Polymer 44 (2003) 2799–2806

polymer

www.elsevier.com/locate/polymer

Miscibility and crystallization in crystalline/crystalline blends of poly(butylene succinate)/poly(ethylene oxide)

Zhaobin Qiu[a,*], Takayuki Ikehara[b], Toshio Nishi[a]

[a]*Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*
[b]*Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*

Received 2 September 2002; received in revised form 27 December 2002; accepted 13 February 2003

Abstract

Miscibility and crystallization behavior have been investigated in blends of poly(butylene succinate) (PBSU) and poly(ethylene oxide) (PEO), both semicrystalline polymers, by differential scanning calorimetry and optical microscopy. Experimental results indicate that PBSU is miscible with PEO as shown by the existence of single composition dependent glass transition temperature over the entire composition range. In addition, the polymer–polymer interaction parameter, obtained from the melting depression of the high-T_m component PBSU using the Flory–Huggins equation, is composition dependent, and its value is always negative. This indicates that PBSU/PEO blends are thermodynamically miscible in the melt. The morphological study of the isothermal crystallization at 95 °C (where only PBSU crystallized) showed the similar crystallization behavior as in amorphous/crystalline blends. Much more attention has been paid to the crystallization and morphology of the low-T_m component PEO, which was studied through both one-step and two-step crystallization. It was found that the crystallization of PEO was affected clearly by the presence of the crystals of PBSU formed through different crystallization processes. The two components crystallized sequentially not simultaneously when the blends were quenched from the melt directly to 50 °C (one-step crystallization), and the PEO spherulites crystallized within the matrix of the crystals of the preexisted PBSU phase. Crystallization at 95 °C followed by quenching to 50 °C (two-step crystallization) also showed the similar crystallization behavior as in one-step crystallization. However, the radial growth rate of the PEO spherulites was reduced significantly in two-step crystallization than in one-step crystallization.

Keywords: Poly(butylene succinate)/poly(ethylene oxide); Miscibility; Crystallization

1. Introduction

Blending of polymers is a useful and economical way to produce new materials with a variety of properties. Miscibility of polymer blends has been studied extensively. Most of the investigated systems represent mixtures of two amorphous polymers, or mixtures in which one of the components is crystalline. However, blends in which both components are crystalline polymers have received much less attention than fully amorphous or amorphous/crystalline systems. It is more complicated and interesting to investigate this special kind of blends of two crystalline polymers since both components are able to crystallize and provide various conditions to study the crystallization behavior and morphology in polymer blends. Up to now, only a small number of works are reported on miscible polymer blends of two crystalline polymers with different chemical structures [1–18]. However, the melting points T_m of the two components in most of these studies were usually about 100 °C apart, and the high-T_m component crystallized first. The low-T_m component crystallized in the constrained space in the spherulites or on the interspherulitic boarders on lowering the crystallization temperature, which was confirmed by the increase in the brightness of the spherulites observed with a polarizing microscope under crossed polars. It indicates that the two components crystallize sequentially, and not simultaneously. However, it is interesting to investigate whether the two components can crystallize simultaneously, and what kind of morphology will arise from the simultaneous crystallization since both of them are crystallizable.

Poly (ethylene succinate) (PES) and poly (ethylene oxide) (PEO) is an example of crystalline/crystalline blends

---

[*] Corresponding author.
E-mail address: zbqiu@yahoo.com (Z. Qiu).

doi:10.1016/S0032-3861(03)00149-6

mentioned above [18,19]. PES and PEO are miscible, and the crystallization kinetics and semicrystalline morphology have been investigated by optical microscopy and small angle X-ray scattering. Because of the similarity in the chemical structure between poly(butylene succinate) (PBSU) and PES, PBSU/PEO might be a new ideal system of blends of two crystalline polymers. However, such kind of work has not been reported in the literature so far.

Our research group has been doing some work on miscibility and crystallization behavior in crystalline/crystalline polymer blends [19–24]. The purpose of this present study is to continue to investigate the miscibility and crystallization behavior in crystalline/crystalline blends to get a better understanding of the nature of this special kind of polymer blends. In this work, we choose PBSU and PEO as the blend system. The two polymers are both crystalline in their neat state, which undergo crystallization over a wide range of temperature. Furthermore, the melting point of PBSU is ca. 115 °C and that of PEO is ca. 67 °C. Therefore, attempts have been made to investigate the crystallization behavior and morphology of the low-T_m component PEO, which much less attention has been paid to in crystalline/crystalline polymer blends.

2. Experimental

PBSU ($M_w = 140,000$) was supplied by Showa High Polymer Co., Ltd., and PEO ($M_w = 100,000$) samples used in this study were purchased from Scientific Polymer Products, Inc. (Ontario, NY). The chemical structures of PBSU and PEO are ($-OCH_2CH_2CH_2CH_2O_2CCH_2CH_2CO-$) and ($-CH_2CH_2O-$), respectively.

