

ISOTHERMAL CRYSTALLIZATION BEHAVIOR AND UNIQUE BANDED SPHERULITES OF HYDROXYAPATITE/POLY(L-LACTIDE) NANOCOMPOSITES*

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Abstract Hydroxyapatite/poly(L-lactide) (HA/PLLA) nanocomposites were prepared by the solvent mixing method. The isothermal crystallization behavior was studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The results show that the crystallization behavior of HA/PLLA composites was strongly affected by the content of HA and crystallization temperature, and the addition of HA could promote nucleation and enhance the crystallization rate. When isothermal crystallization was carried out at 110°C, the HA/PLLA nanocomposite with 1% HA content crystallized most rapidly among all the composites and the half crystallization time was only 1.0 min. Banded spherulites were observed for the HA/PLLA composites, but no banded spherulites were seen in the crystals of PLLA under the same condition.

Keywords: Hydroxyapatite, Polylactide, Crystallization, Nanocomposites, Spherulites.

INTRODUCTION

During the last decades, research about biodegradable and biocompatible polymers has been carried out extensively for both theoretical considerations and practical applications^[1–3]. Among many biopolymers, poly(L-lactide) (PLLA) has been the focus of much attention because it can be made from renewable agriculture materials and can be biodegraded back to water and carbon dioxide after use. Up to now, PLLA has been used in many perspective areas such as orthopedics, drug delivery, sutures and scaffolds because of its wonderful biodegradability and biocompatibility^[4–6].

Hydroxyapatite is a type of biocompatible ceramics and has been an important biomedical material in hard tissue repair and replacement because of its similarity to bone minerals in composition, size, crystal structure and morphology^[7–10]. Therefore, HA has been used to prepare artificial bioceramic/polymer composites^[11–15]. During the recent years, many studies directed to properties including the degradation, biocompatibility and mechanical properties of the HA/PLLA composite have been carried out^[16–19]. The HA/PLLA composite has been used to prepare bioresorbable devices such as miniscrews and miniplates; the composite has also been used to prepare 3-D porous scaffold and used in tissue engineering^[20, 21].

Crystallization is an important factor that affects physical, mechanical and biodegradability properties of PLLA. Many works have been done on the crystallization behavior of PLLA^[22–24], and there are also many

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reports about crystallization behavior of PLLA based nanocomposites, such as poly(L-lactide)/layered double hydroxides, poly(L-lactide)/multiwalled carbon nanotubes, poly(L-lactide)/organoclay, poly(L-lactide)/layered silicate and so on^[25–28]. As for the HA/PLLA composites, which can be made into bone fixation devices or used in bone tissue engineering, the crystallization behavior plays an important role in its final applications, however, to our knowledge, there was hardly any study focused on the crystallization kinetics of HA/PLLA composites that is of great importance in the materials processing and plays an important role in the mechanical properties of HA/PLLA composites. Herein, HA/PLLA composites with different HA contents were prepared, and their isothermal crystallization behavior was studied by differential scanning calorimetry (DSC) and analyzed with the Avrami equation. In addition, the morphology of their crystals was observed by using a polarized optical microscope (POM), and an interesting phenomenon of banded spherulites was observed when the composites isothermally crystallized at 140°C. On the contrary, no banded spherulites were observed when the pure PLLA was crystallized at the same conditions.

EXPERIMENTAL

Materials

PLLA ($M_n = 1.96 \times 10^5$, PDI = 1.16) was synthesized in our lab by the ring opening polymerization of L-lactide with stannous octoate as the catalyst. Hydroxyapatite nanoparticles were synthesized according to the reported method^[29].

Preparation of HA/PLLA Nanocomposites

The nanocomposites were prepared by the solvent mixing method. Briefly, HA was dispersed in dichloromethane by sonication, and then PLLA was dissolved in the suspension. The weight fractions of HA in the HA/PLLA composites were 1%, 3%, 5%, 10% and 20% (the composites were denoted as PLLAHA1, PLLAHA3, PLLAHA5, PLLA10 and PLLA20, respectively). Then the suspension of HA and PLLA was precipitated in ethanol. The composites were dried under vacuum at 40°C for 48 h to completely remove the residual solvent. The dried composites were used directly in the DSC measurement.

