

Control and Development of Crystallinity and Morphology in Poly(β -hydroxybutyrate-co- β -hydroxyvalerate)/Poly(propylene carbonate) Blends

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ABSTRACT: Two different methodologies (reactive blending and mechanical blending) for preparing blends of poly(β -hydroxybutyrate-co- β -hydroxyvalerate) (PHBV) and poly(propylene carbonate) (PPC) were used. The miscibility, chemical structure, thermal behavior, crystallinity, morphology, and mechanical properties of the blends were investigated with Fourier transform infrared spectroscopy, differential scanning calorimetry, polarized optical microscopy, scanning electron microscopy, and tensile tests. A certain extent of hydrogen-bonding interactions between PHBV and PPC took place in the

blends. The graft copolymerization was confirmed in the reactive system. The incorporation of PPC hampered the crystallization process of PHBV and evidently altered the morphology, and the effect was enhanced in the reactive blend. The mechanical properties of PHBV could be changed by 1–2 orders of magnitude by blending modification. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1427–1436, 2005

Key words: biodegradable; blends; crystallization; morphology; reactive processing

INTRODUCTION

Macroscopic properties for polymer blends are strongly affected by their miscibility and microstructure, especially by the allocation of different phases and their level of dispersion and adhesion between the components. In immiscible mechanical blends, the arrangement of the phases is remarkably controlled by the crystallization conditions,¹ and the improvement of mechanical properties has been hampered by the poor interfacial adhesion between the matrix and the dispersed phase. During reactive blending, various chemical reactions such as transesterification, grafting reactions, depolymerization, and repolymerization can occur. Therefore, the interaction between the two phases should be introduced to promote the interfacial adhesion either by the introduction of a preformed compatibilizing agent during blending or by the induction, under appropriate conditions, of reactions between the functional groups of the two incompatible polymers to obtain the formation *in situ* of an interfacial agent.² Thus, through the control of the chemical reactions and blending conditions, the de-

sired mechanical properties and morphological structure of blends can be achieved.

Poly(β -hydroxybutyrate-co- β -hydroxyvalerate) (PHBV) is an optically active thermoplastic aliphatic polyester with high stereoregularity. As an intracellular storage material for carbon and energy, it is produced via a biosynthesis technique by bacterial fermentation with renewable natural materials such as starch. Such a special biological origin results in the absence of any residual contaminating catalysts, which favors its potential use in biomedical materials and in environmental waste management, possibly replacing conventional polymers when recovery for recycling or incineration is difficult or not cost-effective.

However, its prohibitive cost, its narrow processability window, and especially its low impact resistance at room temperature, resulting from its very high crystallinity, hinder its larger commercial applications.

There are many reasons for the brittleness of PHBV. First, because of its high purity and comparatively low crystallization nucleation density, crystallization on rapid cooling in a mold develops at comparatively low temperatures and is followed by secondary crystallization of the amorphous phase at the ambient temperature during storage.^{3,4} Second, the detrimental physical aging process seriously leads to embrittlement as the degree of crystallinity (X_c) increases logarithmi-

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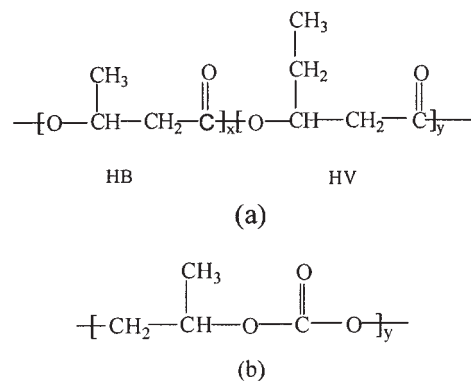
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cally with the storage time; this process tightly constrains the amorphous chains between the crystals by the amorphous-crystalline interface, and there is a corresponding increase in the yield stress and decrease in the impact strength.³⁻⁶ Third, the glass-transition temperature is close to room temperature.⁷ Fourth, large spherulites form easily, with circular breaks around the center and cracks in the radial direction of the spherulites.⁸⁻¹⁰ These factors are responsible for the brittleness breaks of PHBV.

To improve the toughness of PHBV, three kinds of methods have been reported in the literature: the incorporation of nucleating agents,^{9,11} fast cooling during processing, and blending with other polymers. However, the former two methods are not desirable.⁹⁻¹¹ Extensive research has been conducted on blends of PHBV with other polymers recently, and well-reviewed literature is also available.^{1,12-27} Unfortunately, most blends of PHBV are not successful.⁹ The immiscibility of PHBV with most polymers does not permit excellent mixtures. Usually, the compatibilizers are ineffective at improving the brittleness of PHBV in blends of PHBV if they cannot inhibit the crystallization of PHBV.²⁸ Scandola et al.²⁹ concluded that poly[(methyl methacrylate)-*graft*-poly(β -hydroxybutyrate)] [P(MMA-*g*-HB)] is not able to prevent poly(hydroxybutyrate) (PHB) crystallization, and ternary PHB/poly(methyl methacrylate) (PMMA)/P(MMA-*g*-HB) blends remain crystalline and brittle. No compatibilizing effect on PHB/PMMA blends with PHB concentrations higher than 50% has been observed with various amounts of P(MMA-*g*-HB) copolymer. On the other hand, the copolymer has a beneficial effect on the mechanical properties of PHB/PMMA blends with 30–50% PHB, which show a remarkable increase in ductility. The main effect of copolymer addition is the inhibition of PHB crystallization. To improve the performance, achieve high elongation at break, and attain a high degree of flexibility, it is necessary to reduce X_c , reduce the size of the spherulites, and distort the perfection of crystals through the blending of PHBV with other polymers because the brittleness of PHBV is largely due to the presence of large crystallinities in the form of spherulites, which form upon cooling from the melt.⁸

The aim of this work is to develop nonreactive and reactive blends of PHBV with poly(propylene carbonate) (PPC) and to manufacture materials with high performance through the control of the crystallinity and morphology in the PHBV/PPC blends.

