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Miscibility and crystallization of poly(ethylene oxide) and poly(ε-caprolactone) blends

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Abstract

Blends of poly(ethylene oxide) (PEO) with poly(ε-caprolactone) (PCL), both semicrystalline polymers, were prepared by co-dissolving the two polyesters in chloroform and casting the mixture. Phase contrast microscopy was used to probe the miscibility of PEOB/PCL blends. Experimental results indicated that PEO was immiscible with PCL because the melt was biphasic. Crystallization of PEO/PCL blends was studied by differential scanning calorimetry and analyzed by the Avrami equation. The crystallization rate of PEO decreased with the increase of PCL in the blends while the crystallization mechanism did not change. In the case of the isothermal crystallization of PCL, the crystallization mechanism did not change, and the change in the crystallization rate was not very big, or almost constant with the addition of PEO, compared with the change of the crystallization rate of PEO.

Keywords: Poly(ethylene oxide)/poly(ε-caprolactone) blends; Miscibility; Crystallization

1. Introduction

Much attention has been focused on the development and investigation of binary polymer blends, which allow the combination of desirable properties of different polymers with exceptional advantages over the development of novel polymeric materials. 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 have been reported on the miscible polymer blends of two crystalline polymers with different chemical structures, and they may be of considerable technological interest and offer the possibility of investigating crystallization and morphological behavior related to blend miscibility [1–22]. In the case of binary immiscible blends of two crystalline polymers, it is also possible to determine how the crystallinity of one component affects the crystallization process of the other [23–25]. In this work, we report the miscibility and crystallization of poly(ethylene oxide) (PEO) and poly(ε-caprolactone) (PCL) blends. It is really interesting and difficult to study the miscibility and crystallization of PEO/PCL blends since the glass transition temperature (T_g) and the melting point temperature (T_m) of the two components are very close to each other. The T_g is ca. −60 °C, and the T_m is ca. 60 °C. Therefore, the miscibility of PEO/PCL blends cannot easily be determined by the change of T_g with blend composition or the depression in the melting point temperature. Up to now, only one paper reported that PEO and PCL was miscible by the depressed crystallization temperature (T_c) in the blends compared with those of the homopolymers [26]. However, it is questionable to judge the miscibility only by the decrease of T_c.

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Therefore, the miscibility of PEO/PCL blends was examined again by phase contrast microscopy (PCM), and the crystallization of PEO/PCL blends was studied by PCM and differential scanning calorimetry in this paper.

2. Experimental

Both PEO ($M_w = 100,000$) and PCL ($M_w = 14,300$) were purchased from Scientific Polymer Products, Inc. (Ontario, NY) and used as received in this study. PEO/PCL blends were prepared with mutual solvent chloroform at an elevated temperature. 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 PEO.

A PCM (Olympus IMT-2) with a temperature controller (Linkam LK-600PM) was used to probe the miscibility of PEO/PCL blends and to observe the crystallization of PEO and PCL.

Thermal analysis was performed using a TA Instruments differential scanning calorimetry (DSC) 2910 with a Thermal Analyst 2000. Two different procedures were employed:

1. *Nonisothermal crystallization*. The cast samples were first heated from 20 to 90 °C at 10 °C/min (first heating), held at 90 °C for 3 min to destroy any thermal history, cooled to 0 °C at 2 °C/min (first cooling), and then heated to 90 °C at 10 °C/min (second heating).
2. *Isothermal crystallization*. The samples were quenched to 52 °C to crystallize PEO for 1 h after being held at 90 °C for 3 min to destroy any thermal history, and then quenched to 40 °C to crystallize PCL.

The above-mentioned isothermal crystallization conditions consist of the two following steps, namely, the isothermal crystallization of the PEO phase from the melt at 52 °C, and the isothermal crystallization of the PCL from the liquid phase in the presence of previously crystallized PEO at 40 °C. In the case of PEO/PCL blends, the isothermal two-step crystallization described above is possible because PEO and PCL need very different supercooling to crystallize and the difference in the crystallization rate is very large.

