

Compatibility in Immiscible Poly(ether ether ketone)/Poly(ether sulfone) Blends

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SYNOPSIS

Both as-molded and annealed poly(ether ether ketone) (PEEK)/poly(ether sulfone) (PES) blends have been prepared by direct injection molding. The system has been found to be immiscible at all compositions; however, as a result mainly of the produced morphology, it surprisingly maintains to a very great extent the excellent mechanical performance of both of the pure components. This mechanical response is compared with that of the compression molded blends. The ductility of these blends when quenched appears close to the linear between that of the two components. Leaving aside possible morphological and excess free volume of mixing effects, it is in part attributed to the nature of the blend itself.

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INTRODUCTION

The growing demand for polymeric materials with good mechanical properties, high service temperature, and improved chemical resistance has led to active research in the development of new high-performance polymeric materials. A particularly interesting way to obtain new engineering polymers is blending. This is because it allows an ensemble of properties to be obtained that is difficult to achieve in a single polymer. Furthermore, blending gives rise to a range of properties in the final product by changing the blend composition.

Poly(ether ether ketone) (PEEK) is the most common of a class of engineering polymers of recent development: the poly(aryl ether ketones). It is a semicrystalline aromatic thermoplastic with remarkable properties at high temperatures. It offers an excellent balance of properties: toughness, strength, and rigidity, good electrical properties, as well as chemical and radiation resistance. That is why PEEK is generating great interest in applications such as coatings, electrical connectors, impeller housings, molded parts, and high strength composites.

Poly(ether sulfone) (PES) is a typical amorphous engineering thermoplastic: tough, strong, and rigid at room temperature, but distinguished from the others by its high temperature performance, low flammability, and smoke emission. The main applications of PES include coil formers, connectors, terminal blocks, hot water meters, reflectors, medical components, bearings, metal coatings, and the matrix for high-performance composites.

Depending on its crystalline degree, PEEK cannot maintain its stiffness at temperatures higher than its glass transition temperature ($\sim 150^\circ\text{C}$) but can improve the chemical resistance of PES. On the other hand, PES, because of its amorphous nature, is easily attacked by common solvents but it has a higher T_g than PEEK ($\sim 220^\circ\text{C}$) so that it can endure higher temperatures. This is why PEEK and PES seem to be suitable partners to be blended together.

Blends of PEEK and PES have received much attention mainly in the patent literature, both in unreinforced and reinforced states.¹⁻¹⁴ Moreover, the phase behavior and mechanical properties of kneaded melt-blended and compression-molded PEEK/PES blends have been previously studied.^{14,15} Their phase behavior appears unclear because both a single¹⁴ and two almost constant T_g s¹⁵ have been reported. However, to our knowledge, no

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work has been published dealing with the mixing level and properties of PEEK/PES blends directly mixed in an industrial injection machine or with its microscopic structure. This is why the major purpose of this paper is to study the mixing level, structure, and mechanical behavior at room temperature of blends of PEEK and PES. The blends were prepared by direct injection and studied both as-molded (AM) and annealed (AN). Their structure and mechanical behavior were compared with those of compression-molded blends. This study includes (1) DSC, DMTA, WAXS, density, and SEM measurements and (2) the mechanical properties of the blends determined by means of tensile and impact tests.

EXPERIMENTAL

The polymers used in this work were commercial products. PEEK was Victrex 450G, kindly supplied by Imperial Chemical Industries (ICI). It had a melt flow index of 5.0 g/10 min, determined at 370°C and with a 3,800 g load. PES was Ultrason E-2000, and was obtained from BASF. Its average molecular weights were $M_w = 97,000$ and $M_n = 39,000$ as determined by GPC using *N,N*-dimethylformamide as solvent. Both polymers were dried in an air oven at 120°C for at least 18 h before processing.

The polymers were directly melt mixed and injection molded in a Battenfeld BA 230E machine, using a barrel temperature of 370°C and a mold temperature of 16°C. The screw of the plasticization unit was a standard screw with a diameter of 18 mm, L/D of 17.8, compression ratio of 4, and helix angle 17.8°. No mixing devices were present. The injection speed and pressure were 6.6 cm/s and 2,000 bar, respectively. Tensile (ASTM D638 type IV) and impact (ASTM D256) specimens were obtained. Annealing of the injection-molded specimens was carried out in an air oven at 185°C for 24 h. Both tensile and impact specimens were kept hung during the annealing process. The samples which were not annealed (AN) will be called "as-molded" (AM) blends.