Inoue et al.^{30,31} were the first to produce PPC by the copolymerization of carbon dioxide (CO₂) and propylene oxide (PO) in the presence of a diethyl zinc/water complex catalytic system. PPC is low-cost and has good mechanical properties. Moreover, its carboxyl end-capped groups may easily cause special interactions with other components in blends, and its strong polar carbonate group may result in a transesterification reaction, improving the compatibility of



Scheme 1 (a) Structure of PHBV and (b) structure of PPC.

blend systems. Especially through the control of the blending conditions, the *in situ* formation of copolyesters with block or graft chain structures as compatibilizers can be produced, and the miscibility of blends of polyesters can be enhanced.

In this study, the chemical structure, thermal properties, morphological structure, and mechanical properties of PHBV/PPC blends were investigated. The crystallinities and morphologies of blends of PHBV/PPC were controlled and developed by changes in the blend compositions and reactive conditions.

EXPERIMENTAL

Materials

PHBV with nucleation agents was kindly provided by Tianan Biologic Material Co., Ltd. (Ningbo, China). The concentration of hydroxyvalerate (HV) in the copolymer was 4.5 mol %, as measured by proton nuclear magnetic resonance (¹H-NMR) spectroscopy. The weight-average molecular weight (M_w) and the polydispersity index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of the copolymer, determined by gas permeation chromatography (GPC), were 1.25×10^5 and 1.12, respectively.

PPC was synthesized by the copolymerization of CO₂ with PO in an autoclave equipped with a mechanical stirrer in the presence of an Nd(CCl₃COO)₃-based ternary catalyst showing catalytic activity as high as 6500 g/mol of Nd/h. The detailed process was described previously.³² The material was supplied by the synthesis group in our institute, purified and refined, and end-capped with maleic anhydride. M_w and M_w/M_n , measured by GPC, were 3.12×10^5 and 5.30, respectively. The alternative copolymerization ratio of CO₂ to PO was 98.6%. Glycidyl methacrylate (GMA) monomer and dicumyl peroxide (DCP) were used as received in grafting reactions.

The structures of PHBV and PPC are shown in Scheme 1.

Preparation of the PHBV/PPC blends

Two compositions of PHBV/PPC mechanical blends, 30/70 (w/w) and 70/30 (w/w), were prepared in a Brabender instrument operating at 175°C at a rotation speed of 50 rpm for 5 min, were cooled in an air atmosphere, and were put into a desiccator for further use. In the 30/70 (w/w) PHBV/PPC reactive blend, PHBV, premixed with GMA (1 wt %) monomer and DCP (0.2 wt %) as reactive catalysts, was first melted in the Brabender instrument mixing machine (Germany) at the same temperature and rotation speed for 2 min; then, 70 wt % PPC was introduced into the reactor on the molten polymer, thermally stabilized for another 2 min, kept at room temperature, and put into the desiccator for further use. For comparison, pure PHBV was subjected to the same procedure, and a solution blend was prepared by the dissolution of PHBV and PPC with a weight ratio of 30/70 in chloroform at room temperature [3.0% (w/v) solution] for at least a day, casting onto a glass plate, evaporation of the solvent overnight, and drying in an oven at 30°C *in vacuo* for 7 days to remove the residual solvent.

Fourier transform infrared (FTIR) spectra

Infrared measurements were carried out with a Bio-Rad (Cambridge, MA) FTS-135 spectrometer. All FTIR spectra were baseline-corrected and recorded for each sample at a resolution of 4 cm⁻¹ with an accumulation of 16 scans. Thin films of PHBV/PPC blends with weight ratios of 100/0, 70/30, 30/70, and 0/100 and 30/70 (w/w) PHBV/PPC solution and reactive blends were cast from solutions in CHCl₃ and dried at room temperature for examination. The complete removal of CHCl₃ was confirmed by FTIR.

To confirm the reaction between the two components in the reactive system, the 30/70 PHBV/PPC reactive blend was Soxhlet-extracted with acetone for at least 24 h, and the residue was dried and prepared for examination.

Differential scanning calorimetry (DSC)

The crystallization and melting behavior of PHBV, a 70/30 PHBV/PPC mechanical blend, and PHBV/PPC mechanical and reactive blends with the same composition of 30/70 were conducted on a PerkinElmer (New York) DSC-7 apparatus; the temperature scale was calibrated with a high-purity indium standard, and a nitrogen atmosphere was used throughout the study.

The samples, sealed in aluminum pans, were preliminarily heated to 190°C at a rate of 20°C/min and then were maintained at that temperature for 5 min to remove the effects of any previous thermal and mechanical histories; this was followed by cooling to

room temperature at a rate of 20°C/min. Then, they were reheated to 200°C at a rate of 20°C/min. The crystallization temperature (T_c), melting temperature (T_m), apparent melting enthalpy (ΔH_f), and enthalpy of crystallization (ΔH_c) were determined from the thermal curves. T_m and ΔH_f were taken as the peak temperature and the area of the melting endotherm, respectively, whereas T_c and ΔH_c were registered as the temperature and area of the main respective exothermal peak. X_c of the PHBV phase was calculated by

$$X_c(\text{PHBV}) = \Delta H_{f(\text{PHBV})} / \Delta H_{\text{PHBV}}^0 \quad (1)$$

$$X_c = \Delta H_{f(\text{blends})} / w \Delta H_{\text{PHBV}}^0$$

where ΔH_{PHBV}^0 is the enthalpy of melting per gram of 100% crystalline (perfect crystal) (146 J/g); $\Delta H_{f(\text{PHBV})}$ and $\Delta H_{f(\text{blends})}$ are defined as the measured enthalpies of melting for PHBV and blends, respectively; and w is the weight ratio of PHBV in the blend.

