

Nonisothermal Melt-Crystallization Kinetics of Hydroxyapatite-Filled Poly(3-hydroxybutyrate) Composites

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ABSTRACT: The knowledge of biomedical implants ranging from drug delivery devices to tissue engineering and based on bioresorbable polymer composites is increasing, but the study of the crystallization kinetics of these kinds of composites is seldom a concern. The focus of our experimental research was the nonisothermal-crystallization behavior of poly(3-hydroxybutyrate) (PHB)/hydroxyapatite (HA) composites, which was monitored by means of differential scanning calorimetry at different cooling rates. Various macrokinetic models were applied to describe the process of nonisothermal crystallization. The results showed that the modified Avrami model and Mo's approach could describe the nonisothermal crystallization of the composites very well, but the

Ozawa analysis alone was thought to be rather inapplicable. The values of the half-time and kinetic crystallizability showed that the crystallization rate increased with increasing cooling rates for both PHB and the composites. The HA particles served as additional nucleation sites, and low levels of HA resulted in dramatic increases in the crystallization rate with respect to pure PHB; however, high HA contents (> 20 wt %) clearly retarded the growth process. The activation energy for nonisothermal crystallization was evaluated with the Kissinger method and was found to vary with the incorporation of HA. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5388–5395, 2006

Key words: biopolymers; composites; crystallization

INTRODUCTION

Composites with bioactive ceramics [e.g., calcium phosphate, hydroxyapatite (HA), and bioglass] and polymers such as ultrahigh-molecular-weight polyethylene, high-impact polystyrene, and poly(ether ether ketone)^{1–4} have been used as potential materials for bone-tissue replacement. In recent years, there has been much interest in the family of bioresorbable polymer composites reinforced with bioactive ceramics because of their high application potential in the fields of drug delivery devices,^{5–7} nerve regeneration guides,⁸ orthopedic implants for tissue reconstruction,^{9–11} bone fixation,^{12–14} tissue engineering scaffolds,^{15–18} and so forth. The widely used polymer matrices include poly(lactic acid), polyhydroxyalkanoate, polyanhydride, polyorthoester, and their copolymers. Much work has

focused on the preparation, bioactivity, biodegradability, mechanical properties, modification, and utilization of this kind of composite, but very limited studies on the crystallization kinetics can be found so far. Understanding the mechanism and kinetics of crystallization of these materials is vital for determining their ultimate applicability and enabling the design of new polymer composite structures with desirable properties for biomedical applications. Chen and Wang¹⁹ observed the formation of bonelike apatite on the surface of a polyhydroxyalkanoate family blended with HA or tricalcium phosphate after immersion in simulated body fluids and found that the incorporation of bioceramics into biodegradable polymers reduced the crystallinity, and this directly led to a faster rate of degradation of the biopolymer and the reconstruction of new tissue.

Poly(3-hydroxybutyrates) (PHB) is one of the most well known polyhydroxyalkanoates produced from bacteria as intracellular-storage polyesters.^{20,21} Besides being biocompatible, it possesses a high level of crystallinity (60–70%) and exhibits mechanical properties that are similar to or even better than those of tradi-

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tional thermoplastics.²² To improve its toughness, poly(3-hydroxyvalerate) components with various molar ratios are usually introduced, and the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) copolymer is the subject of extensive and ongoing research for biomedical applications.^{23–25} In this study, the main focus was the nonisothermal-crystallization kinetics of poly(3-hydroxybutyrate) (PHB)/HA composites via differential scanning calorimetry (DSC). The effects of the HA content and the cooling rate (ϕ) on the crystallization behavior were particularly examined. Various kinetic models, such as the modified Avrami method, the Ozawa method, and Mo's approach, were applied to describe the process of nonisothermal crystallization and to access the feasibility of each approach. Also, the activation energy for the studied systems was estimated with the Kissinger approach.

EXPERIMENTAL

Materials

PHB powder with a mean particle size of 30 μm and a melting point of about 175°C was provided by Goodfellow Cambridge, Ltd (Huntingdon, England). HA powder with an average particle size of 5 μm was purchased from Berkeley Advanced Biomaterials, Inc. (Berkeley, CA). Chloroform of more than 99.5% purity (International Laboratory, United States) was used as a solvent. In this study, both PHB and HA were used in their as-received state without further treatment.

