Morphology, crystallization kinetics and melting behaviour of the blends of poly(ether ether ketone) with poly(ether sulfone with cardo side group)

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The morphology, crystallization kinetics and melting behaviour of the blends of poly(ether ether ketone) (PEEK) with poly(ether sulfone with cardo side group) (PES-C) prepared by casting from solution were studied using optical microscopy, scanning electron microscopy, wide-angle X-ray scattering and differential scanning calorimetry. The amorphous PES-C was shown to be trapped interfibrillarly or interlamellarly in the spherulites of PEEK at a relatively low crystallization temperature. Its addition causes dilution of the nuclei in PEEK and a great depression in the spherulitic growth rate and overall crystallization rate of PEEK. Also, melting point and crystallinity of PEEK are lowered by PES-C. Besides composition, crystallization temperature was shown to have an influence on the morphology, crystallization kinetics and melting behaviour of the blends.

(Keywords: poly(ether ether ketone); poly(ether sulfone with cardo side group); polyblend; morphology; crystallization kinetics; melting behaviour)

INTRODUCTION

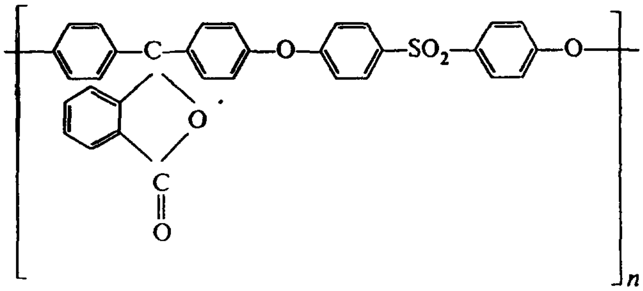
There is growing interest in the practical and theoretical investigation of the properties of polymer blends which involve a crystallizable and an amorphous component[1–7]. The miscibility, morphology, crystallization and melting behaviour of the crystallizable component are the most interesting features of these blends[5]. It is known that the majority of such blends are immiscible, and few of them are fully miscible or partially miscible, and that the morphology, crystallization and melting behaviour of the crystallizable component in the blends depend on the miscibility of the blends. In general, an amorphous component which finally disperses within spherulites or in interspherulitic regions in large domains has been found to have little influence on the crystallization of the crystallizable component in immiscible blends[5,8,9]. In contrast, very fine intraspherulitic dispersion of the amorphous component is usually seen in miscible blends[1,5,10], and in these blends, a large decrease of crystal growth and a change of melting behaviour caused by the amorphous component may appear[3,5,11,12].

In this laboratory, we have studied the blends of poly(ether ether ketone) (PEEK) with poly(ether sulfone with cardo side group) (PES-C) in order to get a new polymeric material with good mechanical properties and high operating temperature. PEEK is a high-performance polymer which has received much interest recently and has found increasing use in many applications. It is a semicrystalline polymer with a glass transition around 145°C[13]. PES-C, also a high-performance polymer, is a recently invented amorphous polymer with a high glass transition temperature of 265°C[14]. It has been revealed that the blends are partially miscible, and the extent of their final mixing depends on the composition and the treatment temperature[15]. In this work, the morphology, crystallization kinetics and melting behaviours of the blends and the effect of crystallization temperature will be considered.

EXPERIMENTAL

Materials

The PEEK used in this work is powder 450P with molecular weight ($\bar{M}_w$) ~4×10^4, produced by Imperial Chemical Industry (ICI), Wilton, UK. PES-C, supplied by Changchun Institute of Applied Chemistry of Academia Sinica, is also a type of powder with a reduced solution viscosity, a quantity related to its molecular weight, of 0.68 ml g^{-1}. Its chemical structure is[14]:



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Cast films of PEEK/PES-C blends were prepared from the α-chloronaphthalene solution of the polymers. Because α-chloronaphthalene is a solvent of PEEK and PES-C, a good polyblend solution can be obtained at 250–260°C. The crystallized samples used for morphology studies were obtained by first melting the films at 400°C for 10 min, then transferring them to an oven which was held at a certain temperature for isothermal crystallization for 10 h.

