# Study of the Miscibility and Crystallization Behavior of Poly(ethylene oxide)/Poly(vinyl alcohol) Blends

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**ABSTRACT:** The miscibility and crystallization behavior of poly(ethylene oxide)/poly(vinyl alcohol) (PEO/PVA) blends were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and polarizing optical microscopy. Because the glass-transition temperature of PVA was near the melting point of PEO crystalline, an uncommon DSC procedure was used to determine the glass-transition temperature of the PVA-rich phase. From the DSC and DMA results, two glass-transition temperatures, which corresponded to the PEO-rich phase and the PVA-rich phase, were observed. It was an important criterion to indicate that a blend was immiscible. It was also found that the preparation method of samples influenced the morphology and crystallization behaviors of PEO/PVA blends. The domain size of the disperse phase (PVA-rich) for the solution-cast blends was much larger than that for the coprecipitated blends. The crystallinity, spherulitic morphology, and isothermal crystallization behavior of PEO in the solution-cast blends were similar to those of the neat PEO. On the contrary, these properties in the coprecipitated blends were different from those of the neat PEO. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1562–1568, 2004

**Key words:** poly(ethylene oxide); poly(vinyl alcohol); blends; miscibility; crystallization

## INTRODUCTION

In recent decades, many polymer blends have been well studied and documented by industrial and scientific research. One of the major concerns in this subject is the miscibility of polymer blends. According to the Flory–Huggins model, some interactions between components of a polymer blend are helpful in forming a miscible polymer blend, such as poly(ethylene oxide)/poly(methyl methacrylate) (PEO/PMMA), poly(ethylene oxide)/poly(vinyl phenol) (PEO/PVPh), poly(vinylidene fluoride)/poly(1,4-butylene adipate) (PVDF/PBA), poly(vinylidene fluoride)/poly(pivalolactone) (PVDF/PPVL), and so on.[1–8] The system of interest here is the PEO/PVA polymer blend. Both PEO and PVA are useful industrial polymers. In particular, PVA has attracted attention and interest because of its environmental issues. PEO contains ether groups, which are expected to induce hydrogen bonds or polar interactions with the hydroxyl groups of PVA chains. Quintana et al.[9] studied the PEO/PVA polymer blend. They found the melting-point depression and negative polymer–polymer interaction parameter $\chi$, which are considered characteristics of a miscible blend. However, they also found that the glass-transition temperature of PEO was not changed with the increase of PVA up to 20 wt % by dynamic mechanical thermal analysis (DMA). Mishra et al.[10] mentioned that weak interchain interactions were evidenced in IR and NMR studies. However, according to the IR spectroscopic studies, Mishra et al.[11] reported that intermolecular hydrogen bonding between PEO and PVA may not be of significance. Based on the results of IR, NMR, and SEM studies,[10,11] Mishra et al. concluded that PEO/PVA is an immiscible system. Furthermore, on the basis of SALS (small-angle light scattering), WAXD, FTIR, and optical microscopy studies, Kondo et al.[12] proposed that the PEO/PVA blend films are immiscible. Also, they demonstrated that only the primary OH in cellulose interacted with the skeletal oxygen of PEO.[13] On the other hand, the OH in PVA, which is a secondary OH, does not interact with the oxygen of PEO. Another important characteristic, which has become standard in judging the miscibility/immiscibility of polymer blends, is whether there is one or multiple glass-transition temperatures ($T_g$) of a polymer blend. The existence of two $T_g$ values indicates immiscible or partial immiscible, whereas one $T_g$ corresponds to a miscible system. Although several experiments have been done to study the miscibility of PEO/PVA, no one has found the existence of two glass-transition temperatures in the PEO/PVA blend system because of the difficulty of such a measurement. Therefore, part of our objective was to measure the glass-transition temperature of PEO/PVA by DSC and DMA.

