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Crystallization Behavior of Biodegradable Poly(ethylene adipate) Modulated by a Benign Nucleating Agent: Zinc Phenylphosphonate*

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Abstract Zinc phenylphosphonate (PPZn), a benign and biocompatible nucleating agent, was prepared and incorporated into the biodegradable poly(ethylene adipate) (PEA) to investigate its effect on the crystallization behavior, crystallization kinetics and spherulite morphology of PEA. Upon addition of PPZn, the crystallization temperature and crystallinity of PEA in the non-isothermal crystallization process increased significantly. Analysis of crystallization kinetics by Avrami equation suggests that the crystallization time shortened greatly and crystallization rate increased markedly after addition of PPZn. In the presence of PPZn, the spherulite size decreased and spherulite density increased significantly. It suggests that PPZn is an efficient nucleating agent for the crystallization of PEA. The accelerated crystallization in the presence of PPZn is mainly attributed to the epitaxial nucleation of PEA crystals on the surface of PPZn crystals, that is, a perfect lattice matching between PEA crystal and PPZn crystal occurs.

Keywords Crystallization kinetics; Epitaxial growth; Poly(ethylene adipate); Nucleating agent

INTRODUCTION

Wide applications (such as food packaging, clothing, transportation, construction, medical and leisure industries) and significantly growing development in products made from traditional petroleum-based polymeric materials, have been witnessed in the recent several decades due to their outstanding mechanical strength, resistance to chemical and biological attack, and low cost[1, 2]. However, the serious and global environmental pollution caused by these non-biodegradable polymeric products has been a main concern by environmentalists, chemists and engineers. Much attention has been paid to polyester materials such as poly(L-lactide)[2] and poly(ε-caprolactone)[3] due to their biodegradability, biocompatibility, recyclability, non-toxicity in degradable products, and excellent mechanical properties.

Poly(ethylene adipate) (PEA), a linear aliphatic polyester made from glycol and diacid, is biodegradable[1] and can be potentially applied in the biomedical field. Hydroxyapatite (HAp)/PEA, as a bioactive composite, was prepared by *in situ* ring-opening polymerization of cyclic oligo(ethylene adipate) within the porous HAp template[4]. Till now, a multitude of works have been focused on the investigation of crystal unit cell and crystalline microstructure[5–11], observation of spherulite or crystal morphology (ring band and ringless

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morphology)[12−22], revealing of the properties (thermal property, degradability)[23−28] of neat PEA or PEA-based composites. It is well known that properties of the polymeric materials are closely related to their crystallization behavior and crystallization kinetics and so control of crystallization behavior and crystallization kinetics is an effective approach to tailor the properties of polymeric materials[1, 29−31]. The crystallization behavior and crystallization kinetics of PEA have been investigated in detail and systematically[1, 32−35], and it is suggested that PEA shows the relatively low crystallization rate[1]. Copolymerization, blending and epitaxial crystallization methods have been used to manipulate the crystallization behavior and crystallization kinetics of PEA[36−39]. However, the biodegradability and biocompatibility of above blends or incorporated nucleating agents (NA) are not unclear, and the copolymerization method is complicated, high cost, and not time saving and eco-friendly.

Recently, a kind of synthetic inorganic/organic composite presenting a layered structure, metal phosphonate, has attracted much attention as a new kind of biocompatible benign filler. After incorporating α-zirconium phosphate, some polymers (such as epoxy[40, 41], poly(acrylamide)[42] and poly(ethylene terephthalate)[43]) show improved mechanical properties and thermal stability. The metal phosphonate has been widely applied as sorbents[44], ion exchange[45], chemical sensor[46] and catalyst[47]. Additionally, the metal phosphonate has also been considered as a versatile biomaterial because phosphate is a naturally occurring functional group. It was well known that calcium phosphate is a potential implant for the bone repair[48]. The metal phosphonates have also been applied in oligonucleotide microarrays, protein binding, and drug-delivery systems[49]. It is indicated that zinc phosphate is a versatile material in biomedical applications, such as bone replacement cements[50]. In particular, *via* changing the types of metal ions or organic group, the properties of metal phosphonates could be tailored. Pan *et al.* reported that zinc phenylphosphonate (PPZn) was an efficient NA to accelerate the crystallization of poly(L-lactide), and increase its tensile and storage modulus[51]. In our most recent work it was observed that PPZn could not only increase the crystallization temperature, shorten the crystallization time, but also facilitate the formation of α-modification and accelerate the β-α phase transition of polymorphic poly(butylene adipate) (PBA)[52].

In this work, PPZn, a benign metal phosphonate, was prepared and used as biocompatible NA that was incorporated into the biodegradable PEA, to investigate its effect on the crystallization behavior in the non-isothermal and isothermal crystallization process, crystallization kinetics in the isothermal crystallization process, and crystalline structure of the PEA by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide angle X-ray diffraction (WAXD). A plausible explanation was also presented and attempted to elucidate the nucleation mechanism in the crystallization process of PEA.

EXPERIMENTAL

Materials

PEA (M_w = 10000 Da) was purchased from Sigma-Aldrich Co. Before use, PEA was purified by precipitating into ethanol from the chloroform solution and then was dried under vacuum at 40 °C for 3 days. $ZnCl_2$, phenylphosphonic acid, and NaOH, which are all analytical grade, were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and used as received.

