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Crystallization kinetics and morphology of poly(butylene succinate)/poly(vinyl phenol) blend

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Abstract

Biodegradable crystalline poly(butylene succinate) (PBSU) can form miscible polymer blends with amorphous poly(vinyl phenol) (PVPh). The isothermal crystallization kinetics and morphology of neat and blended PBSU with PVPh were studied by differential scanning calorimetry (DSC), optical microscopy (OM), wide angle X-ray diffraction (WAXD), and small angle X-ray scattering (SAXS) in this work. The overall isothermal crystallization kinetics of neat and blended PBSU was studied with DSC in the crystallization temperature range of 80–88 °C and analyzed by applying the Avrami equation. It was found that blending with PVPh did not change the crystallization mechanism of PBSU, but reduced the crystallization rate compared with that of neat PBSU at the same crystallization temperature. The crystallization rate decreased with increasing crystallization temperature, while the crystallization mechanism did not change for both neat and blended PBSU irrespective of the crystallization temperature. The spherulitic morphology and growth were observed with hot stage OM in a wide crystallization temperature range of 75–100 °C. The spherulitic morphology of PBSU was influenced apparently by the crystallization temperature and the addition of PVPh. The linear spherulitic growth rate was measured and analyzed by the secondary nucleation theory. Through the Lauritzen–Hoffman equation, some parameters of neat and blended PBSU were derived and compared with each other including the nucleation parameter (K_g), the lateral surface free energy (σ), the end-surface free energy (σ_e), and the work of chain folding (q). Blending with PVPh decreased all the aforementioned parameters compared with those of neat PBSU; however, the decrease extent was limited. WAXD result showed that the crystal structure of PBSU was not modified after blending with PVPh. SAXS result showed that the long period of blended PBSU increased, possibly indicating that the amorphous PVPh might reside mainly in the interlamellar region of PBSU.

Keywords: Poly(butylene succinate)/poly(vinyl phenol) blends; Crystallization kinetics; Morphology

1. Introduction

Biodegradable polymers have received much more attention in the last two decades due to their potential applications in the fields related to environmental protection and the maintenance of physical health. Poly(butylene succinate) (PBSU) is a linear aliphatic biodegradable polyester with the chemical structure of $-(OCH_2CH_2CH_2CH_2O_2CCH_2CH_2CO)-_n$. The crystal structure, crystallization and melting behaviour of PBSU have been reported [1–7]. The nonisothermal crystallization kinetics and subsequent melting behaviour of PBSU were studied in our recent works [8,9]. PBSU was found to be miscible with many polymers, including poly(vinylidene fluoride), poly(vinylidene chloride-*co*-vinyl chloride), and poly(ethylene oxide) in previous works [10–13]. On the other hand, PBSU was found to be immiscible with some biodegradable polymers, including poly(hydroxybutyrate)

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(PHB), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), and poly(ε-caprolactone) [14–16].

Poly(4-vinyl phenol) (PVPh) is an amorphous polymer with high glass transition temperature. PVPh is miscible with various polymers such as poly(ethylene oxide), PHB, poly(hydroxyvalerate) and poly(L-lactide) [17–21]. The miscibility of polymer blends containing PVPh usually arises from the hydrogen bonding interaction between the hydroxyl group of PVPh and other groups of the partners such as the carbonyl group. In previous work, we studied the miscibility and preliminary morphology of PBSU/PVPh blends by DSC and OM [22]. PBSU and PVPh were completely miscible in an amorphous phase over the entire composition range as shown by the single composition dependent glass transition temperature. The negative and composition dependent polymer–polymer interaction parameter indicated that PBSU/PVPh blends were thermodynamically miscible in the melt [22].

It is well known that crystallinity plays an important role in the physical properties and biodegradability of biodegradable polymers. Meanwhile, the crystalline structure and morphology of semicrystalline polymers are also influenced greatly by the thermal history. Therefore, much more attention should be directed to the crystallization kinetics study since it affects not only the crystalline structure and morphology of semicrystalline polymers but also the final physical properties and biodegradability of biodegradable polymers. In this work the overall crystallization kinetics, spherulitic morphology and growth rate, crystal structure and microstructure of neat PBSU and PBSU blended with PVPh were studied in a wide crystallization temperature range by DSC, OM, WAXD and SAXS in detail. It is expected that the results will be helpful for a better understanding of the relationship between structure and properties of biodegradable PBSU/PVPh blends.

2. Experimental section

PBSU ($M_w = 140{,}000$) and PVPh ($M_w = 20{,}000$) were obtained from Showa High Polymer Co. Ltd and Aldrich Company, respectively. PBSU/PVPh blends were prepared with mutual solvent *N*,*N*-dimethylformamide. 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 article, we have only reported neat PBSU and PBSU blended with 20 wt% PVPh, i.e., PBSU/PVPh 80/20, because PBSU did not crystallize or crystallized very slowly in the case of the weight fraction of PVPh greater than 40% [22].

The isothermal crystallization of PBSU/PVPh blend from the melt was examined by a Perkin–Elmer Diamond DSC. The sample was melted at 200 °C for 3 min to destroy any thermal history, cooled to the crystallization temperature (T_c) at a cooling rate of −80 °C/min, and then maintained at the T_c until the crystallization was completed. All operations were performed under nitrogen purge, and sample weight varied between 4 and 6 mg. The exothermal traces were recorded for the later data analysis.

