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Miscibility and crystallization behaviour of biodegradable blends of two aliphatic polyesters. Poly(3-hydroxybutyrate-*co*-hydroxyvalerate) and poly(butylene succinate) blends

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Abstract

Blends of poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) and poly(butylene succinate) (PBSU), both biodegradable semicrystalline polyesters, were prepared with the ratio of PHBV/PBSU ranging from 80/20 to 20/80 by co-dissolving the two polyesters in chloroform and casting the mixture. Differential scanning calorimetry (DSC) and optical microscopy (OM) were used to study the miscibility and crystallization behaviour of PHBV/PBSU blends. Experimental results indicate that PHBV is immiscible with PBSU as shown by the almost unchanged glass transition temperature and the biphasic melt. Crystallization of PHBV/PBSU blends was studied by DSC using two-step crystallization and analyzed by the Avrami equation. The crystallization rate of PHBV decreases with the increase of PBSU in the blends while the crystallization mechanism does not change. In the case of the isothermal crystallization of PBSU, the crystallization mechanism does not change. The crystallization rate of PBSU in the blends is lower than that of neat PBSU; however, the change in the crystallization rate of PBSU was not so big in the blends. The different content of the PHBV in the blends does not make a significant difference in the crystallization rate of PBSU.

Keywords: Poly(3-hydroxybutyrate-*co*-hydroxyvalerate)/poly(butylene succinate) blends; Miscibility; Crystallization

1. Introduction

Biodegradable polymers have received considerable attention in the last two decades due to their potential applications in the fields related to human life such as environmental protection and ecology. According to the difference in the preparation methods, biodegradable polymers can be classified into two types. One is the biosynthetic polymers, such as bacterial polyhydroxyalkanoates (PHAs). Among them poly(hydroxybutyrate) (PHB) is probably the most extensively studied biodegradable thermoplastic polymer. PHB is a truly biodegradable 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 the literature. Miscible blends have been prepared by mixing PHB with poly(vinyl acetate), poly(epichlorohydrin), poly(vinyl phenol), poly(vinylidene fluoride) and poly(ethylene oxide) [2–6]. On the other hand, PHB was known to be immiscible with poly(-caprolactone), poly(cyclohexyl methacrylate), poly(hydroxyoctanoate), high molecular weight poly(L-lactide) and poly(methylene oxide) [7–11]. In our previous work, the miscibility and crystallization behaviour of PHB/poly(vinylidene chloride-*co*-acrylonitrile) (P(VDC-AN)) blends were investigated by differential scanning calorimetry and optical microscopy [12]. On the other hand, another method to improve the mechanical and other physical properties of PHB is the

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development of copolymers of PHB. Among such copolymers, poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) is characterized by better impact resistance and offer 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 miscibility, properties and biodegradability of blends containing either PHB or PHBV, respectively [14,15].

The other type of biodegradable polymers is the chemosynthetic polymers, such as the linear aliphatic polyesters. Poly(butylene succinate) (PBSU) is just one of them. The crystal structure, crystallization and melting behaviour of PBSU have been reported in the literature [16–19]. PBSU was found to be miscible with poly(vinylidene fluoride) and poly(vinylidene chloride-*co*-vinyl chloride) in our previous work [20,21]. Recently, we have studied the miscibility, crystallization and melting behaviour of PBSU blended with poly(ethylene oxide) (PEO) [22,23]. It was found that PBSU was miscible with PEO as shown by the existence of single composition dependent glass transition temperature over the entire composition range. In addition, the polymer–polymer interaction parameter, obtained from the melting depression of the high-T_m component PBSU using the Flory–Huggins equation, was composition dependent, and its value was always negative. The double melting behaviour of isothermally crystallized PBSU blended with PEO was ascribed to the melting and recrystallization model. The miscibility and nonisothermal crystallization in PHB/PBSU blends were also studied in our recent work by differential scanning calorimetry and optical microscopy [24]. It was found that PBSU showed no miscibility with PHB for almost all the blend composition studied, except that PHB showed limited miscibility with PBSU for PHB/PBSU 20/80 blend.

Blends in which both components are crystalline polymers have received much less attention than fully amorphous or amorphous/crystalline systems. Only a small number of works have been reported on the miscible polymer blends of two crystalline polymers with different chemical structures till now, and they may be of considerable technological interest and offer the possibility of investigating crystallization and morphological behaviour related to blend miscibility [25–30]. On the other hand, it is also possible to determine how the crystallinity of one component affects the crystallization process of the other in the case of binary immiscible blends of two crystalline polymer [31,32].

