

Poly(ether ether ketone)/Poly(aryl ether sulfone) Blends: Relationships Between Morphology and Mechanical Properties

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ABSTRACT: Mechanical properties such as the tensile modulus, yield (break) strength, and elongation to break (or yield) are measured for multiphase poly(ether ether ketone) (PEEK)/poly(aryl ether sulfone) (PES) blends. Specimens with three different levels of thermal histories (quenched, as-molded, and annealed) are prepared in order to study their effects on the mechanical properties of PEEK/PES blends. Synergistic behavior is observed in the tensile modulus and tensile strength of the blends in almost the whole range of compositions. The ductility of quenched blends measured as the elongation to break (yield) shows an unexpected synergistic behavior in the blend containing 90 wt % PEEK, although a negative deviation from additive behavior is observed in the rest of the compositions. A ductile–brittle transition is observed between 50 and 75 wt % PEEK in the blend. The ductile–brittle transition in as-molded blends shifts to 75–90 wt % PEEK. Annealed blends show predominantly brittle behavior in the whole composition range. The experimental data are further correlated with the theoretically predicted results based on various composite models.

Although the prediction based on these equations fails to fit the experimental data in the whole composition range, the simplex equations that are normally used for blends showing synergistic behavior produced a reasonable fit to the experimental data. The mechanical properties obtained for different blend compositions are further correlated with their morphology as observed by scanning electron microscopy. Morphological observation shows a two-phase morphology in PES-rich blends, which is an interlocked morphology in which the disperse phase is not clearly visible in PEEK-rich blends, and a cocontinuous type of morphology for a 50/50 composition. Considerable permanent deformation of both the disperse and matrix phase, especially in the case of quenched tensile specimens, demonstrates the remarkable adhesion present between the two phases. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2887–2905, 2003

Key words: poly(ether ketones); poly(ether sulfones); blends; mechanical properties; morphology

INTRODUCTION

Polymer blends have been of great interest particularly in the last two decades or so. The sources that have fueled this interest are the cost and time associated with the development of new polymers and the ability to tailor properties by blending, which may result in new, desirable and, in some cases, unexpected synergistic effects on the properties. Although there are literally 1000s of combinations that could be desirable, only a few exhibit a practical performance profile. In the last few decades, studies in the field of polymer blends have led to the development of a large number of new blend systems, as well as to a simultaneous growth of the science of polymer blends.^{1,2}

Among the development fields in polymer blends, that of high performance polymers is of great interest. This is because of the favorable combination of properties of these polymers, which includes a good level of mechanical properties along with high thermal resistance. High performance materials are sought mainly as an alternative for metals in the structured applications where strength and stiffness are of great importance and the strength to weight ratio is a necessary requirement. One of the leading polymers in this area is poly(ether ether ketone) (PEEK). It is an aromatic semicrystalline thermoplastic that offers an excellent balance of properties: toughness, strength and rigidity, good electrical, as well as chemical and radiation resistance.^{3–9}

Poly(aryl ether sulfone) (PES)^{10,11} is another high performance engineering polymer that is amorphous in nature, unlike PEEK. It exhibits a high glass-transition temperature (T_g , ~220°C), is mechanically tough and rigid, but has a poor resistance to organic solvents.

Blending PEEK with PES is expected to improve the glass-transition behavior and processibility of the

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former and the chemical resistance behavior of the latter. Blends of PEEK with PES have been the focus of attention in recent years, mainly in patent and to some extent in scientific journals.¹²⁻²¹ The blends are reported as being completely miscible,¹²⁻¹⁴ partially miscible,¹⁹ and completely immiscible.¹⁵⁻¹⁸ The method of blending and the structure of PES were found to have considerable influence on the reported miscibility behavior of these blends.^{20,21}

Keeping in view the range of miscibility behaviors reported and the exceptional nature of PEEK/PES blends, we have extensively studied the phase behavior and structure-property relationships of these blends.^{22,23} We found the blends to be completely miscible when solution blended with a lower critical solution temperature of around 340°C and partially miscible when melt mixed. The partially miscible blends had PEEK-rich and PES-rich phases in all compositions.

The study of the mechanical properties of polymer blends is of great importance because these properties determine, in most cases, the possibility of the utilization of a blend. Hence, a better understanding of the relationship between the mechanical properties of blends and their composition is important for their development into various products. These mechanical properties are greatly affected by phase adhesion between the blend components. Miscible blends generally show a linear relationship of the mechanical properties with the blend compositions. However, the variation in the mechanical properties in immiscible and partially miscible blends is more complex and can show from below additive behavior to synergistic behavior. Evidently the factors that decide the final properties in these blends are the viscosity ratio of the component homopolymers, the interfacial adhesion, and, in the case of crystallizable polymers, the amount of the crystalline fraction.

The mechanical properties of PEEK/PES blends have been studied by Malik¹⁹ and Eguiazabal et al.¹⁵⁻¹⁸ According to Malik,¹⁹ the tensile modulus and ultimate strength of a PEEK/PES blend increases significantly with an increasing concentration of PEEK, reaches a maximum at around 40 wt %, and then drops to the value predicted by the rule of mixtures. According to Malik,¹⁹ the synergistic effect was most probably due to the partial miscibility of PEEK/PES systems. Eguiazabal et al.¹⁵⁻¹⁸ found that kneaded and compression molded PEEK/PES blends, when crystallized during slow cooling from the melt, showed the mechanical properties characteristic of immiscible blends. However, quenched amorphous blends showed an unusually positive mechanical behavior, which was attributed to common features of the two components of the blends. Injection molded blends provided mechanically compatible blends, probably due in part to the morphology produced as a conse-

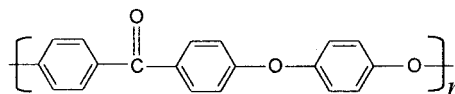
quence of flow during processing. Harris and Roberson^{20,21} reported the compatibility behavior of blends of PEEK with a range of PES compositions. According to them, these blends exhibit excellent compatibility and a significant increase in toughness, especially in the blends of PEEK with a PES containing a biphenylene unit in the backbone.