PBSU/PEO blends were prepared with mutual solvent chloroform. The solution of both polymers (0.01 g/ml) was cast on a petri dish at room temperature. The solvent was allowed to evaporate in a controlled air stream for 1 day and the resulting films were further dried in vacuum at 50 °C for 3 days. In this way, blends were prepared with various compositions ranging from 80/20 to 20/80 in weight ratio, the first number referring to PBSU.

The glass transition temperature (T_g) and the melting point (T_m) of the melt-quenched PBSU/PEO 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 150 °C for 3 min to destroy any thermal history and subsequently quenched into liquid nitrogen. The crystallization exothermic peak temperature was obtained from the DSC cooling exotherm from the crystal-free melt at the cooling rate of 10 °C/min. On the basis of the heat of fusion of 100% crystalline PBSU (200 J/g) [25] and PEO (203 J/g) [26], the degree of crystallinity of both PBSU and PEO components were calculated from the melting endotherms of the melt-quenched sample and normalized with respect to the composition of each component in the blend.

The isothermal crystallization from the melt was also examined by DSC. For PBSU component, the sample was melted at 150 °C for 3 min, cooled quickly to the crystallization temperature (T_c), and then maintained at the T_c until the crystallization completed. After complete crystallization, the sample was heated to 150 °C at a rate of 20 °C/min to measure the melting point temperature (T_m). For PEO component, the sample was first crystallized at 85 °C for 20 min for PBSU component to finish crystallization and then quenched to the T_c for PEO crystallization to get a controlled and reproducible thermal history due to the unavoidable crystallization of PBSU during the direct cooling to the T_c suitable for PEO crystallization.

The morphology was observed under crossed polars with a polarizing microscope (Olympus BHA-P) equipped with a first order retardation plate and a temperature controller (Linkam LK-600PM). The sample was first melt at 150 °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 samples were treated by both one-step and two-step crystallization. For one-step crystallization, the blend samples were quickly quenched to 50 °C from the melt to investigate the possibility of simultaneous crystallization of PBSU and PEO or the effect of the crystals of PBSU formed during the cooling process on the crystallization and morphology of PEO component. For two-step crystallization, the blend samples were first quenched to 95 °C (above the melting point of PEO) to crystallize PBSU until complete crystallization, and then quenched to 50 °C to crystallize PEO to study the effect of crystals of PBSU on the crystallization of PEO. The spherulitic growth rate G was calculated from the change of radius R with time t, i.e. $G = dR/dt$.

3. Results and discussion

3.1. Miscibility study based on the glass transition temperature analysis

It is well known that a single T_g is the most widely and conventionally used criterion for the miscibility of a polymer blend. A single composition dependent glass transition temperature indicates full miscibility with a dimension on the order of 20–40 nm. On the contrary, an immiscible polymer blend exhibits more than one T_g. The dependence of T_g on the composition of the PBSU/PEO blends is shown in Fig. 1. PBSU/PEO blends exhibited a single composition dependent T_g between the T_g of neat PBSU and that of neat PEO, indicating that PBSU and PEO are miscible in the melt over the entire composition range. Various equations, such as Fox equation [27] (Eq. (1)) and Gordon–Taylor equation (Eq. (2)) [28], have been proposed to predict the variation of the glass transition temperature of a random copolymer or miscible blend as a function of

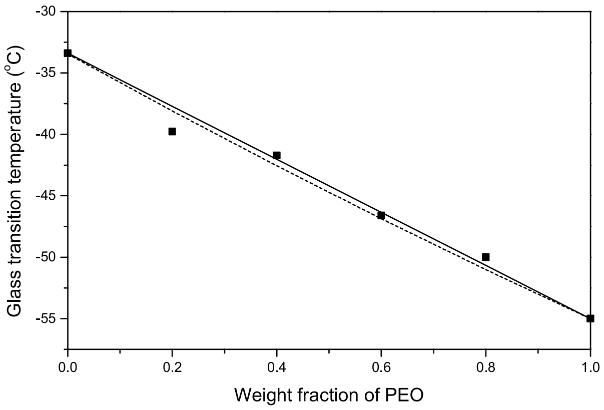


Fig. 1. The glass transition temperature T_g of PBSU/PEO blends as a fuction of PEO weight fraction (the solid line is based on the Gordon–Taylor equation, and the dashed line is based on the Fox equation).

composition:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{1}$$

$$T_g = \frac{W_1 T_{g1} + k(1 - W_1)T_{g2}}{W_1 + k(1 - W_1)} \tag{2}$$

where T_{g1} and T_{g2} are the respective T_gs of the neat component, W_1 and W_2 the weight fraction, and k is the ratio of $\Delta\alpha_2/\Delta\alpha_1$, where $\Delta\alpha$ is the change in the expansion coefficient at T_g, though it is generally used as an empirical parameter in Gordon–Taylor equation. Fig. 1 clearly shows that the experimental T_g against composition curve can fit well with both the Fox and the Gordon–Taylor equation.