Sample preparation

The PHB/HA composites were prepared by a solution method because PHB is a biopolyester, undergoing thermal degradation at temperatures higher than its melting point.^{26,27} Briefly, 10 g of PHB powder was first dissolved in 100 mL of chloroform at 50°C. Then, an appropriate amount of HA particles was added to the PHB solution. The mixtures were magnetically stirred at the same temperature for 3 h, and this was followed by 5 min of sonication in a water bath. Subsequently, the mixing solution was poured into a Petri dish, and a composite film was obtained via drying at 80°C for at least 12 h until a constant sample weight. It has been proved that the combination of a solution-casting method and an ultrasonification technique can enable the even dispersion of a filler in a polymer matrix.^{28,29} In this study, the filler concentrations in the composites were taken to be 10, 20, and 40 wt %, and the related composites were called PHB10, PHB20, and PHB40, respectively, for convenience.

DSC measurements

The crystallization behavior was measured on a Perkin Elmer series DSC 7 differential scanning calorimeter

(Wellesley, MA) under a flowing nitrogen atmosphere. The sample weight was kept at approximately 8.5 mg for all the tests. The temperature and energy readings were calibrated with indium at each ϕ value. For nonisothermal melt crystallization, the raw samples were quickly heated to 190°C at a heating rate of 100°C/min and maintained at 190°C for 5 min in the DSC cells to destroy any nuclei that might act as seed crystals. The samples were then cooled to 25°C at constant ϕ values of 5, 10, 20, and 30°C/min, respectively. The exothermic crystallization peaks were recorded as a function of temperature.

RESULTS AND DISCUSSION

Nonisothermal melt-crystallization behavior

The nonisothermal melt-crystallization exotherms for PHB/HA composites containing various amount of HA at four ϕ values are shown in Figure 1. From these curves, some useful crystallization parameters, such as the peak temperature (T_p), at which the sample has the fastest crystallization, and the onset temperature (T_c), determined with a method described in the literature,³⁰ can be easily obtained. The values of T_p and T_c for all systems in this study are listed in Table I. For a given value of ϕ , all T_p values for the PHB/HA composites are consistently higher than those for pure PHB, suggesting that the addition of HA promotes the crystallization of the polymer. Similar behavior has been observed at other ϕ values (Table I). When comparing the effect of HA on the heat flow of the composites with respect to filler concentrations from 10 to 40 wt %, we find that at low HA concentrations (10 and 20 wt %), T_p and T_c increase with the filler contents, whereas when the HA concentration is up to 40%, both T_p and T_c begin to decrease and are even less than those of the PHB/HA composite (10 wt %). This phenomenon can be related to the combination of two opposite factors. On the one hand, the HA particles serve as additional nucleators, and their introduction promotes the crystallization of PHB. Similar nucleating effects of microscale particles have been reported for polypropylene (PP) composites reinforced with short sisal fibers³¹ and silver-exchanged natural zeolite.³² On the other hand, the addition of a filler reduces the concentration of the polymer in the composite, and this will unavoidably restrict the motion of PHB chains to some degree. At a low HA concentration, the effect of the filler on the polymer concentration is limited, and it is easy for the additional nucleation sites to incorporate the surrounding polymer. However, at a high level of HA, the diffusion of polymer chains to the growing crystallite is evidently hindered, and so the growth process is retarded. In this

