

Miscibility and Crystallization Behaviors of Biodegradable Poly(butylene succinate-co-butylene terephthalate)/Phenoxy Blends

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ABSTRACT: Miscibility and crystallization behaviors of biodegradable poly(butylene succinate-co-butylene terephthalate) (PBST)/poly(hydroxyl ether biphenyl A) (phenoxy) blends were investigated with various techniques in this work. PBST and phenoxy are completely miscible as evidenced by the single composition-dependent glass transition temperature over the entire blend compositions. Nonisothermal melt crystallization peak temperature is higher in neat PBST than in the blends at a given cooling rate. Isothermal melt crystallization kinetics of neat and blended PBST was studied and analyzed by the Avrami

equation. The overall crystallization rate of PBST decreases with increasing crystallization temperature and the phenoxy content in the PBST/phenoxy blends; however, the crystallization mechanism of PBST does not change. Moreover, blending with phenoxy does not modify the crystal structure but reduces the crystallinity degree of PBST in the PBST/phenoxy blends. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 720–726, 2011

Key words: biodegradable; blends; crystallization; miscibility

INTRODUCTION

More and more attention has been paid to biodegradable polymers in recent years owing to the environmental problems caused by conventional plastics. In general, biodegradable polymers can be classified into two types in terms of the preparation methods. One is biosynthetic polymers, such as bacterial poly(hydroxyalkanoates). The other is chemosynthetic polymers, such as the linear aliphatic polyesters. For instance, poly(butylene succinate) (PBS) is known to be an excellent biodegradable polyester with many interesting properties, including biodegradability, melt processability, and chemical resistance. Many investigations on modification via chemical copolymerization have been reported to further extend the practical application of PBS because the physical properties of PBS can be modified through the incorporation of the second comonomer into the backbone of PBS. Thus, some novel biodegradable copolymers have been developed, such as poly(butylene succinate-co-butylene adipate), poly(butylene succinate-co-ethylene succinate), poly(butylene succi-

nate-co-hexamethylene succinate), and poly(butylene succinate-co-propylene succinate).^{1–4} It should be noted that poly(butylene succinate-co-butylene terephthalate) (PBST), a kind of copolyester containing both aliphatic and aromatic units, has also been synthesized. The synthesized PBST copolyesters show random comonomer sequential structures; moreover, the thermal properties and crystallization behavior of PBST depend strongly on their comonomer compositions. The crystal structure of PBST is found to be dependent on the comonomer composition, which changes from monoclinic lattice corresponding to PBS crystal to triclinic lattice corresponding to poly(butylene terephthalate) (PBT) crystal when the butylene terephthalate (BT) comonomer content approaches 30 mol %.⁵ Furthermore, the overall crystallization activation energy of the copolyesters increases with increasing the butylene succinate (BS) unit content during isothermal crystallization process, showing that the BS units on the copolyester chain hinder the crystallizability of the BT units.⁶ The degradation behavior still happens in PBST copolyester with BT content up to 70 mol %; however, the degradation rate of PBST copolyesters decreases with increasing the BT content because the aromatic ester linkage is less degradable than aliphatic ester.⁷

Poly(hydroxyl ether biphenyl A) (phenoxy) is an amorphous polymer with high glass transition temperature. Phenoxy is a proton donor, which offers

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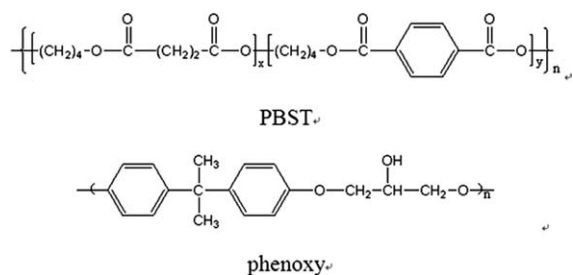
potential for hydrogen-bonding interaction with proton-acceptor polymers. Therefore, it is often used in polymer blending. It is well known that polymer blending is an economic way of designing novel materials with improved properties. The miscibility of polymer blends may benefit from the significant interaction between polymers, such as hydrogen bonding.⁸ Thus, many miscible polymer blends are obtained by blending hydroxyl groups containing polymers such as poly(vinyl phenol) (PVPh) or phenoxy with polymers containing proton-acceptor units. Many polyesters have been found to be miscible with PVPh, such as poly(hydroxybutyrate), poly(ϵ -caprolactone) (PCL), and PBS.^{9–12} In addition, many polyesters have also been found to be miscible or partially miscible with phenoxy, such as PCL, PBT, poly(1,4-butylene adipate), and poly(ethylene adipate).^{10,13,14}