Synthesis of PPZn

PPZn monohydrate was prepared according to the previous method[53]. The detailed procedure is presented as follows. Phenylphosphonic acid (1 g) was dissolved in 40 mL of deionized water. One equivalent of $ZnCl_2$ was dissolved in the deionized water. 20 mL of $ZnCl_2$ solution was then added into the phenylphosphonic acid solution with vigorous stirring and followed by the addition of drops of 0.1 mol·L^{-1} NaOH solution to reach the pH value of 5−6. The sample was filtered and then stirred in the deionized water at 50 °C for 3 days to increase the crystallinity. The resultant sample was filtered once again, washed with the deionized water, and dried at 40 °C under vacuum for 2 days. This obtained product was then dehydrated under vacuum at 200 °C overnight. Eventually, the dehydrated PPZn was milled with a MM200 mixer mill for 3 min at a frequency of 20 Hz.

Preparation of PEA/PPZn

PEA (2 g) and milled PPZn white powder with different weight ratios were mixed in a glass containing 300 mL of chloroform and well stirred to ensure the uniform dispersion of PPZn. After evaporation of the chloroform at the room temperature for 1 day, the obtained film samples were further dried under vacuum at 40 °C for 3 days. The blend films are denoted as PEA/*x*% PPZn, where *x*% is the weight percent of PPZn powder.

Characterization

Thermal behavior of neat PEA and PEA/PPZn blends was investigated using a Pyris Diamond differential scanning calorimetry instrument (Perkin-Elmer Inc., Waltham, U.S.A.) equipped with a Perkin-Elmer intracooler 2P cooling accessory. The temperature and heat flow were calibrated using an indium standard under nitrogen purging. The sample (5–8 mg) was weighed and sealed in an aluminum pan. The samples were heated to 100 °C and held at 100 °C for 3 min to remove the thermal history of PEA. Then they were cooled to −20 °C at 10 K·min^{-1} for the non-isothermal crystallization or quickly cooled at 100 K·min^{-1} to the preset temperature for the isothermal crystallization, followed by a reheating to 100 °C at 10 K·min^{-1} to record the melting curves.

POM observation was made using a XPF550C microscope (Caikon Co., Ltd., Shanghai, China) equipped with a digital camera. The sample was sandwiched between two glass slides, heated to 100 °C on a hot stage and held for 5 min, followed by being pressed to form a thin layer of about 0.1 mm. Then the sample was rapidly transferred to the other hot stage preset to desired temperatures for the isothermal crystallization. The spherulite morphology was recorded after completion of the crystallization.

RESULTS AND DISCUSSION

Preliminary Analysis on Structure of PPZn and PEA/PPZn Composite

WAXD patterns of neat PPZn, neat PEA and PEA/PPZn with various weight percentages of PPZn in the range of 5°–11° are shown in Fig. 1. Here, for the neat PEA and PEA/PPZn composites, the melt-crystallization temperature is 30 °C. For brevity, other WAXD patterns of samples melt-crystallized at 0, 20 and 35 °C are not presented. It can be clearly found that a diffraction peak at 6.25° (for clarity, other WAXD peaks of the PPZn are not shown here) appeared after the addition of the PPZn. In addition, this peak sharpened without any discernible shift, with an increase in the loading of the PPZn. Neat PEA shows no peak in this 2θ range. It was documented that this diffraction peak should be assigned to the (010) reflection[54] and the interlayer *d* spacing of the PPZn (1.414 nm) was obtained according to the 2θ value (6.25°) in this work, which is in good agreement with that (1.434 nm) reported in the previous literature[54]. It reveals that the phenyl rings protrude into the interlamellar region beyond that of the phosphate group on both sides of the layer with enough phenyl-phenyl abutments to

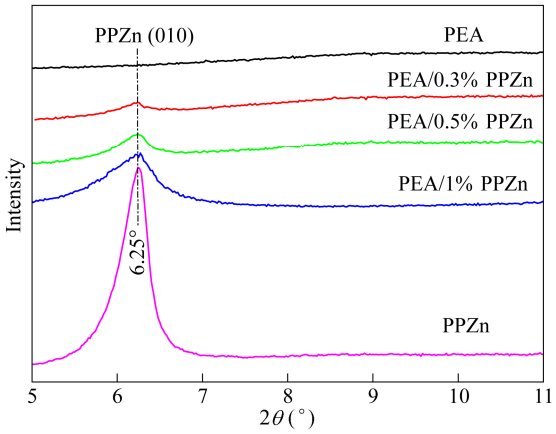


Fig. 1 WAXD patterns of neat PPZn, neat PEA and PEA/PPZn with different loadings of PPZn

hold the layers apart. Also, these results reveal that the PPZn layers were not intercalated or exfoliated by PEA chains in the preparation process, which is probably associated with the narrow spacing between the interlayers and/or strong interlayer force of the PPZn[51]. Chemical modification on the interlayer structure of PPZn may be a feasible way to achieve the nanoscale dispersion in the polymeric matrix, which will be carried out in our future work.