Differential Scanning Calorimetry

Thermal properties of the neat PLLA and the HA/PLLA composites with different HA contents were measured by a differential scanning calorimeter (TA Q100) under nitrogen atmosphere. The samples were heated from 0°C to 200°C and kept at 200°C for 3 min to eliminate the thermal history, and then cooled to 0°C at a rate of 10 K/min and finally the samples were heated to 200°C again.

In the isothermal crystallization process, the samples were heated to 200°C at a rate of 50 K/min and kept at 200°C for 3 min to clear the heat history and then the samples were cooled to the desired crystallization temperature (T_c) at a rate of 50 K/min and kept for 30 min at the T_c . Then the samples were reheated to 200°C at a rate of 10 K/min to measure the melting behavior of the composites.

Polarized Optical Morphology

The morphology of crystallized composites was observed on a Leica DMLP polarizing optical microscope equipped with a digital camera and hot stage. The samples for POM were prepared as follows. First, a certain amount of composite was dispersed in dichloromethane (1 wt%) and the suspension was dip-coated on to a piece of clean glass slide, and then the sample was dried under vacuum at 40°C for 48 h. The sample was melted at 200°C for 3 min and then quenched to 140°C at a rate of 100 K/min; it was maintained at 140°C for 30 min and then cooled to room temperature for the POM observation.

RESULTS AND DISCUSSION

Thermal Properties

The thermal properties of neat PLLA and HA/PLLA composites were measured by scanning the cooling process of melted samples and subsequently the heating process by DSC. The DSC curves are listed in Fig. 1. The exact

thermal properties of different samples are listed in Table 1. The T_c (the peak temperature of the exothermic curves obtained during the cooling process) did not change very much, but $T_{c \text{ onset}}$ (the onset point temperature of crystallization) changed substantially (see Table 1). This could be attributed to the nucleating effect of the HA nanoparticles in the composites; the composites could crystallize at a higher temperature mainly due to a heterogeneous nucleating process. The crystallization enthalpies of the composites were nearly twice that of the neat PLLA, which also demonstrated that the composites could crystallize quickly as compared with the neat PLLA.

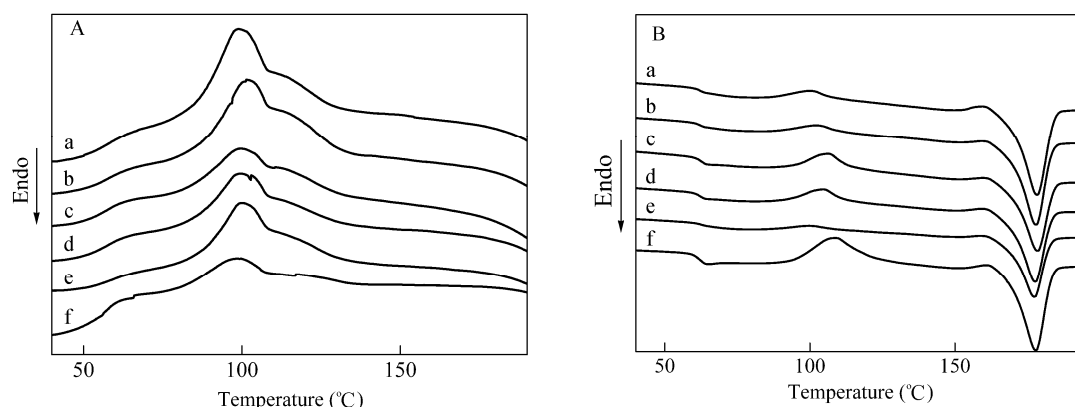


Fig. 1 DSC curves of the melt-crystallization (A) and the subsequent heating process (B) for PLLAHA1 (a), PLLAHA3 (b), PLLAHA5 (c), PLLAHA10 (d), PLLAHA20 (e) and neat PLLA (f)