The spherulitic morphology and growth rate of neat and blended PBSU were studied with a polarizing microscope (Olympus BHA-P) equipped with a first order retardation plate and a temperature controller (Linkam LK-600PM). The samples were first melted at 200 °C for 3 min to destroy any thermal history and then quenched to the T_c at a cooling rate of 100 °C/min. The spherulitic growth rate G was calculated from the change of radius R with time t, i.e., $G = \mathrm{d}R/\mathrm{d}t$.

Wide angle X-ray diffraction and small angle X-ray scattering measurements were performed at room temperature with a Rigaku D/max 2500 PC X-ray diffractometer using CuKα radiation ($\lambda = 0.154$ nm), which was operated at 40 kV and 200 mA. WAXD data were collected from $2\theta = 5$–$60°$ with a step interval of 0.02°. For the SAXS measurements, corrections were made for instrumental background, and the data were collected in the range of $0.1\ \mathrm{nm}^{-1} < s < 2.5\ \mathrm{nm}^{-1}$ ($s = 4\pi/\lambda \sin\theta$), where s is the scattering vector, λ is the X-ray wavelength, and θ is half of the scattering angle. The samples for WAXD and SAXS measurements were prepared as follows. Both neat and blended PBSU were pressed into films at 200 °C, quickly quenched to 90 °C, and annealed at this temperature for 4 h.

3. Results and discussion

3.1. Isothermal crystallization kinetics study of neat and blended PBSU by DSC

As described in Section 2, the overall isothermal crystallization kinetics of neat and blended PBSU was studied by cooling the melt rapidly to the crystallization temperature with DSC. In this work, the crystallization temperature was chosen in the range of 80–88 °C. The exothermal curves were recorded as a function of crystallization time, from which the crystallization enthalpy (ΔH_c) was obtained. The variation of ΔH_c as a function of crystallization temperature is shown in Fig. 1 for neat and blended PBSU. It can be found from Fig. 1 that the value of ΔH_c increases to 67 at 88 °C from

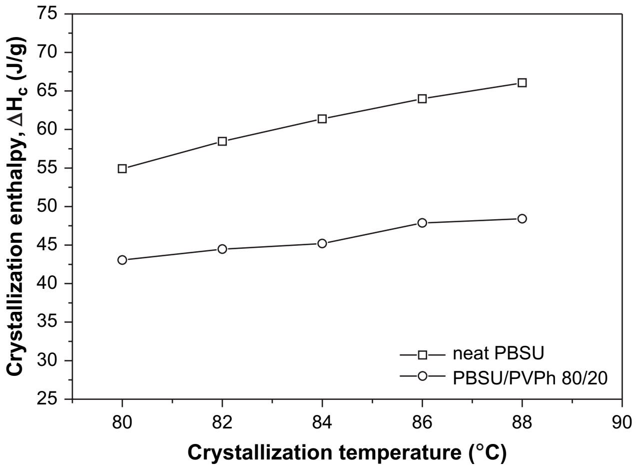

Fig. 1. Crystallization temperature dependence of crystallization enthalpy for neat and blended PBSU.

55 J/g at 80 °C for neat PBSU. In the case of blended PBSU, the value of ΔH_c increases from 43 at 80 °C to 48 J/g at 88 °C. Therefore, it can be concluded that the influence of crystallization temperature has an apparent effect on the crystallization enthalpy for neat PBSU than that of blended PBSU. On the basis of the heat fusion of 100% crystalline PBSU (200 J/g) [6], the degree of crystallinity of neat and blended PBSU was calculated from the values of ΔH_c shown in Fig. 1 and normalized with respect to the composition of PBSU in the blend. Fig. 2 summarizes the degree of crystallinity for neat and blended PBSU.

Fig. 2 shows the similar trend of degree of crystallinity as that of crystallization enthalpy depicted in Fig. 1 for both neat and blended PBSU. The degree of crystallinity of neat PBSU increases from around 27.5 to 33.5% with increasing the crystallization temperature from 80 to 88 °C; however, in the case of blended PBSU the variation is only from around 27 to 30%. The increase of crystallization temperature in the range of 80 to 88 °C does not affect the degree of crystallinity significantly for both neat and blended PBSU.

The well-known Avrami equation was used to analyze the overall isothermal crystallization kinetics of both neat and blended PBSU. It assumes that the relative degree of crystallinity X_t develops as a function of crystallization time t as follows:

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

where X_t is the relative crystallinity at time t, k is the crystallization rate constant depending on nucleation and growth rate, and n is the Avrami exponent depending on the nature of nucleation and growth geometry of the crystals [23]. Since determination of the absolute degree of crystallinity is not necessary in using Avrami analysis, the ratio of the area at time t and the area of whole exotherm was used to get X_t. Fig. 3 shows the development of X_t as a function of crystallization time t for both neat and blended PBSU. It can be seen that the crystallization time increases with increasing crystallization temperature for both neat and blended PBSU, indicating that the crystallization was retarded with the increase of crystallization temperature. At a given crystallization temperature, the crystallization time increases for the PBSU blended with amorphous PVPh compared with that of neat PBSU, indicating that the addition of amorphous PVPh reduces the crystallization rate of PBSU in the blend. The reason for the decrease of crystallization rate of PBSU in the blend will be discussed in the following section.