Non-isothermal Crystallization by DSC

The effect of PPZn on the non-isothermal crystallization behavior of PEA was investigated by DSC. Figure 2 shows the cooling (a) and subsequent heating curves (b) of PEA for neat PEA and the PEA/PPZn composites. It can be clearly seen from Fig. 2(a) that, the non-isothermal crystallization temperature (T_p) of the PEA increased with an increase in the content of the PPZn (C_{PPZn}) and T_p was significantly enhanced from 4.0 °C (for the neat PEA) to 17.6 °C (for the PEA/1% PPZn), as shown in Table 1. It indicates that PPZn is an efficient nucleating agent on which the PEA can nucleate and crystallize at a lower supercooling, compared to the neat one. It is noted that the T_p increased markedly when the C_{PPZn} is lower than 1%, but no distinct enhancement in T_p could be found with a further increase in the C_{PPZn} (from 16.9 °C with C_{PPZn} = 0.5% to 17.6 °C with C_{PPZn} = 1%, as shown in Table 1), suggesting that only lower C_{PPZn} (such as 0.5%) presents pronounced nucleating effect. 1% PPZn provides enough nucleating sites which is much more than those required for the nucleation of PEA, so both 0.5% and 1% PPZn showed the comparative nucleating effect on PEA. In addition, the normalized crystallization enthalpy (ΔH_c) of PEA also increased significantly with an increase in the C_{PPZn}.

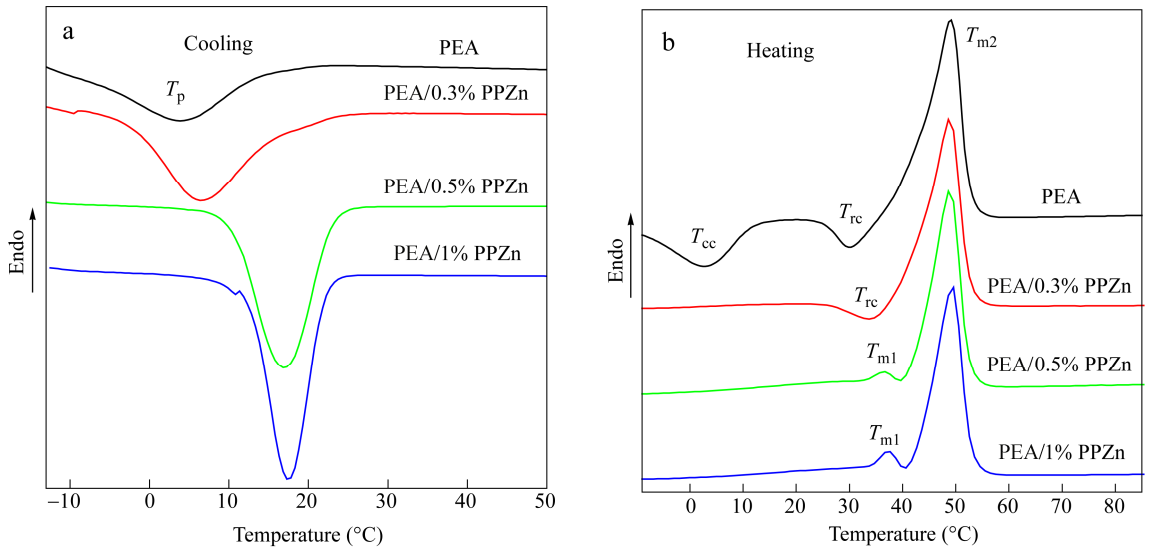


Fig. 2 DSC curves of (a) non-isothermal melt-crystallization and (b) subsequent melting for PEA/PPZn samples with various PPZn loadings (Both the cooling and heating rates are 10 K·min^{-1}.)

Table 1 Thermal parameters of neat PEA and the PEA containing the PPZn in the non-isothermal crystallization and subsequent heating process

Sample	T_p (°C)	ΔH_c (J/g)	T_{cc} (°C)	T_{rc} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	X_c (%)
PEA	4.0	−36.2	2.9	30.3	–	48.9	33.2	28.1
PEA/0.3% PPZn	6.7	−41.5	–	33.6	–	48.8	38.6	32.7
PEA/0.5% PPZn	16.9	−46.8	–	–	36.4	48.7	44.9	38.1
PEA/1% PPZn	17.6	−49.3	–	–	37.3	49.1	48.3	40.9

The neat PEA presented a cold-crystallization (T_{cc} = 2.9 °C), a recrystallization (T_{rc} = 30.3 °C) and a melting peak (T_{m2} = 48.9 °C) in its subsequent heating process, as shown in Fig. 2(b) and Table 1. The cold-

