Synthesis and properties of poly(ether ether ketone)–poly(ether sulfone) block copolymers

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Two series of block copolymers composed of poly(ether ether ketone) (PEEK) and poly(ether sulfone) (PES) components were prepared from the corresponding oligomers via a nucleophilic aromatic substitution reaction. In the first series of block copolymers, the $\bar{M}_n$ of the PEEK segment was fixed at 10000, while the $\bar{M}_n$s of the PES segments ranged from 250 to 9330. (The PES contents of the copolymers varied from 2.2 to 46.2%.) For the other series of block copolymers, the compositions were kept almost constant (PES content ~36%), while the segment lengths were changed. Various properties of the copolymers were investigated by differential scanning calorimetry (d.s.c.), wide-angle X-ray diffraction (WAXD), thermogravimetric analysis (t.g.a.), and dynamic mechanical analysis (d.m.a.). The results showed that the copolymers exhibited no phase separation and the relationship between the glass transition temperature and the compositions of the copolymers approximately followed the formula, $T_g = T_{g1}W_1 + T_{g2}W_2$. The crystallization behaviour, thermal properties and dynamic mechanical behaviour of the copolymers were investigated and it was found that both the PES content and the segment length of the copolymers had a significant influence on their crystallization behaviour.

(Keywords: PEEK; PES; block copolymer)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a crystalline polymer with a melting point of ~334°C and a glass transition temperature (T_g) of 143°C. Its excellent mechanical properties, good environmental resistance and high thermal and thermo-oxidative stability make it very attractive as a high performance engineering thermoplastic[1,2]. Unfortunately, this material has a relatively low T_g, which results in a decrease of the modulus at elevated temperatures. In addition, its price is comparatively high, and this limits its widespread application.

With the development of high technology and the need for materials with comprehensively excellent properties, many papers have appeared in the literature, dealing with blends based on PEEK with other high performance thermoplastics, such as polysulfone (PSF), poly(ether sulfone) (PES), poly(amide imide) (PAI), poly(ether imide) (PEI), poly(phenylene sulfide) (PPS), poly(ether ketone) (PEK), etc.[3–9]. However, most of these blends possess a phase-separated structure, which makes them essentially unusable. Incorporation of the above mentioned polymer blocks into poly(ether ether ketone) may afford new materials with improved properties, and through the judicious choice of molecular weights of the block, either homogeneous or microphase-separated morphologies should be possible. This could provide another means for modifying the properties of PEEK. Although a few patents concerning various copolymers of PEEK have been reported in recent years[10–13], very few fundamental studies on these copolymers can be found in the literature. A random copolymerization approach, as well as an oligomer–monomer approach, have been used as the general synthetic route for the preparation of these copolymers. PES is an amorphous polymer, which possesses excellent properties, in particular a higher T_g, (225°C) and a lower price, when compared with PEEK[14,15]. We have recently demonstrated an alternative synthetic route for the preparation of PEEK/PES block copolymers based on the oligomer–oligomer approach. This present paper covers the synthesis of these kinds of block copolymers, and deals with the miscibility, thermal properties and crystallization behaviour of the copolymers in detail.

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EXPERIMENTAL

Materials

4,4′-Dichlorodiphenylsulfone (m.p. 242°C) (Dalian Santang Chemical Factory, China), 4,4′-dihydroxyldiphenylsulfone (m.p. 142°C) (Yanbian Longjing Chemical Factory, China), hydroquinone, and other reagents used for analysis (Beijing North Suburb Chemical Factory, China), were used without further purification. 4,4′-Difluorobenzophenone (m.p. 103–104°C) and diphenyl-

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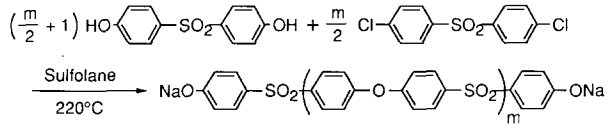
sulfone (m.p. 124–125°C) were prepared in our laboratory by standard procedures.

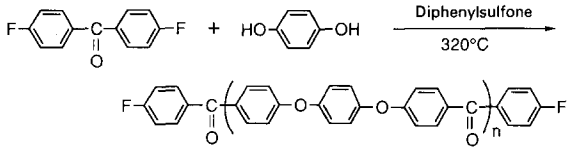
Synthesis of PES oligomers

Dihydroxyl-terminated PES oligomers were prepared by a condensation reaction between 4,4′-dichlorodiphenylsulfone and 4,4′-dihydroxydiphenylsulfone in the presence of aqueous sodium hydroxide in sulfolane[16]. The reaction scheme is shown below:



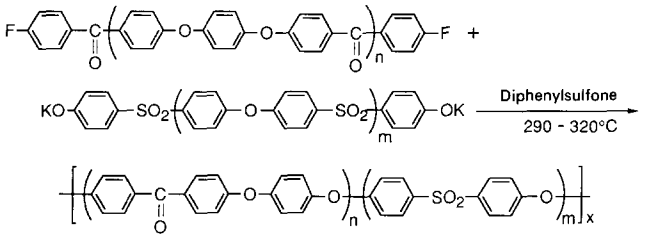
Synthesis of PEEK oligomers

Difluorine-terminated PEEK oligomers were prepared by the reaction of 4,4′-difluorobenzophenone and hydroquinone in diphenylsulfone, in the presence of Na_2CO_3 and K_2CO_3 according to literature procedures[1,17]. The reaction scheme is as follows:



Synthesis of PEEK/PES block copolymers

PEEK/PES block copolymers were prepared from the above two oligomers via a nucleophilic aromatic substitution reaction[18], as follows:



Typical reaction conditions for the copolymer synthesis are as follows: PEEK oligomer (0.2 mol) was prepared first, but was not isolated from the reaction mixture. PES oligomer (5.8 mmol) (solid powder), which had been isolated and characterized, was added to the diphenylsulfone solution of the PEEK oligomer, and the two oligomers were reacted at 260–310°C for 2–4 h. The copolymer solution was then poured into water, and after cooling, the precipitate was crushed, repeatedly washed with acetone and water (for a total of 10 times), and finally dried.