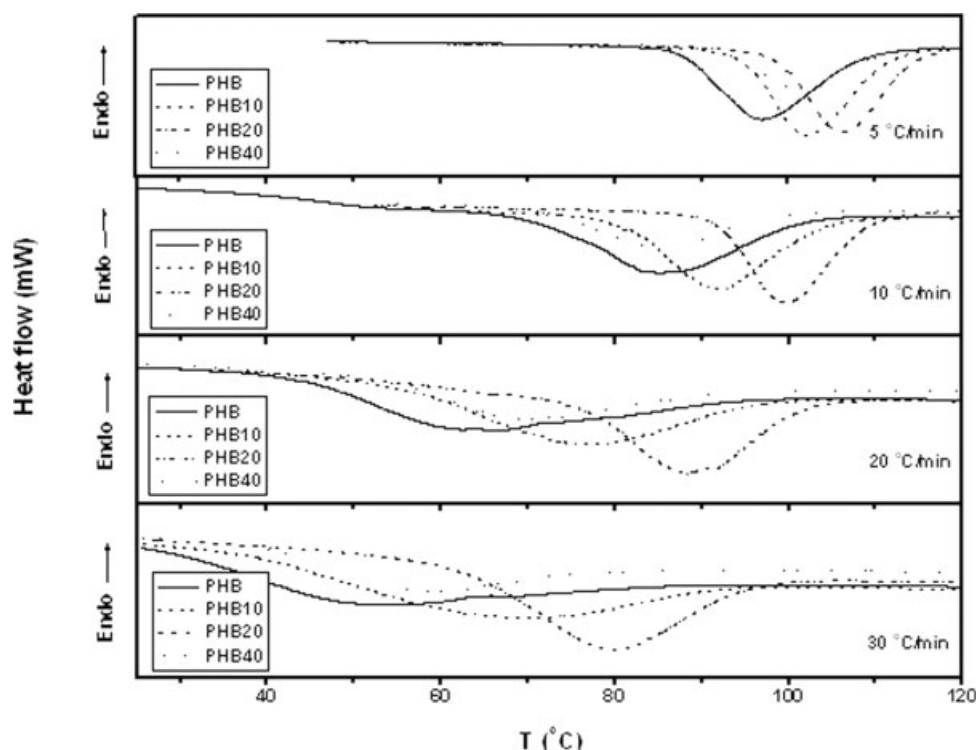


Figure 1 DSC thermograms of nonisothermal crystallization for PHB/HA composites at various ϕ values and HA contents.

study, it is obvious that the latter factor plays the main role for 40 wt % HA. In general, the combination of a larger number of nucleation sites and limited crystal growth is expected to produce crystals of a fine grain size. Wu and Ke³³ reported that different silica size levels all played nucleation roles in poly (ethylene terephthalate). The silica with the smallest size of 54 nm possessed the best capacity for accelerating the crystallization of the polymer because the most nucleation centers were supported in this case. Notably, the aforementioned influence of the filler on polymer crystallization has also been seen in nanocomposite systems, such as clay/nylon nanocomposites.³⁴ Figure 1 and Table I also show that both T_p and T_c decrease, as expected, when ϕ rises. This is attributed to the shorter time required for the polymer to crystallize as ϕ increases. Namely, when the samples are cooled at a lower rate, they have enough time to form the necessary nuclei and to crystallize. However, when a higher ϕ value is used, the motion of polyhydroxybutyrate chains cannot follow the cooling process, and so higher undercooling is required to initiate crystallization.

Nonisothermal-crystallization kinetics

The determination of the absolute crystallinity is not needed for the analysis of the crystallization kinetics,

and the degree of conversion or relative crystallinity (X_t) as a function of temperature can be defined as follows:

$$X_t = \frac{\int_{T_0}^T (dH_c/dT)/dT}{\int_{T_0}^{T_\infty} (dH_c/dT)/dT} \quad (1)$$

where T_∞ is the temperature at the end of crystallization, T_0 is the temperature at which the crystallization begins, and dH/dT is the heat flow rate. During nonisothermal crystallization, time t is determined with the following equation:

$$t = \frac{T_0 - T}{\phi} \quad (2)$$

TABLE I
Nonisothermal Parameters for PHB and PHB/HA Composites Obtained from DSC Exotherms

ϕ (°C/min)	Parameter	PHB	PHB10	PHB20	PHB40
5	T_p	96.91	101.88	106.35	101.37
	T_c	110.51	112.21	115.44	111.06
	$t_{0.5}$	4.01	3.70	3.41	3.86
10	T_p	85.15	91.88	99.67	85.80
	T_c	102.21	104.93	109.40	100.54
	$t_{0.5}$	2.44	2.35	1.81	2.56
20	T_p	65.74	77.40	88.56	70.12
	T_c	94.97	96.68	101.61	92.75
	$t_{0.5}$	1.85	1.48	1.07	1.53
30	T_p	53.94	70.16	79.53	59.23
	T_c	87.27	92.80	95.57	78.46
	$t_{0.5}$	1.26	1.27	0.90	1.21

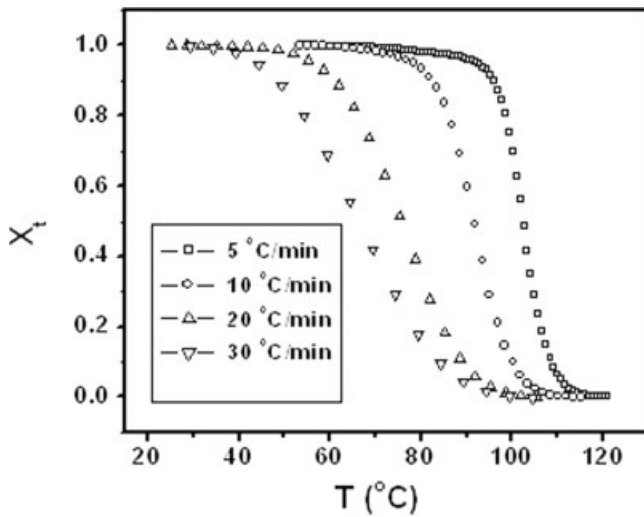


Figure 2 X_t as a function of temperature (T) for PHB10 at various ϕ values.

