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

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Abstract

The glass transition temperatures (T_gs) and rigid amorphous fraction (X_r) of the poly(ether ether ketone) (PEEK) and polyarylate (PAr) blends prepared by screw extrusion have been investigated by differential scanning calorimetry. From the measured T_gs of PEEK and PAr in the PEEK–PAr blends, Flory–Huggins polymer–polymer interaction parameter (χ_{12}) between PEEK and PAr was calculated and found to be 0.058 ± 0.002 at 360°C. From the measured crystallinity and specific heat increment at T_g, the X_r of PEEK in the PEEK–PAr blends was calculated and found to be 0.31, 0.36, and 0.39 for the pure PEEK, 5:5, and 4:6 PEEK–PAr blends, respectively. The increase of X_r with PAr composition suggests that the PEEK crystalline becomes less perfect by the addition of PAr in the PEEK–PAr blends.

Keywords: Polymer blends; Rigid amorphous fraction; Polymer–polymer interaction parameter

1. Introduction

Poly(ether ether ketone) (PEEK) is an aromatic engineering thermoplastic displaying excellent mechanical properties and good thermal stability [1]. The melting behavior, the crystallization behavior, and the rigid amorphous phase of PEEK was studied widely [2–5]. Recently, we reported the glass transition temperatures and rigid amorphous fraction of PEEK in the PEEK–poly(ether imide) blends [2]. Polyarylate (PAr), an amorphous aromatic polyester, which is made from bisphenol-A and isophthalic acids, has good mechanical and flammability properties [6]. For the blends of PEEK with PAr, it was reported that the synergy of the two components leads to an enhancement in impact strength at intermediate compositions [7].

Ryou et al. [8] studied the thermal and mechanical properties of PEEK–PAr blends by dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). From the DMTA and TGA results of the PEEK–PAr blends, they reported that blends of PEEK and PAr are partially miscible, and thermal stability of PAr is improved by the presence of PEEK in the blends. From the results of isothermal and non-isothermal crystallization experiments of PEEK–PAr blends, Krishnaswamy and Kalika [9] reported that the presence of PAr has a strong retarding influence on the rate of crystallization of PEEK in the blends.

Several researchers have studied the rigid amorphous phase for the pure PEEK [10–12] and for the blends [2]. Cheng and coworkers [10] have studied the thermal properties of PEEK using differential scanning calorimetry (DSC) and they have shown that a portion of the amorphous phase of PEEK remains rigid above T_g, since PEEK has a less flexible structure. Similar results for PEEK have been observed by Huo and Cebe [11] and Kalika and Krishnaswamy [12] using the dielectric relaxation of PEEK.

In our present study, we investigate the crystallinity of PEEK and the rigid amorphous fraction of the PEEK–PAr blends by DSC. The Flory–Huggins interaction parameter of the blends of PEEK and PAr was determined experimentally from the glass transition temperatures of the blends by thermal analysis.

2. Experimental

2.1. Polymers

The polymers used in this study were obtained from commercial sources. The characteristics and sources of the polymer samples used in this study are shown in Table 1. PEEK designated Victrex 450G was obtained from ICI Ltd.

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

	$\bar{M}_w$	$\bar{M}_n$	T_g (°C)[a]	ΔC_p^a (J/g K)	T_m (°C)[a]	T_c (°C)[a]
PEEK	39 000[b]	14 000	146.4	0.293	338.3	290.8
PAr	45 800[c]	18 400	195.9	0.151	–	–

[a] Measured in our laboratory by DSC.
[b] Data from Ref. [19].
[c] Measured in our laboratory by GPC.

PAr (Ardel D-100), which is a copolymer of bisphenol-A with a mixture of terephthalic/isophthalic acids (50:50), was supplied by Amoco.

2.2. Blend preparations

The blends of the two polymers were prepared by screw extrusion. The blends with a weight fraction of PEEK from 0.1 to 0.9 with an increment of 0.1 were prepared using a 20-mm diameter laboratory scale screw extruder. The length to diameter ratio (L/D) of the circular die was 20.0 with a diameter of 2 mm. The polymer samples were dried under vacuum at 120°C for 24 h before use. Temperatures of the extruder were set at 360°C in the barrel zones and at 340°C in the die zone.

2.3. Differential scanning calorimetry

The thermal properties of all the samples were analyzed using a Perkin–Elmer DSC, Model DSC-7. Temperature calibration was performed using indium ($T_m = 156.6$°C, $\Delta H_f = 28.5$ J/g). In order to measure the T_g of PEEK and PAr in the PEEK–PAr blends, samples of 5–15 mg were heated in a nitrogen atmosphere from 50 to 360°C at a heating rate of 20 K/min and then cooled to 50°C for the second scan. To prepare the liquid nitrogen quenched samples of the PEEK–PAr blends, the samples were initially heated from 50 to 360°C with a heating rate of 20 K/min and held for 3 min, then the samples were quenched immediately into the liquid nitrogen. The cooling rate of 320 K/min used in DSC stands for natural cooling at room temperature.