It should be noted that few works have been done on the miscibility and crystallization behaviors of biodegradable PBST-based polymer blends. To the best of our knowledge, PBST/phenoxy blends have not been reported in the literature till now. In this work, PBST/phenoxy blends were prepared through solution and casting method. Moreover, miscibility and crystallization behaviors of PBST/phenoxy blends were investigated with various techniques in detail. It is expected that the results reported herein will be of interest and help for a better understanding of structure and properties relationship of biodegradable polymer blends.

EXPERIMENTAL

Materials

PBST ($M_w = 7.35 \times 10^4$ g/mol), a copolymer with 70 mol % butylene terephthalate, was kindly provided by Professor Amin Cao's lab at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Phenoxy ($M_w = 6.5 \times 10^4$ g/mol) was purchased from Scientific Polymer Products. The chemical structures of PBST and phenoxy are shown in Scheme 1.



Scheme 1 Chemical structures of PBST and phenoxy.

Samples preparation

PBST/phenoxy blends were prepared with mutual solvent chloroform (CHCl_3) at room temperature. The polymer mixtures (0.01 g/mL) were stirred for 6–8 h. The solution of both polymers was cast on a dish at room temperature and 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 to ensure total removal of chloroform. In this way, PBST/phenoxy blends were prepared with various compositions ranging from 100/0, 85/15, 70/30, 50/50, 30/70, 15/85 to 0/100 in weight ratio, the first number referring to PBST.

Measurements

Thermal analysis was performed using a TA Instruments differential scanning calorimetry (DSC) Q100 with a Universal Analysis 2000. All operations were performed under nitrogen purge, and the weight of the samples varied between 4 and 6 mg. The glass transition temperature (T_g) of the melt-quenched PBST/phenoxy blends was measured at a heating rate of 20°C/min. The samples were first annealed at 240°C for 3 min to erase any thermal history and subsequently quenched into liquid nitrogen. Nonisothermal melt crystallization and isothermal melt crystallization kinetics of neat PBST and its blends with different phenoxy content were further investigated with DSC. In this work, we only studied neat PBST and the blends with the weight fraction of phenoxy less than 30% because PBST did not crystallize or crystallized very slowly when the phenoxy content was above 50 wt %. For nonisothermal melt crystallization, the crystallization peak temperature was obtained from the DSC traces at a cooling rate of 20°C/min after the sample was first annealed at 240°C for 3 min to erase any thermal history. For isothermal melt crystallization kinetics study, the sample was first annealed at 240°C for 3 min to erase any thermal history, cooled to the crystallization temperature (T_c) at a rate of 60°C/min, and then maintained at T_c until the crystallization is complete.

Spherulitic morphology of PBST/phenoxy blends was observed under crossed polars with a polarizing optical microscope (POM) (Olympus BX51) equipped with a temperature controller (Linkam THMS 600). The samples were first annealed at 240°C for 3 min to erase any thermal history and then cooled to 160°C at 60°C/min.

Wide-angle X-ray diffraction (WAXD) experiments were performed on a Rigaku d/Max2500 VB2+/PC X-ray diffractometer at 40 kV and 20 mA at a scanning rate of 5°/min. The samples for the WAXD experiments were first pressed into films with

