Miscibility and crystallization of poly(ethylene succinate)/poly(vinyl phenol) blends

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Abstract

Miscibility of biodegradable poly(ethylene succinate) (PES)/poly(vinyl phenol) (PVPh) blends has been studied by differential scanning calorimetry (DSC) in this work. PES is found to be miscible with PVPh as shown by the existence of single composition dependent glass transition temperature over the entire composition range. Spherulitic morphology and the growth rates of neat and blended PES were investigated by optical microscopy (OM). Both neat and blended PES show a maximum growth rate value in the crystallization temperature range of 45–65°C, with the growth rate of neat PES being higher than that of blended PES at the same crystallization temperature. The overall crystallization kinetics of neat and blended PES was also studied by DSC and analyzed by the Avrami equation at 60 and 65°C. The crystallization rate decreases with increasing the temperature for both neat and blended PES. The crystallization rate of blended PES is lower than that of neat PES at the same crystallization temperature. However, the Avrami exponent \( n \) is almost the same despite the blend composition and crystallization temperature, indicating that the addition of PVPh does not change the crystallization mechanism of PES but only lowers the crystallization rate.

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1. Introduction

The development and application of biodegradable polymers has recently received more and more attention from the viewpoint of environment protection and resource recycle. Based on the difference in the preparation method, biodegradable polymers can usually be classified into two types. One is the biosynthetic polymer, such as bacterial polyhydroxyalkanoates (PHAs). The other is the chemo-synthetic polymer, such as the aliphatic polyesters.

Poly(ethylene succinate) (PES) is one of the chemo-synthetic biodegradable polyesters, and its chemical structure is \((-\text{OCH}_2\text{CH}_2\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}^-)_n\). The crystal structure, morphology and melting behavior of PES have been reported in the literature [1–4]. In previous works, we studied the nonisothermal crystallization behavior of PES from the amorphous state and the subsequent melting behavior after the nonisothermal crystallization process from the melt [5,6].

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 poly(hydroxybutyrate) (PHB) and poly(ethylene oxide) (PEO) blends [7,8]. 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 [9].

Poly(4-vinyl phenol) (PVPh) is an amorphous polymer with high glass transition temperature. PVPh has been reported to be miscible with various polymers such as poly(ethylene oxide), PHB, poly(hydroxyvalerate) and poly(t-lactide) [10–13]. The miscibility of polymer blends containing PVPh is usually attributed to the hydrogen...
bonding interaction between the hydroxyl group of PVPh and other groups of the partners, such as the carbonyl group. In the previous work, we studied the miscibility and crystallization behavior of poly(butylene succinate) (PBSU)/PVPh blends [14]. PBSU is miscible with PVPh as shown by the existence of single composition dependent glass transition temperature over the entire composition range. Furthermore, the polymer–polymer interaction parameter is always negative and composition dependent, indicating that PBSU/PVPh blends are thermodynamically miscible in the melt. The chemical structure of PBSU is similar to that of PES. They are only different in their numbers of methylene groups between the two ether groups, namely 4 and 2 for PBSU and PES, respectively. Thus PES/PVPh blends may be a new miscible crystalline/amorphous polymer blends model since the carbonyl group of PES is likely to form a hydrogen bond with the hydroxyl group of PVPh as in the case of PBSU/PVPh blends. The properties of PES can thus be modified, and the application field of PES can also be extended. To the best of our knowledge PES/PVPh blends have not been reported so far in the literature. Therefore, the purpose of this manuscript is to investigate the miscibility and crystallization of PES/PVPh blends on the basis of our previous PBSU/PVPh blends study. The miscibility, morphology and crystallization of PES/PVPh blends have been studied with DSC and OM for the first time in this work. PES is found to be miscible with PVPh over the entire composition range as shown by the single composition dependent glass transition temperature.