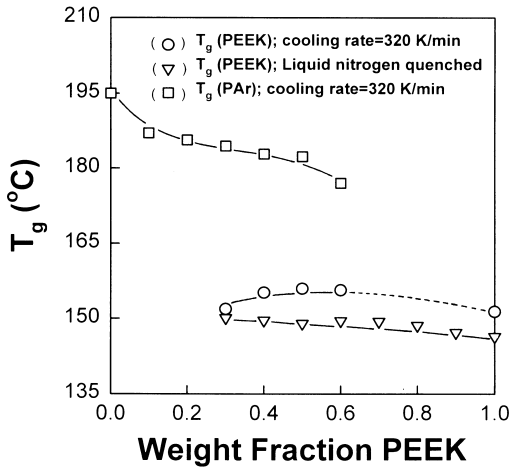

Fig. 1. Effect of blend compositions on the T_gs of PAr and PEEK in the PEEK–PAr blends: (○) T_g of PEEK obtained by 320 K/min cooling; (▽) T_g of PEEK obtained by quenching in liquid nitrogen; (□) T_g of PAr obtained by 320 K/min cooling.

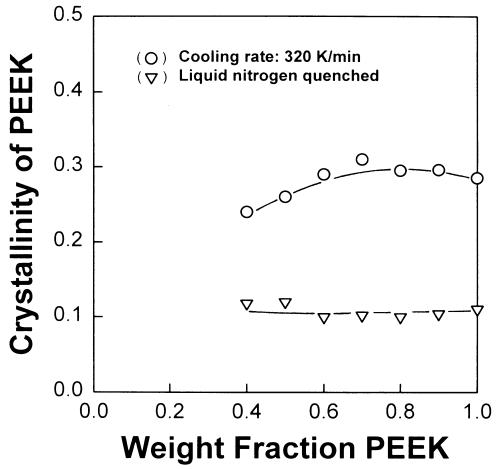

Fig. 2. Effect of blend composition on the crystallinity of PEEK in the PEEK–PAr blends: (○) cooling rate = 320 K/min; (▽) liquid nitrogen quenching.

3. Results and discussion

3.1. T_g of PEEK–PAr blends

The thermal behavior of the PEEK–PAr blends was studied using DSC. Fig. 1 shows the T_g of PEEK in the PEEK–PAr blends with the cooling rates. When the cooling rate is 320 K/min, the T_g of PEEK in the blends increased by about 1–5° with blend composition. For the 9:1, 8:2, and 7:3 PEEK–PAr blends, the T_g of PEEK in the blends was not able to be detected clearly since the T_gs of PEEK and PAr appeared very close to each other. The T_g of PAr in the PEEK–PAr blends is also shown in Fig. 1. From Fig. 1, we can see that the T_g of PAr in the blends decreases by about 7–18° with blend composition. From the results of the T_gs of the PEEK–PAr blends, it is suggested that PEEK and PAr are partially miscible.

From the T_gs of PEEK and PAr in the PEEK–PAr blends, we can estimate the apparent weight fraction of PEEK and PAr dissolved in the PAr-rich phase and the PEEK-rich phase, respectively [13–16]. The apparent weight fractions of PEEK in the PEEK-rich phase and the PAr-rich phase were determined by the Fox equation [17], which is often used to describe the dependence of T_g on composition in a miscible blend system. From the apparent weight fractions which we have calculated from the glass transition temperatures of the blends, we can then estimate the Flory–Huggins polymer–polymer interaction parameter (χ_{12}), provided that the system is at equilibrium or nearly so.

For the partially miscible polymer blends, the χ_{12} of the

polymer blends can be determined by Eq. (1) [13–16]:

$$\chi_{12} = \frac{\{(\phi'_1 2 - \phi''_1 2)[m_2 \ln(\phi''_1/\phi'_1) + (m_1 - m_2)(\phi'_2 - \phi''_2)] + (\phi'_2 2 - \phi''_2 2)[m_1 \ln(\phi''_2/\phi'_2) + (m_2 - m_1)(\phi'_1 - \phi''_1)]\}}{2m_1 m_2(\phi'_1 2 - \phi''_1 2)(\phi'_2 2 - \phi''_2 2)} \quad (1)$$

where ϕ'_1 is the apparent volume fraction of PEEK dissolved in the PEEK-rich phase, ϕ''_1 the apparent volume fraction of PEEK in the PAr-rich phase, and m_1 and m_2 are essentially the number-average degree of polymerization of the PEEK and PAr components, respectively. The volume fraction was obtained from the weight fraction divided by the density of each polymer.