Material preparation

The copolymer samples were moulded into films with a thickness of 0.5 mm, by using a pressure of 10 MPa at 370–380°C for 10 min. To obtain amorphous film samples, the above films were placed on an aluminium plate and then quenched by immediately putting them into an ice/water mixture. Crystalline film samples were prepared by annealing the amorphous films at various temperatures for predetermined periods of time, and then cooling slowly to room temperature.

Measurements

The number-average molecular weights ($\bar{M}_n$s) of the PES oligomers were determined by potentiometric titration in non-aqueous media by means of a glass–calomel electrode system; *N*,*N*-dimethylformamide (DMF) and tetraethylammonium hydroxide were used as the solvent and titrant, respectively. The $\bar{M}_n$s of the PEEK oligomers were determined by ^{19}F n.m.r. spectroscopy, with the spectra being obtained by the use of a Varian FT-80A spectrometer operating at 74.8 MHz, at 25°C. The sample solution (~5 wt%) in H_2SO_4 was prepared at room temperature, with sodium trifluoroacetate used as the internal standard. The inherent viscosities (η_{inh}) of the copolymers were measured in 0.1 wt% H_2SO_4 solution at 25°C. I.r. spectra were measured on a Nicolet 5PC infra-red spectrometer. The thermal analysis was carried out with a Perkin–Elmer DSC-7 instrument, and thermogravimetric analysis (t.g.a.) of the copolymer films was made on a Perkin–Elmer TGS-2 thermogravimetric analyser, using a heating rate of 10°C min^{-1}, in a nitrogen atmosphere. Dynamic viscoelastic measurements were performed on a DDV-II-EA machine, using a heating rate of 2°C min^{-1}, at 3.5 Hz. Wide-angle X-ray diffraction (WAXD) was measured on a Rigaku D/MAX-IIIA X-ray diffractometer, using CuKα radiation, at 40 kV and 30 mA.

RESULTS AND DISCUSSION

Characterization of the block copolymers

In this study, oligomers with various molecular weights were prepared by changing the mole ratio of the two monomers, according to the modified Carothers equation, i.e. $X_n=(1+r)/(1-r)$, where X_n is the number-average degree of polymerization and r is the molar ratio of the two monomers. The PES oligomers were isolated and their number-average molecular weights determined by the convenient and accurate method of potentiometric titration[19]. Owing to the low solubility of PEEK, this method for the molecular characterization of PEEK is limited. Devaux[20] has discussed two independent methods, i.e. gel permeation chromatography (g.p.c.) and ^{19}F n.m.r. end-group analysis, for the determination of $\bar{M}_n$ of PEEK and found end-group analysis by ^{19}F n.m.r. spectroscopy to be a very reliable method. In this present study, ^{19}F n.m.r. measurements were first used to determine the $\bar{M}_n$s of some of the PEEK oligomers which had been isolated before further reaction with the PES oligomer. The $\bar{M}_n$ values determined in this way were in fairly good agreement with calculated values for the oligomers. For example, the $\bar{M}_n$ determined by ^{19}F n.m.r. spectroscopy for a specific PEEK oligomer was 10560, which was very close to the expected (calculated) value of 10000. In the preparation of the PEEK/PES copolymers, the PEEK oligomers were used without isolation or characterization, and the $\bar{M}_n$ was therefore assumed to be the same as that calculated from the feed ratio of 4,4′-difluorobenzophenone to hydroquinone.

In order to investigate the effect of composition on the properties of the PEEK/PES block copolymers, PEEK oligomers with a definite $\bar{M}_n$ (10000, calculated value) were first prepared, while the $\bar{M}_n$ values of the PES oligomers were changed over the range 250–9330; in this way, the PES content in the copolymers varied from 2.2 to 46.2%. The composition of the copolymers and other characterization data are listed in *Table 1*.

Table 1 Compositions and characterization data for the PEEK/PES copolymers

No.	$\bar{M}_n$ of oligomer PEEK[a]	$\bar{M}_n$ of oligomer PES[b]	PES[c] (%)	η_{inh} (dl g^{-1})	T_g (°C)	T_m (°C)	T_c' (°C)	χ_c[d] (%)	χ_c (PEEK)[e] (%)
1	10000	250	2.2	0.93	147	326	181	22.7	23.4
2	10000	1500	12.6	0.92	153	320	199	19.9	22.9
3	10000	2900	22.4	0.83	160	320	214	14.4	18.3
4	10000	3500	25.7	0.85	162	316	231	11.3	15.1
5	10000	5600	35.1	0.85	171	316	(263)	2.0	3.1
6	10000	9330	46.2	0.61	180	–	–	0	0
PEEK			0	0.80	143	334	175	32.6	32.6

[a] Estimated value from feed ratio of 4,4'-difluorobenzophenone and hydroquinone
[b] Determined by potentiometric titration
[c] Calculated by $\{\bar{M}_n(\text{PES})-[\bar{M}_n(\text{PEEK})+\bar{M}_n(\text{PES})]\times\Delta\}\times 100\%/[\bar{M}_n(\text{PEEK})+\bar{M}_n(\text{PES})](1-\Delta)$, where Δ is the fraction of weight loss, and $\bar{M}_n$ (PEEK) and $\bar{M}_n$ (PES) are number-average molecular weights of the PEEK and PES oligomers, respectively
[d] Degree of crystallinity of the copolymers, calculated by d.s.c.
[e] Degree of crystallinity corresponding to the PEEK segments, calculated by d.s.c.

