# Thermal Properties of Melt-Blended Poly(ether ether ketone) and Poly(ether imide)

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ABSTRACT: The thermal properties of blends of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) prepared by screw extrusion were investigated by differential scanning calorimetry. From the thermal analysis of amorphous PEEK–PEI blends which were obtained by quenching in liquid nitrogen, a single glass transition temperature ( $T_g$ ) and negative excess heat capacities of mixing were observed with the blend composition. These results indicate that there is a favorable interaction between the PEEK and PEI in the blends and that there is miscibility between the two components. From the Lu and Weiss equation and a modified equation from this work, the polymer–polymer interaction parameter ( $\chi_{12}$ ) of the amorphous PEEK–PEI blends was calculated and found to range from -0.058 to -0.196 for the extruded blends with the compositions. The  $\chi_{12}$  values calculated from this work appear to be lower than the  $\chi_{12}$  values calculated from the Lu and Weiss equation. The  $\chi_{12}$  values calculated from the  $\chi_{12}$  values calculated from the Weiss equation. The  $\chi_{12}$  values calculated from the  $\chi_{12}$  values calculated from the  $\chi_{12}$  values calculated from the  $\chi_{12}$  value

**Key words:** poly(ether ether ketone); poly(ether imide); blend; glass transition temperature; polymer–polymer interaction parameter

#### INTRODUCTION

The blends of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) are known to be miscible in an amorphous state.<sup>1-6</sup> Recently, many researchers have investigated the mechanism and the morphology of PEEK crystallization in PEEK–PEI blends.<sup>1-4</sup> Crevecoeur and Groeninckx<sup>1</sup> studied the crystallization behavior of PEEK in PEEK–PEI blends using thermal analysis and small-angle X-ray scattering. They reported that the glass transition temperature ( $T_g$ ) of the amorphous samples of the PEEK–PEI blends varies nearly as predicted by the Fox equa-

Contract grant sponsor: Korea Science and Engineering Foundation; contract grant number: 97K3-1005-03-11-3. Journal of Applied Polymer Science, Vol. 72, 733-739 (1999) tion. In semicrystalline samples, because the amorphous phase is enriched in PEI, the glass transition temperature increases. Therefore, the PEEK component in the blends crystallizes as it does in pure PEEK, with the PEI segregating to the amorphous phase.<sup>1,2</sup> From the SAXS measurements, Crevecoeur and Groeninckx<sup>1</sup> concluded that, within the spherulites, PEI is primarily rejected between bundles of lamellae.

Recently, we showed that the blends of PEEK and PEI are miscible in the amorphous state and partially miscible in the semicrystalline state.<sup>3</sup> Also, the rigid amorphous fraction for the semicrystalline PEEK–PEI blends was calculated and found to be 0.117–0.358 with a cooling rate using differential scanning calorimetry (DSC).<sup>3</sup>

Hsiao and Sauer<sup>6</sup> investigated the interaction between PEEK and PEI using the melting-point depression method. They reported that the poly-

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	$\overline{M_w}^{ m \ a}$	$\overline{M_n}^{\mathrm{a}}$	$T_m \; (^\circ \mathrm{C})^\mathrm{b}$	$T_g \; (^{\rm o}{\rm C})^{\rm b}$	$\Delta C_p ~(\mathrm{J/g^oC})^\mathrm{b}$	$ ho (g/cm^3)^c$	$\Delta T \; (^{\circ}\mathrm{C})^{\mathrm{d}}$
PEEK PEI	39,000 30,000	14,000 12,000	338.3 —	$\begin{array}{c} 146.0\\ 218.9\end{array}$	$\begin{array}{c} 0.350\\ 0.241\end{array}$	$\begin{array}{c} 1.26 \\ 1.27 \end{array}$	$5.0\\8.4$

Table I Characteristics of Polymer Samples Used in the PEEK-PEI Blends

<sup>a</sup> Data from ref. 3.

<sup>b</sup> Measured in our laboratory using DSC.

<sup>c</sup> Data from ref. 8.