A different level of miscibility obtained by us for melt mixed PEEK/PES blends necessitates a further examination of the mechanical compatibility in these blends. Hence, in the present investigation we report the mechanical characteristics of PEEK/PES blends. In addition, the thermal history imparted during processing has a large effect on the mechanical properties of a polymer, especially if it is a crystalline one, because the degree of crystallinity and crystal perfection greatly depends on the crystallization conditions, which directly affects the mechanical properties. Thus, the present investigation has been carried out on blends having a range of thermal histories. The mechanical properties thus obtained have been correlated with the morphology of the blends. The results have been further discussed with respect to the different theoretical models that are currently available for predicting the mechanical properties of a multiphase system.

EXPERIMENTAL

Materials

We synthesized PEEK in the laboratory by following the reported procedure.²⁴ The purified polymer was then dried in a vacuum oven at 120°C for 48 h. The inherent viscosity of the synthesized PEEK was measured in an Ostwald viscometer at 25°C using 98% sulfuric acid as a solvent (concentration = 1.00 g polymer/100 mL solvent) and its value was found to be 0.81 dL/g. The polymer has the following general structure:



PES was procured from Amoco Performance Products under the trade name Radel (grade A-300). Although the structure of this polymer has not been disclosed by the manufacturers, Ghosal et al.²⁵ found it to have the following repeating units in its general structure:

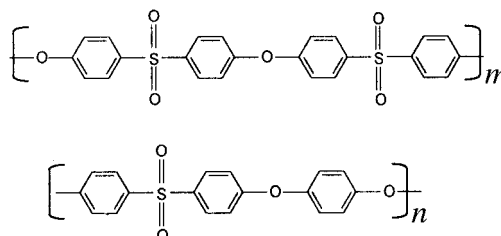


TABLE I
Characteristics of Polymers

Characteristics	PEEK	PES
\bar{M}_w	34.700 ^a	42.500 ^b
Density (g/cm ³)	1.263 ^c	1.370 ^b
T_g (°C)	147.6 ^c	≈223.0 ^d
T_m (°C)	339.1	—

^a The molecular weight measured in our lab.

^b The data provided by the manufacturers.

^c The data for completely amorphous samples.

^d It varies slightly with the thermal history.

The ratio of m/n probably varies in the different grades of Radel A PES that are available. Some of the important characteristics of PES and PEEK that are used in this investigation are listed in Table I.

Preparation of blends

PEEK and PES were blended in ratios of 100/0, 90/10, 75/25, 50/50, 25/75, 10/90, and 0/100 (w/w), respectively. Before blending, the two polymers were completely dried overnight in an air-circulated oven at 150°C. The polymers were melt blended in a Maxwell mixing extruder (model CS-194 AV, Custom Scientific Instruments), which is a laboratory mixing extruder featuring a screwless design. The CS-194 AV extruder has a 0.75-in. diameter rotor and produces a through-put in the range of 200 g/h. The methods to employ this extruder are discussed elsewhere.²⁶ Before melt blending, the two polymers in appropriate weight ratios were thoroughly mixed by hand and then fed to the hopper of the mixing extruder in small batches. The temperature of both the rotor and die zone were set at 350°C, and a rotor speed of 90 rpm was used for all blend compositions. The total residence time of the polymer mixture inside the mixing zone was approximately 30 s, and extrudate were obtained through a die with a 3.5-mm diameter. The extrudates were further chopped into small granules and again passed through the mixing extruder to ensure thorough mixing. The extrudates thus obtained were further converted to granules.

Preparation of moldings

All the samples for mechanical testing were prepared by the compression molding technique. A laboratory hydraulic press was used for preparing the molded samples. Specimens were prepared with an approximate thickness of 0.3 mm. Granules of blends prepared in the extruder and kept between two aluminum foils were placed between the platens of the press, which was already heated to 380°C. A pressure of 100 kg/cm² was applied at this temperature for 10 min and then different treatments were given to the

molded specimens. In the first case, the molded samples were cooled inside the press under pressure in a room temperature environment. In the second case, the molded samples were immediately quenched from 380°C to ice-water temperature. A portion of the quenched samples was annealed in an air oven at 185°C for 24 h.

Tensile tests

The measurements of the tensile properties were made at room temperature by means of a 5000-kg load capacity Universal Testing Machine (model UTB2502, R & D Electronics) at a constant crosshead speed of 10 mm/min. The ASTM D 638 method was followed for carrying out the test. The geometry of the samples was according to the recommendations of group (IV) specimen dimensions under the same ASTM method. The Young's modulus (E) was arbitrarily defined as the secant modulus at 2% elongation (MPa). The ultimate strength (σ_u) and elongation (ϵ_u) were defined as the stress and engineering strain, respectively, at break. The yield strength (σ_y , MPa) and elongation (ϵ_y , %) were taken as the stress and engineering strain at maximum in the stress-strain curve. Suitable instrument and clamp corrections were performed before calculating the elongation and modulus. The values for E , σ , and ϵ were reported as population mean values for at least 8–10 samples.

Scanning electron microscopy

Cross sections of tensile fractured samples were examined with a Jeol (model JSM-35CF) scanning electron microscope at an accelerating voltage of 10 kV. The cross sections of the fractured surfaces of the samples were gold coated prior to examination.

Density measurements

The density of samples was measured by a buoyancy method following ASTM D 792-98, utilizing a Mettler AE-200 balance with an accuracy up to four decimal places. The samples were submerged in xylene with fine copper wire. The density of xylene was measured as 0.8589 g/cm³. The density of the samples was calculated as

$$d = w / (v_{\text{total}} - v_{\text{wire}}) \times d_x \quad (1)$$

where d is the density of the sample (g/cm³), d_x is the density of xylene (g/cm³), v_{total} is the weight of displaced xylene and wire (g), and v_{wire} is the weight of the submerged wire (g). The standard deviation of the measurements was ± 0.0015 g/cm³.

