

# Effect of Nucleating Agents on the Crystallization of Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate)

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**ABSTRACT:** The effect of nucleating agents on the crystallization behavior of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was studied. A differential scanning calorimeter was used to monitor the energy of the crystallization process from the melt and melting behavior. During the crystallization process from the melt, nucleating agent led to an increase in crystallization temperature ( $T_c$ ) of PHBV compared with that for plain PHBV (without nucleating agent). The melting temperature of PHBV changed little with addition of nucleating agent. However, the areas of two melting peaks changed considerably with added nucleating agent. During isothermal crystallization, dependence of the relative degree of crystallization on time was described by the Avrami equation. The addition of nucleat-

ing agent caused an increase in the overall crystallization rate of PHBV, but did not influence the mechanism of nucleation and growth of the PHB crystals. The equilibrium melting temperature of PHBV was determined as 187°C. Analysis of kinetic data according to nucleation theories showed that the increase in crystallization rate of PHBV in the composite is due to the decrease in surface energy of the extremity surface. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2145–2152, 2002

**Key words:** poly(3-hydroxybutyrate-co-3-hydroxyvalerate); crystallization; melting point; biodegradable; thermal properties

## INTRODUCTION

Polymers have found uses in various applications of plastic articles, including films, sheets, fibers, foams, and molded articles, and some other special products, such as packaging, agriculture, household goods, and personal care products. However, polymers usually have a short use period in many application fields; for example, in food packaging, polymers play the role of a protective agent and are quickly disposed of after the contents are consumed. Household products are immediately discarded when the product is used.

The majority of this plastic material is added to the solid waste stream, headed for the rapidly vanishing and increasingly expensive landfill space. Although some efforts<sup>1–3</sup> at recycling have been made, the nature of polymers and the way they are produced and converted to products limits the number of possible recycling applications.

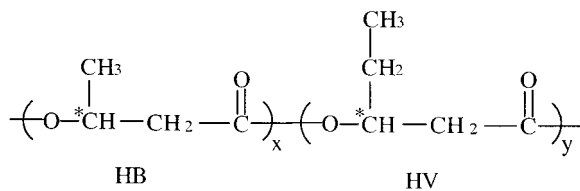
On the other hand, biodegradation and/or bioconversion in controlled environments are the most desirable methods of disposal of wastes and of recycling of resources. The microbial polyester family represents a source of biodegradable materials.<sup>4</sup> Various

biodegradable polymers, such as poly(hydroxyalkanoates), are obtained from several microorganisms.

In the past, the biodegradability and physical properties of the various polyhydroxyalkanoates (PHAs)<sup>5–13</sup> have been studied. PHAs are polyester compounds produced by a variety of microorganisms, such as bacteria and algae. Although PHAs have been of general interest because of their biodegradable nature, their actual use as a plastic material has been hampered by their thermal instability. For example, poly-3-hydroxybutyrate (PHB)<sup>6</sup> is a natural energy-storage product of bacteria and algae. However, it is different from other biologically synthesized polymers such as proteins. PHB is thermoplastic with a high degree of crystallinity and a well-defined melting temperature of ~180°C. Unfortunately, PHB becomes unstable and degrades at elevated temperatures near its melting temperature. Because of this thermal instability, commercial applications of PHB have been extremely limited.

As a result, investigators have studied other PHAs, such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV),<sup>7</sup> in the hopes of discovering a PHA with sufficient thermal stability and other suitable chemical and physical properties for use in practical applications. The processing and the mechanical properties<sup>8</sup> of PHBV have been enhanced over those of PHB. Unfortunately, PHBV presents the following problems to be solved: slow crystallization rate, relatively difficult processing, low elongation at break, and very high crystallinity.

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Scheme 1

Because of the slow crystallization rate, a film made from PHBV will stick to itself even after cooling; a substantial fraction of the PHBV remains amorphous and tacky for long periods of time. However, the properties, processing, and cost of biodegradable polymers, such as PHBVs, can be modified and improved by blending procedures.<sup>6-9</sup>

Although some papers reported the structure, nucleation, properties, and processing of PHBVs,<sup>10-13</sup> to improve the processing properties and quicken the application, it is necessary to study the crystallization and thermal stability of PHBV. In this paper, the effect of nucleating agents on the crystallization behavior of PHBV was studied with a differential scanning calorimeter (DSC).