crystallization and recrystallization peak of the neat PEA in the heating process is indicative of its imperfect crystallization or incomplete adjustment of the PEA molecular chains in the former non-isothermal crystallization process. That is, in the subsequent heating process, the cold-crystallization and recrystallization peaks are attributed to the rearrangement of a part of PEA molecular chains, leading to more perfect and ordered crystallization or thicker crystalline layer. Upon incorporation of 0.3% PPZn, the cold-crystallization peak disappeared, indicating that relatively higher crystallinity compared to the neat PEA, but a small portion of PEA molecular chain was still in disordered or poorly aligned state, as reflected by the fact that a recrystallization peak (T_{rc} = 33.6 °C) appeared in the left side (lower temperature region) of T_{m2} (49.0 °C). It is interesting to note that 2 melting peaks (T_{m1} and T_{m2}) without the cold-crystallization and recrystallization peaks appeared in the heating process for the PEA/0.5% PPZn and PEA/1% PPZn, which implies that both 0.5% and 1% PPZn facilitated the crystallization or increased the crystallinity (X_c) of the PEA, as shown in Table 1. Here, the ΔH_m value is the normalized melting enthalpy of the PEA and the X_c was determined *via* comparing the ΔH_m with the value of an infinitely large crystal (ΔH_m^0 = 118 J/g)[23, 24, 26]. It is mentioned that the crystallization, melting enthalpies and crystallinity presented above by DSC were normalized according to the weight ratio of the PEA. For the neat PEA and PEA/0.3% PPZn, T_{m2} is ascribed to the melting of the crystals formed in the non-isothermal crystallization process, the cold-crystallization and recrystallization in the subsequent heating process. For the PEA/0.5% PPZn and PEA/1% PPZn, T_{m1} and T_{m2} are probably attributed to melt-crystallization-remelt mechanism[15, 27].

Isothermal Crystallization by DSC

Three isothermal crystallization temperatures (T_c = 30, 35 and 38 °C) were chosen for the investigation of the isothermal crystallization behavior of the PEA. The isothermal crystallization DSC curves of the neat PEA and PEA/PPZn composites at 30, 35 and 38 °C are shown in Figs. 3(a), 3(b) and 3(c), respectively. As can be clearly seen that, with the addition of PPZn and an increase in the C_{PPZn}, the isothermal crystallization peak sharpened and the crystallization time shortened greatly. In particular, for those samples melt-crystallized at 35 and 38 °C, the crystallization time decreased markedly, as presented in Figs. 3(b) and 3(c), suggesting that the PPZn accelerated significantly the crystallization rate of PEA.

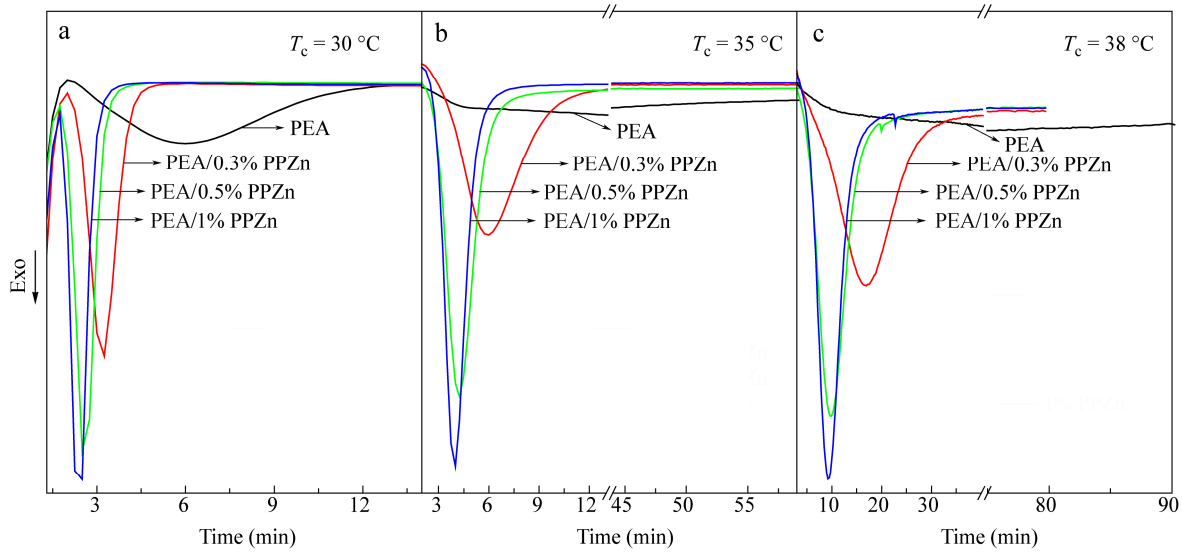


Fig. 3 DSC isothermal crystallization curves of PEA with different C_{PPZn}s melt-crystallized at T_c = (a) 30 °C, (b) 35 °C and (c) 38 °C

The crystallization behaviors of the neat PEA and PEA/PPZn composites melt-crystallized at 30, 35 and 38 °C were quantitatively analyzed according to the Avrami equation[55], and its linear expression can be written in Eq. (1).

$$\lg[-\ln(1 - X_t)] = \lg k + n\lg t \tag{1}$$

where t is the crystallization time (min). X_t is the relative crystallinity at t, which can be calculated from the integrated area of the DSC curve from 0 to t divided by the integrated area of the whole heat flow curve, as expressed in the following Eq. (2).

$$X_t = \frac{\int_0^t \left(\frac{dH}{dt}\right) dt}{\int_0^\infty \left(\frac{dH}{dt}\right) dt} \tag{2}$$

k is the crystallization rate constant. n is the Avrami exponent related to both the nucleation mode (homogeneous or heterogeneous nucleation) and dimension of the crystal growth. It is a combined function of the time dependence of nucleation (n_1) and the number of dimension (n_2) in which crystal growth occurs, and can be expressed as $n = n_1 + n_2$[52, 56–59]. For the heterogeneous nucleation, $n_1 \approx 0$, which means that nuclei emerge all at once in the early stage of crystallization, that is, instantaneous nucleation. For the homogeneous one, $n_1 \approx 1$, and the number of nuclei increases with time. n_2 = 1, 2, and 3 represent 1-, 2-, and 3-dimensional growth, respectively. In practice, the calculated n value by the Avrami equation is not an integer for some uncertain factors.

