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Glass transition temperatures and rigid amorphous fraction of poly(ether ether ketone) and poly(ether imide) blends

Heon Sang Lee and Woo Nyon Kim*
Department of Chemical Engineering, Korea University, Anam-Dong, Seoul 136-701, Korea

Blends of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) prepared by screw extrusion have been investigated using a differential scanning calorimeter. The amorphous samples obtained by quenching in the liquid nitrogen show a single glass transition temperature (T_g). However, semicrystalline samples cooled in d.s.c. show double glass transition temperatures. From these results, it is suggested that the blends of PEEK and PEI are miscible in the amorphous state and partially miscible in the semicrystalline state. From the measured degree of crystallinity (X_c) and specific heat increment (ΔC_p) at T_g, the rigid amorphous fraction (X_r) for the semicrystalline PEEK–PEI blends was calculated and found to be 0.117–0.358 with cooling rates in d.s.c. The effect of cooling rate and PEI composition on the rigid amorphous fraction (X_r) of PEEK in the PEEK–PEI blends are discussed. © 1997 Elsevier Science Ltd.

(Keywords: poly(ether ether ketone); poly(ether imide); rigid amorphous fraction)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is an aromatic engineering thermoplastic displaying excellent mechanical properties and good thermal stability[1-3]. Poly(ether imide) (PEI) is an another high performance and high temperature engineering thermoplastic, which is known to be miscible with PEEK[4-9]. By blending PEEK with PEI, favourable properties of each polymer may be optimized[4]. Recently, many researchers have investigated the mechanism and the morphology of PEEK crystallization in the PEEK–PEI blends[4-9]. Hudson *et al.*[5] have reported that the unit-cell of PEEK crystals is constant at all crystallization temperatures and blend compositions, but the spherulites become more open with the increase of PEI weight fraction. They also reported that the two polymeric components are compatible in the melt, though, phase separation occurs during crystallization of the PEEK component[5].

Crevecoeur and Groeninckx[4] have studied the crystallization behaviour of PEEK in blends with PEI using thermal analysis and small-angle X-ray scattering. They reported that the glass transition of the amorphous samples of the PEEK–PEI blends varies nearly as predicted by the Fox equation[9]. In semicrystalline samples, however, the amorphous phase is enriched in PEI, so the glass transition temperature increases. Therefore, the PEEK component crystallizes as in pure PEEK, with the PEI segregating to the amorphous phase[4,5]. From SAXS measurements, Crevecoeur and Groeninckx[4] concluded that, within the spherulites, PEI is primarily rejected between bundles of lamellae.

In our present study we investigate the thermal behaviour of the amorphous samples and semicrystalline

samples of the PEEK–PEI blends using a differential scanning calorimeter (d.s.c.) to see the single T_g or double T_gs in blends with different thermal history. We also examine thermal properties such as crystallinity of the PEEK and rigid amorphous fraction of PEEK in the semicrystalline PEEK–PEI blends with different thermal history.

EXPERIMENTAL

Polymers

The polymers used in this study were obtained from commercial sources. Poly(ether imide) (PEI) designated Ultem 1000 was supplied by General Electric Co. Poly(ether ether ketone) (PEEK) was supplied by ICI Ltd. The characteristics of polymer samples used in this study are shown in *Table 1*.

Blends preparations

To prepare melt blends, all 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 single screw extruder, with a 24:1 length-to-diameter screw. The length to diameter (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.

Differential scanning calorimetry measurements

The thermal properties of all samples were measured calorimetrically using a Perkin-Elmer differential scanning calorimeter, Model DSC-7. Temperature calibration was performed using indium ($T_m = 156.6$°C, $\Delta H_f = 28.5$ J g^{-1}). To prepare the semicrystalline samples of the PEEK–PEI blends, samples were heated from 50 to

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* To whom correspondence should be addressed

370°C with a heating rate of $20\,\mathrm{K\,min^{-1}}$ and held 1 min and then cooled to 50°C with various cooling rates (1–320 $\mathrm{K\,min^{-1}}$). To prepare the amorphous samples of the PEEK–PEI blends, samples were initially heated from 50 to 370°C with a heating rate of $20\,\mathrm{K\,min^{-1}}$ and held 1 min then the samples were quenched immediately into the liquid nitrogen. The blend samples were then reheated from 50 to 370°C at a heating rate of $20\,\mathrm{K\,min^{-1}}$. In this work, the maximum cooling rate is $170\,\mathrm{K\,min^{-1}}$, which is controlled in d.s.c., therefore the cooling rate of $320\,\mathrm{K\,min^{-1}}$ used in d.s.c. stands for natural cooling at room temperature.

