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# Miscibility of poly(ether ether ketone)/poly(ether diphenyl ether ketone) blends

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Poly(ether ether ketone) and poly(ether diphenyl ether ketone) homopolymers are prepared by nucleophilic substitution routes. Miscibility of PEEK/PEDEK blends has been studied by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (d.s.c.). The results indicate that for PEEK/PEDEK blends, when the PEDEK content (weight fraction) is greater than 0.20 and less than 0.75, PEEK and PEDEK components form independent crystalline regions, i.e. they are immiscible; when the PEDEK content is in the range $W_{\mathrm{PEDEK}} \leqslant 0.20$ or $\geqslant 0.75$, a rich PEEK- or PEDEK-rich content crystallizes from a mixed melt and PEEK and PEDEK are miscible. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: poly(ether ether ketone); poly(ether diphenyl ether ketone); blends)**

## *Introduction*

Poly(ether ether ketone) (PEEK) is a high-performance engineering plastic with excellent thermal, electrical, mechanical and chemical properties, and has been widely applied in the electronic and engineering industries and the aerospace field. Usually, in poly(aryl ether ketone) (PAEK) blends, it is a crystalline polymer blended with an amorphous polymer, for example, poly(ether sulfone)[1,2] and poly(ether imide)[3-5]. Some literature concerned with poly(aryl ether ketone) blends has been reported[6]. In this paper, the miscibility of PEEK/PEDEK [poly(ether diphenyl ether ketone)] blends is investigated.

## *Experimental*

Diphenylsulfone as a solvent was heated until it became a transparent solution, holding at 140 ± 2°C with stirring under a nitrogen atmosphere. Weighed PEEK and PEDEK were dissolved together in this solvent and blended at 260°C for 2 h. The solution was then poured into cold water and a precipitate obtained. After crushing the precipitate, filtering and washing with acetone and distilled water, and drying in an oven at 140°C for 24 h, the powder resin reached a constant weight. The powder resin was wrapped in aluminium foil and moulded on a compression machine at 440°C. In order to obtain an amorphous film, the above film was quenched immediately in an ice/water mixture. A crystalline film with a greater degree of crystallinity is obtained by cooling the film slowly from the melting temperature to room temperature on the compression machine. All samples used in the present paper are film samples. Inherent viscosities of pure PEEK and PEDEK homopolymers are 0.74 and 1.30 $\mathrm{dl\,g^{-1}}$, respectively.

Perkin–Elmer DSC-7 differential scanning calorimetry (d.s.c.) was carried out at a heating rate of 10°C $\mathrm{min^{-1}}$ from 50 to 450°C under a nitrogen atmosphere, and at least 10 mg of the film sample used for d.s.c. measurement.

Wide-angle X-ray difrraction (WAXD) was measured using a PW1700 diffractometer (Philips Co., Holland) with a nickel-filter and Cu$K_{\infty}$ radiation at a scanning rate of 0.3° $\mathrm{min^{-1}}$ in a range of $5° \leqslant 2\theta \leqslant 60°$. All samples were prepared by compression moulding of powder at 440°C for 5 min, then the moulded films were cooled slowly from the melting temperature to room temperature on the compression machine.

## *Results and discussion*

*Single glass transition.* The only difference in chemical structure between PEEK and PEDEK is that PEDEK has a diphenyl group between two ether groups instead of the phenyl group in PEEK. Because diphenyl groups are inserted, the molecular chain rigidity is increased. The PEDEK homopolymer has a $T_g$ at 171°C (measured by d.s.c.). The d.s.c. analysis of PEEK/PEDEK blends is shown in *Figure 1*; before measurement samples were proved to be amorphous by WAXD pattern. Each blend exhibits only a single glass transition which was almost not broadened. The PEEK's $T_g$ was 144 or 145°C and $T_g$ difference between PEEK and PEDEK is in a range of 25–30°C. If the PEEK/PEDEK blend is immiscible, the d.s.c. curve may show

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one or two broadened glass transitions. In fact, each PEEK/PEDEK blend showed only one $T_g$ which seems to imply that PEEK and PEDEK are probably miscible. But the glass transition temperature as a criterion for blend miscibility has some limitations, thus other measurements must be carried out to prove the conclusion.