DSC measurements were carried out with a Dupont DSC cell equipped with a Dupont 2000 Thermal Analyst System. A heating rate of 20°C/min was used, and a nitrogen flow was maintained through the DSC cell. The different parameters related to the thermal transitions were determined in the usual way. The crystallinity of the blends was determined from density and wide angle x-ray scattering (WAXS) measurements. The density values were measured at 23°C by means of a density gradient

column using calcium nitrate solutions. The resolution of the density column was estimated to be 0.0005 g/cm³. The crystallinity of the blends was calculated, assuming volume additivity, by means of the expression

$$1/\rho = X_{\text{PEEK}}/\rho_{\text{PEEK}} + X_{\text{PES}}/\rho_{\text{PES}}$$

$$1/\rho_{\text{PEEK}} = X_c/\rho_c + (1 - X_c)/\rho_a$$

where ρ_c is the density of 100% crystalline (1.4006 g/cm³) and ρ_a that of amorphous PEEK (1.2626 g/cm³).¹⁶

Crystallinity was also measured by WAXS. The scattered intensities were measured as a function of Bragg angle (2θ) for all the blends and pure components. Crystallinity was calculated from WAXS using the relative areas under the crystalline peaks of the annealed (A_c) and amorphous (A_a) backgrounds using the expression¹⁷

$$X_c = (1 + A_a/A_c)^{-1}$$

The maximum crystallinity deviation observed between the two x-ray calculations for each blend composition was $\pm 2.5\%$.

Dynamic mechanical analysis was performed on a Polymer Laboratories DMTA, which provided the storage (E') and loss (E'') moduli and the loss tangent ($\tan \delta$). A heating rate of 4°C/min and a frequency of 1 Hz were employed. Scanning electron microscopy (SEM) on cryogenically or tensile-fractured samples was carried out after gold coating with a Hitachi S-2700 electron microscope operated at 15 kV.

Tensile testing was carried out on an Instron 4301 tensile tester at $23 \pm 2^\circ\text{C}$. A crosshead speed of 10 mm/min was used. High temperature tests at $125 \pm 2^\circ\text{C}$ were performed in an environmental chamber (INSTRON 3110). The different mechanical properties [Young's modulus (E), yield stress (σ_y), and ductility (determined as the nominal deformation at break (ϵ_b))] were determined from the force-displacement curves, and were an average of at least 8 measurements. Izod impact tests were performed in a CEAST pendulum on injection-molded and subsequently notched specimens (notch depth: 2.54 mm; notch radius: 0.25 mm) with a cross section of 12×3.2 mm. The annealed samples were notched prior to annealing. The values obtained for impact strength were an average of at least 8 determinations.

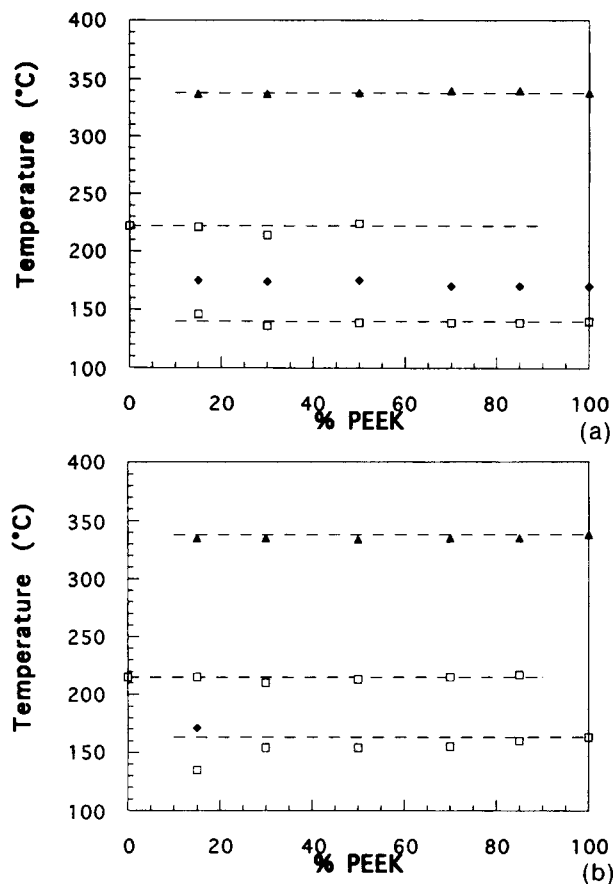


Figure 1 Thermal transitions determined by DSC [T_g (\square), T_c (\blacklozenge), and T_m (\blacktriangle)] of as-molded (a) and annealed (b) injection molded PEEK/PES blends.

