Effect of Poly(propylene carbonate) on the Crystallization and Melting Behavior of Poly(*β*-hydroxybutyrate-*co*-*β*-hydroxyvalerate)

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ABSTRACT: The crystallization and melting behavior of poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate) (PHBV) and a 30/70 (w/w) PHBV/poly(propylene carbonate) (PPC) blend was investigated with differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR). The transesterification reaction between PHBV and PPC was detected in the melt-blending process. The interaction between the two macromolecules was confirmed by means of FTIR analysis. During the crystallization process from the melt, the crystallization temperature of the PHBV/PPC blend decreased about 8°C, the melting temperature was depressed by 4°C, and the degree of crystallinity of PHBV in the blend decreased about 9.4%; this was calculated through a comparison of the DSC heating traces for the blend and pure PHBV. These results indicated that imperfect crystals of PHBV formed, crystallization was inhibited, and the crystallization ability of PHBV was weakened in the blend. The equilibrium melting temperatures of PHBV and the 30/70 PHBV/PPC blend isothermally crystallized were 187.1 and 179°C, respectively. The isothermal crystallization kinetics were also studied. The fold surface free energy of the developing crystals of PHBV isothermally crystallized from the melt decreased; however, a depression in the relative degree of crystallization, a reduction of the linear growth rate of the spherulites, and decreases in the equilibrium melting temperature and crystallization capability of PHBV were detected with the addition of PPC. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2514–2521, 2004

Key words: biodegradable; biopolymers; blends; crystallization; differential scanning calorimetry (DSC); melt

INTRODUCTION

Poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate) (PHBV) is a thermoplastic aliphatic polyester produced by bacterial fermentation with renewable natural materials such as starch. PHBV is potentially useful in biomedical materials, and it is an attractive route to environmental waste management and can replace conventional polymers when recovery for recycling or incineration is difficulty or not cost-effective. When the content of β-hydroxyvalerate (HV) is relatively low (<12 mol %), PHBV is a brittle macromolecular material with an elongation at break of about 6%. Under tensile conditions, it cannot create necking and cannot flow. There are many reasons for the brittleness of PHBV. Because of its high purity, PHBV has a comparatively low crystallization nucleation density, and secondary crystallization of the amorphous phase can take place at the ambient temperature during storage. The solidification process tightly constrains the amorphous chains between the crystals, and this makes the material brittle. Because of the high degree of crystallinity and slow crystallization rate, large spherulites form easily, with circular breaks around the center and cracks in the radial direction of the spherulites. The glass-transition temperature (T_g) of PHBV is close to room temperature. These factors are responsible for the brittleness of PHBV.[1]

Three kinds of methods have been reported for improving the toughness of PHBV. First, by the incorporation of nucleating agents, the nucleation density is increased, the size of the spherulites is reduced, and the crystallization rate is increased.[2,3] Second, fast cooling during the processing of the material reduces the degree of crystallinity and the size of the spherulites. However, the method is not desirable: because T_g of pure PHBV is about 6°C, secondary crystallization takes place during storage at the ambient temperature, and PHBV forms into large spherulites. Third, PHBV can be blended with other polymers.[1–3] Researchers have recently focused on blends of PHBV with other polymers. A large number of studies have been carried out, and well-reviewed publications are also available.[4] Marchessault et al.[5] reviewed the structure and properties of PHBV in search applications. Recently, Ha and Cho,[4] Avella and coworkers,[6–9] Scandola et al.,[10] Pearce and Marchessault,[11] Iannace et al.,[12] Dave et al.,[13] Gassner and Own,[14] and Cyras et

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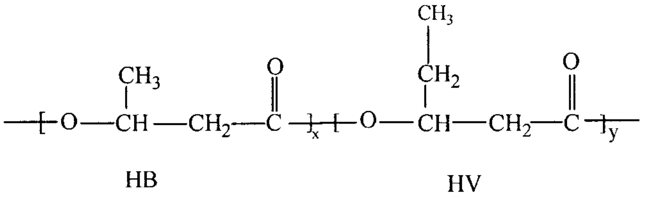


$$-\left[O-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}\right]_x\left[O-\overset{\overset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_2}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}\right]_y-$$

Scheme 1 Molecular structure of PHBV.

al.[15] reviewed the miscibility, morphology, mechanical behavior, and other prominent characteristics of a representative number of blends and composites of poly(β-hydroxybutyrate) (PHB) and PHBV. Unfortunately, most blends of PHBV have not been successful.[2] The immiscibility of PHBV with most polymers does not permit excellent mixtures. Usually, compatibilizers are ineffective in improving the brittleness of PHBV in blends of PHBV if they cannot inhibit the crystallization of PHBV.[16] Scandola et al.[17] concluded that poly(methyl methacrylate-*g*-β-hydroxybutyrate) [P(MMA-*g*-HB)] is not able to prevent PHB crystallization and that ternary PHB/poly(methyl methacrylate) (PMMA)/P(MMA-*g*-HB) blends remain crystalline and brittle. No compatibilizing effect on PHB/PMMA blends with PHB contents higher than 50% has been observed with various amounts of the P(MMA-*g*-HB) copolymer. However, the copolymer has a beneficial effect on the mechanical properties of PHB/PMMA blends with 30–50% PHB; they show a remarkable increase in ductility. The main effect of copolymer addition is the inhibition of PHB crystallization. To improve the performance, achieve a high elongation at break, and attain a high degree of flexibility, depressing the degree of crystallinity, reducing the size of the spherulites, and distorting the perfection of the crystals through the blending of PHBV with other polymers are necessary because the brittleness of PHBV is largely due to the presence of large crystallites in the form of spherulites, which form upon cooling from the melt.[18]

The aim of this work is to develop a new blend of PHBV with poly(propylene carbonate) (PPC).