<sup>d</sup> The width of glass transition, measured in our laboratory using DSC.

mer-polymer interaction parameter  $(\chi_{12})$  between PEEK and PEI must be small and negative since the system is miscible. Chen and Porter<sup>7</sup> studied the PEEK–PEI solution blends and showed that the  $T_g$  of the PEEK–PEI blends obeys the simple Fox equation. Also, they reported that the specific volume of the amorphous PEEK–PEI blends shows a slight negative deviation from linearity and this result is due to a favorable intermolecular interaction between PEEK and PEI.

The method of determining the polymer–polymer interaction parameter between component polymers in a miscible blend has been studied widely.<sup>8–17</sup> Several techniques can be used to determine the thermodynamic polymer–polymer interaction parameter ( $\chi_{12}$ ), such as melting-point depression,<sup>8–10</sup> vapor sorption,<sup>10,11</sup> inverse-phase gas chromatography,<sup>12–14</sup> and some light-scattering methods.<sup>15–17</sup> Only a few methods have been developed which can be applied to incompatible polymer blend systems.<sup>18–21</sup>

In our present study, we investigated the thermal properties such as the  $T_g$  and the specific heat increment  $(\Delta C_p)$  at the  $T_g$  of the amorphous samples of PEEK–PEI blends by DSC. Also, we examined the Flory–Huggins interaction parameter between the PEEK and PEI in the blend by modifying the equation of Lu and Weiss<sup>22</sup> which includes the relationship between the glass transition temperature and the polymer–polymer interaction parameter of miscible binary blends.

#### **EXPERIMENTAL**

#### **Polymers**

The polymers used in this study were obtained from commercial sources. PEI, designated Ultem 1000, was supplied by General Electric Co. PEEK was supplied by ICI Ltd. The characteristics of the polymer samples used in this study are shown in Table I.

#### **Blend Preparation**

To prepare melt blends, all the polymers were dried in a vacuum oven at 120°C for 24 h before use. Blends were prepared using a 20-mm-diameter laboratory-scale screw extruder, with a 24 : 1 length-to-diameter (L/D) screw. The L/D ratio of the circular die was 20.0 with a diameter of 2 mm. The temperature of the extruder was set at 360–370°C in the barrel zones and the temperature of the die was 345°C.

#### **DSC Measurements**

The thermal properties of all the samples were measured calorimetrically using a Perkin–Elmer differential scanning calorimeter, Model DSC-7. Temperature calibration was performed using indium ( $T_m = 156.6^{\circ}$ C,  $\Delta H_f = 28.5$  J/g). To prepare the amorphous samples of the PEEK–PEI blends, samples were initially heated from 50 to 370°C with a heating rate of 20 K/min and held 1 min. Then, the samples were quenched into the liquid nitrogen immediately. The blend samples were reheated from 50 to 370°C at a heating rate of 20 K/min.

#### **RESULTS AND DISCUSSION**

#### T<sub>g</sub> of PEEK–PEI Blends

The blends of PEEK and PEI are known to be miscible at all compositions in the amorphous state.<sup>1-6</sup> Figure 1 shows the glass transition temperatures  $(T_g's)$  of the amorphous samples of the PEEK–PEI blends with various compositions. The samples used in this study were quenched in liquid nitrogen. A single  $T_g$  was observed at all



**Figure 1** Effect of blend composition on the  $T_g$  of the amorphous PEEK–PEI blends. The curve represents a mathematical model of the Fox equation.

compositions. In Figure 1, the experimentally determined  $T_g$  of the PEEK–PEI blends is compared with the  $T_g$  calculated using the Fox equation.<sup>23</sup> The Fox equation is

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1}$$

where  $w_1$  and  $w_2$  are the weight fractions of components 1 and 2, respectively.  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the glass transition temperatures of the blend, component 1, and component 2, respectively. From Figure 1, we can see that the  $T_g$  values determined by the experiments are consistent with the  $T_g$  from the Fox equation. Chen and Porter<sup>7</sup> studied the PEEK–PEI solution blends and reported similar  $T_g$  behavior to that shown in Figure 1.

