# Biphasic Compatible Blends from Injection-molded Poly(ether ether ketone)/Polysulfone

A. ARZAK, J. I. EGUIAZÁBAL, J. NAZÁBAL

Dpto. de Ciencia y Tecnología de Polímeros, Universidad del Pais Vasco, P.O. Box 1072, 20080 San Sebastian (Spain)

**ABSTRACT:** Poly(ether ether ketone)/polysulfone blends were obtained by direct injection molding throughout the composition range. The almost full immiscibility and biphasic nature of these blends was seen by differential scanning calorimetry and dynamic-mechanical thermal analysis and their homogeneously dispersed phase by scanning electron microscopy. The elastic modulus showed an usual behavior slightly below additivity. However, the strain-related break properties such as ductility or impact strength showed a surprising and positive, for an immiscible blend, behavior close to additivity both in as-molded and in annealed blends.

Some possibilities, such as fast cooling, the largely aromatic nature, similar solubility parameters, different dilatation or Poisson coefficients, and the inherent chemical structure of the blends are discussed as reasons for the observed behavior. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1503–1510, 1997

**Key words:** poly(ether ether ketone); polysulfone; miscibility; injection molding; morphology; structure; mechanical properties

## INTRODUCTION

In the last few decades important efforts have been made in the design of new high performance polymers, in particular with high thermal resistance. This has led to the introduction in the market of materials such as semicrystalline poly(ether ketones) and poly(phenylene sulfide), or amorphous polyetherimides and polysulfones. Thermally resistant high-performance thermoplastics give rise to new products, but they are also forerunners when traditional materials are to be substituted. Blending these high-performance polymers constitutes an interesting and easy route to widening their applications; this is by means of specific property combinations based on the properties of the blend components.

Poly(ether ether ketone) (PEEK) is a semi-crystalline aromatic thermoplastic ($T_g = 145°C$, $T_m = 340°C$) with an exceptional balance of properties: toughness, strength, rigidity, and good electrical properties as well as chemical, thermal, and radiation resistance. Polysulfone of bisphenol-A (PSF) is an amorphous thermoplastic with properties intermediate between those of polycarbonate and the higher temperature-resistant engineering poly(ether sulfone) (PES). PSF is clear, rigid, and tough, with a glass transition temperature $T_g$ of 185°C. It has thermal stability and chemical inertness together with excellent hydrolytic stability and good electrical properties. However, like all other amorphous glassy polymers, PSF has poor resistance to organic solvents.

PEEK has been shown to be miscible with amorphous polyetherimide (PEI)[1–3] and poly(ether ketone) (PEK),[4] and PEEK/PES blends appear homogeneous when solution blended.[5] However, heterogeneous PEEK blends are produced with PES when melt-blended,[6–8] with a poly(amide–imide)[9] or with liquid crystalline polymers (LCPs)[10–12] as second components.

PSF has been blended with a great variety of polymeric materials and a patent has been registered on PEEK/PSF blends.[13] Miscibility isfound in PSF blends with poly(N-vinyl pyrrolidone) (PVP),[14] carboxylated-polysulfone (C-PSF),[15] and a phenolphthalein poly(ether ether ketone) (PEK-C).[16,17] However, most PSF blends, as with poly(phenylene sulfide) (PPS),[18–21] high-molecular-weight poly(ethylene oxide),[22] phenoxy,[22] poly(benzimidazole),[23] another polysulfone,[20] and LCPs[24–26] are immiscible. A PSF/PC blend is a commercial product (Mindel, Amoco).

Blending PSF and PEEK might present some benefits because of the complementary properties of both polymers. PSF has a higher $T_g$ than PEEK, which could improve its temperature performance, and the semicrystalline nature of PEEK should be beneficial for the solvent resistance of glassy PSF. Kneaded and compression-molded blends showed almost full immiscibility in the solid state in a recent work[27] in our laboratory. However, when fast-cooled, they showed unexpected mechanical compatibility that could make these blends interesting from an applicative point of view if it were maintained after injection-molding. Although a patent was devoted to PEEK/PSF blends,[13] to our knowledge no systematic study has been published in the open literature on PEEK/PSF blends. Moreover, blends of PEEK with PES, another polysulfone with small structural changes compared with PSF, have given rise to immiscible but clearly compatible blends.[7,8] The origin of this compatibility in fully immiscible blends is not clear. These PEEK/PSF blends, which have a slight chemical structure change, may help explain the reasons for this observed positive mechanical response. Finally, the possibility of direct injection-molding has been seen to be successful in other polymer blends.[8,28] First, this would avoid extrusion processing prior to injection-molding, which might contribute to degradation of the components of the blend; and second, it would render the blend more attractive from an applicative point of view because of its easier production.