Table 1. Thermal properties of neat PLLA and HA/PLLA composites obtained from the DSC curves

Samples	T_c	$T_{c \text{ onset}}$	ΔH_c	T_g	T_{cc}	T_m	ΔH_m	X_c (%)
PLLA	97.9	107.8	7.74	59.4	109.0	177.9	31.1	33.4
PLLAHA1	98.7	129.1	20.8	60.4	100.5	178.2	31.3	34.0
PLLAHA3	101.4	130.5	19.7	60.4	102.9	177.8	31.5	34.9
PLLAHA5	99.8	130.3	14.1	60.5	106.4	178.3	29.5	33.4
PLLAHA10	99.7	133.6	13.7	60.1	104.6	177.6	28.7	34.3
PLLAHA20	100.1	130.7	17.2	60.4	99.9	177.1	26.0	34.9

The glass transition temperature (T_g) and the melting point (T_m , the peak temperature of the endothermic curves) were measured during the second heating scan of PLLA and the HA/PLLA composites, and the DSC curves are listed in Fig. 1B. As shown in Table 1, the T_g and T_m of the neat PLLA were almost the same as that of the composites with different HA contents, and the total crystallization degree (X_c) of the neat PLLA and the HA/PLLA composites did not change very much. X_c was calculated by Eq. (1):

$$X_c = \frac{\Delta H_m}{f \times \Delta H^0} \times 100\% \quad (1)$$

where ΔH_m is the melting enthalpy of neat PLLA or HA/PLLA composites, f is the content of PLLA in the composites and ΔH^0 (93 J/g) is the melting enthalpy of neat PLLA with 100% crystallinity^[28]. In addition, there were some differences in the second heating process, as shown in Fig. 1(B). The cold crystallization of all the composites took place at a lower temperature (T_{cc}) than the PLLA did, and the cold crystallization enthalpy were smaller than that of neat PLLA, showing that the HA particles in the composites could enhance the crystallization rate of the PLLA matrix.

Isothermal Crystallization

The isothermal crystallization behaviors of neat PLLA and the HA/PLLA composites at different temperatures

(T_{ic}) were studied by DSC and the relative degree of crystallinity (X_t) at any given time can be calculated by the following equation:

$$X_t = \frac{X_c(t)}{X_c(t = \infty)} = \frac{\int_0^t (dH_c / dt) dt}{\int_0^\infty (dH_c / dt) dt} \quad (2)$$

where $X_c(t)$ and $X_c(t = \infty)$ are the degrees of the relative crystallinity at time t and at the time when crystallization finishes, respectively. The plots of X_t versus the isothermal crystallization time t at different temperatures are shown in Figs. 2(a)–2(d).