RESULTS AND DISCUSSION

Single T_g of PEEK–PEI blends

The blends of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) are known to be miscible at all compositions in the amorphous state[3-7]. *Figure 1* shows the glass transition temperatures (T_gs) of the semicrystalline samples of the PEEK–PEI blends with various compositions. The samples used in *Figure 1* were cooled with cooling rates of 140 and $320\,\mathrm{K\,min^{-1}}$ in d.s.c. The single glass transition temperature (T_g) is observed at all 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[10].

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (1)$$

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 the difference in T_g values between the experimentally determined T_g of the blends and the T_g from the Fox equation. The increase in T_g compared with Fox equation is more pronounced in the PEEK-rich compositions than in the PEI-rich compositions. The increase of T_g in the PEEK-rich compositions may be due to the increase of crystallinity in the PEEK-rich compositions, which will be explained in *Figure 3*. A similar observation has been reported by Crevecoeur and Groeninckxs[4] that the composition of the amorphous phase has indeed changed upon crystallization of PEEK.

The glass transition temperatures of the PEEK–PEI amorphous blends is shown in *Figure 2*. In this case, the samples were quenched in liquid nitrogen at the melted state. From *Figure 2*, we can see that the experimentally obtained T_g of the PEEK–PEI blends become closer to the T_g calculated by the Fox equation. This may be due to the decrease of crystallinity of PEEK in the PEEK–PEI blends, which will be explained in *Figure 3*.

The crystallinity of pure PEEK and PEEK in the

PEEK–PEI blend is changed with various cooling methods of the samples. Therefore, we performed two different thermal treatments on the PEEK–PEI blends to obtain the semicrystalline and the amorphous blend samples. A slower cooling rate was used to obtain the semicrystalline PEEK–PEI blend samples in the d.s.c. and liquid nitrogen quenching was used to obtain the amorphous PEEK–PEI blend samples. In this study, the degree of crystallinity (X_c) of PEEK were calculated by the following relation: $X_c = \Delta H_f / \Delta H_o$, where ΔH_o is the heat of fusion of the pure crystalline sample, which is $130\,\mathrm{J\,g^{-1}}$ in the literature[11]. ΔH_f is the heat of fusion of the semicrystalline sample, obtained from d.s.c. measurement.

The crystallinity of pure PEEK and PEEK in the

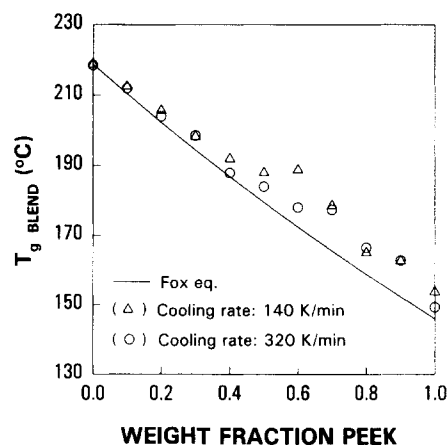**Figure 1** Effect of blend composition on the T_g of the semi-crystalline PEEK–PEI blends obtained (△) by $140\,\mathrm{K\,min^{-1}}$ cooling, (○) by $320\,\mathrm{K\,min^{-1}}$ cooling. The curve represents the mathematical model of the Fox equation[10]
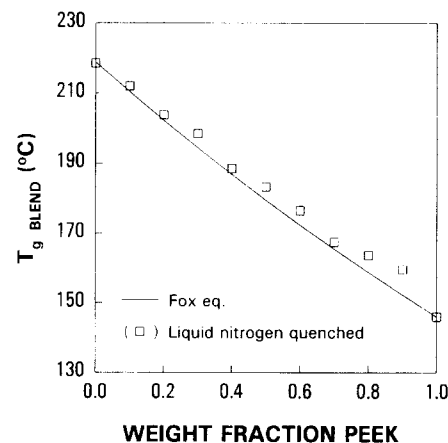

Figure 2 Effect of blend composition on the T_g of the amorphous PEEK–PEI blends. The curve represent mathematical model of the Fox equation[10]

Table 1 Characteristics of polymer samples used in the PEEK–PEI blends

	$M_w{}^a$	$M_n{}^a$	T_m (°C)^b	T_g (°C)^b	ΔC_p (J g^{-1} K^{-1})^b	ρ (g cm^{-3})^c	M_0 (g)	ΔT (°C)^d
PEEK	39 000	14 000	338.3	146.0	0.308	1.26	288	5.0
PEI	30 000	12 000	—	218.9	0.241	1.27	592	8.4

^{a} Data from ref. 5
^{b} Measured in our laboratory using d.s.c.
^{c} Measured in our laboratory using specific gravity chain balance
^{d} The interval of glass transition, measured in our laboratory using d.s.c.

blends is shown in *Figure 3*, we can see that the crystallinity of PEEK in the semicrystalline PEEK–PEI blends (cooling rates in d.s.c.: 140 and 320 K min^{-1}) is found to be 0.080–0.342 with compositions. The crystallinity of PEEK in the amorphous PEEK–PEI blends (liquid nitrogen quenched) is found to be 0.039–0.089 with compositions. From *Figure 3*, 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.