Irrespective of whether it is an immiscible or miscible system, it is able to form a film with good mechanical properties. Obviously, the morphology of film has a major effect on the mechanical properties. Thus the other part of our objective was to study the effect of film-preparation methods on the morphology and crystallization behavior of blends.

## EXPERIMENTAL

### Materials and film-preparation method

PEO with a weight-average molecular weight of 20,000 (Polysciences, Warrington, PA) was used in this study. PVA with a weight-average molecular weight in the range of 85,000–146,000 (Aldrich Chemical Co., Milwaukee, WI) and a degree of saponification of 87–89 mol % was used.

The preparation of PEO and PVA blends was carried out by two different methods, solution casting and coprecipitation. In the former method, mixtures of PEO and PVA with varying weight ratios were dissolved in deionized water. After mixtures were completely dissolved, the solvent (water) was naturally evaporated at room temperature for 5 days. To remove the residual solvent completely, the blend films were placed in a vacuum oven at 90°C for 2 days. In the latter method, PEO and PVA were dissolved in N,N-dimethylformamide (DMF). The solutions were subsequently added dropwise into 20-fold excess of diethyl ether. The precipitate was filtered out and washed several times with diethyl ether. In the solution-casting method, the residual solvent was completely removed by placing the films in a vacuum oven at 90°C for 2 days. For both methods, complete removal of solvent was verified by TGA. The result of TGA showed no weight loss before the degradation temperature of film was reached. Also, it showed no weight loss at 250°C.

### Measurements

Thermal behaviors of PEO/PVA blends were measured with differential scanning calorimetry (DSC). The instrument (Model DSC 2010; TA Instruments, New Castle, DE) was equipped with a liquid nitrogen cooling system and calibrated with an indium standard. The weight of sample used in DSC was in the range of 5–10 mg. All the DSC measurements were under nitrogen atmosphere.

The glass-transition temperature(s) of blends were also conducted with dynamic mechanical analysis (DMA, Model DMA 983; TA Instruments). Samples for DMA testing were prepared by a Polystat 100T hot presser at 200°C for 15 min. The dynamic mechanical behaviors of blends were measured at a fixed frequency of 1 Hz at a heating rate of 3°C/min in the temperature range −100 to 120°C.

The spherulitic morphology of PEO/PVA blends was observed by a Nikon HFX-DX polarizing optical microscope (POM; Nikon, Tokyo, Japan) with a Linkam THMS600 hot stage. The samples were held between two microscope slides. All samples were preheated to 250°C and held for 5 min to erase the thermal history. Then the pressure was applied on the top of slides. The samples were remelted again without the pressure. The samples were then quickly cooled to the desired crystallization temperature (47°C), where the resultant morphology was observed with a video camera mounted on the microscope and analyzed by a digital image analyzer.

The isothermal crystallization of PEO/PVA blends was measured by differential scanning calorimetry (DSC, Model DSC 2010; TA Instruments). The samples were heated to 250°C and held for 5 min on a Linkam THMS600 hot stage, and then quickly moved into the DSC cell, where the temperature was kept at 47°C. After the crystallization peak appeared completely, isothermal crystallization of PEO/PVA blends at 47°C was observed.

