

# Fully biodegradable poly(3-hydroxybutyrate-*co*-hydroxyvalerate)/poly(ethylene succinate) blends: Phase behavior, crystallization and mechanical properties

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Dedicated to Prof. Toshio Nishi of Tokyo Institute of Technology on the occasion of his 65th birthday

## Abstract

Poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) and poly(ethylene succinate) (PES) are both biodegradable semi-crystalline polyesters. Phase behavior, crystal structure, crystallization kinetics, and mechanical properties of fully biodegradable PHBV/PES blends were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), wide angle X-ray diffraction (WAXD), and tensile tests in detail. PHBV is immiscible with PES as evidenced by the two composition independent glass transition temperatures corresponding to those of neat components. Moreover, the biphasic melt further confirms the immiscibility between PHBV and PES. Nonisothermal and isothermal crystallization of PHBV/PES blends were studied by DSC. In the case of isothermal crystallization the crystallization rates of PHBV and PES decrease with increasing the content of the other component for both PHBV-rich and PES-rich blends; however, the crystallization mechanisms do not change. The mechanical properties of PHBV/PES blends were examined by tensile testing. It is found that the tensile strength, elongation at break, Young's modulus, and toughness of PHBV blends can be adjusted by changing blend composition. For PHBV-rich blends, blending some amount of PES can improve the elongation at break significantly while still keeping considerably high tensile strength and Young's modulus.

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**Keywords:** Biodegradable polymer; Crystalline/crystalline polymer blends; Phase behavior

## 1. Introduction

Much more attention has been paid to the development and application of biodegradable polymers

in the last two decades, which can be classified into two types according to the difference in the preparation methods. One is the biosynthetic polymers, such as bacterial poly(hydroxyalkanoates) (PHAs). Poly(hydroxybutyrate) (PHB) is probably the most extensively studied biodegradable thermoplastic polymer among PHAs. PHB is a truly biodegradable

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and biocompatible polymer with relatively high melting point (ca. 180 °C) and crystallinity (more than 50%) [1]. However, practical application of PHB has often been limited by its brittleness and narrow processing window. Therefore, blending of PHB with other polymers has been often reported in literature. Miscible blends have been prepared by mixing PHB with poly(vinyl acetate) (PVAc), poly(epichlorohydrin) (PECH), poly(vinyl phenol) (PVPh), poly(vinylidene fluoride) (PVDF), and poly(ethylene oxide) (PEO) [2–6]. On the other hand, PHB was known to be immiscible with poly( $\epsilon$ -caprolactone) (PCL), poly(cyclohexyl methacrylate) (PCHMAC), poly(hydroxyoctanoate) (PHO), high molecular weight poly(L-lactide) (PLLA), poly(methylene oxide) (POM), and poly(vinylidene chloride-*co*-acrylonitrile) (PVDCAN) [7–12]. Another method to improve the mechanical and other physical properties of PHB is the development of copolymers of PHB. Among such copolymers poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) is characterized by better impact resistance and offers the possibility of processing at lower temperatures than PHB [13]. Compared to PHB few works have been done on PHBV. Recently Di Lorenzo et al. and Ha et al. reviewed the studies of miscibility, properties and biodegradability of blends containing either PHB or PHBV, respectively [14,15].

The other type of biodegradable polymers is chemosynthetic polymers, such as linear aliphatic polyesters. Poly(ethylene succinate) (PES) is just one of them. The crystal structure, morphology and melting behavior of PES have been reported in literature [16–19]. In previous works we studied nonisothermal cold crystallization behavior from the amorphous state and complex melting behavior of PES after nonisothermal melt crystallization process [20,21]. Polymer blending is often a useful and economical way to produce new materials with a variety of properties. However, less work has been done on the blending PES with other polymers. PES was reported to be miscible with PHB and PEO blends [22,23]. PES and PEO were found to be able to form interpenetrated spherulites at 50 °C for PES/PEO 20/80 blend in our recent work [24].

It is well known that the elongation at break of PHBV is very low, limiting its wide application; however, PES is a kind of biodegradable polyester with good mechanical properties, especially its high elongation at break. Thus blending with PES may improve the mechanical properties of PHBV. The main advantages of PHBV/PES blends are summa-

rized as follows. First, PHBV/PES blends are still fully biodegradable polymer blends since both components are biodegradable polyesters. Second, PHBV/PES blends are crystalline/crystalline polymer blends, thus providing various phase behavior and crystalline morphology by changing blend composition and crystallization condition. Third, the mechanical properties of PHBV/PES blends can be modulated by changing blend composition and crystallization condition. In this work we studied the miscibility crystallization behavior and mechanical properties of PHBV/PES blends. To the best of our knowledge, no attention has been paid to the blending of PHBV and PES till now in literature. It is important to understand their miscibility and the crystallization behavior in a cooling process as a model case of processing a biodegradable crystalline polymer blend material. In the present work the results of an investigation concerning the miscibility, phase behavior, crystal structure, nonisothermal crystallization, isothermal crystallization kinetics and mechanical properties of PHBV/PES blends are reported. This work will be helpful for a better understanding of the relationship between structure and properties of biodegradable polymer blends, which should be of great interest and importance to modify the properties and extend the practical application for biodegradable polymers from both academic and industrial viewpoints.

## 2. Experimental part

### 2.1. Materials

PHBV ( $M_w = 4.21 \times 10^5$ ,  $M_n = 1.26 \times 10^5$ ), a copolymer with 8 wt% HV content, was purchased from Aldrich Chemical Co. and PES ( $M_w = 2.13 \times 10^5$ ,  $M_n = 6.80 \times 10^4$ ) was kindly supplied by Shokubai Co. Ltd., Japan. Both PHBV and PES were used as received.