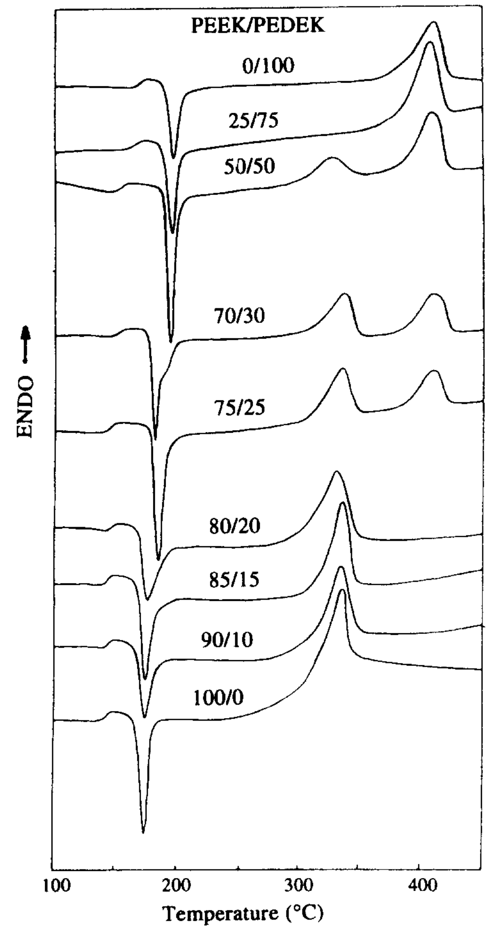

**Figure 1** D.s.c. melting traces of originally amorphous PEEK/PEDEK blends

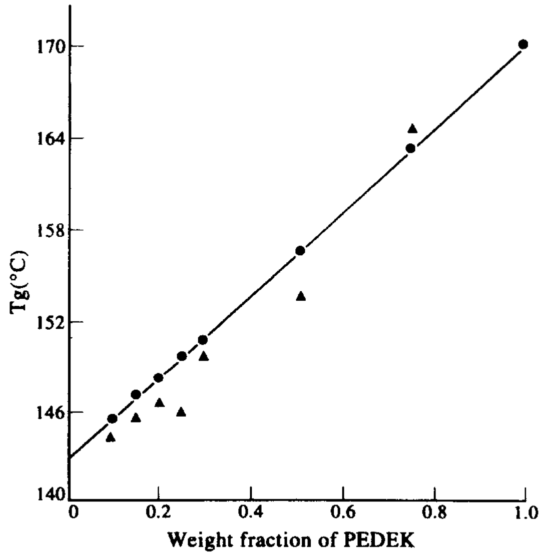

**Figure 2** $T_g$ of PEEK/PEDEK blend as a function of weight fraction of PEDEK in blend: ▲, experimental; ●, calculated from the Fox equation

The $T_g$s of these blends roughly follow the Fox equation: $1/T_g = W_1/T_{g1} + W_2/T_{g2}$, where $T_g$, $T_{g1}$ and $T_{g2}$ are the glass transition temperatures of blend, PEEK and PEDEK, respectively. $W_1$ and $W_2$ are the weight fraction of PEEK and PEDEK, respectively. In *Figure 2*, the experimental $T_g$ of blend is in agreement with calculated values from the Fox equation.

*Crystalline phase.* In *Figure 1* each curve shows a cold crystallization peak; their temperatures are listed in *Table 1*.

Under the same scanning rate, pure PEEK and PEDEK exhibited their cold crystallization peak temperatures at 171 and 198°C. Cold crystallization temperature increased gradually with PEDEK content, i.e. crystal growth temperature rose gradually due to a reduction of mobility (increase in $T_g$). The PEEK/PEDEK 75/25 blend gave a cold crystalization peak temperature at 180°C, and the 70/30 blend at 182°C. Furthermore, the latter showed a shoulder peak at 195°C which suggests that the two crystals grow at different temperatures.

During d.s.c. scanning, the amorphous sample experiences both crystallization and melting processes. If in the course of crystallization two kinds of crystals form independent of each other, two melting processes must be exhibited as long as the difference in the melting point between two pure homopolymers is large enough. *Table 2* lists the melting peak temperatures. When $0.2 < W_{\mathrm{PEDEK}} < 0.75$, two melting peaks are found, the temperatures of which almost correspond to PEEK and PEDEK homopolymers' melting points, except for the 50/50 blend which exhibits the first melting peak at 327°C.

