1. Introduction

In recent years, conventional plastics have been widely used which caused severe environmental problems. Therefore, biodegradable polymers have received more and more attention. Biodegradable polymers can be classified into two types in terms of the preparation methods. One is biosynthetic polymers, such as bacterial polyhydroxyalkanoates (PHAs). The other is chemosynthetic polymers, such as the linear aliphatic polyesters. PBSA, a copolymer of poly(butylene succinate) (PBSU), is one of the biodegradable semicrystalline aliphatic polyesters. PBSA can be synthesized by polycondensation of 1,4-butanediol with succinic and adipic acids. The biodegradability, crystal structure, crystallization kinetics and melting behavior of PBSA have been reported in the literature [1–6]. Compared with PBSU, PBSA is more susceptible to biodegradation because of its lower crystallinity and more flexible polymer chains that can be easily biodegraded by enzymes.

Polymer blending is a simple and economic way to modify the physical properties and extend the practical application fields of biodegradable polymers. On the one hand, PBSA is miscible with poly(ethylene oxide) (PEO) and poly(vinylidene fluoride) (PVDF) [7–9]. The spherulitic growth of PEO was found to continue in the amorphous phase, all become larger with increasing the PVPh content, indicating that PVPh mainly resides in the interlamellar region of PBSA spherulites in the blends. Furthermore, blending with PVPh does not modify the crystal structure of PBSA. The microstructural parameters, including the long period, thickness of crystalline phase and thickness of amorphous phase, all become larger with increasing the PVPh content, indicating that PVPh mainly resides in the interlamellar region of PBSA spherulites in the blends.

* Corresponding author. Tel./fax: +86 10 64412161. E-mail address: qubz@mail.buct.edu.cn (Z. Qiu).
2. Experimental section

PBSA ($M_w = 14,400$) and PVPh ($M_w = 20,000$) were purchased from Aldrich Chemical Company and used as received. The chemical structures of PBSA and PVPh are shown in Scheme 1. PBSA/PVPh blends were prepared with mutual solvent tetrahydrofuran. The solution of both polymers was cast on a petri dish at room temperature and was allowed to evaporate in a controlled air stream for 1 day. The resulting films were further dried in vacuum at 50 °C for 3 days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first 4 days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first days. In this way, PBSA/PVPh blends were prepared with various compositions ranging from 90/10 to 20/80 in weight ratio, the first 4 min to erase any thermal history and then quickly quenched into liquid nitrogen.

Isothermal crystallization kinetics of PBSA/PVPh blends was also investigated by DSC. We only studied neat PBSA and the blends with the weight fraction of PVPh less than 30% because PBSA did not crystallize or crystallized very slowly when the PVPh content was above 40 wt%. The samples were annealed at 130 °C for 4 min, cooled to the crystallization temperature ($T_c$) at a rate of 60 °C/min, and then maintained at $T_c$ until the crystallization completed. The samples were scanned to 130 °C again at 20 °C/min to investigate the melting behavior of PBSA in the PBSA/PVPh blends.

Spherulitic morphology of PBSA/PVPh blends was observed under crossed polars with a polarizing microscope (POM) (Olympus BX51) equipped with a temperature controller (Linkam THMS 600). The samples were first annealed at 130 °C for 4 min to erase any thermal history and then cooled to 65 °C at 4 °C/min.

Wide angle X-ray diffraction (WAXD) experiments were performed on a SAXSess (Anton Paar company) using mono-chromatized CuKα radiation in the diffraction range 2θ = 10–35°. Small angle X-ray scattering (SAXS) measurements were carried out at room temperature with a NanoStar X-ray diffractometer (Buker AXS, Inc.) using CuKα radiation (λ = 0.154 nm) at 40 kV and 30 mA. For the SAXS measurements, corrections were made for instrumental background. The samples for WAXD and SAXS measurements were prepared as follows. The samples were first pressed into films with thickness of around 1 mm on a hot stage at 130 °C as soon as possible and held for 3 days.

3. Results and discussion

3.1. Miscibility study based on the glass transition temperature analysis

Miscibility of PBSA/PVPh blends was studied first by measuring the glass transition temperatures of the melt-quenched samples with DSC. Neat PBSA has a $T_g$ of ca. −43.4 °C and a $T_m$ of ca. 96.4 °C. On the other hand, neat PVPh is an amorphous polymer with a high

 Mig. 1. Variation of $T_g$ and $T_m$ with the PVPh content in the PBSA/PVPh blends. (The dotted line is fitted by the Kwei equation.)

