ABSTRACT: The miscibility of blends of phenolphthalein poly(ether ether sulfone) (PES-C) and poly(ethylene oxide) (PEO) was established on the basis of the thermal analysis results. Differential scanning calorimetry (DSC) studies showed that the PES-C/PEO blends prepared by casting from N,N-dimethylformamide (DMF) possessed a single, composition-dependent glass transition temperature ($T_g$), and thus that PES-C and PEO are miscible in the amorphous state at all compositions at lower temperature. At higher temperature, the blends underwent phase separation, and the PES-C/PEO blend system was found to display a lower critical solution temperature (LCST) behavior. The phase separation process in the blends has also been investigated by using DSC. Annealed at high temperatures, the PES-C/PEO blends exhibited significant changes of thermal properties, such as the enthalpy of crystallization and fusion, temperatures of crystallization and melting, depending on blend composition when phase separation occurred. These changes reflect different characteristics of phase structure in the blends, and were taken as probes to determine phase boundary. From both the thermal analysis and optical microscopy, the phase diagram of the blend system was established. © 1997 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 35: 1383–1392, 1997

Keywords: phenolphthalein poly(ether ether sulfone); poly(ethylene oxide); semicrystalline polymer blends; miscibility; phase separation; thermal properties; LCST behavior

INTRODUCTION

There has been considerable interest in the study of polymer blends because of their importance in academic and technical aspects. Particularly, much attention has been paid to miscibility and phase behavior in polymer blends. Many techniques can be used to study the miscibility and phase behavior of polymer blends. Of them, calorimetric approach has been demonstrated to be powerful. Differential scanning calorimeter can be used for: (1) Measurement of heat of demixing. For the polymer blends with high molecular weight, the combinatorial entropy of mixing ($\Delta S_{\text{mix}}$) is negligibly small and the free volume contribution further increases the free energy of mixing ($\Delta G_{\text{mix}}$). As a result, the miscibility depends on the heat of mixing ($\Delta H_{\text{mix}}$). Therefore, if possible, the measurement of heat of mixing could play an important role in predicting miscibility in polymer blends. However, the direct measurement of heat of mixing is less successful, and at the same time, some indirect methods to estimate $\Delta H_{\text{mix}}$ or miscibility may not always give
reliable results. More recently, differential scanning calorimetry (DSC) studies revealed that several miscible polymer blend systems\(^6^{-12}\) show an endothermic (or exothermic) effect resulting from demixing of components. Ebert et al.\(^7\) argued that the endothermic heat of demixing should roughly correspond to the total heat of mixing, provided that the two phases mainly contain the pure components. The heat of demixing and its concentration dependence can be measured by DSC so that spinodal and bimodal curve can be obtained. (2) Determination of glass transition temperature \((T_g)\). Generally, the use of \(T_g\) in determination of polymer miscibility is based on the judgment that the observation of a single \(T_g\) between those of pure components is taken as the evidence of miscibility, although strictly speaking, a single \(T_g\) is only indicative of state of dispersion, whereas the appearance of two \(T_g\)s stands for occurrence of phase separation. In a miscible amorphous blends, the evolution of two phases when the miscibility gap is entered as a function of annealing temperature and time allows the calculation of composition of the two phases formed, and thus a phase boundary curve can be determined by DSC.\(^13{-16}\) However, for the blends containing one (or more) crystallizable component, it becomes difficult to follow the appearance of phase separation in an isothermal treatment or in a temperature scan since the magnitude and position of \(T_g\) can be strongly affected by the state of crystallization before or after the occurrence of phase separation. However, the changes of other thermal properties, such as enthalpy of crystallization and fusion, temperatures of crystallization and melting, can give some information on phase behavior, which can be taken as adjudgment of phase separation. More recently, Li and Prud’homme\(^17\) studied the phase behaviors in crystalline/miscible blends consisting of poly(\(\varepsilon\)-caprolactone)/poly(styrene-\(\varepsilon\)-co-acrylonitrile), and determined the phase diagram based on the analysis of thermal properties, which was in a good agreement with the result obtained by light scattering.