## EXPERIMENTAL

### Materials and specimens preparation

A random copolymer of 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV), PHBV, was provided by the Microbiology Institute (Beijing), Chinese Academy of Science. The molecular structure of the copolymer is shown in Scheme 1. The content of 3-hydroxyvalerate (PHV) in the copolymer is 6.6 mol %, as measured by nuclear magnetic resonance spectroscopy (NMR). The average molecular weight of the copolymer, obtained by measuring its viscosity in chloroform at 30°C, is  $606 \times 10^3$ . The crystallinity of the copolymer is ~55%, as measured by X-ray diffraction (XRD).

The composites of PHBV and each kind of nucleating agent, such as boron nitride (BN), talc, terbium oxide ( $Tb_2O_3$ ), and lanthanum oxide ( $La_2O_3$ ), were prepared with a Brabender at 165°C. The plain PHBV was subjected to the same procedure as were the composites in the Brabender at 165°C.

### Isothermal crystallization and melting

A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) was employed to detect thermal transitions and to monitor the rate of heat flow from the sample during isothermal crystallization from the melt. The instrument was calibrated with an indium standard, and the measurement was conducted under a nitrogen atmosphere. The sample weight used in the DSC cell was kept in the 8–12-mg range. The samples were first

heated to 190°C at a rate of 80°C/min and then maintained at this temperature for 5 min to remove prior thermal histories. They were cooled to the appropriate crystallization temperature,  $T_c$ , at a rate of 80°C/min. The heat generated during the development of the crystalline phase was recorded up to a vanishing thermal effect and analyzed according to the usual procedure to obtain the relative degree of crystallinity,  $\alpha(t)$ :

$$\alpha(t) = X(t)/X(\infty) = \left( \int_{t_0}^t (dH/dt) / \int_{t_0}^{\infty} (dH/dt) \right) \quad (1)$$

where  $t_0$  is the time at which the sample attains isothermal condition, as indicated by a flat base line after the initial spike in the thermal curve.

The absolute degree of crystallinity of PHBV in its pure state and in the composite was evaluated from the heat evolved during crystallization by the following relationship:

$$X(t) = \left( \int_{t_0}^t (dH/dt) \right) / (1 - \phi)\Delta H_f^0 \quad (2)$$

where  $\Delta H = 1.85 \times 10^8$  J/m<sup>3</sup> is the heat of fusion for 100% crystalline PHB<sup>8</sup> and  $\phi$  is the weight fraction of the filler in the composites.

To observe the melting behavior, some of the isothermally crystallized sample was reheated to 190°C at a rate of 10°C/min. The heat of fusion was calculated from the melting peak area, and the maximum of the endothermic was taken as the melting temperature,  $T_m$ .

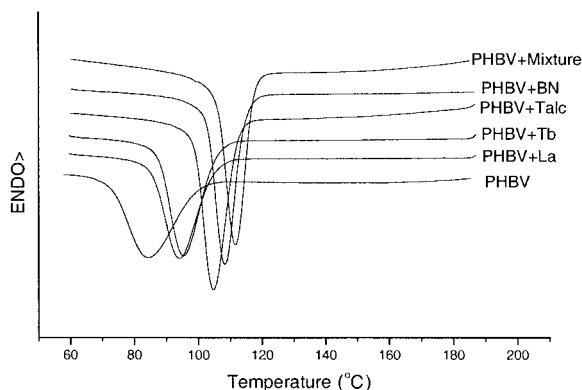
### Crystallization and melting

All the samples were heated to 190°C, then cooled to room temperature at rate of 10°C/min, and then heated to 190°C again. During the cooling and second heating, cooling and heating DSC curves, respectively, were recorded.

## RESULT AND DISCUSSION

### Effect of nucleating agents on the melting and crystallization behavior of PHBV

The effect of nucleating agents on the crystallization behavior of PHBV from the melt is shown in Figure 1. As defined in the figure, four crystallization behavior parameters are listed in Table I. The  $T_c$ s are seen as peaks on DSC scanning curves when the molten samples were cooled from the melt at a cooling rate of 10°C/min. The content of the nucleating agents in