Spherulitic morphology

The spherulitic morphologies of PHBV and the blends were observed with a Leica DML polarized optical microscope (Leica Mikroskopie und Systeme GmbH, Wetzlar, Germany) equipped with an Opton hot stage. We studied the isothermal crystallization behavior by heating the samples on the hot stage at 40°C/min to 190°C, holding them at this temperature for 5 min, and then rapidly quenching them to a desired isothermal crystallization temperature (100°C) and allowing them to crystallize isothermally for an appropriate time (10 min). The morphology of the spherulites was monitored and recorded under crossed polars.

Environmental scanning electron microscope field emission GUN scanning electron microscopy (ESEM)

ESEM was performed with an instrument operating at an accelerating voltage of 20 kV to examine the phase structure on the cryogenically fractured surfaces of specimens of PHBV/PPC blends with weight ratios of 70/30 and 30/70 and a reactive blend (30/70). The fractured samples were prepared by the freeze fracturing of the central part of the dumbbell in liquid nitrogen until they broke. Before observation, the treated samples were coated with a thin layer of gold with a polaron sputtering apparatus.

Mechanical tensile properties

Uniaxial tensile tests were performed at room temperature with an Instron 1121 testing machine (Canton, MA). The measurements were conducted at a cross-head speed of 10 mm/min. At least three runs for each film of PHBV and 30/70 (w/w) PHBV/PPC mechan-

ical and reactive blends were measured and averaged as results. The tensile modulus, yield stress, stress at break, elongation at break, and energies absorbed were determined from the stress-strain curves.

RESULTS AND DISCUSSION

Preparation methodology of the blends and their FTIR spectra

The method of fabrication and the morphology of the blends formed during mixing play critical roles in determining their properties. In this study, the PHBV/PPC blends were prepared by two methodologies: mechanical and reactive blending. In general, the reactive blending methodology generates strong interactions (covalent bonds and ionic bonds) between two incompatible polymers to improve the miscibility and to promote the interfacial adhesion of two immiscible polymers; thus, a positive effect on the final properties of the blends is created. Suitably choosing reactive groups in the components of blends to generate block or graft copolymers is widely used in immiscible polymer blends. These copolymers formed *in situ* during mixing can preferentially extend into their respective homopolymer phases as compatibilizers for controlling the morphology, phase structure, and interfacial adhesion between the phases to obtain an optimized product. PHBV is characterized by the presence of hydroxyl end groups as proton donors that constitute the sites of potential chemical interactions with the carboxyl end groups of PPC as proton acceptors. Generally, the chemical interaction is limited to a few percent of the polymer chains, and this is sufficient to allow good compatibilization between the two polymers. In particular, the chemical interaction between PPC and PHBV during the blending was induced by the thermal decomposition of organic peroxide. FTIR was used to examine the possible interaction between PHBV and PPC qualitatively.

In the hydroxyl vibration regions presented in Figure 1, the absorption peak in pure PHBV is strong and sharp at 3436 cm^{-1} , whereas for PPC, a much weaker and broader band centered at a higher frequency (3478 cm^{-1}) appears. In the spectra of blends with the same weight ratio of 30/70, for the solution blend [Fig. 1(E)], relatively broad and still weak bands centered at 3436 and 3472 cm^{-1} shift to a lower frequency in comparison with that of PPC. For the mechanical one [Fig. 1(C)], the absorption band shifts to a higher frequency, exhibiting three broader and slightly stronger peaks at 3438 , 3474 , and 3569 cm^{-1} ; the former two peaks can be attributed to the characteristics of the respective polymers, whereas the third peak centered at 3569 cm^{-1} is indicative of a certain intermolecular hydrogen-bonding interaction involving the hydroxyl group of PHBV and the carboxyl group of PPC. However, the absorption bands of the reactive blending [Fig.

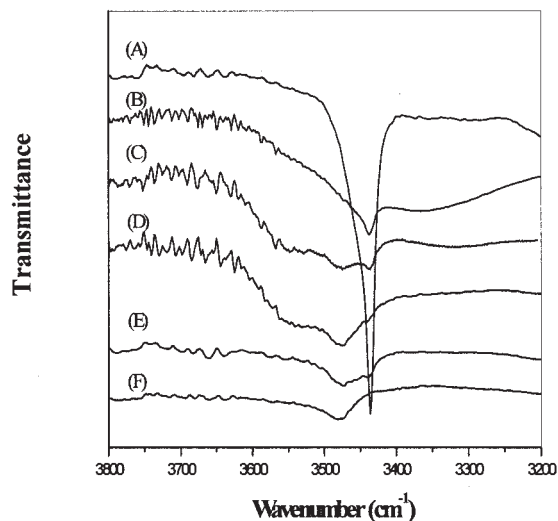


Figure 1 FTIR spectra of the PHBV/PPC blends in the hydroxyl region: (A) 100/0, (B) 70/30 mechanical blend, (C) 30/70 mechanical blend, (D) 30/70 reactive blend, (E) 30/70 solution blend, and (F) 0/100.

1(D)] are strengthened, broadened, and shifted to 3473 and 3565 cm^{-1} , and the characteristic band of PHBV disappears, whereas the characteristic absorption of PPC and the other assigned to the intermolecular hydrogen-bonding absorption peak between PHBV and PPC remains. Polymer-polymer miscibility generally requires specific interactions, such as hydrogen bonding, dipole-dipole interactions, polar interactions, or donor-acceptor interactions. If there exist specific interactions between the two components, the spectrum of the blends should be shifted.^{33,34} Thus, it is thought that the hydrogen bonds between the hydroxyl group of PHBV and the carboxyl group of PPC are responsible for the compatibility in the blend.