PPC is an aliphatic polycarbonate, whereas PHBV is an aliphatic polyester; the transesterification reaction takes place between the two components during the melt-blending process. Furthermore, the carboxylic end groups of PPC and the hydroxy end groups of PHBV react with one another. An evident influence on the crystallization and morphology is created in the blend, and the performance of PHBV is enhanced. The lower cost of PPC, the stronger interaction between the two macromolecules, and the biodegradation of the blend make applications in environmentally friendly packaging possible.

The crystallization, melting behavior, and isothermal crystallization kinetics of the blend were investigated. A remarkable effect of PPC on the crystallization and melting behavior of PHBV was detected. A quantitative evaluation of the crystallization parameters was conducted.

EXPERIMENTAL

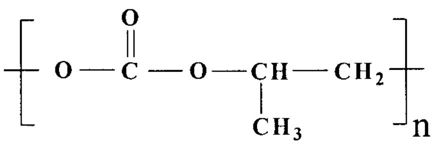
Materials

A random copolymer of β-hydroxybutyrate (HB) and HV, PHBV with nucleation agents, was provided by Tianan Biologic Material Co., Ltd. (Ningbo, China). The molecular structure of the copolymer is shown in Scheme 1. The content of HV in the copolymer was 4.5 mol %, as measured by ^{1}H-NMR. The weight-average molecular weight (M_w) of the copolymer was 1.25×10^5, and the molecular weight distribution index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] was 1.12, as measured by gas permeation chromatography (GPC). The purified sample was treated in a vacuum oven for 24 h at 80°C, sealed, and stored for use at room temperature.

PPC was synthesized through the copolymerization of carbon dioxide (CO_2) with propylene oxide (PO) in an autoclave equipped with a mechanical stirrer in the presence of an $Nd(CCl_3COO)_3$-based ternary catalyst showing catalytic activity as high as 6500 g/mol of Nd/h. The detailed process has been described previously.[19] The material was supplied by the synthesis group in our institute, purified and refined, and end-capped with maleic anhydride (MA). Before it was used, the copolymer was dried *in vacuo* for 24 h at room temperature and sealed for use. The molecular structure is shown in Scheme 2. M_w was 3.12×10^5, and M_w/M_n was 5.30, as measured by GPC; the alternative copolymerization ratio of CO_2 and PO was 98.6%.

Blend preparation

The blend of PHBV and PPC was prepared by melt blending. Because of the cost effect, PHBV and PPC in a weight ratio of 30:70 were blended in a Brabender instrument (Germany) operating at 175°C at a rotation speed of 50 rpm for 8 min, cooled in an air atmosphere, and put into a desiccator for further use. Pure PHBV was subjected to the same procedure for comparison.



$$\left[O-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2\right]_n$$

Scheme 2 Molecular structure of PPC.

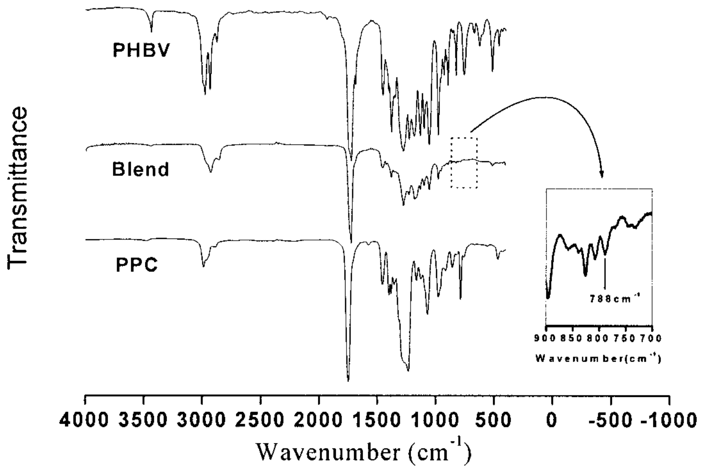


Figure 1 FTIR spectra of PHBV, PPC, and a 30/70 (w/w) PHBV/PPC blend.

Analysis of the properties

Fourier transform infrared (FTIR) characterization

The structural characterizations of PHBV and the PHBV/PPC blend were determined with an FTS-135 FTIR spectroscope (Bio-Rad, Cambridge, MA). Acetone is a good solvent for PPC but a nonsolvent for PHBV. The PHBV/PPC blend was extracted with acetone for 7 days, and the residue was dried and dissolved in chloroform to prepare the solution for examination.