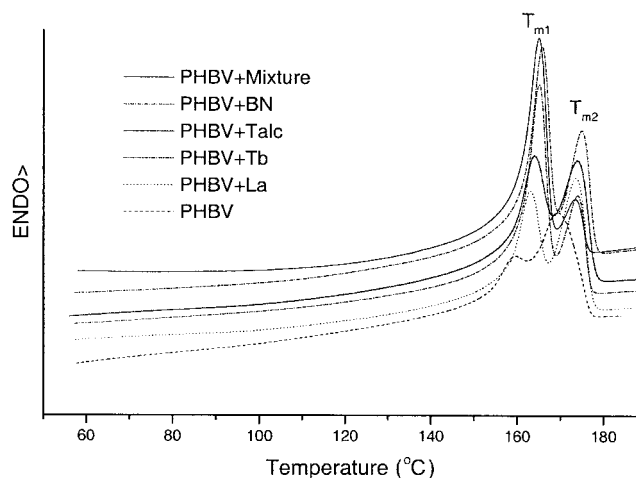
**Figure 1** The DSC scanning traces of PHBVs from melt at a cooling rate of 10°C/min.

these samples is 1 wt % except the content of talc is 5 wt %, as indicated in Table I.

The nucleation effect of these solid additives, drawn from Figure 1 and Table I, is of the order mixture, BN, talc,  $Tb_2O_3$ , and  $La_2O_3$ . If we divide these nucleating agents into two groups, one of them consists of mixture, BN and talc. Their nucleation effect for PHBV is much better than the other group, which consists of  $Tb_2O_3$  and  $La_2O_3$ . The crystallization temperatures,  $T_c$ s, of PHBV containing the nucleating agents in the first group are  $>100^\circ C$  and  $\Delta T$ s are  $<13.8^\circ$ , whereas the onset temperatures increases significantly compared with the neat PHBV. The nucleation effect of the mixture nucleating agents on the crystallization behavior of PHBV is similar to that of BN, and each are slightly better than that of talc (5 wt %). The shifting of  $T_c$  toward higher temperature means that the polymer could crystallize more easily at a relatively lower under-cooling; therefore, reduction of the energy of the driving force for crystallization can be postulated. The higher crystallization rates in PHBV containing nucleating agents were evaluated by the decreasing  $\Delta T$ . The crystallization was completed in 1.2 min, and a 63.4% degree of crystallinity was attained for PHBV with the BN nucleating agent during the cooling scan in the DSC pan from the melt. In contrast, these values are 2.8 min and 58.4%, respectively, for neat PHBV. The crystallization period during the cooling from the melt was shortened  $\sim 2.3$  times by adding the BN nucleat-

**TABLE I**  
Effect of Nucleating Agents on the Crystallization Behavior of PHBV

Nucleating Agent	$T_c, ^\circ C$	$T(\text{onset}), ^\circ C$	$\Delta T, ^\circ C$	$\Delta H_c, J/g$
Mixture	112	117.8	12.0	63.7
BN	109	115.2	12.1	63.4
Talc (5 wt %)	105	113.3	13.8	62.8
$Tb_2O_3$	95	106.6	19.6	60.1
$La_2O_3$	94	105.2	20.3	60.3
None (neat PHBV)	84	100.4	26.2	58.4



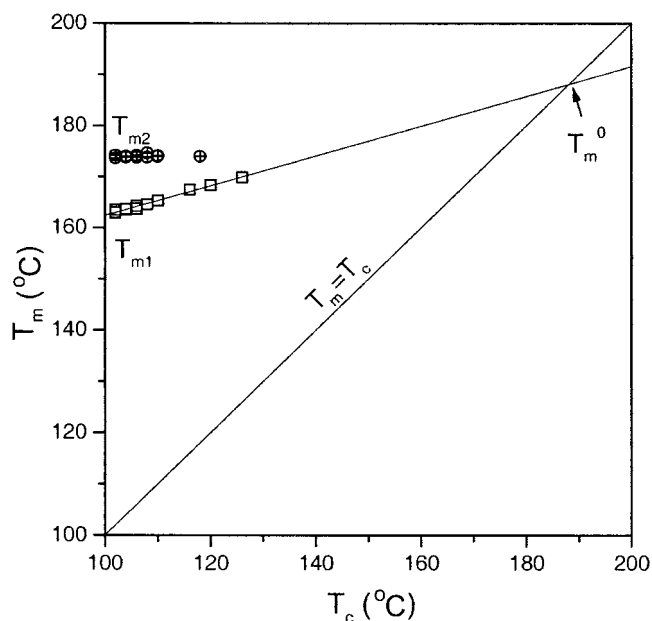
**Figure 2** The melting behavior of PHBVs at a heating rate of 10°C/min.

ing agent to the PHBV. The rare earth oxides,  $Tb_2O_3$  and  $La_2O_3$ , enhanced the crystallization rate and shortened the crystallization duration during cooling from melt of PHBV also, but their nucleation effect is much smaller than that of the nucleating agents BN, mixture, and talc.