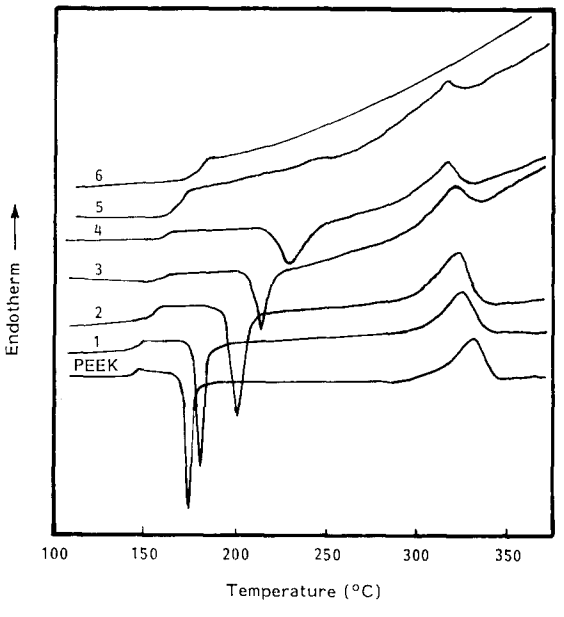


Figure 1 D.s.c. curves of the amorphous PEEK/PES copolymers and PEEK; compositions of the samples are given in *Table 1*

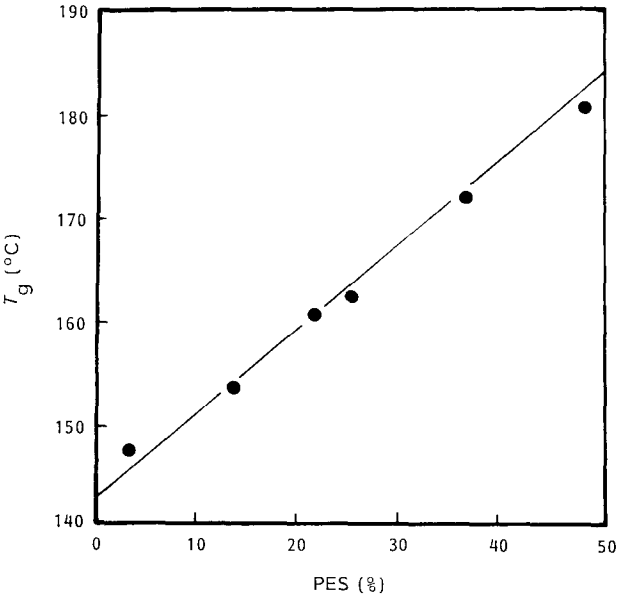


Figure 2 Relationship between T_g and PES content of the PEEK/PES copolymers

The copolymers obtained were extracted with DMF, which is a good solvent for PES, but not for PEEK. The fraction of the weight loss (Δ) of these samples after extraction increased with increasing PES content; for example, the weight losses for samples with PES contents $\leqslant 26\%$ were all less than 0.6%, while the weight loss for a sample with a PES content of 35.1% was 1.25%, and that of a sample with a PES content of 46.2% was 3.8%. The structures of the samples were also confirmed by means of i.r. spectroscopy. Spectra of the samples showed characteristic absorptions, due to the sulfone group, at 1314 and 1152 cm^{-1}, along with an absorption due to the ketone group at 1650 cm^{-1}. In addition, the inherent viscosities of 0.6–0.9 dl g^{-1} suggest that the samples have moderately high molecular weights. These facts indicate that samples prepared via the above methods should be copolymers of the two oligomers, rather than blends of the two components, although the possibility that the residual polymers contain some PEEK oligomer cannot be ruled out completely.

Solubility experiments were also carried out for the copolymers. The results indicate that at room temperature the copolymers did not dissolve in most of the common organic solvents, even in DMF or 1,2-dichloroethane, both of which are good solvents for PES, and could only be dissolved in concentrated sulfuric acid. The chemical resistance properties of these PEEK/PES block copolymers were nearly as good as those of PEEK itself.

