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Phase behaviour and mechanical properties of poly(ether ether ketone)–poly(ether sulphone) blends

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The phase behaviour and the mechanical properties of binary blends composed of poly(ether ether ketone) and poly(ether sulphone) have been studied both in the amorphous state and after crystallization of poly(ether ether ketone).

Differential scanning calorimetry and dynamical mechanical analysis clearly show the existence of phase separation in the blends. Density measurements confirm the absence of strong interactions between the blend components, as well as the slight effect of PES on the crystallization of PEEK.

The mechanical properties of the quenched, amorphous blends remain surprisingly good in spite of the observed immiscibility, however, slowly cooled, crystalline blends appear as brittle materials.

1. Introduction

Engineering polymers with high thermal resistance are of great interest at the present time because they can be used in a variety of applications for which common plastics are inadequate due to their low resistance to temperature. Thermally resistant engineering polymers include such crystallizable materials as poly(phenylene sulphide) and poly(ether ether ketone) and amorphous materials such as polysulphones and, poly(ether imide).

An interesting method for the development of new polymeric materials from these high temperature polymers is blending. Blending makes it possible to obtain a variety of properties in the final products, depending on the blend composition, among other factors. In the case of blends of a crystallizable polymer with an amorphous one, the crystallinity degree and the crystalline morphology may be controlled by varying the processing conditions, principally the cooling rate from the melt.

Another factor which must be taken into account is the influence of blending on the processing conditions of the blends, because of the possible variation of the melt viscosity and thermal transitions of the blends with respect to those of the blend components.

Poly(ether ether ketone) (PEEK) is a semicrystalline polymer with high glass transition and melting temperatures, as well as high thermal resistance. Moreover, this polymer presents high toughness, strength and rigidity, as well as a high resistance to aggressive environments. The applications of this polymer include cable insulation, monofilaments, coatings, moulded parts and high strength composites.

Poly(ether sulphone) (PES) is an amorphous polymer with a high glass transition temperature, and can be classified as a thermally stable polymer. Among other interesting properties of PES are good hydrolitic and thermooxidative stability and high rigidity and creep resistance. The main applications of PES include moulded products as well as fibre-reinforced composites. The high T_g and the properties and applications of PES suggest this polymer as a suitable partner of PEEK when developing PEEK-based blends.

Blends of PEEK with PES have received attention in the patent and paper literature, both in unreinforced and reinforced states [1–7]. In some cases the blends contained a third component, poly(ether imide) for example. No systematic study of the phase behaviour and mechanical properties of these blends has, however, been performed to our knowledge.

In this work we have studied, first, the miscibility of PEEK–PES blends prepared by melt mixing. This study included differential scanning calorimetry, dynamical mechanical analysis and density measurements. Secondly, mechanical properties of the blends were determined by means of the tensile test.

2. Experimental procedure

The polymers used in this work were commercial products. PEEK was Victrex 450 G and was kindly supplied by ICI. It has a melt flow index of 5.0 g per 10 min, determined at 370 °C and with a 3800 g load. PES was Ultrason E, and was obtained from BASF. Its average molecular weights were $M_w = 97000$ and $M_n = 39000$ and were determined by GPC, using

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N,N-dimethylformamide as solvent. Both polymers were dried *in vacuo* at 100 °C for 24 h before mixing.

Melt mixing was carried out in a Brabender Plasticorder at 360 °C and at a mixing blade speed of 30 r.p.m. The torque required to turn the Brabender was registered as a function of mixing time, and the mixing operation was maintained until a constant torque was obtained, at a mixing time of 12 min. For the sake of comparison, the pure blend components were subjected to the same processing conditions.

After blending, the pure PEEK and PES and the blends of both polymers were compression moulded at 370 °C to obtain films of an approximate thickness of 0.1 mm. These films were subjected to two different thermal treatments. In one case, they were rapidly cooled from the melt by immersing them in cold water, to obtain quenched (Q) films. In the second treatment, the films were maintained under pressure during slow cooling of the press by means of a stream of air through the plates. The films obtained after this treatment will be called slowly cooled (SC) films.

Specimens for tensile testing (ASTM D638, type IV) were punched out from the films with a pneumatic die. Samples for calorimetric analysis and density measurements were also obtained from the films. The specimens for dynamical–mechanical analysis, with an approximate thickness of 1 mm, were compression moulded and then quenched.