PES-C was newly developed in China as a high-performance engineering thermoplastic,\(^18\) and it has increasingly been applied since it possesses excellent properties. PES-C was synthesized via condensation reaction of phenolphthalein and 4,4’-dichlorinatediphenylsulfone in a solution and its repeat unit can be schemed as the following:

Referring to its structure, PES-C can be taken as a modified poly(ether sulfone); introduction of the rather bulky and polarizable phenolphthalein group in place of oxygen atom increases the rigidity of the molecular chain, and thus the higher glass transition temperature (258°C) was displayed. Blends of PES-C with several other polymers have been reported.\(^19{-23}\) In the present study, we report on an investigation of the polymer blends composed of the amorphous phenolphthalein poly(ether ether sulfone) (PES-C) and semicrystalline poly(ethylene oxide) (PEO). Miscibility and phase behavior of the blends were given based on the results of DSC measurement. In this system, it was difficult to determine the phase boundary, i.e., a temperature versus composition phase diagram by using DSC to follow appearance of two separate \(T_g\)s at a certain annealing temperature as conventionally shown in amorphous polymer blend systems, since PEO is a crystalline polymer with typically a high degree of crystallinity. However, the change of other thermal properties as functions of annealing temperatures can give some significant information, which can be used to analyze the phase behavior of this system. Hereafter, optical microscopic observation was also be applied to obtain the cloud point curve, and the information gained with the two approaches can establish the miscibility and determine the phase boundary diagram of the system.

EXPERIMENTAL

Materials

The PES-C used in the study is a commercial product and was supplied by Xuzhou Engineering Plastics Factory, Xuzhou, Jiangsu, China. It has a limiting solution viscosity of 0.68 dL/g in the solution of chloroform at 25°C; GPC measurements indicate that the polymer possesses a molecular mass of \(M_n = 1.2 \times 10^4\) and \(M_w = 3.2 \times 10^4\), both expressed as PS equivalent molecular
weight. PES-C has a glass transition temperature of 258°C. The PEO, with a quoted average molecular weight of 20,000, was obtained from Shanghai Chemical Reagent Co., Inc., China. Chloroform and N,N-dimethylformamide (DMF) were A.R. grade and were used as received.

Preparation of Polymer Blends

The PES-C/PEO blends were prepared by solution casting from chloroform at room temperature and from DMF at 50°C. The total polymer concentration was 5% (w/v). To remove the residual solvent, all the blend films obtained were further desiccated in a vacuum oven at 60°C for 2 weeks.

Techniques

Differential Scanning Calorimetry

The calorimetric measurements were performed on a Perkin–Elmer DSC-7 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with Indium standard. In order to obtain glass transition temperature ($T_g$), all the amorphous blend samples (about 15 mg in weight) were first heated up to the temperature between phase separation temperatures and glass transition temperatures ($T_g$) of the samples and held for 5 min to remove the thermal history, followed by quenching to −70°C. For the crystalline blend samples (about 10 mg in weight), the pretreatment temperature was taken as 70°C, which is above the melting point of PEO (65°C) and below the lower critical solution temperature. A heating rate of 20°C/min was used at all cases. Glass transition temperature ($T_g$) was taken as the midpoint of the heat capacity change, while melting temperature ($T_m$) and crystallization temperature ($T_c$) were taken as the maximum of endothermic peak and the minimum of exothermic peak, respectively.

Phase separation processes were investigated by the following procedure. The samples were first annealed at the selected temperature for 5 min, and then quenched to −70°C. The heating thermograms were recorded. Then the sample was annealed at the next higher temperature for 5 min, and quenched. The higher temperature was changed by 10°C (for blend samples with PEO content < 50 wt %) or 5°C (for samples with PEO content > 50 wt %) intervals. This procedure was repeated until the occurrence of phase separation was observed. The annealing temperature corresponding to the first change of thermal behavior was taken as the phase transition temperatures.