In this work, we studied the miscibility and crystallization behaviour of PHBV/PBSU blends on the basis of our previous work of PHB/PBSU blends. Similar to PHB/PBSU blends, both of the components are crystalline and biodegradable in PHBV/PBSU blends. PHBV is a biosynthetic polymer, while PBSU is a chemosynthetic polymer. To the best of our knowledge, no attention has been paid to the blending of PHBV and PBSU till now in the literature. It is important to understand their miscibility and the crystallization behaviour in a cooling process as a model case of processing a biodegradable crystalline polymer blend material. However, an experimental study is not straightforward to conduct because of the dynamic interplay between crystallization and phase separation, or due to crystallization in phase-separated domain structures. In the present paper, the results of an investigation concerning the miscibility, nonisothermal crystallization, subsequent melting behaviour and isothermal crystallization kinetics study of PHBV/PBSU blends were reported.

2. Experimental

PBSU ($M_w = 140,000$) was supplied by Showa High Polymer Co., Ltd, and PHBV ($M_w = 454,000$, $M_n = 153,000$ and $HV\% = 14$) was purchased from Aldrich Chemical Company Inc. PHBV/PBSU 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. The solvent was allowed to evaporate in a controlled air stream for 1 day and the resulting films were further dried in vacuum at 50 °C for 3 days. In this way, blends were prepared with various compositions ranging from 80/20 to 20/80 in weight ratio, the first number referring to PHBV.

Thermal analysis was performed using a TA Instruments differential scanning calorimetry 2910 with a Thermal Analyst 2000. The glass transition temperatures and melting point temperatures of the melt-quenched PHBV/PBSU blends were measured at a heating rate of 20 °C/min. The samples were first annealed at 200 °C for 3 min to destroy any thermal history and subsequently quenched into liquid nitrogen.

Two different procedures were employed to study the crystallization behaviour of PHBV/PBSU blends:

1. *Nonisothermal crystallization*. The cast samples were first heated to 200 °C at 20 °C/min (first heating), held at 200 °C for 3 min to destroy any thermal history, cooled to 0 °C at 5 °C/min(first cooling), and then heated to 200 °C at 20 °C/min(second heating).
2. *Isothermal crystallization*. The samples were quenched to 95 °C to crystallize PBSU for some time until the completion of the crystallization of PBSU after being held at 200 °C for 3 min to destroy any thermal history, and then quenched to 60 °C to crystallize PHBV.

The above mentioned isothermal crystallization conditions consist of the following two steps, namely, the isothermal crystallization of the PBSU phase from the melt at 95 °C, and the isothermal crystallization of the PHBV from the liquid phase in the presence of previously crystallized PBSU at 60 °C. In the case of PHBV/PBSU blends, the isothermal two-step crystallization described above is possible because PBSU and PHBV need very different supercooling to crystallize and the difference in the crystallization rate is very large.

A polarizing microscopy (Olympus BHA-P) with a temperature controller (Linkam LK-600PM) was used to study the miscibility and morphology of PHBV/PBSU blends.

3. Results and discussion

3.1. Study of miscibility of PHBV/PBSU blends based on the glass transition temperature by DSC

Miscibility between the two components plays an important role on the morphology, thermal properties, mechanical properties and biodegradability for the PHBV/PBSU blends. Therefore, the miscibility of PHBV/PBSU blends was first studied by DSC for the melt-quenched samples at a heating rate of 20 °C from the amorphous state. As introduced in Section 2, the PHBV/PBSU blend samples were first annealed at 200 °C for 3 min to destroy any thermal history and then quenched into liquid nitrogen.

Fig. 1 shows the DSC traces of PHBV/PBSU blends. Neat PHBV exhibits a glass transition at −1 °C, an exothermic cold crystallization peak at 69 °C, and two endothermic melting peaks at 132 and 150 °C, respectively. Neat PBSU exhibits a glass transition at −34 °C, an exothermic cold crystallization peak at −5 °C, and an endothermic melting peak at 118 °C. PHBV/PBSU blends show one distinct T_g in DSC measurements at about −35 °C, which is almost unchanged and close to that of neat PBSU. However, the T_g of PHBV cannot be observed in PHBV/PBSU blends since it is actually masked by the cold crystallization of PBSU in PHBV/PBSU blends. The cold crystallization of PHBV is found to shift to high temperature upon the addition of PBSU in the PHBV/PBSU blends compared to that of neat PHBV. For example, the cold crystallization temperature of PHBV is at ca. 88 °C for 80/20 blend, almost 20 °C higher than that of neat PHBV. On the other hand, the cold crystallization temperature of PBSU in the PHBV/PBSU blends does not change so significantly as that of PHBV. With the addition of PHBV, the cold crystallization temperature of PBSU is found to decrease slightly at first for 20/80 blend, and then increase slightly with the increase of PHBV. Finally, the cold crystallization temperature of PBSU is found at ca. 1 °C for 80/20 blend, almost 6 °C higher than that of neat PBSU. The melting endotherms of PBSU and PHBV overlap each other in the PHBV/PBSU blends since the melting point temperatures of the two components are too close. The melting endothermic peak temperature of PBSU in the PHBV/PBSU blends is found to be around 115 °C, which seems unchanged with the PHBV blend composition and 3 °C lower than that of neat PBSU. On the other hand, the melting endotherms of PHBV seem unchanged with the addition of the PBSU content in the PHBV/PBSU blends. But it should be noted that the melting endotherms of PHBV in 20/80 blend cannot be observed when it is heated at a heating rate of 20 °C/min for the melt-quenched sample from the amorphous state, indicating that the crystallization of PHBV is hindered by the presence of the high PBSU content. The above results lead us to the conclusion that PHBV shows no miscibility with PBSU at all with PBSU in the amorphous state for the PHBV/PBSU blends.