THEORETICAL BACKGROUND AND MODEL FITTING

To relate the microstructure and the mechanical behavior of polymer blends, modeling of the mechanical properties of the materials and a comparison with experimental data is a powerful tool. In multiphase polymer systems, the relationship between the mechanical behavior, the composition of the two components, and the morphological (or geometrical) arrangement of each phase has been extensively studied. Several theories and models have been suggested to describe the modulus and strength of multicomponent polymer systems.²⁷

The simplest models for predicting the mechanical properties of blends are series and parallel models. The upper bound parallel or the Voigt model is given by the following rule of mixtures²⁸:

$$P_1 = P_1\phi_1 + P_2\phi_2 \quad (2)$$

where P is the mechanical property of the blend; P_1 and P_2 are the mechanical properties of components 1 and 2, respectively; and ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively. This equation is suitable for models in which the components are arranged parallel to one another and applied stress elongates each component by the same amount. The lower bound series or the Reuss model is given by²⁸

$$1/P_1 = \phi_1/P_1 + \phi_2/P_2 \quad (3)$$

This equation is suitable for models in which the components are arranged in series with the applied stress.

Another widely used model is the Kerner's model.²⁹ It was originally developed for systems having perfect adhesion at the phase boundary and the modulus in this case was predicted by the following equation:

$$E = E_m \left(\frac{(\phi_d E_d)}{[(7 - 5V_m)E_m + (8 - 10V_m)E_d]} + \frac{\phi_m}{15(1 - V_m)} \right) \left(\frac{\phi_d E_m}{[(7 - 5V_m)E_m + (8 - 10V_m)E_d]} + \frac{\phi_m}{15(1 - V_m)} \right) \quad (4)$$

where E , E_m , and E_d are the moduli of the blend, matrix phase, and dispersed phase, respectively; ϕ_d and ϕ_m are the volume fractions of the dispersed and continuous phases, respectively; and V_m is the Poisson ratio of the matrix phase.

Kleiner et al.³⁰ have shown that the moduli of compatible blends fall outside the upper bounds given by eq. (2). Instead of the classical composite results, the

blend moduli are reported to follow a composition dependency given by the general equation cited by Nielsen and Landel²⁸ for one-phase binary mixtures in the specific form given by Kleiner³⁰:

$$E = E_1\phi_1 + E_2\phi_2 + \beta_{12}\phi_1\phi_2 \quad (5)$$

The empirical interaction term (β_{12}) in eq. (5) is given as

$$\beta_{12} = 4E_{12} - 2E_1 - 2E_2 \quad (6)$$

where E_{12} represents the measured modulus of a 50/50 blend. The interaction term (β_{12}) expresses the magnitude of the deviation from the nonlinearity. As an interaction term, β_{12} may be a relative measure of the blend compatibility.

Modeling the tensile strength of a composite system is more complex, because it depends on the area fraction of the dispersed phase, rather than the volume fraction, which is a much more accessible quantity. According to Piggot and Leidner,³¹ the area fraction in systems containing spherical inclusions is proportional to the first power of the volume fraction and the strength at break of an incompatible blend system can be described by the following equation:

$$\sigma = \sigma_m(1 - \phi_d) \quad (7)$$

where σ and σ_m are the tensile strengths of the blend and the matrix, respectively.

Kunori and Geil³² modified eq. (7) for systems having strong interfacial adhesion by assuming that, when a strong adhesive force exists between the blend components, the dispersed phase will contribute to the strength of the blend and the fracture will propagate through the matrix; hence,

$$\sigma = \sigma_m(1 - \phi_d) + \sigma_d\phi_d \quad (8)$$

Equation (8) is same as the upper bound parallel model [i.e., eq. (2)]. If the fracture propagates mainly through the interface, eq. (8) may be written as

$$\sigma = \sigma_m(1 - \phi_d^{2/3}) + \sigma_d\phi_d^{2/3} \quad (9)$$

Apart from the series and parallel models, not much attention has been given to modeling the variation of the percentage elongation at break with composition. Nielsen³³ has suggested that the elongation at break of the composite (ϵ) may be approximated by the following simple equation relating the elongation at break of the matrix (ϵ_m) and the ϕ_d :