In the carbonyl vibration region, as shown in Figure 2, the spectrum of pure PHBV exhibits two bands: a relatively sharp one centered at 1723 cm^{-1} is attributed to PHBV in its preferred conformation (crystalline), and another, a small shoulder at 1737 cm^{-1} , is characteristic of the amorphous state. The amorphous band is characteristically broader than that of the crystalline band, and this reflects an increase in conformational freedom. For PPC, the band centered at 1747 cm^{-1} is characteristic of the carbonate group. The solution blend and the reactive blend present strong bands at 1746 cm^{-1} ; the width of the peak in the former [Fig. 2(E)] is broader than that of the latter [Fig. 2(D)], and a very weak band at 1723 cm^{-1} as a shoulder is slightly stronger in the solution blend. This indicates that at a PPC concentration of 70 wt %, reactive blending makes the system more homogeneous, and the majority of the PHBV component appears amorphous. Perhaps the specific interactions between the two polymers cause the change in the crystallization behavior of PHBV.

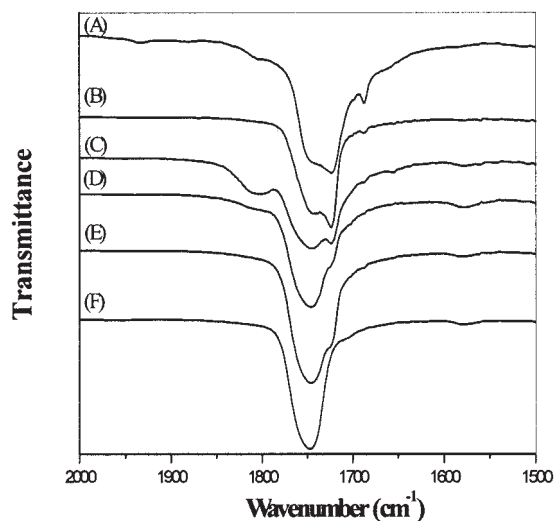


Figure 2 FTIR spectra of the PHBV/PPC blends in the carbonyl region: (A) 100/0, (B) 70/30 mechanical blend, (C) 30/70 mechanical blend, (D) 30/70 reactive blend, (E) 30/70 solution blend, and (F) 0/100.

Changes in the region ranging from 1000 to 1350 cm^{-1} can also be observed in the blends in comparison with the PPC and PHBV polymers (Fig. 3). The band at 1184 cm^{-1} , assigned to the oxygen adjacent to the carbonyl in PHBV, is more intense, and the bands at 1228 cm^{-1} are better defined in the amorphous state. In the crystalline state, the more intense band corresponds to the frequency of 1278 cm^{-1} . While the band at 1234 cm^{-1} corresponds to C—O stretching of PPC, that at 1184 cm^{-1} corresponds to the C—C vibration, and that at 1070 cm^{-1} corresponds to the asymmetrical vibration of C—O—C bonds. Upon blending, the spectrum of the mechanical blend [Fig. 3(C)] consists of two vibration bands centered at 1275 and 1232 cm^{-1} , which are attributed to the respective characteristic of the pure polymers. For the solution blend [Fig. 3(E)], a new weak band centered at 1263 cm^{-1} appears. For the reactive one, as shown in Figure 3(D), the crystalline bands of PHBV disappear, and only the characteristic of PPC could be detected. In the amorphous region, PHBV shows band vibrations at a lower frequency in different blends. The bands vary from 1184 to 1168 cm^{-1} in the reactive blend especially, and this indicates that the crystalline and amorphous regions of PHBV are significantly affected by the incorporation of PPC. On the other hand, the C—O—C vibration of PPC centered at 1070 cm^{-1} exhibits a higher frequency in the reactive blend than that of the other blends, and this is indicative of the strong interaction between the two macromolecules. The described changes are consistent with the results in the hydroxyl-stretching band region of the blends and the mechanism of interaction between the two polymers.

The compositions of the blends also have a significant effect on the chemical structure, as shown in

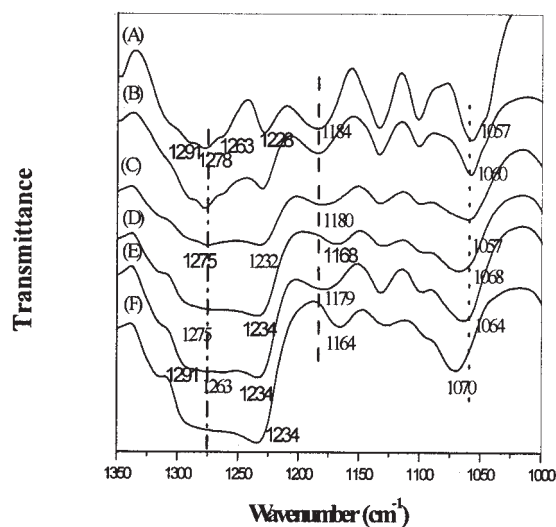


Figure 3 FTIR spectra of the PHBV/PPC blends in the region ranging from 1000 to 1350 cm^{-1} : (A) 100/0, (B) 70/30 mechanical blend, (C) 30/70 mechanical blend, (D) 30/70 reactive blend, (E) 30/70 solution blend, and (F) 0/100.

Figures 1–3. The interaction between the two macromolecules may result from physical factors, such as hydrogen bonds, and chemical reactions, such as grafting and transesterification.