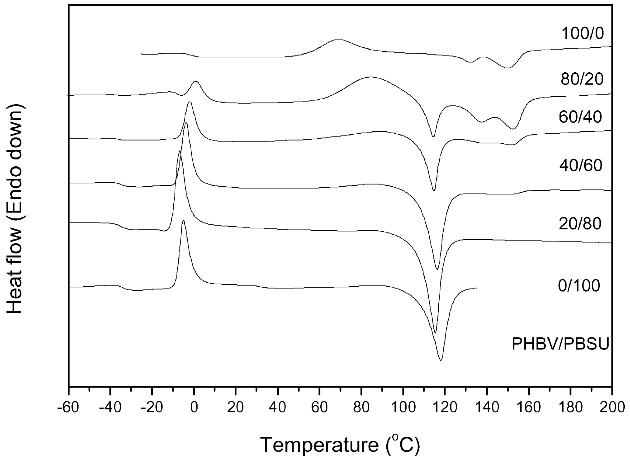


Fig. 1. DSC traces of PHBV/PBSU blends after melt quenching at a heating rate of 20 °C/min.

3.2. Nonisothermal crystallization study by DSC

DSC measurements were also performed to characterize the nonisothermal crystallization from the melt and melting behaviour of PHBV/PBSU blends. The samples were subjected to the thermal treatment as described in Section 2. Fig. 2 shows the DSC traces of neat PHBV, neat PBSU and PHBV/PBSU blends for the cast samples at a heating rate of 20 °C/min. Fig. 3 shows the DSC traces of PHBV/PBSU

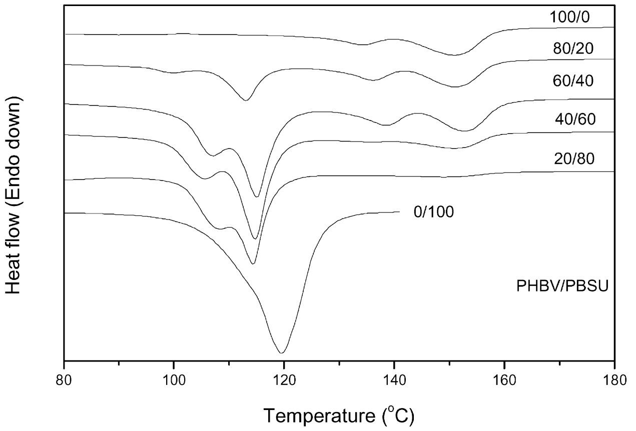


Fig. 2. The first melting behavior of PHBV/PBSU blends for the cast samples at a heating rate of 20 °C/min.

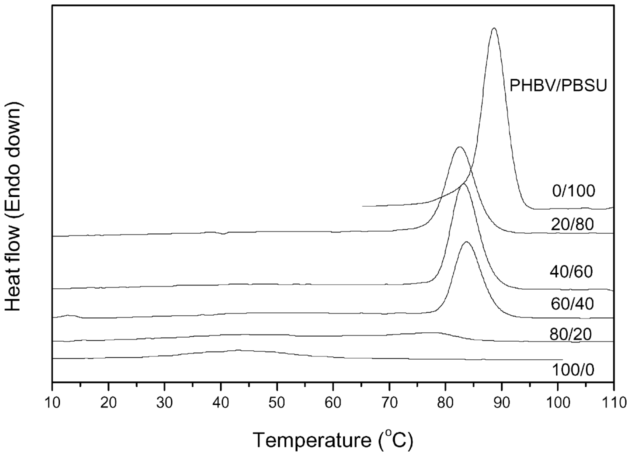


Fig. 3. Nonisothermal crystallization behavior for PHBV/PBSU blends cooled from the melt at a cooling rate of 5 °C/min.

blends at a cooling rate of 5 °C/min from the melt. Fig. 4 shows the DSC traces of PHBV/PBSU blends at a heating rate of 20 °C/min after cooling from the melt at 5 °C/min.