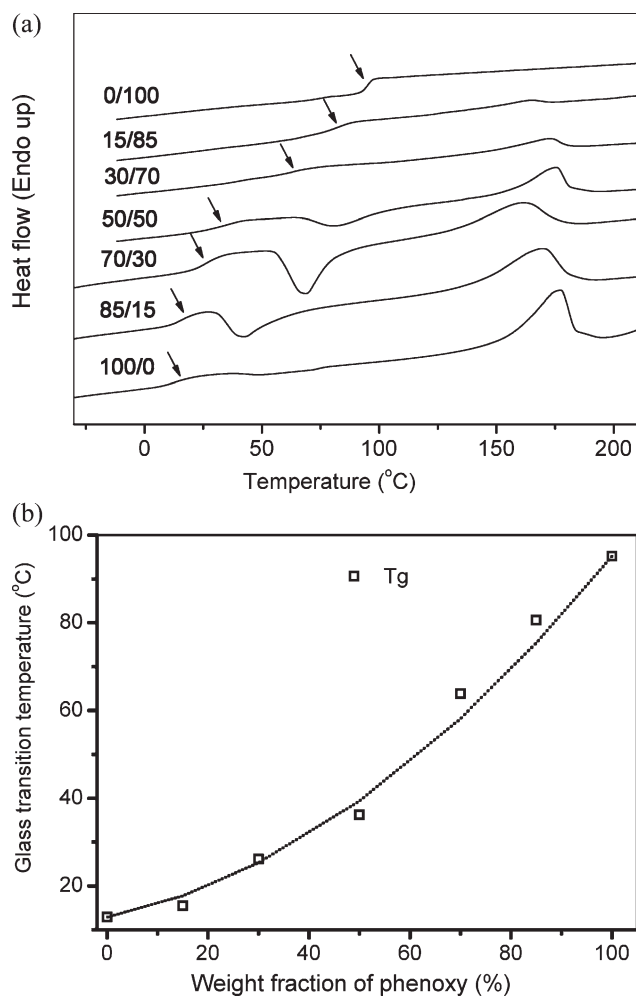


Figure 1 (a) DSC heating traces of PBST/phenoxy blends for the melt-quenched samples at 20°C/min; (b) variation of T_g with the phenoxy content in PBST/phenoxy blends (The dotted line is fitted by the Kwei equation with $k = 1$ and $q = -58$).

thickness of around 1 mm on a hot stage at 240°C for 3 min and then transferred into a vacuum oven at 150°C for 24 h.

RESULTS AND DISCUSSION

Miscibility of PBST/phenoxy blends

The miscibility of PBST/phenoxy blends was first studied by measuring T_g s of the melt-quenched samples with DSC. Figure 1(a) shows the DSC traces of melt-quenched samples. Neat PBST is a semicrystalline polymer with a low T_g of about 12.9°C. In contrast, neat phenoxy is an amorphous polymer with a high T_g of about 95.2°C. It can be found that PBST/phenoxy blends show a single composition-dependent T_g between those of the two neat components, indicating that PBST and phenoxy are miscible over the entire composition range. Figure 1(b) summarizes the variation of T_g with the phenoxy

content for the PBST/phenoxy blends. As shown in Figure 1(b), it is obvious that T_g of the PBST/phenoxy blends increases after blending with high T_g component phenoxy compared with that of neat PBST. As a result, the mobility of PBST decreases with increasing the phenoxy content in the blends.

The Kwei equation is often used to fit the variation of glass transition with blend composition of polymer blends with specific interaction, such as hydrogen bonding,¹⁵ which is also applied in this work as follows:

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1 W_2, \quad (1)$$

where W_1 and W_2 are the weight fraction of neat PBST and neat phenoxy, T_{g1} and T_{g2} are the respective T_g of the neat PBST and neat phenoxy, q is a parameter corresponding to the strength of hydrogen bonding in the blends and reflecting a balance between the breaking of the self-association and the forming of the interassociation hydrogen bonding, and k is a fitting parameter. As shown in Figure 1(b), the Kwei equation fits the variation of T_g with the weight fraction of phenoxy content in PBST/phenoxy blends very well. In this work, a negative q of -58 is obtained in the case of $k = 1$, which is greatly higher than that of -100 for the PCL/phenoxy blends, indicating that the interaction between PBST and phenoxy is stronger than that in the PCL/phenoxy blends.¹⁰ The negative q value in this work indicates that a fraction of self-associated hydrogen bonding of phenoxy is broken to form weaker inter-associated hydrogen bonding. The miscibility between PBST and phenoxy may arise from this specific interaction. The Fourier transform infrared spectroscopy study on the hydrogen bonding between PBST and phenoxy is still underway and will be reported in the near future.