### 2.2. Blends preparations

PHBV/PES blends were prepared with mutual solvent chloroform. The solution of both polymers (0.02 g/ml) was cast on a Petri dish at room temperature and held for 12 h to evaporate the solvent in a controlled air stream. The resulting films were further dried in vacuum at 50 °C for 72 h to remove the solvent completely. PHBV/PES blends were thus prepared with various compositions ranging from 100/0, 80/20, 60/40, 40/60, 20/80 to

0/100 in weight ratio, the first number referring to PHBV.

### 2.3. Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction experiments were performed on a Shimadzu XRD-6000 X-ray Diffractometer at 40 kV and 30 mA. The samples for WAXD experiments were prepared as follows. The samples were first pressed into films with thickness of around 1 mm on a hot stage at 190 °C and then transferred into a vacuum oven at 70 °C for 3 days.

### 2.4. Polarizing optical microscopy (POM)

A polarizing optical microscope (Olympus BX51) equipped with a first-order retardation plate and a temperature controller (Linkam THMS 600) was used to investigate the morphology of PHBV/PES blends.

### 2.5. Differential scanning calorimetry (DSC)

Thermal analysis was performed using a TA Instruments differential scanning calorimetry (DSC) Q100 with a Universal Analysis 2000. The glass transition temperature ( $T_g$ ) and the melting point ( $T_m$ ) of the melt-quenched PHBV/PES blends were measured at a heating rate of 20 °C/min. The samples were first heated to 190 °C at 20 °C/min and held there for 3 min to erase any thermal history and then quenched to -70 °C at a cooling rate of 100 °C/min.

Two different procedures were employed to study the crystallization behavior of PHBV/PES blends:

- (1) *Nonisothermal crystallization.* The samples were first heated to 190 °C at 20 °C/min (first heating), held at 190 °C for 3 min to erase any thermal history, cooled to 10 °C at 10 °C/min (first cooling), and then heated to 190 °C at 20 °C/min (second heating). The crystallization peak temperature was obtained from the first cooling traces.
- (2) *Isothermal crystallization.* The isothermal crystallization of PHBV and PES was studied by DSC. The isothermal crystallization of high- $T_m$  component PHBV at 95 °C was studied for the neat and PHBV-rich blends, i.e., 100/0, 80/20 and 60/40 blend samples. The samples were first annealed at 190 °C for 3 min to erase any thermal history and then

cooled to 95 °C at a cooling rate of 40 °C/min for PHBV to crystallize. The isothermal crystallization of low- $T_m$  component PES was also investigated for the neat and PES-rich blends, i.e., 0/100, 20/80 and 40/60 blend samples. For the isothermal crystallization of neat PES, the sample was first annealed for 3 min to erase any thermal history and then cooled to 70 °C at 40 °C/min for PES to crystallize. For the isothermal crystallization of PES-rich blends, the following procedure was employed. The samples were first crystallized at 95 °C for the high- $T_m$  component PHBV to crystallize as described in the aforementioned section and followed by cooling at 40 °C/min to 70 °C for PES to crystallize. The aforementioned isothermal crystallization conditions consist of the following two steps, namely, the isothermal crystallization of the PHBV phase from the melt at 95 °C, and the isothermal crystallization of the PES from the liquid phase in the presence of previously crystallized PHBV at 95 °C. The aforementioned two-step isothermal crystallization of PHBV/PES blends is possible because PHBV and PES need very different supercooling to crystallize.

### 2.6. Tensile tests

Tensile tests were carried out on an Instron 1185 tensile testing machine at a rate of 10 mm/min at room temperature. Three samples were used at least.

## 3. Results and discussion

### 3.1. Phase behavior of PHBV/PES blends

Whether both components are miscible or not has a significant influence on the morphology, thermal properties, mechanical properties and biodegradability of PHBV/PES blends. In this work PHBV/PES blends were first studied by DSC for the melt-quenched samples at a heating rate of 20 °C/min. As introduced in the experimental section the samples were first annealed at 190 °C for 3 min to erase any thermal history and then quenched to -40 °C at a very fast cooling rate of 100 °C/min. As shown in Fig. 1 neat PHBV exhibits a glass transition ( $T_g$ ) at 2.6 °C, a cold crystallization peak ( $T_{ch}$ ) at 67.2 °C, and two endothermic

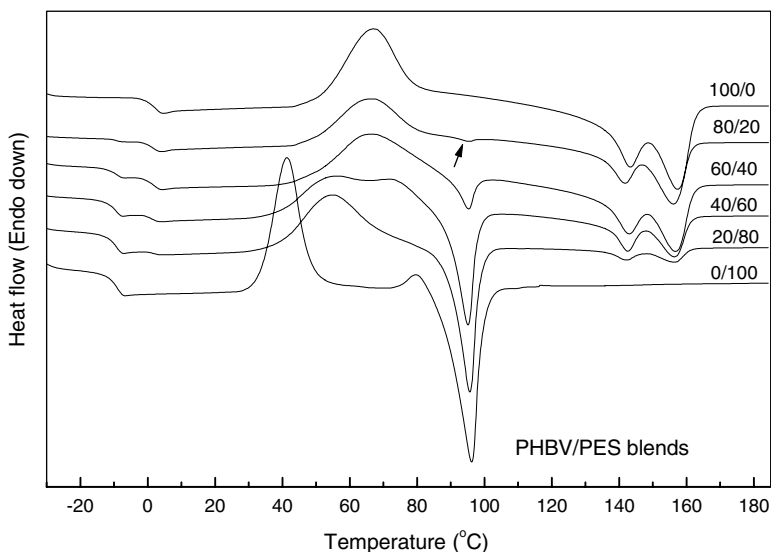


Fig. 1. DSC traces of PHBV/PES blends after melt-quenching at a heating rate of 20 °C/min.

melting peaks ( $T_{ms}$ ) at 143.2 and 157.6 °C, respectively. Neat PES shows a  $T_g$  at  $-8.8$  °C, a  $T_{ch}$  at 41.3 °C, and a  $T_m$  at 96.1 °C. For PHBV/PES blends they show two distinct  $T_g$ s at around  $-9$  and  $2$  °C, corresponding to those of neat components, respectively, indicating that PHBV and PES are immiscible in the amorphous state. On the other hand, two main melting endotherms are found at around 95 and 156 °C, corresponding to  $T_{ms}$  of PES and PHBV. Furthermore, a small melting

endotherm at around 142 °C is also found in the blends, corresponding to  $T_m$  of PHBV. Fig. 2 summarizes the aforementioned thermal properties of PHBV/PES blends. It is clear from Fig. 2 that both  $T_g$ s and  $T_{ms}$  of PHBV and PES remain almost unchanged in the blends, indicating that PHBV/PES blends are immiscible crystalline/crystalline polymer blends.