To investigate the interaction between PHBV and PPC in the reactive blend, solution extraction was performed. Acetone is a good solvent for PPC but is a poor one for PHBV. If the graft copolymerization reaction takes place during blending, a small amount of PPC-g-PHBV in the residue may not dissolve in the acetone, and the characteristic peaks of PPC will appear in the FTIR spectra. As shown in Figure 4, the characteristic band for PPC centered at 800 cm^{-1} exists in the inset figure for PPC-g-PHBV. This is strong

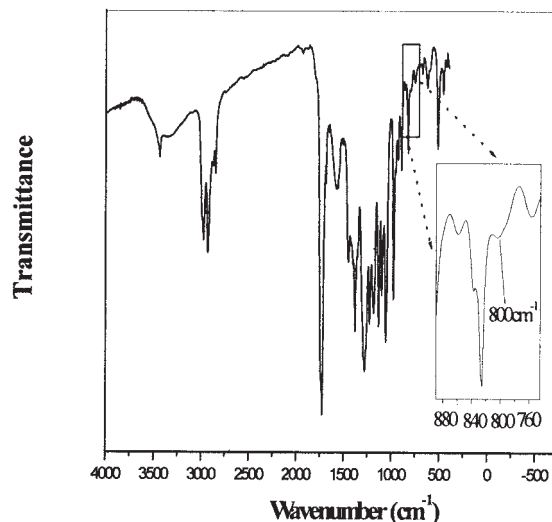


Figure 4 FTIR spectrum of the PHBV-g-PPC residue.

TABLE I
Thermal Properties of PHBV, and the 70/30 PHBV/PPC Blend, 30/70 PHBV/PPC Blend, and Reactive Blend

Sample	T_m (°C)	ΔH_f (J/g)	T_c (°C)	ΔH_c (J/g)	X_c (%)
Pure PHBV	174.3	89.4	109.4	-76.0	61.2
30/70 PHBV/PPC blend	170.4	22.4	101.3	-18.1	51.1
30/70 PHBV/PPC reactive blend	162.5	5.4	Not detected	—	12.3
70/30 PHBV/PPC blend	170.4	49.9	107.9	-44.6	48.8

evidence of a grafting reaction between PHBV and PPC. The copolymer of PHBV and PPC could affect the FTIR spectra mentioned previously for the reactive blend.

Thermal analysis of the PHBV/PPC blends

The thermal properties (T_c , T_m , and X_c) of PHBV and PHBV/PPC blends (mechanical and reactive) were investigated by DSC to determine the influence of the incorporation of PPC on the melting and crystallization behavior of PHBV. The results are listed in Table I. The melting peaks can be detected for pure PHBV and the blends in the DSC heating traces, as shown in Figure 5. T_m decreases by 4 and 12°C in the 30/70 PHBV/PPC mechanical and reactive blends, respectively, with respect to pure PHBV, and this indicates that the perfection of the crystals in the blends decreases, and the lamellar thickness of the crystals becomes smaller, especially in the reactive blend. The decrease in T_m of the crystals under the reactive conditions may result from the transesterification and/or grafting reaction between PPC and PHBV chains dur-

ing sample preparation at 175°C; PHBV-g-PPC copolymers are produced *in situ*. The copolymers act as compatibilizers to improve the miscibility and reduce chain mobility. The interaction between the two components in the blends restricts the regular fold of the macromolecular chain, and this results in the formation of the less perfect crystals of PHBV with lower T_m .

The effect of PPC on the crystallization behavior of PHBV is shown in Figure 6. T_c in the mechanical blend is depressed about 8°C, and for the reactive blend, the crystallization process cannot be detected. The depression of the crystallizability of PHBV in the blends can be observed in comparison with that in pure PHBV. These results indicate that the crystallization of PHBV becomes more difficult and that the potential energy required for crystallization increases in the blends; therefore, the incorporation of PPC hampers the crystallization process of PHBV.

X_c of PHBV and T_m in the reactive blend evidently decrease. They are 12.3% and 162.5°C versus 61.2% and 174.3°C for pure PHBV, respectively; this markedly broadens the processing window and reduces the depolymerization and degradation during processing, ensuring the high performance of PHBV blends.

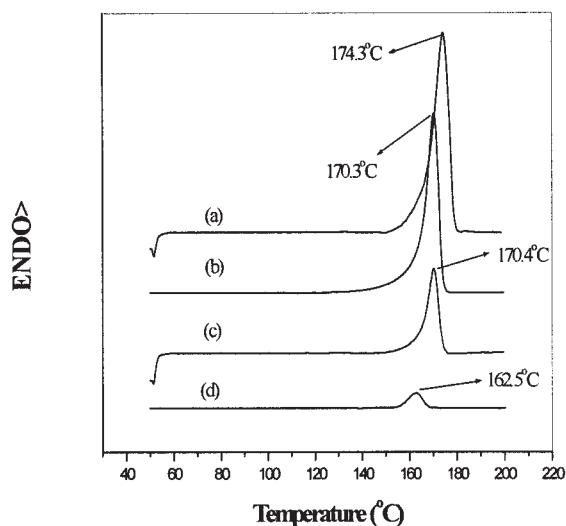


Figure 5 Effect of PPC on the melting behavior of PHBVs at a heating rate of 20°C/min: (a) pure PHBV, (b) 70/30 PHBV/PPC mechanical blend, (c) 30/70 PHBV/PPC mechanical blend, and (d) PHBV/PPC DCP-GMA reactive blend.