RESULTS AND DISCUSSION

Solid State

The thermal transitions of injected PEEK/PES blends as determined by DSC against blend composition are represented both in the case of AM [Fig. 1(a)] and AN [Fig. 1(b)] specimens. Both of them show two glass transitions at temperatures near the T_g s of both pure PEEK and PES, over all the composition range. In some PEEK-rich compositions, the T_g of PES was not detected, probably due to the low PES content, and to the low sensitivity of the calorimeter. The AM blends and the 15/85 AN blend show a practically constant exothermic peak at a temperature just above the T_g of pure PEEK that corresponds to its crystallization during the heating scan. It is to be noticed that the annealing process produces (1) a rise in the T_g of the PEEK-rich phase from 140°C [Fig. 1(a)] to 160°C [Fig. 1(b)] approximately, due to the increased crystallinity that will be seen after and (2) the disappear-

ance of the crystallization exotherm of PEEK in the blend due to the fairly full PEEK crystallization during the annealing process, except in the 15/85 composition. Finally, the melting endotherm of PEEK remains nearly constant with blend composition. All these calorimetric data point out the almost fully immiscibility of the system, and the small effect of PES on the crystallization and melting behavior of PEEK as a consequence of phase separation. These results are in close agreement with previous results.^{1,10,15}

The T_g s of the AM blends measured from the $\tan \delta$ peaks of the dynamic mechanical scans are plotted against composition in Figure 2. Similar features to those that will be commented for AM blends were seen in the case of AN blends. For this reason and because of clarity the T_g s of AN blends are not plotted in Figure 2. Taking into account the composition of the blends, the presence of the other component did not affect the important secondary transitions of both PEEK and PES. As seen in Figure 2, two glass transitions are present in all the composition range at temperatures similar to the T_g s of pure components, in close agreement with DSC results. However, in Figure 2, a slight shift in these two T_g s can be observed. The higher T_g drops by up to 7°C as the PEEK content in the blend increases, whereas the low T_g shifts to a smaller extent to lower temperatures at increasing PES contents. This change of the T_g of PEEK could be due to small, difficult to detect, differences in crystalline contents in the blends. The decrease in T_g of the PES-rich phases, not observed by DSC probably because of the lower resolution available for this method, indicates incomplete phase separation and some interaction between the separated phases. Actually, the existence in PEEK/PES blends of immiscibility,¹⁵ a limited

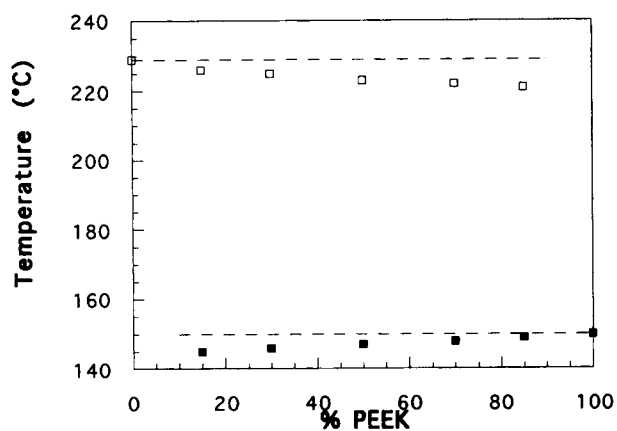


Figure 2 Glass transition determined by DMTA of as-molded PEEK/PES blends.

Table I Crystalline Content of PEEK in PEEK/PES Systems, Calculated from x-Ray Measurements, as a Function of Blend Composition

PEEK/PES	X_c (X-Ray) (%)	
	As-molded	Annealed
100/0	0	17.6
85/15	0	21.1
70/30	0	22.5
50/50	0	25.4
30/70	0	20.0
15/85	0	^a
0/100	0	0

^a Difficult to be measured accurately.

level of miscibility,^{2,5} and, although only stable at temperatures below the T_m of PEEK, even the presence of a single T_g ¹ has been reported. This stability limit gives rise to the fact that in these blends the method and characteristics of blending play a definitive role in the phase behavior and composition obtained. Taking into account the observed T_g s and the long annealing time the blends are practically immiscible at least at 185°C.

The crystallinity of PEEK/PES blends was determined because it strongly influences the mechanical properties. The determination of the crystalline content of a partially crystalline blend presents several problems. At first one could expect that an accurate and easy way to determine X_c would be calorimetry. However, it must be taken into account that in the calorimetric analysis of PEEK recrystallization takes place during the heating scan¹⁸; this additional crystallization may give rise to an overestimation of the X_c values.