The phase morphology of PHBV/PES blends was further studied by POM. It is possible to infer

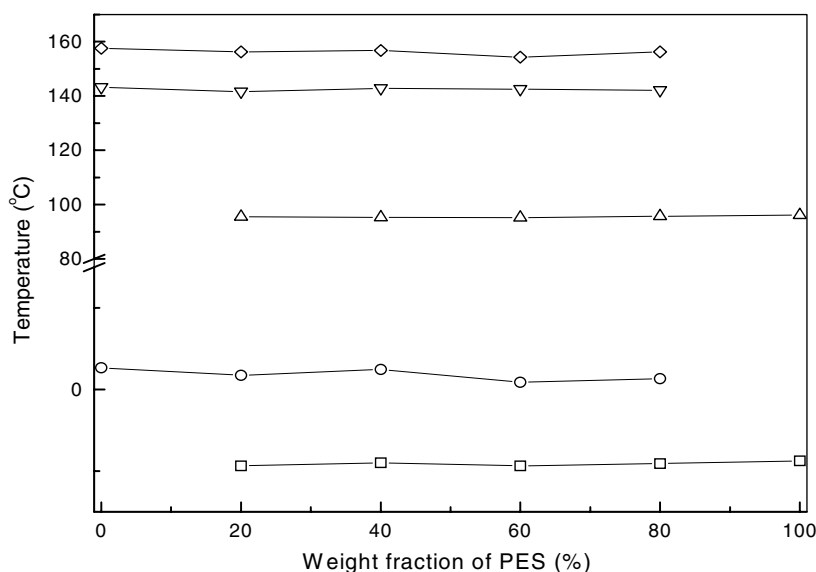


Fig. 2. Summary of the results of  $T_g$  and  $T_m$  of PHBV/PES blends after melt-quenching at a heating rate of 20 °C/min (□, ○:  $T_g$ s of PES and PHBV, respectively; △:  $T_m$  of PES, ▽, ◇:  $T_{ms}$  of PHBV, respectively).



whether the melt is single-phased or biphasic if the refractive indices of PHBV and PES are not the same. Therefore, the single-phased melt should be observed if PHBV and PES are miscible. Otherwise, the biphasic melt should be observed if the two components are immiscible. For all the compositions studied, clearly defined biphasic separation was observed, indicating that PHBV is not miscible with PES in the melt. Fig. 3 shows the spherulitic morphologies of neat and blended PHBV for the PHBV-rich blends. Neat PHBV crystallizes at 95 °C according to a positive banded spherulite pattern from the homogeneous melt; however, PHBV crystallizes through positive banded spherulites from the heterogeneous melt for the PHBV-rich blends, indicating that PHBV and PES are immiscible polymer blends.

WAXD experiments were performed to investigate the crystal structure of PHBV/PES blends. Fig. 4 displays the WAXD patterns of PHBV/PES blends. It has been reported that PHBV crystallizes in either PHB or poly (3-hydroxyvalerate) (PHV) crystalline lattice for HV content lower or higher

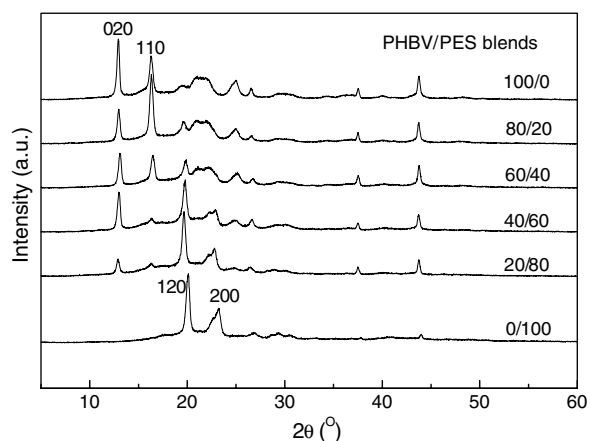


Fig. 4. WAXD patterns of PHBV/PES blends.

than 50 mol% [25]. In the present work, the PHBV sample has an 8 wt% HV content, i.e., low than 50 mol%; therefore, it crystallizes in the PHB crystalline lattice. As a result, neat PHBV studied in this work has the same crystal structure as that of PHB

