

STUDIES OF THE CRYSTALLIZATION BEHAVIOR IN THE CRYSTALLINE/AMORPHOUS POLYMER BLENDS: POLY(ETHYLENE OXIDE)/POLY(METHYL METHACRYLATE) AND POLY(ETHYLENE OXIDE)/POLY(VINYL ACETATE)*

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ABSTRACT

The crystallization process of poly(ethylene oxide) (PEO)/poly(methyl methacrylate) (PMMA) and PEO/poly(vinyl acetate) (PVAc) blends has been characterized by Fourier Transform Infrared (FTIR) spectra in conjunction with Differential Scanning Calorimeter (DSC) measurements. The crystallinity of PEO varies consistently with PEO content in PEO/PVAc blends and the PEO/PMMA blends containing 50 wt% or less PMMA. For the PEO/PMMA blends containing 60 wt% or more PMMA, the crystallinity of PEO decreases more than PEO content but develops with crystallization time. These results can be explained in terms of difference between the crystallization temperature (T_c) and glass transition temperature (T_g) of the blends as a function of content of amorphous component.

INTRODUCTION

Both the crystallization behavior and the structure of the crystallizable component in the crystalline/amorphous polymer blends should affect considerably the overall properties of the blends. In the previous studies, it was observed that if two components in the blends are thought to be compatible in the amorphous state, as the blends are cooled from the melt, crystallization of the crystallizable component occurs, but the total degree of crystallinity of the blend decreases rapidly with increasing content of the amorphous component. A critical composition of crystallizable component, below which no crystallinity develops, is usually observed for several crystalline/amorphous polymer blends^[1]. For example, when poly(vinylidene fluoride) (PVF₂) blended with poly(methyl methacrylate) (PMMA) the crystallinity of PVF₂ rapidly decreased below 80 wt% PVF₂. Even no crystallinity is detected with more than 50 wt% of PMMA component^[2]. Similar result was obtained for the blends of poly(ϵ -caprolactone) (PCL) with poly(bisphenol A carbonate) (PC) in which both polymers are compatible in the amorphous state and capable of crystallization^[3].

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The present paper reports a different analysis on the crystallization behavior in crystalline/amorphous compatible polymer blends. Based on the data obtained from a differential scanning calorimeter (DSC) and Fourier Transform Infrared (FTIR) spectra studies of the poly(ethylene oxide) (PEO)/PMMA and PEO/poly(vinyl acetate) (PVAc) blends, it is possible to influence the level of crystallinity in polymer blends by varying the extent of freezing of motion of segments and molecular chains. The blends are usually in nonequilibrium state, unless the crystallization temperature (T_c) is higher than glass transition temperature (T_g). The crystalline properties will be relevant to the dynamic studies concerning the effect of time change on crystallization process in polymer blends.

EXPERIMENTAL

Materials and blends preparation

The PEO ($MW=1 \times 10^5$) and PMMA ($MW=1.06 \times 10^5$) were products of Scientific Polymer Products Co. and Du pont Co. respectively. PVAc ($MW=1.46 \times 10^5$) was obtained from Beijing Organic Chemicals Co.

Blends of the PEO/PMMA and PEO/PVAc were prepared as thin film by casting onto glass plate from 1% (w/v) solutions in 1,2-dichloroethane. After evaporation of the solvent, the films were dried in a vacuum oven at room temperature. Complete removal of the solvent had occurred at 100–120°C for 20 minutes.

Thin films of PEO/PMMA and PEO/PVAc blends for spectroscopic measurements were prepared by casting onto potassium bromide disks from above solutions. In order to carry out quantitative analysis, it was essential for spectral manipulation to ensure that films were sufficiently thin so that the band intensities are within the absorbance range for which Beer-Lambert Law is obeyed.

Differential Scanning Calorimeter measurements

A Perkin-Elmer DSC 2 type Differential Scanning Calorimeter was used to measure melting point (T_m), glass transition temperature (T_g) and crystallinity of PEO component in the blends. The isothermal crystallization curve, namely the variation of crystallinity with time, was also determined at 30 °C, from which the half-crystallization time ($t_{1/2}$) was calculated. The heat of fusion of crystalline PEO is taken to be 51 cal/g to calculate the degree of crystallinity.

In order to determine the T_g of the blends in amorphous state, the films obtained from solution of the blends were melted in the sample cell of the DSC instrument by heating at 100–120°C and then quenched into liquid nitrogen followed by starting the measurement of the T_g immediately. A heating rate of 20°C/min was used in the DSC measurements. Temperature and fusion heat were calibrated against Indium.