DSC measurements were performed with a DuPont DSC cell equipped with a DuPont 2000 Thermal Analyst System. A heating rate of 20 °C min^{-1} was used, and a nitrogen flow was maintained through the DSC cell. The temperature and the enthalpy were calibrated with reference to indium and tin standards. The different parameters related to the thermal transitions (glass transition temperature, T_g; crystallization temperature, T_c; crystallization heat, ΔH_c; melting temperature, T_m and melting heat, ΔH_m) were determined in the usual way.

The densities of the blends were measured by means of a gradient density column, using sodium nitrate solutions.

Dynamic mechanical analysis was performed on a DMTA from Polymer Laboratories which provided the storage (E') and loss (E'') moduli and the loss tangent (tan δ). A heating rate of 4 °C min^{-1} was employed at a frequency of 1 Hz.

Tensile testing was carried out on an Instron 4301 tensile tester. A cross-head speed of 10 mm min^{-1} was used. The tests were carried out at 23 °C and the different mechanical properties (Young's modulus, E; nominal yield stress, σ_y; nominal break stress, σ_b and ductility, as measured from the nominal deformation at break, ε_b) were determined from the force–displacement curves. A mean of at least eight specimens was tested for the determination of the data. The respective mean typical deviations were ± 100 MPa, ± 2 MPa, ± 5 MPa and ± 3%.

3. Results and discussion

3.1. Phase behaviour

Fig. 1 shows the steadied torque–composition relationship obtained for PEEK–PES blends. As can be seen, the experimental values show a negative deviation with respect to the linear relationship between the values of the pure components. This type of behaviour has been related to the existence of incompatibility between the blend components in the melt [8], although there is sometimes no relationship between compatibility or incompatibility and the existence of positive or negative deviations of the blend viscosity with respect to linearity [9].

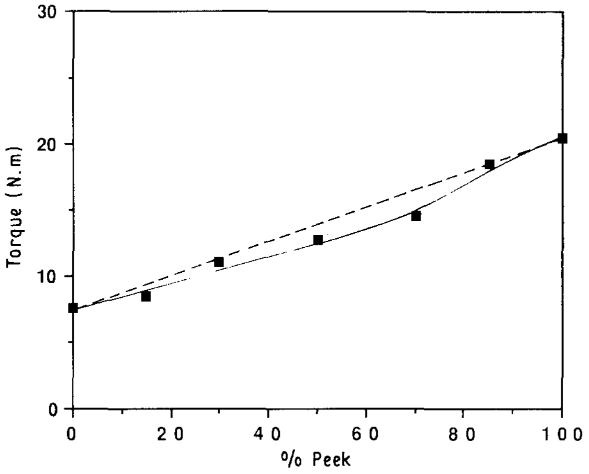

Figure 1 Torque–composition relationship for PEEK–PES blends.

Fig. 2 shows a typical thermogram obtained for the quenched PEEK–PES (50–50) blend. In the case of the slowly cooled sample a very similar plot was obtained except that no exotherm was observed due to the fact that PEEK crystallized during cooling. As can be observed in Fig. 2, two glass transitions at 144 and 220 °C appear in the quenched sample, along with a crystallization exotherm at 180 °C which corresponds to the PEEK crystallization from the glassy state. Finally, the melting endotherm of PEEK is also observed at 335 °C.

In Fig. 3a the thermal transitions of quenched blends are shown as a function of blend composition. The thermal transitions of the SC blends, which are shown in Fig. 3b, will be commented on below.

As can be observed, with reference to the glass transitions, two T_gs appear in all compositions studied, each of them at a temperature practically identical

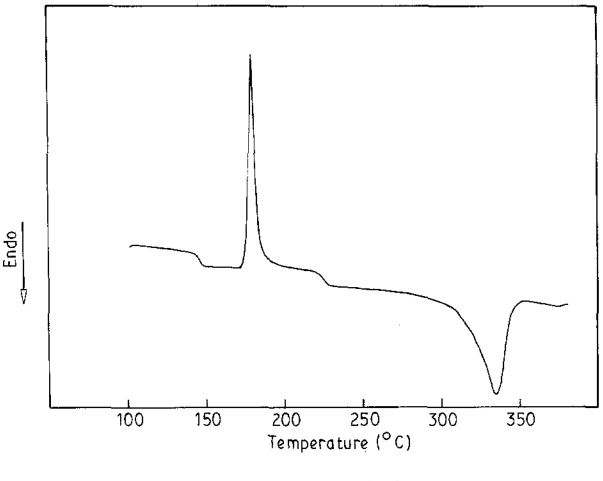

Figure 2 DSC thermogram of a quenched PEEK–PES (50–50) blend.