WAXD patterns are illustrated in *Figure 3*. For PEEK, the four main diffraction peaks are at 18.71°,

**Table 1** Cold crystallization peak temperatures for PEEK/PEDEK blends

| PEEK/PEDEK (weight ratio) | Cold crystallization peak temperature (°C) |
|---|---|
| 100/0 | 171 |
| 90/10 | 174 |
| 85/15 | 175 |
| 80/20 | 177 |
| 75/20 | 186 |
| 70/30 | 182 |
| 50/50 | 195 |
| 25/75 | 196 |
| 0/100 | 198 |

**Table 2** The melting peak temperatures of PEEK/PEDEK blends where the original film samples are amorphous

| PEEK/PEDEK (weight ratio) | $T_{m1}$ (°C) | $T_{m2}$ (°C) |
|---|---|---|
| 100/0 | 336 | — |
| 90/10 | 335 | |
| 85/15 | 335 | — |
| 80/20 | 330 | — |
| 75/25 | 335 | 408 |
| 70/30 | 338 | 407 |
| 50/50 | 327 | 408 |
| 25/75 | — | 407 |
| 0/100 | — | 409 |

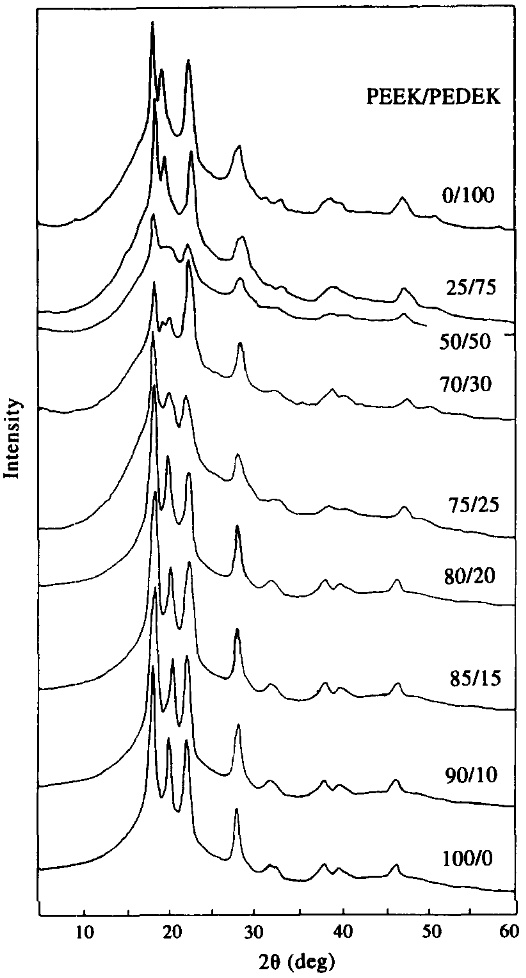

**Figure 3** WAXD patterns of PEEK/PEDEK blends. Film samples were cooled slowly from the melting temperature to room temperature

20.67°, 22.56°, 28.65°, and for PEDEK at 18.42°, 19.588°, 23.645°, 28.20°. An obvious difference between PEEK and PEDEK appears at 20.67° of PEEK and 19.588° of PEDEK. In *Figure 3*, 90/10, 85/15, 80/20, 75/25, 25/75 PEEK/PEDEK blends also show the four main diffraction peaks like PEEK and PEDEK homopolymers, similar to a rich content. But for 70/30, 50/50 PEEK/PEDEK blends the diffraction peaks between 19° and 21° are obviously different from those of the others. The 70/30 blend shows two peaks at 19.678° and 20.49° similar to the combination of PEEK and PEDEK homopolymers, and the 50/50 blend shows a decreased intensity as well as a broadened peak. The above facts imply that the 50/50 and 70/30 PEEK/PEDEK blends, cooled slowly from the melt, contain two kinds of cells which are independent of each other. After the samples were measured by WAXD, they were immediately heated from 100°C by d.s.c. (*Figure 4*). PEEK/PEDEK 90/10, 85/15, 80/20, 25/75 blends all show only one melting peak whose temperature is lower than that of pure PEEK or PEDEK (see *Table 3*). This phenomenon of melting point depression was earlier observed in compatible blends by Nishi and Wang[7] who proposed the relative equation. In our study crystalline/crystalline polymer blends also show melting point depression, indicating PEEK and PEDEK to be miscible at $W_{\mathrm{PEDEK}} \leqslant 0.20$ or $\geqslant 0.75$.