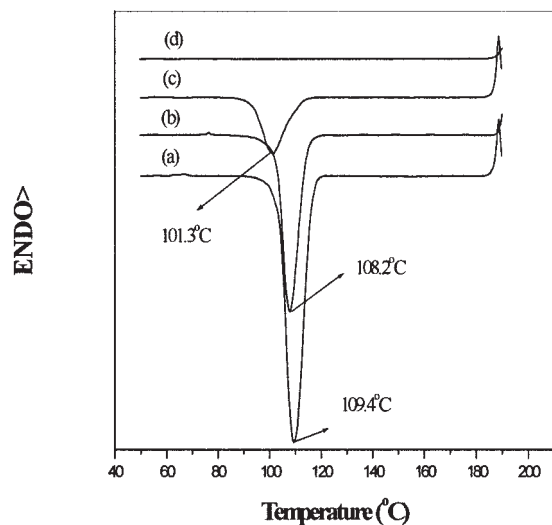


Figure 6 DSC traces of PHBV and PHBV/PPC blends crystallized from the melt: (a) pure PHBV, (b) 70/30 PHBV/PPC mechanical blend, (c) 30/70 PHBV/PPC mechanical blend, and (d) PHBV/PPC DCP-GMA reactive blend.

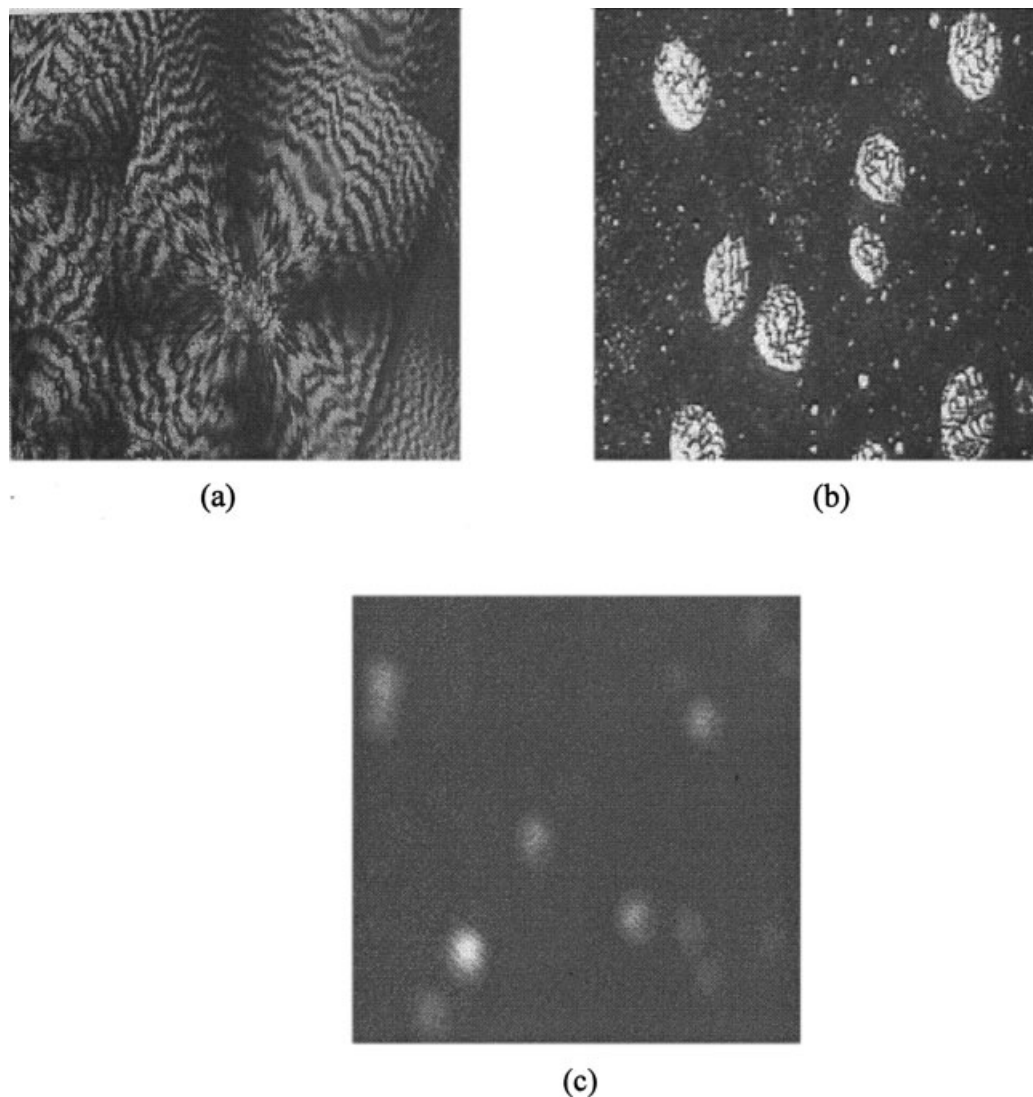


Figure 7 Polarized optical microscopy micrographs of pure PHBV and blends crystallized isothermally at 100°C ($\times 380$): (a) pure PHBV, (b) 30/70 PHBV/PPC blend, and (c) 30/70 PHBV/PPC reactive blend.

Spherulitic morphology

The crystallization behavior in PHBV/PPC blends has shown a depression in the spherulite radial growth and overall crystallization rates of the crystallizable component. Thus, a significant variation in the morphology of the blends has been observed.