Compatibility of the PEEK/PES block copolymers

The d.s.c. curves for the amorphous copolymers are shown in *Figure 1*. It can be seen that the copolymers with different PES contents show single T_gs. The T_g values for the copolymers are shifted to higher temperatures, when compared with that of PEEK, and increase as the PES content is increased. For example, the T_g of the crystalline copolymer (*Table 1*, No. 5) containing 35.1% PES segment was 171°C, ~30°C higher than that of pure PEEK. The plots of these T_g values against the copolymer compositions are shown in *Figure 2*. In this figure, the straight line indicates the calculated values according to the following equation:

$$T_g = T_{g1}W_1 + T_{g2}W_2 \quad (1)$$

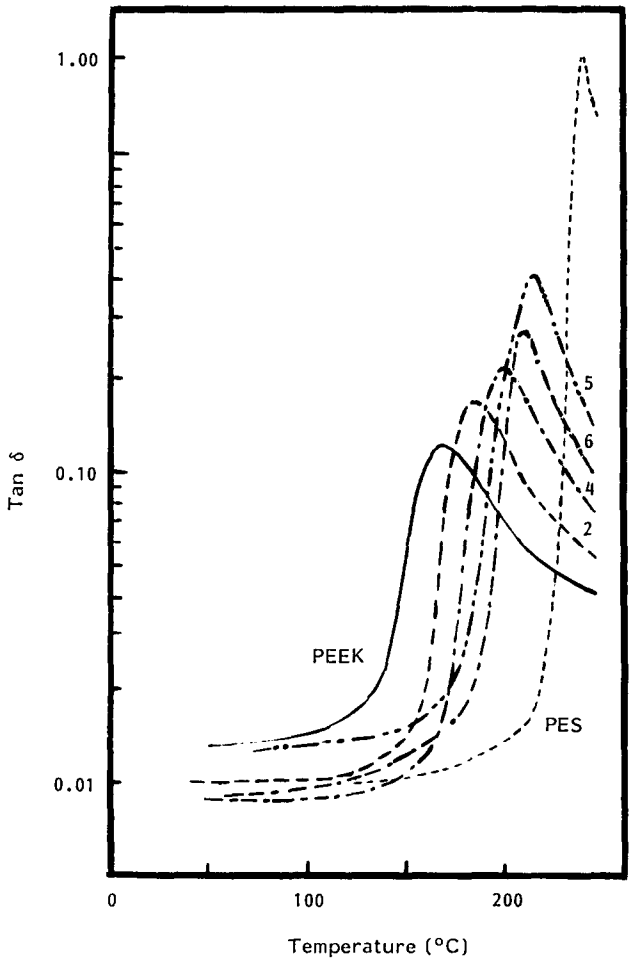


Figure 3 Loss factor curves obtained from dynamic viscoelastic measurements on the PEEK/PES copolymers, PEEK, and PES; compositions of the samples are given in *Table 1*

where T_{g1} and T_{g2} denote the T_g values of PEEK and PES, and W_1 and W_2 the corresponding weight fractions of the PEEK and PES segments in the copolymers, respectively. It can be seen from *Figure 2* that the relationship between T_g and the compositions of the PEEK/PES block copolymers approximately follows that of equation (1).

The samples prepared by compression moulding at 380°C were also investigated by dynamic viscoelastic measurements. Plots of tan δ *versus* temperature (*Figure 3*) also show that each of the copolymers exhibits only a single T_g. These results are consistent with the results from the above mentioned d.s.c. measurements, and suggest that the PEEK/PES block copolymers have homogeneous morphologies over the range of compositions, or block lengths, discussed in this paper. This is different from that observed for the morphologies of PEEK/PES blends. For such blends, the preparation conditions exert an influence over their molecular aggregation behaviour; for example, PEEK is compatible with PES at a processing temperature of 310°C, with the variation of the T_g values with composition obeying the Gordon-Taylor's equation[21], where the adjustable parameter k is 0.43. However, when processing temperatures are above 350°C, phase separation occurs in the PEEK/PES blends[7,9]. Therefore, it may be concluded that the PEEK/PES copolymers have good compatibility when compared with the corresponding PEEK/PES blends. This difference in compatibility could be ascribed to an inherent interaction, due to chemical bonding, existing between the PEEK and PES segments in the PEEK/PES copolymers.

Crystallization behaviour of PEEK/PES block copolymers

Figure 4 shows typical wide-angle X-ray diffraction curves obtained for a crystalline copolymer and pure PEEK. The main diffraction peaks of the copolymer are very similar to those of PEEK. The results suggest that the crystalline structure of the copolymer still belongs to the orthorhombic system[22], and also that the crystalline character still originates in the PEEK segments of the copolymers, whereas the PES segments do not penetrate into the crystalline PEEK segment units.

It can be seen from *Figure 1* that the quenched amorphous samples with a PES content of less than 35.1% show both a cold-crystallization temperature (T_c') and a melting point (T_m). The peak due to T_c' for sample 5 (PES content of 35.1%) is very weak, while the T_m peak is clearly observed. The exothermic peak shows a strong shift toward higher temperatures with increasing PES content and gradually becomes smaller and broader. In contrast, the endothermic peak is shifted to lower temperatures and decreases in intensity with increasing PES content. For example, the T_c' of the copolymer with a PES content of 25.7% is $\sim$56°C higher than that of pure PEEK, while its T_m is $\sim$18°C lower than that of the pure component. The copolymer with a PES content of 46.2% did not show either a T_c' or a T_m peak.