FTIR measurements

All the spectroscopic measurements were carried out on a Nicolet 7199 FTIR. Three hundreds scans of 2 cm⁻¹ resolution were signal averaged. The frequency was calibrated against a reference helium-neon laser to an accuracy of 0.2 cm⁻¹.

RESULTS AND DISCUSSION

1. *The glass transition temperature and compatibility of PEO/PMMA and PEO/PVAc blends in the molten state*

For compatible polymer blends, the T_g of amorphous phase depends on the amorphous composition^[4-6]. Among these theoretical treatments, Couchman's equation is most general, but the data necessary to the equation is rarely available. Therefore, a simplified Couchman's equation, Fox empirical equation is usually used.

For samples of PEO/PMMA blends quenched into liquid nitrogen from the molten state (120°C), the T_g determined by DSC is shown in Figure 1 with mark "▲", while the solid curve in the figure represents T_g -composition relationship calculated from Fox equation.

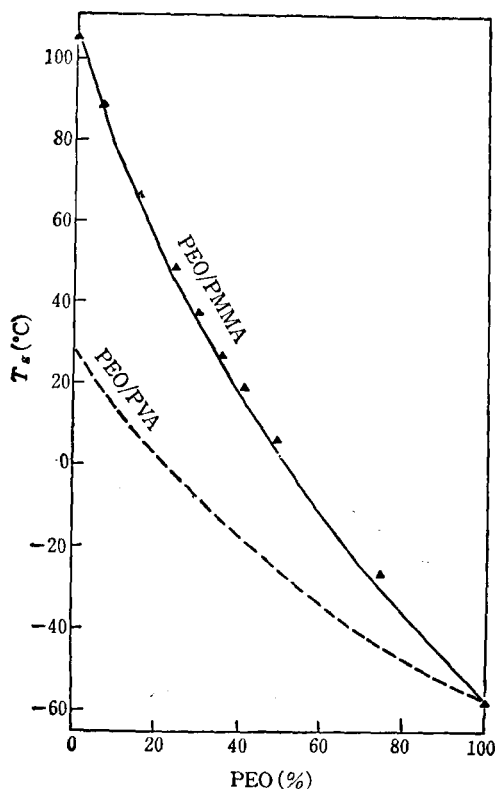


Fig. 1 T_g -composition relationship for PEO/PMMA blends, "▲" is the observed value. Solid curve is calculated from Fox equation

It is clear in Figure 1 that for PEO/PMMA blends with varying compositional ratio and quenched from molten state, the T_g -composition relationship obeys Fox equation and the T_g values all locate between that of unblended PEO (-61°C) and PMMA (105°C). Therefore, these blends are compatible in the molten state^[7-9]. Furthermore, as can be seen in Figure 1 for the blend containing 50 wt% PMMA, the effective T_g in the initial stage to

be close to crystallization temperature (room temperature). Our previous study^[10] indicated that PEO/PVAc blends also is compatible in the molten state and their T_g value are between that of unblended PEO and PVAc (the T_g of pure PVAc is 28°C). The T_g -composition relationship calculated from Fox equation for PEO/PVAc blends is shown as the broken line in Figure 1. It can be seen that the T_g values for PEO/PVAc blends with varying compositional ratios are nearly all below room temperature.

2. Crystallinity and crystallization rate

A plot of crystallinity versus weight percentage of PEO for PEO/PMMA and PEO/PVAc blends is given in Figure 2. For PEO/PMMA blends, initially the crystallinity of PEO component decreases as a function of increasing PMMA (broken line). The decrease of PEO crystallinity is greatly accelerated when above 50 wt% PMMA and deviated substantially from the broken line which represents the crystallinity of PEO in blends when crystallization process is not influenced by the presence of PMMA. No level of crystallinity is detected in the blends with more than 75 wt% of the amorphous PMMA component. These results are compared with that observed for PVF₂/PMMA blends in which the crystallinity of PVF₂ component also decreases with increasing PMMA, but the decreasing rate of PVF₂ crystallinity is much faster than that of PEO/PMMA blends. The deviation from the calculated line is more severe for PVF₂/PMMA, in which the deviation occurs from and above 20 wt% PMMA,