## RESULTS AND DISCUSSION

### Miscibility

From the studies of FTIR, NMR, SALS, and WAXD,[11,12] it was suggested that the PEO/PVA was an immiscible blend. However, no one reported the observation of two glass-transition temperatures, which was an important criterion of the blend's being immiscible. Figure 1(a) and (b) displayed the DSC thermograms of PEO/PVA blends prepared by the solution-casting and the coprecipitation method, respectively. Samples were first heated to 250°C, held for 5 min, and then quenched from 250 to −100°C. The thermograms were then recorded at a heating rate of 10°C/min, from −100 to 200°C. From Figure 1(a) and (b), it was shown that only the glass-transition temperature of neat PVA, 71°C, was observed. The glass-transition temperatures of other blends were not observable. If PEO/PVA was an immiscible blend, it should have two glass-transition temperatures corresponding to the PEO-rich phase and the PVA-rich phase, respectively. Because PEO was a high-crystalline polymer, the difficulty of measuring the glass-transition temperature of the PEO-rich phase by DSC was expected. On the other hand, the glass-transition temperature of the PVA-rich phase was expected to be close to 71°C. Coincidently, it was near the melting point of PEO, 60°C. Therefore, the glass-transition peak of the PVA-rich phase might overlap with the melting peak of PEO in the DSC thermogram and it could be difficult to observe the glass-transition temperature.
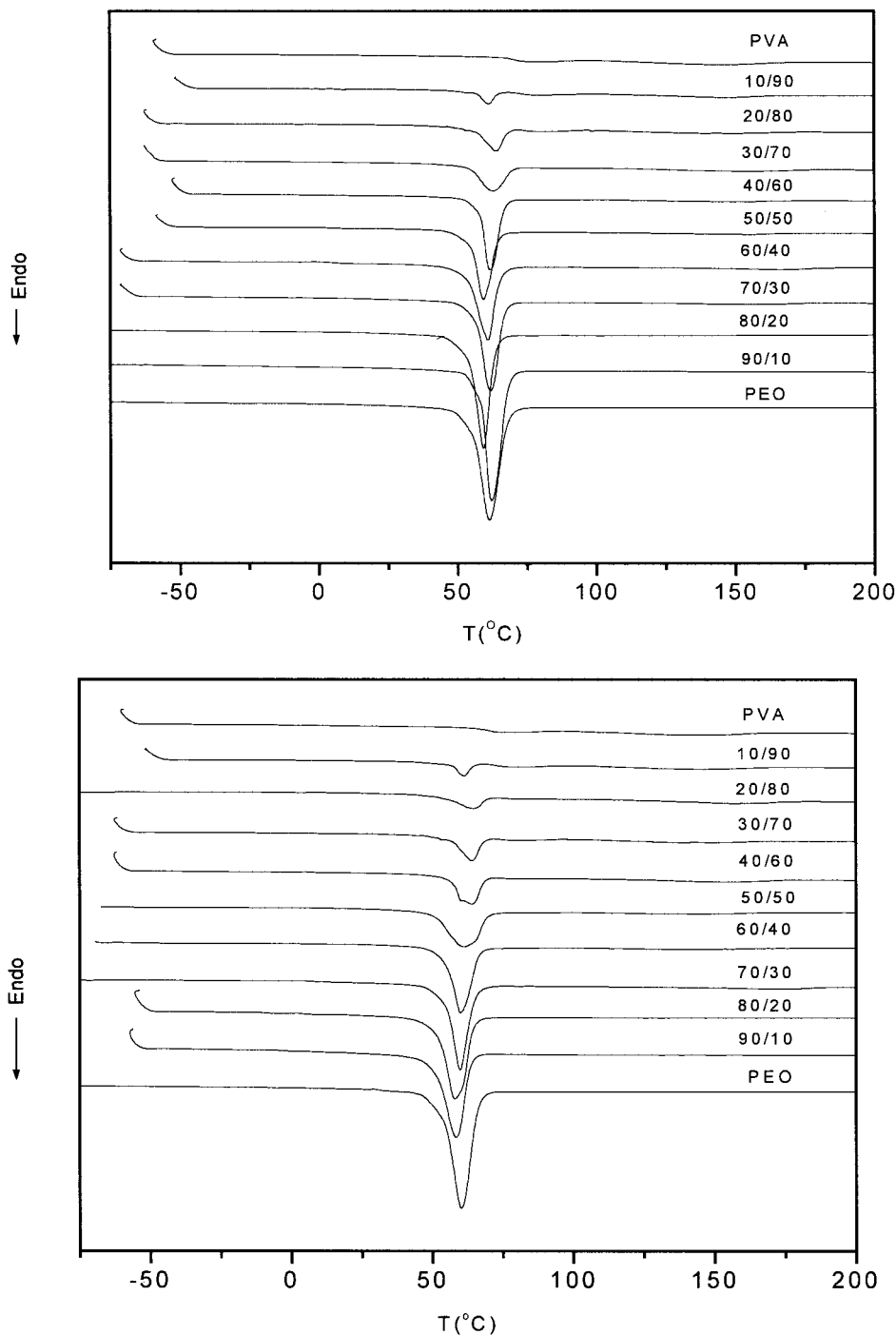
**Figure 1**   DSC thermograms of PEO/PVA blends prepared by (a) solution-casting and (b) coprecipitation.

