the T_g of PLLA. T_{cp} value of PLLA shifts to about 119.4°C, and the crystallization enthalpy increases by 16.06 J/g. With the increasing of PPZn content, T_{cp} values shift to 111.1, 110.1, and 103.9°C with the addition of 0.5 wt % PPZn, 1.0 wt % PPZn, 5.0 wt % PPZn, respectively. It is very apparent that T_{cp} decreases with the incensement of the content of PPZn. The crystallization degree (X_c) of PLLA was evaluated according to the following equation:

$$X_c(\%) = 100(-\Delta H_m) / [(93.0(1 - x_{PPZn}) / 100)]$$

Where ΔH_m is the enthalpy of melting of PLLA, 93.0 J/g is the enthalpy of melting of PLLA crystals having an infinite size,³⁴

and X_{PPZn} is PPZn weight fraction. The value of the crystallinity (X_c) of neat PLLA is 13.08%; X_c of PLLA with 0.1% PPZn is 27.05%, which is about two times that of neat PLLA. Specially, the crystallinity (X_c) of PLLA with 5.0 wt % PPZn reaches to 30.06%. It is shown that the crystallinity of PLLA is enhanced with adding small amount of PPZn.

The melting process of PLLA with different content of PPZn shown in Figure 3(a) appears one or double melting peak. When the content of PPZn is 0.1 wt %, only one endotherm peak appears in the DSC melting curve, the cold crystallization

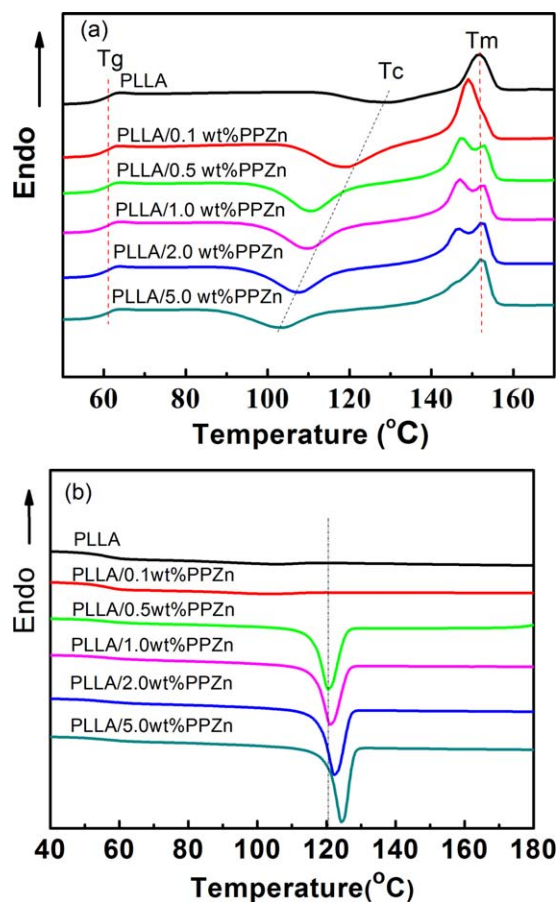


Figure 3. DSC curves of PLLA and PLLA/PPZn samples during non-isothermal crystallization at 10°C/min (a) from 40°C to 190°C; (b) from 190°C to 40°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Thermodynamic Parameters of PLLA and PLLA/PPZn Samples During the Non-Isothermal Cold Crystallization at 10°C/min

Sample	T_g (°C)	T_{cs} (°C)	T_{cp} (°C)	T_{ce} (°C)	ΔH_c (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	X_c (%)
PLLA	61.4	113.7	128.3	142	9.16	—	151.6	12.17	13.08
PLLA/PPZn (0.1 wt %)	61.4	106.8	119.4	140.0	16.06	149.0	152.5	25.14	27.05
PLLA/PPZn (0.5 wt %)	61.3	100.1	111.1	120.7	19.62	147.5	152.8	24.80	27.07
PLLA/PPZn (1.0 wt %)	61.2	98.8	110.1	119.3	18.86	146.9	152.6	24.17	26.25
PLLA/PPZn (2.0 wt %)	61.3	96.1	108.0	116.1	18.75	146.5	152.4	25.88	28.39
PLLA/PPZn (5.0 wt %)	61.0	89.9	103.9	113.6	14.37	145.9	152.4	26.56	30.06