Crystallization behavior of PBST/phenoxy blends

Nonisothermal melt crystallization behavior of neat and blended PBST was studied with DSC. Figure 2 shows the DSC cooling curves of the neat and blended PBST at 20°C/min. As shown in Figure 2, nonisothermal melt crystallization peak temperature (T_{cc}) of neat PBST is found to be around 130°C, whereas for the 85/15 and 70/30 samples, their T_{cc} s decrease to around 127 and 117°C, respectively. The width at half height of crystallization peak for neat PBST, 85/15, and 70/30 is about 11, 13, and 20°C, respectively. Besides, the crystallization enthalpy of neat PBST, 85/15, and 70/30 is 36.7, 33.2, and 28.1 J/g, respectively. All the results above indicate that the crystallization of PBST is suppressed by the addition of phenoxy in the blends.

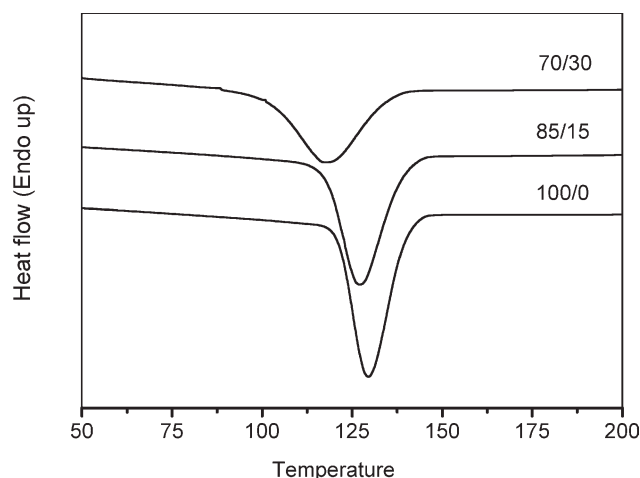


Figure 2 Nonisothermal melt crystallization of neat PBST and its blends at a cooling rate of 20°C/min.

Isothermal melt crystallization kinetics of neat and blended PBST was further investigated with DSC. Figure 3(a) shows the variation of relative crystallinity degree with crystallization time for an 85/15 blend at different T_c s. It can be seen from Figure 3(a) that the crystallization time prolongs with increasing T_c , indicating that the crystallization is retarded at higher T_c . Similar results can also be found for the neat PBST and 70/30 samples. The effect of the phenoxy content on the isothermal melt crystallization of PBST was further studied in this work. Figure 3(b) illustrates the variation of relative crystallinity degree with crystallization time for neat and blended PBST with different phenoxy contents at 150°C. At this T_c , the crystallization time prolongs with increasing the phenoxy content, indicating that the addition of phenoxy reduces the crystallization rate of PBST in the blends compared with that of neat PBST.

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

$$1 - X_t = \exp(-kt^n), \quad (2)$$

where X_t is the relative crystallinity degree 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.^{16–18}

Figure 4(a) shows the Avrami plots for an 85/15 blend at different T_c s. It can be seen from Figure 4(a) that a series of straight lines are obtained, indicating that the Avrami method can describe the development of the relative crystallinity degree as a function of crystallization time very well. Similar results are also found for the neat PBST and 70/30 samples. For

brevery, the results are not shown here. Figure 4(b) shows the Avrami plots for neat and blended PBST at 150°C. It is found that a series of straight lines are obtained, too, indicating that the Avrami method can describe the development of the relative crystallinity degree as a function of crystallization time very well for both neat and blended PBST. Accordingly, the Avrami parameters n and k can be obtained from the slopes and intercepts of the Avrami plots, respectively. The values of n and k for neat and blended PBST are summarized in Table I for comparison. The average value of n is around 2.3 for neat PBST and remains almost unchanged in the PBST/phenoxy blends, i.e., around 2.2 for both 85/15 and 70/30, suggesting that the crystallization of PBST may correspond to three-dimensional truncated spherulitic growth with athermal nucleation.¹⁹ Furthermore, the almost unchanged n indicates that blending with phenoxy does not change the crystallization mechanism of PBST in the PBST/phenoxy blends. It is also of interest to study the effects of T_c and the blend composition on the overall crystallization rate of PBST in the PBST/phenoxy blends. It is