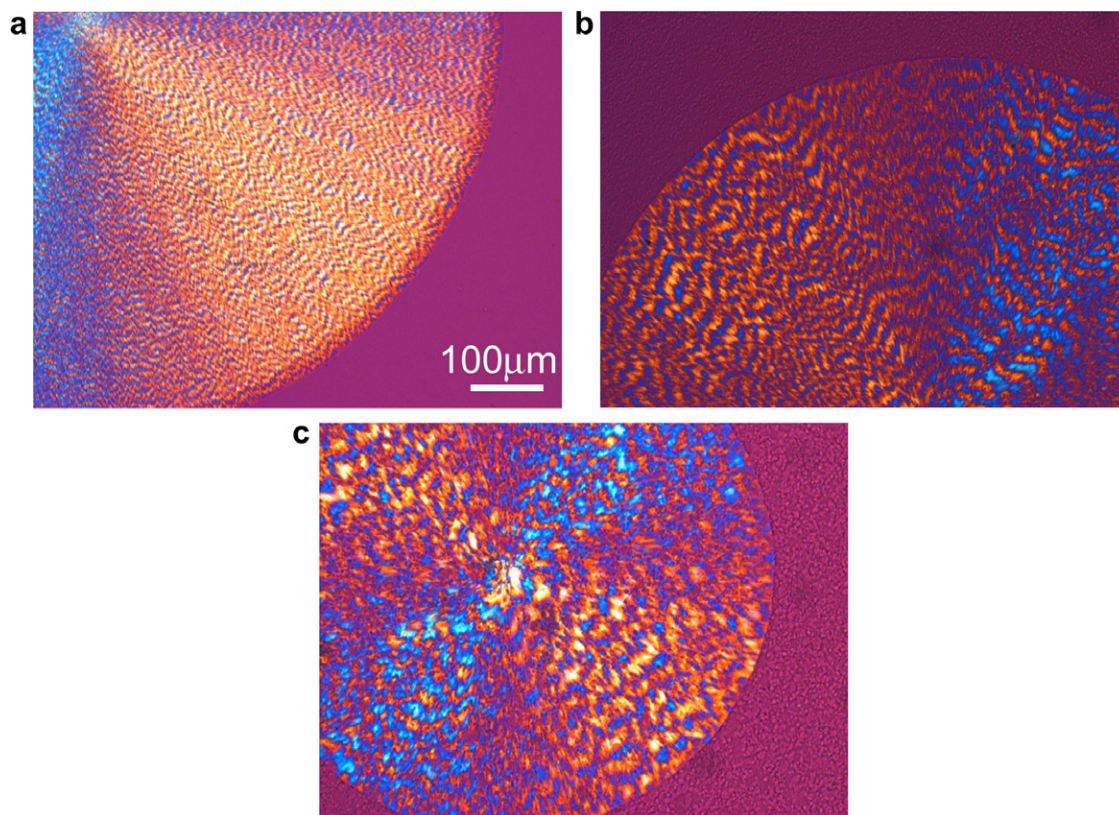


Fig. 3. POM micrographs (same magnification, bar = 100 μm) of neat PHBV and blended PHBV crystallized at 95 °C: (a) neat PHBV, (b) 80/20 blend, and (c) 60/40 blend.

showing the orthorhombic unit cell with  $a = 0.576$  nm,  $b = 1.320$  nm, and  $c$  (fiber axis) = 0.596 nm. As shown in Fig. 4, neat PHBV presents two strong diffraction peaks at around  $12.96^\circ$  and  $16.30^\circ$  corresponding to (020) and (110) planes, respectively [26]. The crystal structure of PES was determined by Ueda et al., and the unit cell of PES is also orthorhombic with  $a = 0.760$  nm,  $b = 1.075$  nm, and  $c$  (fiber axis) = 0.833 nm [16]. Therefore, as shown in Fig. 4 neat PES shows two strong diffraction peaks at around  $20.08^\circ$  and  $23.23^\circ$  corresponding to (120) and (200) planes, respectively. For PHBV/PES blends they involve all the diffraction peaks corresponding to neat PHBV and neat PES; furthermore, the intensity of the diffraction peaks of each component decrease with increasing the other component content in the blends, indicating that PHBV and PES crystallize separately in the blends. Blending with other semicrystalline polymer does not modify the crystal structure in the blends but only reduces the intensity of diffraction peak.

It is well known that crystallinity plays a significant role on the physical properties of biodegradable polymers, such as thermal and mechanical properties, and affects biodegradability, too. Therefore, crystallinity was also studied for PHBV/PES blends before and after blending. As shown in Fig. 4, the diffraction peaks of both components presented and overlapped each other, resulting in that it was difficult to estimate the crystallinity values of each component accurately with WAXD method. Therefore, the crystallinity values of

PHBV/PES blends were determined with DSC for the same samples used for WAXD measurements. DSC traces showed two melting endotherms at low and high temperature range, corresponding to the melting of PES and PHBV, respectively. For brevity, the DSC traces are not shown here. On the basis of the heat of fusion of 100% crystalline PHBV (109 J/g) [27] and PES (180 J/g) [28], the values of crystallinity of both PHBV and PES components were calculated from the melting endotherms and normalized with respect to the composition of each component in the blends. It was found that the values of crystallinity of PHBV decreased gradually from around 71.9% for neat PHBV to around 48.8% for the 20/80 blend; however, the values of crystallinity of PES was around 31% and almost unchanged with the blend composition. Such variation in the crystallinity must affect the mechanical properties of PHBV/PES blends, which will be introduced in the following section.

### 3.2. Nonisothermal crystallization study by DSC

DSC measurements were carried out to investigate the nonisothermal melt crystallization of PHBV/PES blends. Fig. 5 shows the DSC curves of PHBV/PES blends at a cooling rate of  $10^\circ\text{C}/\text{min}$  from the melt. Both neat PHBV and neat PES exhibit the crystallization exotherm as a well-defined peak on cooling from the melt at  $10^\circ\text{C}/\text{min}$ . The crystallization peak temperature ( $T_c$ ) of neat PHBV is around  $49.9^\circ\text{C}$ , while  $T_c$  of neat

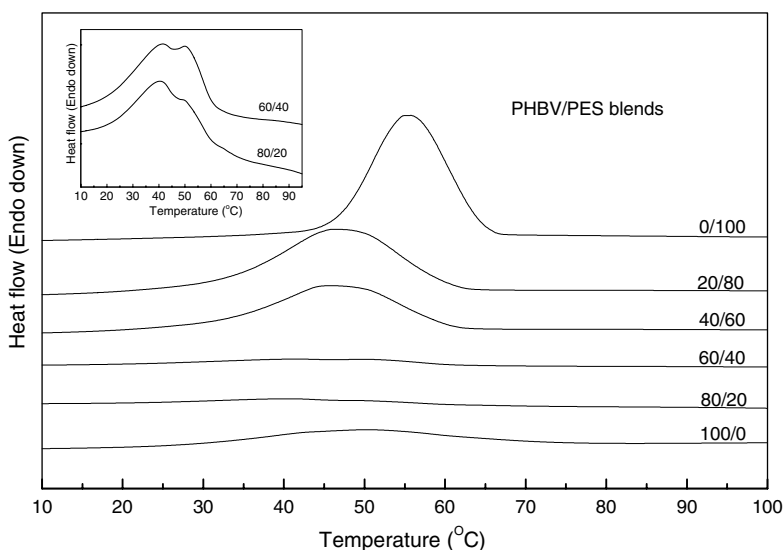


Fig. 5. Nonisothermal melt crystallization of PHBV/PES blends at a cooling rate of  $10^\circ\text{C}/\text{min}$ .