First we studied the melting behaviour of PHBV/PBSU blends for the cast samples at a heating rate of 20 °C/min. The cast samples were prepared by casting the chloroform solution of the PHBV/PBSU blends and removing the chloroform solvent at vacuum oven at 50 °C for 3 days. As shown in Fig. 2, neat PBSU exhibits the T_m as a well-defined peak around 120 °C. However, there are two endothermic peaks or one main endothermic peak with one shoulder corresponding to the melting behaviour of PBSU in the PHBV/PBSU blends. The low endothermic melting temperature (or the shoulder) is found to shift to the high temperature range with the decrease of the PHBV content in the PHBV/PBSU blends, while the high endothermic melting peak (or the main melting peak) is almost unchanged with the change of the PHBV content, and locates around 115 °C, almost 5 °C lower than that of neat PBSU. Meanwhile, it is found that the ratio of area of the endothermic melting peak at low temperature to that of the endothermic melting at high temperature increases with the decrease of the PHBV content in the PHBV/PBSU blends. The above results indicate that the double melting endotherms behaviour of PBSU may arise from the melting and recrystallization mechanism [23]. On the other hand, both neat and blended PHBV show double melting endotherms. The melting endotherm at low temperature shifts to high temperature with the increase of the PBSU content in the PHBV/PBSU blends, while the melting endotherm at high temperature seems not to vary with change of PBSU.

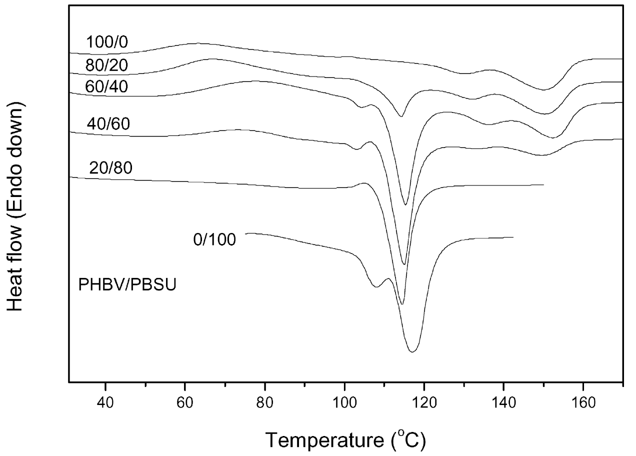


Fig. 4. Subsequent melting behaviour of PHBV/PBSU blends at a heating rate of 20 °C/min after nonisothermal crystallization at a cooling rate of 5 °C/min.

Shown in Fig. 3 is the crystallization behaviour of PHBV/PBSU blends which were cooled from the crystal-free melt at a cooling rate of 5 °C/min. Both neat PHBV and neat PBSU exhibit the crystallization exotherm as a well-defined peak on cooling from the melt at 5 °C/min. The crystallization peak temperature (T_c) of neat PHBV locates at around 43 °C, while the T_c of neat PBSU locates at around 89 °C. The T_c of neat PHBV is lower than that of neat PBSU, although the melting point temperature (T_m) of PHBV is higher than that of PBSU. The above results may be related to the following facts that PHBV is a biosynthetic biodegradable polymer while PBSU is a chemosynthetic biodegradable polymer. The difference in the preparation methods between PHBV and PBSU results in that PHBV lacks the impurities required for the nucleation of the crystallization compared with PBSU. Consequently, the T_c of PBSU is higher than that of PHBV due to the presence of the considerable amount of the impurities. Compared to the T_c of neat PBSU at around 89 °C, the T_c of PBSU in the PHBV/PBSU blends is found to shift to low temperature and vary slightly at around 83 °C with the addition of the PHBV content up to 60 weight percent. However, the T_c of PBSU decreases to around 78 °C for 80/20 blend, indicating that the crystallization of PBSU is restricted by the presence of high PHBV content. The T_c of neat PHBV is at around 43 °C upon cooling from the melt at 5 °C/min. With the addition of PBSU content up to 60 weight percent, the T_c of PHBV varies slightly around 43 °C in the PHBV/PBSU blends. However, the T_c of PHBV cannot be detected for 20/80 blend, indicating that the crystallization of PHBV is hindered in the presence of high PBSU content. The above results confirm again that the crystallizability of PHBV is weaker than that of PBSU.

The subsequent melting behaviour of PHBV/PBSU blends was also investigated by DSC at a heating rate of 20 °C/min after the completion of nonisothermal crystallization at 5 °C/min from the melt. The cold crystallization temperature of neat PHBV can still be observed upon heating to the melt after nonisothermal crystallization from the melt at 5 °C/min, indicating that the crystallizability of PHBV is very weak and most of the melt of PHBV does not crystallize and becomes the amorphous part upon cooling. The cold crystallization temperature of PHBV can still be found with the addition of the PBSU content up to 60 weight percent and varies slightly around 70 °C. In the case of 20/80 blend the cold crystallization temperature of PHBV disappears, and only the melting endotherm of PBSU can be observed, indicating that the crystallization of PHBV is suppressed by the presence of high content PBSU. In the other blends, three melting endotherms appear corresponding to the melting endotherms of PBSU and PHBV, respectively, which is similar to the melting behaviour of PHBV/PBSU blends upon heating from the amorphous state for the melt-quenched samples as shown in Fig. 1. Neat PBSU shows double melting endotherms, which may arise from the melt-recrystallization mechanism.