Differential scanning calorimetry (DSC) characterization

A PerkinElmer DSC-7 instrument (New York) was used to study the crystallization and melting behavior of PHBV and the blend. The instrument was calibrated with an indium standard, and the measurement was conducted under a nitrogen atmosphere. The sample weight used in the DSC pan was kept within 6–8 mg.

The samples were first heated to 190°C at a rate of 40°C/min and then were maintained there for 5 min to destroy all memory of the previous thermal and mechanical histories. They were cooled to room temperature at a rate of 20°C/min and then heated to 200°C at a rate of 20°C/min. The crystallization temperature (T_c) and melting temperature (T_m) were determined from the thermal curves.

In the experiments performed to study the kinetics of isothermal crystallization as a function of the blend and temperature, the samples were heated from 50 to 190°C at a heating rate of 40°C/min, held at 190°C for 5 min, and then cooled to the appropriate T_c. The rate of heat flow generated during the development of the crystalline phase was recorded up to the vanishing thermal effect and was analyzed according to the usual procedure to determine the relative degree of crystallinity [$\alpha(t)$]:

$$\alpha(t) = X(t)/X(\infty) = \int_{t_0}^{t} (dH/dt)\, dt \Big/ \int_{t_0}^{t_\infty} (dH/dt)\, dt \tag{1}$$

where t_0 represents the time at which the sample attains isothermal conditions, as indicated by a flat baseline after the initial spike in the thermal curve, and t_∞ is the time at which the crystallization of the samples is complete.

The absolute degree of crystallinity [$X(t)$] of the samples was evaluated from the heat evolved during crystallization by the following relationship:

$$X(t) = \left[\int_{t0}^{t} (dH/dt)\, dt \right] \Big/ (1 - \Phi)\Delta H_f^0 \tag{2}$$

where ΔH_f^o is the heat of fusion for 100% crystalline PHB (164 J/g) and Φ is the weight fraction of PPC in the blend system.

RESULTS AND DISCUSSION

FTIR characterization

Figure 1 presents the FTIR spectra of the pure PHBV, pure PPC, and PHBV/PPC blend extracted with acetone. The C—O absorbance band at 1737 cm^{-1} of pure PHBV corresponds to the normalized peak, which is insensitive to the composition of PHBV. The considered bands were the C—O—C bonds (1279, 1228, and 1184 cm^{-1}) and the C═O bonds (1723 and 1737 cm^{-1}). By means of FTIR spectra, the crystallinity index (CI) was calculated. The band at 1278 cm^{-1} is characteristic of the crystalline state, and the band at 1723 cm^{-1} corresponds to the ester carbonyl group absorbance, whereas the higher frequency of 1737 cm^{-1} at its side, exhibiting a weaker shoulder peak, corresponds to the amorphous state. The amorphous band is broader than the corresponding one for the crystalline state, reflecting an increase in the conformational freedom. The band at 1380 cm^{-1} corresponds to the stretching of $-CH_3$, which is insensitive to the composition and degree of crystallinity, so it is often chosen as a normalized peak. According to the results of Bloembergen et al.,[20] the CI value of PHBV was calculated to be 0.96, in agreement with that obtained by Bloembergen et al., whereas the corresponding value of the blend is 0.58, which indicates that the incorporation of PPC reduces the degree of crystallinity of PHBV.

The characteristic absorptions bands of PPC are at 1747 (C═O), 1234 (C—O), and 788 cm^{-1}.

Figure 1 shows that the ester carbonyl characterization absorptions for the blend are shifted to 1725 cm^{-1} and narrowed in comparison with neat PHBV, and nearby a weaker shoulder peak reflects the amorphous peak of pure PHBV and the PPC-*g*-PHBV graft copolymer. The band at 788 cm^{-1}, which is the normalized and characteristic peak of PPC, still exhibits a weaker absorption in the blend extracted in acetone. Transesterification (i.e., intermolecular ester–carbonate exchange reactions) between PHBV and PPC takes place during the melt-blending process. The band at 3436 cm^{-1}, resulting from the end hydroxy group absorption of PHBV, disappears in the blend, and this is strong evidence of interactions between the PHBV and PPC macromolecules. Scanning electron microscopy analyses (not shown) show that in this blend PPC serves as a continuous phase, and the dispersed phase is PHBV. Most of the phase domains are 1.4–2.8 μm, and the broken interfaces show plasticity.

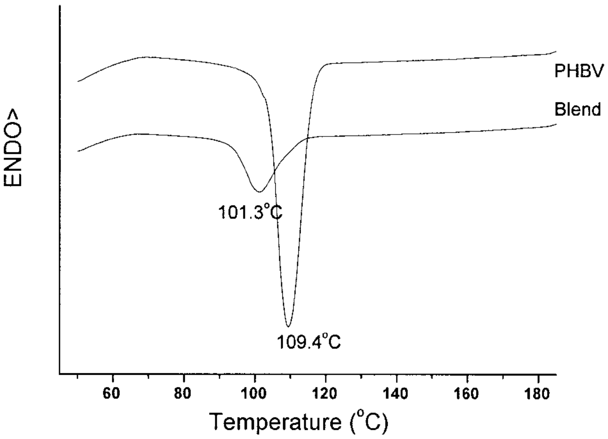


Figure 2 DSC traces of PHBV and a PHBV/PPC blend crystallized from the melt at a cooling rate of 20°C/min.