PES is around 55.7 °C. It should be noted that  $T_c$  of neat PHBV is lower than that of neat PES, although  $T_m$  of PHBV is higher than that of PES. Furthermore, the difference in  $T_c$  of the two components is very small. Such results may be related to the following fact that PHBV is a biosynthetic biodegradable polymer while PES is a chemosynthetic biodegradable polymer. The difference in the preparation methods between PHBV and PES results in that PHBV lacks the impurities required for the nucleation of the crystallization compared with PES. Thus,  $T_c$  of PES is higher than that of PHBV due to the presence of the considerable amount of the impurities. In the blends the crystallization of both components is somewhat complicated because the impurity in PES may disperse from PES to PHBV domain during the blend preparation. Therefore, the crystallization of PHBV would be affected by such a transfer of the impurities. For the PHBV-rich blends, i.e., 80/20 and 60/40, one main exothermic peak and one shoulder are found as shown in the inserted figure. For an 80/20 blend the main exothermic peak and the shoulder are around 50.3 and 40.9 °C, corresponding to  $T_c$ s of PHBV and PES, respectively. For a 60/40 blend they are around 49.9 and 41.5 °C, respectively, also corresponding to  $T_c$ s of PHBV and PES, respectively. It is found that  $T_c$  of PHBV is around 50 °C and almost unchanged irrespective of blending with PES. The almost unchanged  $T_c$ s of PHBV indicate the following two possibilities. One possibility is that the impurities in PES did not disperse from PES to PHBV domain at all. The other possibility is that the quantity of the impurities in PES dispersed from PES to PHBV domain was so small that they could not affect the crystallization of PHBV significantly in the blends. However, for the PES-rich blends, i.e., 40/60 and 20/80, only one exothermic peak is found. Compared to  $T_c$  of neat PES at around 55.7 °C,  $T_c$  of PES in the PHBV/PES blends shifts to low temperature range and varies slightly. In the case of a 40/60 blend the exothermic peak is around 45.7 °C, and in the case of a 20/80 blend it is around 46.3 °C. The decrease of  $T_c$  in the blends indicates that the crystallization of PES is restricted by the presence of high PHBV content. It is clear that the aforementioned peaks should mainly correspond to the crystallization of PES. Since  $T_c$ s of PHBV and PES are very close to each other, the possibility cannot be excluded that  $T_c$  of PHBV is overlapped by that of PES for the PES-rich blends and thus only one exothermic peak is found. In

order to check whether PHBV crystallized or not during the cooling process from the melt, POM experiments are performed using the same procedure as in DSC measurements. It is found that few banded larger PHBV spherulites coexist with lots of small PES spherulites during the cooling process (for brevity, the POM micrographs are not shown), indicative of the crystallization of PHBV.

In the previous section the cold crystallization of PHBV/PES blends was studied from the amorphous state as shown in Fig. 1. The cold crystallization peak temperature ( $T_{ch}$ ) of neat PES is around 41 °C, and that of neat PHBV is around 67 °C. In the blends  $T_{ch}$  of PES increases to around 55 °C, while  $T_{ch}$  of PHBV is almost unchanged. Comparing  $T_{ch}$  shown in Fig. 1 with  $T_c$  shown in Fig. 5, it can be concluded that the crystallizability of PES is always stronger than that of PHBV no matter whether they crystallize from the amorphous state or from the melt since the crystallization of PES is prior to that of PHBV.

### 3.3. Isothermal crystallization study by DSC

The isothermal crystallization of PHBV/PES blends was studied by DSC. In the present work PHBV and PES are both semicrystalline biodegradable polyesters, with PHBV being high- $T_m$  component. According to the characteristics of the two components of PHBV/PES blends, the isothermal crystallization of PHBV was first studied at 95 °C followed by the isothermal crystallization of PHBV at 70 °C as described in the Section 2. The exothermic curves of heat flow as a function of time were recorded and investigated. The plots of relative crystallinity  $X_t$  versus the crystallization time  $t$  are shown in Fig. 6a for the isothermal crystallization of PHBV at 95 °C for neat and PHBV-rich blends. It is found that the crystallization time for PHBV to finish crystallization at 95 °C becomes longer with increasing the PES content in the blends. Crystallization of neat PHBV finished within 45 min. However, in the case of a 60/40 blend the crystallization rate of PHBV was so slow that the time for PHBV to finish crystallization was around 75 min. The well-known Avrami equation is often used to analyze the isothermal crystallization kinetics; it assumes the development of the relative degree of crystallinity with crystallization time  $t$  as

