

Crystallization Kinetics of Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate)/Clay Nanocomposites

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Abstract: The preparation and properties of nanocomposites, consisting of a poly(3-Hydroxybutyrate-co-3-hydroxyvalerate) and an organophilic clay are described. The effect of organophilic clay on the crystallization behavior of (PHBV) was studied. A differential scanning calorimeter (DSC) was used to monitor the energy of the crystallization process from the melt. During the crystallization process from the melt, the organophilic clay led to an increase in crystallization temperature (T_c) of PHBV compared with that for plain PHBV. During isothermal crystallization, dependence of the relative degree of crystallization on time was described by the Avrami equation. The addition of organophilic clay caused an increase in the overall crystallization rate of PHBV, but did not influence the mechanism

of nucleation, and growth of the PHBV crystals and the increase caused by a small quantity of clay is more effective than that large one. The equilibrium melting temperature of PHBV was determined as 186°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. The mechanical test shows that the tensile strength of hybrid increased to 35.6 MPa, which is about 32% higher than that of the original PHBV with the incorporation of 3 wt % clay, and the tensile modulus was also increased. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 655–661, 2004

Key words: crystallization; kinetics; nanocomposites

INTRODUCTION

Biodegradable polymers have been extensively investigated since 1970s, to reduce the environmental pollution caused by plastic wastes.^{1–3} The biodegradability and physical properties of the various polyhydroxyalkanoates (PHAs)^{4,5} have been studied such as poly(3-hydroxybutyrate) (PHB),⁶ which 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.

So investigators have studied other PHAs, such as Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV),⁷ 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 of

PHBV have been enhanced over those of PHB. However, PHBV presents the following problems to be solved: slow crystallization rate, relatively difficult processing, low elongation at break, and very high crystallinity. If the properties of the PHBV, not only crystallization but mechanical, can be further improved by the addition of a small quantity of an environmentally benign material such as clay, this polymer will find applications in more special or severe circumstances.

Inorganic particles are widely used as reinforcement materials for polymers. Among these inorganic materials, clay has been receiving special attention in the field of nanocomposites because of its small particle size and its intercalation properties. Besides economic and environmental factors, its natural abundance, high mechanical strength, and chemical resistance, make clay a useful filler in polymer composites.⁸

Our main research has focused on the synthesis of polymer/clay nanocomposite with good integrated properties.^{9,10} In this article, the effect of clay on the crystallization behavior as well as mechanical property of PHBV was studied.

EXPERIMENTAL

Materials

The montmorillonite (MMT) powders were provided by Jilin Liufangzi Clay Products Co., China, which

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contains exchangeable cations of primarily Na^+ with a cation exchange capacity (CEC) of 100 mEq/100 g. A random copolymer of 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV), PHBV, was supported by Microbiology Institute (Beijing), Chinese Academy of Science. The content of 3-hydroxyvalerate (PHV) in copolymer is 6.6 mol % measured by using NMR. The average molecular weight of the copolymer, obtained by measuring its viscosity in solvent of chloroform at the temperature of 30°C, is 6.06×10^5 g/mol. The crystallinity of the copolymer is about 55%, measured by means of X-ray diffraction.

Preparation of organically modified montmorillonite

Organically modified montmorillonite (OMMT) was prepared by cationic exchange between Na^+ in MMT galleries and hexadecyl-trimethylamine bromide in an aqueous solution in our lab. First, 25 g of MMT was dispersed in 250 mL of distilled water. The hexadecyl-trimethylamine bromide (9.1 g) was then dissolved in 50 mL of distilled water, and it was poured into the MMT-water solution with vigorous stirring for 4 h at 80°C. The exchanged clay was filtered and washed with distilled water until no bromide ion was detected with 0.1 N AgNO_3 solution. It was then dried in a vacuum oven and kept until use.

Preparation of PHBV/clay hybrids

Nanocomposites were prepared by solution intercalation. Solution intercalation was accomplished by adding clay powders to 1% g/mL chloroform solution of PHBV to a final polymer/silicate weight ratio of 100:3 (OMMT3) and 100:10 (OMMT10), respectively. The resulting dispersions were dispersed via ultrasonication for 3 h and allowed to age for 4 days with occasional shaking, then heated for 1 h at 60°C. Nanocomposites were prepared by drying resulting suspension on a glass slide. Samples were dried under vacuum at 40°C for 2 days.