The degree of crystallinity of the copolymers (χ_c) and that which corresponds to the PEEK segments (χ_c(PEEK)) can be estimated from the d.s.c. results by using the following equations:

$$\chi_c = \Delta H/\Delta H_f \quad (2)$$

$$\chi_c(\text{PEEK}) = \chi_c/W_{\text{PEEK}} \quad (3)$$

where ΔH is the heat of fusion of the copolymer

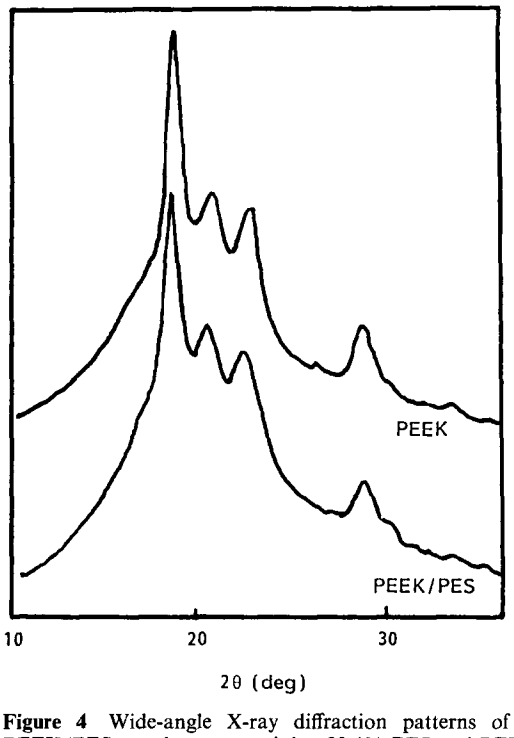


Figure 4 Wide-angle X-ray diffraction patterns of a crystalline PEEK/PES copolymer containing 22.4% PES and PEEK

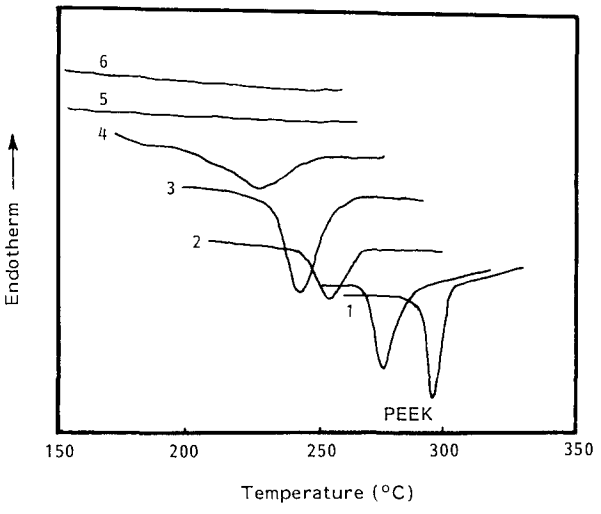


Figure 5 D.s.c. curves of the PEEK/PES copolymers and PEEK obtained after cooling from 400°C at a cooling rate of 10°C min^{-1}; compositions of the samples are given in *Table 1*

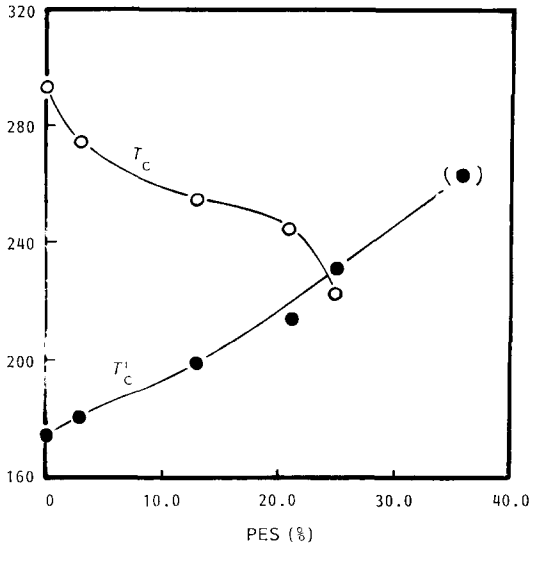


Figure 6 Effect of PES content of the PEEK/PES copolymers on T'_c (●) and T_c (○)

(determined by d.s.c.), ΔH_f is the heat of fusion of 100% crystalline PEEK ($\Delta H_f = 130$ J g^{-1})[22] and W_{PEEK} is the weight fraction of the PEEK segment in the copolymer. The crystallinity data are given in *Table 1*. Both the χ_c and χ_c(PEEK) values of the copolymers decrease with increasing PES content.

Figure 5 shows the d.s.c. curves obtained for the above copolymers, after first melting at 400°C for 2 min, and then cooling, at a rate of 10°C min^{-1}, to room temperature. The copolymers with PES contents of less than 35.1% show an obvious crystallization exotherm temperature (T_c). The T_c of the copolymer with 2.2% PES (1) is 275°C, which is ~20°C lower than that of pure PEEK, but when this copolymer is crystallized from the glassy state, its T'_c is only ~6°C higher than that of pure PEEK (see *Figure 1*). The T_c of the copolymer with a PES content of 25.7% (4) is 223°C, ~70°C lower than that of pure PEEK. The copolymers with PES content ⩾35.1% did not show any obvious crystallization exotherms. Plots of the T'_c and T_c values against the copolymer compositions are shown in *Figure 6*. These results suggest that crystallization of the copolymers becomes more difficult as the PES content is increased.

Figure 7 shows the d.s.c. curves obtained for the copolymer samples (and PEEK) after annealing at 250°C for a long period of time. These curves reveal that crystalline fusion peaks were observed for all of the copolymers examined, indicating that the copolymers discussed above were all crystallizable polymers. Moreover, these isothermally crystallized copolymers also exhibited a double-melting behaviour, as observed for pure PEEK[23]. The low-temperature peaks were smaller, and remained almost constant, regardless of the PES content. The peak maximum temperature for the low-temperature peak (T_{m1}) was ~10°C higher than the annealing temperature. The peak maximum temperatures for the high-temperature melting peaks (T_{m2}) for the PEEK/PES copolymers were lower than that of pure PEEK and decreased as the PES content increased. The values of T_{m1} and T_{m2} are listed in *Table 2*.