peak is higher than 110°C, indicating that PLLA α crystals are mainly formed in the cold crystallization process.^{35,36} When the PPZn content is more than 0.5 wt %, two melting peak or one melting peak and shoulder peak are observed. The corresponding cold crystallization peak temperatures of PLLA are relatively lower than those of neat PLLA (<110°C), thus the less perfect crystals are formed. The lower temperature peak is ascribed to the melting peak of primary crystals, and the higher temperature peak or shoulder peak is corresponding to the melting of the recrystallization crystals. Thus the PLLA/PPZn samples have a melt recrystallization and re-melting process; the different melting behavior of PLLA/PPZn is attributed to the effect of different content of PPZn on the cold crystallization temperature of PLLA.

Figure 4 shows the dependence of crystallization temperature on the PPZn content for PLLA/PPZn samples during non-isothermally crystallization. With the increasing of the PPZn content, T_{cs} , T_{cp} , T_{ce} of PLLA/PPZn samples shift to lower temperature. Specially, T_{cs} , T_{sp} , T_{ce} of PLLA with 5 wt % PPZn are lower about 23.8, 24.4, and 28.4°C than those of neat of PLLA. It can be concluded that the non-isothermal cold crystallization of PLLA are greatly enhanced with the adding small amounts of PPZn relative to neat PLLA, which indicating that PPZn could act as an effective nucleating agent during the non-isothermal

cold crystallization. In a practical processing of PLLA, it is very important to decrease the cold crystallization temperature of PLLA and increase the degree of crystallinity of PLLA.

Isothermal Crystallization of PLLA with Different Content of PPZn

The effect of PPZn content on the isothermal melt crystallization process of PLLA was investigated using DSC measurements. The isothermal crystallization temperature ranges is from 110 to 125°C. Figure 5 shows the representative DSC curves of melting process of PLLA with different content of PPZn isothermally crystallized at 115°C for 30 min. It can be observed that the melting peak temperature of PLLA shifts to a higher temperature because of the presence of PPZn. The dependence of melting temperature (T_m) and the crystallinity of PLLA/PPZn samples on the PPZn content are shown in Figure 6. The melting temperature of PLLA/PPZn blend has an increment trend when the PLLA/PPZn samples were crystallized from 110°C to 120°C, and the degree of crystallinity of PLLA increased with the increase of PPZn content. When PLLA with 0.1–5.0 wt % PPZn isothermally crystallized at 120°C, the crystallinity of PLLA reaches a maximum value.

In fact, the melting behavior of PLLA is closely relative to the crystallization temperature and crystalline structure. In order to

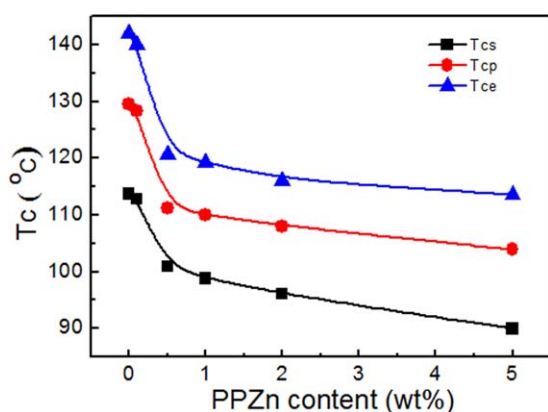


Figure 4. Dependence of crystallization temperature (T_c) on the PPZn content for PLLA/PPZn samples during non-isothermally cold crystallization at heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

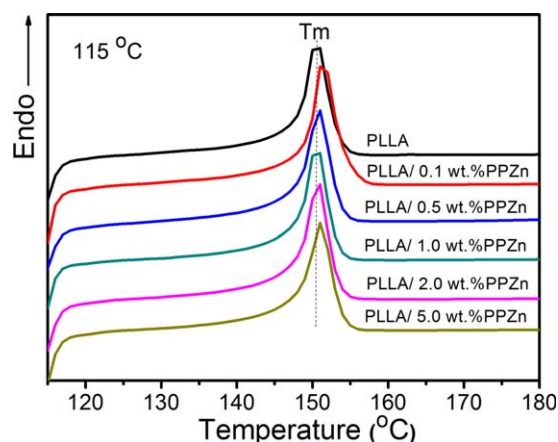


Figure 5. DSC curves of melting behavior after isothermal melt crystallization at 115°C for PLLA and PLLA with different content of PPZn. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