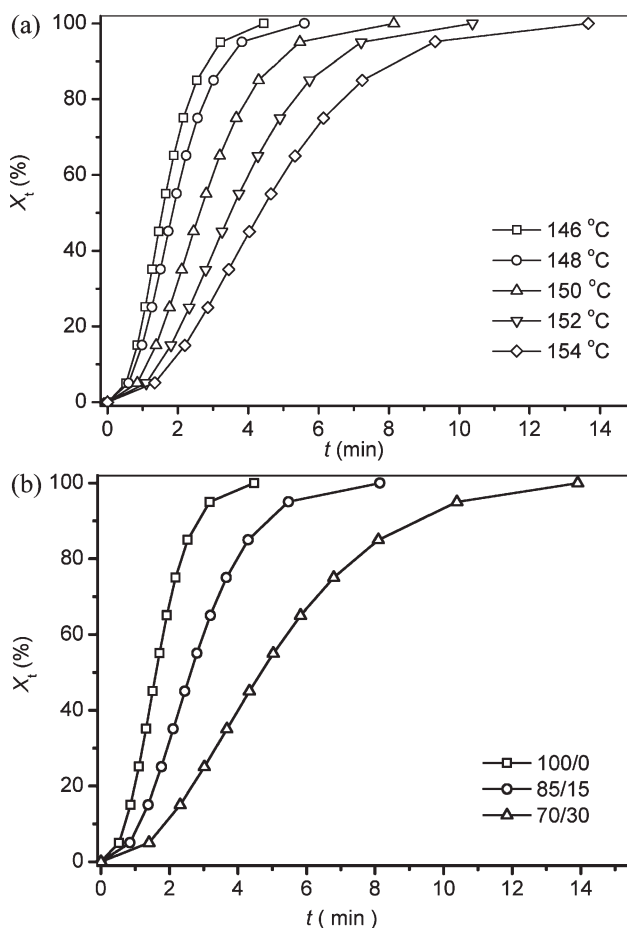


Figure 3 (a) Development of X_t versus t of an 85/15 blend; (b) development of X_t versus t of neat and blended PBST crystallized at 150°C.

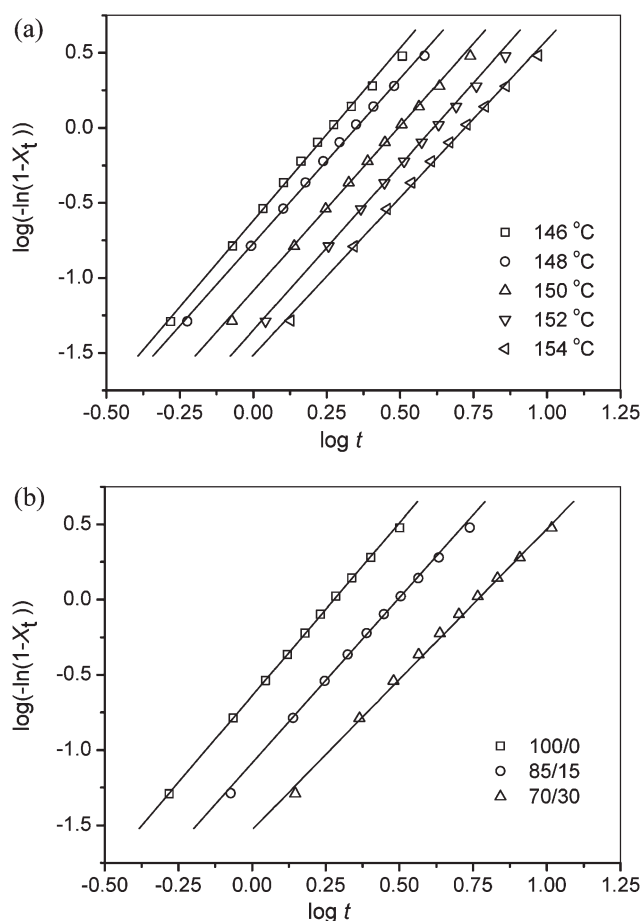


Figure 4 (a) Avrami plots of a PBST/phenoxy 85/15 blend; (b) Avrami plots of neat and blended PBST crystallized at 150°C.

