Polymer Bulletin 33, 113–118 (1994)

**Polymer Bulletin**

# Miscibility of poly(ether imide)/poly(ethylene terephthalate) blends

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## SUMMARY

Miscibility of blends of poly(ether imide) (PEI) and poly(ethylene terephthalate) (PET) were studied by differential scanning calorimetry (DSC). Single and composition-dependent $T_g$'s are observed over the entire composition range, indicating that the blends are miscible in the amorphous region. The overall crystallization rate of PET in the blends decreased with increasing the PEI content. The interaction energy density *B*, which was calculated from the melting point depression of the blends using Nishi-Wang equation, was -5.5 cal/cm$^3$.

## INTRODUCTION

Polymer blends as an excellent way of developing new materials have been of considerable interest in recent years.[1,2] Especially, studies on the blends containing super engineering plastics such as polyimide and polybenzimidazole have been gradually increased in recent years.[3,4]

Poly(ether imide) (PEI) is an high performance polymer with a high glass transition temperature ($T_g$) of 215°C and has good physical properties such as tensile, flexural and compressive strength and electrical insulation. However, although this polymer has been developed to improve the processibility of wholly aromatic polyimides, its processing temperature is still high, about 380°C. Poly(ethylene terephthalate) (PET) on the contrary is a semicrystalline polymer with a $T_g$ of 78°C and a melting temperature of about 255°C; it has an injection-molding temperature of about 270°C for unmodified neat PET.[5] Therefore, blending of PEI and PET may offer an interesting route to combine the complementary properties of both polymers.

In this study, we investigate the miscibility of the PEI/PET blends from analysis of thermal properties such as $T_g$ and $T_m$.

## EXPERIMENTAL

***Materials*** The characteristics of polymers used in this study are described in Table I. The polymers were the product of commercial grades and used as received without further purification. The tradename of the PEI is Ultem 1000.

***Blends preparation*** Blend samples were prepared in the melt state at 320°C for 10 min at 60 rpm using a sigma-blade mixer. Both component polymers were pre-dried under vacuum at 125°C for one day to remove moisture.

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Table I. Properties of Polymers

| polymer | sources | Mw | $T_g$,°C | $T_m$,°C |
|---|---|---|---|---|
| PEI | General Electric Co. | 30,000 | 220 | - |
| PET | Tongyang Nylon Co. | 20,000 | 78 | 255 |

***Thermal Analysis*** Differential scanning calorimetry (DSC) data were recorded on a Perkin-Elmer DSC-7. Indium was used as the temperature and energy calibrator. All samples were heated from room temperature to 280°C (first scan) at a rate of 20°C/min and maintained at that temperature for 5 min. After quenched to room temperature at a rate of 320°C/min, the samples were then reheated to 280°C at a rate of 20°C/min (second scan). The data from the second scan were recorded for all samples. Melt crystallization temperature $T_{cm}$ was obtained during the cooling to room temperature at a rate of 10°C/min after the first scan. The glass transition temperature $T_g$ were defined as the midpoint of the heat capacity change in the glass transition region.

For the measurement of the equilibrium melting temperature, the samples were treated to 280°C for 5 min to ensure complete melting of PBT crystals, quenched to the crystallization temperature $T_c$, kept at $T_c$ for at least 30 min, cooled to room temperature at 20°C/min, and then heated at 20°C/min to observe melting temperature. The reproducibility of $T_g$ or $T_m$ measurements was about ±1.0°C.

Isothermal crystallization exotherms were obtained during maintaining the samples the crystallization temperature $T_c$ for 30 min.

## RESULTS AND DISCUSSION

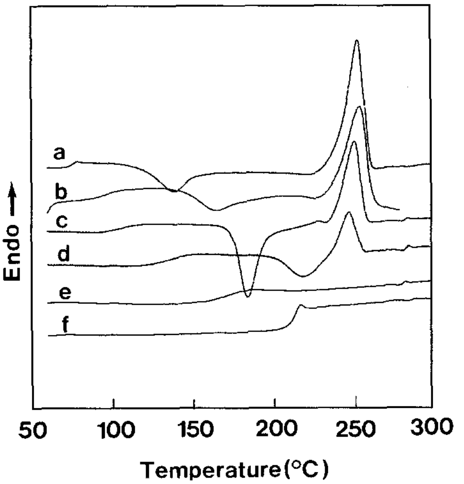

Figure 1. Representative DSC thermograms of PET/PEI blends: (a) 100, (b) 80, (c) 60, (d) 40, (e) 20, and (f) 0 wt% PET.

***Miscibility*** Figure 1 shows the representative DSC thermograms of the PEI/PET blends, and $T_g$, $T_{cm}$ and $T_m$ as a function of blend ratio are summarized in Figure 2. Single and composition-dependent $T_g$'s are observed between those of the pure polymers. As a result, the temperature interval available for crystallization of PET in the blends, $T_m$ - $T_g$, decreases with the addition of PEI. Also, the cold crystallization temperature of PET in the blends increases with increasing the content of PEI. This provides an evidence of the reduction in the crystallization rate of PET with increasing PEI content. Also, there is no trace of crystallinity for the blends containing PET less than 30 wt%. From these results, it is clear that the blends of PEI and PET are miscible over the entire composition range.