Optical Microscopy

Jiangnan XPR-2 optical microscope equipped with a hot stage was used for the cloud point measurement. Films prepared with different compositions of blend were heated at a rate of 5°C/min through the cloud points, and the cloud point defined as the onset of the turbidity. The cloud point curve (CPC) was constructed by plotting the cloud point temperature versus the composition of the blend.

RESULTS AND DISCUSSION

The Thermal Properties and Miscibility of PES-C/PEO Blends

All the blend films cast from chloroform were neither transparent at room temperature nor at elevated temperatures. DSC studies indicate that all these PES-C/PEO blends cast from chloroform solution were not miscible. However, the miscible PES-C/PEO blends were prepared by solution casting from DMF, and they were used throughout this study. The “solvent effect” on the homogeneity of casting polymer blend films has previously been interpreted in terms of the difference in the two polymer–solvent interaction parameters $|\chi_{12} - \chi_{13}|$ or $|\Delta \chi|$ [herein subscript 1 referring to solvent whereas subscript 2 (or 3) standing for polymer]. From a ternary phase diagram, a homogeneous system is attained only with a suitably small $|\Delta \chi|$; in addition, a small polymer–polymer interaction parameter $\chi_{23}$ is necessary.

The PES-C/PEO blends with PEO content < 50 wt % were transparent at room temperature, but the blend samples containing 50 wt % PEO and more increasingly became opaque with increase of PEO content. The polarizing microscopic observation of all these blends with PEO > 50 wt % shows the typical morphology of spherulits. Heated up to 80°C, i.e., above the melting point of PEO (65°C), these opaque films all became clear. This observation indicates that the PES-C/PEO blends present a single homogeneous amorphous phase, i.e., phase separation did not occur, at least on a scale with dimension of phase domains exceeding the wavelength of visible light.

When further heated up to 200°C, all the initially clear samples became turbid in succession, but the remixing did not occur when these sam-
Figure 1. DSC thermograms of PES-C/PEO blends with different blend composition after quenching. Heating rate 20°C/min. For easy comparison all curves are normalized to 1 mg of sample.

Samples were cooled due to kinetic effect. Careful microscopic observations revealed that the turbidity was caused by the formation of a phase-separated structure. These results suggest that the PES-C/PEO blends display a lower critical solution temperature (LCST) behavior, which means that there is a negative enthalpic contribution of mixing.

All the blends were subjected to the studies of thermal analysis. DSC thermograms of the PES-C/PEO blends are shown in Figure 1. It can be seen that each blend displays a single glass transition temperature ($T_g$), intermediate between those of the two pure components and changing with the blend composition. The thermal properties of the blends are summarized in Table I. According to the transparency and glass transition behavior, the conclusion can be reached that the PES-C/PEO blends are completely miscible in the amorphous state, i.e., possess a single, homogeneous, amorphous phase for all composition below the temperature of phase separation. Figure 2 shows the plots of the thermal transitions of the blend as functions of weight fraction of PEO. There are several theoretical and empirical equations to describe the composition dependence of the glass transition temperature. Herein we have applied the Gordon–Taylor equation\(^ {29} \) for this system:

$$T_g = T_{g1} + K(W_2/W_1)(T_{g2} - T_g) \quad (1)$$

where $T_g$ is glass transition temperature of poly-

![Figure 2. Transition behavior of PES-C/PEO blends. (○) $T_g$ (▲) $T_c$, and (△) $T_m$. The dashed line was drawn from the Gordon–Taylor equation with $k = 0.24$.](image)