Fig. 2 shows the variation of the normalized crystallinity with blend composition for each of the blend component. The crystallinity of the PBSU component increased to ca. 50% for the blended materials from ca. 30% for neat PBSU, indicating that the crystallization of PBSU is enhanced by the addition of PEO. This is consistent with the fact that the addition of PEO lowers the T_g of the blend system. However, the crystallinity of PEO was ca. 70% and seemed not to be influenced by the addition of PBSU, except that the crystallinity of 20/80 sample decreased sharply to ca. 25% due to the suppression of the crystallization of PEO by the high PBSU content in this case.

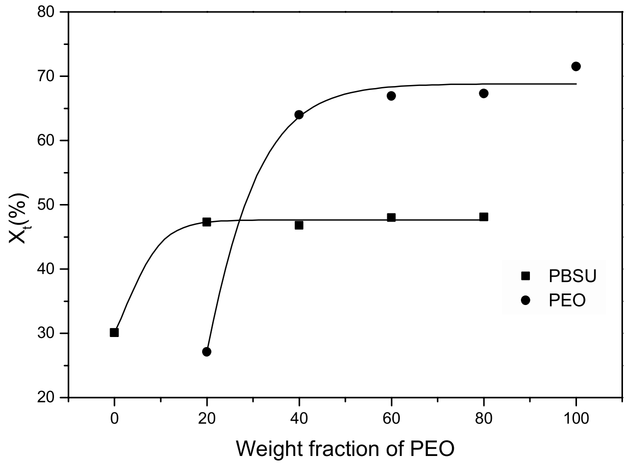


Fig. 2. The crystallinity X_t of PBSU and PEO as a function of the weight fraction of PEO.

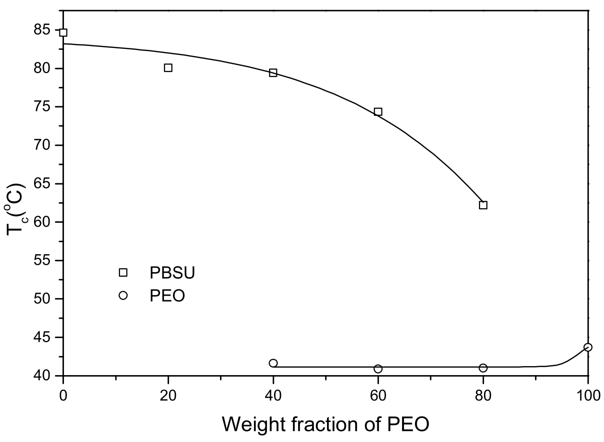


Fig. 3. The crystallization exothermic peak temperature (T_{cp}) of PBSU and PEO as a function of the weight fraction of PEO.

The DSC traces obtained during the nonisothermal crystallization process at the cooling rate of 10 °C/min showed two exothermic peaks corresponding to the crystallization of PBSU and PEO, respectively, except that only one exothermic peak was found for 20/80 sample. Fig. 3 shows the effect of the composition on the crystallization exothermic peak temperature (T_{cp}) for each of the component. It shows that the T_{cp} of PBSU was severely depressed by the presence of the PEO component. On the other hand, blending also affected the T_{cp} of the PEO component. The T_{cp} decreased compared to that of neat PEO but reached approximately a constant value in the blends. This is consistent with the change of the crystallinity of PEO, and such behavior was also found for PES/PEO blend [18].

3.2. Melting behavior and the depression in the equilibrium melting point

The depression in the melting point of a crystalline polymer blended with an amorphous polymer provides important information about its miscibility and its associated polymer–polymer interaction parameter. An immiscible or partially miscible blend typically does not show the depression of the melting point, which is depressed significantly with increasing the content of the amorphous polymer for a miscible blend, especially one containing specific interaction between the components. 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. Therefore, the equilibrium melting point should be used to separate the morphological effect from the thermodynamic effect in discussing the melting point depression as described by the Flory–Huggins theory [29,30].

Hoffman and Weeks [31] have shown a relationship between the apparent melting point T_m and the isothermal crystallization temperature T_c

$$T_m = \eta T_c + (1 - \eta) T_m^0 \tag{3}$$

where T_m^0 is the equilibrium melting point, and η may be regarded as a measure of the stability, i.e. the lamellar thickness, of the crystals undergoing the melting process. The equilibrium melting point can be obtained from the intersection of this line with the $T_m = T_c$ equation.

Fig. 4a shows the melting behavior of PBSU/PEO 20/80 blend after complete isothermal crystallization at various crystallization temperatures. Two melting peaks were observed for the crystallization temperature below 95 °C. The lower melting peak temperature shifted to high temperatures with the crystallization temperature, while the higher melting peak was almost unchanged. Furthermore, the ratio of the area of the lower melting peak to that of the higher melting peak increased with the crystallization temperature. At last the two peaks merged into one peak at temperatures above 95 °C. This fact could be explained by the mechanism of melting, recrystallization and remelting of PBSU crystals [32]. The lower peak is the melting of the crystals formed at the isothermal crystallization temperature which are present prior to the heating scan in DSC, and the higher peak is the melting of the crystals formed by the recrystallization during the heating process. The details about the double melting behavior of PBSU in PBSU/PEO blends will be reported in a separate paper [33]. Hence, the lower melting peaks were used for the analysis with the Hoffman–Weeks equation. Fig. 4b shows the Hoffman–Weeks plot for 20/80, from which the equilibrium melting point T_m^0 was determined to be 125.9 °C. The equilibrium melting point temperature T_m^0 for the neat PBSU and PBSU blended with various fractions of PEO were obtained by the same method. The results are included in Fig. 4c. The equilibrium melting point of neat PBSU was 138.8 °C, which was a little higher than the value of 135 °C reported in the literature [32] because of the high molecular weight sample used in this study. The equilibrium melting point of PBSU decreased with increasing the PEO content.