TABLE I
Effect of PPC on the Crystallization Behavior of PHBV

Sample	PPC (wt %)	T_c (°C)	T_{onset} (°C)	ΔW (°C)	ΔH_c (J/g)	$S_1 = \tan \alpha$
Neat PHBV	None	109.4	116.1	1.0	−76.0	7.9
PHBV/PPC blend	70	101.3	110.7	1.4	−18.1	2.7

ΔH_c = enthalpy of crystallization, which can also be obtained from thermal curves of quenched samples at a heat rate of 20°C/min.

Effect of PPC on the melt and crystallization behavior of PHBV

Figure 2 shows the effects of PPC on the melt and crystallization behavior of PHBV. The parameters of the crystallization process are shown in Table I. At the peak temperature of the crystallization exotherm (T_c), the value of the heat flow is maximum. The initial slope of the exotherm (S_1), which is the slope at inflexion on the high-temperature side of the exotherm, is related to the nucleation rate. $T_{c_{(onset)}}$ is the temperature at the intercept of the tangents at the baseline and the high-temperature side of the exotherm. The width at half-height of the exotherm peak (ΔW) is determined after the normalization of the peak to a constant sample mass. T_c is a function of the cooling rate and is a measure of the supercooling. $T_{c_{(onset)}}$ may have significance similar to that of T_c, except that their interrelationship is inherently dependent on the parameter, which may differ from sample to sample. S_1 is defined as the nucleation rate. The parameter $T_{c(onset)} - T_c$ is a measure of the overall rate of crystallization. The smaller $T_{c_{(onset)}} - T_c$ is, the greater the rate of crystallization is. The smaller ΔW is, the narrower the size distribution of the crystallites is.[21]

The results show that the onset-of-crystallization temperature [T_{onset}(°C)] decreases nearly 6°C, and T_c of the blend decreases 8°C, in comparison with pure PHBV. These results indicate that the crystallization of PHBV becomes more difficult and that the potential energy required for crystallization increases; therefore, the incorporation of PPC hinders the crystallization process of pure PHBV.

It is clear that the value of $T_{onset} - T_c$ for pure PHBV is lower than that for the blend, and this further indicates that pure PHBV exhibits a higher rate of crystallization. According to the polymer crystallization theory, the smaller $T_{onset} - T_c$ is, the greater the rate of crystallization is. With the addition of 70% PPC, the value of the blend decreases 2.8°C in comparison with pure PHBV. PPC reduces the crystallization rate and increases the steric hindrance for the regular fold of PHBV molecular chains.

In general, the observed crystallization rate depression results mainly from (1) a reduction of the driving

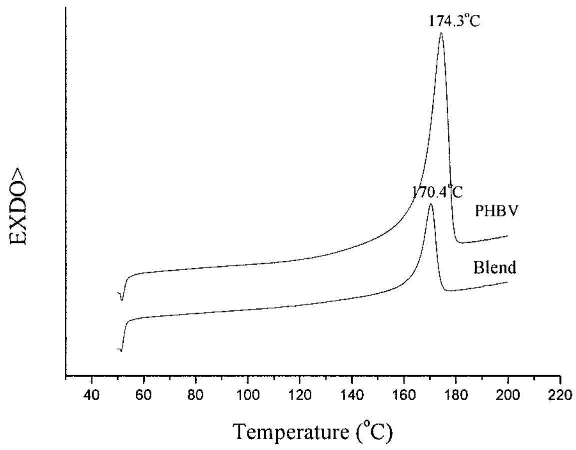


Figure 3 Effect of PPC on the melting behavior of PHBV at a heating rate of 20°C/min.

force for crystallization due to the changes in the equilibrium melting point, (2) a dilution effect that diminishes the formation of a critical nucleus on the front of the growing spherulites, and (3) entropic factors that produce an increase in the energy related to the formation of a nucleus of a critical size.[21]

It is also confirmed in Table I that S_1 of pure PHBV is greater than that of the blend, and this implies that pure PHBV has a greater nucleation rate. Hence, the crystallite size distribution of pure PHBV should be smaller than that of the blend. The analysis agrees with the calculated value of ΔW. PPC may reduce the nucleation and crystallization rates of PHBV and, therefore, lead to an increase in the crystallite size distribution. With polarizing optical microscopy (not shown), two types of break have been found in pure PHBV spherulites: circular breaks around the center and splitting. PHBV forms large, individual spherulites, which depend on the lower nucleation density, but the blend has small, irregular, fine spherulites. The incorporation of PPC evidently changes the crystallization and nucleation behavior of PHBV.