Tensile properties

Tensile properties were recorded with Testometric at a crosshead speed of 5 mm/min using films of 20 mm long and 4 mm width. The tensile properties of each sample were determined from an average of at least five tests.

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

TABLE I
Mechanical Properties of Clay/PHBV Nanocomposites with Various Organophilic Clay Contents

Clay/PHBV (wt/wt)	Tensile strength (MPa)	Strain at break (%)	Modulus (MPa)
0/100	26.9	4.1	1373
3/100	35.6	3.9	1412
10/100	21.8	2.1	1375

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 8–10 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, $\alpha(t)$:

$$\alpha(t) = \frac{X(t)}{X(t_\infty)} = \frac{\int_0^t \frac{dH(t)}{d(t)} dt}{\int_0^{t_\infty} \frac{dH(t)}{d(t)} dt} \quad (1)$$

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:

$$X(t) = \frac{\int_0^t \frac{dH(t)}{d(t)} dt}{(1 - \phi)H_f^0} \quad (2)$$

A random copolymer of 3-hydroxybutyrate (HB) and where $\Delta H = 1.85 \times 10^8$ J/m³ is the heat of fusion for 100% crystalline PHB and ϕ is the weight fraction of the filler in the composites.

RESULTS AND DISCUSSION

Tensile properties of PHBV/clay nanocomposite films

The influence of the clay content on the mechanical properties of the nanocomposites was shown in Table I. With the incorporation of 3 wt % clay, the tensile strength of hybrid increased to 35.6 MPa, which is

about 32% higher than that of the original PHBV, and the tensile modulus was also increased. This behavior can be attributed to the high tensile strength of the silicate layers of clay dispersed in PHBV matrix. When the clay content exceeds 3 wt %, both the tensile strength and the strain at break were decreased. These decreases may be caused by the aggregation of clay, which leads to the loss of the feature of a nanometer composite. The addition of 3 wt % clay not only increased the mechanical property of PHBV but also the crystallization. The following mainly discuss the effect of organophilic clay on the crystallization behavior of PHBV with a differential scanning calorimeter (DSC).

The equilibrium melting temperature of PHBV

Isothermal crystallization from the melt of pure PHBV and PHBV with organophilic clay produces a material exhibiting double melting endotherms on heating as measured by DSC. 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 organophilic clay, the higher the melting point T_{m1} . The melting temperature T_{m2} is independent of the organophilic clay, perhaps because it resulted from the melting of reorganized crystals during the heating of the samples. To evaluate the equilibrium melting temperature, one has to decide which peak temperature corresponds to the crystals formed during 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 1 for all samples, including pure PHBV and PHBV with organophilic clay. 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 186°C, drawn from the intersection of the experimental line with line $T_m = T_c$ shown in Figure 1. This result is in agreement with that of Saghir.¹¹ The thickening factor, γ , is calculated

from the slope of the line in Figure 1 according to the following equation:¹²

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

Because curvature is inherent in the exact form of eq. (3) if γ 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 γ .

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. Because 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

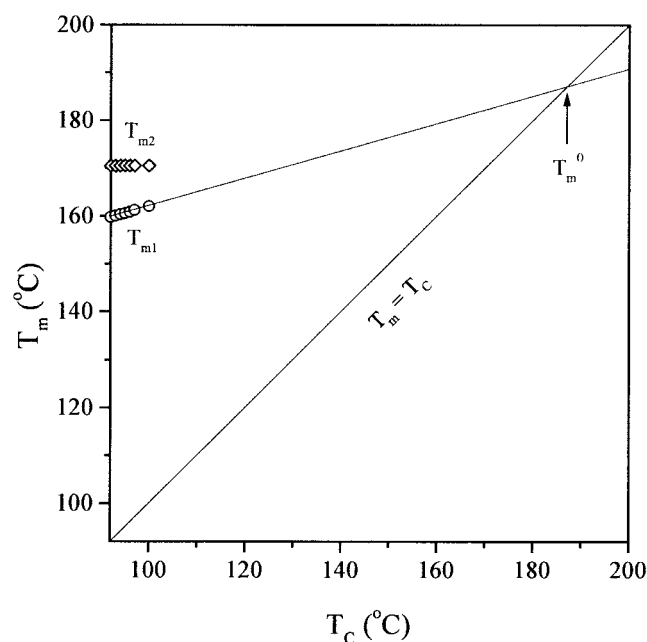


Figure 1 The plot of T_m as a function of T_c for neat PHBV and PHBV with organophilic clay.