The plots of the relative crystallinity (X_t) as a function of the crystallization time (t) for the neat PEA and PEA-based composites melt-crystallized at 30, 35 and 38 °C, are shown in Fig. 4. From Figs. 4(a) (30 °C), 4(b) (35 °C) and 4(c) (38 °C), it can be seen that PEA took much less time to reach the 100% relative crystallinity after the addition of PPZn. Both the 0.5% PPZn and the 1% PPZn enhanced significantly the crystallization rate and shortened greatly the crystallization time of PEA. So from the viewpoint of the cost of the NA, 0.5% should be selected as the optimum content of PPZn to increase the crystallization rate of PEA.

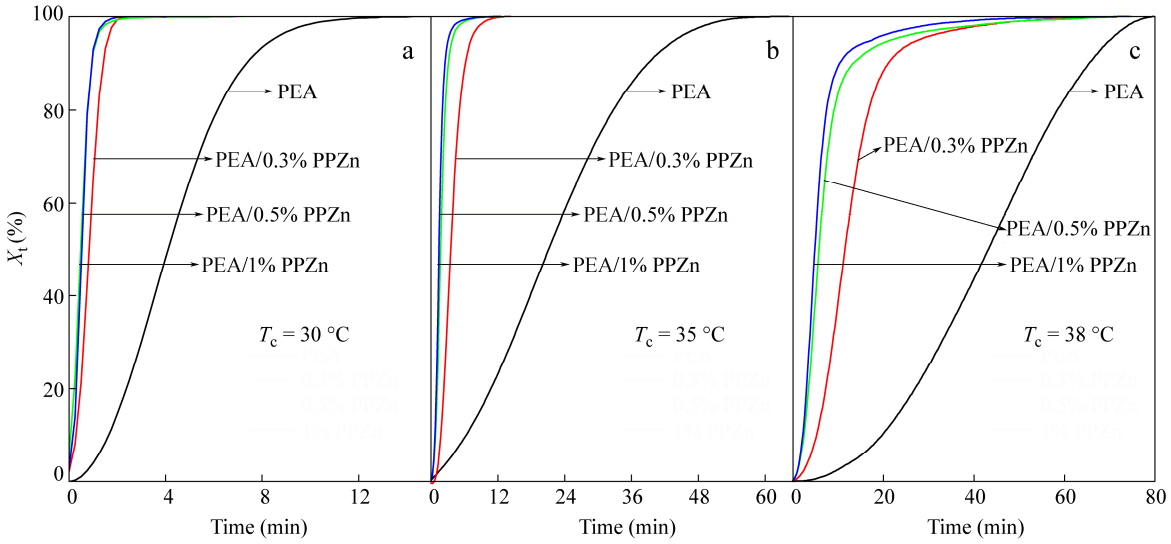


Fig. 4 The relative crystallinity (X_t) as a function of the crystallization time (t) for the neat PEA and PEA-based composites melt-crystallized at (a) 30 °C, (b) 35 °C and (c) 38 °C

The values of $\lg[-\ln(1 - X_t)]$ were also plotted versus that of $\lg t$ and are shown in Fig. 5. Here, for the

calculation of the value of n and k, only the linear portion of the plots of lg[−ln(1 − X_t)] as a function of lg$t$ are presented. As exhibited in Fig. 5, with increasing crystallization temperature, the value of lg$t$ increased when the crystallization was completed. Based on the above Avrami equation, the isothermal crystallization kinetics parameters ($t_{1/2}$, n and k) were obtained and are summarized in Table 2.