The crystallinity of the copolymers decreases with increasing PES content. The above evidence shows that introduction of PES segments into the PEEK molecular chain disturbs the close packing of the PEEK repeat units so that the crystallites become smaller and thus the melting points and the crystallinity of the copolymers are reduced.

In order to investigate the effects of the block length of these copolymers on their crystallization behaviour, another series of PEEK/PES block copolymers with the same composition, but with different segment lengths, was also prepared. In this work, the PES content of the

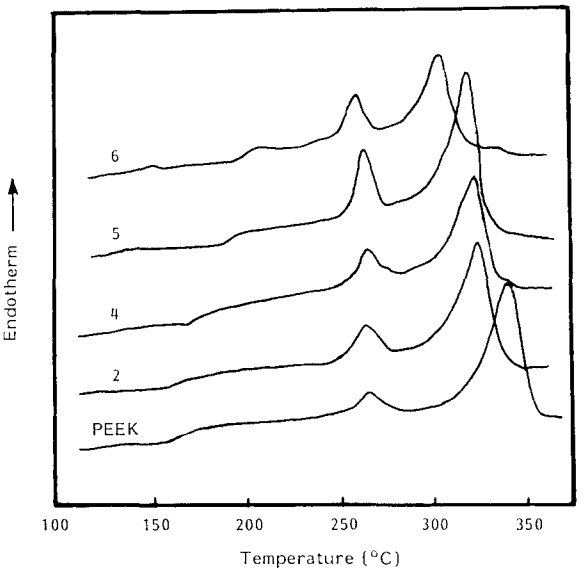


Figure 7 D.s.c. curves of the crystalline PEEK/PES copolymers and PEEK obtained after annealing at 250°C; compositions of the samples are given in *Table 1*

Table 2 Melting points of the PEEK/PES copolymers and PEEK after annealing at 250°C

Sample	T_{m1} (°C)	T_{m2} (°C)
PEEK	261	334
2	262	322
4	262	320
5	262	316
6	263	312

Table 3 Characterization data and properties of the PEEK/PES copolymers with different segment lengths

Sample	$\bar{M}_n$ of oligomer PEEK	$\bar{M}_n$ of oligomer PES	η_{inh} (dl g^{-1})	T_g (°C)	T_m (°C)	T_c' (°C)
7	2080	1150	0.68	168	–	–
8	4660	2600	0.79	170	–	–
9	10000	5600	0.85	171	316	263
10	14900	8370	0.93	170	321	230

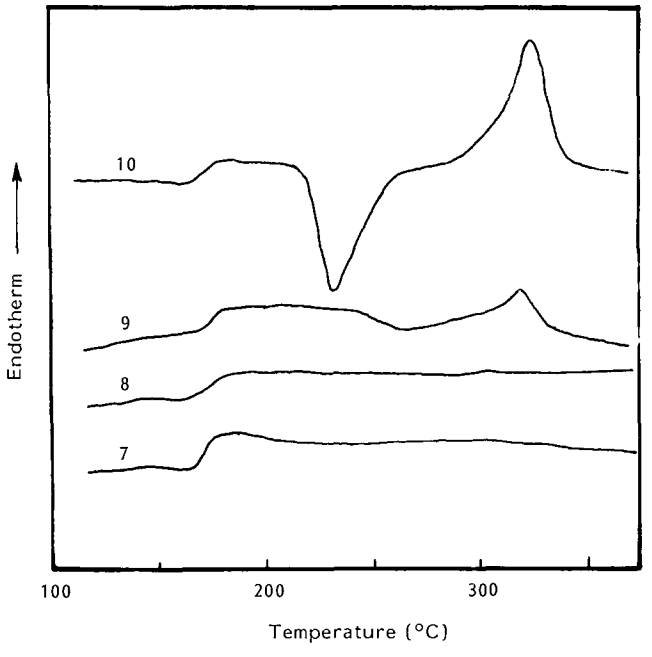


Figure 8 D.s.c. curves of the amorphous PEEK/PES copolymers with different segment lengths; details of the samples are given in *Table 3*

copolymers was fixed at ~36%. The segment lengths of the copolymers and various other properties are listed in *Table 3*.

Figure 8 shows the d.s.c. curves of the melt-quenched, amorphous copolymers. The T_g values of these copolymers are ~170°C and remain almost constant, irrespective of the segment length. The copolymers with PEEK segment lengths ≤4660 (7 and 8) are amorphous, and, with increases in the segment length, the cold-crystallization exothermic peak and crystallization endothermic peak both become obvious. The T_c' shifts towards lower temperatures as the segment length increases; for example, the T_c' of sample 10 is ~33°C lower than that of sample 9, but its melting point is 5°C higher than the latter. These facts suggest that the segment lengths of the copolymers have a great influence on the copolymer crystallization behaviour.