The effect of PPC on the melting behavior of PHBV is shown in Figure 3. The melting peaks can be detected for pure PHBV and the blend in the DSC heating scanning traces. Table II shows that T_m of the blend decreases by 4°C. The perfection of the crystals in the blend decreases, and the lamellar thickness of the crystals seems to be smaller. Reductions of the degree of crystallinity of PHBV and the blend can be observed. They are 54.5 and 45.6% for neat PHBV and the blend, respectively. Usually, as a nucleating agent, the second component would enhance the crystallization of a crystallizable polymer; therefore, PPC would have a positive effect on the crystallization of PHBV according to the polymer nucleation theory. However, the factors that influence the crystallization and melting behavior of PHBV in the blend are complicated. Many factors can retard the crystallization of PHBV in the blend. The apparent effect is controlled by competition among these factors. There are many negative effective factors due to the addition of PPC in the blend that retard the crystallization of PHBV. Besides dilution, transesterification and interaction between two macromolecules, as mentioned previously, hinder the crystallization of PHBV, reduce the crystallization rate of PHBV, increase the number of imperfect crystals, and weaken the crystallization ability of PHBV. As PPC end-capped with MA is an aliphatic polycarbonate with carboxylic end group, whereas PHBV is an aliphatic polyester with hydroxy groups, the hydrogen bond between the two macromolecules would increase their interaction.

The presence of a second component in a crystallizable polymer can lead to relevant modifications of the crystallization, both at the microscopic and molecular level, that affect the process of the structure and morphology formation and the properties of the material. The most important results are connected to the segregation of noncrystallizable chains, the melting point depression of the semicrystalline polymer, the promotion of one polymorph with respect to the others, and the effect on the nucleation density and radial growth rate. From a qualitative point of view, the behavior of a crystallizing blend is rather satisfactory; however, for the prediction of the physical properties of solid materials from a detailed definition of the microstructure and macrostructure, the mechanisms and kinetics of morphology and crystallization are required.

According to polymer crystallization theories, it can be concluded that the incorporation of the second components would cause the following effects on the pure polymer. First, there is the nucleation effect. The second component may increase the crystallization rate and nucleation capability of the original polymer, improve the perfection of the pure PHBV crystallites, and enhance the lamellar thickness. The greater the nucleation effect is of the second component, the higher T_m is of the blend. Second, there is the hindrance effect. The second components added may have a certain miscibility with the pure polymer, and interactions between the two macromolecules will reduce the crystallization rate of the overall material, hinder its crystallization, increase the potential energy

TABLE II
Melting Behavior of PHBV and a PHBV/PPC (30/70) Blend

Sample	PPC (wt %)	T_m (°C)	ΔH_f (J/g)	$X(t_\infty)$ (%)
Neat PHBV	None	174.30	89.41	57.1
Blend	70	170.38	22.45	47.6

ΔH_f = apparent enthalpy of fusion.

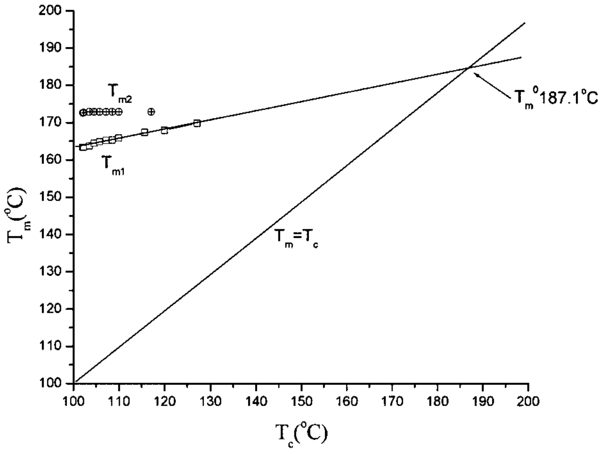


Figure 4 T_m as a function of T_c for neat PHBV.

required and the supercooling degree, affect the regularity of the molecular chain, and widen the crystallite size distribution. Third, there is the dilution effect. The second components added to the crystallizable polymer may be elected as plasticizers, which would cause a reduction of the crystallization behavior and crystallization rate of the crystallizable polymer.

In this blend, PPC hinders the crystallization of PHBV. This may result from the interactions between the two macromolecules as PPC is blended with PHBV under high-speed-mixing and shear conditions. Because of the remarkable effect of PPC on the crystallization of PHBV, the elongation at break of the blend increases to 70%; it is 6 and 13.7% for neat PHBV and PPC, respectively. The energies absorbed by the samples during elongation are 51, 450, and 795 mJ for neat PPC, neat PHBV, and the blend, respectively. These results show that pure PPC has lower values than the PPC/PHBV blend (70/30 w/w), and this demonstrates that the coordination effect exists in the reactive blend. The low tensile toughness of neat PHBV can be related essentially to the large size of the spherulites with cracks and splits. These spherulites with cracks act as gross material defects, causing the premature rupture of the specimen at the beginning of yielding. However, in the PHBV/PPC blend, spherulite size reduction and the depression of the degree of crystallinity, caused by transesterification and interactions between two macromolecules, seem to lead to the improvement of the mechanical properties of the blend.

Equilibrium melting temperature (T_m^0) of PHBV and the PHBV/PPC blend

T_m of the isothermal crystallization samples may be determined by means of DSC, from which T_m^0 can be further drawn. The T_m^0 values of PHBV and the PHBV/PPC blend are 187.1 and 179.0°C, respectively, as shown in Figure 4 for neat PHBV. To avoid the overlapping of points, we have omitted the blend data. The depression of T_m^0 can be strong evidence of strong interactions between the two macromolecules.