Hence, in the present study we have prepared PEEK/PSF blends by direct injection-molding throughout the composition range and observed the morphologies produced. The solid state of the blends was characterized by dynamic-mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), and density measurements. The morphology of the blends was studied by scanning electron microscopy (SEM), and the me-chanical properties of the blends determined by means of tensile and impact tests.

## EXPERIMENTAL

The polymers used in this work were commercial products. PEEK (Victrex® 450G, I.C.I.) had a melt flow index of 5.0 g per 10 min, at 370°C and with a 3,800 g load. PSF (Udel® P1700, Amoco) had a $M_n$ of 31,000.[29] Both polymers were dried at 150°C for 18 h before processing.

The blends were directly melt-mixed and injection-molded in a Battenfeld BA 230E reciprocating screw machine, using a barrel temperature of 370°C and a mold temperature of 16°C. The plasticizer was equipped with a standard screw with a diameter of 18 mm, L/D ratio of 17.8, compression ratio of 4, and helix angle of 17.8 degrees. The injection speed and pressure were 6.6 cm/s and 2,000 bar, respectively. The duration of the molding cycle was 30 s. As-molded (AM) tensile (ASTM D638, type IV) and impact (ASTM D256) specimens were obtained. Annealed (AN) specimens were also obtained by heating in an air oven at 185°C for 24 h. For the sake of comparison, the pure blend components were subjected to the same processing conditions.

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 weight crystalline fraction ($W_c$) of the blends and pure PEEK was calculated from crystallization and melting heats, using the relation

$$W_c = [\Delta H_m - \Delta H_c]/\Delta H_m^0 \qquad (1)$$

where $\Delta H_c$ and $\Delta H_m$ are the crystallization and melting heats during the scan, respectively; and $\Delta H_m^0 = 130$ J/g,[30] the melting heat of 100% crystalline PEEK.

DMTA was performed in a Polymer Laboratories DMTA at a heating rate of 4°C/min and a frequency of 1 Hz.

SEM was carried out with a Hitachi S-2700 electron microscope on cryogenically as well as tensile or impact-fractured samples, after gold coating.

Density measurements were carried out in a density gradient column at 23°C using calcium
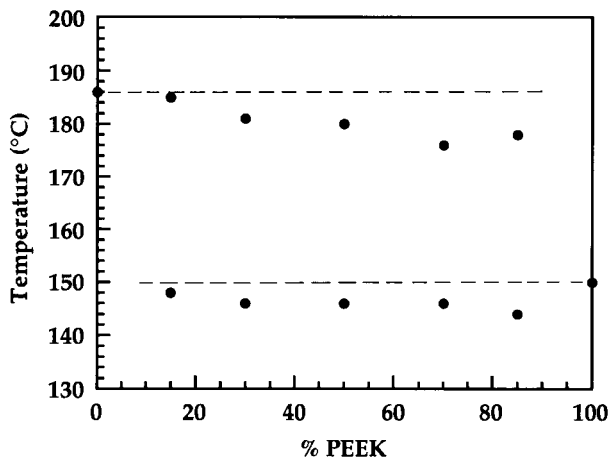
**Figure 1** $T_g$s against composition for AM blends. The values were obtained from the tan $\delta$ peak of the DMTA plots.