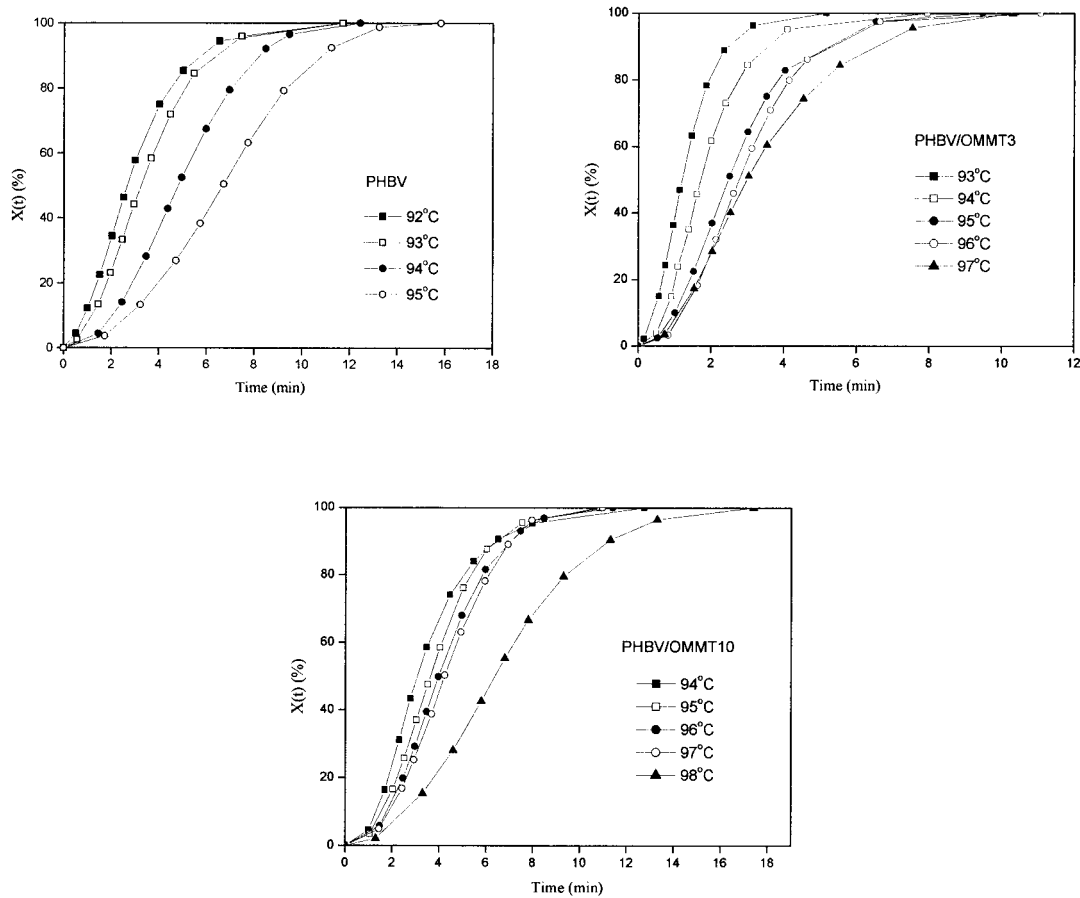


Figure 2 The plots of relative degree of crystallinity of PHBVs as a function of crystallization time under isothermal conditions.

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:¹³

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

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 ~ 0.7 , indicating that other factors not to be considered in the formulation of the theory, such as secondary crystallization, exert influences. The plots of relative degree of crystallinity of PHBVs as a function of crystallization time was shown in Figure 2, and the parameters measured in our study for pure PHBV and PHBV containing the organophilic clay were shown in Table II and Figure 3.

From a qualitative point of view, it can be observed that the addition of organophilic clay into PHBV increases the rate of formation of crystalline phase. This effect can be concluded readily from Table II, where

TABLE II
The Effect of Organophilic Clay on the Crystallization Parameters of PHBV

Sample	T_c (°C)	n	$Z(\text{min}^{-1})$	$Kg(K^2) \times 10^{-5}$	$\sigma_c(\text{J/m}^2)$
PHBV	92	1.9	0.096	18.6	0.11
	93	2.0	0.065		
	94	2.2	0.022		
	95	2.2	0.011		
PHBV/OMMT3	93	2.4	0.50	9.3	0.054
	94	2.6	0.19		
	95	2.5	0.092		
	96	2.5	0.054		
	97	2.7	0.033		
PHBV/OMMT10	94	2.4	0.049	11.7	0.068
	95	2.3	0.037		
	96	2.3	0.029		
	97	2.3	0.025		
	98	2.2	0.011		