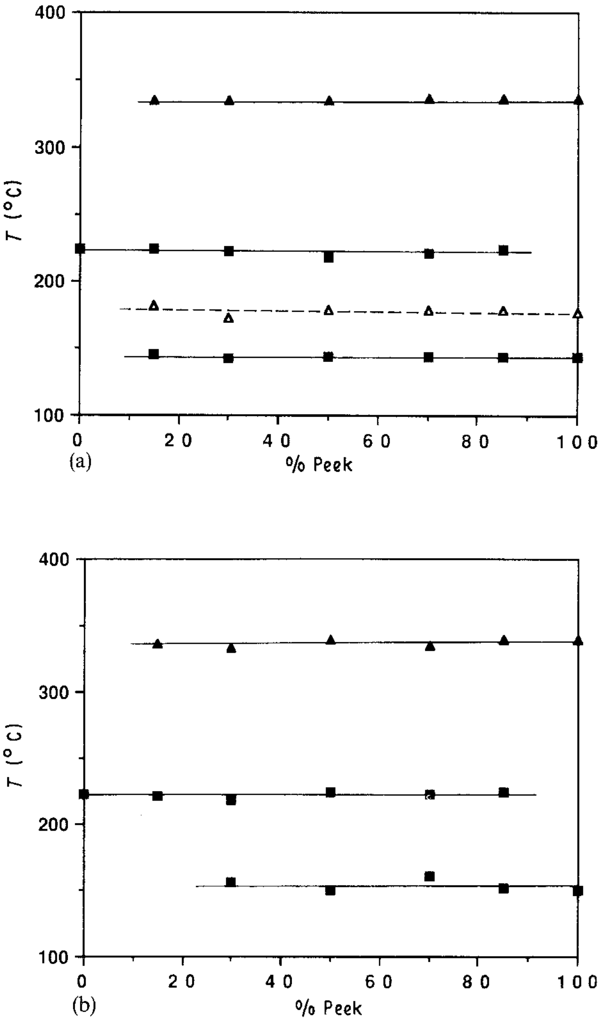

Figure 3 Thermal transitions of PEEK–PES blends. (a) Quenched. (b) Slowly cooled. (■, T_g; △, T_c; ▲, T_m).

to that of each pure component. This indicates the presence of two virtually pure phases in the blends. When the T_g values are determined by dynamic mechanical analysis (Fig. 4), the higher transition appears once again at an approximately constant temperature, whereas the lower one seems to increase slightly as the PEEK content in the blends increases. This could be attributed to a slightly higher crystallinity of PEEK when PEEK content increases in these PEEK-rich blends, as will appear below. Taking into account the differences which are usually observed when the T_gs are determined by DSC and DMTA, and the small variations observed in this case, no clear conclusions can, however, be obtained on this subject. The results concerning the glass transitions of PEEK–PES blends seem to be in close agreement with previous results [1].

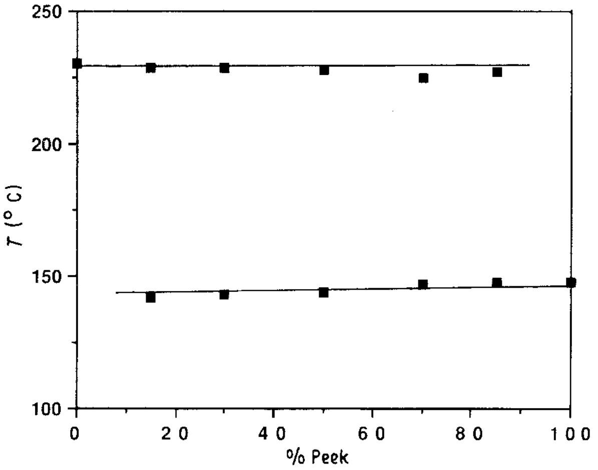

Figure 4 Glass transition temperatures of quenched PEEK–PES blends, measured by dynamic–mechanical analysis.