The effect of the nucleating agents on the melting behavior of PHBV is shown in Figure 2. The double melting temperatures,  $T_{m1}$  and  $T_{m2}$ , were detected for all samples on the DSC heating scanning traces. However, the neat PHBV exhibits the lowest  $T_{m1}$  and  $T_{m2}$ , indicating that the worst crystal perfection with the lowest lamella thickness was created in the neat PHBV. The better the nucleation effect of the agent, the higher the melting point  $T_{m1}$ . The melting temperature  $T_{m2}$  is independent of the nucleating agent, perhaps because it resulted from the melting of reorganized crystals during the heating of the samples (this possibility will be discussed in detail later). The ratios between the melting peaks of  $T_{m1}$  and  $T_{m2}$  for the PHBV containing nucleating agents and pure PHBV are different, as shown in Figure 2. The nucleating agents forced the peak of  $T_{m1}$  to increase and depressed the  $T_{m2}$  peak. The increment of the ratio between the peaks of  $T_{m1}$  and  $T_{m2}$  was enhanced as the nucleation effect of the nucleating agent was improved. These results indicate that the nucleating agents increased the crystallization rate and improved the perfection of the crystals of PHBV.

### The equilibrium melting temperature of PHBV

Isothermal crystallization from the melt of pure PHBV and PHBV with nucleating agents produces a material exhibiting double melting endotherms on heating as measured by DSC. To evaluate the equilibrium melting temperature, one has to decide which peak temperature corresponds to the crystals formed during



**Figure 3** The plot of  $T_m$  as a function of  $T_c$  for neat PHBV and PHBV with added nucleating agents.

primary crystallization. The melt-crystallized PHBVs were heated directly from  $T_c$  after the isothermal crystallization was carried out. We found that the higher temperature peak,  $T_{m2}$ , does not depend on  $T_c$ s. It was postulated that the endothermic peaks at higher temperatures are due to the melting of the crystals that are recrystallized during heating the samples in the DSC pans. On the other hand, the lower temperature peaks,  $T_{m1}$ , are related to the melting crystals formed during isothermal crystallization; they increase steadily with increasing  $T_c$ s. The  $T_{m1}$  data are reported as a function of  $T_c$  in Figure 3 for all samples, including pure PHBV and PHBV with different nucleating agents. All samples are able to crystallize in a reasonable time. The extrapolation procedure is not trivial because reorganization of crystals at  $T_c$  or during heating may improve their stability to different extents at various temperatures. However, we have observed a negligible effect of crystallization time on the peak temperatures of the first endotherm; therefore, the extrapolated  $T_m^0$  should not be greatly affected by crystallization conditions. The equilibrium melting temperature of the PHBV crystals with infinite thickness,  $T_m^0$ , is 187°C, drawn from the intersection of the experimental line with line  $T_m = T_c$  shown in Figure 3. This result is in agreement with that of Saghir.<sup>14</sup> The thickening factor,  $\gamma$ , is calculated from the slope of the line in Figure 3 according to the following equation:<sup>15</sup>

$$T_m = T_m^0 [1 - (1/\gamma)] + (T_c/\gamma) \quad (3)$$

Because curvature is inherent in the exact form of eq. 3 if  $\gamma$  is not strictly a constant at various crystallization

temperatures,  $T_c$ s, this curvature usually tends to give a slightly high value of  $T_m^0$ . When the line of  $T_m$  as a function of  $T_c$  is plotted, one has to consider the deviation resulted from the factor  $\gamma$ .

### Crystallization kinetics

Crystallization kinetics in copolymers is a complex phenomenon that encompasses several processes; viz. production of primary nuclei, formation and spreading of bidimensional surface nuclei, and interdiffusion of crystallizable and noncrystallizable chains at the advancing front of the growing crystallites. These processes are affected to different extents by the thermodynamic conditions in which crystallization takes place, by the molecular characteristics of the components, and by the strength of their mutual interaction. Fortunately, PHB and PHV are miscible. The crystallization behavior of the random copolymer, PHBV, is similar to that of the PHB homopolymer, with some defects consisting of HV segments. In general, the radial growth rate of polymer spherulites can be examined by polarized optical microscopy or DSC. The growth rate of the individual spherulites is measured by the former method, and the growth rate of the overall spherulites is determined by the latter method. According to the phenomenological theory, the relative degree of crystallinity achieved at time  $t$  under isothermal conditions is given by Avrami equation:<sup>16</sup>