Figure 7 shows the spherulites of pure PHBV and PHBV/PPC blends, as observed under crossed polarizers of an optical microscope at 100°C, crystallized isothermally from the melt for 10 min. A comparison of the spherulites of PHBV and a 30/70 PHBV/PPC blend shows that pure PHBV is completely filled with impinged spherulites and exhibits well-developed banded spherulites [Fig. 7(a)], displaying the familiar, smooth, and clear Maltese cross-birefringent pattern, exhibiting circular extinction bands, and forming large banded spherulites with diameters of several millime-

ters (up to 0.3 mm), whereas the spherulites of PHBV in the 30/70 PHBV/PPC sample suffer some morphological changes, as shown in Figure 7(b): the Maltese cross extinction patterns in the nonreactive blend are blurred and indiscernible, displaying noncircular spherulitic borders with less regularity of the contour, and no perfect rings are detected any more. The regularity of the banded spherulites of the original PHBV has disappeared and has been distorted significantly, and the spherulite size is reduced by 1 order of magnitude. These structures are due to the axis orientation or two-dimensional array of the lamellae, no longer in possession of the characteristic symmetric three-dimensional regularity. PHBV macromolecules in the blend cannot form a regular fold chain structure. Rich structural defects and noncrystallizable components exist in the accumulation of the lamellae, and X_c de-

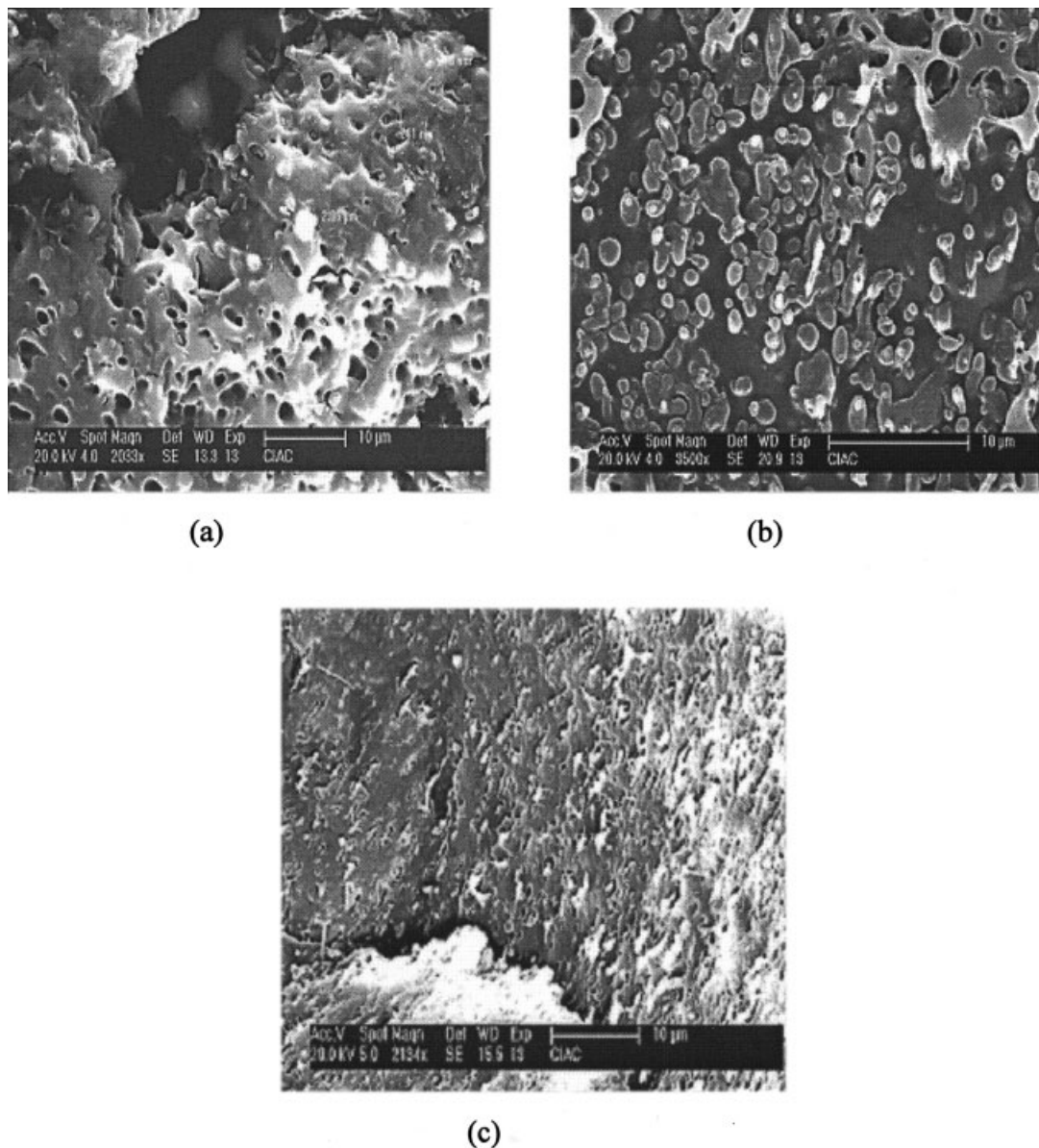


Figure 8 SEM micrographs of cryogenically fractured surfaces of the blends: (a) 70/30 PHBV/PPC blend, (b) 30/70 PHBV/PPC blend, and (c) 30/70 PHBV/PPC reactive blend.

creases remarkably. Despite partial phase separation, there are definite interactions between PHBV and PPC; otherwise, the spherulites would not be much altered by the addition of PPC.

In the 30/70 PHBV/PPC reactive blend, the spherulites exhibit the indistinguishable morphological structure presented in Figure 7(c). From the aforementioned DSC analysis, it can be concluded that X_c for PHBV in the reactive blend has dropped to about 12.3%. In the mechanical tests, the elongation at break increases from 4% for pure PHBV to 1300% for the reactive blend; it has been enhanced by 2 orders of magnitude with respect to pure PHBV. The reactive blend has become one kind of biodegradable macromolecular material with superior toughness. It may be

concluded that transesterification, graft copolymerization, and end-group polycondensation reactions occur during reactive melt blending between the hydroxyl end group of PHBV and the carboxyl end group of PPC. The obtained copolymer destroys the regularity for PHBV molecular chains and limits its crystallization behavior in the blend. PHBV is probably disturbed and repelled to the noncrystallizable domain or located in the surrounding supermolecular structure of developing spherulites.