With respect to the crystallization behaviour, as we have mentioned, after the lower T_g the crystallization exotherm of PEEK appears in the DSC thermograms of quenched samples. No remarkable effect of the blend composition on T_c value is observed in Fig. 3a. This indicates that PES does not affect the crystallization process of PEEK. This accords with the almost full phase separation of the components of the blends. A similar conclusion is reached from the crystallization heats of PEEK in the blends, which are shown as open squares in Fig. 5a because they follow a linear relationship with respect to the blend composition.

The melting behaviour of PEEK is shown by the plot of the melting temperatures obtained for the blends in Fig. 3a and also in Fig. 5a where we show the melting heats of quenched PEEK–PES blends as a

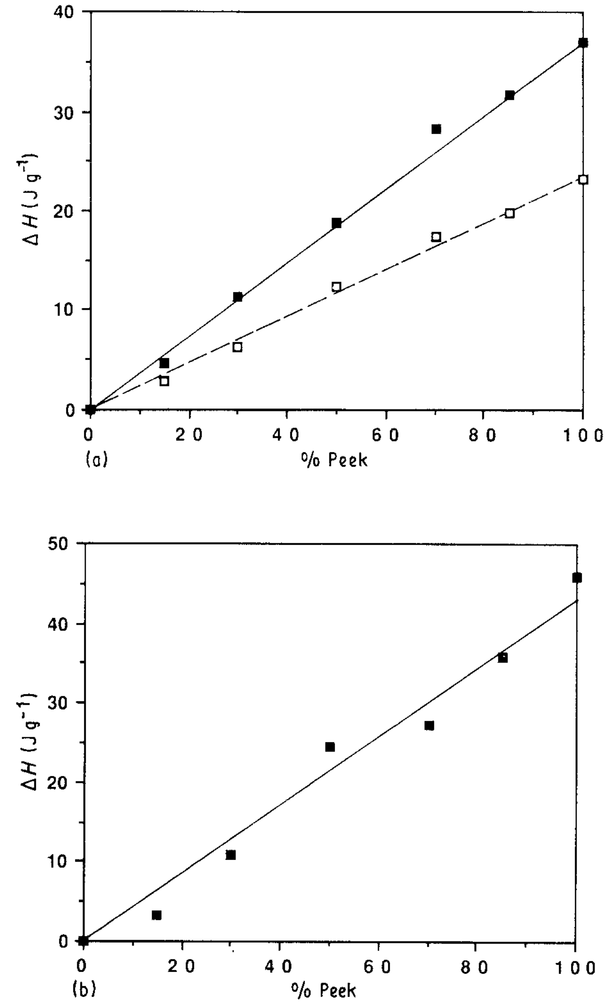

Figure 5 (a) Crystallization (□) and melting (■) heats of quenched PEEK–PES blends. (b) Melting heats of slowly cooled PEEK–PES blends.

function of composition. As is seen in Fig. 5a, a practically linear relationship is obtained, indicating once again the non-existence of any effect of PES in this case on the melting behaviour of PEEK. Moreover, as can be seen in Fig. 3a, the T_m values are practically constant with respect to composition. All these facts are experimental evidence that the crystallization–melting behaviour of PEEK is unrelated to the presence of PES, as a consequence of phase separation.

It is also important to observe that, as seen in Fig. 5a, the crystallization heat of PEEK in quenched blends is lower than the melting heat for all compositions. This seems to indicate that a fraction of PEEK crystallizes during quenching under the conditions applied. This is not clear, however, because it has been reported [10] that in the calorimetric analysis of PEEK, and at low crystallinity levels, additional, undetected crystallization takes place during the calorimetric scan. This, and no crystallization during quenching, would be the reason for the differences observed between the crystallization and melting heats.

The plot of the thermal transitions of the slowly cooled blends, which appears in Fig. 3b, is very similar to that of the quenched blends except for several differences in the values of the transitions and the lack of a crystallization point. The lower glass transition appears in slowly cooled blends at slightly higher temperatures than in quenched ones. This may be attributed to the higher crystallinity of PEEK in SC samples, which reduces the molecular motion of the polymeric chains. The lack of crystallization peak indicates that PEEK crystallizes completely during cooling from the melt. Finally, the melting temperatures were practically identical, as were the melting heats, which, as appears in Fig. 5b, were also linear both for Q and SC blends. These facts are evidence that similar crystalline structure and perfection are finally obtained irrespective of the thermal treatment of the blends.