where T is the temperature at time t . Figure 2 illustrates X_t as a function of the temperature for PHB/HA composites filled with 10 wt % HA at various ϕ values. All the curves have the same sigmoidal shape. Once the X_t - T plot was obtained, the conversion into the X_t - t plot was required because the microkinetic models were used. With eq. (2), the temperature scale of Figure 2 can be changed into the timescale of Figure 3. Figure 3 shows that the higher ϕ is, the shorter the time is for finishing the crystallization.

The half-time of crystallization ($t_{0.5}$), another important parameter, can be obtained from Figure 3 at $X_t = 0.5$. Values of $t_{0.5}$ for all systems under study are also listed in Table I. The $t_{0.5}$ values quite depend on the filler content and ϕ . The reciprocal value of $t_{0.5}$ signifies the bulk crystallization rate. For

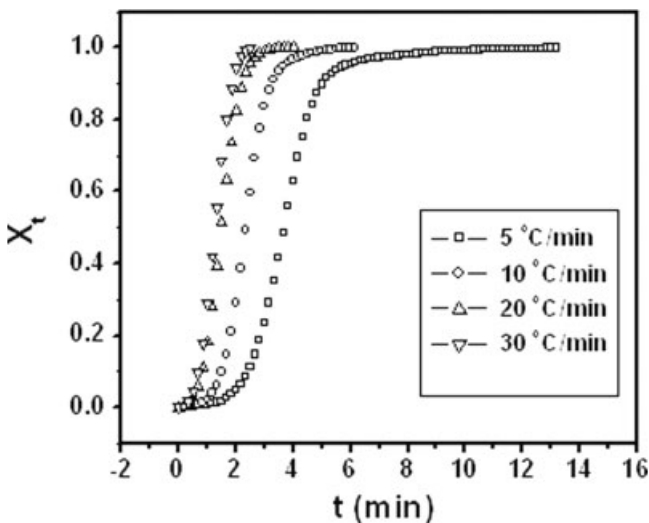


Figure 3 X_t as a function of time (t) for PHB10 at various ϕ values.

a given PHB or PHB/HA composite system, $t_{0.5}^{-1}$ rises with improving ϕ , showing that higher ϕ values promote the crystallization process. On the other hand, a comparison of the $t_{0.5}^{-1}$ values for all HA contents indicates that the composite with 20 wt % HA has the fastest crystallization rate. To explore this effect more clearly, two concepts, the crystallization rate parameter (CRP)³⁵ and crystallization rate coefficient (CRC),³⁶ are introduced; they are determined from the slopes of the $t_{0.5}^{-1}$ - ϕ plot [Fig. 4(a)] and the ϕ - T_p plot [Fig. 4(b)], respectively. Generally, the faster the polymer crystallizes, the higher the CRP (or CRC) value is. Therefore, these two parameters can be used to rank the relative crystallization rates for different polymer systems. Table II summarizes the values of CRP and CRC for PHB and PHB/HA composites. The composite containing 20 wt % HA has both the highest CRP and CRC values of