3.3. Isothermal crystallization study by DSC

The isothermal crystallization of PHBV/PBSU blends was also studied by DSC in this work. In the literature, two-step crystallization was often used to study the isothermal crystallization of binary blends of two semicrystalline polymers whether in miscible or immiscible blends [22, 33]. In our previous work, the isothermal crystallization of poly(ethylene oxide) (PEO)/poly(ε-caprolactone) (PCL) was studied using two-step crystallization procedures by DSC, namely the isothermal crystallization of PEO at 52 ° followed by that of PCL at 40 °C [33].

In the present work PHBV and PBSU are both semicrystalline biodegradable polyesters, with the T_m of PHBV higher than that of PBSU. However, the T_c of PBSU is prior to that of PHBV upon cooling from the melt, indicating that the crystallizability of PHBV is weaker than that of PBSU. Meanwhile, the T_ms of the two components are very close to each other although the T_m of PHBV is a little higher than that of PBSU. Therefore, no attempts have been made to crystallize PHBV above the T_m of PBSU. According to the characteristics of the two components of PHBV/PBSU blends, the isothermal crystallization of PBSU was first studied at 95 °C followed by the isothermal crystallization of PHBV at 60 °C as introduced in 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. 5a for the isothermal crystallization of the neat and blended PBSU at 95 °C. Compared with that of neat PBSU, the crystallization time for PBSU to finish the crystallization at 95 °C becomes longer after the addition of the PHBV content in the PHBV/PBSU blends. Crystallization of PBSU finished within 16 min with the addition of the PHBV content up to 60%. However, in the case of 80/20 blend the crystallization rate of PBSU was very slow and the crystallization time was more than 240 min due to the low PBSU content. It seems that the crystallization of PBSU occurred at the early stage of the crystallization process followed by the crystallization of PHBV at the late stage. The crystallization of PBSU and that of PHBV cannot be separated in this case. Therefore, we cannot study the two-step crystallization of PHBV/PBSU blends for 80/20 blend.

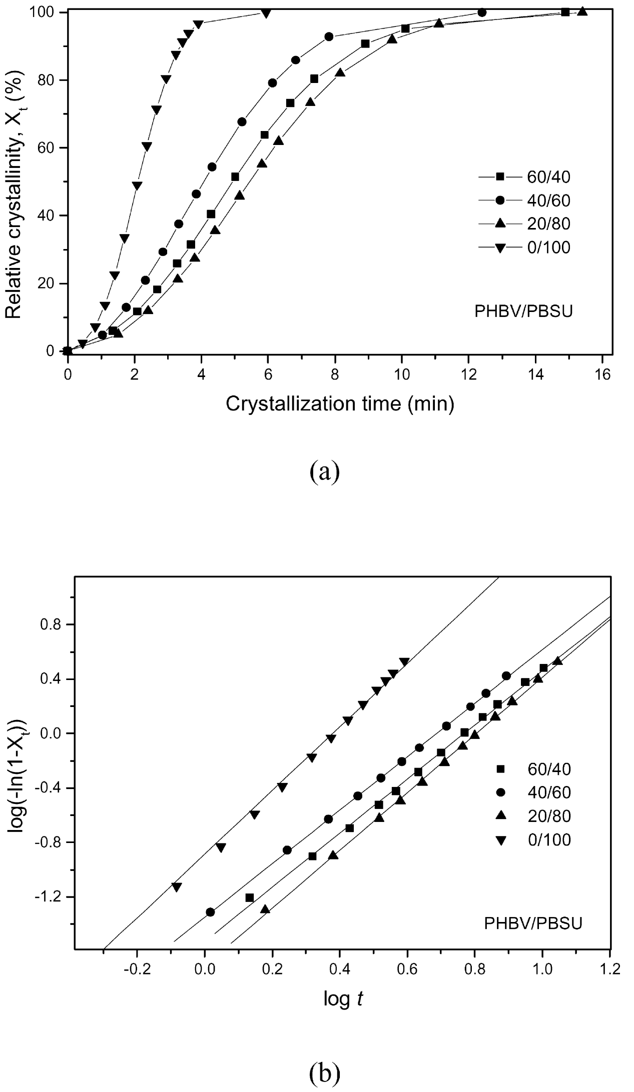


Fig. 5. (a) The plots of relative crystallinity X_t versus crystallization time t of the PBSU crystallization at 95 °C for PHBV/PBSU blends, and (b) the Avrami plots of the PBSU crystallization at 95 °C for PHBV/PBSU blends.

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

$$1 - X_t = \exp(-kt^n) \tag{1}$$

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 [34]. The Avrami parameters n and k are obtained from the plots of $\log(-\ln(1 - X_t))$ versus $\log t$ as shown in Fig. 5b. The Avrami exponents n and crystallization rate constants k of the neat and blended PBSU are listed in Table 1.