Crystallization kinetics

The crystallization kinetics in blends are complex phenomena that encompass several processes: the production of primary nuclei, the formation and spreading of two-dimensional surface nuclei, and the interdiffusion of crystallizable and noncrystallizable chains at the advancing front of the growing crystallization. These processes are affected to different degrees by the thermodynamic conditions under which crystallization takes place, by the molecular characteristics of the components, and by the strength of their mutual interaction. The radial growth rate of the 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. The relative degree of crystallinity achieved at time t [$X(t)$] under isothermal conditions is given by the Avrami equation:

$$X(t) = 1 - \exp(-Zt^n)$$
$$\log\{-\ln[1-X(t)]\} = n \log t + \log Z \tag{3}$$

where n is an index related to the dimensionality of growth and to the way in which primary nuclei are formed and Z is the overall rate constant containing both nucleation and growth contributions. Equation (3) can enable us to evaluate n and Z from the slope and the intercept, respectively. The parameters n and Z for pure PHBV and the PHBV/PPC blend are given in Table III. The half-time ($t_{1/2}$) for crystallization can be determined by the equation $t_{1/2} = (\ln 2/Z)^{1/n}$. Z for the blend is smaller by one order of magnitude at the same T_c in comparison with that for pure PHBV. Plots

TABLE III
Effect of PPC on the Crystallization Parameters of PHBVs

Sample	T_c (°C)	n	Z (min^{-1})	$t_{1/2}$	$K_g \times 10^5$ (k^2)	σ_e (J/m^2)
Neat PHBV	116	2.84	1.16	0.84		
	118	2.89	0.60	1.05		
	120	3.50	0.26	1.32	9.59	0.066
	122	3.52	0.14	1.59		
	124	3.69	0.05	2.07		
PHBV/PPC (30/70)	112	3.39	0.46	1.13		
	114	3.16	0.25	1.38		
	116	3.07	0.15	1.65	6.17	0.056
	118	3.07	0.08	2.02		
	120	3.06	0.03	2.79		

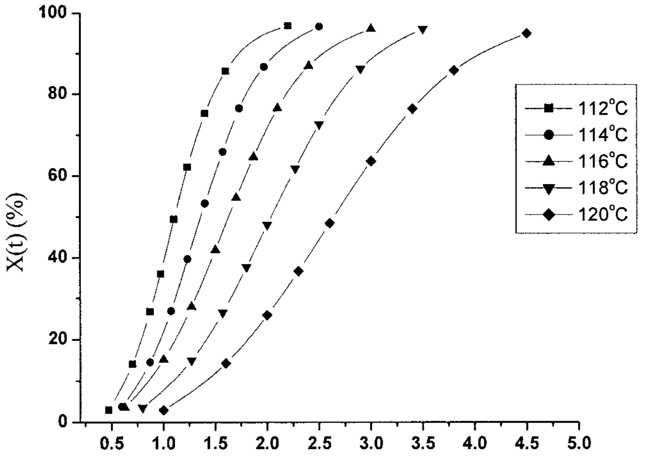


Figure 5 $X(t)$ of a PHBV/PPC blend as a function of the crystallization time under isothermal conditions.

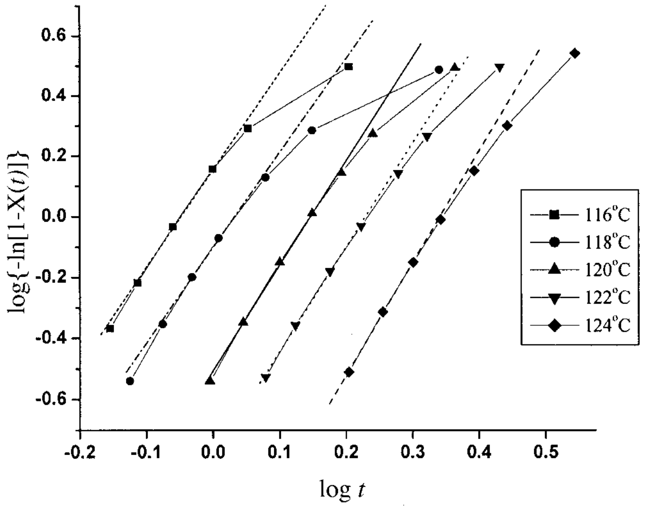


Figure 7 $\log\{-\ln[1 - X(t)]\}$ versus $\log t$ for isothermally crystallized PHBV/PPC at different T_c's.

of the relative crystallinity degree of the PHBV/PPC blend and PHBV as a function of the crystallization time under isothermal conditions are shown in Figures 5 and 6, respectively.

With eq. (3), plots of $\log\{-\ln[1 - X(t)]\}$ versus $\log t$ are shown in Figures 7 and 8. Each curve has a linear portion followed by a derivation at a longer time. The linearity, maintained from the initial stages of crystallization until a high degree of relative conversion, indicates that the Avrami equation correctly describes the crystallization process of PHBV and the PHBV/PPC blend. Moreover, the linear portions are almost parallel, and this implies that the nucleation mechanisms and crystal growth geometries are similar. The deviation at the end portion is considered to be the result of the secondary crystallization, which is caused by spherulite impingement of the crystal perfection.