$$\epsilon = \epsilon_m(1 - \phi_d)^{1/3} \quad (10)$$

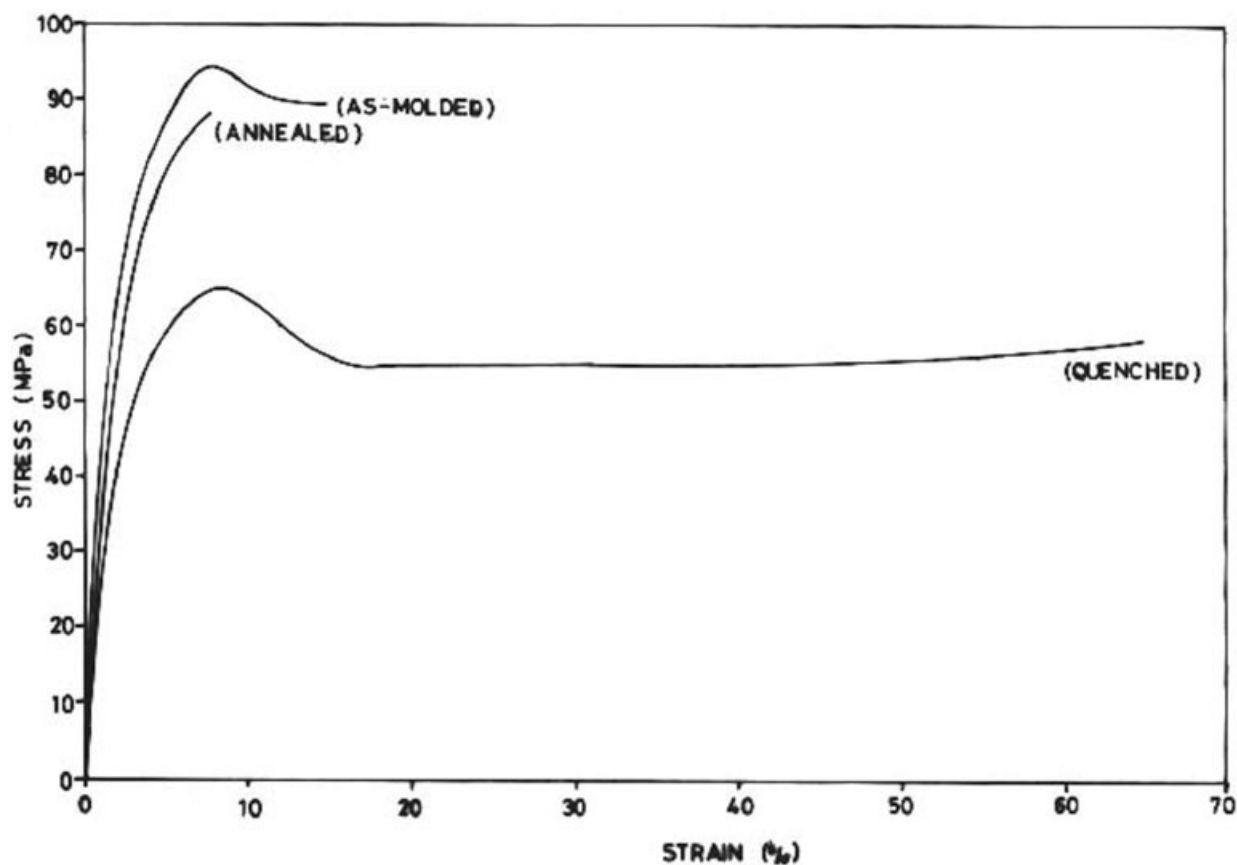


Figure 1 Representative stress-strain curves of PEEK subjected to different thermal treatments.

These theoretical models were initially developed mainly for composites with a soft matrix and rigid filler. The problem with applying these models to polyblend systems is that whereas the ratio of filler modulus to polymer modulus in composites is typically greater than 20, the ratio of moduli for polyblends is nearly equal to unity. Because of this component modulus equivalency in polyblends, the form of the dependence of polyblend moduli on the blend composition may be difficult to model in any meaningful manner with the limitation of the typical scatter of experimental data. Nevertheless, in the last few years, these theoretical models have been successfully applied to a number of polyblend systems.

RESULTS AND DISCUSSION

Figure 1 shows the stress-strain curves of PEEK subjected to different thermal histories. The quenched and as-molded samples show ductile behavior, the quenched samples showing higher elongation at break and hence higher ductility. Annealed samples show a predominantly brittle behavior with samples breaking immediately after yielding. The stress to yield increases in the as-molded and annealed samples because of the development of crystallinity. As-molded

samples show the highest yield stress, probably due to the higher degree of crystallinity in these samples. Surprisingly, annealed samples fail in a predominantly brittle manner, even though they have a lower degree of crystallinity. This could be because of the fact that annealed samples contain a more imperfect crystal microstructure and thus have higher defect concentration within the lamellae.³⁴

Figure 2 shows the stress-strain curves of PES with different thermal histories. Whereas the quenched PES shows ductile behavior with clear neck formation after yielding, the as-molded and annealed PES fail in a brittle manner. This behavior can be understood by the fact that annealing of glassy polymers at temperatures just below their glass transition (T_g) causes a reduction in both volume and enthalpy.³⁵ Naturally, there are accompanying changes in the mechanical properties, and the modulus and strength are expected to increase. However, the more dramatic and serious change is the reduction in ductility (i.e., embrittlement).³⁶ These responses can be interpreted, at least qualitatively, as resulting from the loss in free volume during sub- T_g annealing.³⁷ We must mention here that the as-molded PES can also be considered as annealed samples exposed for shorter annealing times. The annealed PES shows a higher stress at

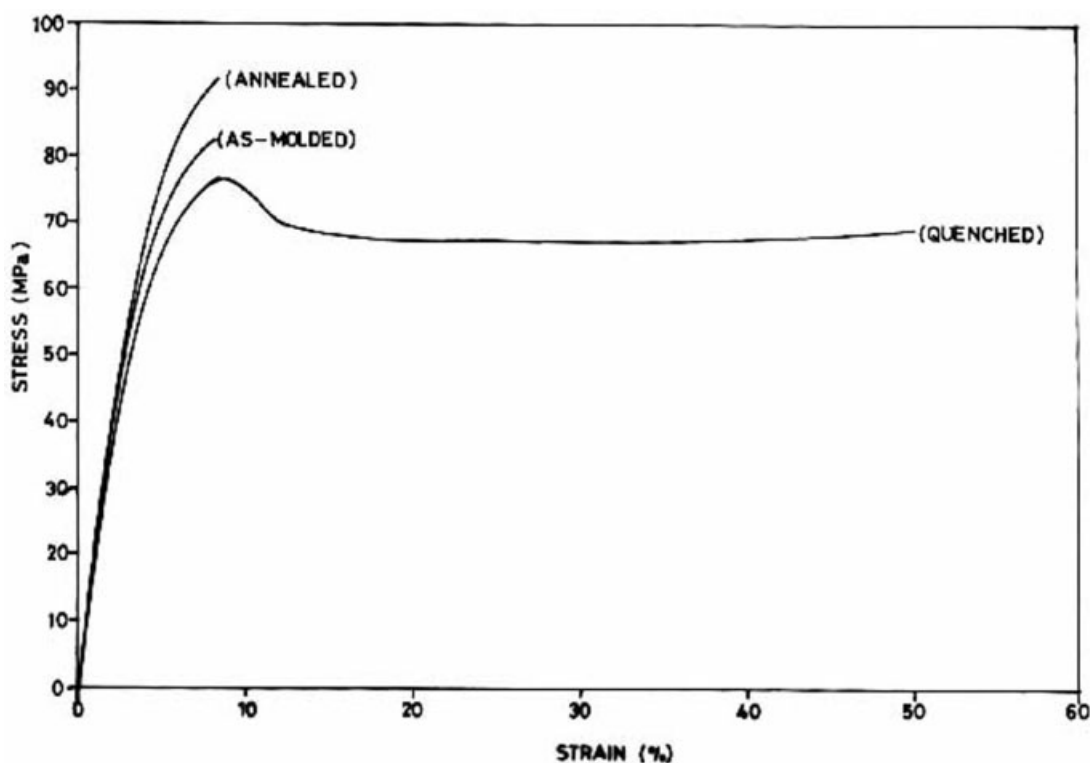


Figure 2 Representative stress-strain curves of PES subjected to different thermal treatments.

failure compared to as-molded PES because of being annealed for a longer duration and hence having lowest free volume.