$$1 - X_t = \exp(-kt^n) \quad (1)$$

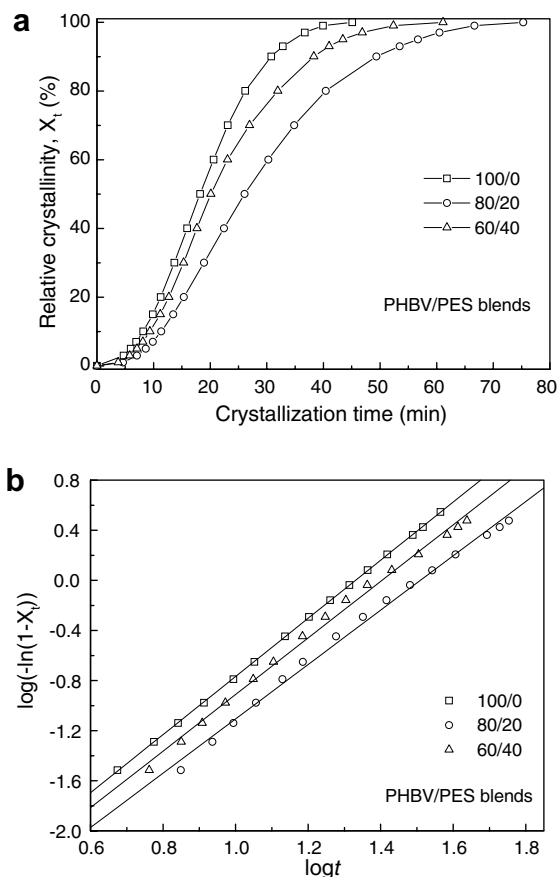


Fig. 6. (a) Development of relative crystallinity  $X_t$  with crystallization time  $t$  of PHBV crystallization at 95°C for neat and PHBV-rich blends and (b) the related Avrami plots of PHBV crystallization.

where  $n$  is the Avrami exponent depending on the nature of nucleation and growth geometry of the crystals, and  $k$  is a composite rate constant involving both nucleation and growth rate parameters [29]. Fig. 6b shows the Avrami plots of the crystallization of PHBV at 95 °C for neat and PHBV-rich blends. The Avrami parameters  $n$  and  $k$  are obtained from the plots of  $\log(-\ln(1 - X_t))$  versus  $\log t$ . The values of Avrami exponents  $n$  and crystallization rate constants  $k$  are listed in Table 1.

It can be seen from Table 1 that the average values of the Avrami exponent  $n$  are around 2.3 for the isothermal crystallization of the neat and blended PHBV. The almost unchanged Avrami exponent  $n$  with the addition of PES indicates that the crystallization mechanism of PHBV is not affected by the presence of PES in the blends. The crystallization rate constant  $k$  of blended PHBV is lower than that

Table 1

The crystallization kinetics parameters of PHBV for neat and PHBV-rich blends after isothermal crystallization at 95 °C

PHBV/PES blends	$n$	$k$ ( $\text{min}^{-n}$ )	$t_{0.5}$ (min)	$1/t_{0.5}$ ( $\text{min}^{-1}$ )
100/0	2.3	$8.16 \times 10^{-4}$	18.77	$5.33 \times 10^{-2}$
80/20	2.2	$5.32 \times 10^{-4}$	26.05	$3.84 \times 10^{-2}$
60/40	2.3	$6.75 \times 10^{-4}$	20.39	$4.90 \times 10^{-2}$

of neat PHBV, indicating that the addition of PES retards the crystallization of PHBV. However, the crystallization rate  $k$  of PHBV in the blends can not be correlated to the PES content in a simple way. The value of  $k$  for the 80/20 blend is lower than that of neat PHBV. With further increasing PES content, the value of  $k$  for the 60/40 blend also increases and higher than that of the 80/20 blend but still low than that of neat PHBV. However, roughly speaking the difference in the crystallization

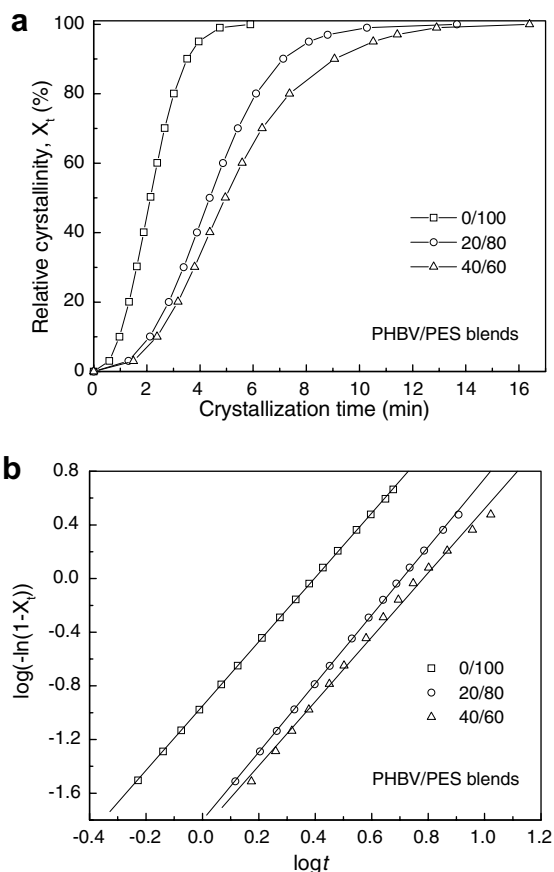


Fig. 7. (a) Development of relative crystallinity  $X_t$  with crystallization time  $t$  of PES crystallization at 70 °C after crystallization of PHBV at 95 °C for neat and PES-rich blends and (b) the related Avrami plots of PES crystallization.



rates of PHBV in the blends is not so significant. In the previous section the spherulitic morphology and growth rates of neat and blended PHBV were studied by POM. It was also found that the spherulitic growth rate of PHBV was almost unchanged irrespective of blending with PES. However, it was found that the nucleation of PHBV in the blends was lower than that of neat PHBV, indicating that the presence of PES melt restricted the nucleation of PHBV. Such results are consistent with the values of  $k$  in PHBV/PES blends studied by DSC.

The half-life crystallization time  $t_{0.5}$ , the time required to achieve 50% of the final crystallinity of the samples, is an important parameter for the discussion of crystallization kinetics. Usually, the crystallization rate is described as the reciprocal of  $t_{0.5}$ . The value of  $t_{0.5}$  is calculated by the following equation:

$$t_{0.5} = (\ln 2/k)^{1/n} \quad (2)$$

where  $k$  and  $n$  are the same as in the Avrami equation. The values of  $t_{0.5}$  and  $1/t_{0.5}$  for the neat and blended PHBV are calculated and are also listed in Table 1. The results further indicate that the addition of PES reduces apparently the crystallization rate of PHBV in the blends compared to that of neat PHBV, but the different content of the PES does not make a significant difference in the crystallization rate of PHBV in the blends.