The crystallization temperature (T_c) of PEEK in the PEEK–PEI blends during cooling in d.s.c. with a cooling rate of 140 K min^{-1} is shown in *Figure 4*. The crystallization temperature of PEEK in the PEEK–PEI blends is shown to decrease with an increase of PEI weight fraction in *Figure 4*, which is consistent with the results by other researchers[4,5,7]. Similar behaviour was observed when the cooling rates were 5, 10 and 20 K min^{-1}. The higher crystallization temperature of PEEK in the PEEK–PEI blends can be explained as PEEK molecules array easily in the unit-cell; crystallization rate is fast. This result is consistent with the result shown in *Figure 3*. That is, the crystallinity is increased in the PEEK-rich compositions.

ΔC_p of PEEK–PEI blends

The values of specific heat increment (ΔC_p) at T_g of the PEEK–PEI blends are shown in *Figure 5*. From this figure we can see that the ΔC_p of amorphous PEEK–PEI blends (liquid nitrogen quenched) increases with an increase of the PEEK weight fraction. While the ΔC_p of semicrystalline PEEK–PEI blends (cooling rates in d.s.c.: 140 and 320 K min^{-1}) decreases with an increase of the PEEK weight fraction. The ΔC_p at T_g corresponds well with the amorphous region of the blends and represent the intensity of glass transition. This result is consistent with the result of crystallinity of the blends which is shown in *Figure 3*.

Cheng and coworkers[12] have studied the thermal properties of PEEK using d.s.c., and they have shown that a portion of the amorphous phase of PEEK remains rigid above T_g, since the PEEK has a less flexible structure. Similar results for the PEEK have been observed by Candia and Vittoria[13] using PEEK membrane, and Huo and Cebe[14], and Kalika and Krishnaswamy[15] using dielectric relaxation of PEEK. They have found that the ΔC_p at T_g is sometimes not consistent with the amorphous weight fraction ($1 - X_c$) for semicrystalline polymers[12,15]. That is, from ΔC_p one can calculate only an overall 'rigid fraction (X_f)' that remains solid beyond the glass transition region by using equation (2)[12]. The overall rigid fraction (X_f) consists of the crystalline fraction (X_c) and the rigid amorphous fraction (X_r). Thus, they[12-15] have incorporated the rigid amorphous fraction (X_r) into the overall rigid fraction (X_f), since the rigid amorphous fraction cannot be detected as a ΔC_p at T_g. The overall rigid fraction (X_f) can be obtained from equation (2)[12].

$$X_f = 1 - \frac{\Delta C_p}{\Delta C_p^a} \tag{2}$$

where X_f is the overall rigid fraction, ΔC_p is the specific heat increment at T_g of the semicrystalline PEEK–PEI blends, and ΔC_p^a is the specific heat increment at T_g of the fully amorphous PEEK–PEI blends. In this work, the

ΔC_p^a values of fully amorphous PEEK–PEI blends were estimated by normalizing the ΔC_p values of the liquid nitrogen quenched PEEK–PEI blends as equation (3):

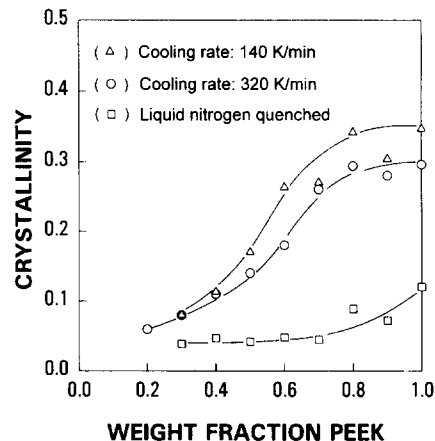$$\Delta C_p^a = \left[\frac{\Delta C_p}{1 - w_1 X_c} \right]_{\text{liquid nitrogen quenched}} \tag{3}$$

Figure 3 Effect of blend composition on the crystallinity of PEEK in the PEEK–PEI blends obtained (△) by 140 K min^{-1} cooling, (○) by 320 K min^{-1} cooling, (□) by quenching in liquid nitrogen
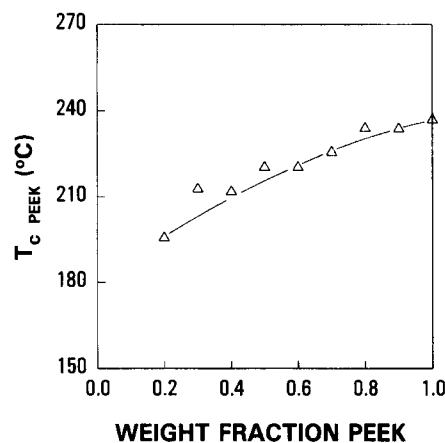