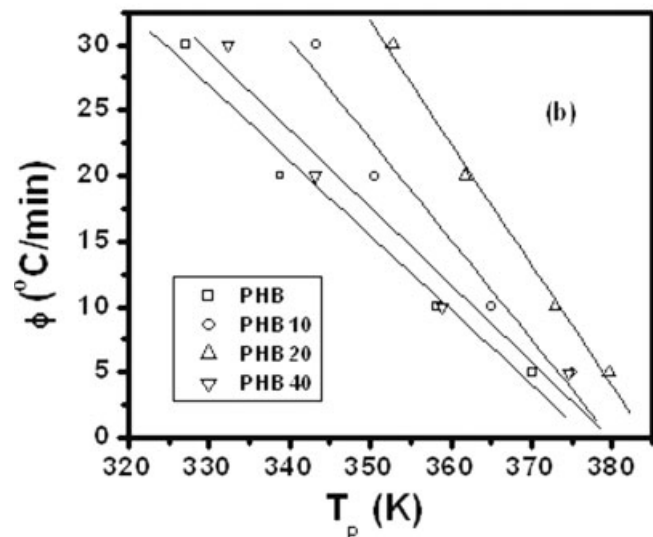
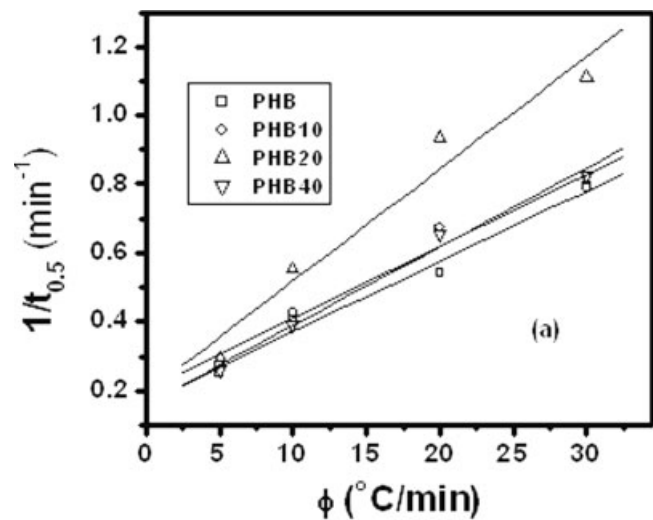


Figure 4 Plots of (a) $1/t_{0.5}$ as a function of ϕ and (b) ϕ as a function of T_p .

TABLE II
CRP and CRC Values for the PHB
and PHB/HA Composites

	PHB	PHB10	PHB20	PHB40
CRP (K ⁻¹)	0.0205	0.0208	0.0326	0.0229
CRC (min ⁻¹)	0.57	0.76	0.93	0.59

0.0326 K⁻¹ and 0.93 min⁻¹, respectively, showing the strongest crystallization ability. When the HA concentration is up to 40 wt %, the composite becomes less crystallizable. That is, a low HA concentration results in dramatic increases in the crystallization kinetics in comparison with pure PHB. However, increasing the concentration of the filler beyond these levels (20 wt % in this study) retards the rate of crystallization. This result is quite identical to the former analysis using parameters of T_p and T_c .

Avrami analysis

The Avrami macrokinetic model³⁷ describes a time-dependent relative crystallinity function $[X(t)]$ for a nonisothermal-crystallization process and can be written as follows:

$$X(t) = 1 - \exp(-Z_t t^n) \quad (3)$$

or

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

where Avrami exponent n is a mechanism constant depending on the type of nucleation and growth process and Z_t is a crystallization rate constant involving both nucleation and growth parameters. Obviously, n and Z_t can be obtained from the slope and intercept, respectively, of the Avrami plots of $\ln[-\ln(1 - X_t)]$ versus $\ln t$.

Considering the nonisothermal character of the process investigated, Jeziorny³⁸ suggested that rate parameter Z_t should be corrected for the influence of ϕ of the polymer. Assuming ϕ to be constant or approximately constant, the final form of the parameter characterizing the kinetics of nonisothermal crystallization can be given as follows:

$$\ln Z_c = \frac{\ln Z_t}{\phi} \quad (5)$$

Z_c apparently represents the kinetic crystallizability at a unit of the cooling rate.

An Avrami analysis was carried out by the direct linear fitting of the plots of $\ln[-\ln(1 - X_t)]$ versus $\ln t$ according to eq. (4). The linear portions of the curves in this study cover a large range of crystallization degrees, about 5–95%, and these portions

have been chosen for the determination of the Avrami parameters. Table III summarizes the values of n , Z_t , and Z_c for PHB and PHB/HA composites. Table III shows that almost all the n values are in the range of 3.0–4.2 and drop with increasing ϕ . The results agree with the values reported by Chen et al.³⁰ for PHB and maleated PHB. As described in the literature,^{39,40} PHB melts undergo homogeneous nucleation. The HA particles act as heterogeneous nuclei for the initial nucleation and should induce the reduction of n . However, in this study, the n values for HA-filled PHB composites are more than that for the pure polymer matrix at the same ϕ value. The reason is that the nonisothermal crystallization of pure PHB might correspond to three-dimensional growth with thermal nucleation, whereas for the composite, the crystallization might be related, to different extents, to three-dimensional growth with athermal nucleation.^{30,41} Parameters Z_t and Z_c strongly depend on ϕ , and at a given value of ϕ , when the HA concentration is more than 20%, these values no longer increase with the HA concentration; this is, as expected, identical to the analysis based on T_p and $t_{0.5}$.