With respect to the use of density for the calculation of X_c , besides crystallinity, there is another parameter which determines density, i.e., the change of volume of mixing that may be produced.¹⁹ In immiscible blends densities should agree with values calculated from the simple additivity rule and thus crystallinity indices can be calculated. However, in the case of PES-rich AM samples as well as in the 15/85 (PEEK/PES) AN blend, incorrect negative values of crystallinity were obtained. Provided the values of the densities of complete crystalline and amorphous PEEK are accurate, this indicates the existence of a surprising positive excess volume of mixing. The change of volume of mixing renders the values of crystallinity calculated from density invalid, so that the crystallinity indices were measured

only by x-ray and are collected in Table I. From the goniometer traces the AM blends appeared amorphous while the crystallinity of PEEK in the AN blends did not significantly change with composition and was close to 20%. The lack of influence of PES on the crystallization of semicrystalline PEEK is probably due to the almost complete phase separation characteristic of the system.

Figure 3 shows the specific volume–composition relationship both in the case of AM and AN blends. There is a decrease in the specific volume of AN blends compared to AM ones, as a consequence of the increased crystalline content after annealing. Both AM and AN samples follow a similar trend vs concentration, that is a positive deviation from the additive rule of mixtures. This excess in volume of mixing could be due to the lack of strong interactions between PEEK and PES, but the effect of crystallinity should also be taken into account. A change in crystallinity from 25 to 21.8% is within the experimental error and it gives rise to a change in specific volume of 0.0025 cm³/g that is of the order of the observed changes. Thus, a positive excess volume of mixing is produced, but its real value may be influenced by the although possibly small, difficult to estimate^{20,21} changes in crystallinity.

Morphology

The surfaces of cryogenically fractured AN blends are shown in Figures 4(a), (b), and (c). The AM injection molded blends showed similar morphologies taking into account the incomplete homogeneity of the blends. As can be seen, in both the 85/15 and 30/70 compositions, Figure 4(a) and (c), a homogeneously dispersed phase appears. The 15/85 blend

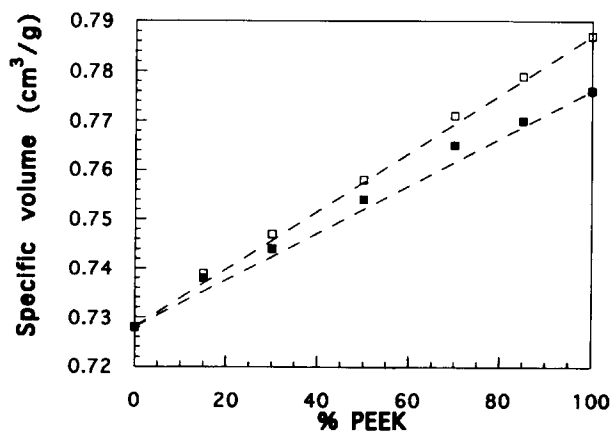
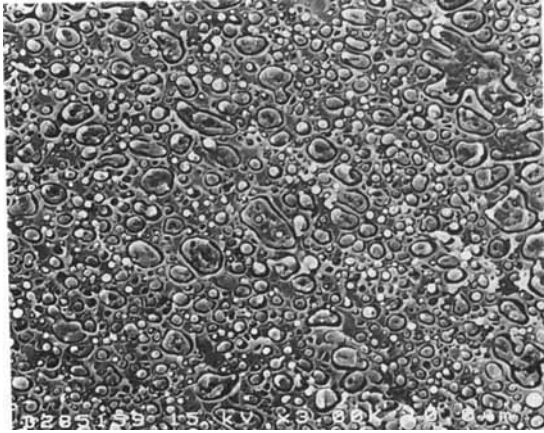
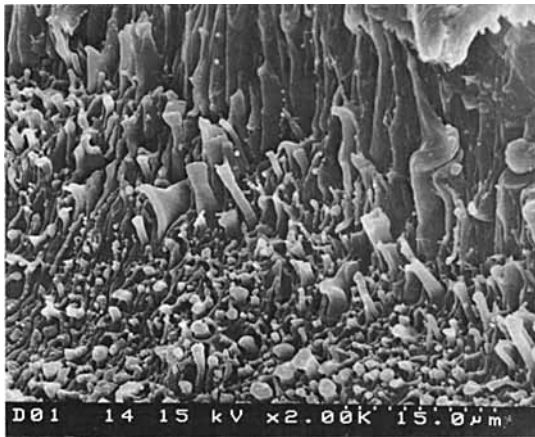


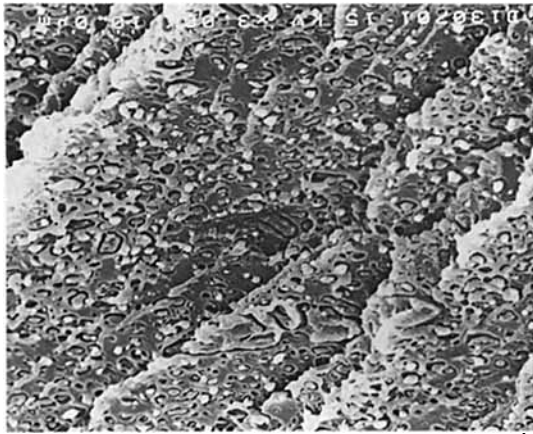
Figure 3 Specific volume–composition relationship of as-molded (white squares) and annealed (black squares) PEEK/PES blends.