Figure 4 Effect of blend composition on the crystallization temperature of PEEK in the PEEK–PEI blends during cooling with cooling rate of 140 K min^{-1}
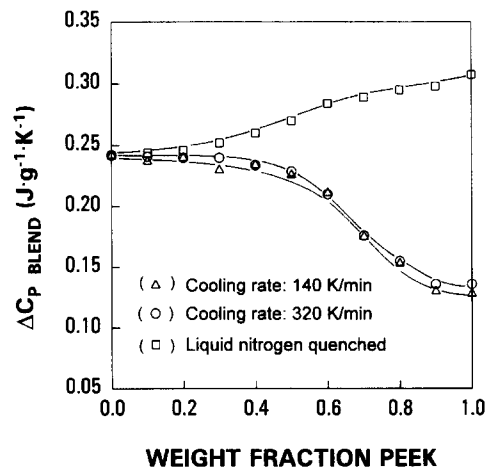

Figure 5 Specific heat increment (ΔC_p) at the T_g of the PEEK–PEI blends obtained (△) by 140 K min^{-1} cooling, (○) by 320 K min^{-1} cooling, (□) by quenching in liquid nitrogen

where w_1 is the weight fraction of PEEK in the PEEK PEI blend.

Rigid amorphous fraction (X_r) of PEEK in the blends

The rigid amorphous fraction (X_r) of PEEK in the PEEK-PEI blends can be defined as equation (4):

$$X_r = \frac{X_f}{w_1} - X_c \qquad (4)$$

Using equations (2) and (4), we can calculate the X_r of PEEK in the blends from the measured ΔC_p and ΔH_f of the blends.

In *Table 2*, the thermal properties such as crystallinity (X_c), specific heat increment (ΔC_p) at T_g, overall rigid fraction (X_f), and rigid amorphous fraction (X_r) of the amorphous PEEK-PEI blend (liquid nitrogen quenched) are presented. The crystallinity (X_c) and the ΔC_p in *Table 2* is from *Figures 3* and *5*, respectively. It is assumed from equation (3) that the rigid amorphous fraction of PEEK in the liquid nitrogen quenched PEEK-PEI blends is zero, since the crystallinity of PEEK in the liquid nitrogen quenched PEEK-PEI blends is too low. In *Table 2*, the ΔC_p^a of fully amorphous PEEK is shown to 0.350 J g^{-1} K^{-1}, which is close to another reported value (0.327 J g^{-1} K^{-1}) by Hsiao and Sauer[8]. Cheng and coworkers[12] have reported the ΔC_p at T_g of PEEK to be about 0.27 J g^{-1} K^{-1} by d.s.c.

In *Table 3*, thermal properties such as crystallinity (X_c), overall rigid fraction (X_f), and rigid amorphous fraction (X_r) of the semicrystalline PEEK-PEI blends (cooling rates in d.s.c.: 140 and 320 K min^{-1}) are presented. The crystallinity (X_c) in *Table 3* was obtained from *Figure 3*. The overall rigid fraction (X_f) is calculated from ΔC_p which are shown in *Figure 5* using equation (2). The rigid amorphous fraction (X_r) is the difference between the overall rigid fraction (X_f) and the crystallinity (X_c). Some researchers[16] have agreed that the X_r does not participate in the glass transition due to 'immobilization' by crystallites. In *Table 3*, the rigid amorphous fraction (X_r) of semicrystalline PEEK is found to be 0.287 in the pure state and 0.117-0.354 in the blends when the cooling rate is 140 K min^{-1}. The rigid amorphous fraction (X_r) of semicrystalline PEEK is 0.315 in the pure state and 0.117-0.358 in the blends when the cooling rate is 320 K min^{-1}. From this result, it can be found that the rigid amorphous fraction (X_r) of semicrystalline PEEK is increased with the increase of the cooling rate in the pure state and in the blends. From *Table 3*, we can see the maximum rigid amorphous fraction (X_r) in the 9/1 PEEK-PEI blend. The rigid amorphous fraction (X_r) of PEEK is initially increased by the incorporation of PEI to the blends. As the amount of PEI is increased in the blends, the rigid amorphous fraction (X_r) of PEEK is decreased. For the 9/1, 8/2, and 7/3 PEEK-PEI blends, the increase of the rigid amorphous fraction (X_r) of PEEK can be explained by the fact that the PEEK crystalline becomes less perfect by the addition of PEI. For the PEI-rich compositions (4/6, 3/7, 2/8, and 1/9 PEEK-PEI blends), the decrease of the rigid amorphous fraction (X_r) of PEEK can be explained by the fact that the values of thermal properties such as T_g, X_c, and ΔC_p are close to those of the amorphous blend samples, which can be seen in *Figures 1-3*, and *5*. Since the rigid amorphous fraction (X_r) is approaching to zero in the two extreme cases: perfect crystalline state and perfect amorphous state[12].