Techniques

A Leitz Orthoplan optical microscope equipped with a heating stage and Hitachi S-520 scanning electron microscope (SEM) were used for morphological observation. Before investigation with SEM, the films, which are much thicker than those used in optical observation, were etched with dichloroethane, a good solvent of PES-C, for 24 h and then coated with gold. A Rigraky Giggefex X-ray machine was used for wide-angle X-ray scattering (WAXS) analysis of the crystallized samples.

The spherulitic growth of PEEK in the blends was determined using the optical microscope. At first, the cast films were melted in the heating stage at 400°C for 10 min, immediately followed by cooling to 300°C, then photographed at appropriate intervals. The overall crystallization of the blends was analysed in a Perkin–Elmer DSC-2 in nitrogen atmosphere by first melting the blends at 400°C for 5 min, then cooling them rapidly at $-320^\circ C\,min^{-1}$ to the predetermined temperature and recording the melt crystallization exotherms. By using the Perkin–Elmer Thermal Analysis Data System supplied in the computer of the differential scanning calorimeter, the baseline, the whole crystallization heat, and the heat as a function of time are given automatically. The error of the heat measurements is known to be $0.8\,J\,g^{-1}$. The data were analysed by the usual method[16].

Analysis of the melting behaviour of the blends was also carried out in a Perkin–Elmer DSC-2 which was calibrated with indium before the experiment. A scanning rate of $20^\circ C\,min^{-1}$ was used, and the heat of fusion was determined in the same way as above. The average values of the heats were used to plot figures into which the corresponding errors were incorporated.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows the morphologies of the blends crystallized at 290°C from the melts of different compositions. Birefringent spherulites of PEEK, as reported previously[17,18], are seen. The samples of the blends are completely filled with spherulites in which there are no large separated domains of PES-C. With increasing PES-C content, the size of the spherulites increases, and the texture of the spherulites becomes open. In particular, for the blends containing 60 wt% PES-C, the spherulitic diameter is much larger but the Maltese cross much weaker. Consequently, amorphous PES-C must be included within the PEEK spherulites in interlamellar or interfibrillar incorporation[6,7]. Open