Table I. Thermal Properties of PES-C/PEO Blends After Quenching

<table>
<thead>
<tr>
<th>PES-C/PEO</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (PEO) (J/g)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (PEO) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>-65</td>
<td></td>
<td></td>
<td>65</td>
<td>160.0</td>
</tr>
<tr>
<td>20/80</td>
<td>-45</td>
<td></td>
<td></td>
<td>63</td>
<td>110.3</td>
</tr>
<tr>
<td>30/70</td>
<td>-50</td>
<td>-27</td>
<td>-35.8</td>
<td>59</td>
<td>49.1</td>
</tr>
<tr>
<td>40/60</td>
<td>-43</td>
<td>35</td>
<td>-4.9</td>
<td>58</td>
<td>7.6</td>
</tr>
<tr>
<td>50/50</td>
<td>-13</td>
<td>44</td>
<td>-0.5</td>
<td>58</td>
<td>0.5</td>
</tr>
<tr>
<td>70/30</td>
<td>58</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80/20</td>
<td>93</td>
<td></td>
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<tr>
<td>90/10</td>
<td>149</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>258</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
mer blends, \( T_{g1} \) and \( T_{g2} \) are those of the pure components 1 and 2, respectively. \( W \) is the weight fraction and \( K \) is an empirical parameter related to the degree of curvature of the \( T_g \) composition diagram. For the crystalline/amorphous polymer blends, the composition of amorphous phase was calculated after subtracting the crystallinity of PEO. The plot of the glass transition temperatures (\( T_g \)s) for the miscible blends versus PEO weight fraction is presented in Figure 2. The prediction \( T_g \) of Gordon–Taylor equation fitting to experimental data yielded a \( K \) value of 0.24, fitting the experimental data quite well.

Prud’homme et al.\textsuperscript{30,31} have suggested that \( K \) can be taken as a semiquantitative measure of the strength of the intermolecular interaction between the components of blends. For instance, in blends of poly(\( e \)-caprolactone) with chlorinated polyethylene, poly(vinyl chloride) (PVC) and chlorinated PVC, \( K \) increases from 0.26 to 1.0. When such an approach is used for the PES-C/PEO blends, the \( K \) value of 0.24 is small, suggesting that the interaction between PES-C and PEO is fairly weak.

Also summarized in Figures 1 and 2 are thermal behaviors of the PES-C/PEO blends. For the pure PEO and the 20/80 PES-C/PEO blend, no cold crystallization exotherm was observed since crystallization was sufficiently rapid to occur completely during the quenching (see Fig. 1). However, for the blends with PES-C content from 30 to 50 wt %, the crystallization temperature (\( T_c \)) increases with increasing PES-C content. This phenomenon indicates that crystallization of PEO becomes progressively difficult in the PES-C-rich blends. Furthermore, the blends with PES-C content of 70 wt % or higher did not show any crystallinity. It was noted that the melting temperature (\( T_m \)) of PEO in the blends apparently decreases with addition of PES-C to the system, which indicates that PES-C hinders the crystallization of PEO in the blends. This is a typical characteristic of a miscible blend composed of an amorphous polymer and a crystallizable polymer in which the glass transition temperature (\( T_g \)) of the amorphous polymer is higher than that of the crystallizable component.

For the miscible polymer blends containing a crystalline component, the interaction energy density \( B \) can be estimated by the apparent melting point depression of crystalline polymer\textsuperscript{32,33}:

\[
T_m = T_m^0 + B \frac{V_{2u}}{D_{H_f}} T_m^0 \frac{\phi_1^2}{T_m^0} \tag{2}
\]

where \( T_m^0 \) and \( T_m \) are the melting points of pure crystalline polymer and the component in the blends, respectively; \( \phi_1 \) is the volume fraction of the amorphous component in the blends. Herein the \( \Delta H_{2u} \) is \( 8.778 \times 10^3 \) J/mol, and \( V_{2u} \) was taken as \( 38.9 \) cm\(^3\)/mol\textsuperscript{34,35} for 100% crystalline PEO. From the plots of \( T_m \) versus \( \phi_1^2 \) (see Table I), a tentative value of \( B \) was found to be \(-16.72 \) J/cm\(^3\) at 65°C for the PES-C/PEO. The negative \( B \) value suggests the negative free energy of mixing (\( \Delta G_{mix} \)). It has to be stressed that this estimate may be subject to some errors since the morphological effect on the melting point depression has not been excluded.