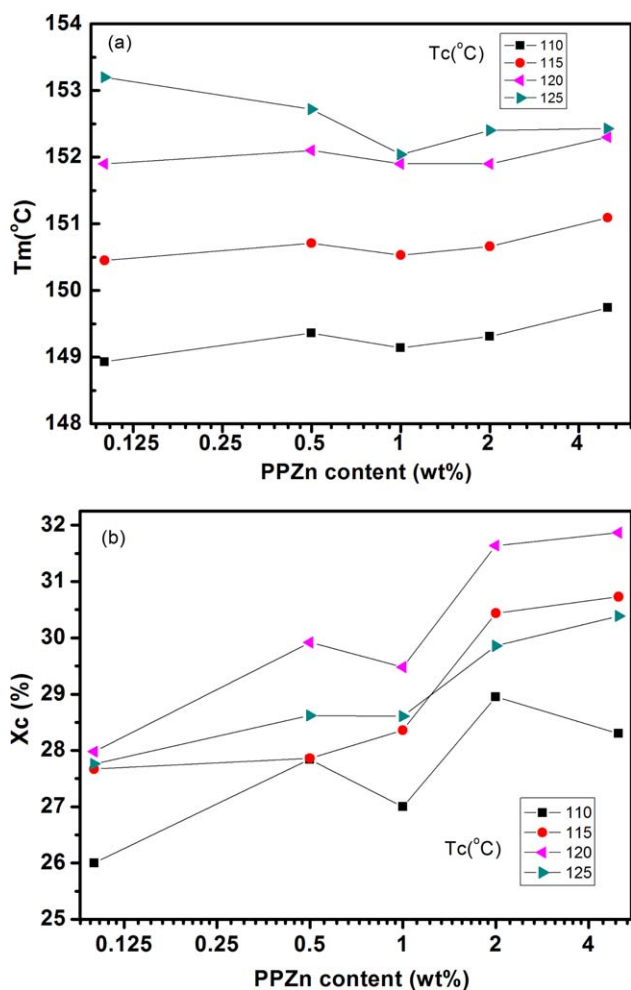


Figure 6. Dependence of (a) melting temperature (T_m) and (b) crystallinity (X_c) of PLLA/PPZn samples on the PPZn contents during isothermal melt-crystallization at different temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

further investigate crystal structure and the melting process of PLLA/PPZn samples at different crystallization temperature, DSC curves of PLLA/1.0 wt % PPZn isothermally crystallized from 80°C to 125°C are shown in Figure 7. We observe the two melting peaks from 130°C to 155°C for PLLA/1.0 wt % PPZn crystallized from 80°C to 90°C, and there is very obvious exothermal process between two melting peaks. With the increasing of isothermal crystallization temperature, the shapes of the two melting peak changes. When the isothermal crystallization temperature is from 105°C to 125°C, respectively; the melting peak become one and the peak shifts to a higher temperature. Zhang et al.³⁶ studied the melting behavior of PLLA by simultaneous WAXD and DSC measurements; they found that PLLA sample demonstrated a peculiar small exothermal peak around 160°C prior to the melting point, while the sample crystallized at temperature around 120°C showed a double melting behavior. It was confirmed that the small exothermal peak corresponded to the phase transition from the disorder α' to order α form, in which the chain packing of the crystal lattice became more compacted.

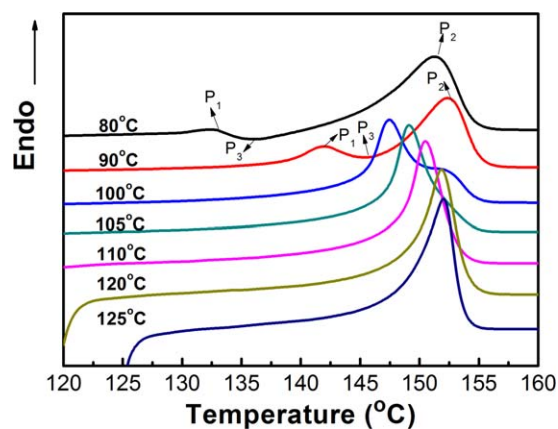


Figure 7. DSC curves of melting behavior of PLLA/PPZn (1.0 wt %) samples after isothermal melt crystallization at 80–125°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For PLLA/1.0 wt % PPZn sample, when the isothermal crystallization temperature ranges is from 80°C to 90°C, the first melting peak obviously appears, which may be corresponding to α'