3. Results and discussion

3.1. Miscibility of PEO/PCL blends by optical microscopy

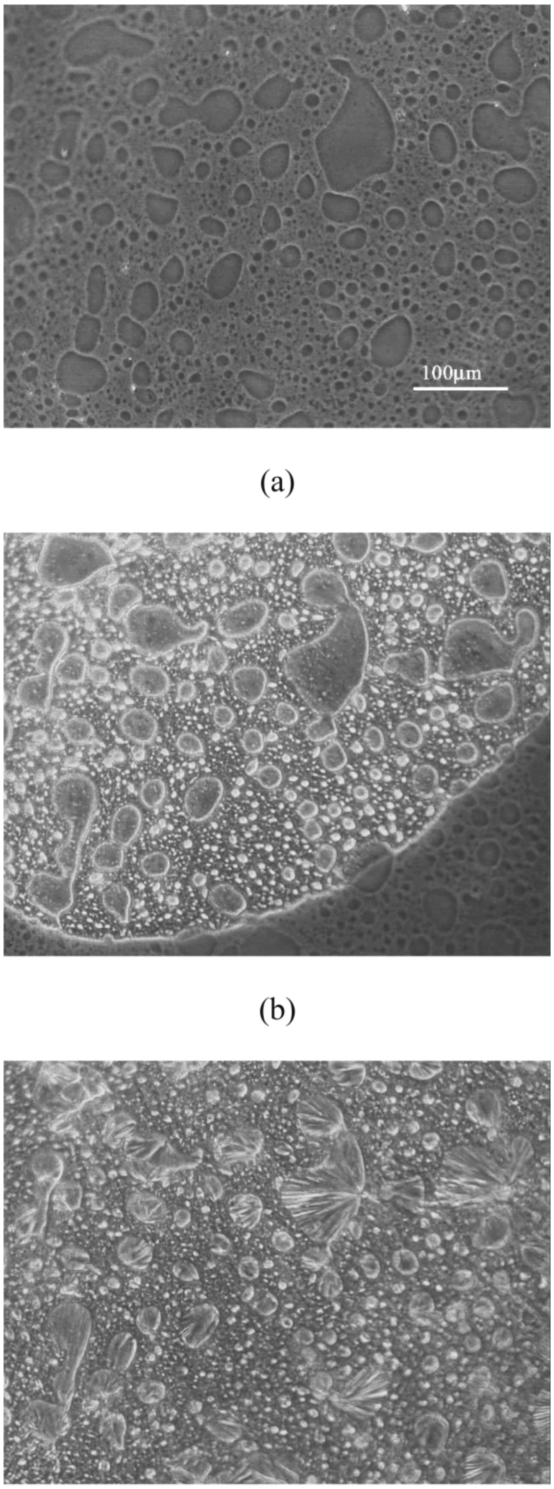
A single T_g is the most widely and conventionally used criterion for the miscibility of a polymer blend. A single composition dependent glass transition indicates full miscibility. On the contrary, an immiscible polymer blend exhibits more than one T_g. But in the case of PEO/PCL blends, the miscibility of PEO/PCL blends can not be determined by this method due to the close T_g of PEO and PCL.

In this paper, the miscibility of PEO/PCL blends was studied by PCM. Provided that the refractive indices of the two components are not the same, it is possible to infer whether the melt is single-phased or biphasic. If PEO is miscible with PCL, the single-phased melt should be observed. Otherwise, if PEO is immiscible with PCL, the biphasic melt should be observed. For all compositions of PEO/PCL blends studied, clearly defined biphasic separation was observed, indicating that PEO is not miscible with PCL in the melt. As an example, the phase separation occurred in the melt of PEO/PCL 60/40 observed by PCM is shown in Fig. 1a. The bright PEO spherulites growing at 52 °C from the heterogeneous melt observed by PCM is shown in Fig. 1b, with small dark domains of PCL melt inside and outside the PEO spherulite. The arc-shaped line is the growth front of the PEO spherulite. Fig. 1c shows the appearance of PCL spherulites after the isothermal crystallization of PCL at 40 °C. In this case, PCL crystallized in the domains in the matrix of PEO spherulites and the dark domains became bright too.