nitrate solutions. The $W_c$ was also determined from density values, assuming volume additivity in the blends. The following expressions were used:

$$1/\rho_{\text{blend}} = W_{\text{PEEK}}/\rho_{\text{PEEK}} + W_{\text{PSF}}/\rho_{\text{PSF}} \qquad (2)$$

$$W_c = [\rho_c(\rho_{\text{PEEK}} - \rho_a)]/[\rho_{\text{PEEK}}(\rho_c - \rho_a)] \quad (3)$$

where $\rho_{\text{blend}}$ is the measured density; $W_{\text{PEEK}}$ and $W_{\text{PSF}}$ are the weight fractions of PEEK and PSF, respectively; $\rho_{\text{PSF}}$ is the density of pure unblended PSF (1.2387 AM; 1.2405 AN); $\rho_{\text{PEEK}}$ is the density of PEEK in the blend, determined by means of equation [2]; $\rho_a$ is the density of noncrystalline PEEK (1.2626 gcm$^{-3}$); and $\rho_c$ is the density of the PEEK crystalline phase (1.4006 gcm$^{-3}$).[30]

Tensile testing was performed on an Instron 4301 tensile tester at 23°C, using a crosshead speed of 10 mm/min. 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 mm × 3.2 mm. The AN samples were notched prior to annealing. The different mechanical properties are an average of at least eight determinations.

## RESULTS AND DISCUSSION

### Phase Behavior

All the blend compositions appeared opaque in the solid state. This is not, however, an indication of immiscibility, taking into account the probable crystallization of PEEK.

Figure 1 shows the composition dependence of

the $T_g$s of AM blends, obtained from DMTA measurements. The AN blends showed very similar behavior, although with a higher PEEK-rich phase $T_g$ as a consequence of its larger crystalline content. As can be seen, two $T_g$s, rather constant with composition, are present at all compositions; one near the $T_g$ of pure PEEK, and the other close to that of pure PSF. The $T_g$ change (maximum 10°C at the PEEK/PSF [70/30] composition in the $T_g$ of the PSF-rich phase) indicates the rather pure nature of the two phases of the blend. The decrease in the $T_g$ of PEEK is probably due to changes in its crystallinity level. That of the PSF phase could indicate some miscibility. The same PEEK/PSF blends obtained by kneading in our laboratory provided similar $T_g$ behavior.[27] This similar $T_g$ behavior between Brabender-mixed and directly injection-molded blends indicates that the presence of only one component almost in every phase of the blends is not due to the direct injection-molding procedure followed but to the intrinsic immiscibility of the blends. However, different miscibility states in PEEK blends with another polysulfone (PES)[5–8] have been reported; this is most likely due to the thermal history or to the different blending conditions used.

The calorimetric analyses of the blends showed concordant results when the transitions were observable. The $T_g$ of the PSF-rich phase of AM blends was observed only in the 15% PEEK composition. In the rest of the blends it was hidden by the PEEK crystallization peak that took place during the calorimetric scan and that was located at approximately 180°C. The positions of the $T_c$ (182°C) and $T_m$ (340°C) were practically constant and close to those of pure PEEK. In AN blends, crystallization did not occur; as a consequence, the two $T_g$s were clearly observed.

The crystallization and melting heats of AM and AN blends followed a practically simple additive rule with blend composition. This, and the lack of change in $T_m$, indicate that strong interactions are not present between the two components of the blends. They also indicate the absence of any important effect of PSF on the crystallization-melting behavior of PEEK, which agrees with the practically total phase separation.

The lack of effect of PSF in PEEK crystallization is also clear when the crystalline content of the AN blends is measured. In Table I the crystalline contents of the blends measured both by DSC and from density data are collected. Given the possibility of recrystallization in the DSC scan,[30–32] the values of crystallinity calculated from those of density (discussed in the next paragraph) are

**Table I   Crystalline Content (%) of PEEK in PEEK/PSF Blends**

|  | AM | | AN | |
|---|---|---|---|---|
| Composition | DSC | Density | DSC | Density |
| 15/85 | 1 | 7 | 18 | 18 |
| 30/70 | 6 | 1 | 32 | 26 |
| 50/50 | 6 | 1 | 29 | 19 |
| 70/30 | 10 | 3 | 28 | 21 |
| 85/15 | 8 | 1 | 27 | 20 |
| 100/0 | 16 | 6 | 27 | 21 |

considered to be more reliable. As seen in Table I, the crystalline content of PEEK by DSC in AM blends is low, and that of AN blends is roughly 25%. Moreover, the crystalline content of PEEK in the blends is rather independent of composition and similar to that of pure PEEK, except in the PEEK/PSF (15/85) composition where a comparatively great experimental error can be expected.