Table 2

The crystallization kinetics parameters of PES for neat and PES-rich blends crystallized at 70 °C after crystallization of PHBV at 95 °C for 100 min

PHBV/PES blends	$n$	$k$ (min <sup>-n</sup> )	$t_{0.5}$ (min)	$1/t_{0.5}$ (min <sup>-1</sup> )
0/100	2.4	$1.12 \times 10^{-1}$	2.14	0.415
20/80	2.5	$1.58 \times 10^{-2}$	4.41	0.227
40/60	2.4	$1.34 \times 10^{-2}$	5.21	0.192

The isothermal crystallization of low- $T_m$  component PES at 70 °C was also studied by DSC and analyzed by the Avrami equation for neat and PES-rich blends. The crystallization process of PES is shown in Section 2 in detail. Fig. 7a shows the plots of relative crystallinity as a function of crystallization time for the neat and blended PES samples. With the increase of the PHBV content, the crystallization time of PES becomes longer. Fig. 7b shows the Avrami plots of the neat and blended PHBV samples. From the straight lines of the Avrami plots, the Avrami exponent  $n$  and crystallization rate constant  $k$  are obtained and listed in Table 2. Furthermore, the values of  $t_{0.5}$  and  $1/t_{0.5}$  are also calculated and shown in Table 2. It is found that the Avrami exponent  $n$  is almost the same for the three samples and varies slightly around 2.4, indicating that the presence of PHBV does not change the crystallization mechanism of PES. On the other hand, the crystallization rate of PES

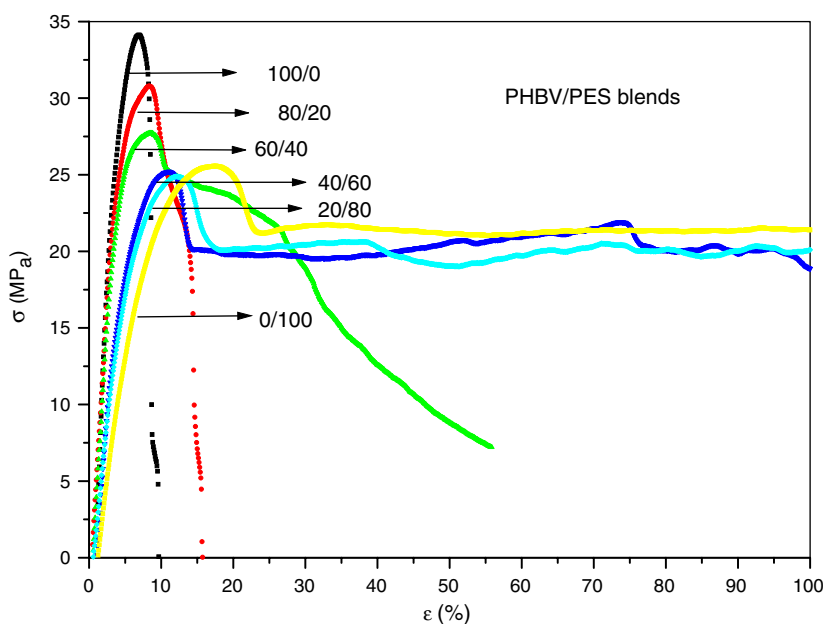


Fig. 8. Typical stress–strain curves for PHBV/PES blends.

