

Miscibility and Crystallization Behavior of Poly(3-hydroxyvalerate-co-3-hydroxyvalerate)/Poly(propylene carbonate) Blends

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ABSTRACT: Blends of synthetic poly(propylene carbonate) (PPC) with a natural bacterial copolymer of 3-hydroxybutyrate with 3-hydroxyvalerate (PHBV) containing 8 mol % 3-hydroxyvalerate units were prepared with a simple casting procedure. PPC was thermally stabilized by end-capping before use. The miscibility, morphology, and crystallization behavior of the blends were investigated by differential scanning calorimetry, polarized optical microscopy, wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS). PHBV/PPC blends showed weak miscibility in the melt, but the miscibility was very low. The

effect of PPC on the crystallization of PHBV was evident. The addition of PPC decreased the rate of spherulite growth of PHBV, and with increasing PPC content in the PHBV/PPC blends, the PHBV spherulites became more and more open. However, the crystalline structure of PHBV did not change with increasing PPC in the PHBV/PPC blends, as shown from WAXD analysis. The long period obtained from SAXS showed a small increase with the addition of PPC. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 4054–4060, 2003

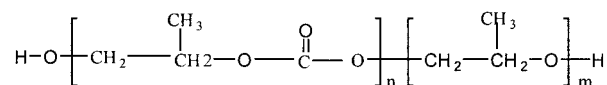
Key words: miscibility; crystallization; blends

INTRODUCTION

Microbially generated polyhydroxybutyrate (PHB) is a biodegradable engineering polymer with important commercial properties.¹ However, it has two main limitations for practical use. One is a narrow processing window. The polymer is thermally unstable at temperatures above its melting point (~ 453 K); that is, a drastic reduction in molecular weight occurs during processing in the temperature range 453–473 K.^{2–4} The other limitation is a relatively low impact resistance. Injection-molded PHB has a high crystallinity, which makes it brittle. To overcome the shortcomings of PHB, efforts have been made to bacterially copolymerize 3-hydroxybutyrate repeating units with other monomers such as 3-hydroxyvalerate (HV),^{5–7} and 4-hydroxybutyrate,^{8–10} hydroxypropionate.¹¹ Among these copolymers, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is the most promising. It possesses a wide range of properties dependent on the HV content.¹² PHBV was first manufactured by ICI in

1983 and was originally intended as a biodegradable substitute for oil-based polyolefins in plastic containers and films.¹³ However, the high cost of production and its narrow processing window prevent it from being used widely. One approach to obtaining a less expensive thermoplastic polymer with improved mechanical properties is to blend PHBV with another suitable polymer. There were studies of blends of PHBV with poly(vinyl chloride),^{14,15} ethylene–vinyl acetate copolymer,¹⁶ poly(*p*-vinylphenol),¹⁷ synthetic atactic PHB,¹⁸ poly(styrene-co-acrylonitrile),¹⁹ polyethylene, and polystyrene,²⁰ but these blends were only partially biodegradable materials because the second component in each blends was not biodegradable.

Polypropylene carbonate (PPC), synthesized by Inoue et al.²¹ first, is an aliphatic polycarbonate composed of carbon dioxide and propylene epoxide with the following molecular structure:²²



The synthesis of PPC can fix and recycle the carbon dioxide in the environment. PPC is also biodegradable,²³ which has been proven by our coworkers. PPC is an amorphous polymer²⁴ that can be used as a toughening agent,²⁵ but until now, no blends of PHBV or PHB with PPC have been reported. The purpose of this study was to investigate the miscibility, crystal-

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lizing behavior, and morphology of PHBV/PPC blends.

EXPERIMENTAL

Material

PHBV containing 8 mol % HV was prepared by the Beijing Biological Institute. The average molecular weight, obtained by the measurement of its viscosity in chloroform at a temperature of 303 K, was 5.8×10^5 . PPC was produced by Changchun Institute of Applied Chemistry. The weight-average molecular weight (M_w) obtained by gel permeation chromatography was 2.3×10^5 , and the polydispersity index (M_w/M_n , where M_n is the number-average molecular-weight) was 2.2.