To overcome the overlap of two peaks and determine the glass-transition temperature of the PVA-rich phase, the crystallization of PEO must be inhibited. Fortunately, it was well known that the crystallization rate would slow down as the crystallization temperature approached the melting temperature for crystalline polymer. Thus, a new strategy was developed. The samples were heated to 250°C and held for 5 min, followed by quenching to 55°C, and then heated to

200°C again at a heating rate of 10°C/min. The thermograms during heating from 55 to 250°C are shown in Figure 2. To ensure there was no significant crystallization of PEO during the process, the isothermal crystallization of PEO at 55°C was monitored using POM with a temperature-controlling hot stage. The result showed that no significant spherulites were formed within 30 min. Also, the same procedure was performed by DSC and neither the crystallization exo-
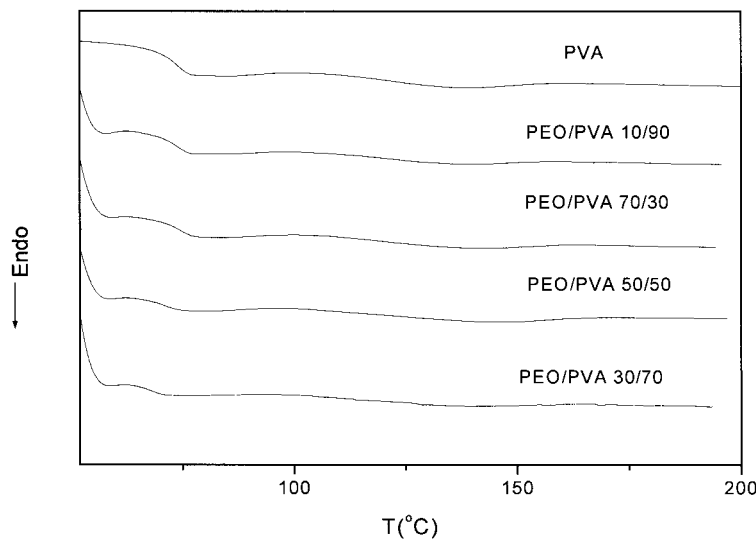
**Figure 2** DSC thermograms of PEO/PVA blends prepared by coprecipitation.

therm nor the melting endotherm was observed for isothermal crystallization at 55°C, for 30 min. Therefore, no significant crystallization of PEO was optically observed to interfere with the DSC observation of the glass transition of the PVA-rich phase. Also, the possibility of PVA crystallization during the quenching from 250 to 55°C was checked using the thermogram shown in Figure 2.

Figure 2 shows that the crystallization peak of PVA occurred after the glass-transition peak and then the melting peak of PVA was observed. Furthermore, the area under the crystallization peak was about the same as the area of melting peak (for 20/80 PEO/PVA, exotherm = 5.04 J/g; endotherm = 5.09 J/g), which meant that no PVA crystallization was formed during the quenching from 250 to 55°C. Now let us examine the thermogram shown in Figure 2. The glass transition of the PVA-rich phase for each composition is shown clearly now without the interference of PEO melting peak. The results are listed in Table I. The glass-transition temperature was taken as the midpoint of the change of slope in the DSC curve. Considering the degree of heterogeneity attributed to phase separation, it could be concluded that the glass-transition temperature of the PVA-rich phase was the same as that of neat PVA for every composition of the blend.