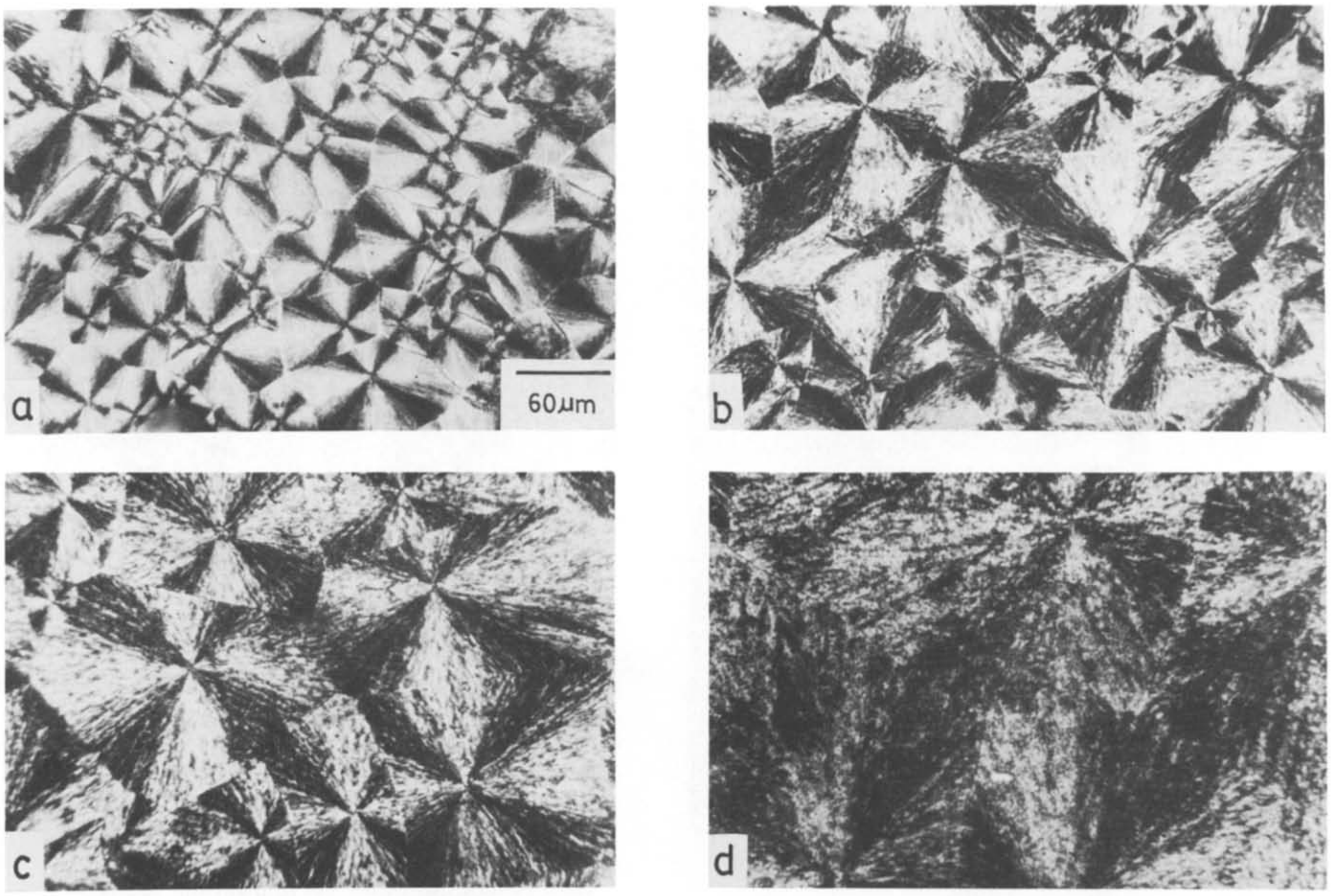

Figure 1 Spherulitic morphology of PEEK/PES-C blends isothermally crystallized at 290°C for 10 h. Blends are: (a) 100/0; (b) 80/20; (c) 60/40; (d) 40/60. All micrographs are to the same scale

texture, which means a relatively small overall crystallinity of a spherulite and is related to the presence of an amorphous component[19], was once observed in the blends of polycaprolactone (PCL) and poly(vinyl chloride) (PVC)[10]. Its appearance in the PEEK/PES-C blends was confirmed in the crystallinity determination.

To obtain further information about the intraspherulitic dispersion of PES-C, SEM was used to examine the spherulites. In *Figure 2*, a micrograph of the etched surface of the blends is shown. Etching with dichloroethane, a good solvent for PES-C, was carried out for long enough to ensure that PES-C was removed to an appropriate depth from the surface. In the figure, the fibrillar texture of PEEK within the spherulites can be seen. This indicates that the PES-C molecules are probably confined to interfibrillar regions of the spherulites in this case. In other words, PES-C might be trapped between the lamellar bundles of PEEK within the spherulites. The partial miscibility of PEEK/PES-C blends revealed previously[15] might be related to such a morphology. Usually, the amorphous component in partially miscible blends is difficult to segregate in interlamellar regions of the crystallizable component, although it can be trapped intraspherulitically in a very fine dispersion. This can be seen in other systems. The blends in which the amorphous components were reported to disperse interlamellarly are miscible ones, such as PCL/PVC, poly(hydroxy ether of bisphenol A) (phenoxy) with PCL[20], poly(vinylidene fluoride) (PVF2) with poly(methyl methacrylate) (PMMA)[2,12], poly(ethylene oxide) (PEO) with PMMA[3,5], and poly(phenylene oxide) (PPO) with isotactic polystyrene (iPS)[4], while those in which interfibrillar dispersion was mainly seen are often partially miscible, like the blends of chlorinated polyethylene (CPE) with PCL[21].

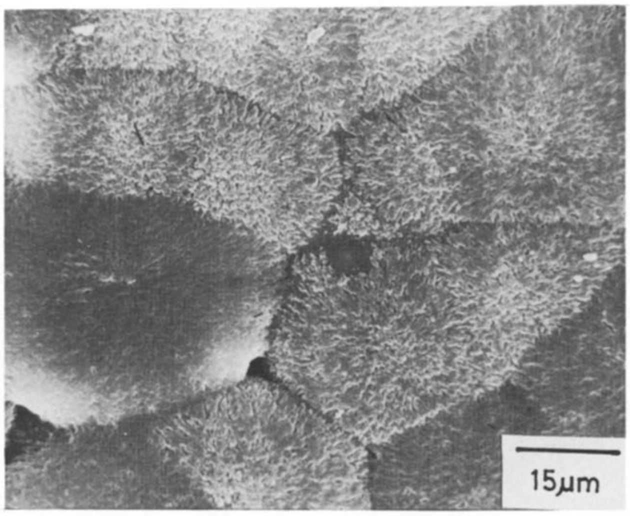

Figure 2 Scanning electron micrograph of etched surface of PEEK/PES-C 40/60 blend crystallized at 290°C