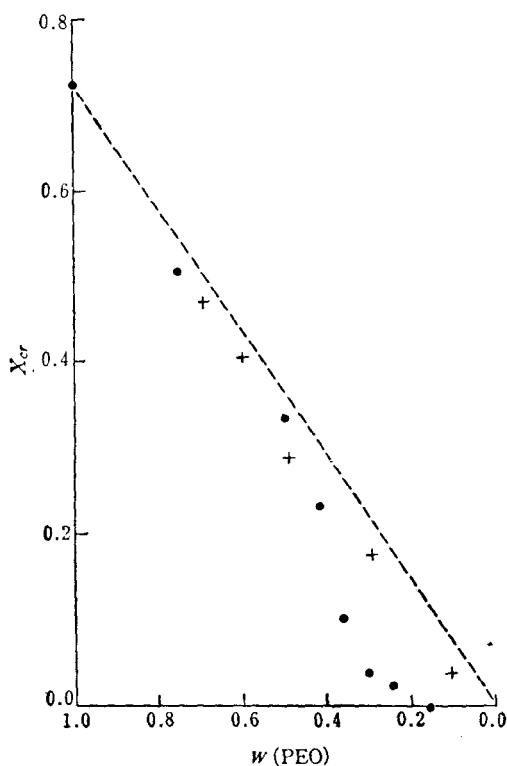


Fig. 2 Degree of crystallinity measured for PEO/PMMA blends (●) and PEO/PVAc blends (+) as a function of PEO composition

than PEO/PMMA blends. However, for PEO/PVAc blends, the degree of PEO crystallinity is a linear function of PEO content in whole compositional range.

The difference in the crystallinity for these blends can be interpreted in terms of chain mobility. Sufficient chain mobility is a major factor in the crystallization of polymers. As the T_g of the crystallizable polymer is well below room temperature (crystallization temperature T_c), sufficient chain mobility exists for the polymer to crystallize. In contrast, if the T_g of a polymer is close to or above the T_c then the polymer chains will be "frozen" and will not have sufficient mobility to form ordered structures. The T_g of polymer is time dependent. In general, the W-L-F equation is used to describe the time-dependence of T_g . Sufficient chain mobility (T_g is below T_c) is also needed for crystallizable/amorphous blends which is compatible in amorphous state. The time-temperature superposition principle is also suitable to the T_g of blends. Another factor should also be mentioned. Since T_g is a function of blend compositions, not only does it depend on the initial amorphous composition of the blends, but also influenced by the extent and process of crystallization. For example, after initial fraction of low T_g component has crystallized, the resultant amorphous phase composition becomes richer in amorphous component and the effective T_g will rise gradually. When T_g is close to crystallization temperature, the molecular chains of crystallizable component in the blends are "frozen" into the glassy state and there is insufficient chain mobility to rearrange them into an ordered structure. Therefore the extent of decrease of crystallinity with increasing amorphous content in the initial composition of the blends is time dependent and greater than that predicted by Fox equation.

Based on above discussion, T_g values are all below T_c in case of PEO/PVAc blends in whole compositional range and PEO/PMMA blends containing less than 50 wt% PMMA causes the degree of PEO crystallinity to be a linear function of PEO composition in the blends. If PMMA content in PEO/PMMA blends is more than 50 wt% but less than 75 wt%, T_g is close to or a little higher than T_c , crystallization is still possible and time dependent. In this case, the crystallinity is usually lower than calculated from blend's composition. No PEO crystallinity can be observed when PMMA content is more than 75 wt%, in which T_g is higher than T_c that the segmental motion in molecular chain of PEO has been "frozen" and therefore, there is no longer enough mobility for the amorphous PEO component to rearrange into the crystal lattice in the experimental period.

For crystalline/amorphous blends, T_g rising in amorphous phase implies increasing viscosity of the blends, and therefore, inhibiting chain mobility at a greater extent. In contrast, lower T_g value means that chain motion is easier and so that crystallization processes proceed more rapidly. Figure 3 shows the logarithmic half-crystallization time $t_{1/2}$ as a function of PEO/PVAc blends composition during isothermal crystallization ($T_c = 30^\circ\text{C}$). When unblended PEO sample was quenched from molten state to 30°C for isothermal crystallization, the half-crystallization time was about 2 minutes. By blending with PVAc, it increased to 10 minutes for the blend containing 50 wt% PVAc. However, the crystallization of PEO in these blends still goes on rapidly because of relative lower T_g than T_c for PEO/PVAc blends with most compositional ratios. For example, even for the blend containing 80 wt% PVAc, the T_g is still lower than T_c (see Figure 1), and the crystallization of PEO finished in several hours (Figure 3). Therefore, for PEO/PVAc blends with every kind of compositional ratios,

the crystallinity of PEO corresponding to its content in the blends can be detected in the experimental period.