Representative stress-strain curves of quenched, as-molded, and annealed PEEK/PES blends are shown in Figure 3(a-c). As Figure 3(a) illustrates, almost all the quenched blend compositions fail in a ductile manner, although the fraction of samples failing by brittle fracture increases as the PEEK concentration in the blend decreases. Hence, whereas blends containing 75 and 90 wt % PEEK fail by predominantly ductile fracture, those containing 10, 25, and 50 wt % PEEK fail predominantly by brittle fracture. The fact that some tensile specimens break by ductile failure while others break by brittle failure at the same blend composition can be explained in terms of failure criteria proposed by Nicolais and Dibenedetto.³⁸ According to these criteria, the brittle failure will occur if an individual sample defect grows to a critical defect size before the stress-strain curve reaches a maximum. Variations in the defect size and defect size distribution within a tensile sample population results in a proportion of some samples failing in a brittle mode and some failing in the ductile mode within the same embrittlement region. Another remarkable feature of the stress-strain curves in Figure 3(a) is the increase in the stress at yield (or break) to a maximum at around 50 wt % PEEK content. A similar synergistic dependence of the tensile strength on blend compositions has also been reported for other blend systems.^{39,42} Similarly, the

elongation at break reaches a maximum at 90 wt % PEEK content in the blend. There can be several reasons for these synergistic behavior, which are discussed later in this article. Figure 3(b), which represents the stress-strain curve of as-molded samples, shows nearly similar behavior to the quenched samples, except for the fact that the break (or yield) stress is higher and elongation to break is lower in the as-molded blends compared to quenched blends. In addition, except for the composition having 90 wt % PEEK, all other blend compositions show brittle failure. The composition with 75 wt % PEEK does appear to initiate a neck region, but failure occurs shortly after the yield point. All the annealed blend samples including the homopolymers fail by brittle failure as shown in Figure 3(c). The tensile stress at break in annealed blends varies in a nearly similar fashion as the quenched and as-molded samples.

The above observations of the tensile stress-strain curve of PEEK/PES blends are discussed below with respect to the inherent compatibility and morphology of the blend system, and they are modeled with respect to current theories of polymer composite behavior.

Tensile or Young's modulus behavior

The tensile modulus of the blends as a function of volume fraction of PEEK for quenched, as-molded, and annealed samples is shown in Figure 4(a-c). The experimental moduli are plotted with the curves de-

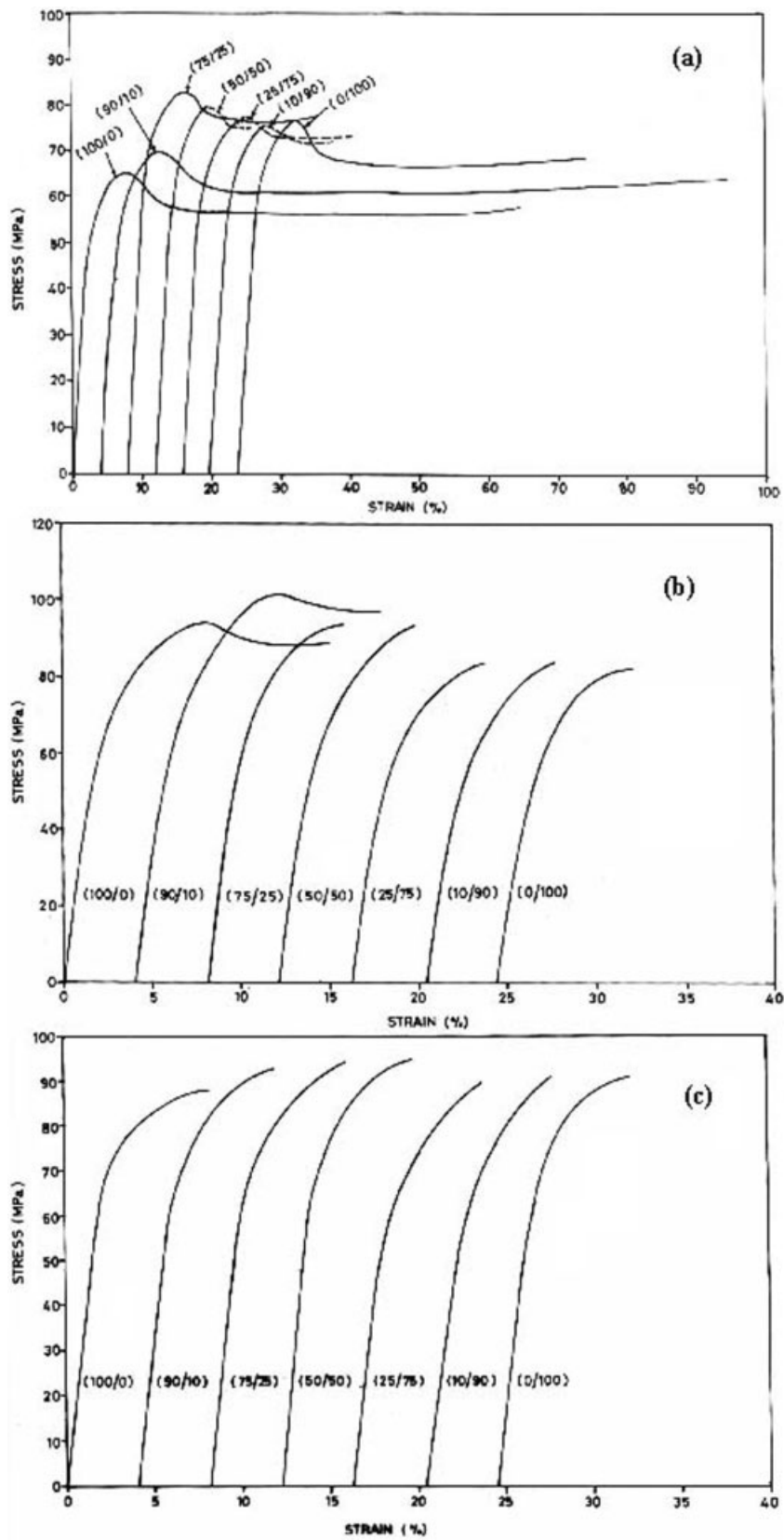


Figure 3 Representative stress-strain curves of various compositions of PEEK/PES blends subjected to different thermal treatments: (a) quenched, (b) as-molded, and (c) annealed. The curves are sequentially shifted 4% in strain along the abscissa for the purpose of comparison.

