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The multiple melting behaviour of immiscible poly(ether ether ketone)/poly(ether diphenyl ether ketone) blend

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Poly(ether ether ketone)/poly(ether diphenyl ether ketone) blend containing 30 wt% PEDEK was used to investigate the melting behaviour of immiscible PEEK/PEDEK blends. The results measured from differential scanning calorimetry (d.s.c.) and wide-angle X-ray diffraction (WAXD) showed that immiscible PEEK/PEDEK blends isothermally crystallized at a temperature between T_g and T_{m_2} (PEEK's normal melting point) from the glassy state also exhibited the multi-melting behaviour like poly(aryl ether ketones) homopolymers. In addition, the low-temperature melting peak was independent of composition of poly(aryl ether ketones) blends and only associated with the thermal history. © 1997 Elsevier Science Ltd.

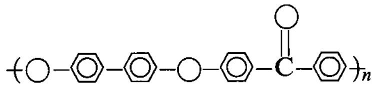
(Keywords: multiple melting behaviour; PEEK/PEDEK blends; immiscible)

INTRODUCTION

Some polymers crystallized from the melt or from the glassy state exhibit the multiple endotherms in melting experiments, for example, PE, PP, nylon 6, nylon 66, iPS, PET. One of them, iPS could yield from one to three endothermal peaks under different crystallization conditions[1,2]. Zhou[2] studied PET isothermally crystallized from the melt on a DSC. Subsequent melting curves showed three endotherms under many crystallization conditions, which are attributed to the melting of crystallites formed during primary and secondary crystallization processes and the melting of crystals formed during recrystallization during the melting scan. Yagpharov[3] extensively investigated a few linear crystalline polymers and considered that two types of crystal formation exist in all the typical linear crystallizing polymers, secondary crystallization formed the crystals of 'fringed micelle' and these crystals have a number of properties with differ greatly from those of the primary crystals.

Poly(ether ether ketone) (PEEK) as a semicrystalline thermoplastic resin with excellent mechanical property and temperature resistance has been applied in the electronic engineering industry and aerospace fields[4]. Since the double-melting phenomenon of PEEK was first reported by Blundell and co-workers[5], some researchers have extensively studied this behaviour for the poly(aryl ether ketones) family[6–20]. Two main hypotheses are put forward. Hypothesis I considered that the double-melting peaks were attributable to melting and recrystallization during d.s.c. scanning; hypothesis **II** proposed that two melting peaks originated from the two different morphological crystals.

We have studied the double-melting behaviour of pure PEDEK homopolymer with the following chemical structure



PEDEK has a T_g of 171°C and a T_m of 408°C. *Figure 1* shows the d.s.c. curves of PEDEK crystallized from the glassy state at different temperatures. Its double-melting phenomenon is similar to that of PEEK. According to PEDEK data, we propose a viewpoint to explain the double-melting behaviour of *para*-substituted poly(aryl ether ketones) when a sample is crystallized at a temperature from the glassy state. The double-melting behaviour of PAEKs isothermally crystallized from the glassy state is associated with the perfect crystal and imperfect crystal. The perfect crystal gives rise to the high-melting peak (also called normal melting point); the imperfect crystal results in the low-melting peak. When the crystallization temperature is high enough ($T_{m2} - T_c \leq 20$°C), the imperfect crystal is close to the perfect one[21].