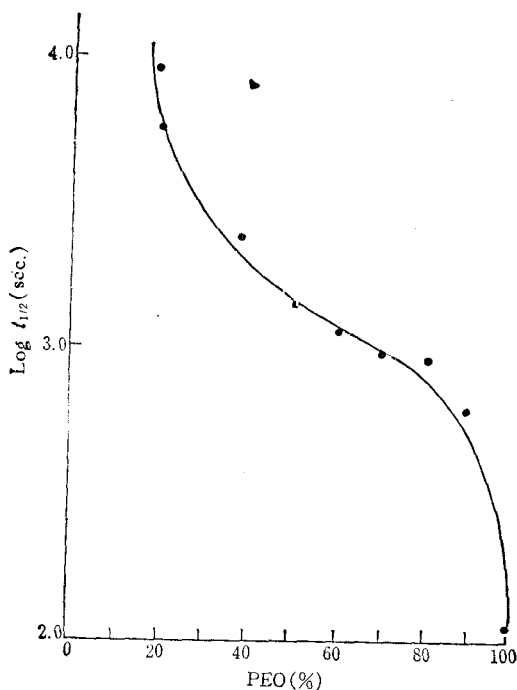


Fig. 3 Logarithmic half-crystallization time $t_{1/2}$ as a function of PEO/PVAc blend's composition during isothermal crystallization ($T_c = 30^\circ\text{C}$)

In PEO/PMMA blends, the T_g value increases with increasing PMMA content in the blends. Because of much higher T_g value for PMMA than PVAc, the rate of T_g increase with increasing PMMA content in PEO/PMMA blends is much higher than that with increasing PVAc content in PEO/PVAc blends and therefore, the rate of decreasing PEO crystallinity with increasing PMMA or PVAc content is much faster for PEO/PMMA blends than that for PEO/PVAc blends.

In the case of PEO/PMMA blends containing PMMA concentrations of 50 wt% or less, the T_g of the PEO/PMMA blends is lower than T_c . There is sufficient chain mobility for PEO to crystallize with crystallization rate rapid enough so that the degree of "equilibrium" crystallinity corresponding to the PEO content in the blends can be observed in the experimental period.

As expected, the crystallinity of PEO relative to its own weight percentage keeps relatively constant in the compositional range of lower PMMA content. However, when PMMA concentration is up to 50 wt%, the blend's T_g increased up to 0°C , the chain mobility decreases and the half-crystallization time ($t_{1/2}$) is about 10^3 times longer than that in pure PEO due to lowering the crystallization rate. In the compositional range of 50–75 wt% PMMA in the blends, the T_g of the blends is close to or above T_c then the chain mobility is inhibited severely and the crystallization rate drops sharply. In addition, one would expect the cessa-

tion of crystallization as soon as enough PEO has crystallized such that the amorphous $T_g = T_c$ even though the T_g of original mixture is below T_c . As a result, dramatically decreasing the crystallinity of PEO in the blends occurs in this compositional range and the "equilibrium" crystallinity can not arrive within the experimental period.

From this consideration the rapid decrease of the crystallinity of PVF₂ with increase of PMMA content in PVF₂/PMMA blends can be explained clearly. T_g corresponding to 50 wt% PMMA content in the blends is about 45°C, higher than T_c . Therefore, no crystallinity of PVF₂ can be detected within experimental period. But one can expect that the crystallinity of PVF₂ can be developed and observed by heat treatment (raising T_c) or long time annealing at room temperature.

Therefore, the crystallization behavior of crystalline/amorphous polymer blends can be interpreted on the base of crystallization kinetics but not thermodynamic equilibrium.