The crystallinity of pure PEEK and PEEK in the liquid nitrogen-quenched blends is shown in Figure 2. In Figure 2, we can see that the crystallinity of PEEK in the liquid nitrogen-quenched PEEK–PEI blends is 0.03–0.12 with the compositions. From Figure 2, it is observed that the crystallinity is decreased more significantly in the PEEK-rich compositions of the blends when the samples are quenched in liquid nitrogen. Therefore, it is suggested that the liquid nitrogenquenched PEEK–PEI blends are amorphous PEEK–PEI blends since the crystallinity of PEEK in the blends is very low.

#### $\Delta C_p$ of PEEK–PEI Blends

The values of the specific heat increment  $(\Delta C_p)$  at  $T_g$  of the amorphous PEEK–PEI blends are shown in Figure 3. From this figure, we can see that the  $\Delta C_p$  of amorphous PEEK–PEI blends (liquid nitrogen-quenched) increases with increase of the PEEK weight fraction and is smaller than the  $\Delta C_p$ , which is expected on the basis of the simple additivity rule.

From the difference in the  $\Delta C_p$  values between the experimentally determined  $\Delta C_p$  of the blends and the  $\Delta C_p$  from the simple additivity rule, it is found that the excess heat capacities of mixing have negative values. The negative excess heat capacities of mixing were observed in the miscible blends by other researchers,  $^{24,25}$  such as in poly( $\varepsilon$ caprolactone)-polychlorostyrene by Allard and Prud'homme.<sup>24</sup> Wang and coworkers<sup>25</sup> observed the negative excess heat capacities of mixing for the several miscible blends having hydrogen bonding between the two polymers. Chen and Porter<sup>7</sup> studied the amorphous PEEK–PEI blends by density measurement. They reported that the specific volume of the blends shows a slight negative deviation from linearity, indicating a favorable intermolecular interaction between PEEK



**Figure 2** Effect of blend composition on the crystallinity of PEEK in the PEEK–PEI blends obtained by quenching in liquid nitrogen



**Figure 3** Specific heat increment  $(\Delta C_p)$  at the  $T_g$  of the amorphous PEEK–PEI blends. The curve represents the simple additivity rule.

and PEI. Hsiao and Sauer<sup>6</sup> reported a negative interaction parameter even though the interaction between PEEK and PEI is not strong. By comparing our results of the PEEK–PEI blends with those of other researchers,<sup>6,7</sup> it is suggested that there is a favorable interaction between the PEEK and PEI in the blends from the results of the negative excess heat capacities and the single glass transition temperature of the PEEK–PEI blends, which is similar to the results of other researchers.<sup>6,7</sup>

## Polymer–Polymer Interaction Parameter ( $\chi_{12}$ ) of PEEK–PEI Blends

Lu and Weiss<sup>22</sup> derived the relationship between the glass transition temperature and the interaction parameter of miscible binary polymer blends. The equations are as follows:

$$T_{gm} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + \frac{A w_1 w_2}{(w_1 + k w_2)(w_1 + b w_2)(w_1 + c w_2)^2}$$
(2)

where

$$A = \frac{\chi_{12} R (T_{g1} - T_{g2}) c}{M_1 \Delta C_{p1}}$$
(3)

where

$$k = \frac{\Delta C_{p2} - w_1 \delta C_p^1}{\Delta C_{p1} - w_2 \delta C_p^g} \tag{4}$$

where  $T_{gm}$  is the observed  $T_g$  of the blend;  $w_1$ , the weight fraction of polymer 1 having  $T_{g1}$ ; and  $w_2$ , the weight fraction of polymer 2 having  $T_{g2}$ .  $b = M_2/M_1$ , where  $M_1$  and  $M_2$  are the molecular weight of the repeating unit in polymers 1 and 2, respectively.  $c = \rho_1/\rho_2$ , where  $\rho_1$  and  $\rho_2$  are the densities of pure components 1 and 2, respectively.  $\chi_{12}$  is the Flory–Huggins polymer–polymer interaction parameter.  $\Delta C_p = C_p^{\rm l}(T_g) - C_p^{\rm g}(T_g)$ = the specific heat increment at  $T_g$ , and  $\delta C_p$  is the specific heat change due to mixing. Because  $\delta C_p$  is usually small compared with  $\Delta C_p$ , the right side of eq. (4) can be replaced by  $\Delta C_{p2}/\Delta C_{p1}$ .<sup>22</sup> Lu and Weiss<sup>22</sup> treated the glass transition as