2. Experimental

PES ($M_w = 10,000$) and PVPh ($M_w = 20,000$) samples used in this study were purchased from Scientific Polymer Products, Inc. (Ontario, NY) and Aldrich Company, respectively. PES/PVPh blends were prepared with mutual solvent $N,N$-dimethylformamide at an elevated temperature. The solution of both polymers (0.02 g/ml) was cast on a petri dish, and the solvent was allowed to evaporate in a controlled air stream for 1 day. The resulting films were dried further in vacuum at 50 °C for 3 days to remove the solvent completely. PES/PVPh blends were thus prepared with various compositions ranging from 80/20 to 20/80 in weight ratio, the first number referring to PES.

The glass transition temperature ($T_g$) and the melting point ($T_m$) of the melt-quenched PES/PVPh blends were measured by a TA Instruments differential scanning calorimetry (DSC) 2910 with a Thermal Analyst 2000 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. In the case of neat PES, the annealing temperature was chosen as 130 °C.

The spherulitic morphology was observed with a polarizing microscope (Olympus BHA-P) equipped with a temperature controller (Linkam LK-600PM). The PES/PVPh blend samples were first held at 200 °C for 3 min to destroy any thermal history and then quenched to the crystallization temperature $T_c$ at a cooling rate of 100 °C/min. In the case of neat PES, the temperature was chosen as 130 °C to melt the sample. The spherulitic growth rate $G$ was calculated from the change of radius $R$ with time $t$, i.e., $G = dR/dt$.

The isothermal crystallization of PES/PVPh blends was also examined with DSC from the melt. The sample was melted at 200 °C for 3 min, cooled quickly to the $T_c$, 60 and 65 °C in this work, and then maintained at the $T_c$ until the crystallization completed. The crystallization exothermic curves were recorded and analyzed with the Avrami equation.

3. Results and discussion

3.1. Miscibility study

Miscibility of PES/PVPh blends was studied first by DSC. Fig. 1 shows the DSC traces of the melt-quenched samples of PES/PVPh blends. Neat PES has a $T_g$ of ca. −16 °C, a cold crystallization peak temperature of ca. 51 °C and a $T_m$ of ca. 102 °C. On the other hand, neat PVPh is an amorphous polymer with a high $T_g$ of ca. 175 °C. It can be seen from Fig. 1 that PES/PVPh blends show a single composition dependent $T_g$ between the $T_g$s of neat PES and neat PVPh, indicating that PES and PVPh are miscible over the entire composition range. The cold crystallization peak temperature of PES is also found to shift to high temperature range in the blends compared with that of neat PES, indicating that the crystallization of PES is suppressed in the presence of PVPh. The $T_g$ of the PES/PVPh blends was increased due to the blending with the high $T_g$ component PVPh, resulting in the decrease of the mobility of PES in the blends. The crystallization of PES is, therefore, hindered by the presence of PVPh. The cold crystallization temperature

![Fig. 1. DSC traces of melt-quenched PES/PVPh blends at a heating rate of 20 °C/min.](image-url)
of PES could not be detected in the blends containing PVPh above 40 weight percent because of the high $T_g$ of the blends. The $T_m$ of PES is also found to shift to low temperature range upon the addition of PVPh in the PES/PVPh blends; however, the decrease of the $T_m$ is very slight. The $T_m$ of PES could not be detected with PVPh above 40 weight percent in the blends, which is similar to the trend of the cold crystallization temperature.

The composition dependence of $T_g$ of the PES/PVPh blends is summarized in Fig. 2. Meanwhile, the composition dependence of the cold crystallization temperature and the $T_m$ of PES is also shown in Fig. 2. It can be concluded more clearly from Fig. 2 that PES is miscible with PVPh from the composition dependence of $T_g$ of the blends, the increase of the cold crystallization peak temperature of PES and the depression of the $T_m$ of PES with the increase of PVPh. The miscibility of PES/PVPh blends may arise from the hydrogen bonding formed between the carbonyl group of PES with the hydroxyl group of PVPh, which will be investigated further by FT-IR.