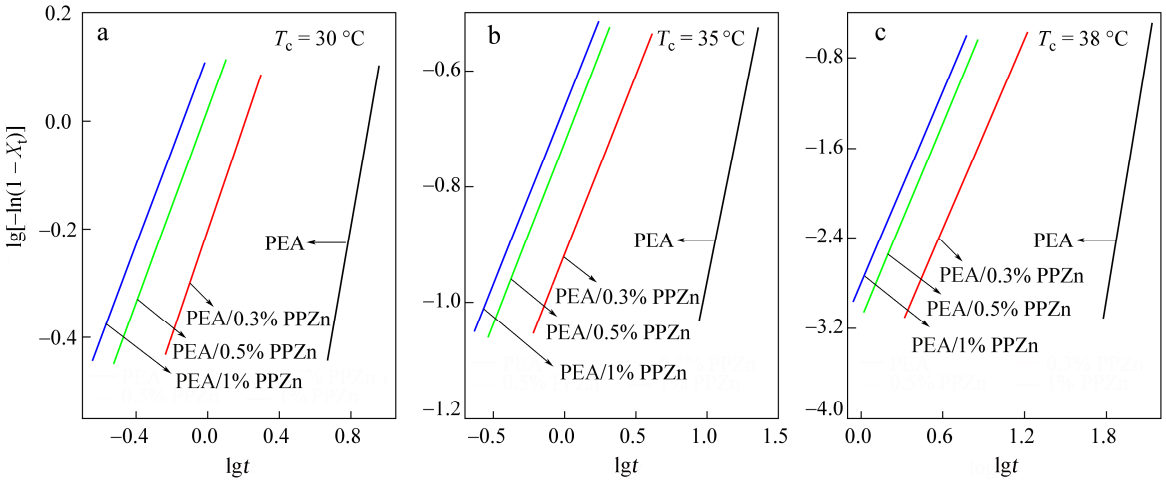


Fig. 5 lg[−ln(1 − X_t)] as a function of lg$t$ for the neat PEA and PEA-based composites melt-crystallized at (a) 30 °C, (b) 35 °C and (c) 38 °C

Table 2 Kinetics parameters of the PEA in the isothermal crystallization process (T_c = 30, 35 and 38 °C) for the neat PEA and PEA/PPZn composites

Sample	Isothermal crystallization								
	T_c = 30 °C			T_c = 35 °C			T_c = 38 °C		
	$t_{1/2}$ (min)	n	k (min^{-1})	$t_{1/2}$ (min)	n	k (min^{-1})	$t_{1/2}$ (min)	n	k (min^{-1})
PEA	5.2	3.6	0.038	23.7	3.7	0.003	45.2	3.8	0.000174
PEA/0.3% PPZn	1.2	2.7	1.158	10.8	2.8	0.037	13.7	2.9	0.00758
PEA/0.5% PPZn	0.5	2.8	2.371	2.4	2.8	0.159	8.4	2.7	0.0187
PEA/1% PPZn	0.5	2.8	2.529	2.2	2.7	0.373	7.9	2.8	0.0304

$t_{1/2}$ is the crystallization half time, which can be defined as the time when it reaches 50% of the relative crystallinity. From Table 2, it can be found that after addition of PPZn, $t_{1/2}$ of PEA at the same crystallization temperature depressed greatly, and k increased significantly. Especially, at T_c = 38 °C, the $t_{1/2}$ value shortened by about 5 times and the k value increased by 174 times for the PEA upon incorporation of 1% PPZn. The n value of the neat PEA is close to 4 regardless of the T_c, implying that the neat PEA spherulites probably grow in a homogeneous mode (n_1 = 1) with a 3-dimensional manner (n_2 = 3). After the addition of PPZn, the n value is about 3, indicating that the PEA spherulites still grow with a 3-dimensional manner (n_2 = 3) but in a heterogeneous mode (n_1 = 0).

Figure 6 shows the DSC heating curves of neat PEA and the PEA with different C_{PPZn}s after the isothermal crystallization at T_cs = 30, 35 and 38 °C, respectively. Multiple melting peaks (two or three melting peaks) can be found, in good agreement with previous report[27]. Figure 6(a) exhibits 3 melting peaks, but both Figs. 6(b) and 6(c) show two melting peaks (except for the shoulder peak, as denoted by the arrow in Fig. 6b). Multiple melting behaviors have been widely studied and the mechanism is very complicated. Based on our previous report[1], the crystalline structure (aggregation structure) of the PEA is not crystallization temperature-dependent, that is, no polymorphic crystalline structure in the melting-crystallization process of the PEA can be found. Therefore, multiple melting peaks of the PEA in its heating process may be attributed to melting-crystallization-

remelting mechanism[27]. Similar result has been reported for the α-modification of the poly(butylene adipate)[29, 30]. The PEA at T_c = 30 °C exhibits less perfect crystallization or less ordered (regular) molecular chain than those at T_c = 35 and 38 °C, so a more complicated melting-crystallization process is needed for achieving of a more perfect crystallization or more ordered molecular chain rearrangement.