an Ehrenfest transition of second order. In the case of a second-order transition, a plot of a primary quantity shows an abrupt change in the slope, while a plot of a secondary quantity (such as specific heat) then shows a sudden jump. But the glassy state is not completely defined by the normal state variables P, V, and T, and the glass transition is not a real thermodynamic secondorder transition.<sup>26</sup> Schneider et al.<sup>27</sup> reported that the  $T_g$  range becomes larger with higher polydispersity. Because the transition region of the specific heat between the glass state and the liquid state is not considered in the Lu and Weiss equation, we modified eq. (2) by using the glass transition temperature obtained by the midpoint method.<sup>28,29</sup> We assumed, from the DSC thermogram, that the specific heat in the glass transition region depends on the temperature linearly. The specific heat in the glass transition region can be expressed as follows:

$$C_p^T = C_p^g + (T - T_1) \frac{\Delta C_p}{\Delta T}$$
 (5)

Equation (5) can be alternatively expressed as follows:

$$C_p^T = C_p^1 - (T_2 - T) \frac{\Delta C_p}{\Delta T}$$
(6)

where  $C_p^T$  is the specific heat of the glass transition region;  $C_p^g$  and  $C_p^l$ , the specific heat of the glassy state and the liquid state, respectively;  $\Delta T$ , the width of the glass transition; and  $T_1$  and  $T_2$ , the onset and end temperatures of the glass transition, respectively. The temperature dependence of the  $C_p$  of the glassy state and the liquid state is neglected in eqs. (5) and (6).

The enthalpy change of the blend can be given as described in Lu and Weiss's work<sup>22</sup>:

$$\Delta H_{\text{blend}} = x_1 \Delta H_1 + x_2 \Delta H_2 + \Delta H_m(T_{g2}) - \Delta H_m(T_{g1}) \quad (7)$$

where  $\Delta H_1$ ,  $\Delta H_2$ , and  $\Delta H_{\text{blend}}$  are the changes of the enthalpies when the temperature is increased from  $T_{g1}$  to  $T_{g2}$  at a constant pressure for polymer 1, polymer 2, and their blend, respectively.  $x_1$  and  $x_2$  are the mole fractions of polymers 1 and 2, respectively.  $\Delta H_{\text{m}}(T_{g1})$  and  $\Delta H_m(T_{g2})$  are the excess enthalpies of mixing at  $T_{g1}$  and  $T_{g2}$ .

For the Lu and Weiss work, the enthalpy change corresponding to heating the blends from  $T_{g1}$  to  $T_{g2}$  is given by eq. (8)<sup>22</sup>:

$$\Delta H_{\rm blend} = \int_{T_{g1}}^{T_{gm}} C_{p,{\rm blend}}^{g} \, dT + \int_{T_{gm}}^{T_{g2}} C_{p,{\rm blend}}^{1} \, dT \quad (8)$$

where  $T_{gm}$  is the observed  $T_g$  of the blend.  $C_{p,\text{blend}}^g$  and  $C_{p,\text{blend}}^1$  are the specific heats of the blend in the glassy state and the liquid state, respectively. In eq. (8), it is assumed that the specific heat at  $T_g$  of the blend shows a sudden jump from the glassy state to the liquid state.