Cheng and coworkers[12] have reported that the rigid amorphous fraction (X_r) of pure PEEK was observed to be 0.05, 0.09, and 0.11 with a cooling rate in d.s.c. of 0.31, 2.5, and 10 K min^{-1}, respectively. In this work, we have used the cooling rate of 5 K min^{-1} for the pure PEEK and the X_r was observed to be 0.188 (*Table 4*) which is close to the values with other workers[12]. For the pure PEEK crystallized isothermally in the temperature range 190-300°C, the rigid amorphous fraction (X_r) has been reported as 0.08-0.14 by Cheng and coworkers[12] using d.s.c. and 0.24-0.32 by Huo and Cebe[14] using the dielectric relaxation test.

Table 2 Thermal properties of the amorphous PEEK-PEI blends (liquid nitrogen quenched)

Blend[a]	X_c[b]	ΔC_p^c (J g^{-1} K^{-1})	$\Delta C_p^{a\,d}$ (J g^{-1} K^{-1})	X_f[e]	X_r[f]
10/0	0.120	0.308	0.350	0.120	0.000
9/1	0.072	0.298	0.319	0.072	0.000
8/2	0.089	0.295	0.318	0.089	0.000
7/3	0.045	0.289	0.299	0.045	0.000
6/4	0.048	0.284	0.292	0.048	0.000
5/5	0.042	0.270	0.276	0.042	0.000
4/6	0.047	0.260	0.265	0.047	0.000
3/7	0.039	0.252	0.255	0.039	0.000
2/8		0.246			
1/9		0.244			
0/10	0.000	0.241	0.241	0.000	0.000

[a] Blend composition given as the overall weight fraction PEEK in the PEEK-PEI blend
[b] Crystallinity of PEEK in the PEEK-PEI blend: data from *Figure 3*
[c] Specific heat increment at T_g of the liquid nitrogen quenched PEEK-PEI blend: data from *Figure 5*
[d] Specific heat increment at T_g of fully amorphous PEEK-PEI blend: $\Delta C_p^a = \Delta C_p/(1 - X_c w_1)$, where w_1 is weight fraction of PEEK in the PEEK-PEI blend
[e] The overall rigid fraction of the PEEK-PEI blend: $X_f = 1 - \Delta C_p/\Delta C_p^a$
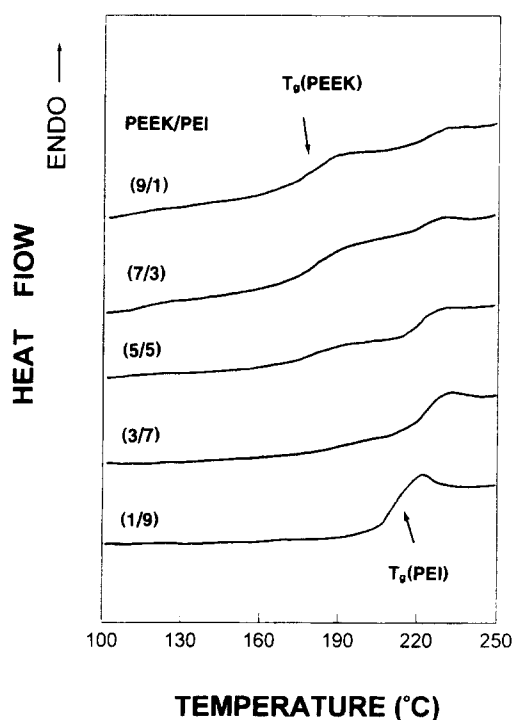[f] The rigid amorphous fraction of PEEK in the PEEK-PEI blend: $X_r = X_f/w_1 - X_c$

Figure 6 Thermogram showing the double T_gs behaviour in the semicrystalline PEEK-PEI blends obtained by slow cooling (5 K min^{-1})

Table 3 Thermal properties of the semicrystalline PEEK–PEI blends

Blend[a]	X_c[b] 140 K min^{-1}[e]	X_c[b] 320 K min^{-1}[f]	X_f[c] 140 K min^{-1}[e]	X_f[c] 320 K min^{-1}[f]	X_r[d] 140 K min^{-1}[e]	X_r[d] 320 K min^{-1}[f]
10/0	0.347	0.296	0.634	0.611	0.287	0.315
9/1	0.304	0.280	0.592	0.574	0.354	0.358
8/2	0.342	0.294	0.519	0.513	0.307	0.347
7/3	0.270	0.260	0.415	0.411	0.323	0.327
6/4	0.263	0.180	0.277	0.281	0.199	0.288
5/5	0.170	0.140	0.181	0.170	0.192	0.200
4/6	0.113	0.110	0.117	0.117	0.180	0.183
3/7	0.080	0.080	0.059	0.059	0.117	0.117
2/8	—	—	0.024	0.024	—	—
1/9	—	—	0.029	0.012	—	—
0/10	0.000	0.000	0.000	0.000	0.000	0.000