All the results so far reported clearly indicate the almost absolute phase separation which takes place in PEEK–PES blends. The study of the phase behaviour will be complemented by means of the density and crystallinity values obtained for both sets of blends.

Fig. 6 shows the density–composition relationships obtained from the gradient density column. As is seen, a linear relationship is found for quenched blends; this linear relationship indicates the non-existence of strong interactions between the blend components which would give rise to densification, i.e., a positive deviation from linearity of the density–composition relationship [11].

The crystallinity levels of PEEK calculated from the density values are almost 0% in all compositions. This indicates that practically no crystallization takes place during cooling. It may thus be concluded that the differences between the crystallization and melting heats observed in the calorimetric scans (Fig. 5) are due to the previously mentioned undetected crystallization during the scan.

As far as the density–composition relationship for the SC samples is concerned, it also appears in Fig. 6.

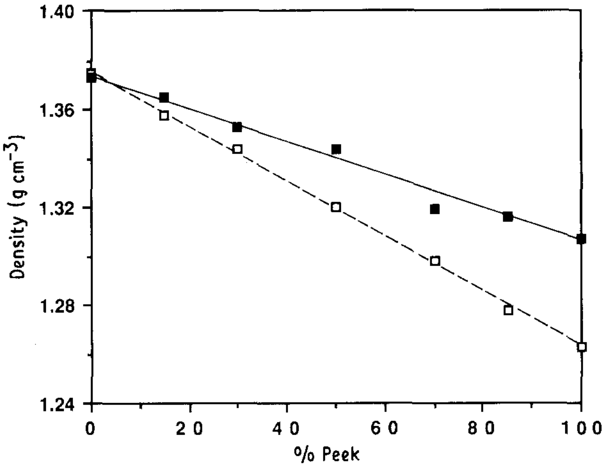

Figure 6 Density–composition relationship for quenched (□) and slowly cooled (■) PEEK–PES blends.

As can be observed, an approximately linear relation appears. The values obtained for the SC blends are higher than those obtained for Q ones, as expected taking into account the higher crystallinity values of PEEK in SC samples, which were seen because of the latter's ΔH_c and ΔH_m values. These crystallinity values of PEEK in SC blends, obtained from density measurements, are collected in Table I.

3.2. Mechanical properties

In Fig. 7 we show the Young's modulus–composition relationship for quenched and slowly cooled PEEK–PES blends. As can be observed, the values obtained for this low-strain mechanical property are generally higher for SC blends. This is true except at the lower PEEK contents, in which case both types of materials show approximately the same value. This behaviour is clearly a consequence of the higher crystallinity level of PEEK in the SC samples.

As is also observed in Fig. 7, the modulus–composition relationship for quenched samples is practically linear, a result which is unexpected, as the usual behaviour for incompatible blends is a negative deviation from linearity [12]. Incompatibility is the expected consequence of the almost full immiscibility of the blend. This unexpected behaviour, which has been observed also in other immiscible polymer blends [13–15], may be explained on the basis of adhesion level between the phases, good enough to be able to transmit the stress to the dispersed phase at least after the small deformations and at the low stress

TABLE I Crystallinity values of PEEK in SC PEEK–PES blends from density measurements

Composition (PEEK–PES)	Crystallinity (%)
0–100	0
15–85	4.6
30–70	8.1
50–50	17.9
70–30	16.6
85–15	26.7
100–0	31.9

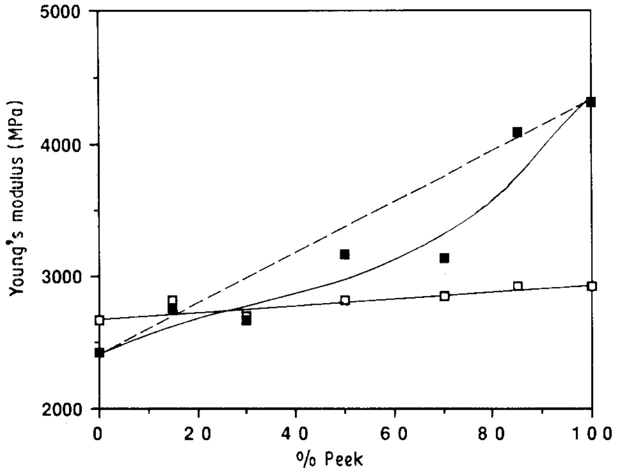

Figure 7 Young's modulus of quenched (□) and slowly cooled (■) PEEK–PES blends.

characteristic of the measurement of the Young's modulus.