The melting endotherm of PES could not be detected with the PVPh content above 40 weight percent for the melt-quenched PES/PVPh blends samples. But the melting endotherm of PES for each of the PES/PVPh blends has been found for the as cast samples as shown in Fig. 3. The thermal history is different in these two cases. Therefore, PES is expected to have a larger mobility to crystallize for as cast samples than that for melt-quenched samples. Neat PES has an endotherm at ca. 104 °C in Fig. 3. However, the melting endotherm shifts to low temperature range in PES/PVPh blends compared with that of neat PES. Furthermore, two melting endotherms are found for PES/PVPh 80/20 blend sample. The multiple melting endotherms are often found for the as cast polyester blends and are attributed to the melting and recrystallization model [14]. The multiple melting endotherms of PES/PVPh blends may also arise from the melting and recrystallization model. The apparent melting fusion enthalpy ($\Delta H_m$) was measured for each of PES/PVPh blends of the as cast samples. The value of $\Delta H_m$ was plotted as a function of the blend composition in Fig. 4, which decreased almost linearly with the increase of PVPh in the PES/PVPh blends.

3.2. Spherulitic morphology and overall crystallization

Spherulitic morphology and the growth rates of neat and blended PES were also studied by OM. In this work, we only studied the spherulitic morphology and the growth rates of PES/PVPh 80/20 and compared them with those of neat PES. Shown in Figs. 5 and 6 are the spherulitic morphology of neat and blended PES, respectively, which crystallized in the temperature range of 45–65 °C. Both neat and blended PES shows compact spherulites with clear Maltese. The spherulites size increases with the crystallization temperature for both neat and blended PES, indicating that the nucleation density decreases with the crystallization temperature. On the other hand, the spherulites of PES in the
blends become larger than those of neat PES crystallized at the same temperature, indicative of a decrease in the nucleation density with the addition of PVPh. PES spherulites are space-filling in the blends, indicating that PVPh is rejected in the crystallization process as a noncrystallizable component and resides primarily in the interlamellar and interfibrillar domains of the PES spherulites [15].

The spherulitic growth rates of neat and blended PES were also measured by following the development of radius with time. Both neat and blended PES spherulites show a linear growth until the contact with other spherulites during the crystallization process. As an example, shown in Fig. 7(a) is the time dependence of the radius of PES/PVPh 80/20 spherulites growing at 60 °C. The linear growth rate was estimated to be 22.62 μm min from the slope of the straight...
line. Using the same method, the growth rates of both neat and blended PES spherulites have been measured in the crystallization range of 45–65 °C. Shown in Fig. 7(b) is the temperature dependence of the spherulitic growth rates of neat and blended PES. Both neat and blended PES exhibited a bell shape for the growth rates in the crystallization temperature range of 45–65 °C. Neat PES showed a maximum value for the growth rate at around 55 °C, while blended PES showed a maximum value at around 58 °C. Furthermore, it was also found that the growth rate of neat PES was higher than that of blended PES crystallized at the same temperature, indicating that the addition of PVPh reduced the growth rates of PES in the blends. The decrease of the growth rates of PES in the blends with the addition of PVPh may be related to the following three facts. First, the addition of high $T_g$ component PVPh increased the $T_g$ of...
PES/PVPh blends, resulting in the decrease of the mobility of PES compared with that of neat PES. Second, the added PVPh is a diluent to PES in the miscible blends, resulting in the dilution of PES chains at the spherulites growth front. Third, the decrease of the melting point temperature in the blends may drop the thermodynamic driving force required for the growth of PES spherulites.

The overall crystallization kinetics of neat and blended PES was also investigated with DSC. As introduced in the experimental section, we only studied the isothermal crystallization of neat PES and PES/PVPh 80/20 blend at 60 and 65 °C from the melt. The crystallization exothermic curves of heat flow as a function of time were recorded and investigated. The relative crystallinity $X_t$ at time $t$ is defined as the ratio of the area under the exothermic curve between the onset crystallization time and the crystallization time $t$ to the whole area under the exothermic curve from the onset crystallization time to the end crystallization time. The plots of relative crystallinity $X_t$ as a function of crystallization time $t$ are shown in Fig. 8(a) for the isothermal crystallization of the neat and blended PES at 60 and 65 °C. The crystallization time $t$ increases with increasing the crystallization temperature from 60 to 65 °C for both neat and blended PES. At the same crystallization temperature, the crystallization time of blended PES is longer than that of neat PES. The results indicate preliminarily that the crystallization rates of neat and blended PES reduce with the increase of crystallization temperature from 60 to 65 °C. Meanwhile, it also indicates the crystallization of PES is suppressed in the blends compared with neat PES. The trend is consistent with that of the spherulitic growth rate shown in Fig. 7(b).