$T_g$ of ca. 171.1 °C. Fig. 1 summarizes the variation of $T_g$ and $T_m$ with increasing the PVPh content. It can be seen from Fig. 1 that PBSA/PVPh blends show a single composition dependent $T_g$ between those of the two neat components, indicating that PBSA and PVPh are miscible over the entire composition range. It is obvious that $T_g$ of the PBSA/PVPh blends increases after blending with the high $T_g$ component PVPh, resulting in the decrease of the mobility of PBSA in the blends. Therefore, the crystallization of PBSA is hindered by the presence of PVPh. As a result, $T_m$ of PBSA shifts to low temperature range upon the addition of PVPh in the blends; however, the decrease of $T_m$ is very slight. It should be noted that $T_m$ of PBSA/PVPh blends could not be detected with the PVPh content above 40 wt% in the blends.

Furthermore, the Kwei equation [24] is applied in this work to fit the variation of $T_g$ as a function of composition as follows.

$$T_g = \frac{W_1T_{g1} + kW_2T_{g2}}{W_1 + kW_2} + qW_1W_2$$

(1)

where $W_1$ and $W_2$ are the weight fraction of two pure components, $T_{g1}$ and $T_{g2}$ are the respective $T_g$ of the neat component, $q$ is a parameter corresponding to the strength of hydrogen bonding in the blends, reflecting a balance between the breaking of the self-association and the forming of the inter-association hydrogen bonding, and $k$ is a fitting constant. As showed in Fig. 1, the Kwei equation fits $T_g$ of PBSA/PVPh blends very well. In this work, a negative $q$ of −160 is obtained in the case of $k = 1$, which is greatly lower than that of −85 for PCL/PVPh blends [19], indicating that the interaction between PBSA and PVPh is weaker than that in the PCL/PVPh blends.

3.2. The depression of the equilibrium melting point of PBSA in the PBSA/PVPh blends

The depression of the melting point of crystalline polymer blended with an amorphous polymer provides important information of its miscibility. An immiscible blends or partially miscible blends do not show the depression of melting point significantly. However, the melting point of a polymer is affected not only by the thermodynamic factors but also by the morphological factors such as crystalline lamellar thickness and the perfection of spherulites. Therefore, the equilibrium melting point ($T_m^e$) is introduced to separate the morphological effect from the thermodynamic effect in discussing the melting point depression as described by the
Flory–Huggins theory [25]. $T_m^o$ can be derived from the Hoffmann–Weeks equation [26]:

$$T_m = \eta T_c + (1 - \eta)T_m^o$$

where $T_m$ is the apparent melting point, $T_c$ is the crystallization temperature, and $\eta$ may be regarded as a measure of the stability.

The melting behavior of PBSA/PVPh blends was studied with DSC. As an example, Fig. 2a shows the melting behavior of a 90/10 blend crystallized isothermally at various $T_c$s. Two endothermic melting peaks are observed. The lower endothermic peak ($T_m^o$) shifts to higher temperature range with increasing $T_c$, while the higher endothermic peak ($T_m^2$) is almost unchanged. Moreover, the magnitude of the area of $T_m^o$ increases and that of $T_m^2$ decreases with the increase of $T_c$. This is also observed in the 80/20 and 70/30 blends. Such melting behavior can be explained by the melt-recrystallization model [7,27–29]. $T_m^o$ is the melting of the crystals formed during the isothermal crystallization process which are present prior to the heating scan, and dependent greatly on $T_c$. $T_m^2$ is the melting of the crystals formed through the recrystallization during the heating process.

Therefore, $T_m^o$ is used for the analysis of the Hoffman–Weeks equation. Fig. 2b shows the Hoffman–Weeks plots for neat PBSA and the blends. From Fig. 2b, the values of $T_m^o$s are determined to be around 120, 113.2, 102.6, and 100.6 °C for neat PBSA, 90/10, 80/20, and 70/30 blends, respectively. It is clear that $T_m^o$ of PBSA decreases with increasing the PVPh content. The depression of $T_m^o$ indicates again that PBSA and PVPh are miscible polymer blends. $T_m^o$s obtained on this study is further analyzed by the Nishi–Wang equation [30] based on the Flory–Huggins theory [25]:

$$\frac{1}{T_m^o(b)} - \frac{1}{T_m^o(p)} = -\frac{RV_2}{\Delta H^oV_1} \left[ \ln \phi_1 + \frac{1}{m_2} - \frac{1}{m_1} + \phi_1^2 \right]$$