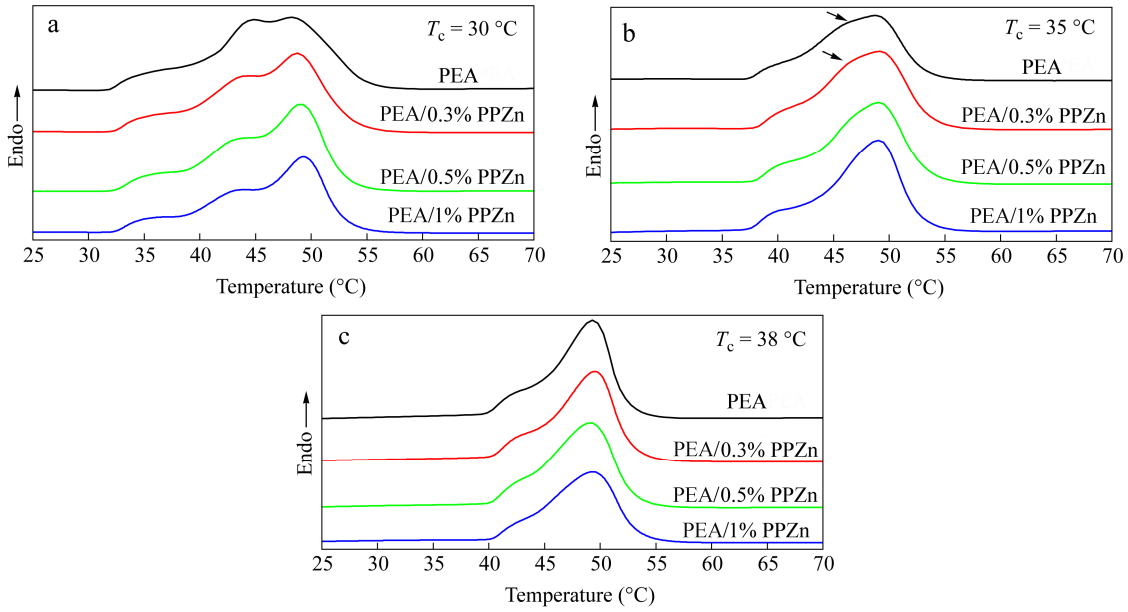


Fig. 6 DSC heating curves of neat PEA and the PEA with different C_{PPZn}s after the isothermal crystallization at T_c = (a) 30 °C, (b) 35 °C and (c) 38 °C

Spherulite Morphology Observation by POM

To evaluate the effect of PPZn on the spherulite morphology of PEA, the POM observation was performed for the neat PEA and PEA/PPZn composites melt-crystallized at 28, 33 and 35 °C, respectively, and the images are shown in Fig. 7. At T_c = 28 °C, the neat PEA showed the ring band spherulites (panel a1), probably associated with the lamellar twisting of the PEA at a specific crystallization temperature region[27]. When T_c was raised to 33 °C (panel a2), the spherulite size increased slightly, spherulite density decreased slightly, and no ring band spherulite could be found. With increasing T_c to 35 °C (panel a3), the spherulite size further increased and the spherulite density further decreased. In general, the spherulite number of the polymer decreases when T_c is increased, because of the difficulty in the nucleation at the smaller undercooling (that is, the higher crystallization temperature).

Upon incorporation of 0.3%, 0.5% and 1% PPZn, the spherulite size decreased significantly and spherulite density increased markedly at the same T_c, compared with that of the neat PEA. The POM observation further revealed that the PPZn exhibited the excellent nucleation ability on the crystallization of the PEA, in good agreement with the DSC results aforementioned. PPZn, serving as heterogeneous nuclei, decreased the free energy for the formation of a critical nucleus of the PEA and facilitated the formation of the nuclei of PEA at a higher temperature. Thus, at the same T_c, more nuclei of the PEA are available in the presence of PPZn, greatly accelerating the crystallization rate and increasing the spherulite density of PEA. The nucleation mechanism of the PEA in the presence of PPZn will be presented in the later section.

Proposed Mechanism for Nucleation of PEA in the Presence of PPZn

Generally speaking, the accelerated nucleation of the NA-containing polymer can be ascribed to the chemical or epitaxial nucleation. There is a chemical reaction between the polymer and NA during the chemical nucleation, resulting in a new nucleating substance on which other polymer chains can nucleate. It was reported that the chemical nucleation occurs for the PET/organic salt composite[60]. In this work, the chemical reaction is not

expected to occur between PEA and PPZn. Thus the chemical nucleation should be excluded in the PEA/PPZn composites.