It can be seen from Table 1 that the average value of the Avrami exponent n is around 2.1 for the isothermal crystallization of the neat and blended PBSU. The almost unchanged Avrami exponent n with the addition of PHBV

Table 1
Crystallization kinetic parameters of PBSU in PHBV/PBSU blends at 95 °C

PHBV/PBSU	n	k (min^{-n})	$t_{0.5}$ (min)	$1/t_{0.5}$ (min^{-1})
0/100	2.34	1.29×10^{-1}	2.05	0.488
20/80	2.12	1.96×10^{-2}	5.37	0.186
40/60	1.97	4.46×10^{-2}	4.04	0.248
60/40	1.99	2.97×10^{-2}	4.88	0.205

indicates that the crystallization mechanism of PBSU is not affected by the presence of PHBV in PHBV/PBSU blends. The crystallization rate constant k of blended PBSU is lower than that of neat PBSU, indicating that the addition of PHBV retards the crystallization of PBSU. However, the crystallization rate k of PBSU in the blends cannot be correlated to the PHBV content in a simple way. The value of k of 20/80 is lower than that of neat PBSU. With the increase of the PHBV content, the value of k of 40/60 still decreases. However, with still the increase of PHBV the value of k of 60/40 increases and it is higher than that of 40/60 blend though it is lower than that of 20/80 blend. It is expected that the value of k will be the lowest for 20/80 blend although the exact value cannot be calculated. But roughly speaking the difference in the crystallization rate of PBSU is not so big, and the content of PHBV does not exert a significant influence on the crystallization rate of PBSU in the blends.

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:

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

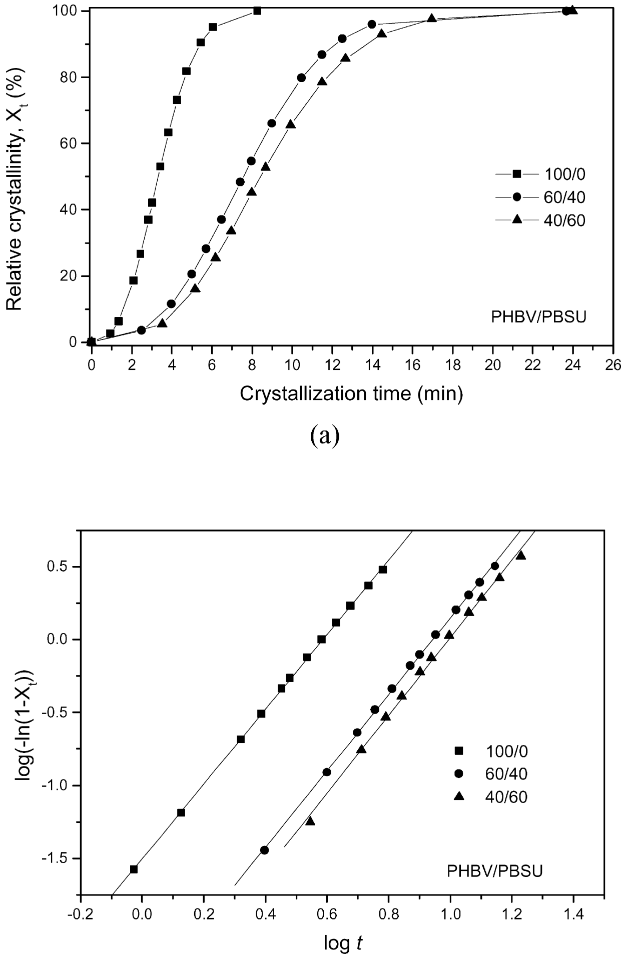
where k and n are the same as in the Avrami equation. The values of $t_{0.5}$ and $1/t_{0.5}$ for the neat and blended PBSU were calculated and are also listed in Table 1. The value of $t_{0.5}$ for neat PBSU is around half of those for the blended PBSU; however, the difference in the values of $t_{0.5}$ of the blended PBSU is not so big. On the other hand, the value of $1/t_{0.5}$ for neat PBSU is more than two times than those for the blended PBSU, and the difference in the values of the $1/t_{0.5}$ for blended PBSU is not so big. The above results indicate that the addition of PHBV reduces apparently the crystallization rate of PBSU in the blends compared to that of neat PBSU, but the different content of the PHBV does not make a significant difference in the crystallization rate of PBSU in the blends.