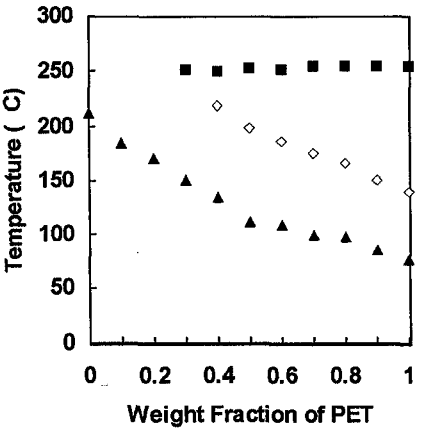

Figure 2. $T_g$, $T_m$ , and $T_{c,\ cold}$ *versus* the weight fraction of PET: (▲) $T_g$, (■), $T_m$, and (◇) $T_{c,\ cold}$. $T_{c,cold}$ means the cold crystallization temperature of PET in the blends.

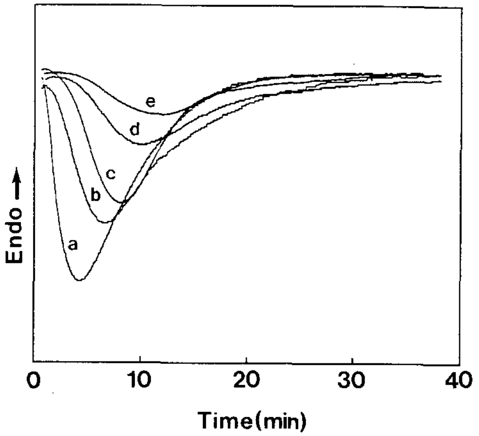

Figure 3. Representative DSC exotherms of isothermal crystallization at 230°C for the PET/PEI blends: (a) 100, (b) 90, (c) 80, (d) 70, and (e) 60 wt% PET.

***Crystallization Kinetics*** Formation of miscible blends will affect the temperature interval available for crystallization, $T_m$ - $T_g$ (see Figure 2), and thus influence the crystallization kinetics. The effect of PEI on crystallization kinetics is illustrated in Figure 3. The crystallization isotherms are obtained at the crystallization temperature of 230°C. As the content of the PEI increases, the isotherms are shifted to longer time, and the overall crystallization rate becomes progressively slower. The kinetics of isothermal crystallization was analyzed using the Avrami equation:[6]

$$1 - X_t = \exp(-Kt^n) \qquad (1)$$

where $X_t$ is the fraction of material crystallized after time $t$, $K$ the kinetic rate constant, and $n$ the Avrami exponent which depends on the nature of the primary nucleation and the geometry of growing crystals. $X_t$ is calculated from the ratio of the heat generated at time $t$ to the total heat corresponding to the completion of crystallization. Equation (1) can be transformed into Eq (2)

$$\log[-\ln(1 - X_t)] = n\log t + \log K \qquad (2)$$

The values of $K$ and $n$ can be determined from the intercept and slope of Eq (2). The kinetics parameters at the temperature of 230°C are listed in Table II.

As shown in Table II, $t_{1/2}$ increases with the addition of amorphous PEI component. This indicates that the rate of crystallization of PET in the blends decreases with increasing the content of PEI, because the reciprocal of the crystallization half-time $t_{1/2}$ is directly proportional to the rate of crystallization. This result is well consistent with the general theory of the crystallization rate of miscible crystalline-amorphous polymer blends which have different $T_g$'s.[7] The addition of an amorphous polymer to a crystallizable one will lower the crystallization rate if the glass transition temperature of the blend is higher than that of the crystalline one, since the transport of the crystallizable polymer onto the crystal growth surface is retarded.

Table II. Kinetic Data for the Isothermal Crystallization of the PEI/PET Blends

| PET/PEI blend | *n* | *logK* | $t_{1/2}$[a], min |
|---|---|---|---|
| 100/0 | 1.63 | -1.51 | 6.59 |
| 90/10 | 1.79 | -1.72 | 8.15 |
| 80/20 | 1.69 | -1.72 | 11.69 |
| 70/30 | 2.52 | -2.77 | 12.12 |
| 60/40 | 2.61 | -2.90 | 12.30 |

[a] $t_{1/2}$, the half-time of crystallization is defined as the time for half of crystallinity to develop.

In summary, an increase in the $T_g$'s of the blends with the PEI content (shown in Figure 2) will retard molecular motion in the amorphoud region. Therefore, the diffusion of PET molecules to the crystal growth sites becomes difficult, and thus the crystallization rate decreases.