3.2. Nonisothermal crystallization study by DSC

DSC measurements were performed to characterize the crystallization and melting behavior of PEO/PCL blends. The samples were subjected to the thermal treatment described in the experimental part. The nonisothermal crystallization of PEO/PCL blends was first studied by DSC. Fig. 2 shows the DSC traces of neat PEO, neat PCL and PEO/PCL blends for the cast samples at a heating rate of 10 °C/min. Fig. 3 shows the DSC traces of PEO/PCL blends at a cooling rate of 2 °C/min from the melt. Fig. 4 shows the DSC traces of PEO/PCL blends at a heating rate of 10 °C/min after cooling from the melt at 2 °C/min. Fig. 5 summarizes the melting point temperature (T_m) and crystallization temperature (T_c) of PEO/PCL blends from Figs. 2 to 4. From the above figures, the following conclusions can be obtained.

(1) Both neat PEO and neat PCL exhibit the T_m as a well-defined peak, with the T_m of PEO being higher than that of PCL. However, in the blends there are two melting peaks or one peak and one shoulder corresponding to the T_m of the two components, respectively, and the shape of the area of the melting peaks changes with the blend composition. The T_m of PEO gradually decreases with the increase of PCL, while the T_m of PCL is almost unchanged. Differences between the values of the first (Fig. 2) and second (Fig. 4) heating are due to the different thermal history of the samples. In the case of the first heating, the cast samples



(a)

(b)

(c)

Fig. 1. PCM micrographs (same magnification, bar = 100 μm) of PEO/PCL 60/40: (a) the melt at 90 °C for 10 min, (b) crystallization of PEO at 52 °C for 22 min, and (c) crystallization of PCL at 40 °C for 20 min after crystallization of PEO at 52 °C for 1 h.

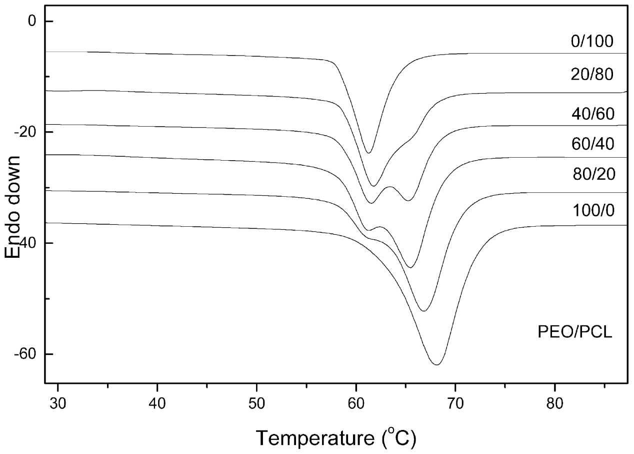


Fig. 2. The first melting behavior of PEO/PCL blends for the cast samples at 10 °C/min.

were crystallized by annealing at 50 °C for 3 days, whereas in the case of the second heating, the samples were crystallized nonisothermally at a cooling rate of 2 °C/min from the crystal-free melt.

(2) Both neat PEO and neat PCL exhibit the T_c as a well-defined peak on cooling from the melt at a 2 °C/min, with the T_c of PEO being higher than that of PCL. However, in the blends there are two separate crystallization temperature peaks corresponding to the T_c of PEO and PCL, respectively. And the shape of the area of the crystallization peaks changes with the blend composition too. The T_c of PEO is almost unchanged, whereas the T_c of PCL first increases and then decreases with the increase of PEO content in the blends.

(3) The higher the PEO percentage, the higher the apparent fusion enthalpy (ΔH_m) and crystallization enthalpy (ΔH_c) of the blends. This is because the ΔH_m and ΔH_c of neat PEO is higher than those of neat PCL.