clear from Table I that the k values decrease with increasing T_c for both neat and blended PBST, indicating that the overall crystallization rate is reduced at higher T_c . Moreover, at a given T_c of 150°C, the k values decrease with increasing the phenoxy content,

TABLE I
Isothermal Crystallization Kinetics Parameters of Neat and Blended PBST Based on the Avrami Equation

Samples	T_c (°C)	n	k (min ⁻ⁿ)	$t_{0.5}$ (min)
100/0	150	2.3	2.30×10^{-1}	1.61
	152	2.3	1.33×10^{-1}	2.05
	154	2.3	4.42×10^{-2}	3.31
	156	2.3	2.82×10^{-2}	4.03
	158	2.2	2.05×10^{-2}	4.96
85/15	146	2.3	2.42×10^{-1}	1.58
	148	2.2	1.70×10^{-1}	1.89
	150	2.2	8.21×10^{-2}	2.64
	152	2.2	4.51×10^{-2}	3.46
	154	2.1	3.08×10^{-2}	4.40
70/30	142	2.3	9.73×10^{-2}	2.35
	144	2.3	6.08×10^{-2}	2.88
	146	2.2	4.83×10^{-2}	3.36
	148	2.1	4.12×10^{-2}	3.84
	150	2.0	2.96×10^{-2}	4.84

indicating that blending with phenoxy decreases the overall crystallization rate of PBST in the PBST/phenoxy blends relative to neat PBST.

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

$$t_{0.5} = (\ln 2/k)^{1/n}, \quad (3)$$

where n and k are the same as in the Avrami equation. Table I summarizes the values of $t_{0.5}$ for both neat and blended PBST. It is obvious that the values of $t_{0.5}$ increase with increasing T_c for both neat and blended PBST. Moreover, it can also be found that the values of $t_{0.5}$ are smaller in neat PBST than those in the blends at a given T_c , indicating that the crystallization rate of PBST becomes slower after blending with phenoxy.

To show the effects of blend composition and crystallization temperature on the crystallization rate of PBST clearly, Figure 5 summarizes the temperature dependence of $1/t_{0.5}$ for neat and blended PBST. As shown in Figure 5, the overall crystallization rates of PBST decrease with increasing T_c for both neat and blended PBST, resulting from the difficulty in nucleation at high T_c . On the other hand, the overall crystallization rates decrease with increasing the phenoxy content, indicating that blending with amorphous phenoxy retards the crystallization of PBST in the blends. The reduction of the crystallization rate of PBST with increasing the phenoxy content in the blends may be attributed to the following factors. First, the addition of high T_g

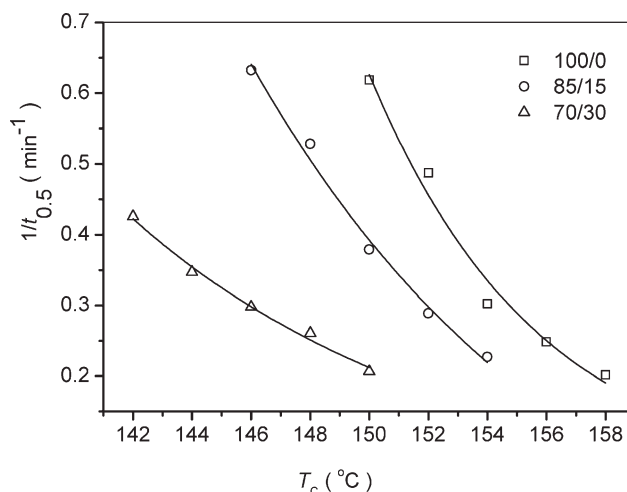


Figure 5 Crystallization temperature dependence of $1/t_{0.5}$ for neat and blended PBST.