End-capping PPC

PPC was treated with some stabilizing agents before use. PPC (5 g) was dissolved in 150 mL of solvent. After 0.01 mol of treating agent, such as maleic anhydride, was added, the solution was stirred for 4 h at a temperature of 333 K. The reaction products were precipitated in methanol and purified by Soxhlet extraction for about 24 h.

Preparation of the blends

PHBV/PPC blends with weight ratios from 100/0 to 0/100 were prepared by solution blending and were then cast from chloroform and dried *in vacuo* at 353 K to a constant weight. Specimens for the wide-angle X-ray diffraction (WAXD) study were compression-molded and isothermally crystallized at 393 K for 4 h.

Experimental conditions for the measurements

A PerkinElmer DSC-7 differential scanning calorimeter was used to study the glass-transition temperature (T_g) and the melting and crystallization behaviors of the blends. About 10 mg of each sample was heated from room temperature to 463 K (run I) and was then maintained at 463 K for 2 min before it was quenched to 223 K. The samples were then reheated to 463 K (run II). After they were held for 2 min at 463 K, the samples were cooled down to 223 K (run

III). A scan rate of 20 K/min was used throughout. The midpoints of the transitions in the traces recorded in the second heating scan (run II) were taken as the values of T_g . The exothermic and endothermic peaks of the thermograms in the second heating scan were taken as the cold crystallization temperature (T_{cc}) and the melting temperature (T_m), respectively. The heat of fusion (run II) was estimated as the integral of the endothermic curves. The exothermic peaks of the thermograms by the third heating scan were taken as crystallization temperatures (T_c 's; run III).

A PerkinElmer 7s thermal analysis system was used to determine the decomposition temperature of treated and untreated PPC. The sample weight was about 10 mg and the heating rate is 10 K/min. The flowing rate of purging gas (nitrogen and air) was 20 cm³/min.

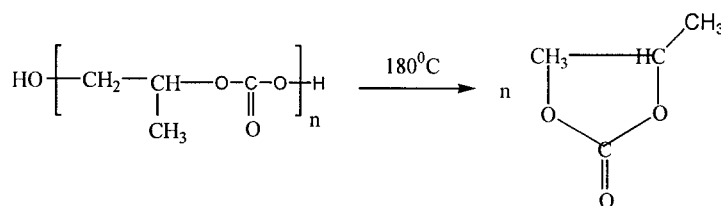
The morphological structure of PHBV spherulites was observed with an OPTON polarizing optical microscope equipped with a hot stage. Each specimen was sandwiched between two thin glass slides, kept at 463 K for 2 min on one hot stage, and then transferred as quickly as possible onto another hot stage, which was held at a prefixed temperature. The specimens were crystallized isothermally at a given T_c . The growth of the spherulite radius was monitored as a function of time. The slope of the line obtained from a plot of the spherulitic radius versus time was taken as the radial growth rate of the PHBV spherulites.

WAXD experiments were performed with a Philips PW1700 X-ray diffractometer using Cu K α X-rays at a voltage of 40 kV and a current of 30 mA. Small-angle X-ray scattering (SAXS) measurements were also performed with a compact Kratky system connected with the PW1700 diffractometer.

RESULTS AND DISCUSSION

Thermal stabilization of PPC

Unlike aromatic polycarbonate, PPC, which is an aliphatic polycarbonate, shows low thermal stability. Even at temperatures of only about 453 K, PPC undergoes a reduction in molecular weight in which the "back-biting" reactions of the free hydroxyl groups are said to play a significant part.²⁶