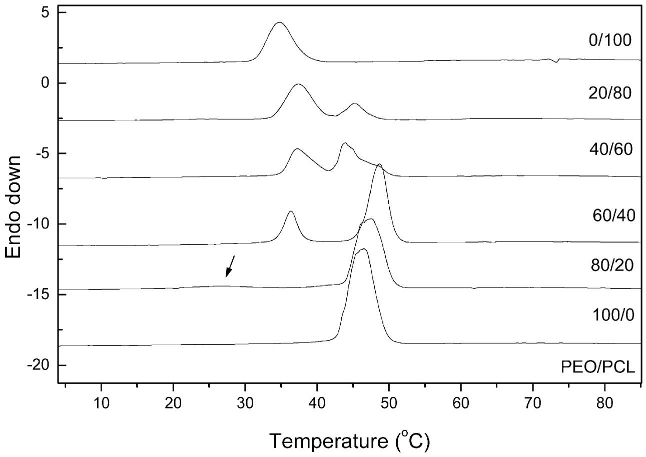


Fig. 3. Nonisothermal crystallization behavior for PEO/PCL blends cooled from the melt at 2 °C/min. The arrow is indicative of the T_c of PCL.

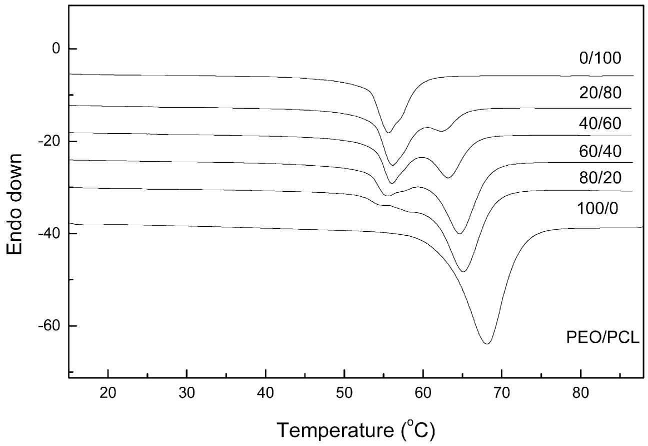


Fig. 4. The second melting behavior of PEO/PCL blends at 10 °C/min after cooling from the melt at 2 °C/min.

3.3. Isothermal crystallization study by DSC

The isothermal crystallization of PEO/PCL blends was also studied by DSC. According to the procedure described in Section 2, the process of the isothermal crystallization of the PEO/PCL blends was investigated at two crystallization temperatures: 52 °C for PEO, and 40 °C for PCL.

The exothermic curves of heat flow as a function of time were recorded and investigated. The relative crystallinity X_t is a function of crystallization time t and calculated by

$$X_t = \frac{\int_{t_0}^{t} \left(\frac{\mathrm{d}H_c}{\mathrm{d}t}\right)\mathrm{d}t}{\int_{t_0}^{t_\infty} \left(\frac{\mathrm{d}H_c}{\mathrm{d}t}\right)\mathrm{d}t} \tag{1}$$

where $\mathrm{d}H_c/\mathrm{d}t$ is the rate of heat evolution, and t_0 and t_∞ are the onset and end time of crystallization time, respectively. The plots of relative crystallinity X_t versus the crystallization time t are shown in Fig. 6 for the isothermal crystallization of the neat and blended PEO at 52 °C. It should be noted that the crystallization of PEO blended with 80% PCL was not observed within the crystallization time 1 h used in this study. The well-known Avrami equation is often used to analyze the isothermal crystallization kinetics; it assumes that the relative degree of crystallinity develops with crystallization time t as

$$1 - X_t = \exp(-kt^n) \tag{2}$$

where 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 [27]. The Avrami parameters n and k are obtained from the plots of $\log(-\ln(1 - X_t))$ versus $\log t$ as shown in Fig. 7. The Avrami exponents n and crystallization rate constants k of the neat and blended PEO are listed in Table 1.