The specific volume values of the blends are shown against PEEK content in Figure 2. Both AM and AN blends follow an additive behavior that agrees with the lack of strong interactions between the blend components[33] and with the practically full immiscibility of the blends. As a consequence of the almost full immiscibility and volume additivity, the crystallinity degrees may be calculated from density. They are very low in all compositions of AM samples and fairly similar to those determined by DSC in AN blends, as seen in Table I. The relative high crystallinity value of the 15/85 AM blend is probably due to the large measurement error as a consequence of the very low crystallinity content of the blend.

Both the additivity of the specific volume plot, and the constant crystallinity follow the general behavior of immiscible blends. In this case, interactions between the two components are very difficult and, as a consequence, crystallization and solidification take place within a domain of nearly pure resin, thus almost unaffected by the presence of other macromolecules.[34]

## Morphology

The fracture surfaces of some AN tensile and impact specimens are shown in Figure 3. The rest of the compositions, as well as the AM specimens, gave similar surfaces. No relevant difference was observed between tensile and impact specimens. As can be seen, the presence of a homogeneously dispersed phase with a small phase size disper-

sion is clear. This indicates that direct injection-molding is possible in these PEEK/PSF blends. The differences between Figure 3(a) (tensile) and (b) (impact) are mainly due to the cryogenic nature of the fracture of the tensile specimen that was used to better show its morphology before deformation in the solid state. Thus, despite the larger thickness of impact specimens, their morphology and that of tensile specimens are similar. No large orientation of the dispersed phase, which may appear after injection-molding,[35] is seen in these blends under the conditions used.

These AM and AN morphologies are clearly different from those obtained in the same blend[27] after kneading, compression-molding, and quenching. In these compression-molded blends, in minoritary zones, the matrix and the dispersed phase were able to elongate, but in most zones the dispersed phase was clearly integrated into the matrix up to the point of being difficult to be observed. In the AM blends of this work, however, debonding is clearer, not only in the cryogenically fractured Figure 3(a), but also in the impact broken Figure 3(b) and (c).

When the morphologies of this work were compared with those of injection-molded PEEK/PES blends of a previous work in our laboratory,[8] as in this case, the morphologies did not change with annealing. However, the minoritary and deformed polysulfone dispersed phase that appeared in that blend is not seen in this case. The main injection conditions are the same, so this morphology difference must be due to the differences in viscosity between PSF and PES.

## Mechanical Properties

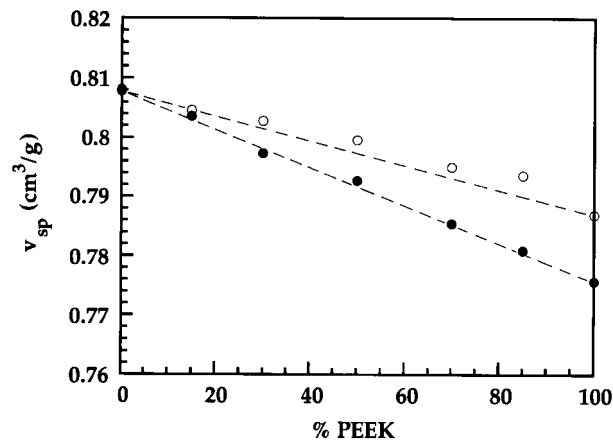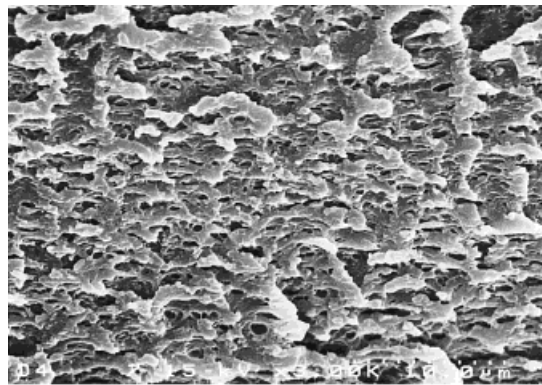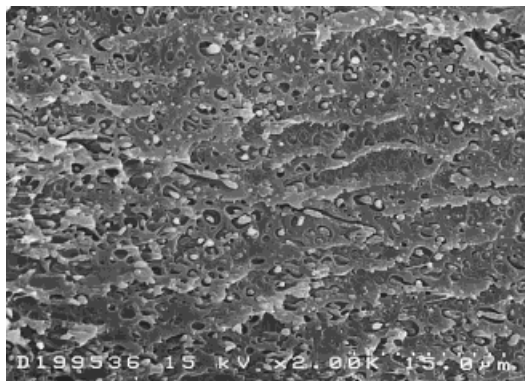The moduli of elasticity of both AM and AN blends are shown in Figure 4. The values from a previous