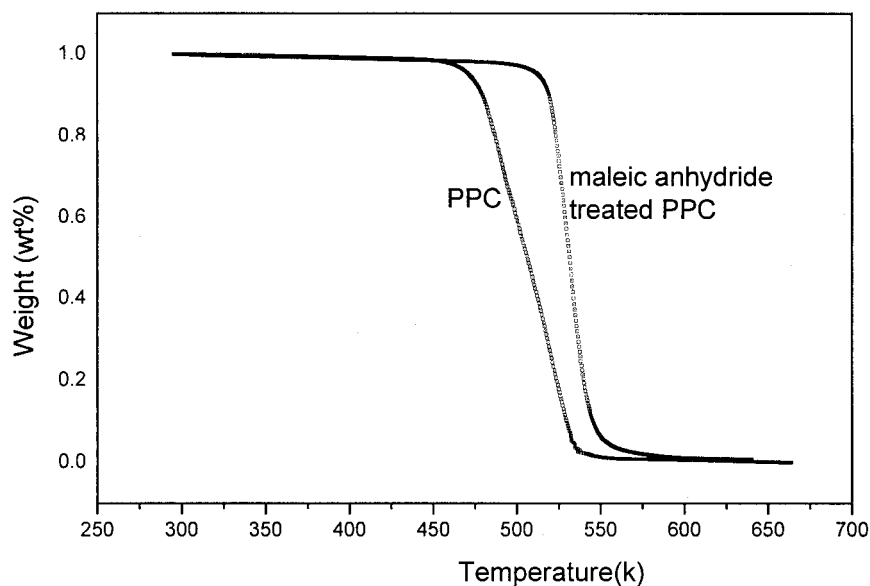


Figure 1 TGA curves of treated and untreated PPC in N_2 .

Hence, it was unsuitable for PPC to blend with PHBV (containing 8 mol% HV) whose equilibrium T_m was more than 443 K, nor could it be processed in practice by injection-molding or extrusion.

It was reported that end-capping can improve thermal stability.²⁷ In our experiment, we selected maleic anhydride, benzoyl chloride, and tolylene diisocyanate as end-capping agents.

The thermogravimetric analysis (TGA) curves of the untreated and the maleic-anhydride-treated PPC obtained under flowing nitrogen are shown in Figure 1, and the decomposition temperatures of the treated and untreated PPC are listed in Table I. As shown in the table, the decomposition temperatures of the treated PPC samples were higher than that of the untreated PPC. During end-capping, the nucleophilic terminal hydroxy groups in PPC were replaced with less reactive groups. Although the tendency for depolymerization via chain scission was not affected by the transformation, the depolymerization via chain unzipping was prevented due to the formation of a five-membered ring in the chain end after end-capping.

Miscibility

The thermal characterization of polymer blends is a well-known method for the determination of the mis-

cibility of polymer blends. The miscibility between any two polymers in the amorphous state is detected by the presence of a single T_g peak intermediate between those of the two component polymers. So, the T_g behavior of PHBV/PPC blends was studied to examine their miscibility.

Figure 2 shows the differential scanning calorimetry (DSC) curves of the quenched PHBV/PPC blends (run II). Two T_g 's, which were almost not changed with the PHBV contents, were observed in the 60/40, 40/60, and 20/80 wt % PHBV/PPC blends. One was about 276 K, closed to the T_g of PHBV. The other was not evident because it was affected by the T_{cc} peak, close to the T_g of pure PPC. In the 80/20 wt % PHBV/PPC blend, only one T_g (about 276 K) was observed. The possible reason was that the T_g of PPC was veiled by the T_{cc} peak of PHBV.

The T_{cc} and T_m in the heating scan of the quenched blends (run II) could also be used to examine the miscibility of the system. In general, cold crystallization took place at a temperature above the T_g of the blends in which the crystallizable polymer chains possessed enough segmental mobility to crystallize. As shown in Figure 2, the cold crystallization peak of the quenched blends shifted a little toward higher temperatures. Especially for the quenched blend with a 60/40 composition, the T_{cc} increased from 334.4 K (for pure PHBV) to 338.7 K (for the 60/40 wt % PHBV/PPC blend). This could be explained by the weak miscibility of PHBV/PPC blends in the melt. The existence of PPC obstructed the segmental motion of PHBV, and thus, the T_{cc} moved to a higher temperature. The 40/60 wt % PHBV/PPC blend had about the same T_{cc} as pure PHBV. This could be attributed to the influence of the glass transition of PPC in the blend.