Figure 3 shows the crystallinity of PEO, as a function of blend composition, which was calculated from the following equation:

\[
X_c = \frac{\Delta H_f - \Delta H_c}{\Delta H_f^0} \tag{3}
\]

where \( X_c \) is percent crystallinity. \( \Delta H_f \), \( \Delta H_c \) are the enthalpy of fusion and crystallization of PEO. \( \Delta H_f^0 \) is the fusion enthalpy of perfectly crystalline PEO, and has been reported to be 213 J/g.\textsuperscript{36} The crystallinity of PEO in the blends containing PES-C less than 20 wt % does not deviate much from the dashed line (Fig. 3), which stands for the crystallinity of PEO in the blends if the crystallization process is not influenced by the presence of PES-C. However, there is a dramatic decrease in crys-
PES-C/PEO 70/30 (wt) blends were representatively described based on the evolution of thermal properties as a function of annealing temperature. A series of thermograms of the 70/30 PES-C/PEO blends was obtained after annealing at temperatures between 80 and 200°C and then quenching to −70°C (Fig. 4). It can be seen that when annealed below 110°C, the DSC scans show no obvious changes, but the significant difference was observed as the annealing temperature is higher than 110°C. There appear minor melting peaks of PEO in the DSC heating thermograms, and the area under the melting peaks increases with increasing annealing temperature, reaching a plateau when the annealing temperature is higher than 140°C (Fig. 5). The melting temperature ($T_m$) increases dramatically after annealing up to 110°C and thereafter only gradually increases (Fig. 5). The appearance of the crystallization of PEO in the blends is indicative of the occurrence of phase separation, i.e., the PEO-rich phase has separated from the initial homogeneous amorphous PES-C/PEO mixture. With phase separation taking place, PEO gradually concentrates from the original homogeneous blends and both the PEO-rich phase and PEO-lean phase are simultaneously formed, resulting in the appearance of the crystallization and fusion of PEO during the process of quenching and heating run. The higher the annealing temperature, the larger the area under the melting peaks, which suggest the phase separation performs more completely.

Figure 4. DSC thermograms of the 70/30 PES-C/PEO blend for various annealing temperature between 85 and 190°C. The annealing time was 5 min.

Phase Separation of PES-C/PEO Blends Studied by DSC

As shown above, there are different thermal behaviors for the miscible blends of PES-C and PEO, depending on the blend composition. Blends with different composition display different changes of thermal properties while phase separation occurs. Therefore, the investigation of phase separation should be performed in the light of the blend compositions. The studies of phase separation process are discussed in detail as follows.

PES-C/PEO Blends Containing Less Than 50 wt % PEO

All the PES-C/PEO blends containing less than 50 wt % PEO do not show crystallization phenomena under the experimental conditions (Fig. 1). Herein, the results of DSC measurement for the
Hence, the occurrence of the melting at a particular annealing temperature should be considered as the beginning of phase separation. From Figure 4, it is observed that \( T_g \) of the blends became broad in the vicinity of the onset of phase separation. The width of the glass transition may reflect the magnitude of local compositional fluctuations in the polymer blends, implying the relative homogeneity or miscibility of the system. However, the transition temperatures do not change until the appearance of a minor melting peak in the DSC curve, indicating the occurrence of phase separation. With the phase separation occurring, the \( T_g \)s gradually shift to lower temperature, although they increasingly became indistinguishable at higher annealing temperature due to its higher crystallinity after more complete phase separation. It is noted that the second \( T_g \), i.e. that of the PES-C-rich phase, cannot be seen in Figure 4. However, there is an apparent deviation of DSC curves from the baseline after the melting peaks of PEO. The higher the annealing temperature, the larger the deviation, which suggests a broaden range of glass transition of the PES-C-rich phase after the multistage thermal treatment. It should be pointed out that the heating rescans after the appearance of the melting peaks of PEO does not show the cold crystallization of PEO, which indicates that the crystallization of PEO in the newly separated PEO-rich phase mainly occurs during the quenching process.