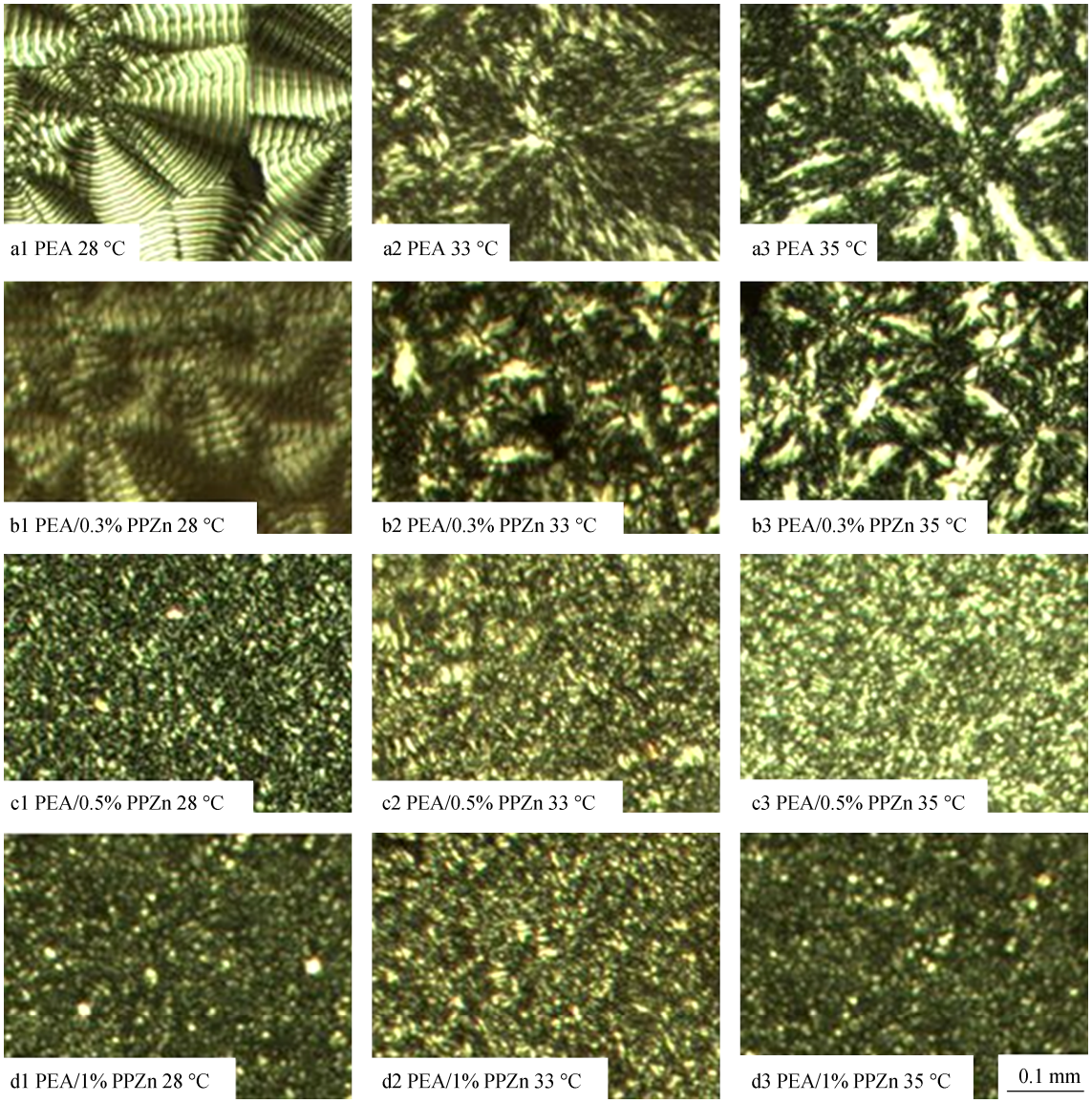


Fig. 7 POM pictures for the neat PEA and PEA/PPZn composites (with 0.3%, 0.5% and 1% PPZn) melt-crystallized at various T_cs (Scale bar in each picture is 0.1 mm.)

In terms of the epitaxial nucleation, the crystal of the polymer can grow on the surface of the NA. That is, the growth of the polymer crystal on the NA surface is governed by the excellent matching of the lattice plane between the polymer and NA[61]. It was documented that the nucleation mechanisms of some polymer/NA composites are attributed to the epitaxial nucleation, such as PBA/PPZn[52], PBA/cyanuric acid (CA)[57], PBA/polyethylene[62], PBA/isotactic polypropylene (*i*PP)[63], *i*PP/γ-quinacridone[64], *i*PP/4-fluorobenzoic acid[64], and PET/talc[65]. It was reported that the PPZn crystal is an orthorhombic unit cell with lattice parameters of a = 0.566 nm, b = 1.445 nm, and c = 0.480 nm[53]. For the PEA crystal, its chains are packed in a monoclinic unit cell with the dimensions of a = 0.547 nm, b = 0.723 nm, c = 1.172 nm and the monoclinic angle of α = 113.5°[8, 9, 27]. The value (1.445 nm) of the b axis of the PPZn crystal is almost 2 times (1.446 nm) that of the b

axis of the PEA crystal, suggesting that a perfect lattice matching between the PEA and PPZn crystal. This perfect lattice matching indicates that the PEA crystal might preferentially grow on the PPZn surface *via* the epitaxial nucleation mechanism. For a better understanding, a schematic diagram used for illustrating the epitaxial growth of the PEA crystal on the surface of the PPZn crystal is shown in Fig. 8.

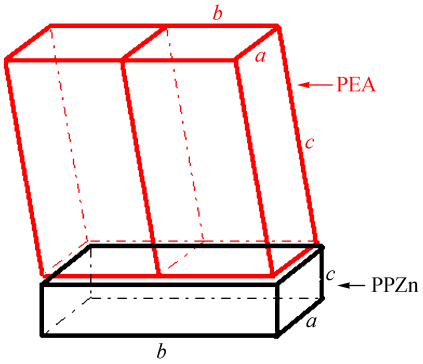


Fig. 8 Schematic illustration for epitaxial growth of the PEA crystal on the surface of the PPZn

CONCLUSIONS

The incorporated layered PPZn was not intercalated or exfoliated by PEA chains in the PEA/PPZn composite. After addition of PPZn, the crystallization temperature of the PEA increased from 4.0 °C (the neat PEA) to 17.6 °C (PEA/1% PPZn) and the crystallinity increased from 28.1% (the neat PEA) to 40.9% (PEA/1% PPZn). Crystallization kinetics data in the isothermal crystallization process suggest that the crystallization time decreased significantly and crystallization rate increased greatly, but the growth mode (3-dimentional growth) did not alter. PPZn increased the spherulite density and decreased significantly the spherulite size of the PEA. The epitaxial nucleation mechanism could be used for explaining the growth of the PEA crystals on the surface of PPZn, because the value of the *b* axis of the PPZn crystal is almost 2 times that of the *b* axis of the PEA crystal.

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