TABLE I
Thermal Properties of Treated and Untreated PPC Samples

Treated agent	Decomposition temperature (K)		
	Untreated	Maleic anhydride	Benzoyl chloride
Air	476	516	518
N_2	473	510	515

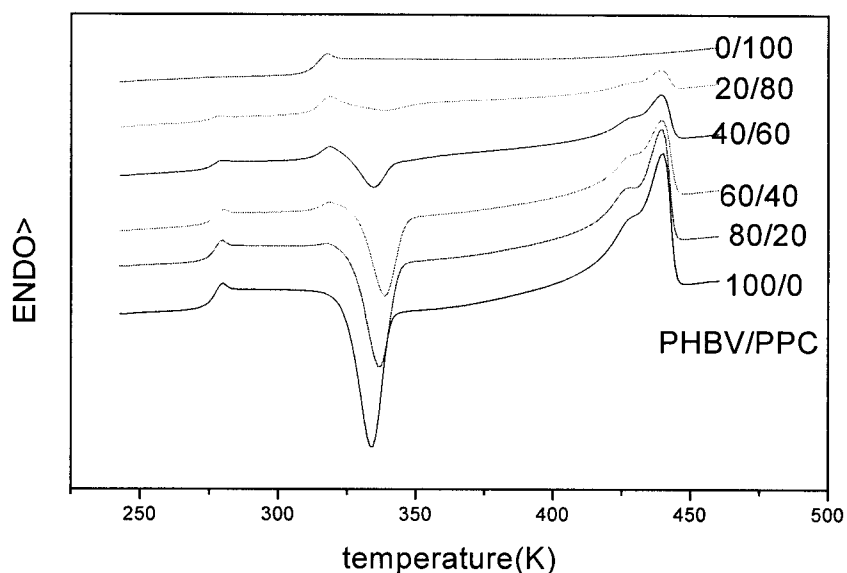


Figure 2 DSC curves of quenched PHBV, PPC, and their blends.

In another aspect, the melting behavior of the crystallizable component was affected by the amorphous component in miscible blends, whereas the melting behavior was not affected by the second amorphous component in immiscible blends. For PHBV/PPC blends, the T_m decreased slightly with increasing PPC content of the blends. From the thermal behavior of the PHBV/PPC blends, we concluded that the PHBV/PPC blends were partially miscible in the melt state. However, the miscibility was very poor. This is further illustrated in the following discussion of the crystallization behavior and morphology of the PHBV/PPC blends.

Nonisothermal crystallization

PHBV is a highly crystalline polymer²⁸ that will crystallize when cooled from the melt. The peaks in the DSC traces of the nonisothermal crystallization of the blends varied with the blend composition, as shown in Figure 3.

As shown in Figure 3, the T_c of PHBV in the blends decreased with increasing PPC content in the blends. The exothermic peak for 20PHBV/80PPC was not evident due to the effect of the T_g of PPC. The undercooling temperature (ΔT) was defined as the temperature difference between the T_m in the second run and

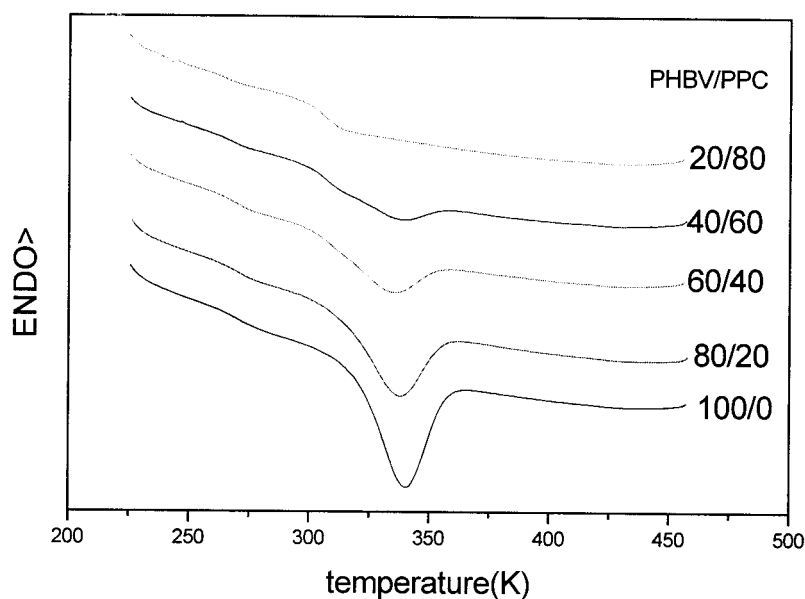


Figure 3 DSC curves of PHBV and its blends cooled from 463 to 223 K.