$$X(t) = 1 - \exp[-Zt^n] \quad (4)$$

where  $n$  is an index related to the dimensionality of growth and to the way primary nuclei are formed, and  $Z$  is the overall rate constant containing both nucleation and growth contributions. Linearization of eq. 4 enables one to evaluate  $n$  and  $Z$  from the slope and the intercept, respectively, of the best straight lines fitting the experimental points at low degree of transformation. In agreement with previous kinetic investigations, we found that deviation from linearity starts when  $X$  is  $\sim 0.7$ , indicating that other factors not to be considered in the formulation of the theory, such as secondary crystallization, exert influences. The parameters measured in our study for pure PHBV and PHBV containing the nucleating agents were shown in Table II and Figures 4 and 5.

From a qualitative point of view, it can be observed that the addition of nucleating agents into PHBV increases the rate of formation of crystalline phase. This effect can be concluded readily from Table II, where the apparent overall rate constant  $Z$  as a function of temperature is shown for various nucleating agents. The results clearly indicate that incorporation of the nucleating agents enhances the crystallization rate of PHBV.

**TABLE II**  
Effect of Nucleating Agents on the Crystallization Parameters of PHBVs

Sample	$T_c$ (°C)	$n$	$Z$ (min <sup>-1</sup> )	$K_g$ (K <sup>2</sup> )	$\sigma_e$ (J/m <sup>2</sup> )
PHBV	98	2.2	$4.6 \times 10^{-1}$	5.3	0.037
	100	2.1	$2.3 \times 10^{-1}$		
	104	2.2	$1.2 \times 10^{-1}$		
	106	2.0	$1.1 \times 10^{-1}$		
	108	2.2	$7.7 \times 10^{-2}$		
PHBV-La	102	2.4	$9.5 \times 10^{-2}$	4.6	0.032
	104	2.5	$7.2 \times 10^{-2}$		
	106	2.7	$3.3 \times 10^{-2}$		
	108	2.6	$2.0 \times 10^{-2}$		
	110	2.5	$1.8 \times 10^{-2}$		
PHBV-Tb	102	2.1	$1.9 \times 10^{-1}$	4.0	0.028
	104	2.1	$1.0 \times 10^{-1}$		
	106	2.4	$6.2 \times 10^{-2}$		
	108	2.5	$4.7 \times 10^{-2}$		
	110	2.8	$1.8 \times 10^{-2}$		
PHBV-Talc	112	2.2	$2.7 \times 10^{-1}$	3.9	0.027
	114	2.8	$6.4 \times 10^{-2}$		
	116	2.9	$4.9 \times 10^{-2}$		
	118	2.9	$2.0 \times 10^{-2}$		
	120	2.8	$1.4 \times 10^{-2}$		
PHBV-BN	118	2.1	$3.0 \times 10^{-1}$	3.4	0.024
	120	2.4	$1.6 \times 10^{-1}$		
	122	2.4	$1.1 \times 10^{-1}$		
	124	2.6	$4.3 \times 10^{-2}$		
	126	2.8	$1.1 \times 10^{-2}$		

According to the nucleation theories it is possible to discuss the overall crystallization behavior of PHBV by using calorimetric data obtained under isothermal conditions. In fact, it can easily be shown that, under isokinetic conditions for nucleation rate, the linear growth rate,  $G$ , is related to  $n$  and  $Z$  by the following simple relation:<sup>17,18</sup>

$$G \propto Z^{1/n} \quad (5)$$

The theory of surface nucleation can be used to account for the effect of nucleating agents on the linear growth rate of the spherulites developing in an undercooled homogenous PHBV. The equation<sup>19</sup> commonly used to describe the linear growth kinetics reads as follows:

$$G = \phi_2 G_0 \exp \left[ -U/R(C_2 + T - T_g) \right] \exp \left[ -r b_0 \sigma \sigma_e T_m^0 / [k f \Delta H_m^0 T_c \Delta T] \right] \exp \left[ 2 \sigma T_m^0 \ln \phi_2 / b_0 f \Delta H_m^0 \Delta T \right] \quad (6)$$