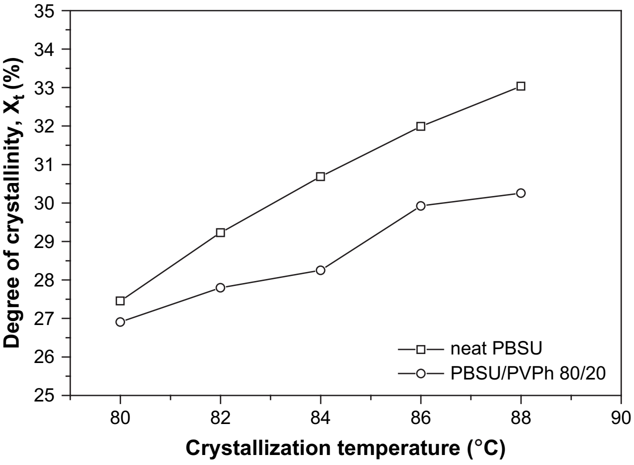

Fig. 2. Crystallization temperature dependence of crystallinity for neat and blended PBSU.

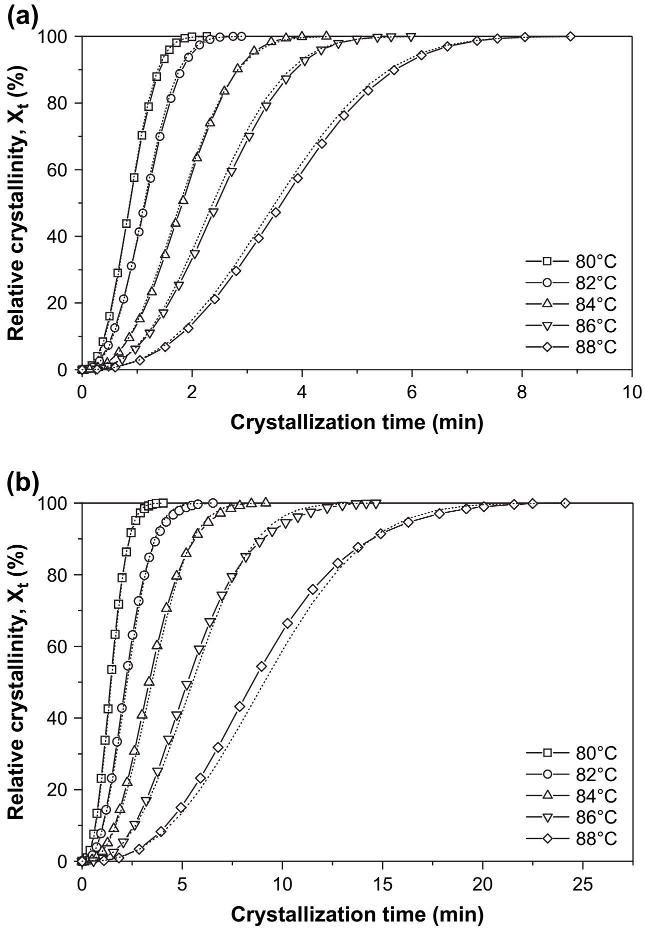

Fig. 3. Development of relative degree of crystallinity as a function of crystallization time for neat and blended PBSU; (a) neat PBSU, and (b) blended PBSU (solid line: the experimental crystallinity; dot line: the calculated crystallinity on the basis of the Avrami parameters n and k shown in Table 1).

Fig. 4 shows the Avrami plots for both neat and blended PBSU. It can be seen from Fig. 4 that the Avrami method can describe the development of the relative degree of crystallinity as a function of crystallization time very well. Accordingly, the Avrami parameters n and k can be obtained from the slope and intercept, respectively in the plots of $\log(-\ln(1-X_t))$ vs. $\log t$ as shown in Fig. 4. The values of n and k are summarized in Table 1. The values of n are almost unchanged with the crystallization temperature and blend composition, indicating that the crystallization mechanism of PBSU does not change in the investigated crystallization temperature range as well as blend composition. Moreover, the values of k decrease with increasing crystallization temperature for both neat and blended PBSU, indicating that the

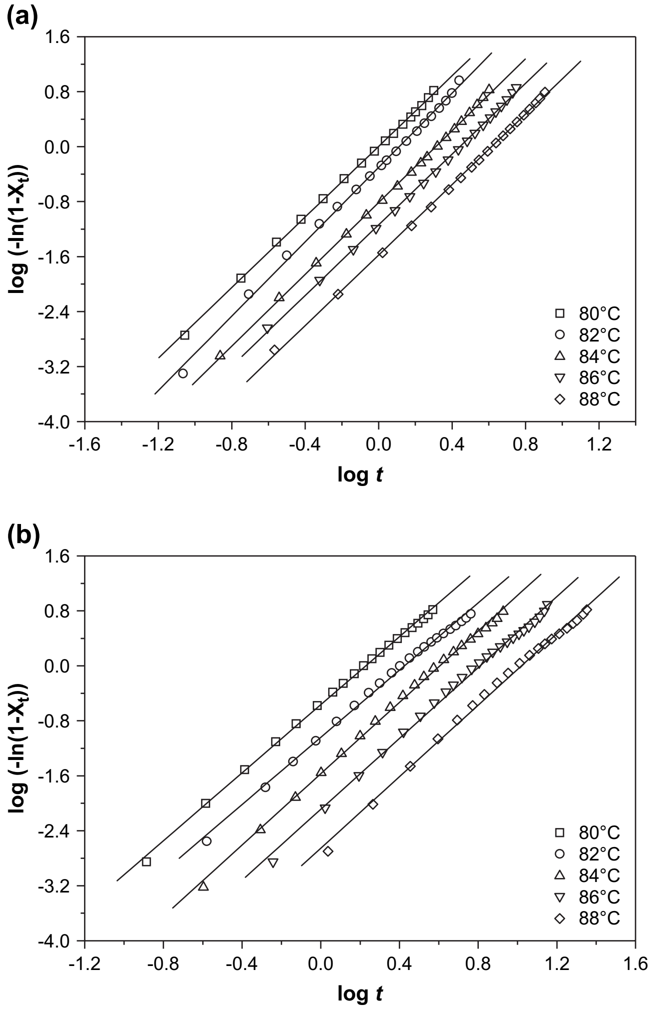

Fig. 4. Avrami plots of neat and blended PBSU; (a) neat PBSU, and (b) blended PBSU.