Ozawa analysis

Ozawa⁴² extended the Avrami equation for a nonisothermal treatment. Assuming that the nonisothermal-crystallization process is composed of infinitesimally small isothermal-crystallization steps, X_t at temperature T can be calculated as follows:

$$1 - X_t = \exp[-k(T)/\phi^m] \quad (6)$$

where m is the Ozawa exponent, which depends on the dimensions of the crystal growth, and k is the cooling crystallization function, which is related to

TABLE III
Kinetic Parameters for the PHB and PHB/HA Composites
Obtained from Avrami Analysis

ϕ (°C/min)	Avrami	PHB	PHB10	PHB20	PHB40
	parameter ^a				
5	n	3.71	4.01	4.19	4.10
	Z_t	0.004	0.004	0.004	0.003
	Z_c	0.330	0.323	0.324	0.305
10	n	3.35	3.83	4.05	3.85
	Z_t	0.033	0.025	0.060	0.021
	Z_c	0.710	0.691	0.755	0.680
20	n	2.94	3.04	3.22	3.32
	Z_t	0.126	0.206	0.483	0.166
	Z_c	0.902	0.924	0.964	0.914
30	n	2.54	2.99	3.18	3.35
	Z_t	0.387	0.366	0.947	0.472
	Z_c	0.969	0.967	0.998	0.975

^a Z_t and Z_c are given in units of min⁻¹.

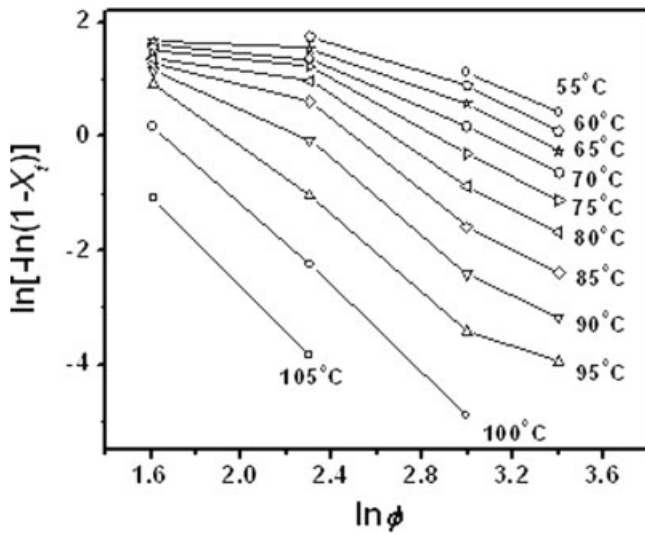


Figure 5 Typical Ozawa plots for PHB10.

the overall crystallization rate. Taking the double-logarithmic form, we can rewrite this equation as

$$\ln[-\ln(1 - X_t)] = \ln k(T) - m \ln \phi \quad (7)$$

If the Ozawa method is valid, plots of $\ln[-\ln(1 - X_t)]$ versus $\ln \phi$ should be straight lines, and kinetic parameters $k(T)$ and m should be obtainable from the intercept and slope of the lines, respectively. Figure 5 presents typical Ozawa plots for a PHB/HA composite containing 10 wt % filler. In the Ozawa plots, a characteristic curvature can be observed, preventing an accurate analysis of the nonisothermal-crystallization data. The continuous change in the slope with temperature makes it clear that m is not constant during crystallization, and the cooling crystallization function $k(T)$ cannot be determined because of the nonlinearity of the curves. The most likely reason for the unsatisfactory description is the assumption during the application of the Ozawa method that the secondary crystallization and dependence of the fold length on the temperature can be ignored and exponent m is a constant independent of the temperature.⁴³ In fact, except for PHB/HA composites, the crystallization kinetics of some polymer composites, including nanocomposites,⁴⁴⁻⁴⁶ has also been proved not to be described well by the Ozawa method because for these polymer systems, a large part of the overall crystallization is due to secondary crystallization.