The WAXS curves of PEEK/PES-C blends which crystallized at 290°C from melt are shown in *Figure 3*. Since the positions of the four sharp crystalline reflections of PEEK are independent of the blend composition, it is known that the unit cell dimensions of PEEK remain unchanged after blending with PES-C. By drawing a straight baseline between 10° and 36°, then using the diffraction profile from the amorphous sample to fit a scaled amorphous curve under the diffraction peaks of the crystallized sample with the same composition in the manner described by Blundell and Osborn[22], the crystallinities of the blends were determined as the ratios of the crystalline peaks to the total areas with an error of 0.9%. They decrease with increasing PES-C content as shown in *Table 1*. Furthermore, based on the wt% of PEEK in the blends, the crystallinity of PEEK was obtained and found to decrease.

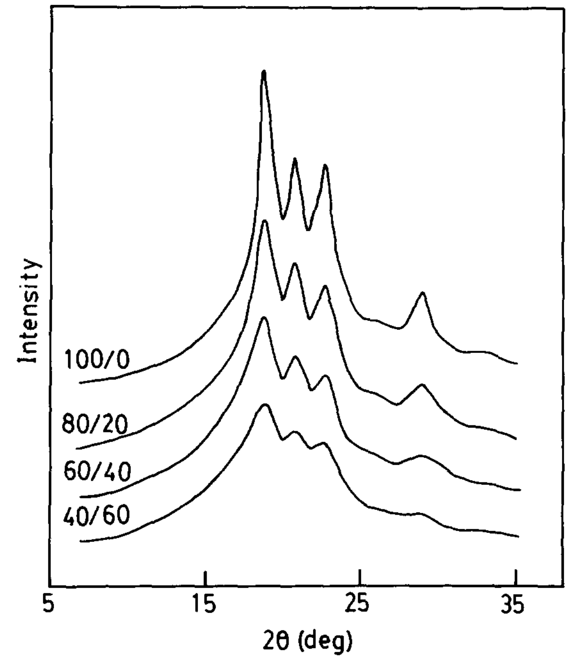

Figure 3 WAXS curves of PEEK/PES-C blends crystallized at 290°C

Table 1 Crystallinity of PEEK/PES-C blends measured by WAXS

PEEK/PES-C	Crystallinity (%)[a] based on total wt	Crystallinity (%) based on wt of PEEK
100/0	30.1	30.1
80/20	22.7	28.4
60/40	16.0	26.6
40/60	10.3	25.7

[a] Error is 0.9%

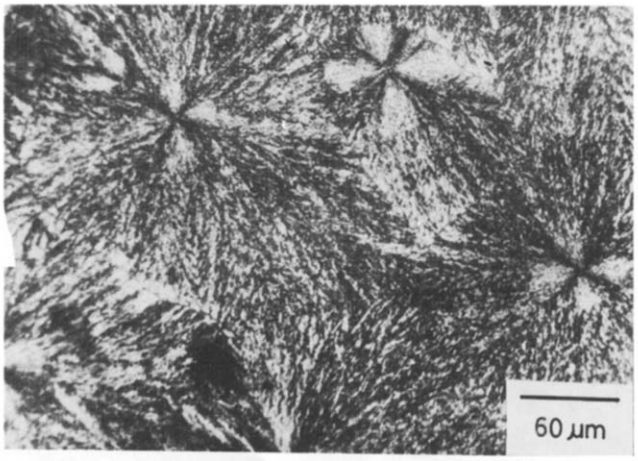

Figure 4 Spherulitic morphology of PEEK/PES-C 40/60 blends isothermally crystallized at 315°C for 10 h

Besides composition, crystallization temperature is also a factor which may affect the morphology of the blends. As shown in *Figure 4*, the morphology of

PEEK/PES-C 40/60 crystallized at 315°C from the melt is different from that crystallized at 290°C (*Figure 1d*). The Maltese cross is more significant in the central region of the spherulites but cannot be seen in the other parts, and the darker regions may be seen at the boundaries of the spherulites. This indicates that PES-C has been rejected from the spherulites to some extent in this case. Therefore, segregation is significant at high crystallization temperatures. A similar phenomenon was observed in the blends of PEEK with poly(ether imide) (PEI), in which PEI is rejected from the spherulites at high crystallization temperatures[23]. The growth mechanism of PEEK lamellar bundles and the slow growth rate of spherulites at this temperature were thought to be responsible for such a morphology.