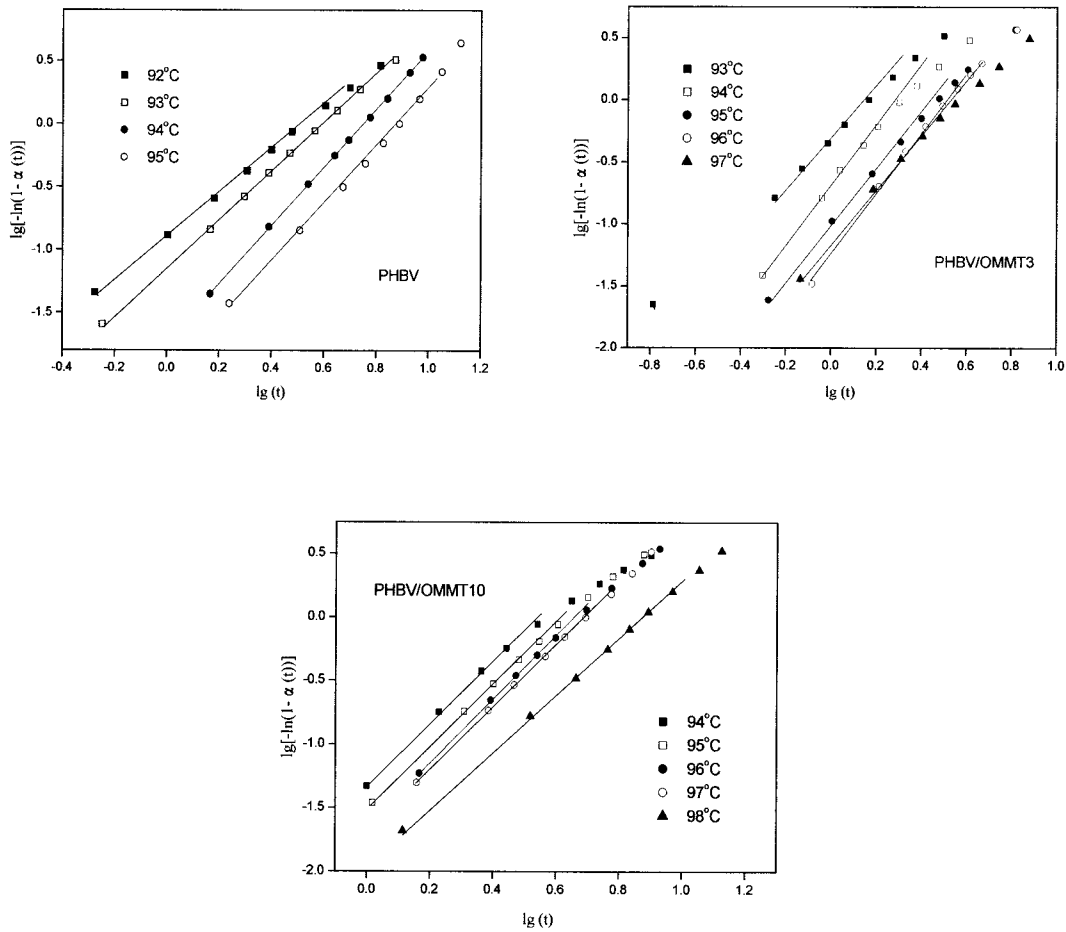


Figure 3 The plots of $\log[-\ln(1 - X(t))]$ as a function of $\log(t)$ for PHBV and PHBV added organophilic clay.

the apparent overall rate constant Z as a function of temperature is shown for organophilic clay. The results clearly indicate that incorporation of the organophilic clay enhances the crystallization rate of PHBV and the small amount of clay is more effective than large one.

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:^{14,15}

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

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 equation¹⁶ commonly used to describe the linear growth kinetics reads as follows:

$$G = \phi_2 G_0 \exp\left[\frac{-U}{R(C_2 + T_c - T_g)}\right] \exp\left[-\frac{rb_0\sigma\sigma_e T_m^0}{(kf\Delta H_{mm}^0 T_c \Delta T)}\right] \exp\left[\frac{2\sigma T_m^0 \ln\phi_2}{b_0 f \Delta H_m^0 \Delta T}\right] \quad (6)$$

where ϕ_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 $f = 2T_c/(T_m^0 + T_c)$. σ and σ_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.¹⁷ 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 $\Delta T = T_m^0 - T_c$.