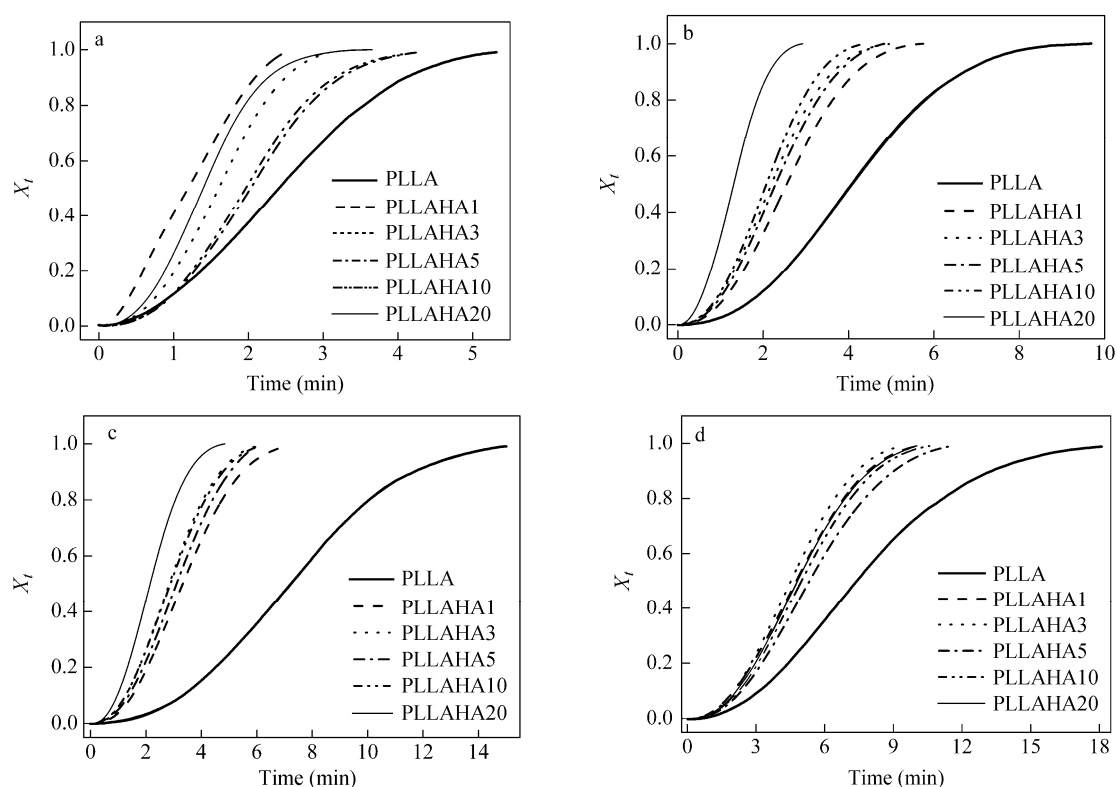


Fig. 2 The relative degree of crystallinity for PLLA and HA/PLLA composites versus crystallization time at 110°C (a), 120°C (b), 130°C (c) and 140°C (d), respectively

The Avrami equation is widely used to describe the isothermal crystallization behavior of polymers:

$$1 - X_t = \exp(-kt^n) \quad (3)$$

where X_t is the relative crystallinity at time t , k and n are the crystallization rate constant and the Avrami equation exponent, respectively, which are related to the crystallization rate and to the geometry of crystal growth. From Eq. (3), the following equation could be obtained:

$$\lg[-\ln(1 - X_t)] = \lg k + n \lg t \quad (4)$$

By plotting $\lg[-\ln(1 - X_t)]$ versus $\lg t$, a linear line would be obtained. From the line, the intercept and slope of the line can be calculated, which are the values of $\lg k$ and n , respectively. In addition, $t_{1/2}$ is also an important parameter to describe the isothermal crystallization of a polymer system and can be obtained by the following equation:

$$t_{1/2} = (\ln 2/k)^{1/n} \quad (5)$$

where $t_{1/2}$ is the half crystallization time that is defined as the time required when the relative crystallinity is 50%.

As shown in Figs. 2(a)–2(d), the isothermal processes of the composites required shorter time than that of neat PLLA at all the crystallization temperatures, mainly because of the nucleating effect of HA nanoparticles. The nanocomposites with the same HA content demonstrated different crystallization rates at different isothermal crystallization temperatures. At a certain T_{ic} , the composites with different filler contents could also have different crystallization rates and there were no consistent trend between different T_{ic} . For example, when the isothermal crystallization was carried out at 110°C, the composite with 1% HA content crystallized most rapidly; but when T_{ic} was 120°C, the composite with 20% HA content crystallized more rapidly than other composites. The inorganic particles in the composites could work as a nucleating agent, so the crystallization rate of the composites was higher than that of neat PLLA. However, the inorganic particles could also prevent the growth of the crystals, so there was a competition between the nucleating effect and retardance effect. There was no clear relationship between the crystallization rate and the filler content, but on the whole, the introduction of HA into PLLA played an important role as a nucleating agent, and the HA/PLLA composites crystallized more quickly than the pure PLLA.