TABLE II
 T_c and ΔH_c from the Melt

Sample code	T_c (K)	ΔT (K)	ΔH_c (J g ⁻¹)	ΔH_c^{PHBV} (J g ⁻¹)
PHBV	340.1	99.8	45.6	45.6
PHBV/PPC 80/20	337.3	102.2	34.3	42.9
PHBV/PPC 60/40	333.8	105.6	21.6	36
PHBV/PPC 40/60	335.8	103.4	17.3	42

the T_c in the third scan ($\Delta T = T_m - T_c$). ΔT was used to describe the kinetic crystallizability during the nonisothermal crystallization process. A higher ΔT suggested a lower kinetic crystallizability in the range of T_m to T_g . T_c , ΔT , and the enthalpy of the nonisothermal crystallization of the PHBV phase in the blends (ΔH_c^{PHBV}) are listed in Table II. ΔH_c^{PHBV} was calculated from the enthalpy of the blends (ΔH_c ; $\Delta H_c^{\text{PHBV}} = \Delta H_c / W_{\text{PHBV}}$). As shown in Table II, ΔT increased and the enthalpy of the PHBV phase in the blends decreased with increasing PPC content in the blends. This indicated that there existed an effect of PPC on the crystallization of PHBV. Although in the second run, two T_g 's were observed, the change in T_c implied that there was some PPC in the enriched PHBV phase.

Isothermal crystallization

It was previously pointed out (see Fig. 3) that during the nonisothermal crystallization of the PHBV/PPC blends, PPC affected the crystallization of PHBV. Further evidence was obtained from the isothermal crystallization of the PHBV/PPC blends. In this study, the measurement of spherulitic growth rates (G_s) was used to study the isothermal crystallization behavior.

The G_s of pure PHBV and the PHBV/PPC blends were determined with a polarizing optical microscope. Thin films of PHBV and PHBV/PPC blends were isothermally crystallized at a selected temperature. The temperature range was from 358 to 393 K. At a selected temperature, the spherulites were observed to grow at a constant rate until impingement occurred for all of the compositions examined with PHBV in them. This result implied that the composition of the melts remained constant during the crystallization process, and the amorphous component did not migrate to enrich the melts in the proximity of growing lamellae²⁹ (either interlamellarly or between bundles of lamelle).

The dependence of G on T_c for PHBV and PHBV/PPC blends is shown in Figure 4, where it is shown that the G values decreased with increasing PPC content in the blends. The effect was very weak, especially in the higher temperature region of the curves. This was accounted for by the dilution effect of amorphous PPC on the PHBV crystallization front.

Morphology

Optical micrographs of the PHBV/PPC blends (isothermally crystallized at 363 K) taken with crossed polars are shown in Figure 5, where it is shown that with increasing PPC content in the PHBV/PPC blends, the PHBV spherulites became more and more open. Especially in the specimen with 20/80 wt % PHBV/PPC, the microcrystals of PHBV were dispersed in the PPC matrix. The Maltese cross became vague with increasing PPC content in the blends. In blends containing more than 60 wt % PPC, the Maltese cross could not be seen. In the blend of 40/60 wt % PHBV/PPC, the Maltese cross was not clear, but the