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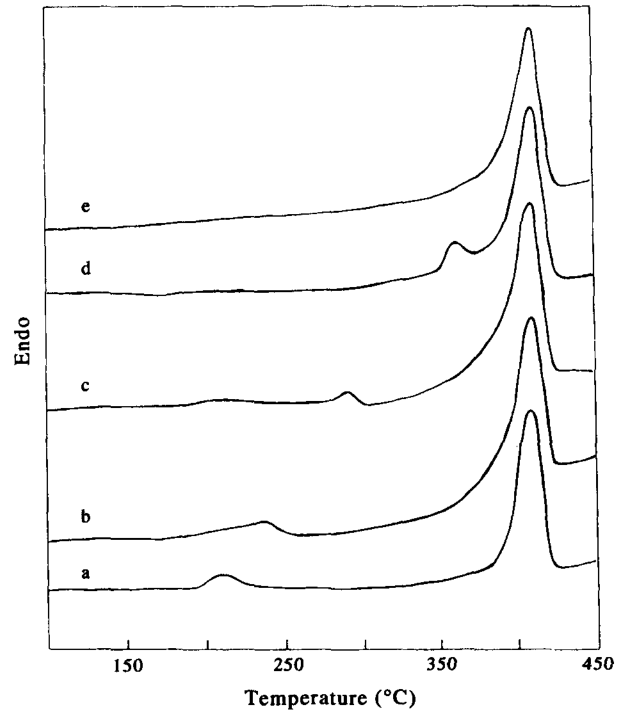

Figure 1 D.s.c. traces of pure PEDEK film isothermally crystallized from the glassy state at a temperature for 30 min. (a) 200°C, (b) 230°C, (c) 280°C, (d) 350°C, (e) 390°C

Usually, poly(aryl ether ketone) is a crystalline polymer blended with an amorphous polymer, such as poly(ether sulfone)[22,23] and poly(ether imide)[24–26]. Relatively few studies have paid attention to two poly(aryl ether ketone) blends[27]. Poly(ether diphenyl ether ketone) have blended with PEEK and experimental results (*Figure 2* exhibited the d.s.c. and WAXD results of different content of PEDEK, and ref. 28 gave the detailed discussion) indicated that PEEK and PEDEK were miscible in the range $W_{\mathrm{PEDEK}} \leqslant 0.20$ or $\geqslant 0.75$, namely, immiscible in the range $0.20 < W_{\mathrm{PEDEK}} < 0.75$[28]. For immiscible PEEK/PEDEK blends, PEEK and PEDEK form crystalline regions respectively. We select a blend with 30 wt% PEDEK to study the melting behaviour which has been widely studied in poly(aryl ether ketones) homopolymers.

EXPERIMENTAL

Both PEEK and PEDEK were synthesized through the nucleophilic route and their inherent viscosities were 0.74 and 1.30 dl g^{-1} in 98% sulfuric acid, respectively. Pure PEDEK had a T_g of 171°C and a T_m of 408°C measured by d.s.c.

Diphenylsulfone as a solvent was heated until it became a transparent solution, holding at 140 ± 2°C with stirring under a nitrogen atmosphere. PEEK and PEDEK were weighed in the given proportion and added to the solvent, then blended at 260°C for 2 h. The solution was poured into cold water and the precipitate was obtained. After the crude blend was crushed, filtered, washed and dried, a fine powder resin was finally obtained.