According to the nucleation theories, the linear growth rate (G) is related to n and Z expressed in the following simple relation:

$$G \propto Z^{1/n} \tag{4}$$

The theory of surface nucleation can be used to account for the effect of the second component on the spherulites developing in pure PHBV. The following equation can describe the linear growth kinetics:[22]

$$\begin{aligned}\alpha = \ln Z/n + U^*/R[C_2 + T_c - T_g] \\ - [1 + 2\sigma T_m^0/b_0 f \Delta H_m^0 \Delta T] \ln \Phi_2 \\ = \ln G_0 - r b_0 \sigma \sigma_e T_m^0/[k f \Delta H_m^0 T_c \Delta T]\end{aligned} \tag{5}$$

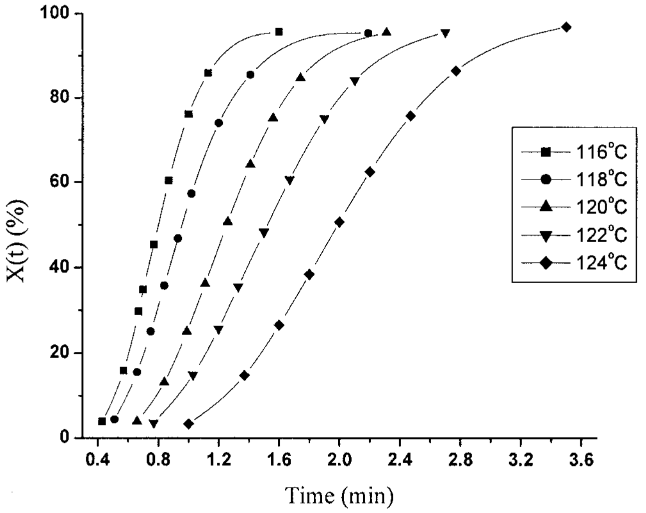


Figure 6 $X(t)$ of PHBV as a function of the crystallization time under isothermal conditions.

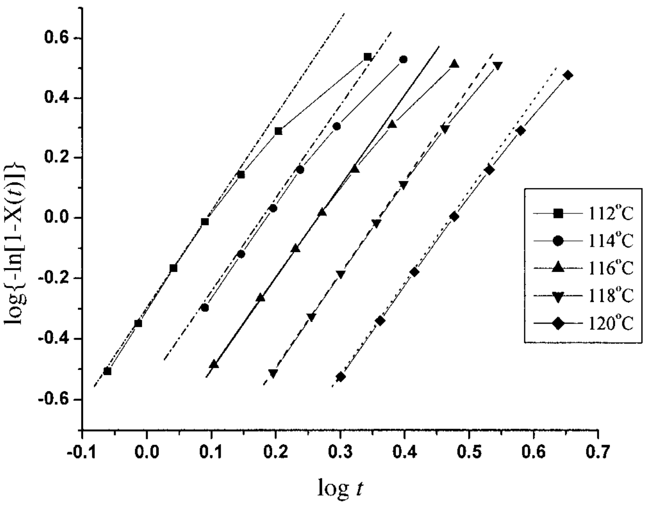


Figure 8 $\log\{-\ln[1 - X(t)]\}$ versus $\log t$ for an isothermally crystallized 30/70 PHBV/PPC blend at different T_c's.

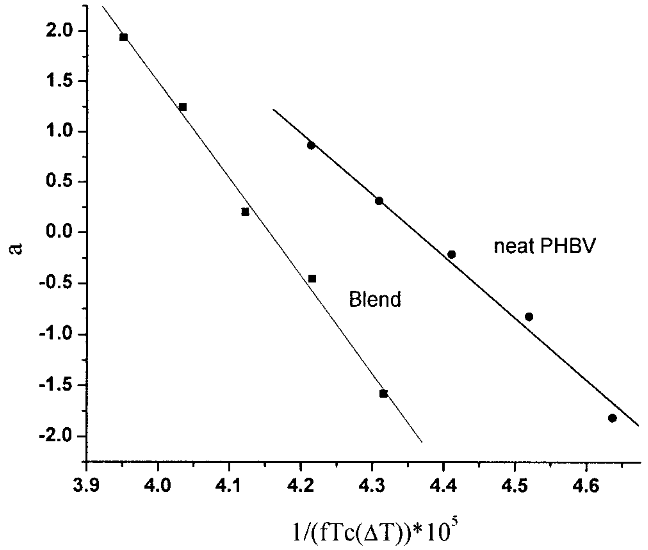


Figure 9 Kinetic data according to eq. (5) for PHBV and a 30/70 PHBV/PPC blend.

where $f = 2T_c/(T_m^0 + T_c)$ is a correction factor for the temperature dependence of the enthalpy of fusion; U^* is the activation energy for the transport of segments to the crystal front through the subcooled melt; and σ and σ_e are the lateral and fold surface free energies of the developing crystals, respectively. The former parameter, $\sigma = 2.8 \times 10^{-2}$J/m^2, was obtained from our previous work.[3] In our previous work, C_2 is a constant usually assumed to be 51.6°C, b_0 is the layer thickness, and the parameter r is related to the characteristic of the growth regime: $r = 4$ in regimes I and III and $r = 2$ in regimes II and III are fit for our studies. The undercooling degree is $\Delta T = T_m^0 - T_c$. For PHBV, T_g is 6°C, T_m^0 is 187.1°C, and U^* is 10.25 kJ; b_0 was calculated from the average dimensions of the orthorhombic unit cell [a = 0.576 nm, b = 1.320 nm, c (fiber axis) = 0.595 nm, and space group = $p2_12_12_1$] of PHBV in the temperature range of interest.