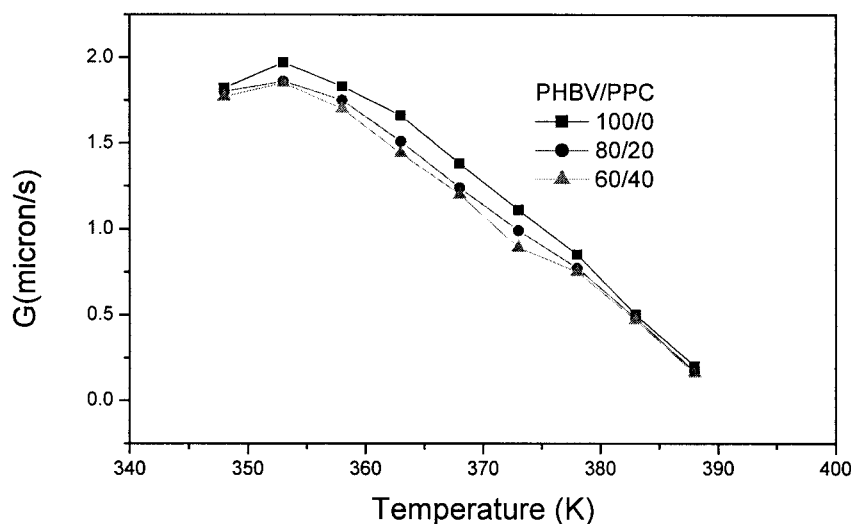


Figure 4 G as a function of T_c for the PHBV/PPC blends.

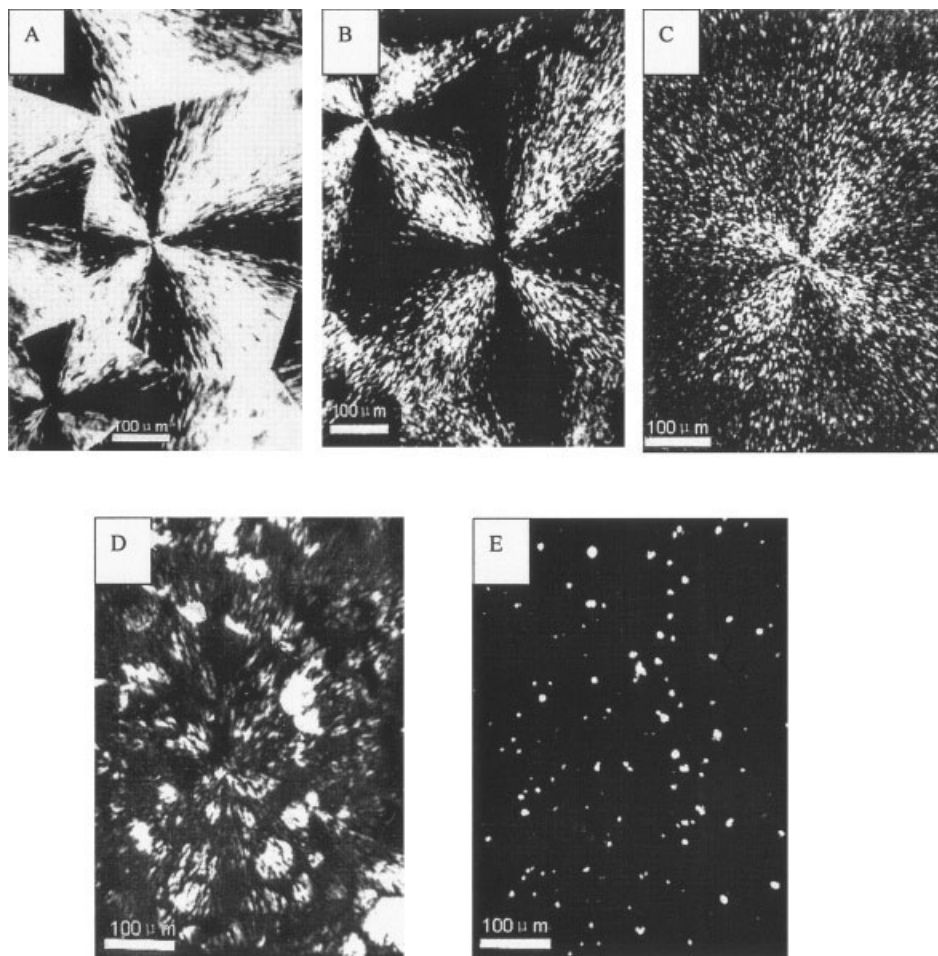


Figure 5 Optical micrographs of isothermally crystallized (at 368 K) pure PHBV and the PHBV/PPC blends: (A) 100/0, (B) 80/20, (C) 60/40, (D) 40/60, and (E) 20/80.

microcrystals of PHBV in the blend still grew along the radius of the spherulite. This may have been due to PHBV and PPC both being continuous phases in the blend of 40PHBV/60PPC.