(a)



(b)



(c)

Figure 4 Cryogenically fractured surfaces of PEEK/PES annealed specimens: (a, b) 85/15; (c) 30/70 compositions.

showed a similar structure. The 50/50 and 70/30 compositions appeared cocontinuous. Figure 4(b) was taken at 60° from the vertical axis and corre-

sponds to very minority zones of the 85/15 composition, that also appeared in other compositions.

Figure 4(a) clearly shows that the amount of dispersed phase is much larger than the 15% that composition indicates. This is because PEEK is present inside the dispersed PES phase. This gives rise to a more massive PES presence than that composition indicates and is experimental evidence of the very finely mixed structure obtained, despite immiscibility, by direct injection molding. Similar morphology was seldom observed in the case of PES-rich blends and in the 50/50 composition.

As can be also seen in Figure 4(b), the morphology of the 85/15 blend seen in Figure 4(a) as well as that of the other compositions was not sphere-like as might be supposed from Figure 4(c) but thin cylinders perpendicular to the fracture surface. This morphology is more clear in Figure 5 where the fracture surface of a 30/70 blend after tensile testing at room temperature is seen at an angle of 50° from the vertical. Figure 5 corresponds to roughly a 15% of the fracture surface. The rest was similar to the interfibrillar areas of Figure 5. As can be seen, and as it took place in the rest of compositions, the general debonding observed after cryogenic fractures develops ductile fracture at room temperature with rough fracture surfaces without any sign of debonding, despite the almost complete immiscibility of the blend.

Small Strain Mechanical Properties

The Young's moduli of PEEK/PES blends as a function of blend composition are shown in Figure 6. They follow a practically linear relationship with blend composition, with a small negative deviation

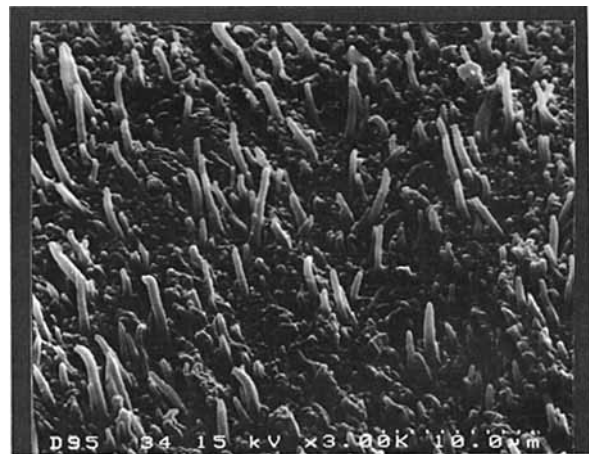


Figure 5 Tensile fracture surface of PEEK/PES 30/70 annealed specimen.

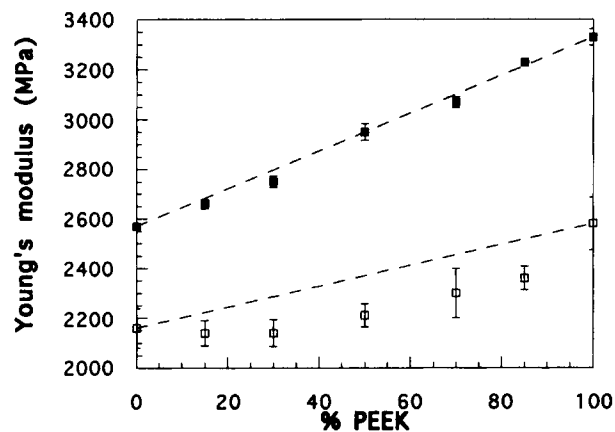


Figure 6 Young's modulus-composition relationship for PEEK/PES as-molded (white squares) and annealed (black squares) blends.

from linearity, higher in the case of AM than in AN samples. This behavior, despite immiscibility, has often been observed in several blends,^{15,22} and has been explained on the basis of a minimum adhesion between the phases of the blend, that would be good enough to be able to transmit the stress to the dispersed phase at least at the low stress and deformation characteristic of the Young's modulus measurements.