Mo's analysis

As discussed previously, nonisothermal crystallization is difficult to describe with a single equation because there are a lot of parameters that have to be taken into account simultaneously.⁴³ For the study of

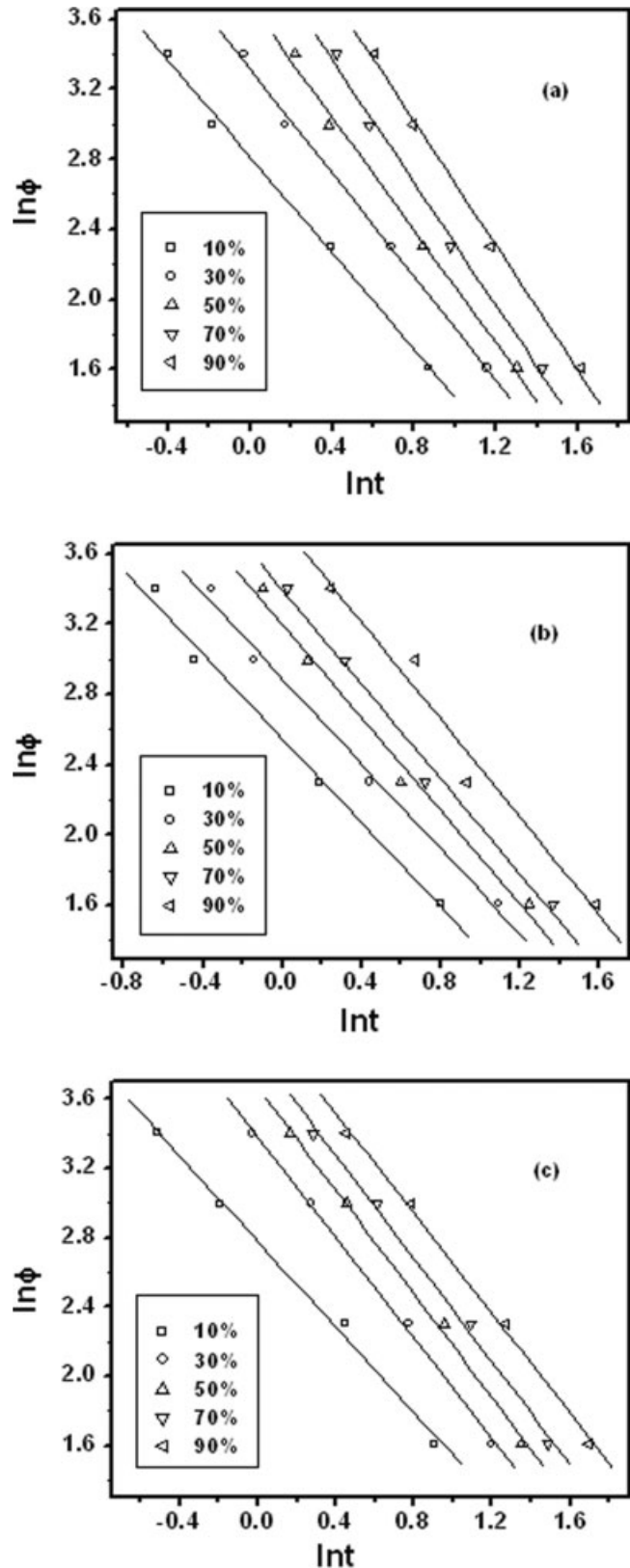


Figure 6 Plots of $\ln \phi$ versus $\ln t$ as a function of X_t for (a) PHB10, (b) PHB20, and (c) PHB40.

nonisothermal-crystallization kinetics, another model, a combined Avrami–Ozawa approach, was proposed by Mo et al.⁴⁷ It can be easily seen that the left forms of eqs. (4) and (7) are the same. By combining these two equations, we can define the relationship for a given degree of crystallization between ϕ and t as follows:

$$\ln Z_t + n \ln t = \ln k'(T) - m \ln \phi \quad (8)$$

By rearrangement at a certain crystallinity and solving for ϕ , we can simplify eq. (8) as

$$\ln \phi = \ln F(T) - a \ln t \quad (9)$$

where $F(T) = [k'(T)/Z_t]^{1/m}$ refers to the cooling rate required within a unit of the crystallization time when the measured system has a certain degree of crystallinity and a is the ratio of n to m , that is, n/m . The importance of this method is that it correlates ϕ with the temperature, time, and morphology. According to eq. (9), at a given crystallinity value, the plots of $\ln \phi$ versus $\ln t$ should be a straight line with an intercept of $\ln F(T)$ and a slope of $-a$. The plots of $\ln \phi$ against $\ln t$ as a function of X_t for PHB/HA composites are shown in Figure 6. A good linear relationship can be observed, indicating that the combination of the Avrami and Ozawa equations exhibits great advantages in treating nonisothermal-crystallization kinetics. The values of $\ln F(T)$ and a are summarized in Table IV. The values of a range from 1.23 to 1.75 for PHB and PHB/HA composites, and both a and $F(T)$ increase with increasing X_t in almost all cases. However, when we compare the effects of the fillers, a turning point in $F(T)$ at each X_t , similarly to the analysis of T_p and $t_{0.5}$, is also found. That is, when the HA concentration exceeds 20 wt %, the dropping trend of $F(T)$ values as a function of the filler content is terminated. This confirms in the same way the existence of a combined effect of two contradictable factors: the acceleration and retardancy of fillers on the crystallization. Besides, Mo's method has also been applied successfully in analyzing the nonisothermal-