The equilibrium melting point data obtained in this study were analyzed by the Nishi–Wang equation [30] based on the Flory–Huggins theory [29]. The melting point depression is given by Eq. (4),

$$\frac{1}{T_m^0(\text{blend})} - \frac{1}{T_m^0(\text{pure})} = -\frac{RV_2}{\Delta H^0 V_1}\left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)\phi_1 + \chi_{12}\phi_1^2\right] \tag{4}$$

where T_m^0(pure) and T_m^0(blend) are the equilibrium melting point of the pure crystallizable component and of the blend, respectively. ΔH^0 is the heat of fusion of the perfectly

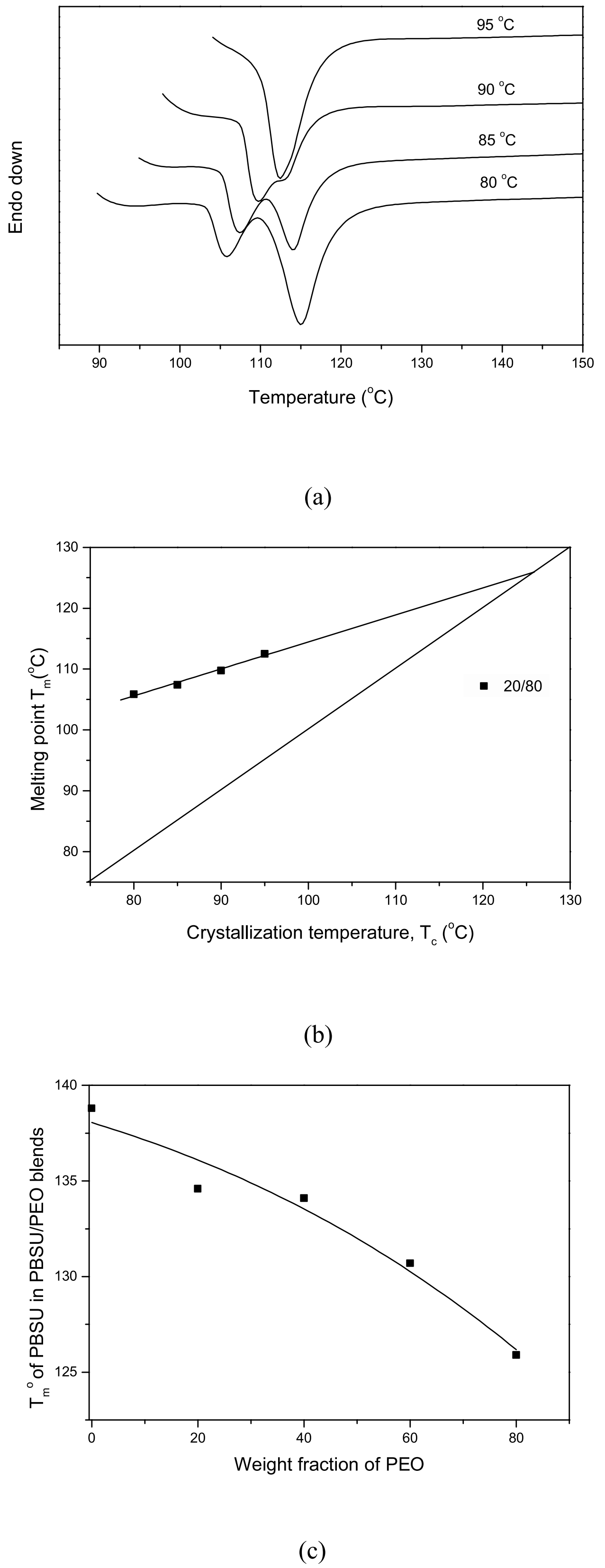


Fig. 4. (a) Melting behavior of PBSU component for 20/80 sample, (b) Hoffman–Weeks plot of the PBSU component for 20/80 blend, and (c) the equilibrium melting point of PBSU in PBSU/PEO blends vs. weight fraction of PEO.

crystallizable polymer per mole of the repeat unit, V is the molar volume of the repeating units of the polymers, m and ϕ are degree of polymerization and the volume fraction of the component in the blend, respectively. Subscripts 1 and 2 refer to the amorphous and crystalline polymer, respectively. R is the universal gas constant, and χ_{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. (4) can be neglected. The interaction parameter χ_{12} can be written as

$$-\frac{\Delta H^0 V_1}{R V_2}\left(\frac{1}{T_m^0(\text{blend})}-\frac{1}{T_m^0(\text{pure})}\right)=\chi_{12}\phi_1^2 \qquad (5)$$

For PBSU/PEO blends, the crystallization temperature used to obtain the equilibrium melting point for PBSU was higher than the melting point of PEO, i.e. PBSU was the crystalline polymer, while PEO acted as an amorphous diluent in such a case. Eq. (5) can therefore be applied to get the polymer–polymer interaction parameter χ_{12}.