If we compare the Young's moduli of the AN with those of the AM specimens the former are higher. This behavior agrees with the higher crystallinity level of PEEK attained in the AN samples. However, in the case of pure PES, the reason for the increased modulus must, of course, be different. As is known,²³ an increase in the Young's modulus during an annealing or aging process could also be due to the package or reorganization of polymeric chains leading to vitrification and to a decrease in free volume and, thus, mobility. In fact amorphous PES has been aged at 185°C, a temperature below its T_g ($\sim 220^\circ\text{C}$) but higher than its important γ ($\sim -100^\circ\text{C}$) and β (~ 110) transitions. This vitrification, although not detected by the density measurements, can take place.²⁴ To confirm this, the dynamic mechanical tests of AM and AN PES are shown in Figure 7. As can be seen, after annealing, a clear decrease in $\tan \delta$ occurs from roughly 0°C until T_g . This loss of mobility must be the reason for the observed modulus increase in AN blends at room temperature. To prove this, modulus and ductility were measured at 125°C , that is, in the region where the $\tan \delta$ decrease is mainly observed. Modulus increases were also observed and ductility decreased much more than at room temperature, due to the loss of mobility after annealing.

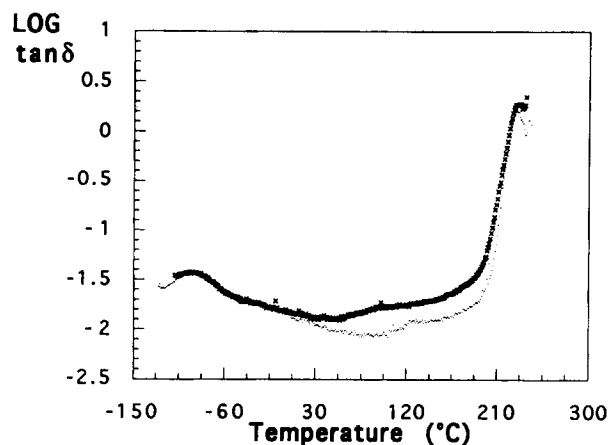


Figure 7 Loss tangent of PES before (x) and after annealing (·) as a function of temperature.

After annealing of pure PES, an increase in density, typically less than 0.5%, should also take place.²⁵ It is not observed in Figure 3 so that it ought to be less than the estimated resolution of the density column of 0.0005 g/cm^3 (0.036%). This agrees with our previous results¹⁵ and with the results of Golden et al.²⁶ who reported the apparent maintenance of the density after annealing treatments concomitant with the increase in small strain properties. Thus, there is additional experimental evidence for the fact that in amorphous polymers, annealing may produce rigidity without, although present,²⁷ a significant decrease in the free volume of the blend.

The yield stress (σ_y) of the blends is shown in Figure 8 as a function of blend composition. It exhibits a slight negative deviation from linearity in the case of AM blends and a nearly linear relation-

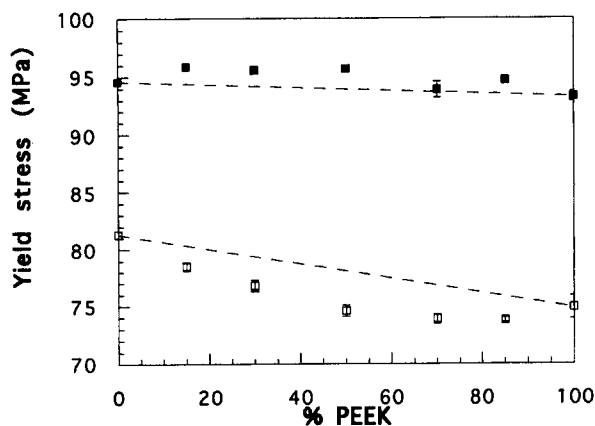


Figure 8 Yield stress-composition relationship for PEEK/PES as-molded (white squares) and annealed (black squares) blends.

ship for the AN samples. These data of σ_y vs composition follow a similar trend to the Young's modulus vs composition data and indicate the existence of good adhesion between the phases of the blend. When the AM and AN values are compared, a very noticeable rise in σ_y of PEEK/PES blends after annealing appears. This must be due to the increased crystalline content of the PEEK-rich phase of the blends, concomitant with the previously reported loss of mobility of PES as a consequence of thermal aging.