crystallization is suppressed with the increase of crystallization temperature. On the other hand, the values of k decrease with the addition of PVPh at the same crystallization temperature. The reason why the addition of PVPh reduces the crystallization rate may be related to the following three factors. First, the addition of high T_g component PVPh increases the T_g of PBSU/PVPh blends, resulting in the decrease of the mobility of blended PBSU compared with that of neat PBSU. Second, the decrease of the melting point temperature of PBSU in the blend may reduce the thermodynamic driving force required for the crystallization of PBSU. Third, the added PVPh may have a diluent effect on the crystallization of PBSU at the crystal growth front. Similar results were also found for the crystallization of poly(ethylene succinate)/PVPh blends in our previous work [24]. In order to check the validity of the Avrami method of studying the isothermal crystallization kinetics of neat and blended PBSU, we calculated the crystallinities using the values of n and k listed in Table 1 for each crystallization temperature, which was shown as dot lines in Fig. 3. It could be found that the dot line and the solid line are very consistent, indicating that the Avrami method could describe the isothermal crystallization process very well.

Table 1
Parameters n, k, and t_{max}, from the Avrami analysis of isothermal melt crystallization for neat and blended PBSU

	T_c (°C)	n	k (min^{-n})	t_{max} (min)
PBSU	80	2.6	1.008	0.823
	82	2.7	4.978×10^{-1}	1.091
	84	2.6	1.539×10^{-1}	1.702
	86	2.6	7.279×10^{-2}	2.288
	88	2.6	2.645×10^{-2}	3.406
PBSU/PVPh 80/20	80	2.5	0.272	1.374
	82	2.5	9.121×10^{-2}	2.145
	84	2.6	2.694×10^{-2}	3.344
	86	2.6	8.180×10^{-3}	5.327
	88	2.6	2.220×10^{-3}	8.701

Since t_{max} is the solution of $dQ/dt = 0$ ($Q(t)$ being the heat flow), it can be written in terms of n and k as follows:

$$t_{max} = \left(\frac{(n-1)}{nk}\right)^{1/n} \tag{2}$$

By using the values of n and k listed in Table 1, the values of t_{max} were obtained and listed in Table 1, too. It can be seen that the values of t_{max} increase with the crystallization temperature for both neat and blended PBSU. Furthermore, it increases with the addition of PVPh in the blend compared with that of neat PBSU. The half-life crystallization time $t_{0.5}$, which is defined as the time at $X_t = 0.5$, is an important parameter for the discussion of crystallization kinetics; it can also be calculated using the relation:

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \tag{3}$$

Usually, the crystallization rate can also be described as the reciprocal of $t_{0.5}$, i.e., $1/t_{0.5}$. By using the data listed in Table 1 and the aforementioned two equations, the values of $t_{0.5}$ and $1/t_{0.5}$ were obtained and plotted in Fig. 5 as a function of crystallization temperature and blend composition. It can be seen from Fig. 5 that the value of $t_{0.5}$ increases for neat and blended with the increase of the crystallization temperature. The value of $t_{0.5}$ for neat PBSU is lower than that for blended PBSU. The difference in $t_{0.5}$ becomes more apparent with the increase of crystallization temperature. On the other hand, the value of $1/t_{0.5}$ decreases with increasing crystallization temperature as well as the addition of PVPh, indicative of the reduction of crystallization rate. The results are consistent with the trend of k listed in Table 1. All the aforementioned results can lead us to a conclusion that the addition of PVPh does not change the overall crystallization mechanism of PBSU, but only reduces the crystallization rate in the PBSU/PVPh blend. The reduction of crystallization rate of PBSU was mainly caused by increase of the glass transition temperature and depression of the melting point after adding PVPh content in blends. First, the addition of high T_g component PVPh increased the T_g of PBSU/PVPh blend, resulting in the