Using Eq. (1), the χ_{12} from the measured volume fractions for the PEEK–PAr blends was calculated. The values of $m_1 = 39.2$ and $m_2 = 51.4$ were used. A repeat unit of PAr has been chosen as a lattice site volume. The χ_{12} values of the PEEK–PAr blends are found to be 0.058 ± 0.002 at 360°C. The critical value of χ_{12}, $(\chi_{12})_c$ was also calculated and found to be 0.045 for the PEEK–PAr blends [18]. It can be surmised that if $\chi_{12} < (\chi_{12})_c$ is observed, then the polymers are compatible with each other and there will be no phase separation. If $\chi_{12} > (\chi_{12})_c$ is observed in the blends, phase separation will occur. For the above PEEK–PAr blends, the values of χ_{12} are greater than the values of $(\chi_{12})_c$ which indicates that the PEEK–PAr blends are immiscible under the mixing condition.

3.2. Rigid amorphous fraction of PEEK in the PEEK–PAr blends

The crystallinity of PEEK in the PEEK–PAr blends is shown in Fig. 2. The degree of crystallinity (X_c) of PEEK was calculated by the following relation: $X_c = \Delta H_f/\Delta H_0$, where ΔH_0 is the heat of fusion of the pure crystalline sample, which is 130 J/g in the literature [4]. ΔH_f is the heat of fusion of PEEK in the PEEK–PAr blends, obtained from DSC measurement. In Fig. 2, we can see that the crystallinity of PEEK in the blends is found to be 0.24–0.32 with cooling rates in DSC. The crystallinity of PEEK in the PEEK–PAr blends quenched in the liquid nitrogen is found to be 0.10–0.12 with composition.

Several researchers have studied the rigid amorphous phase for pure PEEK [10–12] and for the blends of PEEK and poly(ether imide) [2]. Cheng and coworkers [10] have studied the thermal properties of PEEK using DSC and they have shown that a portion of the amorphous phase of PEEK remains rigid above T_g, since PEEK has a less flexible structure. Similar results for PEEK have been observed by Huo and Cebe [11] and Kalika and Krishnaswamy [12] using the dielectric relaxation of PEEK. They have found that the specific heat increment (ΔC_p) at T_g is sometimes not consistent with the amorphous weight fraction ($1 - X_c$) for semicrystalline polymers [11,12]. That is, from ΔC_p one can calculate only an overall 'rigid fraction (X_f)' that remains solid beyond the glass transition region by Eq. (2). The overall rigid fraction (X_f) consists of the crystalline fraction (X_c) and the rigid amorphous fraction (X_r). Thus, they 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 Eq. (2) [10]:

$$X_f = 1 - \frac{\Delta C_p}{\Delta C_p^a} \quad (2)$$

where X_f is the overall rigid fraction, ΔC_p the specific heat increment at T_g of the semicrystalline PEEK in the PEEK–PAr blends, and ΔC_p^a the specific heat increment at the T_g of the fully amorphous PEEK in the PEEK–PAr blends. $\Delta C_p/\Delta C_p^a$ is the flexible amorphous fraction. The ΔC_p^a values were estimated by normalizing the ΔC_p values of the liquid nitrogen quenched PEEK–PAr blends as Eq. (3):

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

Then, the rigid amorphous fraction (X_r) of PEEK in the PEEK–PAr blends can be determined as Eq. (4):

$$X_r = 1 - \frac{\Delta C_p}{\Delta C_p^a} - X_c. \quad (4)$$

Using Eqs. (2) and (4), we can calculate the X_r of PEEK in the PEEK–PAr blends from the measured ΔC_p and ΔH_f of PEEK in the blends which are shown in Table 2. In Table 2, the X_f, X_c, and X_r of PEEK for the 10:0, 5:5, 4:6 PEEK–PAr

Table 2
Thermal properties of the PEEK–PAr blends which were cooled with a cooling rate of 320 K/min

Blend[a]	ΔC_p[b] (J/g K)	ΔC_p^a[c] (J/g K)	ΔC_p[d] (J/g K)	X_f[e]	X_c[f]	X_r[g]
1.0	0.293	0.330	0.133	0.59	0.28	0.31
0.5	0.264	0.281	0.107	0.62	0.26	0.36
0.4	0.262	0.275	0.102	0.63	0.24	0.39

[a] Blend composition given as overall weight fraction PEEK in the PEEK–PAr blends.
[b] Specific heat increment at T_g of PEEK in the liquid nitrogen quenched PEEK–PAr blends.
[c] Specific heat increment at T_g of PEEK in the fully amorphous PEEK–PAr blends, data from Eq. (3).
[d] Specific heat increment at T_g of PEEK in the PEEK–PAr blends: cooling rate = 320 K/min.
[e] The overall rigid fraction of PEEK in the PEEK–PAr blends: $X_f = 1 - \Delta C_p/\Delta C_p^a$.
[f] Crystallinity of PEEK in the PEEK–PAr blends, data from Fig. 2.
[g] The rigid amorphous fraction of PEEK in the PEEK–PAr blends: $X_r = X_f - X_c$.

blends are also presented. In Table 2, we can see that the X_r of PEEK in the 5:5 and 4:6 PEEK–PAr blends is larger than the X_r of pure PEEK. The increase of X_r with PAr composition suggests that the PEEK crystalline becomes less perfect by the addition of PAr in the PEEK–PAr blends.

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