TABLE IV
Kinetic Parameters for PHB and PHB/HA Composites at Various X_t Values from Mo's Analysis

	Kinetic parameter	X_t (%)				
		10	30	50	70	90
PHB	a	1.35	1.51	1.60	1.70	1.67
	$\ln F(T)$	2.88	3.49	3.88	4.22	4.50
PHB10	a	1.37	1.47	1.61	1.75	1.77
	$\ln F(T)$	2.81	3.31	3.69	4.07	4.43
PHB20	a	1.20	1.21	1.32	1.35	1.39
	$\ln F(T)$	2.55	2.89	3.20	3.40	3.76
PHB40	a	1.23	1.45	1.49	1.49	1.44
	$\ln F(T)$	2.78	3.38	3.67	3.87	4.09

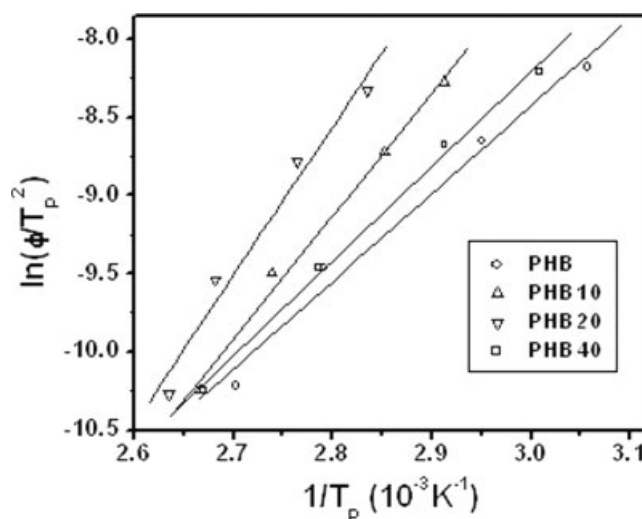


Figure 7 Plots of $\ln(\phi/T_p^2)$ versus $1/T_p$ for PHB and PHB/HA composites.

crystallization processes of other systems, such as high-density polyethylene/SiO₂ composites,⁴⁸ polyoxymethylene (POM)/clay,⁴⁹ and nylon 6/graphite⁴⁴ nanocomposites.

Activation energy

The activation energy of crystallization for PHB/HA composites can be evaluated with the Kissinger approach⁵⁰ as follows:

$$\frac{d[\ln \phi/T_p^2]}{d(1/T_p)} = -\frac{\Delta E}{R} \quad (10)$$

where ΔE is the effective energy barrier and R is the gas constant. The other parameters have the same meanings earlier mentioned. From the slope of the plot of $\ln \phi/T_p^2$ against $1/T_p$ presented in Figure 7, the activation energy of nonisothermal crystallization for PHB and PHB/HA composites has been obtained. As shown in Table V, the calculated ΔE values of the composites vary with the presence of HA and fall in the range of 50–79 kJ/mol.

CONCLUSIONS

The nonisothermal-crystallization behavior of PHB/HA composites has been investigated with DSC at different values of ϕ . The Ozawa analysis fails to provide an adequate description of the nonisother-

TABLE V
 ΔE for the PHB and PHB/HA Composites

Sample	PHB	PHB10	PHB20	PHB40
ΔE (kJ/mol)	46.6	64.9	78.8	50.2

mal-crystallization process in neat PHB and the composite samples. However, both the modified Avrami method and the combination of the Avrami and Ozawa equations proposed by Mo et al.⁴⁷ provide a satisfactory description of the experimental data. The values of $t_{0.5}$ and Z_c show that the crystallization rate increases with increasing ϕ for both PHB and the composites. The HA particles serve as additional nucleation sites. The composite containing 20 wt % HA had the fastest crystallization rate, reflecting the existence of a combination of acceleration and limitation effects on the crystallization. At low amounts of HA, the promotion function plays the main role, and the crystallization process is accelerated compared with that of pure PHB, whereas, when a higher filler content is used, the concentration of the polymer in the composite decreases and the motion of PHB chains is restricted to some extent; this results in slower crystallization.

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