In the case of slowly cooled blends, the Young's modulus–composition relationship shows a negative deviation from linearity. This negative deviation indicates that the crystallization of PEEK, which has no clear influence on such properties as Young's modulus or ductility [16], has in this case a negative effect on this mechanical property of the blends. As we shall see, this negative influence also appears in other mechanical properties.

Fig. 8 shows the yield stress of the blends as a function of composition. In the case of quenched blends, the experimental values are slightly higher than the additive ones, indicating once again the existence of good phase adhesion between the phases of the blends.

In the case of slowly cooled blends, only the pure components undergo the yield process. The σ_y value is slightly higher for SC PES than for Q PES, whereas it is much higher for SC PEEK than for Q PEEK, as a consequence of the higher crystallinity degree of slowly cooled PEEK. Slowly cooled PEEK–PES blends do not yield, but break before the yield point. This is an initial indication that the crystallinity of PEEK increases the brittleness of the blends. Other results concerning mechanical properties of the blends also show this brittleness, as we shall see.

As a consequence of the results obtained in the analysis of the small-strain properties of the blends, it appears that in the case of quenched, non-crystalline blends, blending has a rather favourable effect on the properties, whereas in the case of slowly cooled blends, although the modulus is maintained at a high level, the brittleness of the blends has as a consequence the absence of the yield process.

The break properties of PEEK–PES blends also show a different behaviour depending on the thermal treatment imposed on the samples. In Fig. 9 we have represented the break stress as a function of composition for the two sets of samples. Negative deviations from linearity are generally found in both cases. These deviations are more important in the intermediate compositional range and in the case of slowly cooled, and hence highly crystalline blends. Thus, although the break stress of the pure components is slightly higher when they are slowly cooled from the melt than when they are quenched, the opposite takes place in most of the blends due to their biphasic nature.

Finally, the effect of the thermal treatment undergone by the blends on ductility, measured as the nominal deformation at break, is shown in Fig. 10. As can be seen, in the case of SC blends the ductility is very low in all compositions, as has already been mentioned, and the blends must be considered brittle. This embrittlement must be due to the fact that the deformation at fracture of the crystalline PEEK at ambient temperature in the used processing conditions (7%) is very close to the brittle–ductile transition, that is, as usually considered, to the deformation at yield, thus, a small decrease in the ductile nature of the material gave rise to a marked decrease in the deformation at fracture. This is in accord with the observed behaviour of tensile strength, where clear decreases were observed due to the fact that fracture took place before yielding. This is because before yielding a small ductility change produces a clear change in the tensile strength. This is a negative conclusion because PEEK is chiefly used at its high

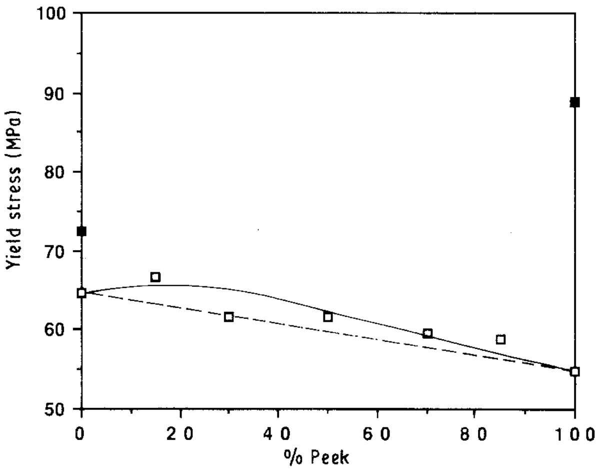

Figure 8 Yield stress of quenched (□) and slowly cooled (■) PEEK–PES blends.