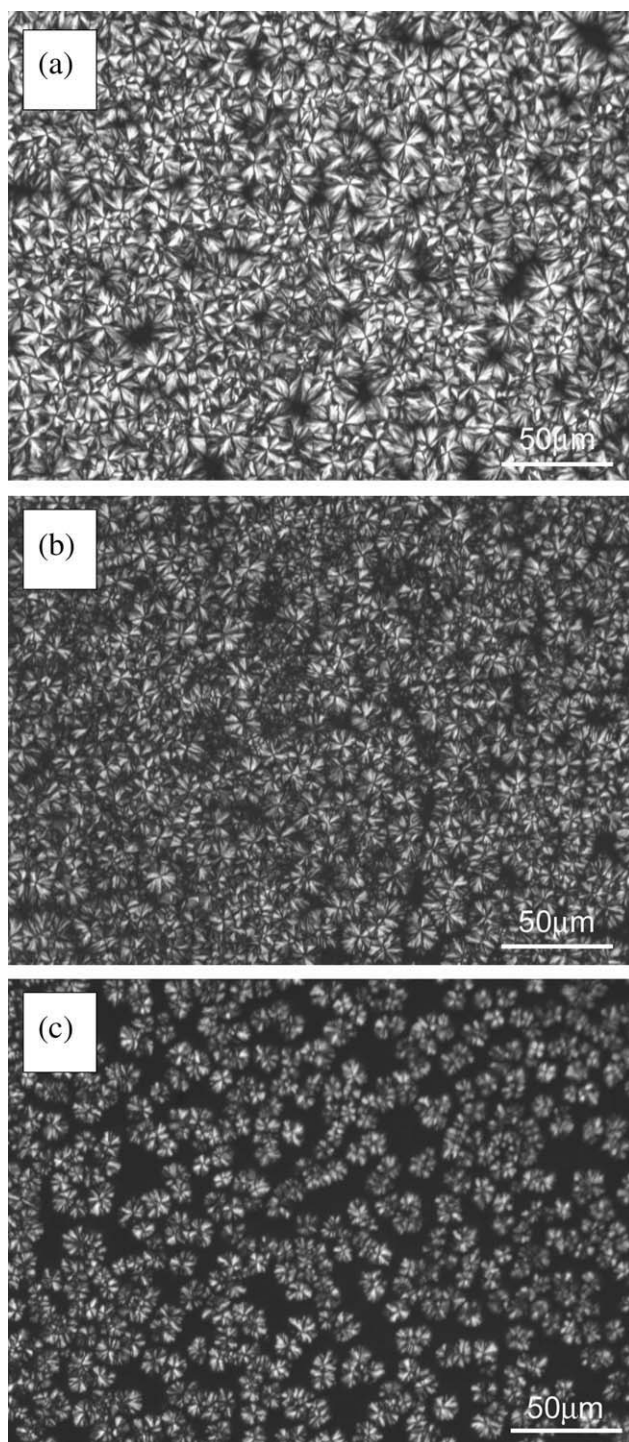


Figure 6 POM graphs of the spherulitic morphology of neat and blended PBST crystallized at 160°C for 30 min. (a) 100/0; (b) 85/15; and (c) 70/30.

component phenoxy increases T_g s of PBST/phenoxy blends, resulting in the decrease of the mobility of PBST compared with that of neat PBST. Second, the addition of phenoxy may play a role of a diluent to PBST in the miscible blends, resulting in the dilution of PBST chains at the spherulites growth front.

The spherulitic morphology of neat PBST and its blends was studied with POM in this work. Figure 6 shows the POM images of neat and blended PBST crystallized at 160°C for 30 min. After a given crystallization time of 30 min, the whole space is filled with PBST spherulites for neat PBST as shown in Figure 6(a), while there are still some uncrystallized areas for both 85/15 and 70/30 as shown in Figure 6(b,c), especially for the 70/30 sample. It is clear that the size of the spherulites is bigger in neat PBST than in the PBST/phenoxy blends after isothermal crystallization at 160°C for 30 min, suggesting that the spherulitic growth rate of neat PBST should be higher than those of the PBST/phenoxy blends. However, it is difficult to measure the spherulitic growth rates for both neat and blended PBST accurately because the size of the spherulites is too small. The slow down of the spherulitic growth of PBST in the presence of phenoxy is consistent with the DSC results in the previous section, which may be attributed to the following factors, i.e., the lower mobility of PBST and the diluent effect of phenoxy in the blends.