Phase structure

The mechanical properties of immiscible blends are strongly dependent on their morphologies; therefore,

TABLE II
Mechanical Properties of PHBV and Its Blends

	Yield stress (MPa)	Stress at break (MPa)	Elongation at break (%)	Tensile modulus (MPa)	Energies absorbed (mJ)
Pure PHBV	38.2	38.2	4.0	1515	25.3
30/70 PHBV/PPC mechanical blend	17.7	9.7	74	1096	428
70/30 PHBV/PPC reactive blend	3.8	3.6	1300	66.6	4236

the control of the morphology of an immiscible polymer melt is of vital importance for the tailoring of the final properties of the product.

The morphological analyses were performed on the fractured surfaces of 30/70 PHBV/PPC blends (non-reactive and reactive) and a 70/30 PHBV/PPC blend by means of scanning electron microscopy (SEM). In the fractured surface of the 70/30 PHBV/PPC blend [Fig. 8(a)], black holes in the micrographs represent the PPC microdomains located in the PHBV matrix. PHBV acts as a continuous phase, whereas PPC acts as a dispersed phase, distributed as a spherical shape in the matrix, and most of the domains for the dispersed phase are less than 1 μm in size. In the 30/70 PHBV/PPC blend shown in Figure 8(b), PPC becomes a continuous phase, and the dispersed phase is PHBV distributed as a spherical shape. Most of the phase domains are 1.4–2.8 μm in diameter. There exists a clear two-phase structure in the blend; however, between the phase domains, no distinct interspaces exist, and this indicates that a certain interfacial adhesion remains between PHBV and PPC. In particular, the cryogenically fractured interfaces exhibit plasticity.

Figure 8(c) shows the fractured surfaces of the 30/70 PHBV/PPC reactive blend. Although the two-phase morphology still exists, the reactive blend forms the dispersed phase with rather small droplets. PHBV is well covered by the PPC matrix, and a fairly smooth fracture surface is evident; better interfacial adhesion generated by the compatibilizer can be deduced, giving rise to better final properties.

The SEM observations show that the reactive blend displays highly compatible features. The reactive approach used to prepare the blends allows a better interaction between the functional groups of PHBV and the reactive carboxyl group of the PPC chain, giving rise to the formation of a copolymer that can act as an emulsifying agent to reduce the coalescence effect in immiscible polymer blends by lowering the interfacial tension between the blend components, causing good stress transfer between the matrix and well-dispersed PHBV domains, and may lead to a well-dispersed morphology.

Mechanical properties

Improved mechanical properties might be obtained by the optimization of the blend morphology during pro-

cessing. The tensile properties for pure PHBV and 30/70 PHBV/PPC mechanical and reactive blends are summarized in Table II. A reduction in the tensile modulus and stress at break of PHBV by the addition of amorphous PPC was detected. On the other hand, the elongation at break of PHBV was enhanced. Pure PHBV is a brittle macromolecular material with an elongation at break of about 4%. Under tensile conditions, it cannot create necking and cannot flow. The elongation at break of the 30/70 PHBV/PPC reactive blend (1300%) is almost 325 times higher than that of pure PHBV (4.0%) and 18 times higher than that of the nonreactive blend (74%). The energies absorbed by the samples during elongation for the reactive blend are 4236 mJ, that is, 167 and 9.9 times those of pure PHBV (4.0 mJ) and the mechanical blend (74.0 mJ), respectively. The properties of PHBV can be changed by 1–2 orders of magnitude by blending modification. It has been confirmed that samples with low PHBV contents retain their ductile behavior, whereas composites with high contents of PHBV present the behavior of a rigid material. A series of new materials can be produced from brittle plastics to high-toughness elastomers by changes in the constituents of the blends and by the control of the reactive blending morphology.

The low tensile toughness of pure 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. Although the reduction of the spherulite size and the depression of X_c in the blends, caused by transesterification and interactions between two macromolecules, seem to lead to an improvement in the mechanical properties of PHBV, the tensile strength of the polymeric matrix deteriorates in the presence of the PPC phase for the nonreactive composite and is even inferior to that of the reactive type. PPC can probably act as a defect and stress concentration in the blends. These results can be justified by the good compatibilization reached between the two polymers by means of the reactive catalyst.

CONCLUSIONS

PHBV and PPC had a certain extent of reaction in different blending processes. The graft copolymeriza-

tion was confirmed in the reactive system. T_m of the nonreactive 30/70 PHBV/PPC blend and the reactive blend decreased by 4 and 12°C, respectively, in comparison with that of pure PHBV, because the PHBV/PPC copolymers were produced *in situ* during mixing and the miscibility of PHBV/PPC was improved in the reactive blend. T_c of the nonreactive blend decreased about 8°C, and for the reactive one, the crystallization process could not be detected. X_c of PHBV in the nonreactive and reactive blends decreased from 61.2% to 51.1 and 12.3%, respectively, and this indicated that the incorporation of PPC hampered the crystallization process of pure PHBV, even in the reactive blend. The spherulites of PHBV were irregular and distorted in the nonreactive blend, and the size of the crystallites was lowered, whereas in the reactive blend, the spherulites were difficult to distinguish. The SEM measurements revealed that a phase inversion occurred between the 30/70 PHBV/PPC blend and 70/30 PHBV/PPC blend. The cryogenically fractured interfaces exhibited plasticity, especially in the reactive blend. The mechanical properties varied considerably with the blend composition. The properties of PHBV could be changed by 1–2 orders of magnitude by blending modification. A series of new materials can be produced from brittle plastics to high-toughness elastomers by changes in the composition and by control of the reactive blending morphology.

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