**Figure 2**   Specific volume of the AM ($\bigcirc$) and AN ($\bullet$) blends against composition.

(a)



(b)



(c)

**Figure 3** Fracture surfaces of AN blends observed by SEM. (a) 30/70 tensile specimen after cryogenic fracture; (b) 30/70 impact specimen after fracture at room temperature; (c) 50/50 impact specimen after fracture at room temperature.

$$E_m = E_1\phi_1 + E_2\phi_2 + \beta_{12}\phi_1\phi_2 \qquad (4)$$

which provides a suitable way to quantify the deviation from simple additivity, was applied to these blends, negative $\beta_{12}$ values of only $-700$ MPa and $-325$ MPa were obtained, respectively, for AM and AN blends. These slight deviations from additivity are not surprising in immiscible blends, because the effect of immiscibility is slight due to the small deformations at which the moduli of elasticity are measured.

Volume additivity is very likely to take place due to the almost fully pure nature of the two phases, so that the amount of free volume of the amorphous phase is not a parameter to be considered an influence on the modulus behavior. As a consequence, the differences between the modulus values of AM and AN blends have to be due to the higher crystalline content of AN blends.

All the blends gave yield stress values slightly below the simple additivity rule between those of AM PEEK (76.0 MPa) and PSF (68.4 MPa), and also AN PEEK (93.3 MPa) and PSF (81.8 MPa). The mean negative deviation from linearity was 5.5% in AM and 2.6% in AN blends. The yield stress values of Robeson and Harris[13] ranged between those of the two additive lines of this work. The fairly similar behavior of the modulus of elasticity and of the yield stress is not surprising because the relation between both properties is rather common in polymers.[36]

The break stresses of both the AM and AN blends are seen in Figure 5. They show almost additive values with respect to those of the pure components. The higher values of PEEK-rich AN
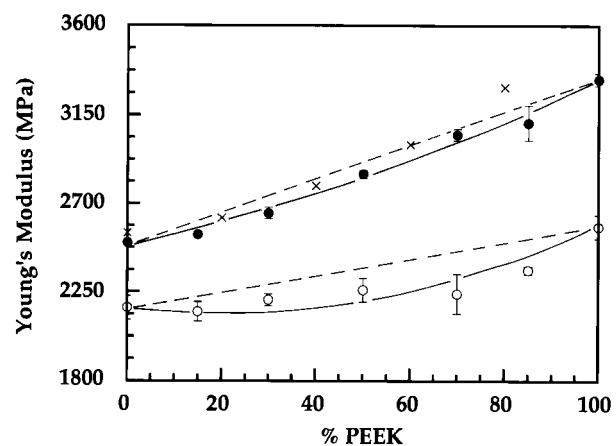


**Figure 4** Modulus of elasticity of the blends against composition. Symbols as in Figure 2. Values of the moduli of the blends from Robeson and Harris[13] ($\times$) are also collected.

patent[13] are also collected as a reference. They are more or less superimposable on those of AN blends. As can be seen, both AM and AN blends show a small negative departure of modulus from additivity, which is slightly higher in the case of the AM blends. When the equation

**Figure 5** Break stress of the blends against composition. Symbols as in Figure 2.



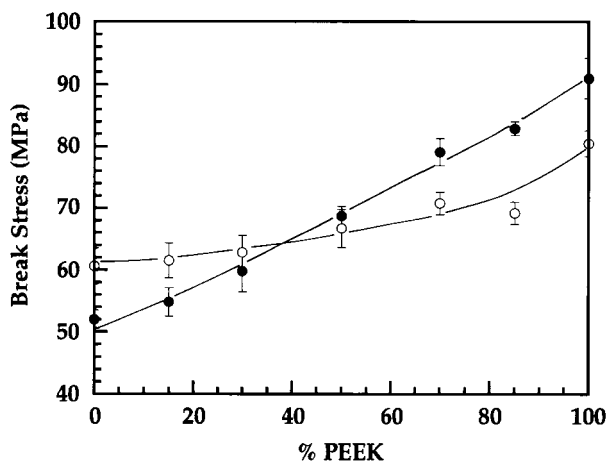**Figure 7** Impact strength of the blends against composition. Symbols as in Figure 2.