[a] Blend compositions given as the overall weight fraction PEEK in the PEEK–PEI blend
[b] Crystallinity of PEEK in the PEEK–PEI blend: data from *Figure 3*
[c] The overall rigid fraction of the PEEK–PEI blend: $X_f = 1 - \Delta C_p/\Delta C_p^a$
[d] The rigid amorphous fraction of PEEK in the PEEK–PEI blend: $X_r = X_f/w_1 - X_c$
[e] All data were obtained at heating rate of 20 K min^{-1} after the blend's being cooled at cooling rate of 140 K min^{-1}
[f] All data were obtained at heating rate of 20 K min^{-1} after the blend's being cooled at cooling rate of 320 K min^{-1}

Double T_gs of PEEK–PEI blends

The PEEK–PEI blends are completely miscible at all compositions in the amorphous state[4–9]. But phase separation may occur because of the crystallizable property of PEEK in the PEEK–PEI blends[5–7]. Isothermal crystallization mechanism of the PEEK–PEI blends have been investigated by some researchers[4–7]. Crevecoeur and Groeninckxs[4] reported that the glass transition temperature of the PEEK–PEI blends shifted to higher temperature as PEEK crystallizes in the blends and observed a single T_g in the PEEK–PEI blends. In *Figures 6* and *7*, we used a very slow cooling rate (5 K min^{-1}) when the blends were cooled from the melted state above T_m. From *Figures 6* and *7*, we can see the double glass transition regions: the upper one is the PEEK-rich phase and the lower one is the PEI-rich phase. In *Figure 7*, there is a slight increase of T_g (PEEK) up to 20 K with composition compared to the T_g of pure PEEK. Also there is a slight decrease of T_g (PEI) up to 8 K with composition compared to the T_g of pure PEI. A miscible polymer blend will exhibit a single glass transition between the T_gs of the components while for partially miscible systems the T_gs approach each other but do not become identical[17–19]. From the T_g values of *Figure 7*, we can say that the PEEK–PEI blends become partially miscible when the cooling rate is slow at the melted state above T_m. This result comes from the fact that the PEI is rejected between bundles of lamellae during the crystallization of PEEK in the PEEK–PEI blends[4]. At weight fraction of 0.1, 0.2, and 0.3 of PEEK in the PEEK–PEI blends, it was difficult to observe double T_gs of the blends because of the d.s.c. sensitivity.

The thermal properties of the semicrystalline PEEK–PEI blends (cooling rate in d.s.c.: 5 K min^{-1}) such as specific heat increment (ΔC_p), crystallinity (X_c), overall rigid fraction (X_f), and rigid amorphous fraction (X_r) are presented in *Table 4*. The specific heat increment (ΔC_p) at T_g of PEI in the PEEK–PEI blends is found to be from 0.112 to 0.177 J g^{-1} K^{-1}, which is shown to decrease with the increase of PEEK weight fraction in *Table 4*. The reduction of ΔC_p at T_g of PEI may be due to the dissolution of PEI in the conjugate phase[18]. Thus the

Table 4 Thermal properties of the semicrystalline PEEK–PEI blends which were cooled with cooling rate of 5 K min^{-1}

Blend[a]	ΔC_p (PEEK)[b] (J g^{-1} K^{-1})	ΔC_p (PEI)[c] (J g^{-1} K^{-1})	X_c[d]	X_f[e]	X_r[f]
10/0	0.129	—	0.443	0.630	0.188
9/1	0.126	0.112	0.442	0.576	0.198
8/2	0.127	0.115	0.442	0.510	0.195
7/3	0.127	0.116	0.443	0.446	0.194
6/4	0.127	0.118	0.443	0.382	0.194
5/5	0.128	0.160	0.444	0.317	0.190
4/6	0.127	0.177	0.443	0.255	0.191
0/10	—	0.241	0.000	0.000	0.000

[a] Blend composition given as the overall weight fraction PEEK in the PEEK–PEI blend
[b] The specific heat increment at T_g of PEEK in the PEEK–PEI blend
[c] The specific heat increment at T_g of PEI in the PEEK–PEI blend
[d] Crystallinity of PEEK in the PEEK–PEI blend
[e] The overall rigid fraction of the PEEK–PEI blend: $X_f = [1 - \Delta C_p(\text{PEEK})/\Delta C_p^a(\text{PEEK})] \times w_1$, where w_1 is weight fraction of PEEK in the PEEK–PEI blend
[f] The rigid amorphous fraction of PEEK in the PEEK–PEI blend: $X_r = X_f/w_1 - X_c$
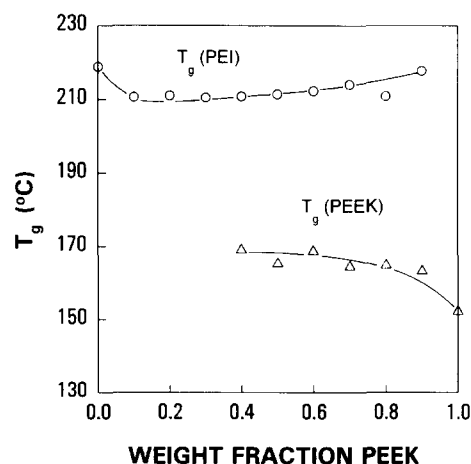