Because PEO was a high-crystalline polymer, the glass transition was difficult to observe by DSC. Thus, the glass-transition temperature of the PEO-rich phase was observed using DMA. From the DMA result, a $T_g$ of −26°C for neat PEO was observed. Also, a $T_g$ of 74°C for neat PVA was found from the DMA results. They were about the same as those reported in Quintana et al.[9] Coincidentally, the DMA results of neat PVA also showed another broad loss peak around −28°C

that was near the glass-transition temperature of PEO. It was a subglass-relaxation peak of neat PVA. Again, the glass-transition peak of the PEO-rich phase overlapped with the subglass-relaxation peak of the PVA-rich phase in the blends. However, it was well known that the subglass relaxation was associated with a very local molecular motion. Therefore, in an immiscible blend, it was not expected that the broadness of the subglass relaxation would be influenced by the other component except for overlapping with another relaxation. Thus, it was possible to check whether the loss peak around −28°C was attributed to one or two relaxation processes for the PEO/PVA blends. Given that the relaxation was influenced not only by the morphology but also by the temperature, it was necessary to normalize the experimental data.[14,15] A normalized loss moduli ($E''/E''_{max}$) versus $(1/T) - (1/T_{max})$ is shown in Figure 3. The subscript max indicates the peak value of the loss modulus curve. From

**TABLE I**
**PVA $T_g$ of PEO/PVA Blends Prepared by the Coprecipitation Method**

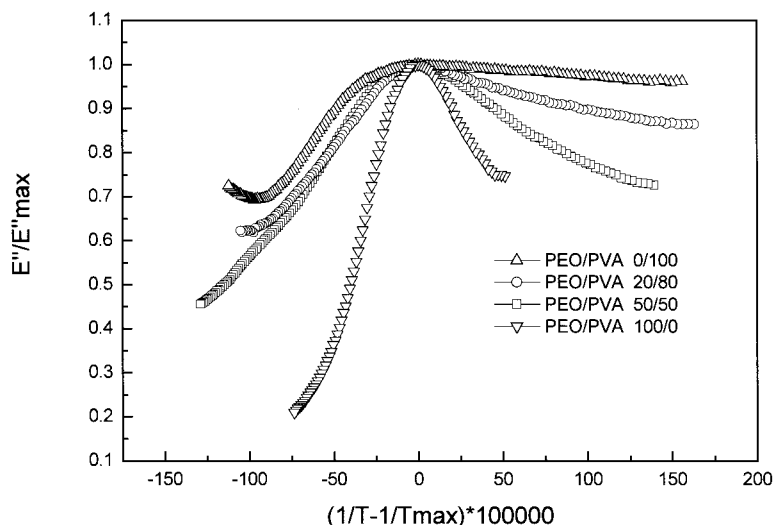| PEO/PVA (wt %) | $T_g$ (°C) |
|---|---|
| 0/100 | 71.01 |
| 10/90 | 70.52 |
| 20/80 | 70.91 |
| 30/70 | 70.15 |
| 40/60 | 68.35 |
| 50/50 | 70.62 |
| 60/40 | 68.55 |
| 70/30 | 70.97 |
| 80/20 | 68.45 |
| 90/10 | —[a] |

[a] Value not obtained.

**Figure 3** Normalized loss moduli ($E''/E'$) versus $[(1/T) - (1/T_{max})]$ of PEO/PVA blends.

this figure, it may be observed that the shape of loss modulus around −28°C becomes narrower with the increasing PEO component. Thus, it was believed that the relaxation peak around −28°C of PEO/PVA blend resulted from the overlapping of subglass relaxation of the PVA-rich phase and glass transition of the PEO-rich phase.