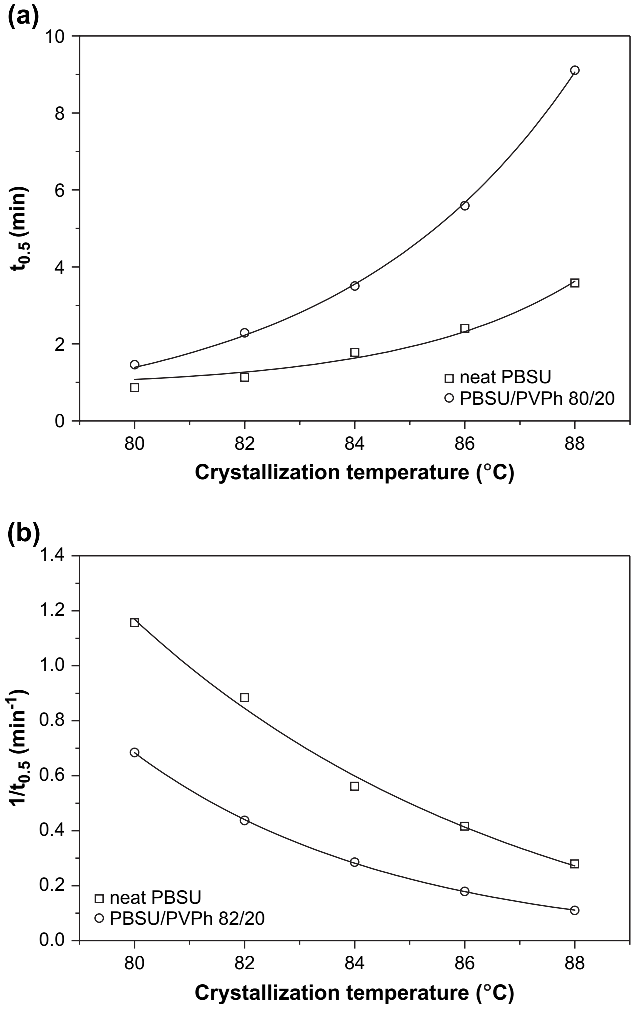

Fig. 5. Crystallization temperature dependence of $t_{0.5}$ of neat and blended PBSU (a), and crystallization temperature dependence of $1/t_{0.5}$ of neat and blended PBSU (b).

decrease of the mobility of PBSU compared with that of neat PBSU. In this work, the T_g of blended PBSU was 10 °C higher than that of neat PBSU. Second, the equilibrium melting point temperature of blended PBSU was almost 6 °C lower than that of neat PBSU, which may drop the thermodynamic driving force required for the growth of PBSU spherulites. Third, the added PVPh may play a role of a diluent to PBSU in the miscible blends, resulting in the dilution of PBSU chains at the spherulites growth front.

3.2. Spherulitic morphology and growth of neat and blended PBSU by POM

The preliminary morphology of PBSU/PVPh blends was once studied by optical microscopy in previous work for neat and blended PBSU crystallized at 85 °C. The spherulitic morphology and growth rate of neat and blended PBSU were studied in this work with hot stage OM in a wide crystallization temperature range of 75–100 °C as mentioned in Section 2.

Fig. 6 shows the spherulitic morphology of neat and blended PBSU crystallized at 75, 85 and 95 °C, respectively, as examples. Both neat and blended PBSU show banded spherulites with concentric extinction bands at low crystallization temperature of 75 °C. Both neat and blended PBSU do not exhibit banded spherulites any more at crystallization temperatures higher than 80 °C. It can also be found that the spherulites of neat PBSU are very compact while those of blended PBSU are coarse at the same crystallization temperature. The bundles of lamellae of blended PBSU spherulites are fewer, but thicker than those for neat PBSU. The coarseness of PBSU spherulites becomes more apparent with increasing crystallization temperature, especially in the blend, indicating that blending with amorphous PVPh increases the coarseness of PBSU spherulites. Moreover, both neat and blended PBSU spherulites are space filling. The fact that blended PBSU spherulites are space filling indicates that amorphous PVPh is rejected during the crystallization process as a noncrystallizable component and resides primarily in the interlamellar and/or interfibrillar domains of the PBSU spherulites [25,26].

The spherulitic growth rate of neat and blended PBSU was also measured by following the development of radius with time. Both neat and blended PBSU spherulites show a linear growth with crystallization time until the contact with other spherulites during the crystallization process. Fig. 7 shows the temperature dependence of the spherulitic growth rates of neat and blended PBSU. It can be seen that the spherulitic growth rates of both neat and blended PBSU decrease with increasing temperature. The growth rate of neat PBSU spherulites was higher than that of blended PBSU at the same crystallization temperature. The trend of spherulitic growth rates is similar to that of $1/t_{0.5}$ shown in Fig. 5b. The difference in the growth rate of neat and blended PBSU spherulites becomes more apparent at low crystallization temperature, indicating that the addition of the amorphous component PVPh reduces significantly the growth rate at crystallization temperature with large degree of supercooling. The decrease in the growth rate of blended PBSU may be related to the following factors, i.e., the lower mobility, the lower thermodynamic driving force required for the growth of PBSU spherulites, and the diluent effect of PVPh in the blend.

In order to further investigate the crystal growth kinetics of neat and blended PBSU isothermally crystallized from the melt, the secondary nucleation theory called usually as the Lauritzen–Hoffman equation was applied in this work to analyze the spherulitic growth rate of neat and blended PBSU. On the basis of this theory [27], the crystal growth rate G at a given crystallization temperature T_c is expressed by the following equation

$$G = G_0 \exp\left[-\frac{U^*}{\mathrm{R}(T_c - T_\infty)}\right] \exp\left[-\frac{K_g}{T_c(\Delta T)f}\right] \qquad (4)$$

where G_0 is a preexponential factor, U^* is the activation energy for transporting the polymer chain segments to the crystallization site, R is the gas constant, T_∞ is a temperature below which the polymer chain movement ceases, ΔT is the degree of supercooling described as $T_m^0 - T_c$ with T_m^0 being the equilibrium melting point, f is a correction factor