Figure 9 shows the d.s.c. curves obtained (in the heating mode) for the above samples after being isothermally crystallized at 250°C for a long period of time. These curves show that after annealing all of these copolymers also exhibit double-melting behaviour, indicating that all of them including those with $\bar{M}_n$ of segments as small as 2080, are crystallizable polymers. The values of T_{m1} and T_{m2} are listed in *Table 4*. T_{m1} is almost constant, irrespective of the segment lengths, while T_{m2} increases with an increase in segment length; for example, the value of T_{m2} for sample 7 is ~30°C lower than that of sample 10. This suggests that crystallites of the copolymers become less perfect as the segment length decreases. The crystallinity of the copolymers, as observed from the intensities of the endothermic peaks, decreases with decreasing segment length. These facts may be explained in the following way. As the lengths of the PEEK and PES segments increase, the number of linkages between them becomes smaller (in terms of the weight average), and the interaction between the PES and PEEK segments decreases. Moreover, the longer the PEEK segments, then the more closely they pack overall, and thus the crystallizability of the copolymers is improved with increasing segment length.

Thermal stability and dynamic mechanical behaviour of PEEK/PES block copolymers

The thermal stability of the PEEK/PES copolymers was evaluated by t.g.a. *Figure 10* shows typical t.g.a. traces in nitrogen for two of the copolymers, together with that of pure PEEK. The decomposition temperatures (T_ds), at which a weight loss reaches 2.5% of the original sample weight, were 536, 494 and 550°C, for samples 4, and 6, and PEEK, respectively. The thermal stability of the copolymers is somewhat reduced by the incorporation of the PES segments (relative to pure PEEK) and the T_d values decrease with increasing PES content, but were still higher than 490°C. In addition, the thermal stability of the copolymers with a PES content less than 26% is still very good.

Figure 11 shows the temperature dependence of the storage modulus, E', for copolymer samples which have been obtained by compression moulding at 380°C. The modulus of PEEK starts to decrease at ~150–180°C and

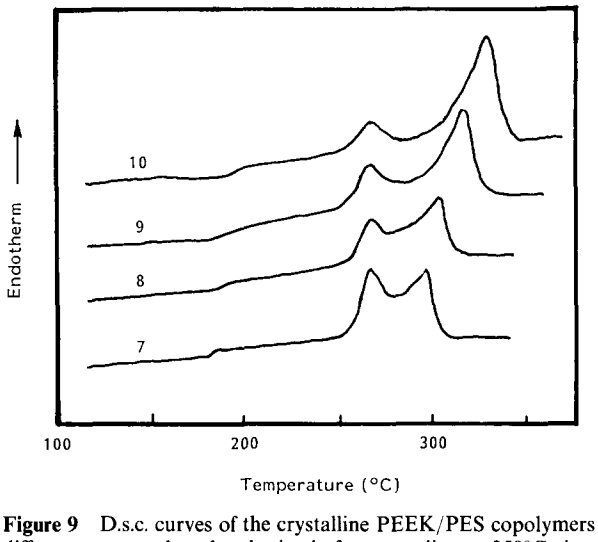


Figure 9 D.s.c. curves of the crystalline PEEK/PES copolymers with different segment lengths obtained after annealing at 250°C; details of the samples are given in *Table 3*

Table 4 D.s.c. analysis of the PEEK/PES copolymers of fixed composition, with different segment lengths, after annealing at 250°C

Sample	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)
7	181	265	295
8	181	264	301
9	186	265	314
10	190	265	325

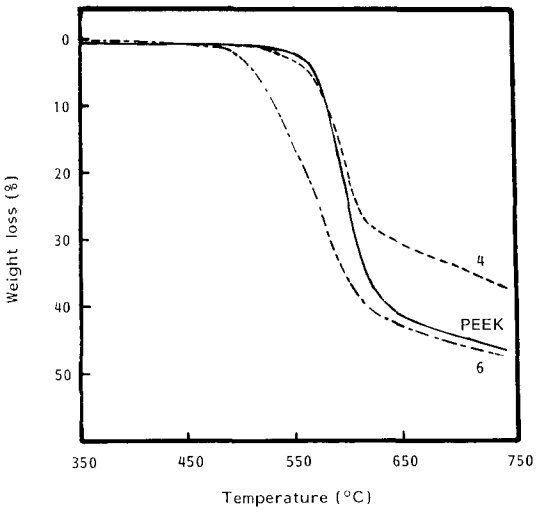


Figure 10 T.g.a. curves of the PEEK/PES copolymers and PEEK; compositions of the samples are given in *Table 1*