Studies on the structure of the crystallized PHBV in the blends were also carried out with WAXD and

SAXS. The WAXD results are shown in Figure 6. When the spectrum of the pure PHBV were compared with those of the blends, we could see that the *d*-spacing values were constant for the (1 1 0), (0 0 2), and (0 2 0) crystallographic planes, which indicated

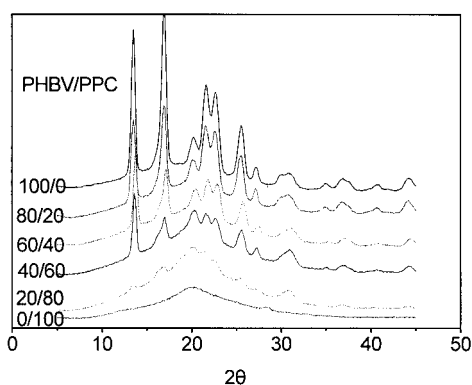


Figure 6 WAXD profiles of the isothermally crystallized (at 393 K) PHBV/PPC blends.

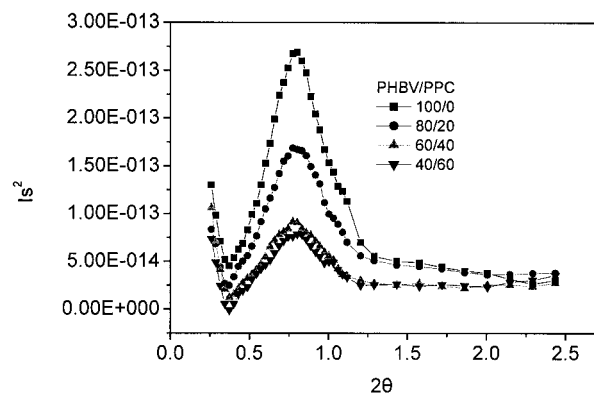


Figure 7 Desmeared SAXS curves of PHBV and the PHBV/PPC blends.

TABLE III
 L_p Values of PHBV and the PHBV/PPC Blends

Code	L_p (nm)
PHBV	10.2
80PHBV/20PPC	10.5
60PHBV/40PPC	10.5
40PHBV/60PPC	10.5

that the PHBV unit cell was not changed in the blends.

The desmeared SAXS profiles of the isothermally crystallized pure PHBV and PHBV/PPC blends (Fig. 7) showed the presence of a maximum, which was associated with the period between the centers of adjacent lamellas. As shown in Figure 7, the peaks showed little change in position with increasing PPC content. According to Bragg's law, the reciprocal of the long period ($L_p = 2\pi/q_{\max}$) is proportional to the value in q_{\max} (scattering vector, $q = 4\pi \sin \theta/\lambda$). The value is listed in Table III. As shown in Table III, L_p increased a little with the addition of PPC. However, L_p was the same for the 80/20, 60/40, and 40/60 wt % PHBV/PPC blends. This implied that during the crystallization of PHBV from the melt a small amount of PPC, which was dissolved in the enriched PHBV phase, was ejected into the interlamellar region of PHBV. However, most of the PPC, which was ejected into the interfibrillar region, was in the enriched PPC phase.

CONCLUSIONS

The thermal stability of PPC was improved by end-capping with different agents. The miscibility, crystallization behavior, and morphology of PHBV and PPC blends were studied by DSC, optical microscopy, WAXD, and SAXS. PHBV/PPC blends formed a weak miscible blend in the melt state. The addition of PPC decreased G of PHBV. With the increasing PPC content in the PHBV/PPC blends, ΔT also increased. However, as shown by WAXD analysis, the crystalline structure of PHBV did not change with the increasing PPC content in the blends. The L_p 's of the blends obtained by SAXS showed a little increase with the addition of PPC. However, the L_p was the same for the 80/20, 60/40, and 40/60 wt % PHBV/PPC blends. This indicated that during the crystallization of PHBV

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