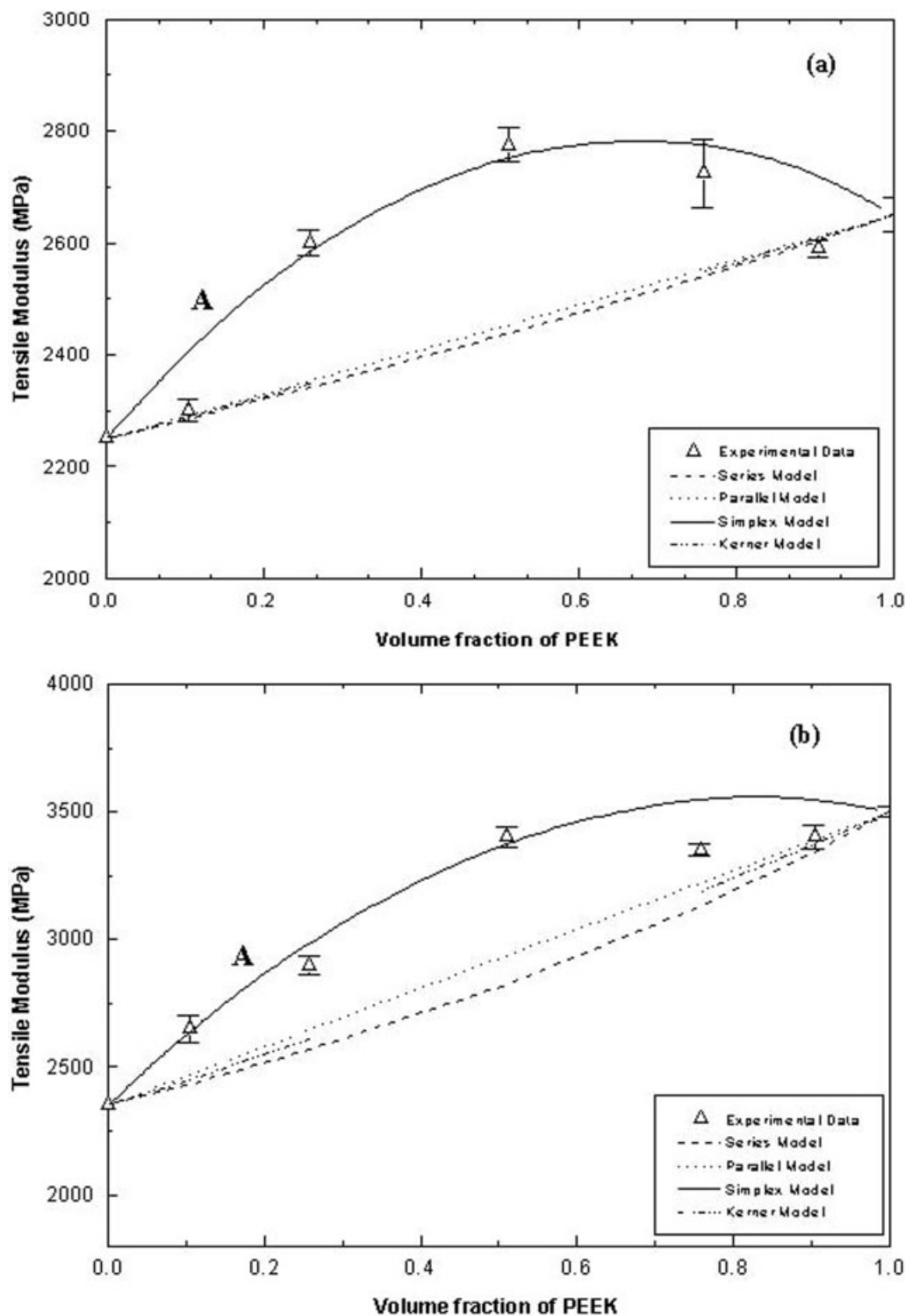


Figure 4 The tensile modulus as a function of the volume fraction of PEEK for PEEK/PES blends and a comparison with theoretically predicted variations for (a) quenched, (b) as-molded, and (c) annealed blends.

rived by the described theoretical equations. Because compositions with 50 wt % PEEK are close to a phase inversion composition, the properties for this composition have not been predicted by some of the equations. Thus, the theoretical curve based on these equations shows discontinuity around this particular com-

position. The left-hand curves in Figure 4 represent the PES matrix with PEEK as the dispersed phase, and the right-hand curves refer to the PEEK matrix with PES as the dispersed phase. Here, a Poisson ratio of 0.44 was used for both PEEK and PES and the volume fractions were calculated assuming constant density