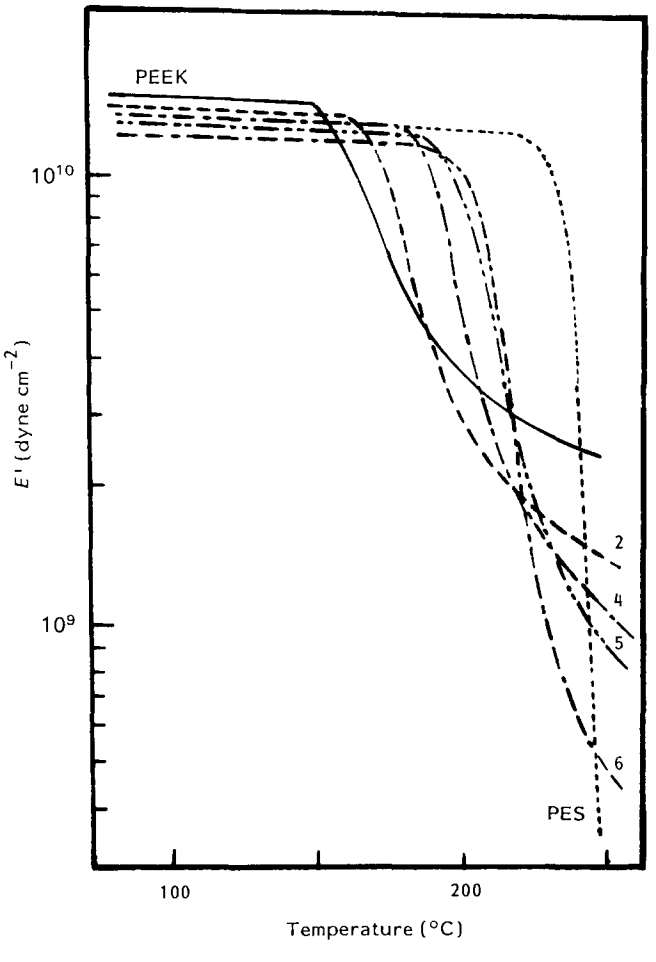


Figure 11 Storage modulus as a function of temperature for PEEK, PES, and the PEEK/PES copolymers; compositions of the samples are given in *Table 1*

tends to reach a plateau, while the modulus of PES drops dramatically at 230–250°C. For the PEEK/PES copolymers, the temperatures at which the modulus starts to decrease are higher than that of the pure PEEK. The temperature dependence of E' for the copolymers with the higher PEEK contents resembles that of crystalline PEEK, i.e. the modulus decreases slowly to a value at which it begins to show a tendency to level out and form a plateau. As the PES content increases, however, the modulus decreases more and more rapidly, becoming similar to the behaviour shown by amorphous PES.

The extent of lowering of the storage modulus with increasing temperature can be expressed by the modulus-maintaining ratio, namely the ratio of the modulus at a particular temperature, relative to the constant value at a lower temperature (see *Figure 11*). The modulus-maintaining ratio of the copolymers at 170, 200 and 250°C, as a function of the PES content, is shown in *Figure 12*. At 170°C, the modulus-maintaining ratio increases with PES content over the range 0–26%. When the PES content is above 26%, it almost remains constant. At a temperature of 200°C, the ratio increases significantly with increasing PES content. However, at 250°C, the ratio decreases slowly with increasing PES content. This is because there are now two phases present in the copolymers; one is the amorphous phase, containing PEEK and PES components, while the other is the PEEK crystalline phase. The modulus of the copolymers is affected by these two phases. When the temperature is below the T_g of PES, this component in the copolymers can maintain very good mechanical properties. The miscible amorphous phase is a critical factor affecting the modulus of the copolymers, because the T_g of this phase increases with PES content. Therefore, the modulus-maintaining ratio also increases with PES content. When the temperature is higher than the T_g of PES, the modulus of the amorphous phase shows a large decrease, and therefore the presence of the PEEK crystalline phase is the main factor affecting the modulus of the copolymer. Since the crystallinity of the copolymers decreases with increasing PES content, the modulus-maintaining ratio also decreases as a result of this.

CONCLUSIONS

PEEK/PES block copolymers were successfully prepared from dihydroxyl-terminated PES oligomers and difluorine-

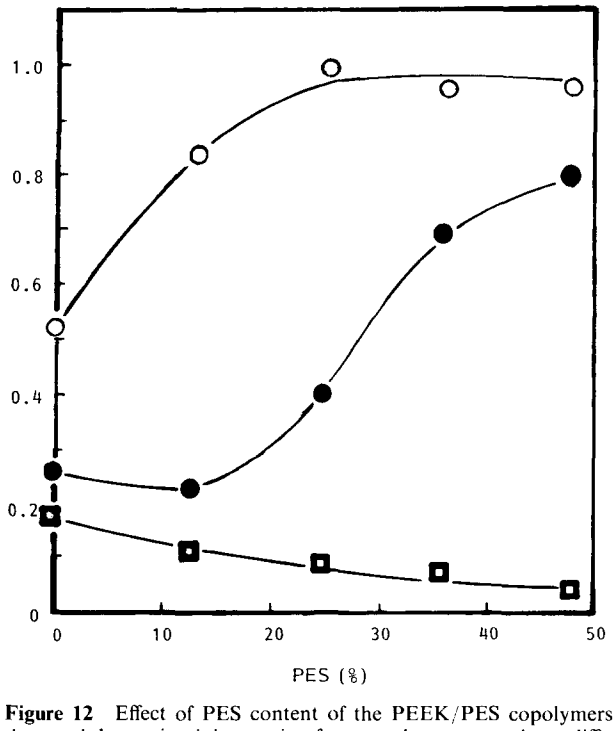


Figure 12 Effect of PES content of the PEEK/PES copolymers on the modulus-maintaining ratio, for samples measured at different temperatures: (○) 170°C; (●) 200°C; (□) 250°C

terminated PEEK oligomers in diphenylsulfone in the presence of K_2CO_3. No phase separation was observed for these copolymers. The relationship between T_g and the composition of the copolymers follows the equation, $T_g = T_{g1}W_1 + T_{g2}W_2$. The PEEK/PES copolymers are a compatible system, with their crystalline structures being similar to that of PEEK. The PES content and the segment length of the copolymers have a significant influence on their crystallization behaviour. As the amorphous PES content increases, or the segment length decreases, the melting points and the crystallinity of the copolymers decrease and crystallization of the PEEK segments in the copolymers becomes more difficult. The PES content in the copolymers also exerts an influence on both the thermal stability and the dynamic mechanical behaviour of the copolymers. Overall, the copolymers synthesized in this work have very good chemical resistance, high-temperature stability and high-temperature mechanical properties.

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