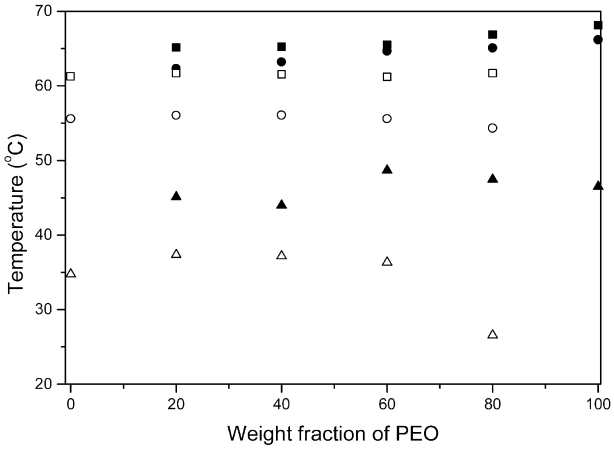


Fig. 5. Summary of the results of T_m and T_c for the nonisothermal crystallization of PEO/PCL blends (■, □: the T_m of PEO and PCL, respectively, for the cast samples; ●, ○: the T_m of PEO and PCL, respectively, after cooling from the melt; and ▲, △: the T_c of PEO and PCL cooling from the melt, respectively).

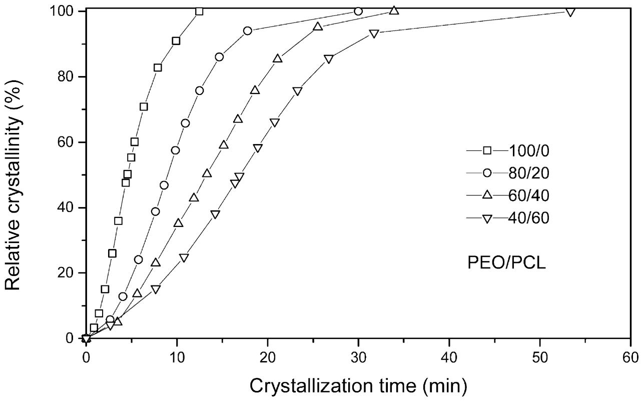


Fig. 6. The plots of relative crystallinity X_t versus crystallization time t of the crystallization of PEO at 52 °C for PEO/PCL blends.

From Table 1, it could be seen that the average value of the Avrami exponent n is around 2.0 for the isothermal crystallization of the neat and blended PEO. The almost unchanged Avrami exponent n with the addition of PCL

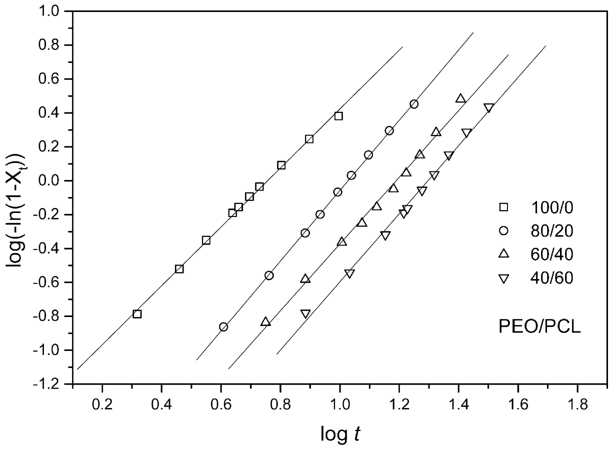


Fig. 7. The Avrami plots of the crystallization of PEO at 52 °C for PEO/PCL blends.

Table 1
Crystallization kinetic parameters of PEO in PEO/PCL blends at 52 °C

PEO/PCL	n	k (min^{-n})	$t_{0.5}$ (min)
100/0	1.8	4.42×10^{-2}	4.65
80/20	2.0	7.75×10^{-3}	8.92
60/40	2.0	4.45×10^{-3}	12.50
40/60	2.0	2.46×10^{-3}	16.50
20/80	No	Peak	

indicates that the crystallization mechanism of PEO is not affected by the presence of PCL in PEO/PCL blends. This is consistent with the observation by PCM.