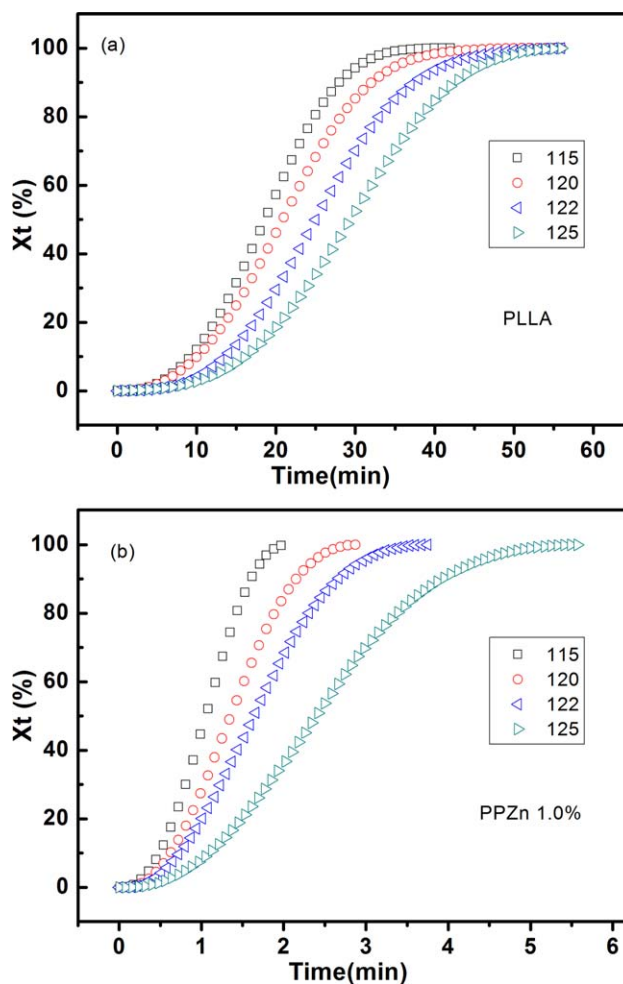


Figure 8. The relationship between the relative crystallinity and crystallization time of PLLA and PLLA/PPZn (1.0 wt %) samples at different isothermal crystallization temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

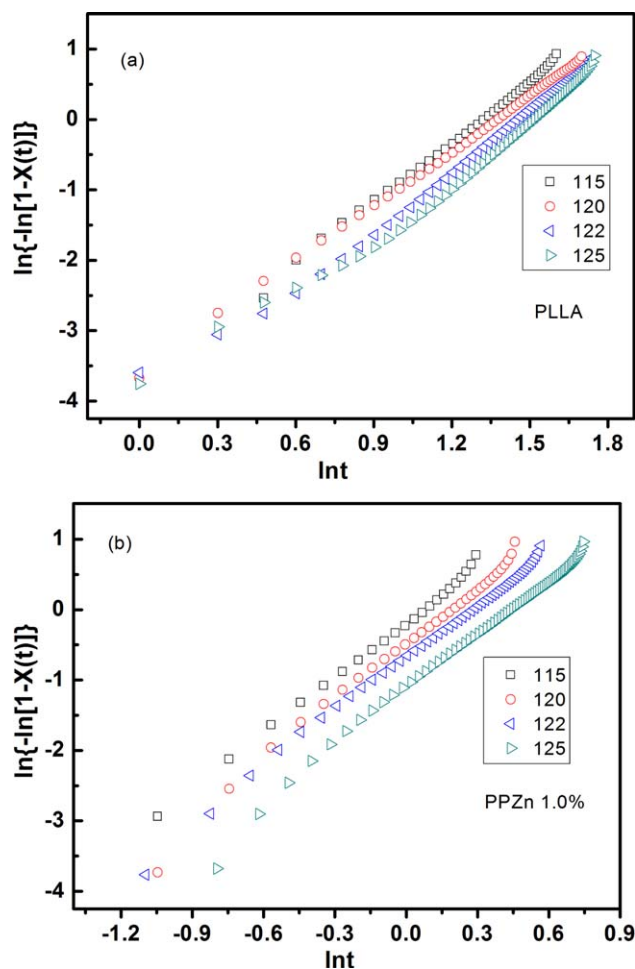


Figure 9. The Avrami plots between $\ln\{-\ln[1 - X(t)]\}$ and $\ln t$ of PLLA and PLLA/PPZn (1.0 wt %) samples at different isothermal crystallization temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