Figure 7 Double T_gs of the semi-crystalline PEEK–PEI blends obtained by slow cooling (5 K min^{-1}) with the blend composition (○) T_g of PEI of the PEEK–PEI blends, (△) T_g of PEEK in the PEEK–PEI blends

undissolved part of the PEI would show a reduced ΔC_p by d.s.c. In *Table 4*, the crystallinity (X_c) of PEEK in the semicrystalline PEEK–PEI blend (cooling rate in d.s.c.: $5\,K\,min^{-1}$) is shown to be from 0.442 to 0.444, which are almost constant with blend compositions. This indicates that PEEK in the blends have enough time to crystallize when the blends are cooled at a cooling rate of $5\,K\,min^{-1}$ even though PEI reduces the rate of crystallization of PEEK. The rigid amorphous fraction (X_r) of PEEK in the semicrystalline PEEK–PEI blends (cooling rate in d.s.c.: $5\,K\,min^{-1}$) is found to be from 0.190 to 0.198, which are somewhat higher than that of pure PEEK (0.188) in *Table 4*. This is due to the reduction of ΔC_p at the T_g of PEEK in the blends, which is resulted from the dissolution of PEEK in the conjugate phase. From the results of *Tables 3* and *4*, it can be founded that the rigid amorphous fraction of PEEK in the semicrystalline PEEK–PEI blends is increased with the increase of the cooling rates in d.s.c., since the crystalline of PEEK may become less perfect in the PEEK–PEI blends at a higher cooling rate.

In order to examine whether the blends exhibit double T_gs or a single T_g, we have tested the PEEK–PEI blend at various cooling rates $(1-170\,K\,min^{-1})$ in d.s.c. The T_gs of the PEEK–PEI (7/3) blend are shown in *Figures 8* and *9* with various cooling rates. When the blend was cooled at slow cooling rates (1 and $10\,K\,min^{-1}$), the PEEK–PEI (7/3) blend shows double T_gs in *Figure 8*, which are T_g (PEI), associated with the PEI-rich phase, and T_g (PEEK), associated with the PEEK-rich phase. As the cooling rate becomes faster (40 and $80\,K\,min^{-1}$), the double T_gs of the PEEK–PEI (7/3) blend become closer to the centre of the T_g of each pure component. Finally the double T_gs of the PEEK–PEI (7/3) blend become a single T_g when the cooling rate is $140\,K\,min^{-1}$ and faster than $140\,K\,min^{-1}$, which are shown in *Figure 9*.

From the results of *Figures 1, 2, 7,* and *9*, it can be concluded that the PEEK–PEI blends exhibit single T_g in the amorphous state but show double T_gs in the semicrystalline state due to the phase separation during the crystallization of PEEK in the blends. This result is consistent with the results of crystallinity (X_c) of the PEEK in the PEEK–PEI blends, which is shown in *Tables 2–4*. However, one question remains to be answered: why do the semicrystalline PEEK–PEI blends (cooling rates in d.s.c.: 140 and $320\,K\,min^{-1}$) exhibit single T_g in *Figure 1*? It can be surmised that the single T_g of the semicrystalline PEEK–PEI blends (cooling rates in d.s.c.: 140 and $320\,K\,min^{-1}$) comes from the broadening of the T_gs of PEEK-rich phase and PEI-rich phase. There is a phase separation between the PEEK-rich and the PEI-rich phase in the semicrystalline PEEK–PEI blends (cooling rates in d.s.c.: 140 and $320\,K\,min^{-1}$), however the double T_gs of the blends may look like single T_g in a d.s.c. thermogram, since the two T_gs are so close each other.

Maximum rigid amorphous fraction (X_r) *of PEEK*

In the previous sections, it has been reported that the crystallinity (X_c) of PEEK in the blends decreases with the increase of cooling rates in d.s.c., while the X_r of PEEK in the blends increases with the increase of cooling rates in d.s.c. In *Tables 3* and *4*, the X_c and X_r of PEEK in the blends depend on the PEI-composition, also.