where $T_m^o(p)$ and $T_m^o(b)$ are the equilibrium melting points of the pure crystallizable polymer and of the blend, respectively. $\Delta H^o$ is the fusion heat of the perfectly crystallizable polymer per mole of the repeat unit, $V$ is the molar volume of the repeating units of the polymers, $m$ and $\phi$ are degree of polymerization and the volume fraction of the component in the blends, respectively. Subscripts 1 and 2 refer to the amorphous and crystalline polymer, respectively. $R$ is the universal gas constant, and $\chi_{12}$ is the polymer–polymer interaction parameter. When both $m_1$ and $m_2$ are large, for high molecular weight polymers, these related terms in Eq. (3) can be neglected. The interaction parameter $\chi_{12}$ can thus be written as

$$\frac{\Delta H^oV_1}{RV_2} \left( \frac{1}{T_m^o(b)} - \frac{1}{T_m^o(p)} \right) = \beta = \chi_{12}\phi_1^2$$

In order to calculate the left-hand side term of Eq. (4), the following parameters are used: $V_1 = 100$ cm$^3$/mol [31], $V_2 = 135.1$ cm$^3$/mol, and $\Delta H^o = 20.304$ J/mol [32]. The weight fraction of amorphous polymer is transformed to volume fraction.

![Fig. 2.](image)

*(a) Melting behavior of a 90/10 blend isothermally crystallized at various $T_c$s from the melt; (b) Hoffman–Weeks plots of neat and blended PBSA for the estimation of the equilibrium melting points.*

**3.3. Isothermal crystallization of PBSA/PVPh blends**

Isothermal crystallization kinetics of PBSA/PVPh blends was investigated by DSC. Fig. 4a shows the variation of relative crystallinity with crystallization time for a PBSA/PVPh 90/10 blend. It can be seen that the crystallization isoformers display the characteristic sigmoidal shape. Moreover, the crystallization time
The values of $n$ can be obtained from the slopes and intercepts, respectively. The apparent $T_c$ prolongs with the increase of crystallization temperature for both neat and blended PBSA.

The Avrami equation is usually employed to analyze the isothermal crystallization kinetics of crystalline polymers, which describes the development of relative degree of crystallinity with crystallization time $t$ as

$$1 - X_t = \exp(-kt^n)$$  \hspace{1cm} (5)

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 [33–35].

Fig. 4b shows the Avrami plots for a PBSA/PVPh 90/10 blend. It can be seen that a series of straight lines are obtained, which indicates 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 slopes and intercepts, respectively. The values of $n$ and $k$ for neat and blended PBSA are summarized in Table 1. The values of $n$ for neat PBSA and PBSA blends are between 2 and 3, suggesting that the crystallization of PBSA may correspond to three-dimensional truncated spherulitic growth with athermal nucleation [36]. Furthermore, blending with PVPh does not change the crystallization mechanism of PBSA in the blends apparently.

The half-time of crystallization ($t_{0.5}$), defined as the time required to half completion of the final crystallinity, can be obtained by Eq. (6). The overall crystallization rate can be simply represented by $1/t_{0.5}$.

$$t_{0.5} = \left(\frac{\ln 2}{k^*}\right)^{1/n}$$  \hspace{1cm} (6)

On the basis of the values of $n$ and $k$, the values of $t_{0.5}$ and $1/t_{0.5}$ were calculated. Table 1 summarizes the values of $t_{0.5}$ for both neat and blended PBSA. It is obvious that the values of $t_{0.5}$ increase with the increase of $T_c$ for both neat PBSA and its blends with PVPh at different content. Moreover, it is also found that the values of $t_{0.5}$ are smaller in the neat PBSA than those in the blends at a given $T_c$, indicating that the crystallization rate of PBSA becomes slower after blending with PVPh.

In order to show the effects of blend composition and crystallization temperature on the crystallization rate of PBSA clearly, Fig. 5 summarizes the temperature dependence of $1/t_{0.5}$ for neat and blended PBSA.

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<th>$T_c$ (°C)</th>
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<th>$k$ (min⁻¹)</th>
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Table 1

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Fig. 4. (a) Development of relative crystallinity $X_t$ versus crystallization time; (b) Avrami plots of a PBSA/PVPh 90/10 blend.

Fig. 5. Crystallization temperature dependence of $1/t_{0.5}$ for neat and blended PBSA.
rates decrease with increasing the PVPh content at a given $T_c$, indicating that blending with amorphous PVPh retards the crystallization of PBSA in the blends. The reduction of the crystallization rate of PBSA in the blends may be attributed to the following factors. First, the addition of high $T_g$ component PVPh increases $T_g$s of PBSA/PVPh blends, resulting in the decrease of the mobility of PBSA compared with that of neat PBSA. Second, the equilibrium melting point temperatures of blended PBSA were lower than that of neat PBSA, which must drop the thermodynamic driving force required for the crystallization of PBSA. Third, the addition of PVPh may play a role of a diluent to PBSA in the miscible blends, resulting in the dilution of PBSA chains at the spherulites growth front [21,23,38].