form melting peak, the second peak is corresponding to α form melting peak. And the exothermal peak between two melting peaks may be corresponding to the phase transition from α' form to α form. When the isothermal crystallized temperature is increased by 100°C, the shape of two melting peaks changes, the peak at lower temperature (P1) is ascribed to the melting peak of primary crystals, and the peak at higher temperature (P2) is corresponding to the melting peak of the recrystallization crystals. With the isothermal crystallization temperature is increased from 105°C to 125°C, the melting peak becomes one and the peak shifts to higher temperature, which means that α form is mainly developed, and the α' form crystals become perfect. As is well known in the literatures,^{35,36} for neat PLLA, α form was formed at higher 120°C, and α' form was mainly formed at lower 100°C, α and α' form were formed between 100 and 120°C. The above experimental result shows that α form is mainly formed at higher 105°C by adding 1.0 wt % PPZn. It is speculated that PPZn particles acted as heterogeneous nuclei during PLLA crystallization process and reduced the free energy for the formation of a critical nucleus, thus the formation of α crystals could be formed at relatively low temperature.

Isothermal Crystallization Kinetics of PLLA with Different Content of PPZn

Figure 8 shows the plots of the relative crystallization and crystallization time for PLLA and PLLA/PPZn blends during different isothermal melt crystallization process. The Avrami equation is used to analyze the isothermal crystallization kinetics of PLLA. The relative degree of crystallization with crystallization time is in the following form.^{37,38}

$$\ln[-\ln(1 - X_t)] = \ln k + n \ln t$$

Where X_t is the relative degree of crystallinity, t is crystallization time, n is Avrami exponent depending on the nature of nucleation and growth geometry of the crystals, and k is the crystallization rate constant involving both nucleation and growth rate parameters. Figure 9 shows the Avrami plots of neat PLLA and PLLA/1.0 wt % PPZn isothermal crystallized at 115, 120, 122, and 125°C. The Avrami parameters n and k can be obtained from the slopes and the interceptions of these fitting linear curves. The half-life $t_{1/2}$ is an important parameter for the crystallization kinetics and can be expressed as follows:

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

The parameters of crystallization kinetics calculated from Figure 9 are summarized in Table III. In general, the Avrami exponent

Table III. Isothermal Melt Crystallization Kinetics Parameters of PLLA and PLLA/PPZn Samples at Different Crystallization Temperature (T_c) Based on the Avrami Equation

Sample	T_c (°C)	k (min ⁻ⁿ)	n	$t_{1/2}$ (min)
PLLA	115	1.65×10^{-4}	3.58	18.08
	120	2.54×10^{-4}	3.42	20.33
	122	9.08×10^{-5}	3.38	24.85
	125	7.53×10^{-5}	3.12	28.37
PLLA/PPZn (0.1 wt %)	115	7.84×10^{-2}	3.04	2.04
	120	2.43×10^{-2}	3.16	2.78
	122	1.76×10^{-2}	3.09	3.27
	125	7.5×10^{-3}	3.06	4.37
PLLA/PPZn (0.5 wt %)	115	0.51	2.86	1.11
	120	0.33	2.41	1.36
	122	0.18	2.96	1.56
	125	0.06	2.76	2.37
PLLA/PPZn (1.0 wt %)	115	0.68	2.68	1.00
	120	0.31	2.77	1.32
	122	0.20	2.58	1.6
	125	0.07	2.70	2.39
PLLA/PPZn (2.0 wt %)	115	2.35	2.61	0.62
	120	1.11	2.30	0.81
	122	0.70	2.52	0.99
	125	0.21	2.48	1.60