The schematic curves of the specific heat at the glass transition temperature are shown in Figure 4. In Figure 4, the  $T_g$ 's of polymer 1, polymer 2, and their blend are shown as  $T_{g1}$ ,  $T_{g2}$ , and  $T_{gm}$ , respectively. In Figure 4,  $T_{b1}$  and  $T_{b2}$  are the onset temperature and the end temperature of the glass transition of the blend, respectively. Equation (8) can be modified by using eq. (5) or eq. (6), which represents the slope of the transition region of specific heat at  $T_g$ . The modified enthalpy change of the blend is obtained as in eq. (9):

$$\Delta H_{\text{blend}} = \int_{T_{g1}}^{T_{b1}} C_{p,\text{blend}}^{g} dT + \int_{T_{b1}}^{T_{gm}} C_{p,\text{blend}}^{T} dT + \int_{T_{gm}}^{T_{b2}} C_{p,\text{blend}}^{T} dT + \int_{T_{b2}}^{T_{g2}} C_{p,\text{blend}}^{1} dT \quad (9)$$



### Temperature (°C)

**Figure 4** Schematic curves showing the  $T_g$  of polymer 1  $(T_{g1})$ , the  $T_g$  of polymer 2  $(T_{g2})$ , and the  $T_g$  of the miscible blend  $(T_{gm})$ , respectively.

where  $C_{p,\text{blend}}^T$  is the specific heat of the blend in the glass transition region and given by eq. (5).  $T_{b1}$  and  $T_{b2}$  are the onset temperature and the end temperature of the glass transition of the blend, respectively.  $C_p$ , blend is given by the mixing law as eq. (10)<sup>30</sup>:

$$C_{p,\text{blend}} = x_1 C_{p1} + x_2 C_{p2} + x_1 x_2 \delta C_p \qquad (10)$$

where  $x_1$  and  $x_2$  are the mole fractions of polymers 1 and 2, respectively, and  $\delta C_p$  is the specific heat change due to mixing. Similarly, the changes of the enthalpies of polymers 1 and 2 are given by eqs. (11) and (12), respectively:

$$\Delta H_1 = \int_{T_{g1}}^{T_{12}} C_{p1}^T \, dT + \int_{T_{12}}^{T_{g2}} C_{p1}^1 \, dT \qquad (11)$$

$$\Delta H_2 = \int_{T_{g1}}^{T_{21}} C_{p2}^g \, dT + \int_{T_{21}}^{T_{g2}} C_{p2}^T \, dT \qquad (12)$$

where  $T_{i1}$  is onset temperature of the glass transition of polymer *i* and  $T_{i2}$  is end temperature of the glass transition of polymer *i*. The enthalpy of mixing can be given by the van Laar relationship:

$$\Delta H_m(T) = \chi_{12} R T \phi_1 \phi_2 \tag{13}$$

where  $\phi_i$  is the volume fraction of component *i*; *R*, the gas constant; and  $\chi_{12}$ , the polymer–polymer interaction parameter.

After substitution of eqs. (9)–(13) into eq. (7), we can obtain the modified equation, eq. (14), which includes  $\Delta T_1$  and  $\Delta T_2$ , which are the width of the glass transition region of components 1 and 2, respectively. Then, eq. (14) is given by

$$T_{gm} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + \frac{A w_1 w_2}{(w_1 + k w_2)(w_1 + b w_2)(w_1 + c w_2)^2} + \frac{k w_2 \Delta T_2 - w_1 \Delta T_1}{8(w_1 + k w_2)} \quad (14)$$

where A and k are shown in eqs. (3) and (4), respectively.

The  $\chi_{12}$  values of the PEEK–PEI blends which are obtained by eq. (2) (Lu and Weiss equation) were found to be -5.91, -3.77, -7.57, -2.76, -4.23, -4.36, and -2.76 for the 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, and 7/3 PEEK/PEI blends, respectively. The  $\chi_{12}$  values of the PEEK–PEI blends obtained by eq. (14) (this work) were found to be -8.08, -4.67, -8.04, -3.00, -4.32, -4.34, and -2.59 for the 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, and 7/3 PEEK/PEI blends, respectively.