In order to calculate the left-hand side term of Eq. (5), the following parameters were used: $V_1 = 44\ \text{cm}^3/\textbf{mol}$ [1], $V_2 = 145.9\ \text{cm}^3/\text{mol}$, and $\Delta H^0 = 34435$ J/mol [25]. The plot of the left-hand side of Eq. (5) versus ϕ_1^2 is shown in Fig. 5. The fact that the line does not pass through the origin according to the prediction of the Eq. (5) indicates the polymer–polymer interaction parameter χ_{12} is composition dependent. The values of χ_{12} obtained from the broken lines in Fig. 5 were negative for all investigated compositions, indicating that PBSU and PEO are thermodynamically miscible in the melt.

The melting behavior of the low-T_m component PEO was also studied for PEO rich blends using the Hoffman–Weeks extrapolation method as the PBSU component. However, the isothermal crystallization process used for PEO component was different from that for PBSU component. For PEO component, the blend sample was first crystallized at 85 °C for 20 min for PBSU component to finish crystallization as the process introduced in the experimental part and then quenched to the T_c for PEO crystallization. Fig. 6 shows the Hoffman–Weeks plots for PEO in PEO rich blends. A small depression in the equilibrium melting point of PEO was found.

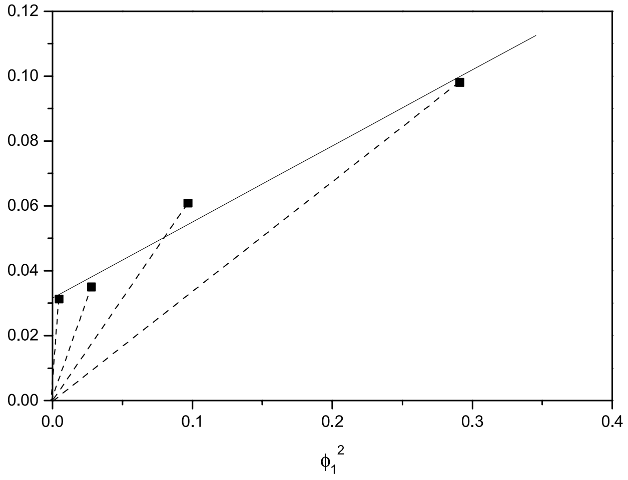


Fig. 5. Equilibrium melting point depression of PBSU as a function of blend composition, plotted according to the Nishi–Wang equation (the y-axis was the left-hand side of Eq. (5)).