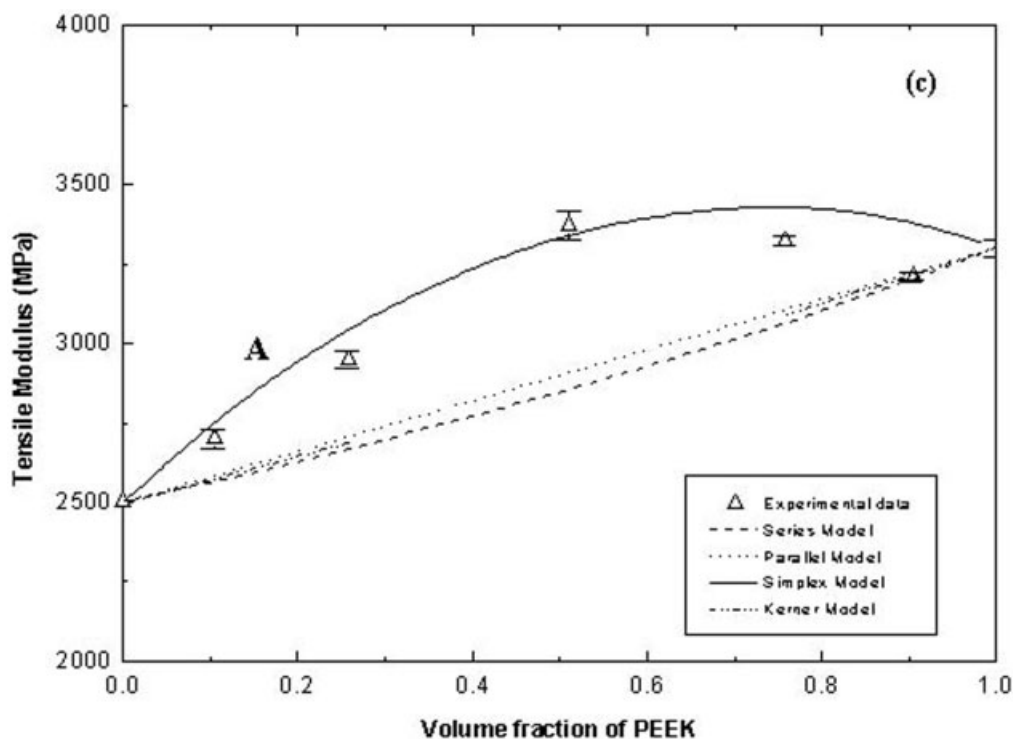


Figure 4 (Continued from the previous page)

for the two components through the whole composition range. This assumption is justified by the small variation of the degree of crystallinity of PEEK in the blends.⁴³ Respective density values of 1.31 and 1.37 g/cm³ were used for PEEK and PES. In addition, in agreement with others,^{44,46} we assume that, although different from the theoretical condition of 0.50, the actual Poisson ratios can be applied to our case.

As can be seen from Figure 4(a–c), the blend moduli show a positive deviation from linearity in all cases. The above behavior appears more clearly in the intermediate compositions. The results are remarkable in the sense that this kind of behavior is generally observed in miscible blends and, as reported previously,²³ the present blend system shows very limited miscibility, although such synergistic behavior in the blend moduli has also been reported in other immiscible blend systems.^{39,41,47}

In addition, the Figure 4 shows that no composite equation is able to model the experimental modulus data of this blend system in an exact manner. The linear curves are those that normally predict the property of a miscible blend or of immiscible blends with perfect adhesion between the phases, whereas the curves below the additive behavior are those that usually predict the property of an immiscible blend system with poor interfacial adhesion. As discussed by Kleiner et al.³⁰ normally such systems, which show positive deviation from linearity, can be modeled by simplex equations such as eq. (5). Curve A in Figure 4(a–c) shows the theoretical curve based on eq. (5).

The value of β_{12} in eq. (5), which can be taken as a relative measure of compatibility, was found to be 1300, 1900, and 1880 MPa for quenched, as-molded, and annealed blend systems, respectively. These values are greater or comparable to those obtained for some other compatible systems.^{30,39,41} They also show a high degree of mechanical compatibility in as-molded and annealed blends compared to quenched blends, at least at the low strains at which the moduli values are normally measured. Although simplex equations can be generated to model modulus–composition empirical data, they give no indication of any correlation with the molecular structure. As has been mentioned by Kleiner et al.,³⁰ the packing density, cohesive energy density, and glass-transition temperature are (in the order given) the major factors that determine the numerical magnitude of the modulus and the density and packing density are the key to understanding the modulus.

Figure 5(a,b) shows the variation of the density with composition in quenched and as-molded PEEK/PES blends. Annealed blends behave more or less similar to as-molded blends. The experimental density data have been compared with the additivity behavior. In the case of density, it is given by the following relationship:

$$1/\rho = w_1/\rho_1 + w_2/\rho_2 \quad (11)$$

where ρ , ρ_1 , and ρ_2 are the densities of the blend and homopolymers 1 and 2, respectively; and w_1 and w_2