The slow-down of the crystallization rate of PBSU in the blends may be related to the following two reasons. One possible reason is the presence of the PHBV suppresses the nucleation of the PBSU in the blends. In other words, the presence of PHBV has a negative effect on the primary nucleation of PBSU. The number of heterogeneous primary nuclei of PBSU may decrease with the addition of PHBV in the blends because of the migration of heterogeneity from PBSU to PHBV. Similar results were also recently reported on the crystallization behaviour of PHBV/PCL blends [35]. Similar to PHBV/PBSU blends of this study, PHBV and PCL are both biodegradable semicrystalline polyesters. The crystallization rate of PHBV decrease with the addition of PCL since PCL has a negative effect on the primary nucleation of PHBV. Another possible reason of the slow-down of the crystallization rate of PBSU may be considered to occur from a physical restriction to the growth of PBSU spherulites by the PHBV domains due to the not large phase separation between PBSU and PHBV [36]. Conclusively the presence of PHBV in the PHBV/PBSU blends does not change the crystallization mechanism of PBSU, but reduces the crystallization rate of PBSU in the blends compared with neat PHBV when they crystallized isothermally at a given crystallization temperature.

The isothermal crystallization of PHBV at 60 °C was also studied by DSC and analyzed by the Avrami equation in PHBV/PBSU blends after the samples were held at 95 °C to finish the crystallization of PBSU. As mentioned above, the crystallization of PBSU and PHBV could not be separated at 95 for 80/20 blend, namely the crystallization of PHBV had occurred at 95 °C so that it did not crystallize any more upon cooling the crystallization temperature to 60 °C. On the other hand, PHBV did not show any traces to crystallize for 20/80 blend upon cooling the crystallization temperature to 60 °C after the completion of PBSU crystallization at 95 °C, indicating that the crystallizability of PHBV was suppressed by the presence of PBSU due to the low content of PHBV. Similar results are also found that PHBV cannot crystallize for 20/80 blend when the samples are heated from the amorphous state after melt-quenching (Fig. 1) or the samples are cooled from the melt at 5 °C/min (Fig. 3) and then heated to the melt (Fig. 4). In both cases, the melting point temperatures of PHBV cannot be observed, indicating the absence of the crystallization of PHBV. Therefore, we can only present here the results of PHBV crystallization at 60 °C for neat PHBV, 60/40 and 40/60 blend samples. Shown in Fig. 6a are the plots of relative crystallinity as a function of crystallization time for the neat and blended PHBV samples. With the increase of the PBSU content, the crystallization time of PHBV becomes longer. Fig. 6b 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 were obtained and listed in Table 2. Furthermore, the values of

Table 2
Crystallization kinetic parameters of PHBV in PHBV/PBSU blends at 60 °C

PHBV/PBSU	n	k (min^{-n})	$t_{0.5}$ (min)	$1/t_{0.5}$ (min^{-1})
100/0	2.57	3.13×10^{-2}	3.35	0.299
60/40	2.63	3.34×10^{-3}	7.63	0.131
40/60	2.67	2.22×10^{-3}	8.61	0.116



(a)

(b)

Fig. 6. (a) The plots of relative crystallinity X_t versus crystallization time t of the PHBV crystallization at 60 °C for PHBV/PBSU blends, and (b) the Avrami plots of the PBSU crystallization at 60 °C for PHBV/PBSU blends.

$t_{0.5}$ and $1/t_{0.5}$ were 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 2.6, indicating that the addition of PBSU does not the change the crystallization mechanism of PHBV. The crystallization rate of PHBV is found to decrease with the increase of PBSU. PHBV and PBSU are both crystalline polymers. From the above studies, PHBV and PBSU are immiscible. In the case of PBSU crystallization at 95 °C, PBSU crystallized in the presence of the phase separated melt of PHBV. However, in the case of PHBV crystallization at 60 °C, PHBV crystallized in the presence of PBSU crystals formed previously at 95 °C. The presence of the PBSU crystals may have two different influences on the crystallization of PHBV. One is the possible positive effect on the nucleation of PHBV spherulites. The other is the possible negative effect on the crystal growth of PHBV spherulites. The slow-down of the crystallization rate of PHBV may arise from the competition between the two opposite effects. The negative effect of the presence of the PBSU crystals on the spherulitic growth of PHBV seems to play a dominant role during the crystallization of PHBV. Conclusively, the crystallization mechanism of PHBV does not change with the addition of PBSU in the PHBV/PBSU blends; however, the crystallization rate of PHBV decreases with the increase of the PBSU content in the presence of the previously formed PBSU crystals at high temperature.