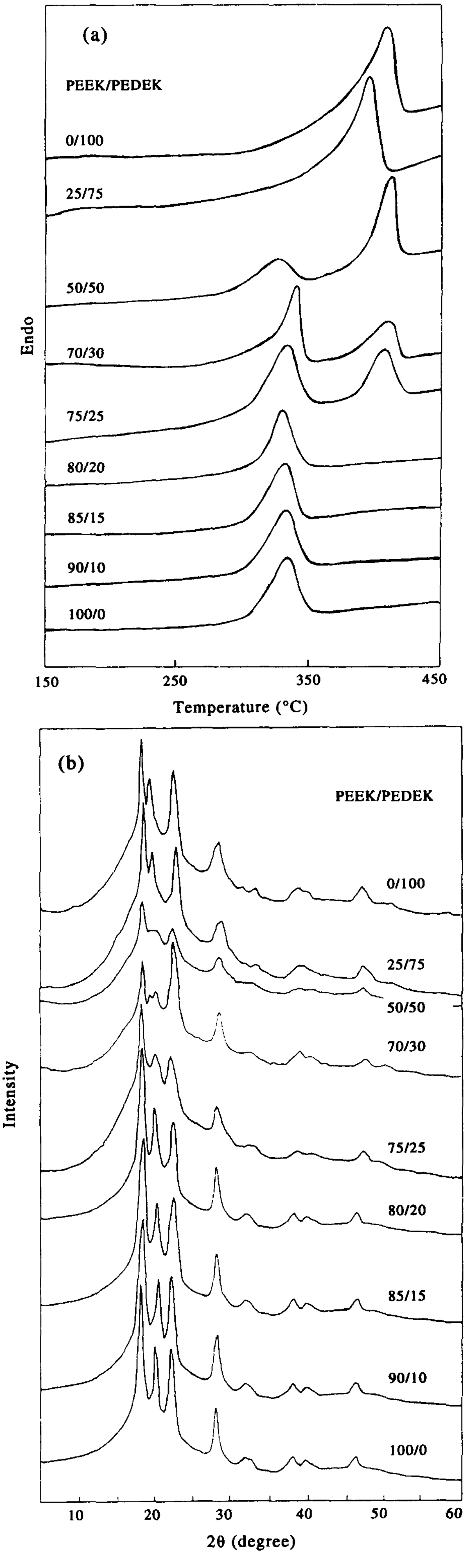

Figure 2 Miscibility of PEEK/PEDEK blends, film samples cooled slowly from the melting temperature to room temperature. (a) D.s.c. melting traces at a heating rate of 10°C min^{-1}, (b) WAXD patterns

The powder resin wrapped up in an aluminium foil was moulded on a compression machine at 440°C. The moulded film was quenched into an ice/water mixture as quickly as possible in order to get an amorphous sheet.

Isothermally crystallized sample: an amorphous sheet was put into an oven controlled at a temperature for 30 min, then was withdrawn to ambient temperature.

Perkin–Elmer DSC-7 d.s.c. was carried out at a heating rate of $10°C\,min^{-1}$ from 50 to 450°C under a nitrogen atmosphere.

Wide-angle X-ray diffraction (WAXD) was measured by a PW1700 diffractometer from Philips Co. (Holland) with CuK_α radiation and nickel-filtered at a scanning rate of $0.3°\,min^{-1}$ from 5 to 60°.

RESULTS AND DISCUSSION

PEEK/PEDEK blend containing 30 wt% PEDEK proved by d.s.c. and WAXD was immiscible[28]. *Figure 3* shows the d.s.c. curves of originally amorphous PEEK blend (30 wt% PEDEK) and PEDEK. The PEEK and PEDEK showed their cold crystallization peaks at 171 and 198°C, respectively. But the cold crystallization peak of the blend appeared at 182°C with a shoulder peak of 190°C which suggested that in this temperature range from 171 to 214°C two kinds of crystals grew which melted at 338°C and 405°C similar to the melting point of pure PEEK and PEDEK, 335°C and 405°C.

The d.s.c. traces of blend annealed at different temperatures are given in *Figure 4*. The blend showed its T_g at 150°C. As the sample was crystallized at 150°C, the cold crystallization peak appeared at 185°C but a shoulder peak cannot be seen; when the blend was crystallized at 230, 280, 290°C, the low-temperature melting peaks exhibited at 239, 288 and 297°C, respectively. However, this phenomenon has been observed in many poly(aryl ether ketone) homopolymers. The plot of one low and two high temperature melting peaks vs crystallization temperature are shown in *Figure 5*. The low-temperature peak appeared at about 10°C above T_c, but two high-temperature melting peaks nearly kept constant values with crystallization temperature. If PEEK and PEDEK content in the blend is independent of each other, the blend annealed at 350°C must exhibit a low-temperature peak at 360°C or so like pure PEDEK. In fact, there was not a so-called low-temperature peak, only two melting peaks at 334°C and 402°C corresponding to the PEEK and PEDEK contents.