Crystallization kinetics

The addition of PES-C to PEEK has an obvious effect on the nucleation density and the number of spherulites per unit volume. As shown in *Figure 5*, in thin films of PEEK/PES-C blends, the number of spherulites per unit area ($\bar{N}$) decreases with increasing content of PES-C, and also decreases as the crystallization temperature increases for a given composition. Therefore, PES-C may dilute the nuclei in PEEK during the process of mixing. This explains the increase in the spherulitic size caused by the addition of PES-C as mentioned above, and will affect the crystal growth of PEEK.

In *Figure 6*, the spherulitic radius is plotted against time at a given crystallization temperature for several compositions. A substantial decrease of the growth rate with increasing PES-C content is observed. Since T_g of PES-C is much higher than that of PEEK[13,14], it is reasonable that the blends show a depression in the radial growth rate of the spherulites. In this context, the T_g of the amorphous component may alter the transport term associated with the solid–liquid interface, and finally change the growth rate[3]. However, another mechanism, such as a thermodynamic melting point depression, may be responsible for this[3,21]. The dependence of the spherulitic growth rate on the PES-C content is thought to be related to the miscibility of the blends. It was found that the coprecipitated samples and quenched samples of the blends showed two distinct T_g values which are lower than the T_g of PES-C with the same treatment and higher than that of PEEK, indicating the presence of a PEEK-rich phase and a PES-C-rich phase in the blends and the molecularly partial miscibility of PEEK with PES-C[15]. A large depression in the spherulitic rate of the crystalline component caused by the amorphous component was previously reported to occur in fully miscible or partially miscible blends, while a small depression was seen in immiscible blends[5,6,21].

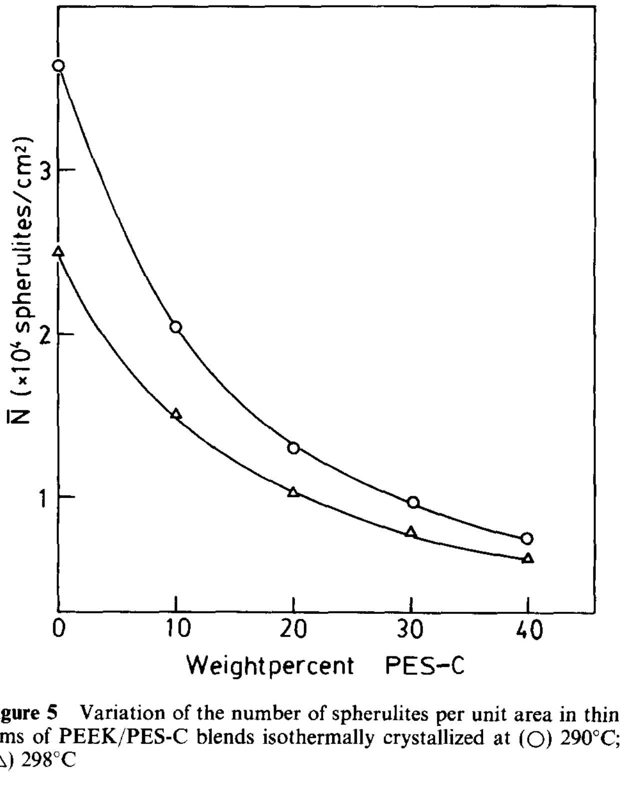

Figure 5 Variation of the number of spherulites per unit area in thin films of PEEK/PES-C blends isothermally crystallized at (○) 290°C; (△) 298°C