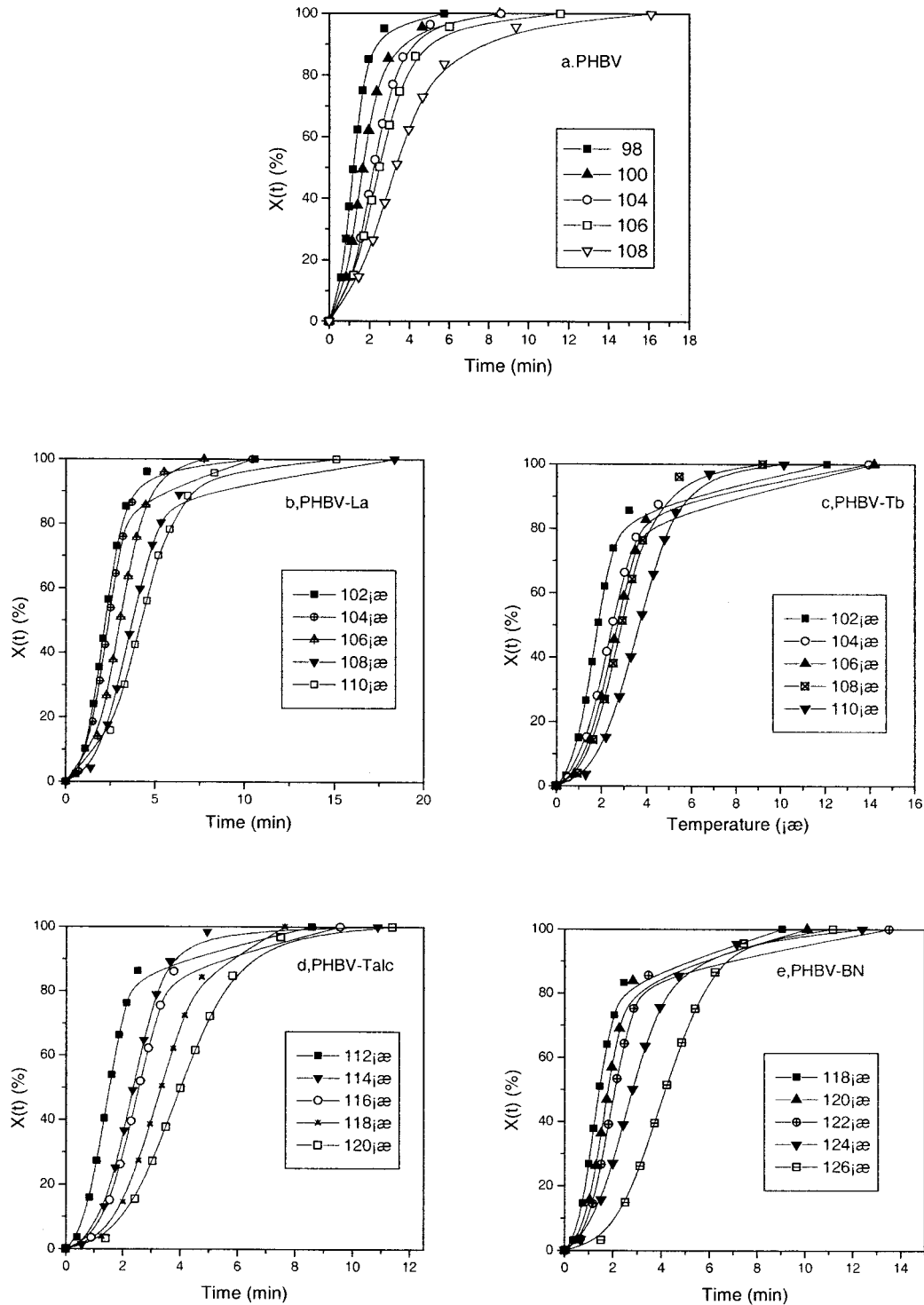
where  $\phi_2$  is the volume fraction of crystallizable component in the copolymer,  $U$  is the activation energy for transport of segments to the crystal front through the subcooled melt,  $T_g$  is the glass transition temperature of PHBV,  $C_2$  is a constant usually assumed as 51.6°C,  $f$  is correction factor for the temperature dependence of the enthalpy of fusion and can be expressed as  $f = 2T_c / (T_m^0 + T_c)$ .  $\sigma$  and  $\sigma_e$  are the lateral and fold surface free energy of the developing crystals, respectively,

and  $b_0$  is the layer thickness. The parameter  $r$  is related to the characteristic of the growth regime:  $r = 4$  in regimes I and III, and  $r = 2$  in regime II.<sup>20</sup> It is expected that transition from regime I to II to III should be observed on increasing the ratio between surface nucleation rate and the rate of spreading of the secondary nucleus on the substrate. The undercooling degree is  $\Delta T = T_m^0 - T_c$ .