n is thought to be associated with the crystal growth dimensional and nucleation modes. For the heterogeneous nucleation system, the crystal growth dimensional is equal to n , whereas it is equal to $n - 1$ for homogeneous nucleation mode. From Table III, it can be seen that the average value of n for neat PLLA is about 3.38. It is suggested that the crystallization start from homogeneous nucleation and the crystal growth corresponds to either 2-D ($n = 3$) or 3-D ($n = 4$) crystallization. With the adding of PLLA, the Avrami exponent n becomes smaller than that of neat of PLLA. For PLLA with 0.5 wt % PPZn, the Avrami exponent n is about 2.86 at 115°C. It is suggest that crystallization of PLLA/PPZn starts from heterogenous nucleation and crystal growth corresponds to between three-dimensional and two-dimensional. The crystallization rate of PLLA could be described by k or $t_{1/2}$. In Table III, $t_{1/2}$ of neat PLLA at 120°C is 20.33 min; $t_{1/2}$ of PLLA/1.0 wt % PPZn is only 1.32 min at same crystallization temperature. Figure 10 shows the variation of $t_{1/2}$ with crystallization temperature (T_c) for neat PLLA and PLLA/PPZn. It can be clearly seen that $t_{1/2}$ decreases with the increasing of PPZn content at same crystallization temperature (T_c), and $t_{1/2}$ of PLLA/PPZn at 115°C are smallest. In brief, the isothermal melt crystallization process of PLLA is greatly accelerated by PPZn as an effective nucleating agent; and the enhancement of the crystallization rate of PLLA is influenced by PPZn content and T_c . It has been speculated that PPZn accelerated nucleation of PLLA by the mechanisms of epitaxial nucleation from the literature.³² The PPZn crystal possess an

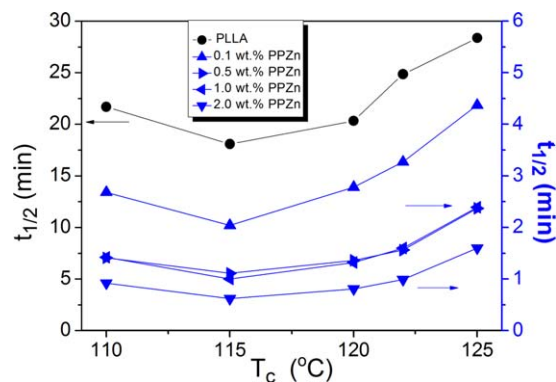


Figure 10. Variations of $t_{1/2}$ with crystallization temperature (T_c) of neat PLLA and PLLA/PPZn samples during different isothermal crystallization temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

orthorhombic cell with lattice parameters $a = 0.566$ nm, $b = 1.445$ nm, and $c = 0.480$ nm.³³ In the PLLA α crystal, the chains pack in an orthorhombic or pseudo-orthorhombic unit cell with dimensions $a = 1.034$ nm, $b = 0.597$ nm, and $c = 2.88$ nm.³⁹ The length of the c -axis of the PLLA α crystal is twice that of the b -axis of the PPZn crystal. This excellent matching was suggested that PLLA crystals might grow on the PPZn surface by an epitaxial mechanism, which the (0 0 1) lattice plane of PLLA along the (0 1 0) direction of PPZn crystals.