Our previously proposed viewpoint[21] can explain the above phenomena. First, both PEEK and PEDEK molecules exist in the PEEK/PEDEK blend, which was

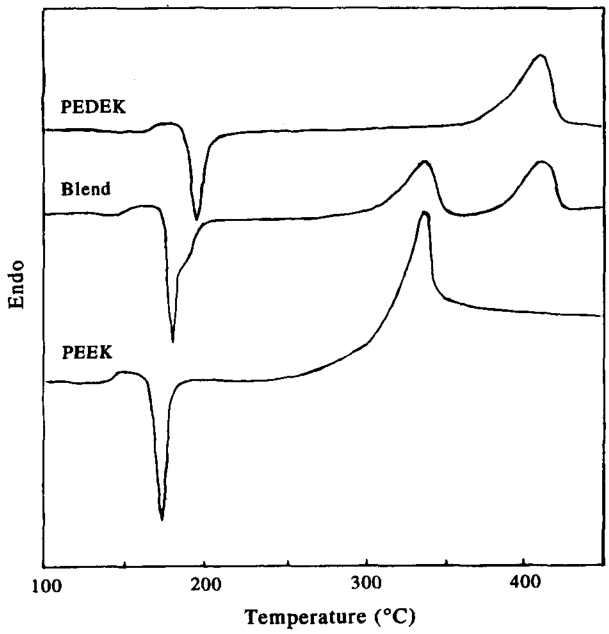

Figure 3 D.s.c. traces of originally amorphous PEEK, PEEK/PEDEK blend, PEDEK at a heating rate of $10°C\,min^{-1}$

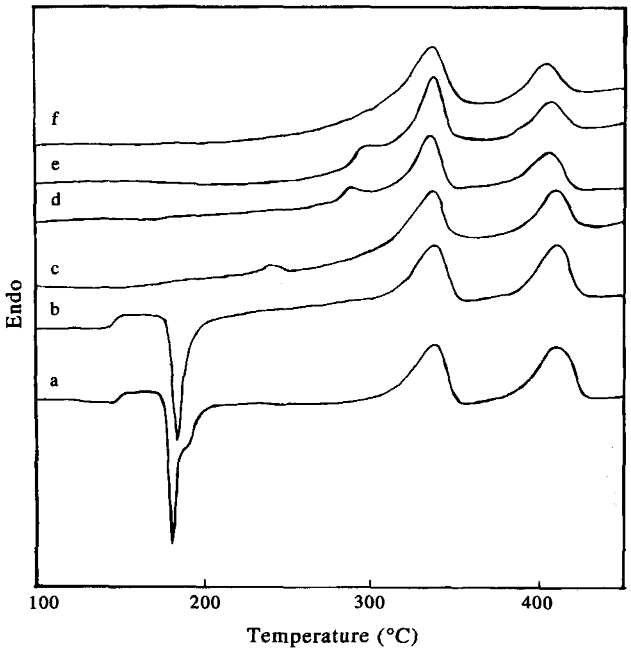

Figure 4 D.s.c. traces after blend was isothermally crystallized at different temperatures for 30 min. (a) Originally amorphous, (b) 150°C, (c) 230°C, (d) 280°C, (e) 290°C, (f) 350°C

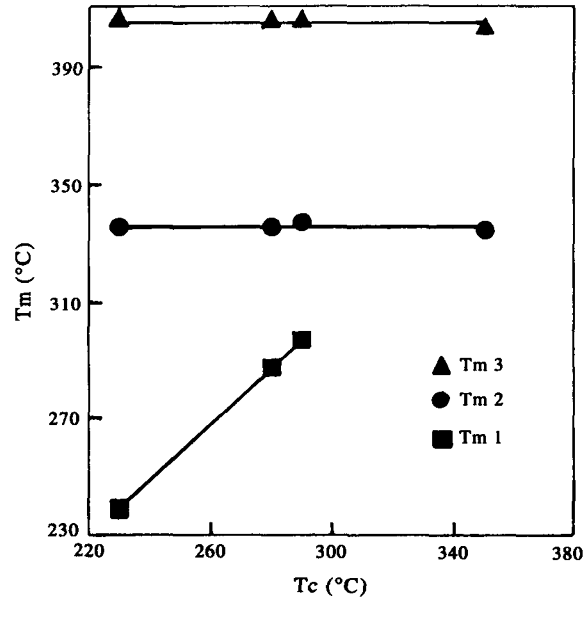

Figure 5 Variation of the low and high melting peak temperatures with crystallization temperature