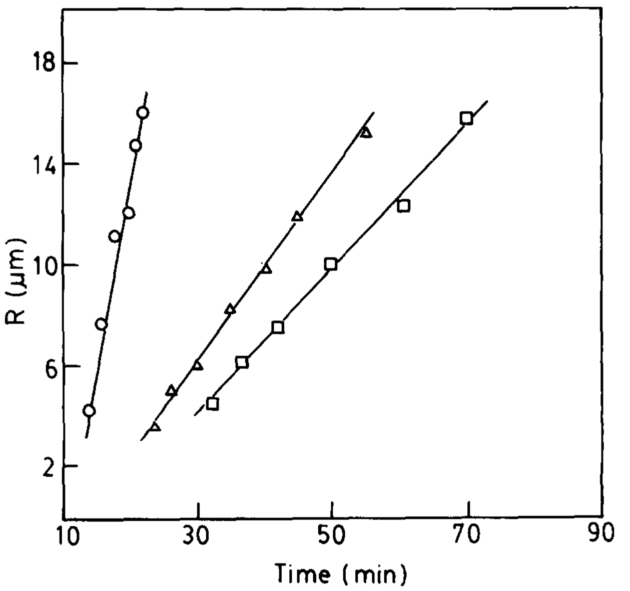

Figure 6 Spherulite growth in PEEK/PES-C blends isothermally crystallized at 302°C. Blends are (○), 100/0; (△) 80/20; (□) 60/40

The combination of the effect of the dilution of nuclei and depression of spherulite growth rate caused by PES-C can be observed in the overall isothermal crystallization of the blends. Using d.s.c., the fraction weight crystallinities $X(t)$ of the blends at different times were found. By plotting $X(t)$ *versus* time and calculating the time at which $X(t) = 0.5$, half-crystallization time $t_{0.5}$ was obtained with an error of 0.04 min. *Figure 7* shows $1/t_{0.5}$, a measure of the overall crystallization rate, as a function of crystallization temperature T_c. It is clearly seen that $1/t_{0.5}$ decreases with increasing amorphous PES-C content at a given T_c. The depression is very significant at low T_c, while it tends to vanish at very high T_c. This phenomenon could be an indication that the depression is mainly due to the influence of the dilution effect with higher T_g on the transport term mentioned above. Since diffusion of the amorphous component must occur in order for the crystallization to proceed[3], a larger diffusion rate at higher T_c will increase the influence and consequently weaken the depression.

The reduction in the spherulite growth rate and overall crystallization is very similar to what happens in the blends in which the amorphous component is incorporated interlamellarly or interfibrillarly within the spherulites[5-7,9,21]. So, a similar dispersion of PES-C in PEEK spherulites could be expected from the

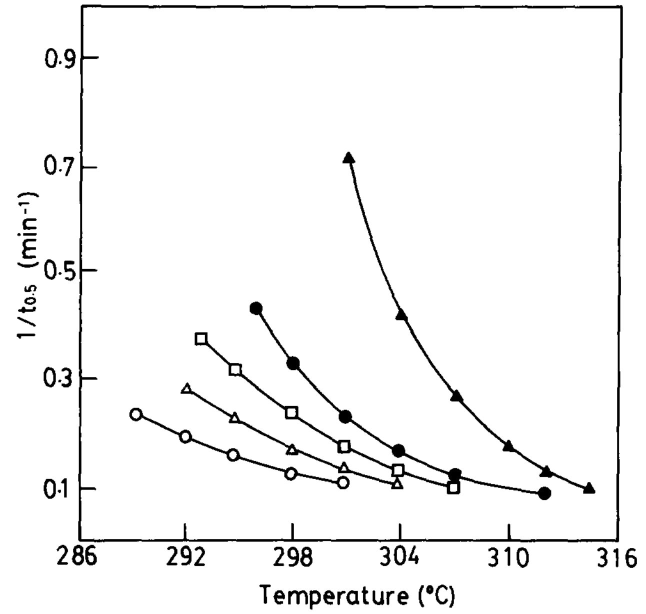

Figure 7 Reciprocal of the time of half-crystallization $1/t_{0.5}$ *versus* T_c for PEEK/PES-C blends. Blends are (▲) 100/0; (●) 80/20; (□) 60/40; (△) 40/60; (○) 20/80