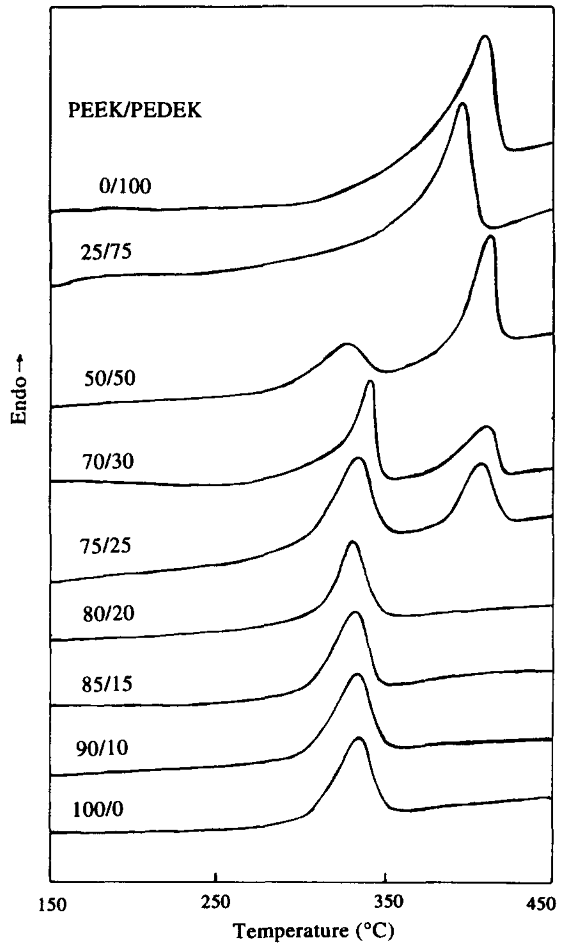

**Figure 4** D.s.c. melting traces of PEEK/PEDEK blends. Film samples were cooled slowly from the melting temperature to room temperature

PEEK/PEDEK 75/25, 70/30, 50/50 blends show two melting peaks, the temperatures of which almost correspond to the melting points of pure PEEK and PEDEK, which indicates that in the above ratio blends PEEK and PEDEK crystallize independently and form separate cells. Although PEEK is independent of PEDEK, the two still interact. The 50/50 blend exhibits a first melting point at 327°C lower than that of pure PEEK.

## *Conclusion*

The crystalline polymers PEEK and PEDEK have similar chemical structures. In the PEEK/PEDEK

**Table 3** The melting peak temperatures of PEEK/PEDEK blends where the film samples were cooled slowly from the melting temperature to room temperature

| PEEK/PEDEK (weight ratio) | $T_{\mathrm{m1}}$ (°C) | $T_{\mathrm{m2}}$ (°C) |
|---|---|---|
| 100/0 | 334 | — |
| 90/10 | 333 | — |
| 85/15 | 332 | — |
| 80/20 | 330 | — |
| 75/25 | 334 | 405 |
| 70/30 | 341 | 410 |
| 50/50 | 325 | 411 |
| 25/75 | — | 396 |
| 0/100 | — | 413 |

blends, when PEDEK is in the range 0.20–0.75, PEEK and PEDEK are immiscible, forming their own crystalline regions, i.e. one is independent of the other; when the PEDEK content is in the range $\leqslant 0.20$ or $\geqslant 0.75$, PEEK and PEDEK are miscible.

## REFERENCES

1 Wu, Z., Zheng, Y., Yan, H., Nakamura, T., Nozawa, T. and Yosomiya, R. *Angew. Makromol. Chem.* 1989, **173,** 163

2 Yu, X. M., Zheng, Y. B., Wu, Z. W., Tang, X. Y. and Jiang, B. Z. *J. Appl. Polym. Sci.* 1990, **41,** 2649

3 Torre, L. and Kenny, J. M. *Polym. Compos.* 1992, **13,** 380.

4 Chen, H. L. and Porter, R. S. *J. Polym. Sci. Part B: Polym. Phys.* **1993; 31,** 1845.

5 Sauer, B. B. and Hsiao, B. S. *J. Polym. Sci. Part B: Polym. Phys.* 1993, **31,** 917

6 Sham, C. K., Guerra, G., Karasz, F. E. and MacKnight, W. J. *Polymer* 1988, **29,** 1016

7 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8,** 909