By combining eqs. 5 and 6 and after some rearrangements,

$$\alpha = \ln(Z)/n + U/R[C_2 + T_c - T_g] - [1 + 2\sigma T_m^0 / b_0 f \Delta H_m^0 \Delta T] \ln \phi_2 = \ln G_0 - r b_0 \sigma \sigma_e T_m^0 / [k f \Delta H_m^0 T_c \Delta T] \quad (7)$$

The straight lines with slopes,  $K_g$ , related to the surface energies of the lamellar crystals were obtained by plotting  $\alpha$  as a function of  $1/f T_c \Delta T$ . The results are shown in Figure 6 for pure PHBV and PHBV with nucleating agents. The parameters  $n$  and  $Z$  in eq. 7 have been evaluated from the preceding Avrami analysis and  $U^* = 10.25$  KJ and  $C_2 = 51.6$ °C have been taken from literature.<sup>21, 22</sup> The equilibrium melting temperature,  $T_m^0$ , and the glass transition temperature,  $T_g$ , of PHBV were measured as already mentioned. The layer thickness,  $b_0 = 0.72$  nm, was calculated<sup>23</sup> from the average dimensions of the orthorhombic unit cell [ $a = 0.576$  nm,  $b = 1.320$  nm,  $c$  (fiber axis) = 0.595



**Figure 4** The plots of relative degree of crystallinity of PHBVs as a function of crystallization time under isothermal conditions.

nm, space group  $p2_12_12_1$ ] of PHBV in the temperature range of interest. The experimental data in Figure 6 obey eq. 7 for all samples, regardless of the kind and amounts of nucleating agents.

To determine the kinetic value of the end surface energy and its dependence on the nucleating agents, the lateral surface free energy,  $\sigma$ , has to be estimated

first. The fold surface free energy can then be calculated by the Thomas–Staveley equation:<sup>24</sup>

$$\sigma = \beta \Delta H_m^\circ A_o^{1/2} \quad (8)$$

where  $A_o$  is the cross-sectional area of a chain of PHB crystal and  $\beta$  is a constant that is 0.24 for polyesters