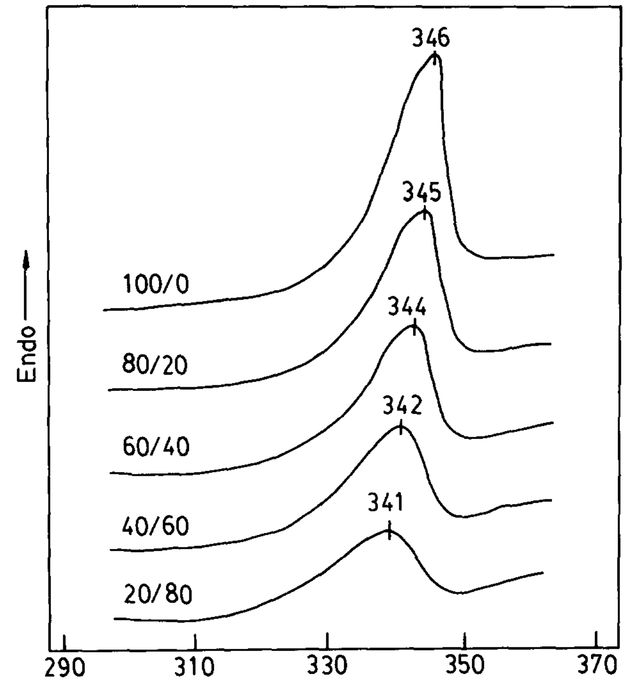

Figure 8 D.s.c. curves of PEEK/PES-C blends isothermally crystallized at 290°C for 10 h. Scanning rate 20°C min^{-1}

crystallization kinetics of PEEK/PES-C blends and from the optical observation of their morphology.

Melting behaviour

PEEK/PES-C blends isothermally crystallized at 290°C from the melt exhibit a single melting peak (*Figure 8*). The peak temperature decreases with increasing PES-C content. It can be explained in two ways. First, the dilute effect caused by PES-C might lead to thinning of PEEK lamellae[5,21]. Secondly, a negative interaction parameter χ might result in a melting-point depression[3]. The former can be supported by the results of morphology and crystallization kinetics, while the partial miscibility of PES-C with PEEK in the melt is believed to be a reason that PES-C might have an influence on the formation of PEEK lamellae.

Also, the melting enthalpy of PEEK is affected by the addition of PES-C. As shown in *Figure 9*, the enthalpy in the blends is lower than that calculated based on the value of pure PEEK and the content of PEEK in the blends, with the consideration of measurement error. Since melting enthalpy is a measure of the degree of

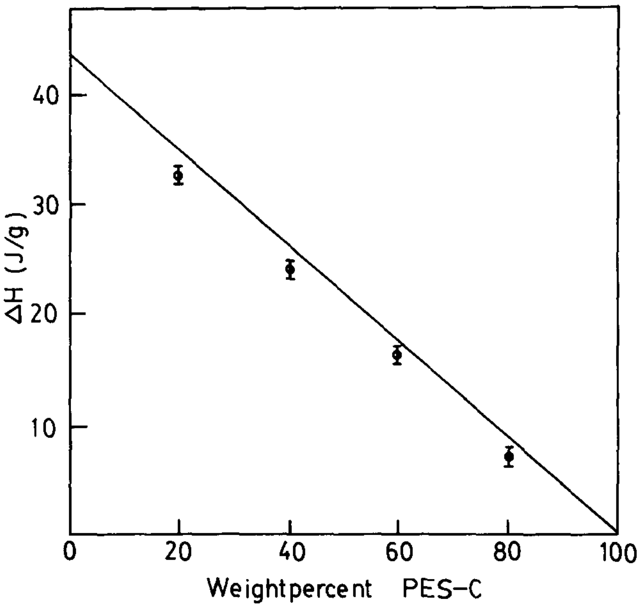

Figure 9 Influence of PES-C content on the melting enthalpy of PEEK in PEEK/PES-C blends isothermally crystallized at 290°C for 10 h. The straight line represents the values calculated based on the melting enthalpy of pure PEEK and the content of PEEK in the blends