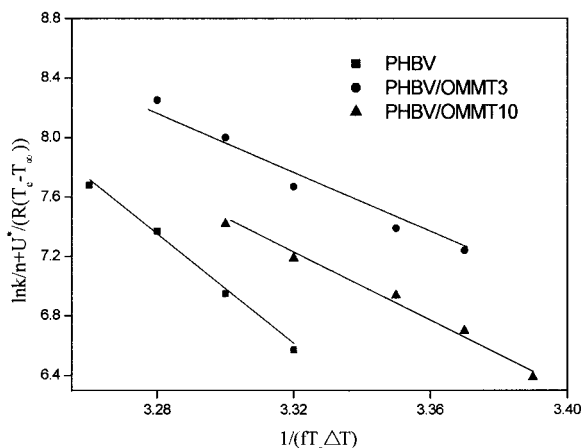


Figure 4 The plots of kinetic data according to eq. (7).

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

$$\begin{aligned} \alpha &= \ln(Z)/n + U/R(C_2 + T_c - T_g) \\ &\quad - (1 + 2\sigma T_m^0/b_0 f \Delta H_m^0 \Delta T) \ln \phi_2 \\ &= \ln G_0 - rb_0 \sigma \sigma_c T_m^0 / (kf \Delta H_m^0 T_c \Delta T) \quad (7) \end{aligned}$$

The straight lines with slopes, K_g , related to the surface energies of the lamellar crystals were obtained by plotting α as a function of $1/fT_c\Delta T$. The results are shown in Figure 4 for pure PHBV and PHBV with organophilic clay. The parameters n and Z in eq. (7) have been evaluated from the preceding Avrami analysis and $U^* = 10.25$ kJ and $C_2 = 51.6^\circ\text{C}$ have been taken from the literature.^{18,19} 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 calculated²⁰ from the average dimensions of the orthorhombic unit cell [$a = 0.576$ nm, $b = 1.320$ nm, c (fiber axis) = 0.595 nm, space group $p2_12_12_1$] of PHBV in the temperature range of interest. The experimental data in Figure 4 obey eq. (7) for all samples, regardless of the presence of organophilic clay or not.

To determine the kinetic value of the end surface energy and its dependence on the nucleating agents, the lateral surface free energy, σ , has to be estimated first. The fold surface free energy can then be calculated by the Thomas-Staveley equation:²¹

$$\sigma = \beta \Delta H_m^0 A_0^{1/2} \quad (8)$$

where A_0 is the cross-sectional area of a chain of PHB crystal, and β is a constant that is 0.24 for polyesters and 0.1 for polyolefins, according to Marand and Hoffman.²² The value of $\beta = 0.24$ is suitable for PHBV because PHBV is a polyester. From the accepted unit

cell dimensions of PHB, $\sigma = 2.8 \times 10^{-2}$ J/m² was calculated.

From the slopes of the straight lines, K_g , in Figure 4, 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 $\sim 60^\circ\text{C}$, σ_c were obtained for neat PHBV and PHBV with added the organophilic clay, 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 organophilic clay in the copolymer. However, when the content of organophilic clay is larger than 3 wt %, it is noted that the crystallinity decreases with increasing content of clay. Thus, it can be said that a small amount of clay in the blend accelerates the crystallization of PHBV, while a large clay content delays it.²³ The overall isothermal crystallization rate is thought to be governed by two terms, namely, diffusion and nucleation. The diffusion term is related to the activation free energy for transporting a polymer segment to a growing crystal face, and the nucleation term is related to the thermodynamic driving force for nucleation of new layers on the crystal. Considering these two terms, a small amount of clay seemed to serve as a nucleating agent, whereas a large amount of it seemed to hinder the transportation of polymer segments. Accordingly, we found that the clay has two opposing effects on the crystallization of PHBV, and further, that these effects are dependent on the clay content.

CONCLUSIONS

The organophilic clay used in this study enhanced the crystallization rate and improved the perfection of the PHBV crystals. The equilibrium melting temperature of PHBV is 186°C . The free energy for PHBV crystals formed during isothermal crystallization from melt decreased by adding nucleating agents to the copolymer. The tensile properties of composites were improved by incorporation of 3 wt % clay. The nucleation effect of the organophilic clay and the tensile properties of composites decreases with the increase of clay content.

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