The  $\chi_{12}$  values calculated by eqs. (2) and (14) are not segmental  $\chi_{12}$  values if the heat of mixing  $(\Delta H_m)$  is defined as in eq. (13). The segmental  $\chi_{12}$  values can be defined by using eq. (15)<sup>19,31,32</sup>:

$$\Delta H_m(T) = \chi_{12} R T \phi_1 \phi_2 (m_1 n_1 + m_2 n_2) \quad (15)$$

where  $\phi_i$  is the volume fraction of component i;  $n_1$ and  $n_2$ , the number of moles of the PEEK and PEI in the blend, respectively; and  $m_1$  and  $m_2$ , the number of lattice sites of the PEEK and PEI molecules, respectively.  $m_1$  and  $m_2$  can be obtained by the following relation<sup>20</sup>:  $m_1 = V_1/V_0$  and  $m_2 = V_2/V_0$ , where  $V_1$ ,  $V_2$ , and  $V_0$  are the molar volume of PEI, PEEK, and the repeating unit of PEEK, respectively. The segmental  $\chi_{12}$  values of the PEEK–PEI blends can be obtained by dividing the  $\chi_{12}$  values calculated from eqs. (2) and (14) by the average value of  $m_1$  and  $m_2$ . The values of  $m_1$ = 48.6 and  $m_2$  = 41.3 were used for the PEEK and PEI, respectively. A repeating unit of the PEEK was chosen as a site volume.

Table IIPolymer-Polymer InteractionParameter for the AmorphousPEEK-PEI Blends

Blends (PEEK–PEI)	$\chi_{12}{}^{\mathrm{a}}$	$\chi_{12}{}^{\mathrm{b}}$
1:9	-0.132	-0.196
2:8	-0.084	-0.104
3:7	-0.168	-0.179
4:6	-0.061	-0.067
5:5	-0.094	-0.096
6:4	-0.097	-0.097
7:3	-0.061	-0.058

 $^{\rm a}$  All  $\chi$  values are calculated from eq. (2) (Lu and Weiss equation).

<sup>b</sup> All  $\chi$  values are calculated from eq. (14) (from this work).

In Table II, the segmental  $\chi_{12}$  values of the PEEK–PEI blends are presented. From Table II, it is shown that the  $\chi_{12}$  values of the PEEK–PEI blends decrease with increase of the PEI weight fraction in the blends. In Table II, the  $\chi_{12}$  values of the PEEK-PEI blends which are calculated from eq. (2) (Lu and Weiss equation) are shown to be  $-0.115 \pm 0.054$  with the blend composition. Also, the  $\chi_{12}$  values of the PEEK–PEI blends which are calculated from eq. (14) (this work) are shown to be  $-0.127 \pm 0.069$  with the blend composition. In Table II, we can see that the  $\chi_{12}$ values calculated from this work appear to be lower than the  $\chi_{12}$  values which are calculated from the Lu and Weiss equation. The  $\chi_{12}$  values shown in Table II appear as small negative values approaching zero, which is consistent with the results of Hsiao and Sauer,<sup>6</sup> such that the interaction parameter between PEEK and PEI must be small and negative since the system is miscible. However, they did not report the  $\chi_{12}$  values of the PEEK–PEI blends. From the results of the  $\chi_{12}$ values which are shown in Table II, the interaction parameter of the PEEK-PEI blends was found to range from -0.058 to -0.196 with the compositions.

#### CONCLUSIONS

In the study of the amorphous PEEK–PEI blends which are obtained by quenching in liquid nitrogen, a single glass transition temperature  $(T_g)$  is observed at all blend compositions. The values of the specific heat increment at  $T_g$  for the amorphous PEEK–PEI blends are smaller than those expected on the basis of a simple additivity rule. From the above results, it is concluded that there is a favorable interaction between the PEEK and PEI in the blends and that there is a miscibility between the two components. From the Lu and Weiss work, a modified equation which represents the slope of the transition region of the specific heat at  $T_g$  was derived. From the Lu and Weiss equation and the modified equation from this work, the polymer-polymer interaction parameter  $(\chi_{12})$  of the amorphous PEEK–PEI blends was calculated and found to range from -0.058 to -0.196 for the extruded blends with the compositions. The  $\chi_{12}$  values which are calculated from this work appeared to be lower than the  $\chi_{12}$  values which were calculated from the Lu and Weiss equation. The  $\chi_{12}$  values calculated from the  $T_g$  method both ways decreased with the increase of the PEI weight fraction.

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