Fig. 6 shows POM images of neat and blended PBSA crystallized at 65 °C. The spherulites of neat PBSA are compact. In the case of the PBSA/PVPh blends, PBSA spherulites become coarser compared with those of neat PBSA. For an 80/20 blend, the bundles of lamellae are fewer but thicker than those for neat PBSA, and assume a feather-like pattern. The fact that PBSA spherulites are space-filling indicates that PVPh is rejected in the crystallization process and may reside primarily in the fibrillar and lamellar domains of PBSA spherulites.

3.4. WAXD and SAXS studies of neat and blended PBSA

The crystal structure and microstructure of PBSA before and after blending with PVPh were investigated with WAXD and SAXS in the present work. Fig. 7 shows the WAXD patterns of neat and blended PBSA crystallized at 65 °C for 3 days. It can be seen from Fig. 7 that both neat and blended PBSA exhibit almost the same diffraction peaks at the same location. However, the intensity of the diffraction peaks decreases with increasing the PVPh content. It indicates that blending with amorphous PVPh does not modify the crystal structure of PBSA, but decreases the crystallinity of PBSA in the blends.

The microstructure of the PBSA/PVPh blends was studied by SAXS. The morphological parameters in the lamellar level, such as long period ($L_P$), crystal layer thickness ($L_c$), and amorphous layer thickness ($L_a$) are determined by one-dimensional correlation function [37],

$$\gamma(z) = \frac{1}{\gamma(0)} \int_0^\infty I(q)q^2 \cos(qz) dq$$

(7)

where $z$ is the correlation distance, $\gamma(0)$ is the scattering invariant, $q$ is the scattering vector, which was calculated from $q = 4\pi \sin(\theta)/\lambda$ ($\lambda = 0.154$ nm), $2\theta$ is the scattering angle, and $I$ is the scattering intensity distributions.

The curves of normalized one-dimensional correlation function $\gamma(z)$ are shown in Fig. 8 for neat and blended PBSA. From Fig. 8, the values of $L_P$, $L_c$ and $L_a$ are obtained. Fig. 9 summarizes the variation of $L_P$, $L_c$ and $L_a$ for both neat PBSA and its blends with different PVPh contents.
Fig. 9. Variation of microstructural parameters with PVPh content for the PBSA/PVPh blends crystallized at 65 °C for 3 days: (□) long period; (<>) crystal layer thickness; and (∆) amorphous layer thickness.

As shown in Fig. 9, the values of \( L_P, L_c \), and \( L_a \) are 9.49, 3.35 and 6.14 nm, respectively, for neat PBSA. For an 80/20 blend, they increase to be 12.09, 3.70 and 8.39 nm, respectively. With further increasing the PVPh content, indicating that PVPh mainly resides in the interlamellar region of PBSA spherulites. Accordingly, the \( L_P \) values increase from 9.49 for neat PBSA to 12.09 and 14.96 nm for the 80/20 and 60/40 blends, respectively. The increase in \( L_P \) mainly arises from the increase in \( L_a \) although there is also a small increase in \( L_c \) in the PBSA/PVPh blends. Similar results were also found in PCL/phenolic blends [38].

4. Conclusions

Miscibility, isothermal crystallization kinetics, crystal structure, and microstructure of biodegradable PBSA/PVPh blends were investigated with DSC, POM, WAXD, and SAXS in detail in this work. The following conclusions are obtained:

(1) PBSA and PVPh are miscible crystalline/amorphous polymer blends. Miscibility of PBSA/PVPh blends is evidenced by the single composition dependent glass transition temperature over the entire blend compositions. The negative polymer–polymer interaction parameter, obtained from the melting depression of PBSA using the Nishi–Wang equation, further indicates that PBSA/PVPh blends are thermodynamically miscible.

(2) Isothermal crystallization kinetics study of neat and blended PBSA indicates that the crystallization mechanism of PBSA does not change, but the crystallization rate decreases with increasing the PVPh content in the blends.

(3) The crystal structure of PBSA is not modified in the PBSA/PVPh blends. However, the values of \( L_P, L_c \), and \( L_a \) become larger with increasing the PVPh content, indicating that PVPh mainly resides in the interlamellar region of PBSA spherulites.

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References