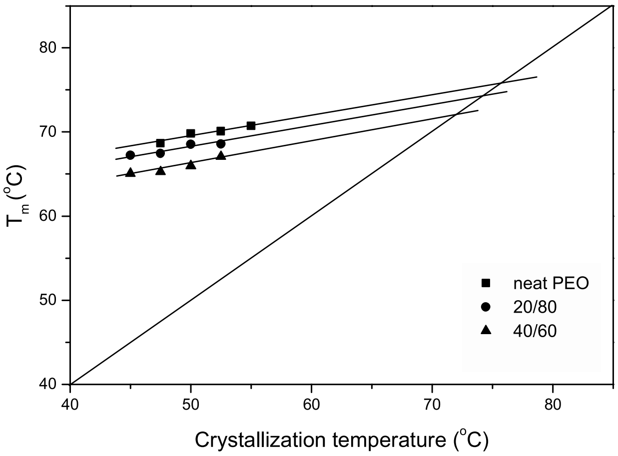


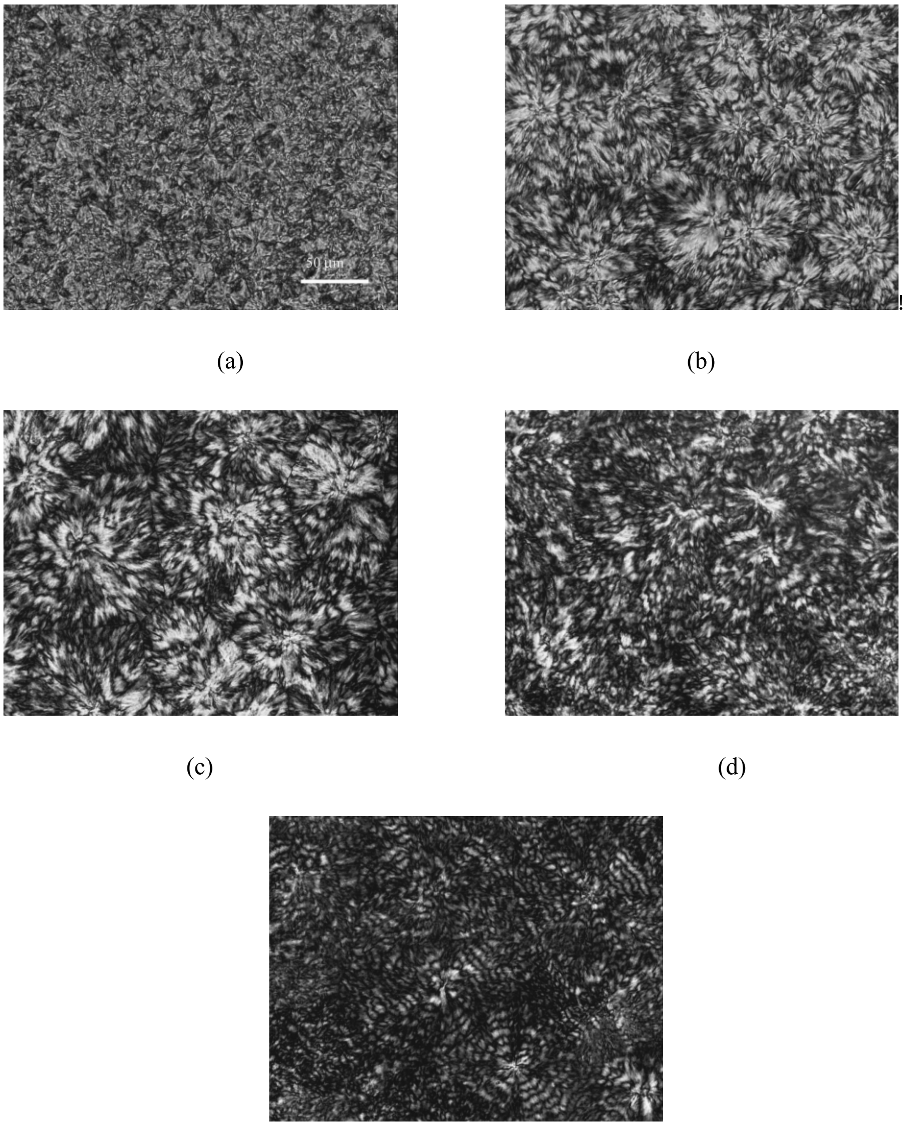
Fig. 6. Hoffman–Weeks analysis of the PEO component in PBSU/PEO blends.

3.3. Morphology study on PBSU/PEO blends

For miscible blends of two crystalline polymers the crystallization and morphology of high-T_m component have been investigated extensively, whereas much less attention has been paid to those of the low-T_m component. It is usually difficult and complicated to study the crystallization and morphology of the low-T_m component in crystalline/crystalline blends since the high-T_m component may partially crystallize before the crystallization temperature of the low-T_m component is reached. Therefore, the unavoidable crystallization of the high-T_m component must have a certain effect on the crystallization and morphology of the low-T_m component. For PBSU/PEO blends investigated in this study, the difference in T_m is not so large than those in the blend system in the literature, such as PVDF/PBA [7] and PHB/PEO [1], where the difference in T_m is ca. 100 °C. Therefore, it is possible and interesting that both components are able to crystallize simultaneously at the T_c below the T_m of PEO.

In this paper, the high-T_m component PBSU was studied by quenching the melt directly to the T_c above the T_m of PEO to study the effect of the presence of the PEO component on the crystallization and morphology of PBSU as in amorphous/crystalline polymer blends. For the low-T_m component PEO, the crystallization and morphology was investigated through both one-step crystallization and two-step crystallization as introduced in the experimental part.

For the high-T_m component PBSU, the crystallization temperature T_c was chosen to be 95 °C above the melting point T_m of PEO. Under such a condition, PEO acts as a noncrystallizable component. Fig. 7 shows the spherulitic