**PES-C/PEO Blends Containing 50 wt % PEO**

For the PES-C/PEO 50/50 blends, the amorphous and homogeneous mixture was obtained after quenching from 80°C to -70°C in terms of the comparison of the area under the crystallization and melting peaks, since there are equal values of the enthalpy between the two transitions (Table I). Figure 6 shows a series of heating thermograms of the 50/50 PES-C/PEO blend annealed at different temperatures between 80 and 130°C. Below 105°C, the endothermic enthalpy remains unchanged and equal to exothermal one, which indicates that PEO crystallizes only during the heating run of DSC after quenching. When the annealing temperature is 105°C or above, both the enthalpy values began to increase dramatically, and the enthalpy of fusion even began to surpass that of crystallization in contrast to the cases at the annealing temperatures below 105°C. At the same time, the cold crystallization temperatures (\( T_c \)) shifted to lower temperatures whereas the melting temperatures (\( T_m \)) increased.

![Figure 6.](image)

These results clearly display that, at annealing temperatures above 105°C, PEO began to crystallize not only during the heating scan but also during the quenching process. The shift of the crystallization peaks to lower temperature indicates that the composition might have changed somewhat during annealing. In other words, on annealing, two separated amorphous phases are formed, i.e., one is the PES-C-rich phase whereas the other corresponds to the PEO-rich phase. The PEO-rich phase can crystallize during quenching process, and its thermal behavior is just similar to that of the 30/70 PES-C/PEO blend (Fig. 1). The cold crystallization of PEO becomes easier, i.e. the hindrance effect of PES-C on PEO crystallization reduces because the content of the amorphous component (PES-C) with higher \( T_g \) in the newly formed PEO-rich phase reduces. As a consequence, the enthalpy values of crystallization and fusion increased, and \( T_m \) increased since more perfect crystals could be formed. It is assumed that the shift of crystallization peak at a particular annealing temperature can correspond to the beginning of phase separation. Of course, the annealing time is an important factor which affects the shift and magnitude of crystallization peak after the phase separation occurs. The one-phase temperature zone is reserved only if every parameter remain constant: enthalpy of fusion (\( \Delta H_f \)), enthalpy of crystallization (\( \Delta H_c \)), \( T_c \), and \( T_m \) (Fig. 7).
PES-C/PEO Blends Containing More Than 50 wt % PEO

When PEO content in the blends was more than 50 wt %, only the crystalline blends were obtained under the experimental condition used since PEO crystallization can occur during the quenching process, and at the same time there was cold crystallization phenomenon during the heating scan. With increase of PEO content, the cold crystallization peak in the heating thermograms became fairly indistinguishable when PEO was more than 80 wt % in the blends. Representatively, Figure 8 gives a series of thermograms of the 30/70 PES-C/PEO blend annealed at different temperatures ranging from 85 to 110°C. It is observed that the thermal enthalpy values of crystallization and melting transition change depending upon the annealing temperature. The plot of thermal enthalpy of crystallization and fusion as a function of annealing temperature is shown in Figure 9. It is noted that, at or below 80°C, the two enthalpy values almost remain constant, which indicates that the composition of the blends does not change during the annealing process, and namely the phase separation does not take place. However, when the annealing temperature is above 80°C, the enthalpy of crystallization gradually decreases with increasing annealing temperature, whereas the enthalpy of fusion increases. It is reasonable to believe that the changes of thermal enthalpy are caused by the occurrence of phase separation during annealing. Therefore, the phenomenon is indicative of the occurrence of phase separation. With increasing annealing temperature, the area under the melting peaks became larger whereas the enthalpy of crystallization be-
MISCIBILITY AND PHASE SEPARATION IN PES-C/PEO BLENDS

The blends exhibit single, composition-dependent glass transition temperatures that obey the Gordon–Taylor equation quite well. The crystallization of PEO in the blends was obviously hindered by PES-C, as shown by the dramatic lowering of the PEO crystallinity and the decrease of PEO crystallization rate.