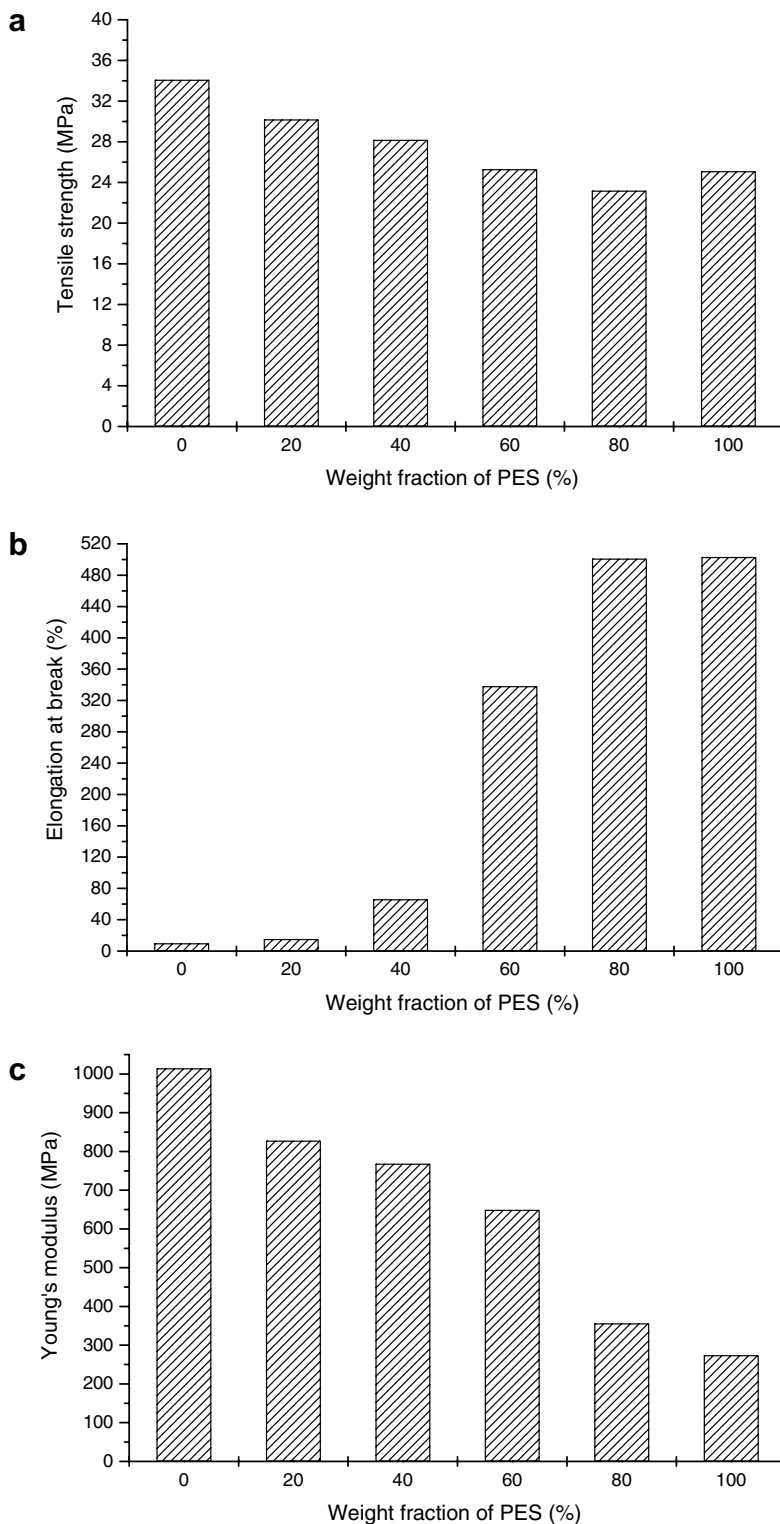


Fig. 9. Mechanical properties of PHBV/PES blends: (a) tensile strength, (b) elongation at break and (c) Young's modulus.

decreases with increasing the PHBV content. The slow-down of the crystallization rate of PES may be explained as follows. In this work both PHBV and PES are both crystalline polymers. From the above studies, PHBV and PES are immiscible. For the crystallization of high- $T_m$  component PHBV at 95 °C, PHBV crystallizes in the presence of the phase separated melt of PES; however, in the case of the crystallization of low- $T_m$  component PES at 70 °C, PES must crystallize in the presence of PHBV crystals formed previously at 95 °C. It is expected that the presence of the PHBV crystals may have two different influences on the crystallization of PES. One is the possible positive effect on the nucleation of PES spherulites. The other is the possible negative effect on the crystal growth of PES spherulites. The slow-down of the crystallization rate of PES arises from the competition between the two opposite effects. The effect of the presence of the PHBV crystals on the spherulitic growth of PES may play a dominant role during the crystallization of PES, resulting in the fact that the crystallization rate of PES decreases with increasing the PHBV content in the blends. Conclusively, the crystallization mechanisms of PHBV and PES do not change in the blends; however, the crystallization rate of each component decreases in the blends with the addition of the other component.

### 3.4. Mechanical properties

The aforementioned results indicate that PHBV and PES are immiscible and crystallize separately in the blends. In this work tensile test experiments were also carried out in order to investigate the effect of blending with PES on the mechanical properties of PHBV. Fig. 8 shows the typical stress–strain curves of PHBV/PES blends. From Fig. 8, the mechanical properties of PHBV/PES blends were determined. The values of Young's modulus of PHBV/PES blends, obtained from the slopes of the stress–strain curves, decrease with increasing PES content. The values of tensile strength also decrease with increasing PES content in the blends. On the other hand, the elongation at break and the toughness increased with increasing PES content in the blends. Fig. 9 demonstrates the mechanical properties of PHBV/PES blends in detail. Neat PHBV has a tensile strength of 34.1 MPa, an elongation at break of 10.0% and a Young's modulus of 1014.7 MPa. On the other hand, neat PES has a tensile strength of 25.1 MPa, an elongation at break of 503.3% and a

Young's modulus of 274.4 MPa. Comparing the mechanical properties of the two neat components, it can be found that they have comparable values of tensile strength. Furthermore, PHBV has a very high Young's modulus with rather low elongation at break, while PES has a very low Young's modulus with rather high elongation at break. Therefore, it is expected that the mechanical properties of PHBV/PES blends can be adjusted by tuning the blend composition to meet some practical application. The Young's modulus of neat PHBV is around 1015 MPa and decreases steadily to be around 828 and 768 MPa for PHBV-rich blends, namely, PHBV/PES 80/20 and 60/40. On the contrary, the Young's modulus of neat PES is around 274 MPa, and increases to be around 356 and 649 MPa for PES-rich blends, namely, PHBV/PES 20/80 and 40/60. Moreover, it should be noted that the elongation at break of PHBV/PES blends increases significantly with respect to that of neat PHBV. The elongation at break is only around 10.0% for neat PHBV, increases to be around 15.4% for a PHBV/PES 80/20 blend, and further increases tremendously to be around 66.2% for a PHBV/PES 60/40 blend. It is clear that the elongation at break of PHBV increases by around 0.5 and 5 times in the PHBV-rich blends (i.e., PHBV/PES 80/20 and 60/40 blend compositions). However, the Young's modulus of PHBV only decreases by 18% and 24%. The practical application of PHBV is thus expected to extend, especially in some cases where excellent mechanical properties are required.

## 4. Conclusions

In this work fully biodegradable polymer blends have been prepared by blending PHBV with PES. Phase morphology, crystal structure, crystallization behavior, and mechanical properties of PHBV/PES blends were investigated by DSC, POM, WAXD, and tensile tests in detail. It is found that PHBV is immiscible with PES as evidence by the two composition independent glass transition temperatures and the biphasic melt. Crystallization of PHBV/PES blends was studied by DSC using two-step crystallization condition and analyzed by the Avrami equation. The crystallization rates of PHBV and PES decrease with increasing the content of the other component; however, the crystallization mechanisms do not change. The mechanical properties study indicates that tensile strength, elongation at break and Young's modulus of PHBV/PES blends can be adjusted by changing blend composition.

Blending some amount of PES can improve the elongation at break significantly while still keeping considerably high tensile strength and Young's modulus for the PHBV-rich blends. Such improvement is expected to be of great importance to the practical application of PHBV in some fields, where excellent mechanical properties are necessary.

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