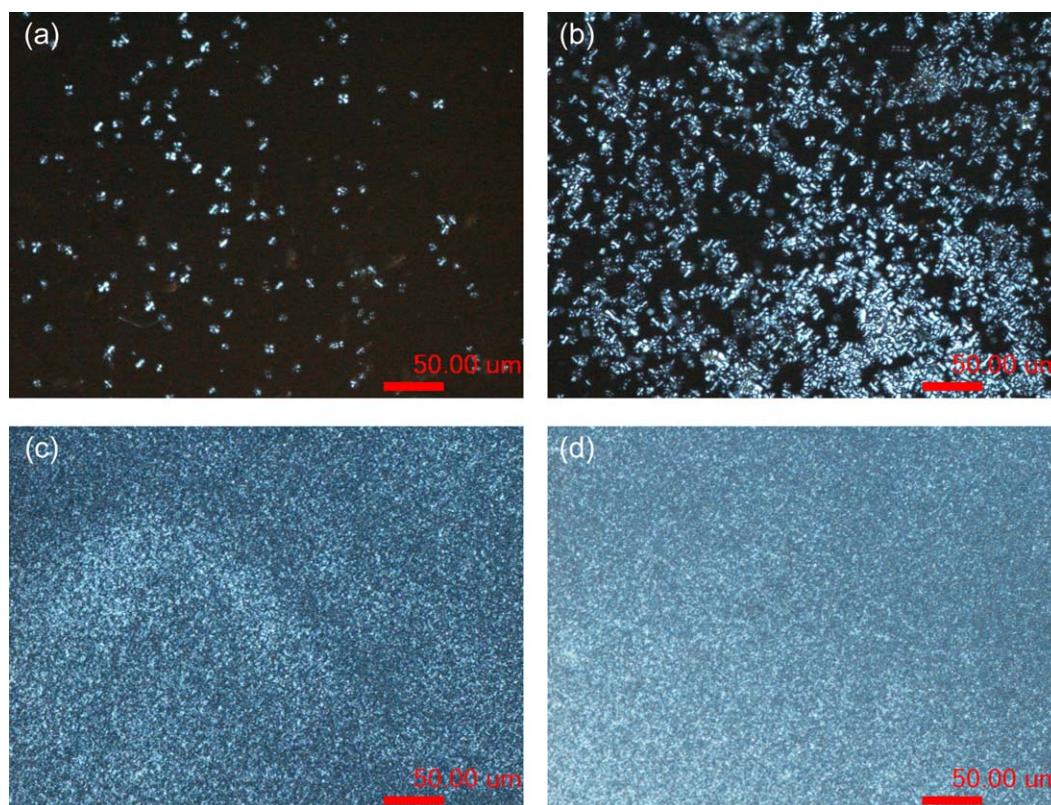


Figure 11. POM images of neat PLLA and PLLA/NAs isothermal crystallization at 110°C for different time. (a) PLLA 90 min, (b) PLLA/1.0 wt % PCL 5 min, (c) PLLA/1.0 wt % PEG 5 min, (d) PLLA/1.0 wt % PPZn 5 min, (e) PLLA/2.0 wt % PPZn 5 min, and (f) PLLA/5.0 wt % PPZn 5 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

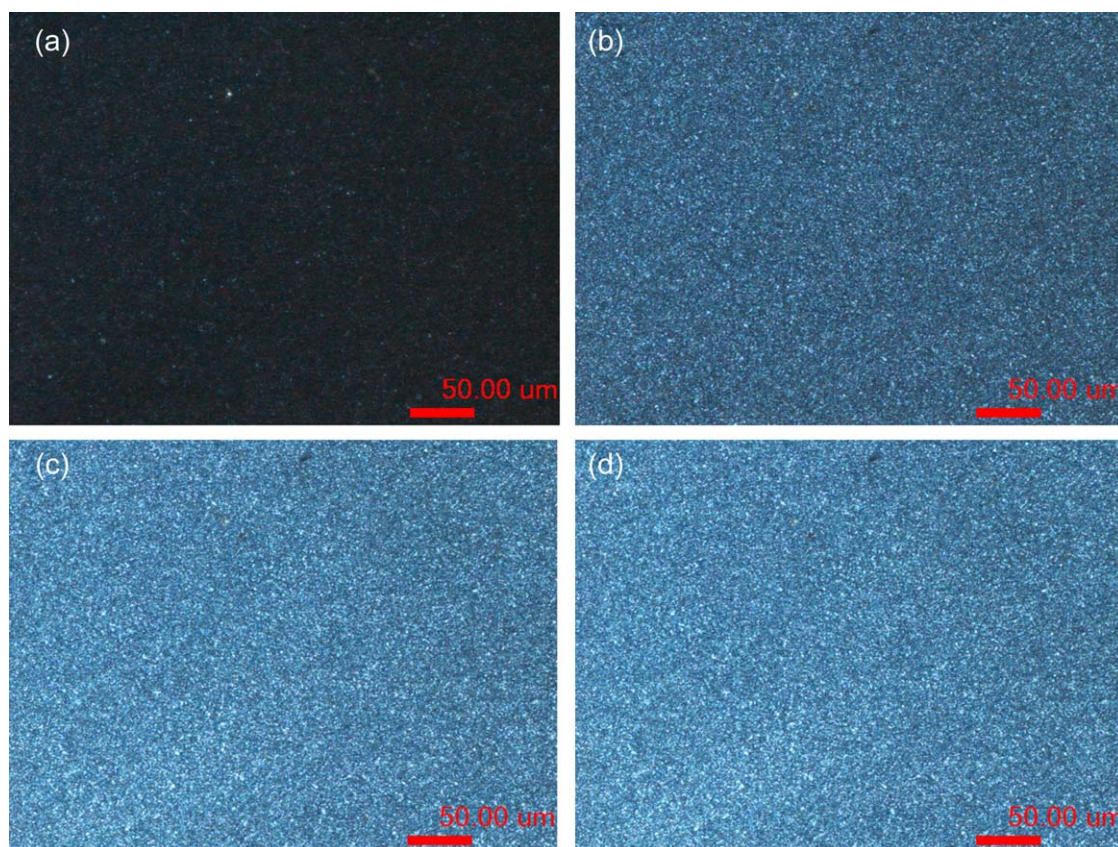


Figure 12. POM images of PLLA/PPZn (0.5 wt %) samples during isothermal crystallization process at 115°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