Table 2. The Avrami parameters at different crystallization temperatures for PLLA and HA/PLLA composites

Samples	T_c (°C)	n	k (min ⁻ⁿ)
PLLA	110	2.3	1.12×10^{-1}
PLLAHA1	110	2.2	6.60×10^{-1}
PLLAHA3	110	2.4	2.17×10^{-1}
PLLAHA5	110	2.5	1.23×10^{-1}
PLLAHA10	110	2.5	1.29×10^{-1}
PLLAHA20	110	2.5	3.09×10^{-1}
PLLA	120	2.4	2.40×10^{-2}
PLLAHA1	120	2.3	7.94×10^{-2}
PLLAHA3	120	2.3	1.12×10^{-1}
PLLAHA5	120	2.3	1.02×10^{-1}
PLLAHA10	120	2.3	1.26×10^{-1}
PLLAHA20	120	2.2	3.80×10^{-1}
PLLA	130	2.5	5.13×10^{-3}
PLLAHA1	130	2.4	3.89×10^{-2}
PLLAHA3	130	2.3	6.03×10^{-2}
PLLAHA5	130	2.3	5.13×10^{-2}
PLLAHA10	130	2.3	6.17×10^{-2}
PLLAHA20	130	2.4	1.15×10^{-1}
PLLA	140	2.3	6.92×10^{-3}
PLLAHA1	140	2.3	2.09×10^{-2}
PLLAHA3	140	2.4	1.91×10^{-2}
PLLAHA5	140	2.4	1.35×10^{-2}
PLLAHA10	140	2.3	1.66×10^{-2}
PLLAHA20	140	2.4	1.58×10^{-2}

Figures 3(a)–3(d) show the plots of $\lg[-\ln(1-X_t)]$ versus $\lg t$ at different temperatures. The values of parameters k and n obtained from the plots are listed in Table 2. All the composites and neat PLLA showed much similar n values in the range of 2.2–2.5, showing that the crystallization proceeded in a three dimension

growth manner. The parameter k is the rate constant of the crystallization process and the larger the k is, the higher the crystallization rate is. As shown in Table 2, the k values are related to both the content of the HA nanoparticles and the crystallization temperature. The $t_{1/2}$ values are the most evident results to characterize the crystallization rate, and the composite with a shorter $t_{1/2}$ can crystallize faster than the composites with a longer $t_{1/2}$. As shown in Fig. 4, the HA content and isothermal crystallization temperature (T_{ic}) played an important role in the values of $t_{1/2}$. When T_{ic} was 110°C, the composite with 1% HA content had the smallest $t_{1/2}$ value; when T_{ic} was 120°C, the composite with 20% HA content crystallized most rapidly. In addition, when the isothermal crystallization was carried out at 140°C, the composite with 3% HA content crystallized most quickly.