At higher temperatures, the PES-C/PEO blends underwent phase separation, which indicates the existence of a lower critical solution temperature (LCST). Based on the DSC studies and optical microscopy, the phase separation process was investigated. Annealed at the selected temperature and then quenched, the blends can display apparent changes of thermal behavior depending on the blend composition while phase separation takes place. (1) For the blends containing PEO less than 50 wt %, no crystallization phenomenon of PEO was observed after quenching, but there appears a minor melting peak when the samples were annealed at a particular higher temperature. The occurrence of melting peak after annealing is assumed to correspond to the beginning of phase separation. (2) For the amorphous blends obtained via quenching, crystallization is observed (e.g., PES-C/PEO 50/50 blends), positions of the crystallization and melting peaks, enthalpy of crystallization and fusion do not change until the blends are annealed at a particular higher temperature. The changes of thermal properties of blends composed of a crystalline polymer and an amorphous polymer can provide information about the occurrence of phase separation, and thermal analysis can be used to determine the phase boundary of such blends.

On the basis of above-mentioned analysis of thermal properties and microscopic observations, the temperatures of phase separation were determined and a phase boundary diagram was established, as shown in Figure 10. It can be seen that the temperatures determined by optical observation were higher than those determined by thermal analysis.

The asymmetrical phase diagram has the minimum around 20 wt % PEO and the system exhibits a typical lower critical solution temperature behavior (LCST) just as in PES/PEO blend system.37,41

CONCLUSIONS

Miscibility and phase behavior in blends of PES-C and PEO have been investigated by differential scanning calorimetry and optical microscopy. The blends are completely miscible in the amorphous state over the entire composition range at temperature $T < T_{\text{cut}} = 75^\circ\text{C}$ as judged from the transparency of blend films and the glass transition behavior. The blends exhibit single, composition-dependent glass transition temperatures that obey the Gordon–Taylor equation quite well. The crystallization of PEO in the blends was obviously hindered by PES-C, as shown by the dramatic lowering of the PEO crystallinity and the decrease of PEO crystallization rate.

At higher temperatures, the PES-C/PEO blends underwent phase separation, which indicates the existence of a lower critical solution temperature (LCST). Based on the DSC studies and optical microscopy, the phase separation process was investigated. Annealed at the selected temperature and then quenched, the blends can display apparent changes of thermal behavior depending on the blend composition while phase separation takes place. (1) For the blends containing PEO less than 50 wt %, no crystallization phenomenon of PEO was observed after quenching, but there appears a minor melting peak when the samples were annealed at a particular higher temperature. The occurrence of melting peak after annealing is assumed to correspond to the beginning of phase separation. (2) For the amorphous blends obtained via quenching, crystallization is observed (e.g., PES-C/PEO 50/50 blends), positions of the crystallization and melting peaks, enthalpy of crystallization and fusion do not change until the blends are annealed at a particular higher temperature. The changes of the thermal properties at the annealing temperature can be taken as the onset of phase separation. (3) As for the blends rich in PEO, the crystallization of PEO occurs not only during the heating scan but also during the quenching process. In this case, the changes of enthalpy values of crystallization and fusion are sensitive to the onset of phase separation. Prior to the occurrence of phase separation, the thermal properties remain constant. With phase separation occurring at a particular higher temperature, the enthalpy of crystallization decreases but that of fusion increases with increase of the annealing temperature. In short, the changes of thermal properties of blends composed of a crystalline polymer and an amorphous polymer can provide information about the occurrence of phase separation, and thermal analysis can be used to determine the phase boundary of such blends.

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REFERENCES AND NOTES