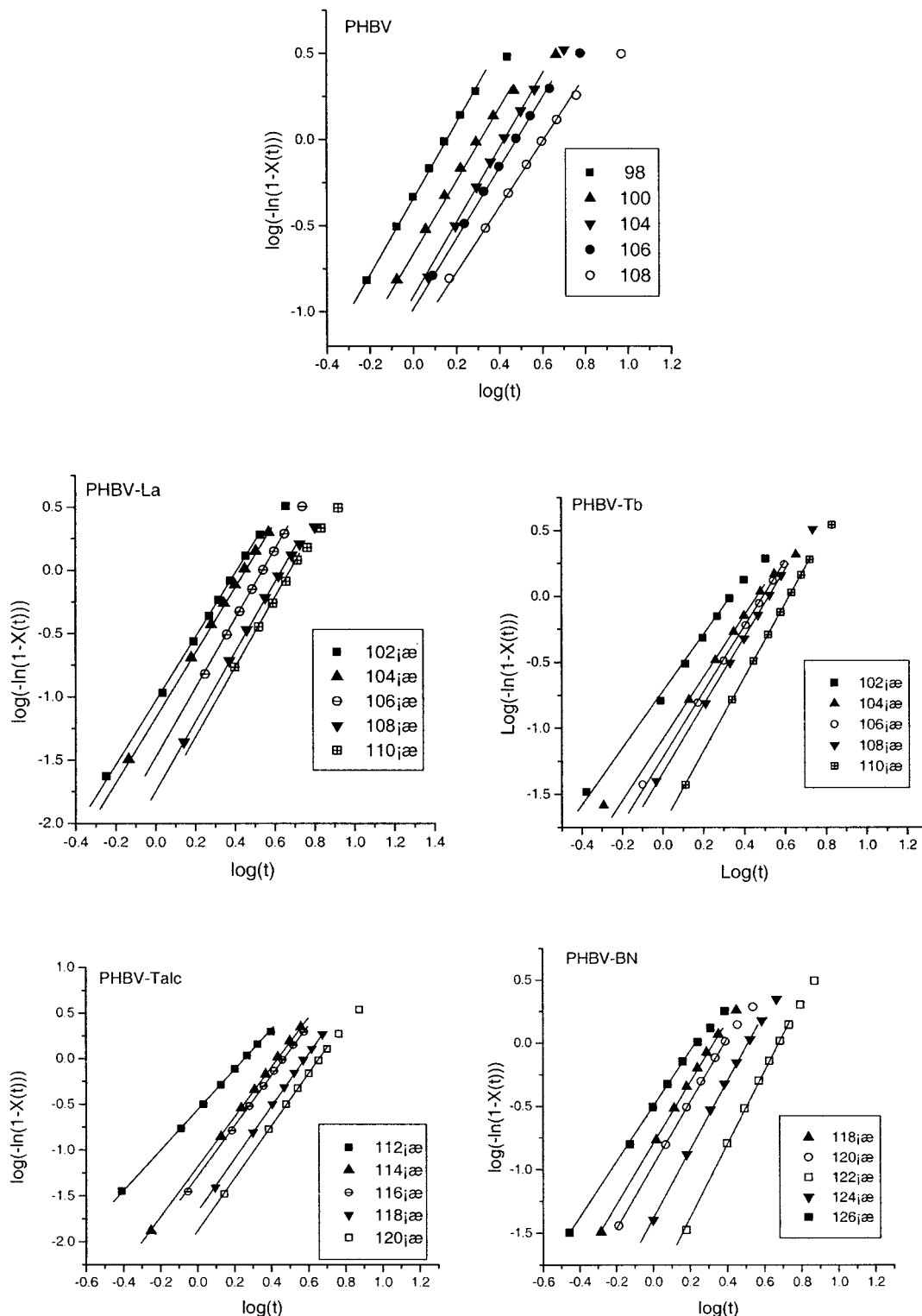
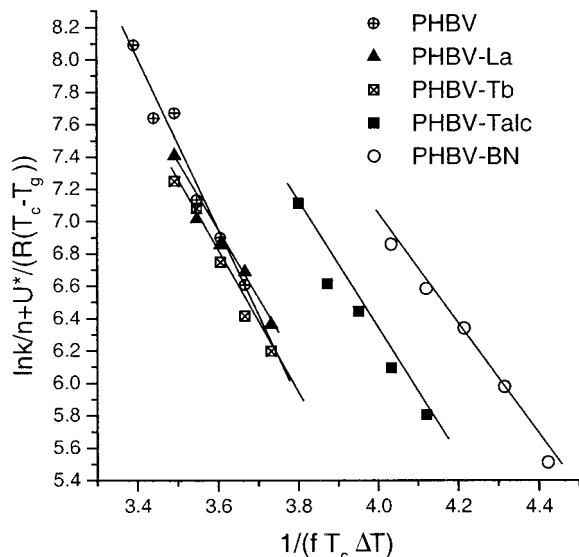


Figure 5 The plots of  $\log[-\ln(1 - X(t))]$  as a function of  $\log(t)$  for PHBV and PHBV added nucleating agents.

and 0.1 for polyolefins, according to Marand and Hoffman.<sup>25</sup> The value of  $\beta = 0.24$  is suitable for PHBV because PHBV is a polyester. From the accepted unit cell dimensions of PHB,  $\sigma = 2.8 \times 10^{-2} \text{ J/m}^2$  was calculated.

From the slopes of the straight lines,  $K_g$ , in Figure 6, the fold surface free energies can readily be calculated provided the growth regime is known. On the assumption that regime III is operative at supercoolings of the order  $\sim 60^\circ\text{C}$ ,  $\sigma_e$  were obtained for neat PHBV



**Figure 6** The plots of kinetic data according to eq. 7.

and PHBV with added the nucleating agents, and these results are listed in Table II.

The free energy for PHBV crystals formed during the crystallization isothermally from melting state decreased by adding the nucleating agents in the copolymer. The nucleation effect of the solid additives decreases in the order BN, talc,  $Tb_2O_3$ , and  $La_2O_3$ . These results are in agreement with those from DSC scans in the cooling and heating modes, as already mentioned.

### CONCLUSIONS

1. The crystallization and melting behavior of PHBV was affected by adding nucleating agents. The nucleating agents used in this study enhanced the crystallization rate and improved the perfection of the PHBV crystals.
2. The equilibrium melting temperature of PHBV is  $187^\circ C$ .
3. The free energy for PHBV crystals formed during isothermal crystallization from melt decreased by adding nucleating agents to the copolymer.

4. The nucleation effect of the solid additives decreases in order BN, talc,  $Tb_2O_3$ , and  $La_2O_3$ .

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