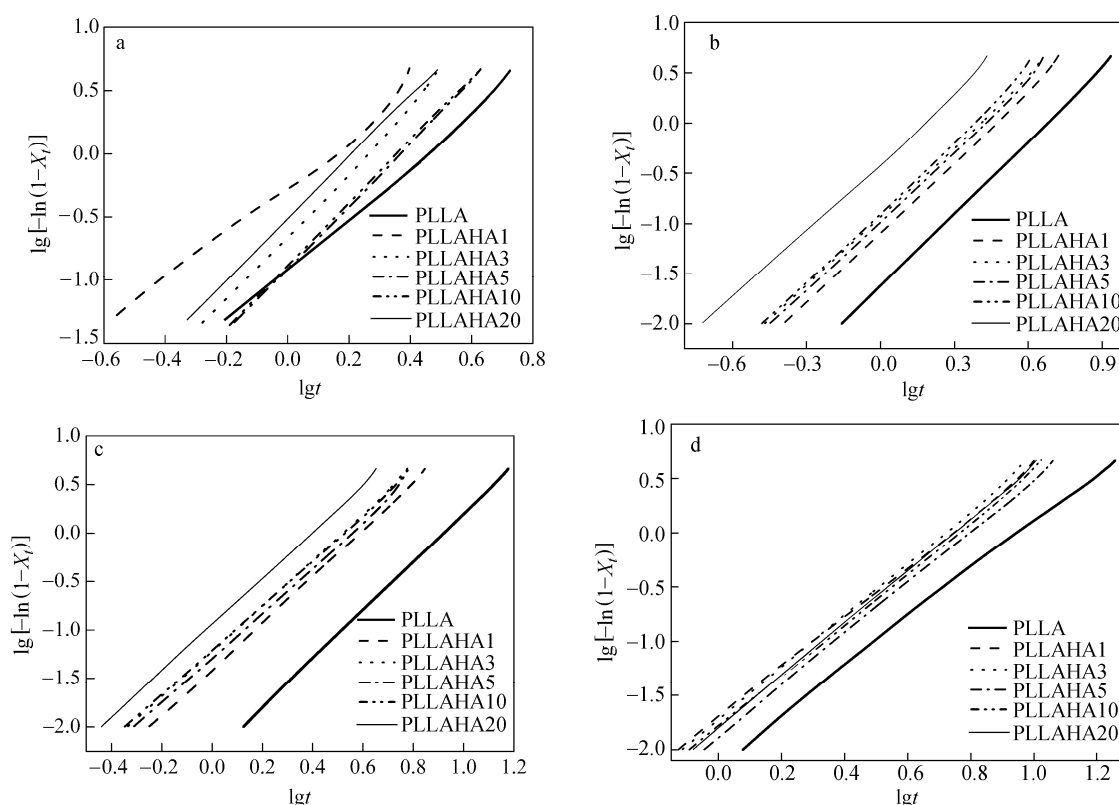


Fig. 3 Avrami plots for PLLA and HA/PLLA composites at 110°C (a), 120°C (b), 130°C (c) and 140°C (d), respectively

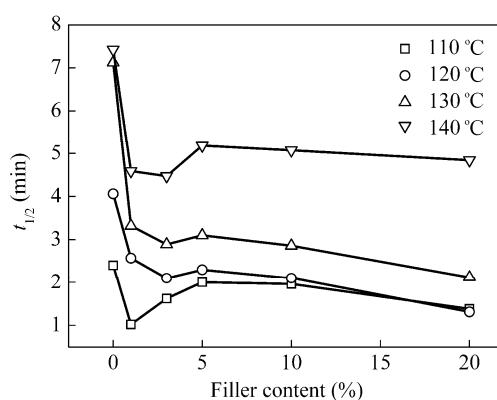


Fig. 4 Half crystallization time for PLLA and HA/PLLA composites at different temperatures

Melting Behavior

From the DSC curves of the subsequent heating scan after the isothermal crystallization, the T_m and melting enthalpy of the PLLA and the composites were obtained and the results are listed in Table 3. Compared with the T_m value listed in Table 1, the T_m after isothermal crystallization was higher than that of the nonisothermal counterparts, and in addition, with the increase of the T_{ic} , the T_m of all the samples also increased, showing that the samples crystallized more orderly. However, compared with neat PLLA, a minor decrease of the crystalline degree for the composites was observed, demonstrating that the addition of inorganic particles into the composites had a retardance effect for the arrangement of polymer chains, and thus would decrease the total crystalline degree.

Table 3. T_m and X_c of the PLLA and HA/PLLA composites after isothermal crystallization at different temperatures

Samples	$T_{ic} = 110^\circ\text{C}$		$T_{ic} = 120^\circ\text{C}$		$T_{ic} = 130^\circ\text{C}$		$T_{ic} = 140^\circ\text{C}$	
	T_m ($^\circ\text{C}$)	X_c (%)	T_m ($^\circ\text{C}$)	X_c (%)	T_m ($^\circ\text{C}$)	X_c (%)	T_m ($^\circ\text{C}$)	X_c (%)
PLLA	178.0	36.7	178.6	38.3	181.4	41.2	183.8	46.6
PLLAHA1	177.3	32.3	178.4	36.3	180.8	40.9	184.1	41.7
PLLAHA3	176.9	36.3	177.9	36.7	181.7	37.7	184.2	43.1
PLLAHA5	177.5	36.6	178.4	37.0	181.1	40.1	184.3	41.4
PLLAHA10	177.3	36.5	178.6	35.8	180.8	39.4	183.5	41.6
PLLAHA20	177.7	34.7	178.1	36.1	180.3	40.0	182.8	44.8