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

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

(1)

Here $n$ 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 [16]. Shown in Fig. 8(b) are the Avrami plots of $\log(-\ln(1 - X_t))$ versus $\log t$ for neat and blended PES crystallized at 60 and 65 °C, from which the Avrami parameters $n$ and $k$ were obtained. The Avrami exponent $n$ and crystallization rate constants $k$ of the neat and blended PES are listed in Table 1. From Fig. 8(b) and Table 1, it is seen that the Avrami exponent $n$ is almost the same despite the blend composition and the crystallization temperature, suggesting that the crystallization mechanism remains the same. However, the crystallization rate constant $k$ decreases with the increase of crystallization temperature from 60 to 65 °C for both neat and blended PES. Moreover, the value of $k$ for the blended PES reduces compared with that of neat PES at the same crystallization temperature, indicating the crystallization of PES was hindered with the addition of PVPh. The trends are the same as those of Fig. 8(a). All the results mentioned above show that the addition of PVPh does not change the overall crystallization mechanism of PES but only reduces the crystallization rate in the PES/PVPh blends. The reduction of the crystallization rate of PES can also be explained by the increase of the glass transition temperature and the depression of the melting point after adding the PVPh content in the blends.

Now let us compare the similarity and differences of PES/PVPh blends and PBSU/PVPh blends simply. Both PES and PBSU can form miscible blends with PVPh due to the similarity of the chemical structures of the two polymers, which may arise from the hydrogen bond formation between the carbonyl groups of the two biodegradable polyesters and the hydroxyl group of PVPh. However, the presence of PVPh may have different effect on the morphology and crystallization of PES and PBSU in the blends. In the PES/PVPh blends, the presence of PVPh does not have any significant effect on the morphology and crystallization mechanism of PES, and only lowers the crystallization rate. In the PBSU/PVPh blends, the presence of PVPh has a significant effect on the morphology of PBSU, which varied apparently as a function of blend composition [14].

### Table 1

<table>
<thead>
<tr>
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<th>$T_c$ (°C)</th>
<th>$n$</th>
<th>$k$ (min$^{-n}$)</th>
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<tr>
<td>PES</td>
<td>60</td>
<td>2.44</td>
<td>6.74 x 10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>2.35</td>
<td>2.67 x 10$^{-3}$</td>
</tr>
<tr>
<td>PES/PVPh 80/20</td>
<td>60</td>
<td>2.35</td>
<td>5.52 x 10$^{-3}$</td>
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<td></td>
<td>65</td>
<td>2.24</td>
<td>1.44 x 10$^{-3}$</td>
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4. Conclusions

Miscibility and crystallization of PES/PVPh blends have been studied with DSC and OM in this work. PES shows miscibility with PVPh as shown by the single composition dependent glass transition temperature through the DSC study of the melt-quenched PES/PVPh blend samples. OM experiments indicate that both neat PES and PES/PVPh 80/20 show compact spherulites with clear Maltese. The spherulitic growth rates of neat and blended PES were also measured as a function of crystallization temperature. Bell shape curves were found for the growth rate of both neat and blended PES in the crystallization temperature range of 45–65 °C, which exhibited a maximum value at ca. 55 and 58 °C, respectively, for neat and blended PES. The growth rate of neat PES was higher than that of blended PES crystallized at the same temperature, indicating that the addition of PVPh reduced the spherulitic growth of PES in the blends. The overall crystallization kinetics of neat and blended PES was also studied by DSC and analyzed by the Avrami equation at 60 and 65 °C. The Avrami exponent $n$ remained almost the same despite the blend composition and crystallization temperature. However, the crystallization rate decreased with increasing the temperature for both neat and blended PES. The crystallization rate of blended PES was lower than that of neat PES at the same crystallization temperature. It can thus be concluded that the addition of PVPh does not change the crystallization mechanism of PES but only lowers the crystallization rate.

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