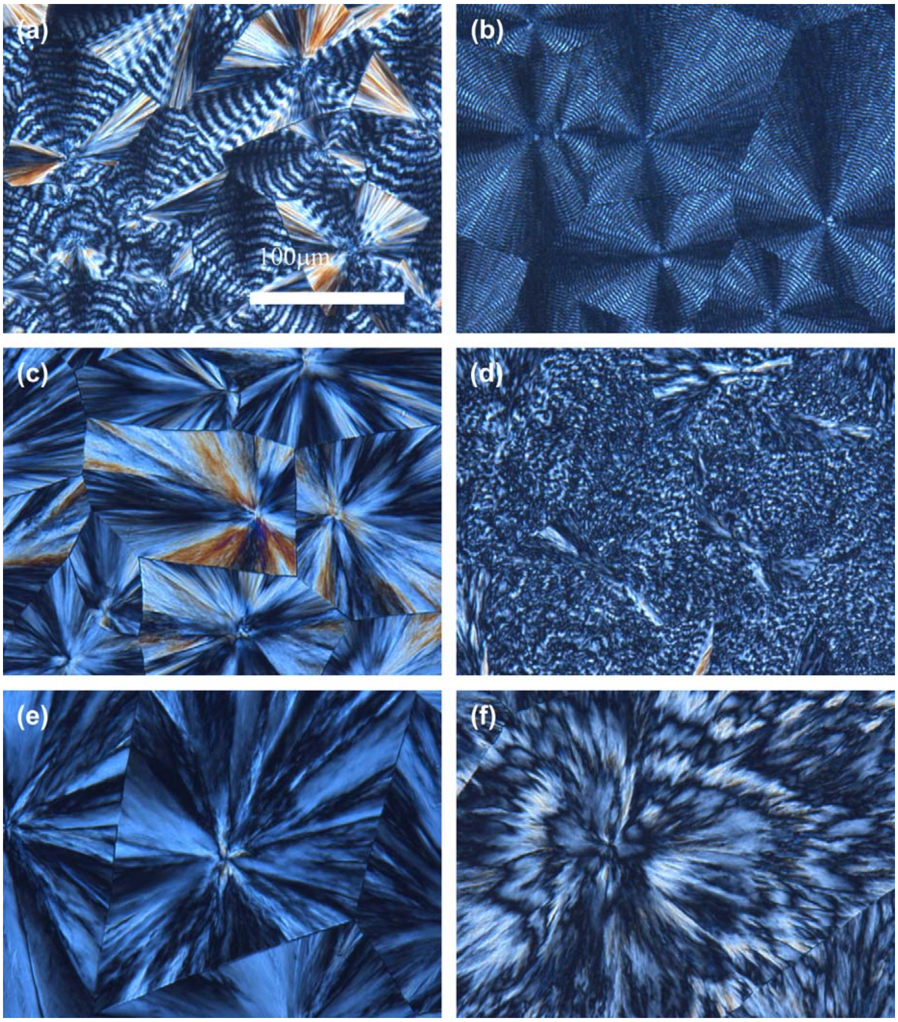

Fig. 6. Optical micrographs (same magnification with bar = 100 μm) of the spherulitic morphology of neat and blended PBSU crystallized at various temperatures; (a) neat PBSU at 75 °C for 1 min, (b) blended PBSU at 75 °C for 2 min, (c) neat PBSU at 85 °C for 8 min, (d) blended PBSU at 85 °C for 10 min, (e) neat PBSU at 95 °C for 25 min, and (f) blended PBSU at 95 °C for 50 min.

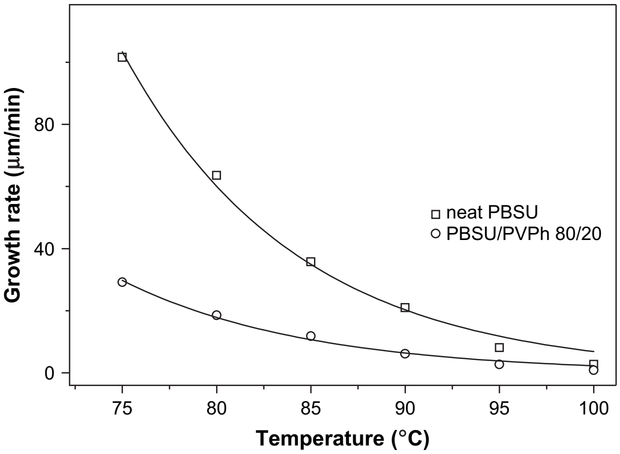

Fig. 7. Crystallization temperature dependence of spherulitic growth rate of neat and blended PBSU.

accounting for the variation in the enthalpy of fusion given as $f = 2T_c/(T_m^0 + T_c)$, and K_g is the nucleation constant as shown in

$$K_g = \frac{nb_0\sigma\sigma_e T_m^0}{\Delta h_f k} \tag{5}$$

where σ and σ_e are the lateral surface free energy and end-surface free energy, respectively, b_0 is the molecular thickness, Δh_f is the heat of fusion per unit volume, k is the Boltzmann constant, and the value of n is dependent on the crystallization regime. For practical convenient use, Eq. (4) is usually rewritten as follows

$$\ln G + \frac{U^*}{\mathrm{R}(T_c - T_\infty)} = \ln G_0 - \frac{K_g}{T_c(\Delta T)f} \tag{6}$$

In this work, the universal values of $U^* = 1500$ cal/mol and $T_\infty = T_g - 30$ K were used in all calculations [7,27]. The spherulitic growth rates shown in Fig. 7 were applied, and the values of the T_g and T_m^0 of neat and blended PBSU have been obtained in previous work [22]. The plot of the left-hand side of Eq. (6) vs. $1/(T_c\Delta Tf)$ gives the slope $-K_g$. Hence, the K_g of neat PBSU was estimated as 1.872×10^5 K^2, and that of blended PBSU was determined to be 1.411×10^5 K^2.