Morphology of the Crystals

Figure 5 shows the POM photographs of the pure PLLA and the HA/PLLA composites. The crystal morphology of pure PLLA (Fig. 4a) showed a typical spherulitic structure and the spherulite diameter was about 250 μm . The spherulite diameter of HA/PLLA composites decreased greatly with the incorporation of the nucleating agent and the spherulite number was much more than that of pure PLLA. The most interesting phenomenon was that the banded spherulites appeared in the crystals of the nanocomposites (Fig. 4). The banded spherulites have been observed in PLLA, PS-PLLA block copolymer and PLLA/PCL blends, and it is generally believed that the periodic bands are derived from the lamellar twisting in the radial direction during the crystal growth^[30, 31]. As for the banded spherulites of the HA/PLLA composites, the inorganic particles dispersed in the polymer matrix, interrupted the homogeneousness of the polymer phase, and it caused the unbalanced stress at the lamellar surface, which was widely accepted as the drive force of lamella twisting^[32].

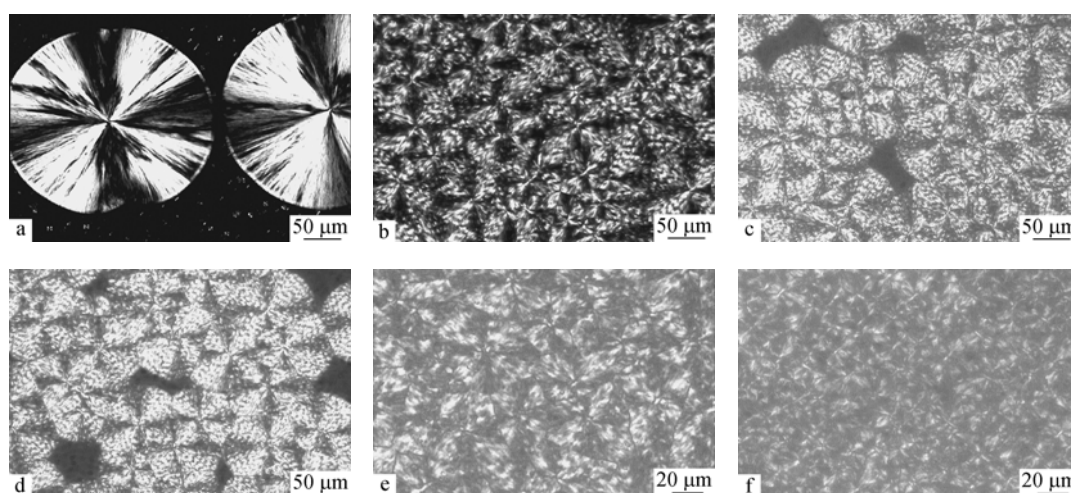


Fig. 5 Polarized optical micrographs of neat PLLA (a), PLLAHA1 (b), PLLAHA3 (c), PLLAHA4 (d), PLLAHA5 (e) and PLLAHA (f) isothermally crystallized for 30 min at 140 $^\circ\text{C}$

CONCLUSIONS

In the present work, HA/PLLA nanocomposites were prepared by the solvent mixing method and their crystallization behaviors of the as-prepared composites were studied by DSC thermal analysis and the crystal morphology was also investigated by POM. The thermal properties showed that the HA particles could take a nucleating effect. All the composites could crystallize more quickly than the pure PLLA and the half time of crystallization for the HA/PLLA composites were shorter than that of neat PLLA. However, the composites with lower HA contents can crystallize much faster than the composites with higher HA contents at 110°C and 140°C, showing that there was also a retardation effect from the HA particles at higher HA contents. After isothermal crystallization, the T_m of the composites increased higher than that of the composites without the isothermal crystallization process, so it can be concluded that the composites crystallized more orderly and completely under the isothermal crystallization conditions. As for the morphology of HA/PLLA composites, banded spherulites were observed, but there were no banded spherulites in the PLLA crystallized under the same crystallization condition.

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