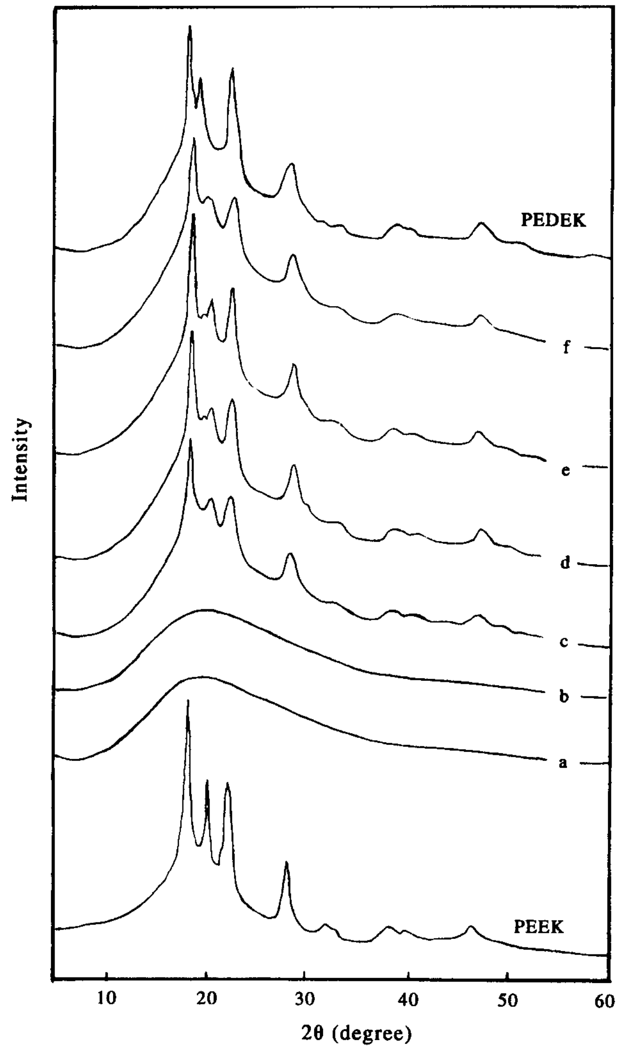

Figure 6 WAXD patterns after blend was isothermally crystallized at different temperatures for 30 min. (a) Originally amorphous, (b) 150°C, (c) 230°C, (d) 280°C, (e) 290°C, (f) 350°C. PEEK and PEDEK homopolymers as references

crystallized at a temperature (lower than 334°C) from the glassy state. On the one hand, two kinds of molecular chains can arrange regularly to form perfect PEEK and PEDEK crystals which cause two high-temperature melting peaks. Again, a few imperfect PEEK and PEDEK crystals were also formed whose regularity was related to crystallization temperature and independent of composition of poly(aryl ether ketone), namely the low-temperature melting peak was just associated with the thermal history. In *Figure 4*, the curve f did not show a low-temperature melting peak, why? When the blend was isothermally crystallized at 350°C, PEDEK molecules can arrange regularly to form its crystalline region, but most of the PEEK melted and its molecules moved vigorously and randomly and destroyed a few imperfect PEDEK forming crystals. After annealing, a sample was laid in the ambient atmosphere, where the PEEK content still had a little crystallinity which was proved by WAXD patterns (shown in *Figure 4*). It was obvious that the diffraction intensity of the PEEK content at 20.6° decreased in that, meanwhile, PEDEK at 19.6° increased compared with the blend crystallizing at 290°C. When sample f was scanned by d.s.c., the PEEK content crystallized rapidly and melted at 334°C (peak temperature). This PEEK crystallization prevented a few imperfect crystals forming in a PEDEK content, so a low-temperature melting peak cannot be observed.

CONCLUSIONS

The immiscible PEEK/PEDEK blend isothermally crystallized under the PEEK melting point also exhibited the multiple melting behaviour of poly(aryl ether ketones) homopolymers. But when the blend crystallized at a temperature between PEEK and PEDEK melting points, during d.s.c. scanning, PEEK content crystallized dominantly and made it impossible to form a few imperfect crystals in the PEDEK content, so there was no low-temperature melting peak at all.

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