From the results of DSC and DMA, it was suggested that the PEO/PVA was an immiscible blend, which is consistent with the results of FTIR, NMR, SALS, and WAXD.[11,12]

**Effect of film-preparation methods on PEO/PVA blends**

Morphology

PEO/PVA blends were prepared by either the solution-casting or coprecipitation method. The effect of preparation methods on the spherulitic morphology and crystallization behavior of PEO in the blends was studied by POM and DSC.

Figure 4 shows the final spherulitic morphologies crystallized at 47°C for the neat PEO, solution-cast, and coprecipitated PEO/PVA 70/30 samples. PVA was not able to crystallize during the quenching from the melt. Also, the crystallization temperature was too low for PVA to crystallize. Therefore, only the PEO was able to crystallize in such conditions. It was observed that the spherulitic morphologies of PEO in the solution-cast blend were the same as those of the neat PEO and were not influenced by the presence of PVA. On the contrary, the spherulites of PEO in the coprecipitated blend were different from those of the neat PEO. The cross pattern of spherulites became more coarse and unclear. Furthermore, the situation of phase separation could be found by examining the

whole sample rather than a local part of the sample. Results are shown in Figure 5, which is the schematic plot of the dispersion of PVA in the PEO-rich phase. The PVA-rich phase was dispersed in the PEO-rich phase. The domain size of the PVA-rich phase in the solution-cast blend was significantly larger than it in the coprecipitated blend.

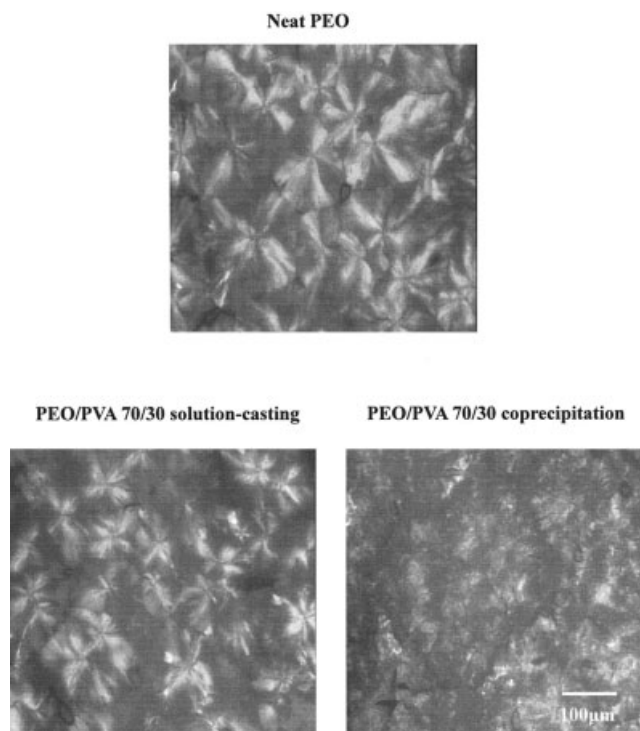It was known that the morphology of the blend could be influenced by the solvent used in the sample



**Figure 4** Final spherulitic morphologies crystallized at 47°C for the neat PEO, solution-cast, and coprecipitated PEO/PVA 70/30 samples.
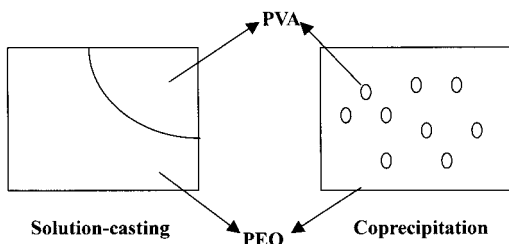
**Figure 5** Schematic representation of the dispersion of PVA in the PEO-rich phase by different film-preparation methods.