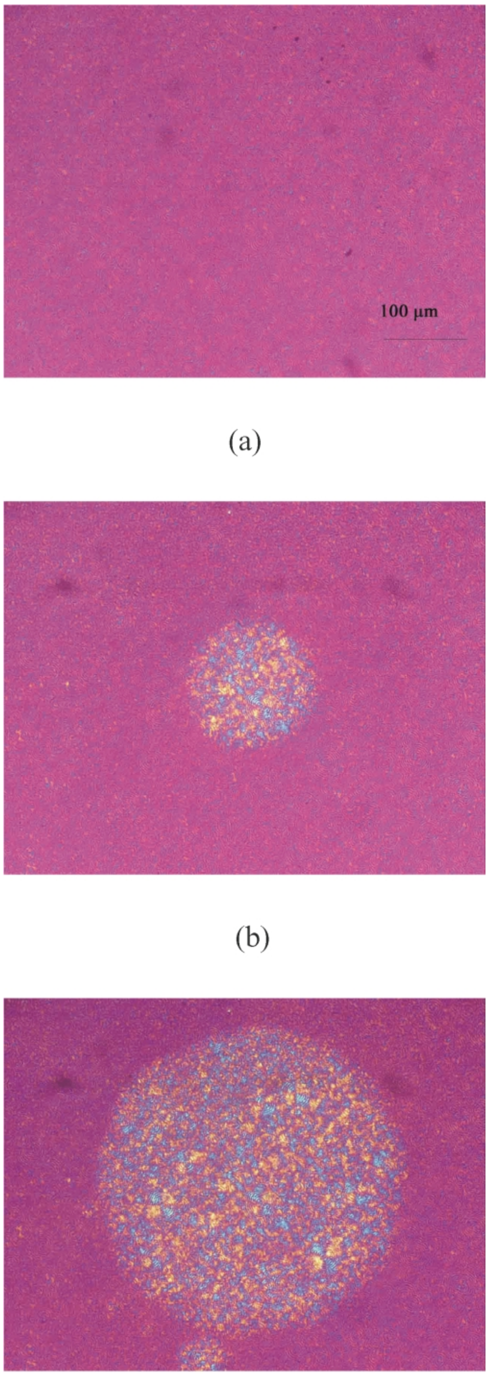


(a) (b) (c) (d) (e)

Fig. 7. Optical micrographs of the spherulitic morphology of PBSU in various blends with PEO after complete crystallization at 95 °C: (a) neat PBSU, (b) 80/20, (c) 60/40, (d) 40/60, and (e) 20/80.

morphology of the neat and blended PBSU after complete crystallization at 95 °C. It is seen that the spherulites of PBSU became larger with the PEO content, indicative of a decrease in the nucleation density. The coarseness of PBSU spherulites increased with increasing the PEO content in the blends, too. The fact that PBSU spherulites are almost space-filling even at the high PEO content indicates that only PBSU component crystallizes from the blends under the experimental condition and that PEO is rejected in the crystallization process as a noncrystallizable component and reside primarily in the interlamellar and interfibrillar domains of the PBSU spherulites [34,35]. Such behavior is typical for the high-T_m component in crystalline/crystalline blends [1,4,6,7,18–24].

It is more complicated and interesting to study the crystallization and morphology of the low-T_m component PEO. In PBSU/PEO blends, it was found that the crystallization of PEO was affected significantly by the presence of the crystals of PBSU formed through both one-step and two-step crystallization process. First, attempts have been made to investigate the possibility of the simultaneous crystallization of PBSU and PEO at the T_c below the T_m of PEO by one-step crystallization, i.e. quenching the melt directly to the T_c. The T_c chosen in this study was 50 °C. However, PBSU always crystallized first and filled the whole space before PEO started to crystallize, indicating that PBSU and PEO crystallize sequentially and not simultaneously. For the PBSU rich blends, PBSU crystallized and filled the whole space before the T_c was reached even at the fastest cooling rate 100 °C/min. The crystallization of PEO was not perceptible within the experimental time 2 h in this study. However, one interesting phenomenon was found for 20/80 and 40/60 blend samples when they crystallized at 50 °C by one-step crystallization. For the PEO rich blends, PBSU started to crystallize before the T_c was reached and filled the whole space soon after the T_c was reached. The one-step crystallization process for 20/80 sample is shown in Fig. 8. PBSU crystallized first from the homogeneous melt and filled the whole space (Fig. 8a). Because of the high supercooling (ca. 85 °C), the nucleation density of PBSU was very high, so the size of PBSU spherulites was very small and they were not easy to be observed. After the volume-filling crystallization of PBSU, a bright PEO spherulite started to crystallize in the matrix of the PBSU spherulites (Fig. 8b). In this case, the fibrils (stacks of lamellae) of PEO may grow in the interfibrillar region of PBSU spherulites, which made the negative spherulites of PBSU where the crystallization of PEO occurred easier to be observed and the rest where the crystallization of PEO had not occurred still not easy to be observed. The bright pattern of PEO continued to grow until it collided with another PEO spherulite (Fig. 8c). At last, the whole space was filled with PEO spherulites crystallized in the matrix of the PBSU spherulites. Such crystallization behavior was also found in our recent work for poly(ester carbonate) (PEC) and poly(L-lactic acid) (PLLA) blends [24]. For comparison, the PEO rich blends were also studied through two-step crystallization. The blends were first quenched to 95 °C and held until complete crystallization of PBSU and then quenched to 50 °C to crystallize PEO. It was found that the crystallization of PEO proceeded through the same spherulitic growth process as in one-step crystallization. This is different form the study for the low-T_m component in crystalline/crystalline polymer blends reported in the literatures, where the low-T_m component crystallized only in the interspherulitic domains of the preexisted high-T_m component and within the spherulitic domains of the preexisted high-T_m component, and could not crystallize according to the spherulitic growth [8,20]. It should be noted that the growth rate for 20/80 through two-step crystallization was 48 μm/min, only ca. one third of the growth rate 131 μm/min through one-step crystallization. This indicates that the crystallization condition, one-step or two-step crystallization, has a significant effect on the crystallization of the low-T_m component PEO. The reasons can probably be explained as follows. The crystals of the high-T_m component PBSU formed through one-step crystallization are not so perfect than those obtained through two-step crystallization. Furthermore, it is more difficult for PEO spherulites to grow within the matrix of the perfect crystals of PBSU. As a result, the growth rate of the PEO spherulites is affected significantly by the presence of the preexisted crystals of PBSU formed through the different crystallization process.