***Determination of Interaction Energy Parameter*** In miscible polymer blends in which one component can crystallize, melting temperature depression has been observed.[8-10] This phenomenon has been frequently used to determine the interaction parameter between blend components. The relation between the melting temperature depression and the interaction parameter has been proposed by Nishi and Wang as follows:[11]

$$T_m^0 - T_{mb}^0 = -T_m^0\left(BV_{2u} / \Delta H_{2u}\right)\Phi_1^2 \tag{3}$$

where $\Delta H_{2u} / V_{2u}$ denotes the latent heat of fusion of 100% crystalline component per unit volume, $B$ is the interaction energy density between blend components, and $\Phi_1^2$ is the amorphous component. According to eq (3), $B$ value for PEI/PET blends are determined from the slope of the straight line in the plot of $\Delta T_m$ (= $T_m^0$-$T_{mb}^0$) *versus* the square of the volume fraction of PEI in the blends.

However, since the melting temperature of miscible polymer blends is depressed by the kinetic effect as well as the thermodynamic reason,[12] this unfavorable effect must be eliminated to correctly determine the $B$ parameter. The method of Hoffman and Weeks has been used to obtain the equilibrium melting temperatures free from the kinetic or morphological effect.[13] Table III shows the equilibrium melting temperatures of pure PET and PEI/PET blends obtained from the method of Hoffman and Weeks (not shown here). The equilibrium melting temperature obtained here for pure PET is slightly small, as compared with the value found in the lterature the value found in the lterature.[14]

Figure 4 shows the plot of $\Delta T_m$ (= $T_m^0$-$T_{mb}^0$) *versus* the square of the volume fraction of PEI in the blends. The value of $B$ from the slope is -5.5 cal/cm$^3$. The negative $B$ values means that there exists a specific intermolecular interaction between PEI and PET.

Table III. Equilibrium Melting Temperatures of Pure PET and PEI/PET Blends

| PET/PEI (wt/wt) | $T_{mb}^0$,°C | PET/PEI (wt/wt) | $T_{mb}^0$,°C |
|---|---|---|---|
| 100/0 | 262.5 | 70/30 | 255.1 |
| 90/10 | 257.7 | 60/40 | 254.2 |
| 80/20 | 255.6 | | |

DSC analysis is the most widely used technique for determining the miscibility in semicrystalline/ amorphous polymer blends. However, this technique has several experimental difficulties on the use of $T_g$ or $T_m$ for quantitative analysis, although experimental conditions have been selected carefully to optimize the experimental factors that can make thermal analysis difficult.[15] Also, the use of DSC analysis to determine accurate crystallization rate constants for semicrystalline polymers has some limitations such as the lack of sensitivity of the calorimeter and the inability to follow crystallization process to higher conversion and longer time.[16] In addition to these limitations, the statistical scatter in a straight line, as shown in Figure 4, may affect the accuracy of the values of the crystallization kinetic and interaction parameters. However, uncertainties in the parameters has been not estimated in this study.

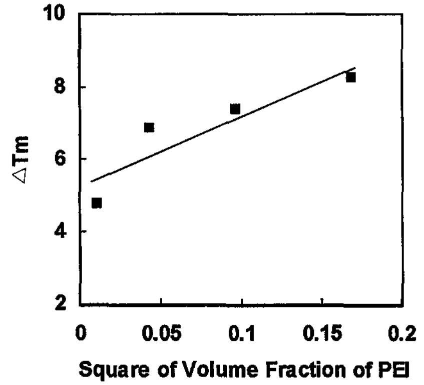

Figure 4. Plots of equilibrium melting temperature depression *versus* the square of the volume fraction of PEI.

Fourier Transform infrared (FTIR) spectroscopy has been often used in characterizing the presence and nature of specific intermolecular interactions in miscible polymer blends.[17] Composition-dependent frequency shifts and broadenings for miscible blends have been ascribed to specific intermolecular interactions and to changes in chain conformations. However, in the present systems no major frequency shifts in the spectra of the blends are observed.

## CONCLUSIONS

Miscibility, crystallization and melting behavior in blends of PEI and PET have been examined using DSC. The blends exhibit single and composition-dependent $T_g$'s over the entire composition range, indicating the miscibility of the PEI/PET blends in the amorphous region. Also, the temperature interval available for crystallization of PET in the blends, $T_m$ - $T_g$, are decreased with the addition of PEI.

The crystallization kinetics of the PEI/PET blends was investigated by employing the Avrami equation. The reciprocal of the crystallization half-time corresponding to the rate of crystallization decreases with increasing the content of PEI in the blends. This results from an increase of the $T_g$'s of the blends with the addition of PEI.

The equilibrium melting temperatures of PET in the blends, which are determined from the Hoffman-Weeks plot, are depressed with increasing the PEI content. The value of interaction energy density $B$ calculated from Nish-Wang equation is -5.5 cal/cm$^3$.

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Accepted March 26, 1994 Shi