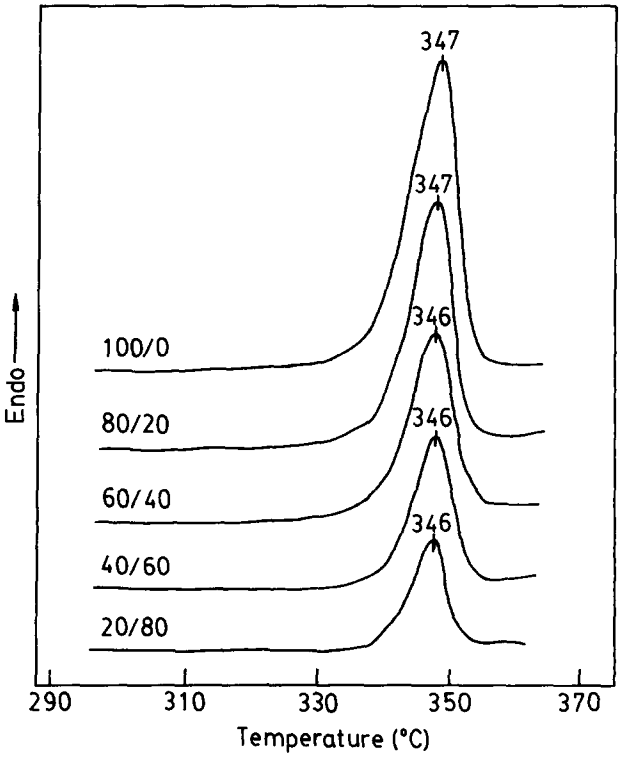

Figure 10 D.s.c. curves of PEEK/PES-C blends isothermally crystallized at 315°C for 10 h. Scanning rate 20°C min^{-1}

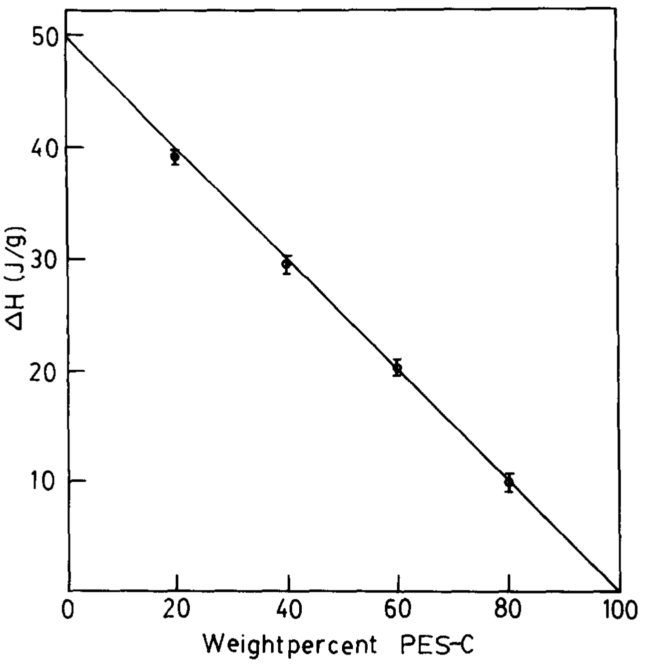

Figure 11 Influence of PES-C content on the melting enthalpy of PEEK in PEEK/PES-C blends isothermally crystallized at 315°C for 10 h. The straight line represents the values calculated based on the melting enthalpy of pure PEEK and the content of PEEK in the blends

crystallinity, it is known that the crystallinity of PEEK in the blends is relatively low. This is in agreement with the WAXS results. The kinetic effect caused by PES-C is considered to be the reason for such depression of crystallinity.

As observed from morphology and kinetics, crystallization temperature also has a pronounced effect on the melting behaviour of the blends. When crystallized at 315°C for the same time period as at 290°C, PES-C has little effect on the melting point of PEEK (*Figure 10*). In this case, the melting enthalpy of PEEK in the blends is also close to the calculated value (*Figure 11*). This indicates that PES-C obstructs the crystallization of PEEK less at higher temperatures, in agreement with the kinetic behaviour of the blends at higher T_c, arising from the significant segregation during crystallization at this temperature.

CONCLUSION

When crystallized at lower temperatures, the spherulites of PEEK/PES-C blends up to 60% PES-C are volume-filling, and the amorphous PES-C is probably interfibrillarly dispersed in the spherulites. On the other hand, more PES-C is trapped near and at the borders of the spherulites at higher temperatures due to the more significant segregation. PES-C has a dilution effect on the nuclei in PEEK and causes a great decrease of spherulite growth rate and overall crystallization rate of PEEK. The rate depression is very significant at a lower crystallization temperature T_c and tends to vanish at higher T_c. Also, melting point and crystallinity in the blends were shown to decrease with decreasing T_c.

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