PBST crystallized in triclinic lattice of PBT when the BT content was 70 mol %.⁵ The BT content of the PBST used in this study is 70 mol %; therefore, the crystal structure of PBST is the same as that of PBT. Figure 7 shows the WAXD patterns of neat and blended PBST crystallized at 150°C for 24 h. It can be seen from Figure 7 that both neat and blended PBST exhibit almost the same diffraction peaks at the same location. The main peaks located at 17.2°, 23.2°, and 25.2° correspond to (010), (100), and ($\bar{1}11$) planes of PBST, respectively.²⁰ The intensity of the diffraction peaks of PBST decreases with increasing the phenoxy content, indicating that the crystallinity degree of PBST may decrease with the addition of

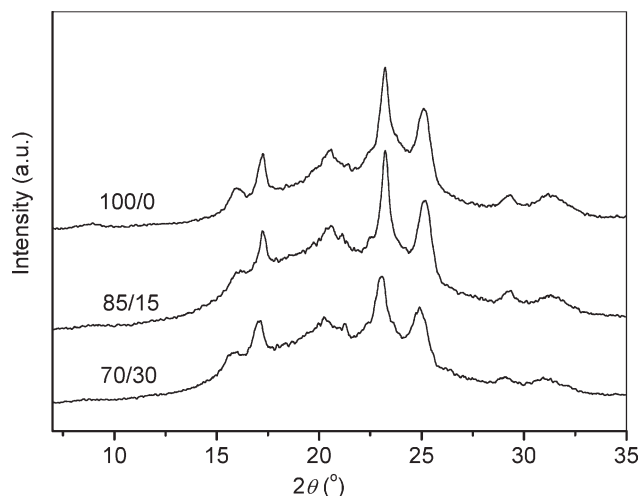


Figure 7 WAXD patterns of neat and blended PBST crystallized at 150°C for 24 h.

phenoxy. The crystallinity degree values may be calculated by the ratio of the area under the crystalline peaks to the whole area under both the crystalline peaks and the amorphous background on the basis of the WAXD patterns; thus, the crystalline degree values are estimated to be around $30\% \pm 3\%$ for neat PBST and 85/15 and $23\% \pm 3\%$ for 70/30 in this work. Such results indicate that blending with amorphous phenoxy does not modify the crystal structure but decreases the crystallinity degree of PBST in the blends.

In the above sections, miscibility and crystallization behaviors of PBST/phenoxy blends were studied in detail with various techniques. However, it should be noted that the PBST sample used in this work is a copolymer; thus, it is clear that the miscibility between PBST and phenoxy and the crystallization behavior of PBST in its pure state and in the PBST/phenoxy blends must depend strongly on the comonomer composition of PBST. We should be very careful to deduce the related conclusions about miscibility and crystallization behaviors of PBST/phenoxy blends in case other PBST samples with different comonomer compositions are used.

CONCLUSIONS

Miscibility and crystallization behaviors of biodegradable PBST/phenoxy blends were investigated with DSC, POM, and WAXD in this work. PBST and phenoxy are miscible crystalline/amorphous polymer blends over the whole compositions as evidenced by the single composition-dependent T_g . Nonisothermal melt crystallization behavior and isothermal melt crystallization kinetics of neat and blended PBST were studied in detail. The experimental results show that crystallization of PBST is suppressed by the presence of phenoxy in the blends for both nonisothermal and isothermal melt crystallization. Moreover, the overall crystallization rate of

PBST decreases with increasing crystallization temperature and the phenoxy content in the PBST/phenoxy blends; however, the crystallization mechanism of PBST does not change in the case of isothermal melt crystallization. It is also found that blending with phenoxy does not modify the crystal structure but reduces the crystallinity degree of PBST in the PBST/phenoxy blends.

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