(a)

(b)

(c)

Fig. 8. The one-step crystallization process for 20/80 sample at 50 °C: (a) 0.5 min, (b) 2.5 min, and (c) 3 min.

4. Conclusions

PBSU and PEO 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 was calculated from the equilibrium melting depression of PBSU. The morphological study of the isothermal crystallization at 95 °C (where only PBSU crystallized) showed the similar crystallization behavior as in amorphous/crystalline blends. The spherulites of PBSU became larger with PEO content, indicative of a decrease in the nucleation density. The coarseness of PBSU spherulites increased with increasing the PEO content in the blends, too. The crystallization and morphology of the low-T_m component PEO was studied through both one-step and two-step crystallization. The crystallization of PBSU component was always prior to that of PEO component, indicating that the two components crystallized sequentially not simultaneously when the blends were quenched from the melt directly to 50 °C (one-step crystallization). The PEO spherulites crystallized within the matrix of the crystals of the PBSU. Crystallization at 95 °C followed by quenching to 50 °C (two-step crystallization) showed the similar crystallization behavior as in one-step crystallization. However, the radial growth rate of the PEO spherulites was reduced significantly in two-step crystallization than in one-step crystallization. The crystallization of PEO was affected clearly by the presence of the crystals of PBSU formed through different crystallization processes.

Acknowledgements

Part of this work was supported by Grant-in-Aid for Scientific Research on Priority Areas (A) ‘Dynamic Control of Strongly Correlated Soft Materials’ (No. 413/13031012) from the Ministry of Education, Science, Sports, Culture, and Technology, Japan. Z. Qiu thanks the Japan Society for the Promotion of Science for providing the fellowship and the grant-in-aid to do this research at the University of Tokyo. The authors thank the reviewer for valuable suggestions.

References

[1] Avella M, Martuscelli E. Polymer 1988;29:1731.
[2] Avella M, Martuscelli E, Greco P. Polymer 1991;32:1647.
[3] Avella M, Martuscelli E, Raimo M. Polymer 1993;34:3234.
[4] Marand H, Collins M. ACS Polym Prep 1990;31:552.
[5] Edie SL, Marand H. ACS Polym Prep 1991;32:329.
[6] Chiu HJ, Chen HL, Lin JS. Polymer 2001;42:5749.
[7] Penning JP, Manley RStJ. Macromolecules 1996;29:77.
[8] Penning JP, Manley RStJ. Macromolecules 1996;29:84.
[9] Fujia K, Kyu T, Manley RStJ. Macromolecules 1996;29:91.
[10] Liu LZ, Chu B, Penning JP, Manley RStJ. Macromolecules 1997;30:4398.
[11] Cheung YW, Stein RS. Macromolecules 1994;27:2512.
[12] Cheung YW, Stein RS, Lin JS, Wignall GD. Macromolecules 1994;27:2520.
[13] Cheung YW, Stein RS, Wignall GD, Yang HE. Macromolecules 1993;26:5365.
[14] Cheung YW, Stein RS, Chu B, Wu G. Macromolecules 1994;27:3589.
[15] Blümm E, Owen AJ. Polymer 1995;36:4077.
[16] Liu AS, Liau WB, Chiu WY. Macromolecules 1998;31:6593.
[17] Liau WB, Liu AS, Chiu WY. Macromol Chem Phys 2002;203:294.
[18] Chen HL, Wang SF. Polymer 2000;41:5157.
[19] Qiu Z, Ikehara T, Nishi T. Macromolecules 2002;35:8251.
[20] Lee JC, Tazawa H, Ikehara T, Nishi T. Polym J 1998;30:327.
[21] Lee JC, Tazawa H, Ikehara T, Nishi T. Polym J 1998;30:780.
[22] Ikehara T, Nishi T. Polym J 2000;32:683.
[23] Terada Y, Ikehara T, Nishi T. Polym J 2000;32:900.
[24] Hirano S, Nishikawa Y, Terada Y, Ikehara T, Nishi T. Polym J 2002;34:85.
[25] Miyata T, Masuko T. Polymer 1998;39:1399.
[26] Wunderlich B, Macromolecular physics, New York: Academic Press; 1980. vol. 3.
[27] Fox TG. J Appl. Bull Am Phys Soc 1956;1:123.
[28] Gordon M, Taylor JS. J Appl Chem 1952;2:493.
[29] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.
[30] Nishi T, Wang TT. Macromolecules 1975;8:909.
[31] Hoffman JD, Weeks JJ. J Chem Phys 1965;42:4301.
[32] Yoo ES, Im SS. J Polym Sci Polym Phys 1999;37:1357.
[33] Qiu Z, Ikehara T, Nishi T. Submitted for publication.
[34] Keith HD, Pdden Jr FJ. J Appl Phys 1964;35:1270.
[35] Keith HD, Pdden Jr FJ. J Appl Phys 1964;35:1286.