blends with respect to AM blends are probably due to their higher crystalline content. The higher tensile strength of PSF and PSF-rich AM blends is a consequence of their larger ductility which allows a larger load increase after yield.

The ductility and impact strength of the blends are shown, respectively in Figures 6 and 7. Both properties lie near additivity, independent of the thermal treatments applied. When the equation used for the modulus is applied to ductility, thanks to the lack of important change of concavity in the ductility plot of AN blends, a positive deviation in ductility of $\beta_{12} = 20\%$ in these blends is calculated. It is to be noted that AN blends, in which PEEK attains a crystalline degree of approximately 20%, are ductile materials. This agrees with the lack of morphological change of the fracture surfaces observed with respect to AM
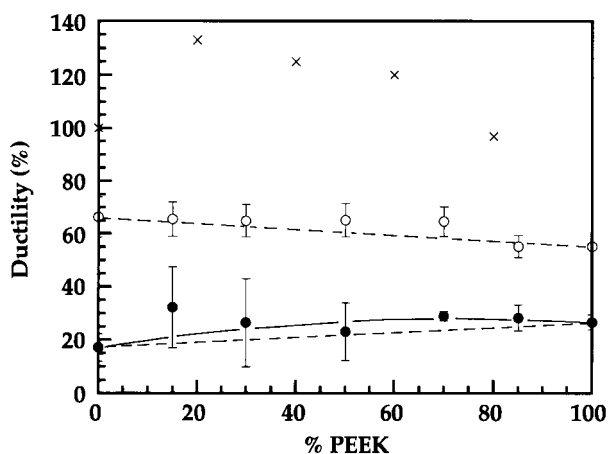


**Figure 6** Ductility of the blends against composition. Symbols as in Figure 4.
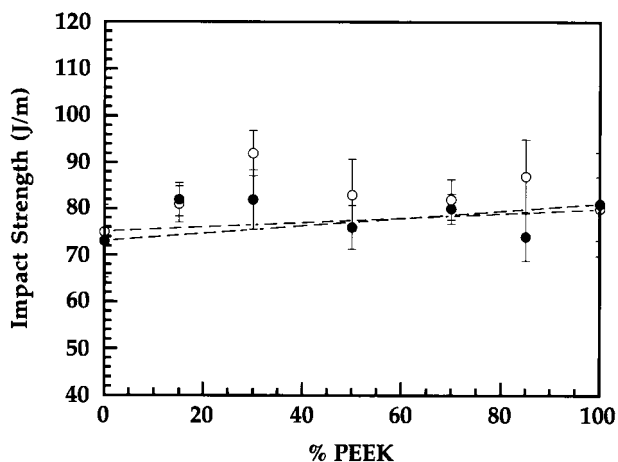
blends; so there is not an intrinsically negative influence of crystallization on the mechanical compatibility of the blend. This is important, because PEEK is chiefly used at high crystalline contents.

As can be seen, the ductility values from a previous work [13] are higher than those reported here, both in the case of AM and also in the AN blends which provided a very similar modulus of elasticity. This is despite both the fact that eight specimens were used to determine each value, and the habitual typical deviations observed. The quality of the surface of the specimens is usually similar in injected blends. The crystallinity level could not be low in Robeson and Harris [13] because the moduli of elasticity were those of the AN blends reported in this work. The different processing conditions, which are known to have a profound influence on the mechanical properties of the blends, [37] might account for the observed differences.