**TABLE II**
**Crystallinity of PEO/PVA Blends Prepared by Two Different Preparation Methods**

| PEO/PVA (wt %) | $X_c$/PEO (in %) | |
| --- | --- | --- |
| | Solution-casting | Coprecipitation |
| 100/0 | 91.88 | 91.67 |
| 90/10 | 93.15 | 75.33 |
| 80/20 | 90.60 | 78.19 |
| 70/30 | 89.59 | 76.57 |
| 60/40 | 92.13 | 80.89 |
| 50/50 | 94.67 | 78.06 |

preparations.[16–18] In this study, solvents used in the solution-cast blends were different from those used in the coprecipitated blends. Thus, the effect of solvent on morphology was examined. A sample was prepared using the same procedure of previous cast blends except the casting solvent was DMF. The POM results showed that the morphology of DMF-cast blend was the same as that of the water-cast blend. Therefore, it was suggested that the morphology of the cast blend was not influenced by the solvent, but rather was influenced by the preparation methods. One possible reason was the time allowed for the phase separation. In the solution-cast method, it took 5 days to evaporate the water, whereas only a very short time was needed for the coprecipitation method.

## Crystallinity

The fusion heat of PEO in the blend was obtained by integration of the area under the melting peak of the DSC curve. Samples were first heated to 250°C, held for 5 min, and then cooled to −100°C. At a heating rate of 10°C/min, samples were heated from −100 to 200°C, and the fusion heat of PEO was obtained. The crystallinity of PEO in the blend was calculated by the following equation:

Crystallinity

$$= \Delta H_f/\Delta H_f^\circ/\text{weight fraction of PEO in the blend}$$

where $\Delta H_f$ is the fusion heat of PEO and $\Delta H_f^\circ$ is the fusion heat of perfect PEO crystal (196.46 J/g).[19] The results are listed in Table II, which shows that the crystallinity of PEO in the solution-cast blend was not influenced by blending with PVA. On the other hand, the cystallinity of PEO in the coprecipitated blends was less than that in the neat PEO. Obviously, the crystallization was influenced by adding PVA because of the relatively better distribution of PVA in PEO. However, the crystallinity of PEO in coprecipitated blends did not change significantly with the increase of PVA.

## Isothermal crystallization

The kinetics of isothermal crystallization was analyzed using the Avrami equation[20–22] with the double-logarithmic form:

$$\log[-\ln(1 - X_t)] = \log K_n + n\log t$$

where $n$ is the Avrami exponent related to the geometry of the spherulitic growth and the mechanism of the nucleation; $K_n$ is the overall kinetic rate constant. Table III shows values of $n$ and $K_n$ of the Avrami equation at a crystallization temperature of 47°C for both solution-cast and coprecipitated blends. In spite of the different preparation methods of samples, the overall kinetic rate constants ($K_n$ values) of the blends were about the same. Moreover, the $K_n$ values of the blends were not changed with the composition, which could further verify that PEG/PLLA blends constitute immiscible systems. The $K_n$ values of the blends were reasonable compared with the data reported by Qiu et al.[23] ($4.42 \times 10^{-2}$ min$^{-n}$) but was higher than that reported by Zhong and Guo[24] ($3.6 \times 10^{-4}$ min$^{-n}$) and Guo et al.[25] ($3.19 \times 10^{-5}$ min$^{-n}$). It was hard to make a direct comparison because of the different materials and crystallization temperature they used. However, the Avrami exponents ($n$) were dependent on the preparation methods of samples. The Avrami exponents of PEO in the solution-cast blends were the same as those of the neat PEO (about 2.5). However, in the

**TABLE III**
**Crystallization Rate Constants and Avrami Exponents of PEO/PVA Blends Crystallized at 47°C, and the Samples Were Prepared by Two Different Methods**