It is clear that the addition of amorphous PVPh reduces the value of K_g in the blend compared with that of neat PBSU (Fig. 8).

It should also be noted that no crystallization regime transition was found in the crystallization temperature range used in this study for both neat and blended PBSU. On the basis of OM results and Ref. [7], the crystallization regime in the present crystallization temperature range is regime III; therefore, the value of n in Eq. (5) is 4. In order to calculate the value of $\sigma\sigma_e$ of neat PBSU on the basis of Eq. (5), the following parameters were used in this study. The values of b_0, T_m^0, and Δh_f are 0.404 nm, 411.9 K, and 2.68×10^8 J/m^3, respectively [4,6,22]. Thus, the value of $\sigma\sigma_e$ is determined to be 1.040×10^{-3} J^2/m^4. Using the same method, the value of $\sigma\sigma_e$ of blended PBSU is estimated to be 7.955×10^{-4} J^2/m^4. The value of $\sigma\sigma_e$ can be used further to calculate the surface free energy σ, σ_e and the work of chain folding q. According to the secondary nucleation theory σ, σ_e and q can be determined from the following equations:

$$\sigma = \alpha(a_0 b_0)^{1/2}\Delta h_f \tag{7}$$

$$\sigma_e = \sigma\sigma_e/\sigma \tag{8}$$

$$q = 2a_0 b_0 \sigma_e \tag{9}$$

where a_0 is the width of a molecular chain, $a_0 b_0$ is the cross-section area per chain molecules. The values of a_0 and b_0 are 0.525 and 0.404 nm for PBSU, respectively, if the crystal growth front is assumed to be the (110) plane [4]. As to the value of α, it is an empirical parameter varying between 0.1 and 0.3. Generally, α is usually assumed to be 0.1 for polyolefins and 0.25 for polyesters. In this work, α is chosen to be 0.25 for further calculation since PBSU is a kind of biodegradable polyester. Thus, the values of σ, σ_e and q were determined to be 3.086×10^{-2} J/m^2, 3.370×10^{-2} J/m^2, and 8.605×10^3 J/mol, respectively, for neat PBSU on the basis of the aforementioned equations using the related parameters.

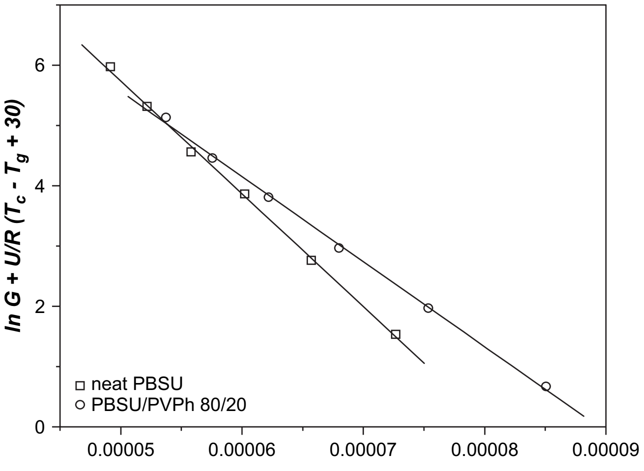

Fig. 8. The Lauritzen–Hoffman plots for the estimation of nucleation parameter of neat and blended PBSU.

Table 2
Thermal properties and kinetic parameters of the secondary nucleation analysis for neat and blended PBSU

Parameter	Neat PBSU	PBSU/PVPh 80/20
T_g (K)	239.5	249.2
T_m^0 (K)	411.9	406.1
K_g (K^2)	1.872×10^5	1.411×10^5
$\sigma\sigma_e$ (J^2/m^4)	1.040×10^{-3}	7.955×10^{-4}
σ (J/m^2)	3.086×10^{-2}	2.469×10^{-2}
σ_e (J/m^2)	3.370×10^{-2}	3.222×10^{-2}
q (J/mol)	8.605×10^3	8.225×10^3

Using the same method, the values of σ, σ_e and q for blended PBSU were determined to be 2.469×10^{-2} J/m^2, 3.222×10^{-2} J/m^2, and 8.225×10^3 J/mol, respectively. All the obtained values are listed in Table 2. For further comparison, the values of T_g, T_m^0, and K_g for neat and blended PBSU are also listed in Table 2. It can be found that blending with amorphous PVPh reduces all the related parameters compared with those of neat PBSU, except increasing the value of T_g. However, the decrease extent is also limited since the weight fraction of the amorphous component PVPh is only 20 wt% in the blend. The decrease of the aforementioned crystallization parameters might be attributed to the fact that the amorphous PVPh in the blend disrupted the lamellae in PBSU during the crystallization process. Similar results were often found in miscible crystalline/amorphous blends such as PHB/PVPh blends [28] and poly(trimethylene terephthalate)/PVPh blends [29].