These mechanical properties are interesting in fully immiscible blends. Moreover, the same PEEK/PSF blends but compression-molded after kneading also gave a slightly synergistic behavior when quenched. [27] Such a positive behavior also took place in some PEEK/PES blends. These blends appear as immiscible [7,8] but it seems that they may also appear as miscible when melt-molded at 310°C. [5] Thus the presence of the other component only in the surface of the dispersed phase could not be excluded, because when cooled it should have passed through a miscibility zone. The fact that in both PEEK/PES [7,8] and PEEK/PSF [27] blends the ductility values close to additivity were seen only in thin and, thus, very fast-quenched blends, but not in slowly cooled blends,

might point to a processing-related parameter as that responsible for such behavior. However, this does not take place in all immiscible blends[38] with such a thermal treatment. This is because very thin and fast-cooled polyethylene/polystyrene compression-molded films processed in our laboratories provided bad ductility values in the three compositions obtained. Additionally, large ductility also takes place in much thicker injection-molded and thus more slowly cooled PEEK/PSF specimens. As a consequence, a fast cooling and the related improved free volume and ductility of the components is not the only reason for such ductility behavior.

In other cases, these unexpectedly good mechanical properties are a consequence of very oriented structures[39] which are often produced in injection-molding,[8,35] or of interpenetrated structures[40] typical of nonindustrial blending methods. Oriented structures were seen in injection-molded PEEK/PES blends,[8] but no such structure is seen here, despite the fact that besides cryogenic fracture surfaces, impact and tensile broken surfaces are shown. As is seen, mainly in Figure 3(b), the slight orientation produced is not the general orientation that is seen in other injected immiscible blends[35] with favorable mechanical properties. Thus this is an immiscible blend that offers significant good mechanical properties, without apparent morphological reasons.

A similar mechanical behavior has been reported, besides for PEEK/PES,[7,8] for POM/phenoxy in the phenoxy-rich compositions[41] and also for PPS with both PEI and PSF.[19] The largely aromatic nature of the components was tentatively related[19] to their good mechanical properties. PEEK, PSF, and PES are largely aromatic, but it is not easy to find a more concrete inherent link between PEEK and PPS. Both have a common semicrystalline character; but it does not seem probable that this influences the mechanical compatibility between both almost-pure phases.

The correlation between the segment interaction parameter and the interphase width in polymer blends, which must be related to compatibility, has been studied.[42] Moreover, a small solubility parameter difference between the two components helps miscibility by giving rise to an interaction parameter close to zero.[43] PSF also has a solubility parameter ($21.3$ MPa$^{1/2}$) fairly similar to that of PEI ($21.5$ MPa$^{1/2}$), which is miscible and consequently compatible with PEEK. It is also not very far from that of PES ($22.1$ MPa$^{1/2}$), which also provides[8] compatible blends with PEEK. But this is not the only condition, because there are many other incompatible blends with similar solubility parameters.

Another possibility is that a different dilatation coefficient or bulk modulus of the components could produce a larger expansion of the dispersed phase during cooling in the mold or in the deformation on testing. This would give rise to a compressive hydrostatic stress that would clearly hinder debonding. However, this expansion situation would take place only in one side of the property–composition plot. This is because when the dispersed phase is the matrix at the other side of the plot, the situation should be the opposite; and this does not take place either in these blends or in PEEK/PES blends. However, a small difference in elastic properties between the components of the blends is a parameter that could help compatibility, because polycarbonate/Hytrel blends, which are miscible in most compositions,[44] should be prone to maintain their compatibility after phase separation. However, they are brittle materials after separation[45] of the rubber-like Hytrel-rich phase which presents elastic properties very different from those of the fairly rigid PC-rich matrix.

Thus, leaving aside a small difference in elastic properties, the appearance of another blend with (1) slightly different chemical structure from the PEEK/PES blends but with identical diphenylene ether units, (2) related chemical structure of both components, and (3) unexpected compatibility, strengthens the possibility of a structure-related parameter such as preferential surface enrichment,[46] a large aromatic character,[19] or the actual nature of the blend's components[8] as that responsible for the observed mechanical behavior.

## CONCLUSIONS

PEEK/PSF blends are constituted by two almost pure and homogeneous phases after direct injection-molding, as determined by DMTA and DSC. The phase separation in PEEK/PSF blends allows PEEK to crystallize as in the unblended state. No change in the specific volume of the blends takes place as a result of blending, both in AM and AN blends. As usual, the moduli of elasticity were almost additive, but both ductility and impact strength showed an additive response. Several possibilities have been discussed as reasons for this unexpected behavior.

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