Ultimate Mechanical Properties

In Figure 9 the ductility of the injection molded blends (full lines, squares) is shown. As can be seen, despite the complete immiscibility of the blends, their ductility values are almost a linear combination of the contribution of each component, because when deviation takes place it is comparable to the typical deviation of the measurement. This takes place both in the case of AM (empty squares) and in the AN blends (full squares). The decrease in ductility of the AN blends is due to their semicrystalline nature, to the decrease in free volume of the amorphous phase, and to the weakening of the secondary transition on annealing.²⁸

The impact strength of the blends against composition is shown in Figure 10. As can be seen, this impact strength behavior agrees with that of ductility because it is not at all common in immiscible blends. The impact strength of AN and AM pure PEEK is the same; this agrees with previous results²⁹

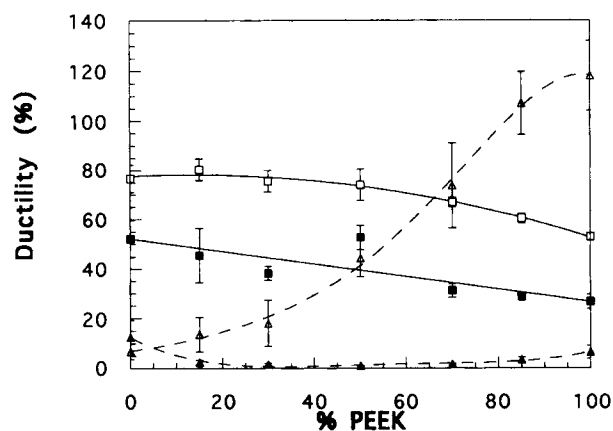


Figure 9 Ductility-composition relationship for PEEK/PES blends. Squares correspond to injection molded blends [as-molded (\square) and annealed (\blacksquare)] and triangles to melt kneaded and compression molded blends from Arzak et al.¹⁵ [quenched, amorphous (\triangle) and slowly cooled, crystalline (\blacktriangle)].

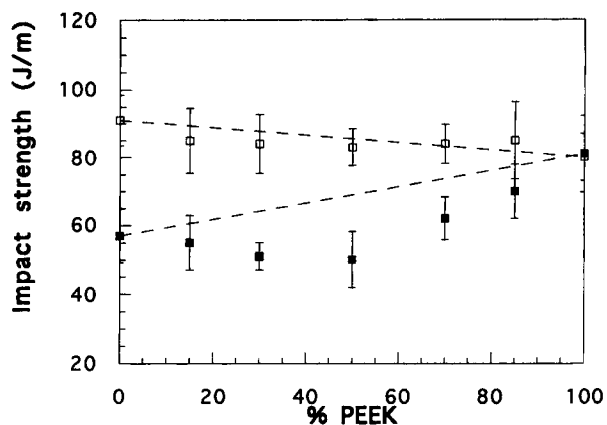
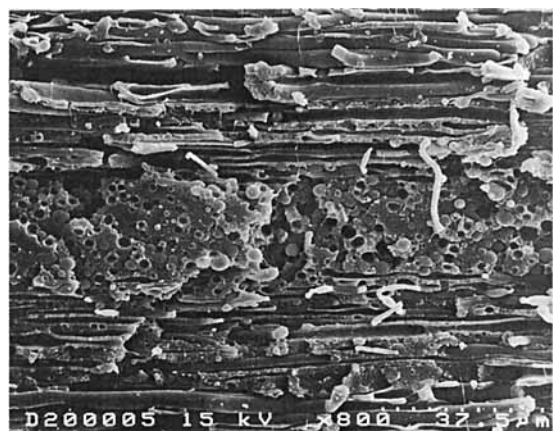


Figure 10 Impact strength-composition relationship for PEEK/PES as-molded (white squares) and annealed (black squares) blends.

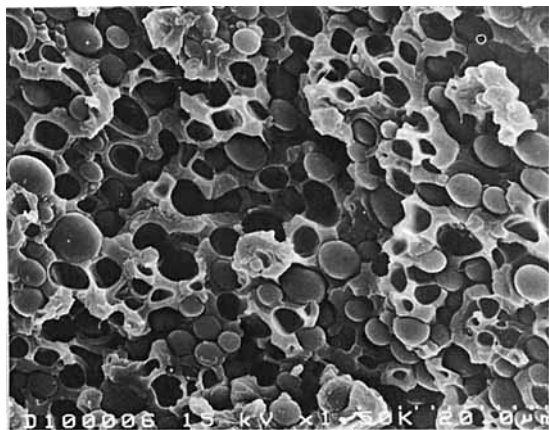
and is due to the contribution of strength, besides that of ductility, to impact resistance.

These high-performance results in fracture properties, more usual in monophasic blends, are not entirely unexpected, because injection molding is able to give rise^{30,31} to very oriented structures with elongation properties³² much higher than those expected from immiscible blends. In this way the presence of oriented structures, although not as developed as in other blends,³⁰ was clearly seen in Figures 4 and 5. Moreover, as seen in Figure 4(a) and (c) the component which forms the matrix is often present inside the dispersed phase. Thus, the appearance of this hardly anisotropic morphology is enough to explain the high ductility of these practically immiscible blends.