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

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

where k and n are the same as in the Avrami equation. The values of $t_{0.5}$ for the neat and blended PEO were calculated and are also listed in Table 1. It is clear that at a given crystallization temperature the value of $t_{0.5}$ increases with the increase of PCL, indicating that the crystallization rate of PEO decreases with the increase of PCL. The slow-down of the crystallization rate of PEO may be considered to occur from a physical restriction to the growth by the PCL domains [28]. Conclusively the presence of PCL in the PEO/PCL blends does not change the crystallization mechanism of PEO, but reduces the crystallization rate of PEO in the blends compared with neat PEO when they crystallized isothermally at a given crystallization temperature.

The isothermal crystallization of PCL at 40 °C was also studied by DSC and analyzed by the Avrami equation in PEO/PCL blends after the samples was held at 52 °C for 1 h to finish the crystallization of PEO. It should be noted too that the crystallization of PCL blended with 80% PEO was not observed due to the short crystallization time 1 h used in this study and the very slow crystallization rate of PCL. The results are listed in Table 2. The average Avrami exponent is around 2, and does not change with the addition of PEO. On the other hand, it is found that k increased and $t_{0.5}$ decreased for PCL with the increase of PEO in the blends except that the value of k in PEO/PCL 20/80 was smaller than that in PEO/PCL 40/60 while the value of $t_{0.5}$ in PEO/PCL 40/60 was larger than that in PEO/PCL 20/80. The increase of the crystallization rate of PCL with the increase of PEO may be explained as follows. The temperature for the isothermal crystallization of PCL in PEO/PCL blends was chosen to be 40 °C, which was a suitable crystallization temperature to investigate the crystallization process of PCL in the blends with PEO in the presence of the crystals of PEO formed at a higher crystallization temperature 52 °C by considering the crystallization time required for PCL and the differences in supercooling needed to crystallize for PEO and PCL. Meanwhile, the crystallization peak temperature T_c of PCL cooled from the melt at 2 °C/min first increased with the increase of PEO in the blends (Fig. 5), indicating that the temperature gap between the isothermal crystallization temperature 40 °C and the crystallization peak temperature T_c decreased with the increase of PEO. This was probably the reason why the crystallization rate of PCL increased with the increase of PEO since it was reasonable that PCL crystallized faster at a crystallization temperature close to T_c (crystallization peak temperature) than at a crystallization temperature far away from T_c in the crystallization temperature range higher than T_c when PCL crystallized from the melt. However, the changes in k and $t_{0.5}$ were not so big, or almost constant, compared with the changes of k and $t_{0.5}$ of PEO in Table 1.

Table 2
Crystallization kinetic parameters of PCL in PEO/PCL blends at 40 °C

PEO/PCL	n	k (min^{-n})	$t_{0.5}$ (min)
0/100	1.7	1.14×10^{-1}	2.82
20/80	2.2	9.84×10^{-2}	2.38
40/60	1.9	1.19×10^{-1}	2.51
60/40	2.0	1.68×10^{-1}	2.05
80/20	No	Peak	

4. Conclusions

The miscibility and crystallization of PEO/PCL blends have been studied by PCM and DSC in this work. The following conclusions were obtained:

1. PCM study showed that PEO is immiscible with PCL. Though the molecular weight of the samples used in this study is not the same as those of the literature, the conclusion is really questionable that PEO was miscible with PCL from the change of T_c [26].
2. A small change of T_c of PEO/PCL blends was actually found. The T_m of PEO decreases with the increase of PCL, but the T_m of PCL is almost the same in the blends. However, these results cannot be used to conclude that PEO and PCL are miscible.
3. The crystallization rate of PEO decreases with the increase of PCL in the blends while the crystallization mechanism does not change. The slow-down of the crystallization rate of PEO may be considered to occur from a physical restriction to the growth by the PCL domains. The crystallization mechanism of PCL does not change with PEO, and the change in the crystallization rate was not so big, or almost constant, compared with the change of the crystallization rate of PEO.

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