POM experiments were performed to investigate the crystal morphology of neat PLLA and PLLA with different of nucleating agents. Figure 11 displays the crystal morphology of PLLA with different nucleating agents crystallized at 115°C. In Figure 11(a–c) illustrates the POM images of PLLA with 1.0 wt % PCL, 1.0 wt % PEG, 1.0 wt % PPZn crystallized for 5 min at 115°C, respectively. It is very obvious that the crystallization rate for PLLA/PPZn is fastest than that of PLLA/PCL and PLLA/PEG, and the number of PLLA spherulites is greatest than those of PLLA/PCL and PLLA/PEG blends. The size of spherulites of PLLA in PLLA/PPZn blends is too small to measure. With the increasing of PPZn content, it is no obvious difference in PLLA/1.0 wt % PPZn and PLLA/2.0 wt % PPZn blends shown in Figure 10(c) and (d). Figure 12 (a–d) illustrates the isothermal crystallization process of PLLA with 0.5 wt % PZ at 115°C. In Figure 12(a), it is a little dark in the visual field crystallized at 115°C for 1 min, and some small crystal could be identified, then it becomes lighter in Figure 12(b) crystallized for 2 min, and after 3 min, it changes very little in Figure 12(c) and (d), which indicates that the isothermal crystallization continues for about 3–4 min. Compared with neat PLLA, the crystallization time of PLLA/0.5 wt % PPZn is dramatically shortened about 30 times. The POM results are consistent with the result of isothermal crystallization kinetics by DSC measurement.

CONCLUSION

The non-isothermal cold and isothermal melt crystallization processes of PLLA with different content of PPZn at various

crystallization temperatures were investigated by DSC and POM measurement. It is found that the non-isothermal cold crystallization temperature of PLLA with different content of PPZn is obviously lower than that of neat PLLA, and the addition of PPZn on the PLLA matrix dramatically increases the crystallinity of PLLA. The isothermal melt crystallization results show that the crystal structure of PLLA in PLLA/PPZn blend depends on the crystallization temperature. When the isothermal crystallization temperature was below 100°C, there was very obvious exothermal peak between two melting peaks for PLLA/1.0 wt % PPZn, which may be corresponding to phase transition peak from α' to α form. When the isothermal crystallization temperature was increased over 110°C, α form is mainly developed, and α form crystal become perfect. It is a little ahead in the formation of α crystal because of the presence of PPZn. The isothermal crystallization kinetics results show that k for PLLA with several percents of PPZn is much larger than that of neat PLLA, and the half-time ($t_{1/2}$) of PLLA/PPZn blend is dramatically smaller than that of neat PLLA. It indicates the crystallization rates of PLLA in PLLA/PPZn blends are greatly faster than that in neat PLLA, and the enhancement of the crystallization rate of PLLA is influence by PPZn content and crystallization temperature.

PPZn has some influence on nucleation mechanism and crystal growth. For neat PLLA, the crystallization start from homogeneous nucleation and the crystal growth corresponds to either 2-D ($n = 3$) or 3-D ($n = 4$) crystallization. With the different

content of PPZn, the Avrami exponent n is from 2.48 to 3.09. It is suggested that the crystallization mechanism for PLLA/PPZn starts from heterogeneous nucleation and the crystal growth corresponds to between three dimensional and two dimensional. POM images show that the number of PLLA spherulites in the PLLA/PPZn blend is greater than in neat PLLA; and the size of PLLA spherulites in PLLA/PPZn is smaller than in neat PLLA. The crystallization time in PLLA/PPZn is dramatically shorter than that in PLLA. The increased nucleation density of PLLA spherulites in the PLLA/PPZn indicates that PPZn could act as a very effective nucleating agent either the cold crystallization or melt crystallization.

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