Plots of α versus $1/[fT_c(\Delta T)]$ are shown in Figure 9; calculated from the slopes of the straight lines, K_g is 9.59×10^5 and 6.17×10^5 for PHBV and the blend, respectively. From the values of K_g, the σ_e values for PHBV and PHBV/PPC blend have been calculated. These results are listed in Table III. The free energy for the formed PHBV crystals decreases with the incorporation of PPC. The nucleating effect of PPC has been confirmed.

CONCLUSIONS

1. PHBV and PPC undergo a certain degree of transesterification during the melt-blending process, and a certain interaction has been observed between the two macromolecules.
2. During the crystallization process from the melt, T_c of the PHBV/PPC blend decreases by 8°C in comparison with that for plain PHBV, and T_m decreases by 4°C. This indicates that the introduction of PPC reduces the perfection of crystals of PHBV, inhibits the crystallization of PHBV, and weakens its crystallization ability.
3. The T_m^0 values of PHBV and the PHBV/PPC blend (30/70) isothermally crystallized are 187.1 and 179°C, respectively.
4. σ_e of the developing crystals of PHBV isothermally crystallized from the melt decreases; however, the degree of crystallinity, the radial growth rate of spherulites, T_m^0, and the crystallization capability of PHBV decrease with the addition of PPC.

References

1. Hobbs, J. K.; McMaaster, T. J.; Miles, M. J.; Barham, P. J. Polymer 1996, 37, 3241.
2. El-Hadi, A.; Schnabel, R.; Straube, E.; Miller, G.; Henning, S. Polym Test 2002, 21, 665.
3. Liu, W. J.; Yang, H. L.; Wang, Z.; Dong, L. S.; Liu, J. J. J Appl Polym Sci 2002, 86, 2145.
4. Ha, C. S.; Cho, N. J. Prog Polym Sci 2002, 27, 759.
5. Marchessault, R. H.; Blunm, T. L.; Deslandes, Y.; Hamer, G. K.; Orts, W. J.; Sundararajan, P. R.; Taylor, M. G. Macromol Symp 1988, 19, 235.
6. Avella, M.; Martuscelli, E.; Raimo, M. J Mater Sci 2000, 35, 523.
7. Avella, M.; Errico, M. E. J Appl Polym Sci 2000, 77, 232.
8. Avella, M.; Errico, M. E.; Immirzi, B.; Malinconico, M.; Falcigno, L.; Paolillo, L. Macromol Chem Phys 1998, 199, 1901.
9. Avella, M.; Errico, M. E.; Rimedio, R.; Sadocco, P. J Appl Polym Sci 2002, 83, 1432.
10. Scandola, M.; Focarete, M. L.; Adamus, G.; Sikorska, W.; Baranowska, I.; Swierczek, S.; Gnatowski, M.; Kowalczuk, M.; Jedlinski, Z. Macromolecules 1997, 30, 2568.
11. Pearce, R. P.; Marchessault, R. H. Macromolecules 1994, 27, 3869.
12. Iannace, S.; Amreoaio, L.; Huang, J.; Nicolais, L. J Appl Polym Sci 1994, 54, 1525.
13. Dave, P. B.; Ashar, N. J.; Gross, R. A.; McCarthy, S. P. Polym Prepr 1990, 31, 442.
14. Gassner, F.; Owen, A. J. Polym Int 1996, 39, 215.
15. Cyras, V. P.; Fernandez, N. G.; Vazquez, A. Polym Int 1999, 48, 705.
16. Scandola, M.; Ceccorulli, G.; Pizzoli, G. Macromolecules 1992, 25, 6441.
17. Ceccorulli, G.; Scandola, M.; Adamas, G. J Polym Sci Part B: Polym Phys 2002, 40, 1390.
18. Barham, P. J.; Keller, A. J Polym Sci Part B: Polym Phys 1986, 24, 69.
19. Liu, B. Y.; Zhao, X. J.; Wang, X. H.; Wang, F. S. J Polym Sci Part A: Polym Chem 2001, 39, 2751.
20. Bloembergen, S.; Holden, D. A.; Humer, G. K.; Bluhm, T. L.; Marchessault, R. H. Macromolecules 1986, 19, 2865.
21. An, Y. X.; Dong, L. S.; Li, G.; Mo, Z. S.; Feng, Z. L. J Polym Sci Part B: Polym Phys 2000, 38, 1860.
22. Alfonse, G. C.; Chiappa, V.; Liu, J. J.; Sadiku, E. R. Eur Polym J 1991, 27, 795.