Now, we can examine the relationship between the X_r and X_c of PEEK in the blends, which has been shown in *Figure 10*. *Figure 10* is obtained from *Tables 3* and *4*. The
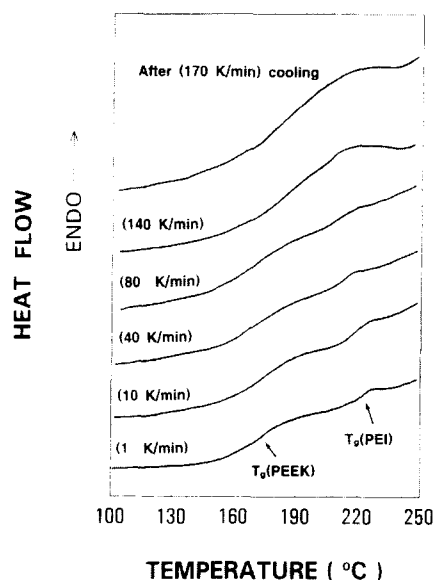

Figure 8 Thermograms showing the double T_gs of the semi-crystalline 7/3 PEEK–PEI blend at various cooling rates
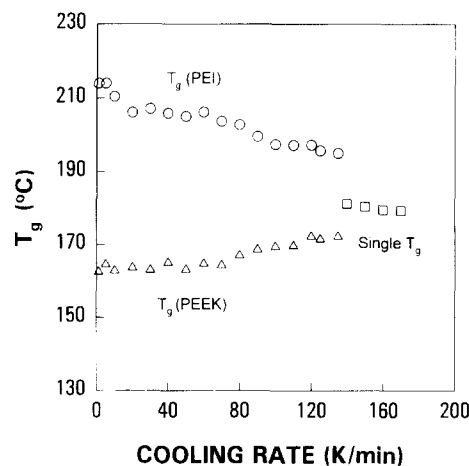

Figure 9 Effect of cooling rates on the double T_gs of the semicrystalline 7/3 PEEK–PEI blend
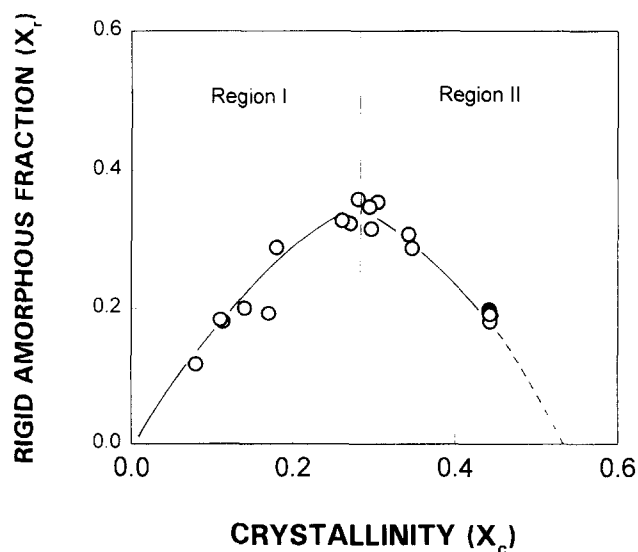

Figure 10 The rigid amorphous fraction (X_r) of PEEK as a function of the crystallinity (X_c)

maximum X_r is observed about $X_c = 0.3$ which is inbetween the minimum crystalline state (amorphous state) and the maximum crystalline state. In region I of *Figure 10*, the crystallization of PEEK may induce the formation of the rigid amorphous region, therefore, X_r increases with the increase of the X_c. While in region II of *Figure 10*, X_r decreases with the increase of X_c. The decrease of X_r in region II may be due to the fact that the crystalline region has become a more ordered crystalline structure as X_c is increased.

CONCLUSIONS

In the thermal analysis of PEEK–PEI blends, it can be concluded that the PEEK–PEI blends exhibit a single T_g in the amorphous state but show double T_gs in the semicrystalline state due to the phase separation during crystallization of PEEK in the blends.

For the amorphous PEEK–PEI blends, the ΔC_p increases with an increase of the PEEK weight fraction. For the semicrystalline PEEK–PEI blends, the ΔC_p decreases with an increase of the PEEK weight fraction. The crystallinity (X_c) of PEEK in the amorphous and semicrystalline PEEK–PEI blends is found to be 0.039–0.089 and 0.080–0.342, respectively. From the results of ΔC_p and crystallinity (X_c) of the blends, the rigid amorphous fraction (X_r) of the PEEK has been calculated and found to be 0.117–0.358 with the PEI composition and cooling rates in d.s.c.

The rigid amorphous fraction (X_r) of PEEK in the semicrystalline PEEK–PEI blends increases with the increase of cooling rates in d.s.c., since the crystalline of PEEK may become less perfect in the PEEK–PEI blends at a higher cooling rate.

The rigid amorphous fraction (X_r) of PEEK increases initially by the addition of PEI, then the X_r decreases as more PEI is added to the blends. The maximum X_r was observed at 9/1 PEEK–PEI blend. The increase of X_r of PEEK in the PEEK-rich composition can be explained by the fact that the PEEK crystalline becomes less perfect by the addition of PEI. For the PEI-rich composition, the values of T_g, X_c, and ΔC_p which determine the X_r show close to those of the amorphous blend samples, therefore the value of X_r of PEEK is decreased.

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