Although DSC or depolarizability measurements have been extensively employed to follow the development of the crystallinity in polymer blends as a function of time, they are not generally considered to be techniques applicable to the study of very slow crystallization process. Because Infrared spectroscopy is very sensitive to the change of chain conformation of PEO in crystalline region of the blends, it is usually used to determine the degree of crystallinity and monitor the development of crystallinity in polymers, especially those with low crystallinity, as a function of time. In the infrared spectrum of PEO, the 1359 and 1343 cm⁻¹ doublet is associated with CH₂ wagging motion in PEO crystalline region⁽¹¹⁾. This doublet disappeared in the molten state and is replaced by the 1349 cm⁻¹ band attributed to the CH₂ wagging in the amorphous region. Therefore, the relative intensity ratio of the 1359 and 1343 cm⁻¹ doublet to the 1349 cm⁻¹ band can be used to characterize the PEO

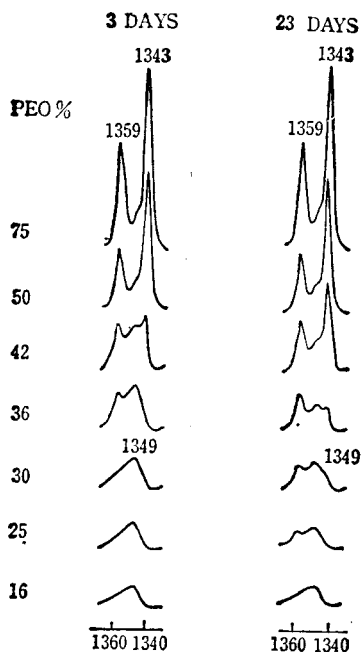


Fig. 4 CH₂ wagging bands of PEO infrared spectra for PEO/PMMA blends

crystallization process. Figure 4 shows the bands associated with CH_2 wagging motion of PEO chains in infrared spectra obtained from PEO/PMMA blends as a function of composition. In Figure 4, the fact that the crystalline band doublet at 1359 and 1343 cm^{-1} is gradually replaced by the amorphous band at 1349 cm^{-1} indicates that the crystallinity of PEO decreases with increasing PMMA content. Furthermore, the fact that relative intensity change with crystallization time at different rates suggests the crystallization rate decreases also by the addition of PMMA component.

As seen in Figure 4 for samples containing PEO concentration of 50 wt% and less (42, 36, 30 wt%), the intensity of crystalline bands for the samples after 23 days is higher than that after 3 days. More obviously, the intensity of crystalline bands for the sample containing 25 wt% PEO only can be observed after 23 days. Therefore, the fact that the decreasing rate of PEO crystallinity with increasing PMMA content after 3 days crystallization is faster than that after 23 days shows the time dependence of the relationship between crystallinity and blend's composition. In contrast, for the blends containing 50 wt% or more PEO, no further spectroscopic changes occur after 3 days. However, for samples containing 42–25 wt% PEO, the fact that the relative intensity of the bands continues to change even after 3 days, namely the amorphous band at 1349 cm^{-1} continues to decrease and the crystalline bands at 1359 and 1343 cm^{-1} continue to increase, indicates that crystallization is continuing to take place. As for the sample containing 16 wt% PEO, no intensity of crystalline bands is seen even after 23 days.

As mentioned previously, these above results can be interpreted on chain mobility. T_g is intermediate between the high value of pure PMMA and the low value associated with pure PEO and can be predicted from the Fox equation shown in Figure 2. In the case of PEO content of 50 wt% or more, the T_g is well below T_c , so that the crystallization proceeds rapidly and the "equilibrium" crystallinity arrives in 3 days and therefore, no crystallization is continuing to take place after this period. Decreasing PEO content down to 42–25 wt%, the T_g is close to T_c and the crystallization rate drops dramatically, so that continuous growing of the crystallinity can be observed in very long period. For the samples containing 16 wt% or less PEO, the T_g (above 40°C) is well above T_c , so that molecular chains of PEO have been "frozen" and no crystallinity can be observed in this case.

In summary, the glass transition temperature T_g performs an important role in the crystallization process of crystalline/amorphous polymer blends.

CONCLUSION

1. Change of PEO crystallinity in PEO/PVAc blends is consistent with compositional change in the blends. For PEO/PMMA blends, the crystallinity decreases with increasing PMMA content in the blends, and the variation of crystallinity is consistent with the variation of composition in the range of 50 or less weight percent PMMA but it drops sharply in the case of containing PMMA above 50 wt%. The rate of decreasing crystallinity with increasing PMMA content in blends is lower for PEO/PMMA blends than PVF₂/PMMA blends.
2. The degree of crystallinity observed in crystalline/amorphous polymer blends is the results

of crystallization kinetics and depends on T_g of the blends greatly. Also it is time dependent.

3. FTIR can be very well used to follow the crystallization process of polymer blends.

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