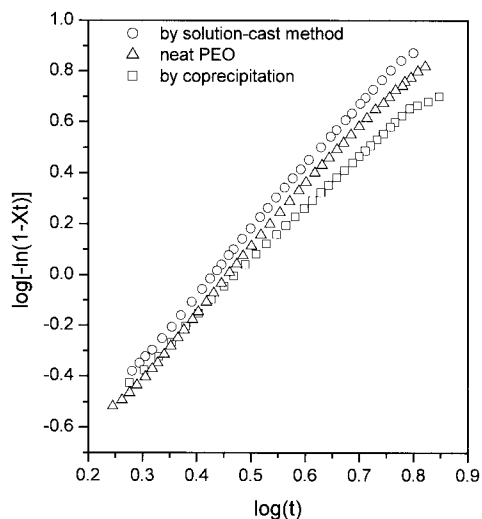| PEO/PVA (wt %) | Solution-casting | | Coprecipitation | |
| --- | --- | --- | --- | --- |
| | $n$ | $K_n$ (min$^{-n}$) | $n$ | $K_n$ (min$^{-n}$) |
| 100/0 | 2.51 | $8.95 \times 10^{-2}$ | 2.50 | $8.83 \times 10^{-2}$ |
| 90/10 | 2.57 | $10.2 \times 10^{-2}$ | 1.94 | $9.96 \times 10^{-2}$ |
| 80/20 | 2.60 | $9.12 \times 10^{-2}$ | 2.02 | $10.5 \times 10^{-2}$ |
| 70/30 | 2.52 | $8.45 \times 10^{-2}$ | 2.16 | $7.91 \times 10^{-2}$ |
| 60/40 | 2.48 | $10.3 \times 10^{-2}$ | 2.18 | $9.15 \times 10^{-2}$ |
| 50/50 | 2.55 | $8.68 \times 10^{-2}$ | 2.09 | $9.45 \times 10^{-2}$ |

**Figure 6** Avrami equation plot {log[−ln(1 − $X_t$)] versus log($t$)} of 70/30 wt % PEO/PVA blends isothermally crystallized at 47°C.

coprecipitated blends they were less (∼ 2.0) than that for the neat PEO. Again, the Avrami exponents of PEO in the coprecipitated blends did not change significantly with the increasing amount of PVA.

From the POM observation, the final size, the density, and the time at which spherulites appeared were about the same for both the solution-cast and the coprecipitated blends. Thus, the mechanism of nucleation was independent of the preparation method of blends. However, it was expected that the crystallization would be influenced when spherulites reach the boundary between the PEO-rich phase and the PVA-rich phase. Also, from POM observations, it was shown that the domain size of the PVA-rich phase dispersed in the PEO-rich matrix was much larger for the solution-cast blend. That is, the coprecipitated blend has more boundaries than the solution-cast blend. Therefore, it was expected that the crystallization of PEO in the coprecipitated blend would deviate from the neat PEO much more easily. Figure 6 shows the plot, log[−ln(1 − $X_t$)] versus log($t$), of 70/30 PEO/PVA blends isothermally crystallized at 47°C. It was found that it deviated from a linear relationship much earlier for the coprecipitated blend than that for the solution-cast blend.

## CONCLUSIONS

From the viewpoint of thermodynamics, the existence of specific interactions, such as hydrogen bonding and polar interaction, between two components in a polymer blend could induce miscibility. PEO and PVA contained ether groups and hydroxyl groups, respectively. However, it was found that PEO/PVA blends were immiscible from the DSC and DMA results. Two glass-transition temperatures corresponding to PEO-rich and PVA-rich phases were observed. Although PEO/PVA was immiscible, the crystallization behavior and morphology were dependent on the preparation methods of blends. One possible reason was the time allowed for the phase separation. The domain size of the dispersion phase (PVA-rich) for the solution-cast blends was much larger than that for the coprecipitation blends. The crystallinity, spherulitic morphology, and isothermal crystallization behavior of PEO in the solution-cast blends were similar to those in the neat PEO. They were not influenced by PVA. In contrast, they were influenced by PVA in the coprecipitation blends.

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