3.4. Optical microscopy study

Optical microscopy was also used to study the miscibility and crystallization behaviour of PHBV/PBSU blends. Provided that the refractive indices of the two components are not the same, it is possible to infer whether the melt is single-phased or biphasic. If PHBV is miscible with PBSU, the single-phased melt should be observed. Otherwise, if PHBV is immiscible with PBSU, the biphasic melt should be observed. PHBV/PBSU blends samples were first melted at 200 °C and then were observed by optical microscopy. For all the compositions studied, clearly defined biphasic separation was observed, indicating that PHBV is not miscible with PBSU in the melt. As an example, shown in Fig. 7 are the phase separation and crystallization of PHBV and PBSU for 60/40 blend observed by OM. Fig. 7a shows the bright spherulites of PBSU, which were crystallized at 90 °C from the crystal-free melt and dispersed in the dark matrix of PHBV melt. The crystallization rate of PBSU is higher than that of PHBV as introduced in the previous sections, so PHBV was still in the melt when PBSU crystallized at 90 °C. On cooling the sample to a low temperature, PHBV can also crystallize and coexists with the PBSU crystals. Fig. 7b shows the banded spherulites of PHBV, which were crystallized at 60 °C in the presence of the PBSU crystals formed at 90 °C. The PBSU spherulites are brighter than the PHBV sherulites. On heating the sample to 120 °C which is above the apparent T_m of PBSU but below that of PHBV, the PBSU spherulites disappeared, while only the banded PHBV spherulites still existed (Fig. 7c). In such a case, it is easier to conclude that the PHBV phase is the continuous phase while PBSU is the dispersed phase for 60/40 blend.

4. Conclusions

The miscibility of PHBV/PBSU blends was investigated by DSC and OM. PHBV was found to show no miscibility with PBSU at all, from the independence of the glass transition temperature and the phase separated melt. The crystallizability of PHBV is weaker than that of PBSU. The isothermal crystallization of PHBV/PBSU blends were studied using two-step crystallization process, the low melting point component with strong crystallizability PBSU at 95 °C and the high melting point component with weak crystallizability PHBV at 60 °C. The crystallization rate of PHBV decreases with the increase of PBSU in the blends

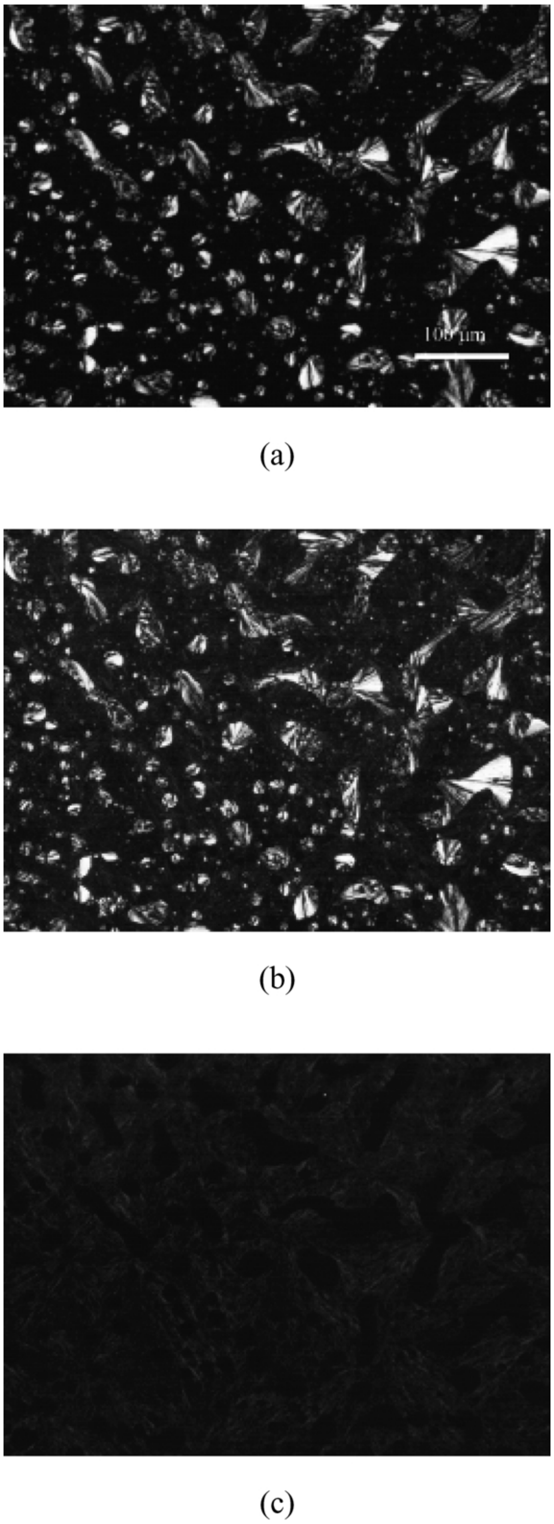


Fig. 7. OM micrographs (same magnification, bar = 100 μm) of PHBV/PBSU 60/40: (a) crystallization of PBSU at 90 °C, (b) crystallization of PHBV at 60 °C after completion of crystallization of PBSU at 90 °C, and (c) morphology of PHBV/PBSU 60/40 reheated above the melting point of PBSU while below that of PHBV.

while the crystallization mechanism does not change. The slow-down of the crystallization rate of PHBV may be considered to occur from a physical restriction to the growth by the PBSU crystals formed previously at high crystallization temperature. The crystallization mechanism of PBSU does not change with PHBV. The crystallization rate of PBSU in the blends is lower that of neat PBSU; however, the change in the crystallization rate of PBSU was not so big in the blends.

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