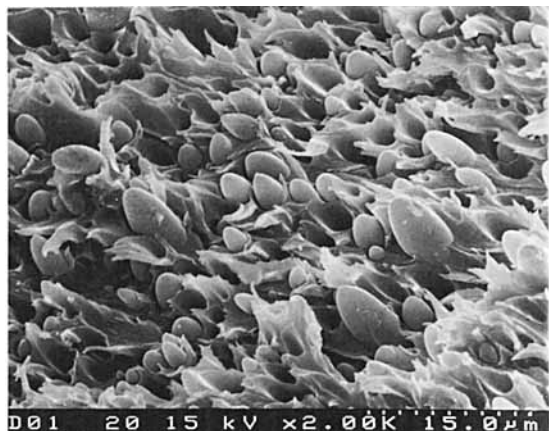
With the aim of verifying this proposition, the morphology and ductility of the injection molded blends of this work were compared with those of compression molded PEEK/PES blends. The ductility values were collected from Arzak et al.¹⁵ and are shown in Figure 9 (dotted lines, triangles). The morphology was observed after melt blending in a Brabender mixer, compression molding, quenching or slow cooling, and tensile fracture, and is shown in Figure 11. Cryogenically fractured specimens showed similar morphologies. As can be seen in Figure 11(a), the 70/30 slowly cooled (SC) composition is rather cocontinuous, as is the 50/50 blend due to the proximity of both compositions to the phase inversion composition. The morphologies of the 30/70 composition, Figure 11(b), and those of the 15/85 and 85/15 that were very similar, are that of a typical brittle polymer blend, i.e., a fine dispersion of slightly deformed spheres that has been debonded from the matrix. Similar structures, but more de-



(a)



(b)



(c)

Figure 11 Tensile fracture surface of compression molded PEEK/PES. (a) 70/30 and (b) 30/70 compositions slowly cooled; (c) 30/70 composition quenched.

formed, are seen in Figure 11(c) at 50° from the vertical axis for the quenched (Q) amorphous blends obtained by compression molding. As can be seen, the morphology of the SC blends agrees with their

low ductility values. However, the compression molded Q blends show a surprising positive response.

This excellent performance in ductility of compression-molded immiscible blends is very unusual.³³ Given the amorphous state of the components, it may be due to any of the following parameters: flow-induced orientation in the tensile direction, change in the free volume of the blends, or the nature of the blend itself.

With respect to flow-induced orientation, such a fibrous structure scarcely starts to appear in these blends, as seen in Figure 11(c). A free volume increase in the blends due to blending does not take place to an important extent, as seen in Figure 3. Thus, although such a large ductility is not found in the brittle slowly cooled compression-molded blends, the nature of these ductile blends itself seems to be one reason for the observed ductility behavior. Nature is used here to mean (1) a largely aromatic character that has been proposed³⁴ to be the reason for compatibility in PPS blends, or (2) a limited miscibilization of both polymers only at the interfacial surface that would not be clearly reflected in the T_g values. In fact, the mechanical properties of an immiscible blend may depend on enthalpic interactions and related polymer-polymer adhesion between the phases.³⁵ Moreover, these blends have identical structural diphenylene ether units in the molecular chain and the possibility of preferential surface adsorption³⁶ and thus surface enrichment,³⁷ as takes place in other materials, has been postulated for polymers by means of x-ray photoelectron spectroscopy (XPS).

Thus, there is evidence of immiscible blends with a reasonable level of mechanical properties, without structural reasons. This suggests that either partial miscibility, specific morphologies, or the presence of a third component in both phases of an immiscible blend is not a precondition to achieve compatibility in an engineering ductile polymer blend. Moreover, it offers a possible new direction in the research and development of valuable new polymeric materials in the near future.

CONCLUSIONS

Directly injection-molded blends of PEEK and PES are composed of two almost pure phases over the entire range of compositions. Injection molding is a suitable way of mixing and, despite immiscibility, it provides mechanically compatible blends with improved mechanical properties with respect to those

of compression molding, mainly due to the morphology produced.

Compression molded and quenched ductile PEEK/PES blends also constitute unexpected mechanically compatible materials, despite immiscibility and the lack of favorable morphology. The good adhesion that must exist is mainly attributed to the nature of the blend, i.e., to a large aromatic character in both components, or to miscibilization only at the surface.

This work has been supported by the University of the Basque Country (Project 084/90). A. Arzak wishes to thank to the Basque Government for the award of a grant for the development of this work.

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Received January 11, 1995

Accepted March 28, 1995