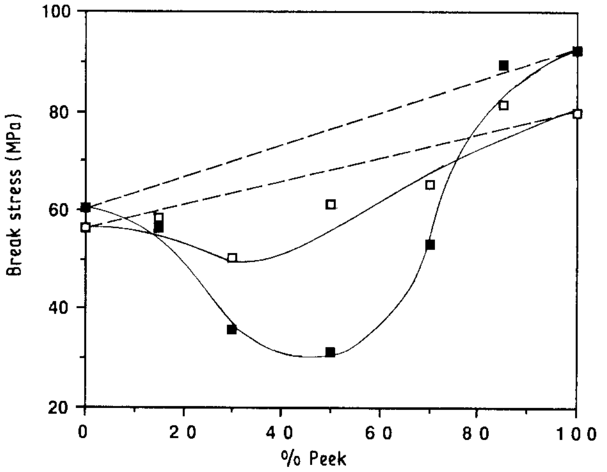

Figure 9 Break stress of quenched (□) and slowly cooled (■) PEEK–PES blends.

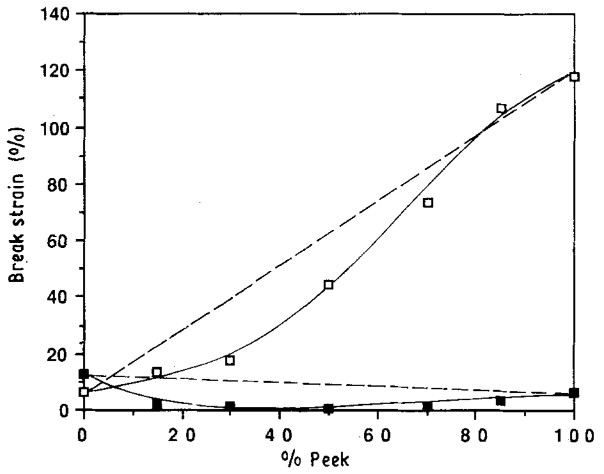

Figure 10 Break strain of quenched (□) and slowly cooled (■) PEEK–PES blends.

crystalline contents. The ductility increase necessary to overtake the deformation of the yield point is, however, small, so, any small ductility improvement, by means of a slight decrease of the crystalline content or any other change, would have a much greater effect on the tensile strength and probably on the tensile toughness.

Regarding the ductility of the Q blends, Fig. 10 shows a small negative deviation from linearity except at the higher PEEK contents. This behaviour is important and unusual in immiscible blends. Unusual because immiscible blends that have not been compatibilized by means of grafting, for instance, normally show very brittle behaviour. Even the presence of significant amounts of plasticizer [15] or of one of the components [13] in both phases of the blend are not active enough to produce a material of ductility similar to that of the components. In this case, however, in spite of almost complete immiscibility – the T_gs are those of the pure components – a 50–50 blend, close to the maximum negative deviation from linearity, shows a deformation at fracture of 44%. This is a ductile material.

This behaviour of the ductility of the Q blends cannot be explained as a result of the used moulding method [13] because it does not produce any remarkable anisotropy, so it must be attributed to the nature of the blend itself. This behaviour of blends with near-maximum immiscibility but with a reasonable level of mechanical properties has been found in other polymer blends [14, 17] and suggests that either miscibility, or even partial miscibility, or the presence of a third component in both of the phases of the blends is not a precondition to achieving compatibility, that is, good mechanical properties, in an engineering polymer blend. This offers a possible new direction in the development of valuable new polymeric materials in the near future.

4. Conclusions

PEEK–PES blends are immiscible, as indicated by the results obtained from calorimetric and dynamic–mechanical analysis. Two phases are present in the blends, each of them almost totally composed of each pure component. Density measurements indicate the non-existence of strong interactions between the blend components. The crystallization–melting behaviour of PEEK is little affected by the presence of PES in the blends.

The SC, partially crystalline blends exhibit a Young's modulus below, but rather close to linearity; however, the long-term mechanical properties suffer a clear deterioration due to the combined effect of both crystallization and blending on the ductility of the blends.

The mechanical properties of the quenched blends are maintained at a good level in spite of phase separation. The high-strain properties, such as break stress and ductility, show slight negative deviations from linearity, while Young's modulus and yield stress appear as linear or even above linearity. Intermediate materials between Q and SC blends with tailored Young's modulus and ductility could be produced by controlling the crystalline content of the blends.

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