3.3. WAXD/SAXS studies of neat and blended PBSU

The crystal structure and microstructure of PBSU before and after blending with amorphous PVPh were also investigated with WAXD and SAXS. Fig. 9 shows the WAXD patterns of neat and blended PBSU crystallized at 90 °C for 4 h. It can be seen from Fig. 9 that both neat and blended PBSU exhibit almost the same diffraction peaks at almost the same locations, indicating that blending with amorphous PVPh does not modify the crystal structure of PBSU, and

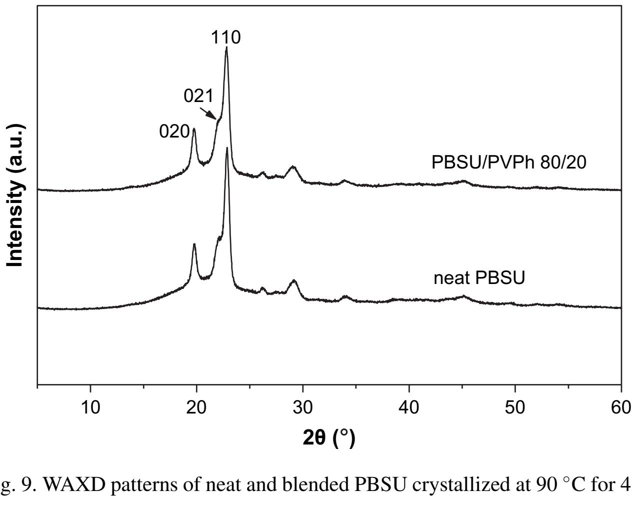

Fig. 9. WAXD patterns of neat and blended PBSU crystallized at 90 °C for 4 h.

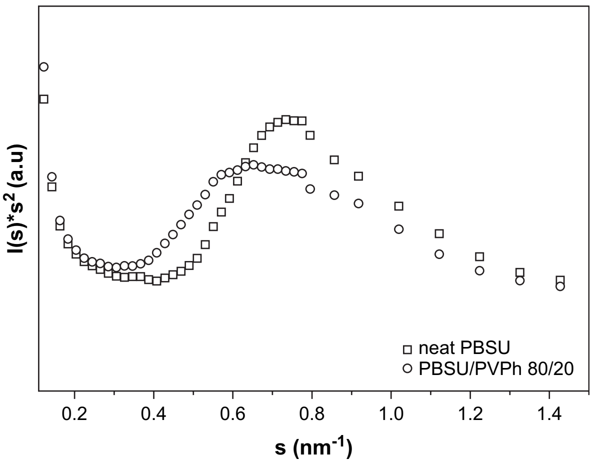

Fig. 10. SAXS profiles of neat and blended PBSU crystallized at 90 °C for 4 h.

PVPh exists in an amorphous state and is excluded from the crystal region of PBSU. The three main peaks located at around 19.4, 21.9, and 22.6° correspond to (020), (021), and (110) planes of PBSU, respectively. The heats of fusion of neat and blended PBSU crystallized at 90 °C for 4 h were measured to be 73.37 and 55.29 J/g, respectively. Thus, the crystallinity of neat and blended PBSU is estimated to be around 37% and 35%, respectively, indicating that blending with 20 wt% amorphous PVPh does not influence the crystallinity of PBSU significantly. It can also be expected that the biodegradability of PBSU will also remain almost the same after blending with PVPh on the basis of crystallinity.

The microstructure of neat and blended PBSU was investigated with SAXS, too. Fig. 10 shows the Lorentz-corrected SAXS profiles of neat and blended PBSU crystallized isothermally at 90 °C for 4 h. Both neat and blended PBSU show well-defined peaks, indicating fairly well lamellar stacks in the samples. The peak of blended PBSU shifts to low scattering vector compared with that of neat PBSU. The long period associated with the lamellar stacks were calculated from the peak maximum using Bragg's equation, $L = 2\pi/s_{\max}$. Thus, the long periods of neat and blended PBSU were estimated as 8.56 and 9.63 nm, respectively. The increase of the long periods indicates that the amorphous component PVPh might reside mainly in the interlamellar region of PBSU. However, the increasing long period might be also due to the thickening of the lamellae in the lamellar stacks. Further investigation is still necessary to give an exclusive conclusion about the exact locations of the amorphous component.

4. Conclusions

Isothermal crystallization kinetics and morphology of miscible biodegradable crystalline/amorphous blend of PBSU and PVPh was investigated with DSC, OM, WAXD and SAXS in detail in this work. The overall isothermal crystallization kinetics of neat and blended PBSU was studied with DSC and analyzed by the Avrami equation. The Avrami exponent n was almost unchanged despite the crystallization temperature as well as the addition of amorphous PVPh, indicating that blending with PVPh did not change the crystallization mechanism of PBSU within the crystallization temperature range of 80–88 °C. However, the crystallization rate decreased with the increase of crystallization temperature and the blending. The decrease of the overall crystallization rate was attributed to three factors, including the depression of T_m^0, the increase of T_g, and the diluent effect of PVPh on the crystallization of PBSU in the blends. The spherulitic morphology and growth were observed with hot stage OM in a wide crystallization temperature range of 75–100 °C. The spherulitic morphology of PBSU was influenced apparently by crystallization temperature and the blending with PVPh. On the basis of the secondary nucleation theory, some crystallization parameters of neat and blended PBSU were derived and compared with each other including the nucleation parameter, the lateral surface free energy, the end-surface free energy, and the work of chain folding. Blending with PVPh decreased all the aforementioned parameters compared with those of neat PBSU. The crystal structure of PBSU was not modified by the blending, and the crystallinity changed very slightly from the WAXD measurement. On the basis of SAXS measurement, it was found that the long period PBSU increased in the blend, indicating that the amorphous PVPh resided mainly in the interlamellar region of PBSU.

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