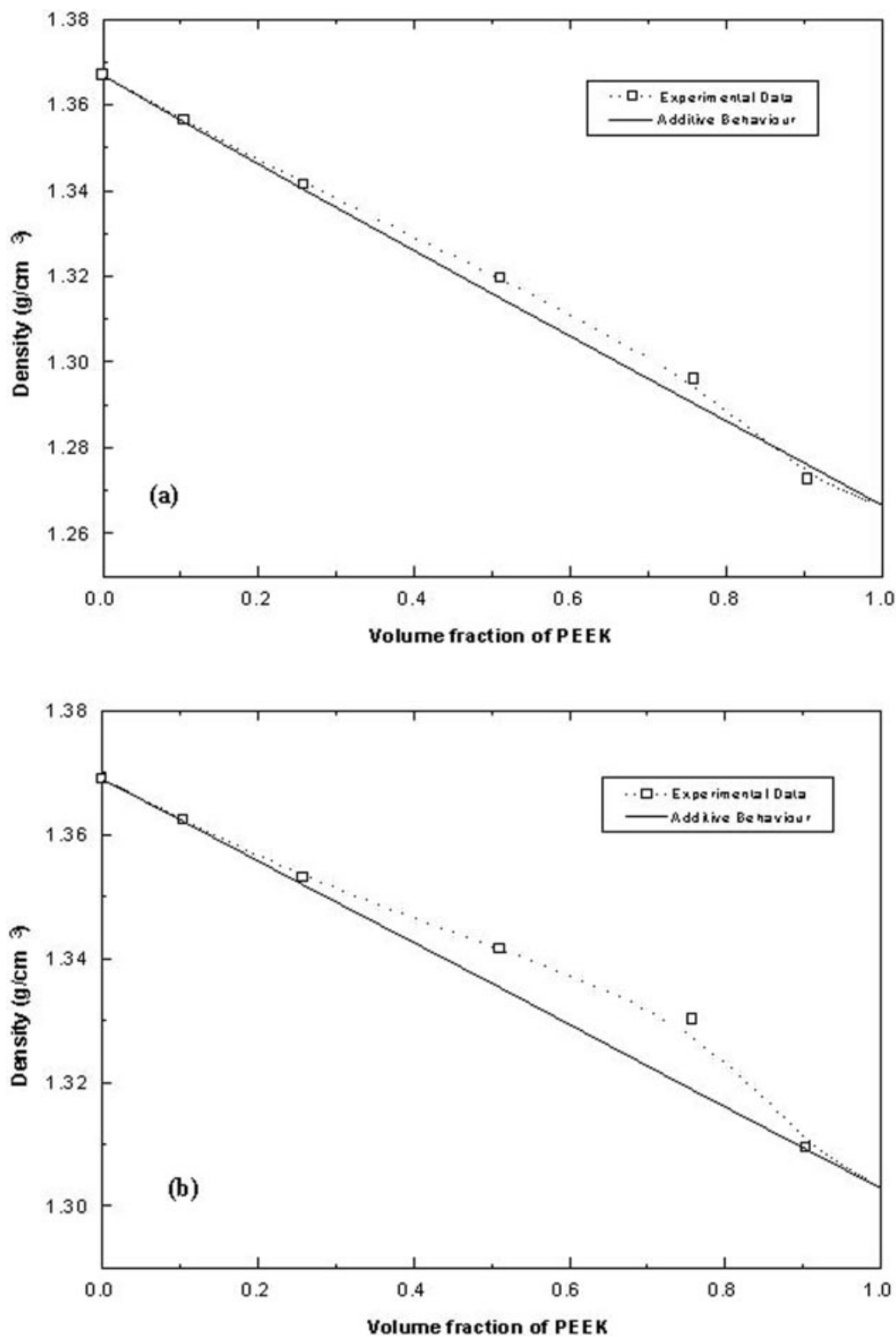


Figure 5 The density as a function of the volume fraction of PEEK for (a) quenched and (b) as-molded PEEK/PES blends.

are the weight fractions of the respective homopolymers. From Figure 5(a,b) it can be observed that the variation of the density with the composition follows a trend that is more or less similar to the modulus behavior and hence signifies the importance of the correlation between the density and modulus.

Tensile strength behavior

Figure 6(a–c) shows the variation of the strength at yield (or break) with the volume fraction of PEEK for quenched, as-molded, and annealed blends. Observe that the blends show an apparent synergism in the

tensile strength compared to the homopolymers. This synergism is more visible in the PEEK-rich compositions than in the PES-rich compositions. In Figure 6(a), which shows the strength at break (or yield) of quenched blends, it can be observed that whereas both homopolymers break by ductile failure, the blends show a region of transition from predominantly ductile failure to predominantly brittle failure. This transition occurs at a composition of around 50–75 wt % PEEK. Compositions having a PEEK content higher than 50–75 wt % PEEK break predominantly by ductile failure, whereas compositions having a PEEK content lower than 50–75 wt % PEEK fail predominantly by brittle failure. As mentioned previously, even in compositions failing by brittle fracture, some specimens break in a ductile manner. The fraction of total samples that fail by ductile mode is indicated within the parentheses for each composition (Fig. 6).

Although the tensile strength data for as-molded and annealed blends vary in a way similar to those observed for quenched blends, the embrittlement region in as-molded blends shifts to the 75–90 wt % PEEK region. In annealed blends, as expected based on the tensile behavior of homopolymers, all blends fail by brittle failure. There is also an increase in the tensile strength values of as-molded and annealed blends compared to quenched blends, which was discussed earlier.

As can be observed from Figure 6(a–c), most of the composite equations fail to predict the tensile strength data of the present blend system, at least in the PEEK-rich compositions. Although not applied previously, we propose that simplex equations of the form used to model the synergistic behavior in the modulus data can also be generated for predicting the tensile strength values. Curve A in Figure 6(a–c) is drawn based on such simplex equations, and it reasonably fits the experimental data.

Fried et al.³⁹ have discussed various reasons for the synergism in tensile strength in polymer blends. One of the reasons is based on an extension of the rubber network theory,⁴⁸ which suggest that an increase in strength could result from an increase in the number of network chains per unit volume formed by the entanglements. Increased entanglement density may occur as a result of specific interchain interactions. However, in the present blend system, any interactions will not be strong enough to let the above reason be valid for the observed synergism in tensile strength. Another explanation for the above behavior may be taken from the same packing density argument proposed by Kleiner et al.³⁰ to explain the observed synergism in modulus values, and the maximum blend strength may be directly related to the maximum blend density. The above fact, to some extent, seems to correlate well with the experimental data, but it cannot explain the increase in strength values at a 90 wt % PEEK composition, where the density value is near to

the additive value. The other reason for the synergism in the tensile strength data for PEEK-rich compositions could be due to the more compatible nature of the blend at these compositions.²³ This could result in the suppression of the secondary relaxation of PEEK and thus raise the stress level required to activate significant strain softening. This has also been found in several other blend systems.^{41,49}

Elongation at break (or yield) behavior

Figure 7(a–d) shows the elongation at break (or yield) of quenched, as-molded, and annealed PEEK/PES blends. As already mentioned, in quenched PEEK/PES blends, some specimens of a blend composition fail in a ductile manner while other show brittle failure. Figure 7(a) shows the elongation at yield of quenched specimens failing via ductile mode or the elongation at break of specimens failing via brittle mode. Figure 7(b) shows the elongation at break of quenched specimens showing ductile failure. From the figures it can be seen that whereas the PEEK-rich compositions in quenched PEEK/PES blends fails predominantly by ductile failure and shows high elongation at break, most of the specimens in PES-rich compositions fail as soon as the yield point is reached. This could be because of the multiphase nature and low miscibility of the blends at these compositions. Thus, although the interfacial adhesion in these compositions is good enough for excellent small strain deformation properties like the modulus and yield strength, it is not sufficient to overtake the deformation of the yield point and hence blends fail as soon as the yield point is reached. Figure 7(a) shows that the elongation at yield (or break) in PEEK-rich compositions of quenched PEEK/PES blends is above that predicted by additive behavior, whereas in PES-rich compositions it shows a negative deviation and falls more or less near to that predicted by the Nielsen model. From Figure 7(b) it can be observed that, although most of the blend compositions show a negative deviation of the elongation at break from those predicted by additive behavior, the composition containing 90 wt % PEEK shows an unusual synergistic ductile behavior with an elongation at break greater than both of the homopolymers. Although unexpected in a partially miscible blend system like the present one, such behavior has also been observed in other blend systems. We do not have any explanations for this behavior. However, it must be mentioned here that this particular blend composition shows the highest miscibility for PEEK/PES blends, as has been reported previously.^{22,23} In addition, the increase in ductility corresponds well with the earlier observed decrease in the modulus and increase in the yield strength.

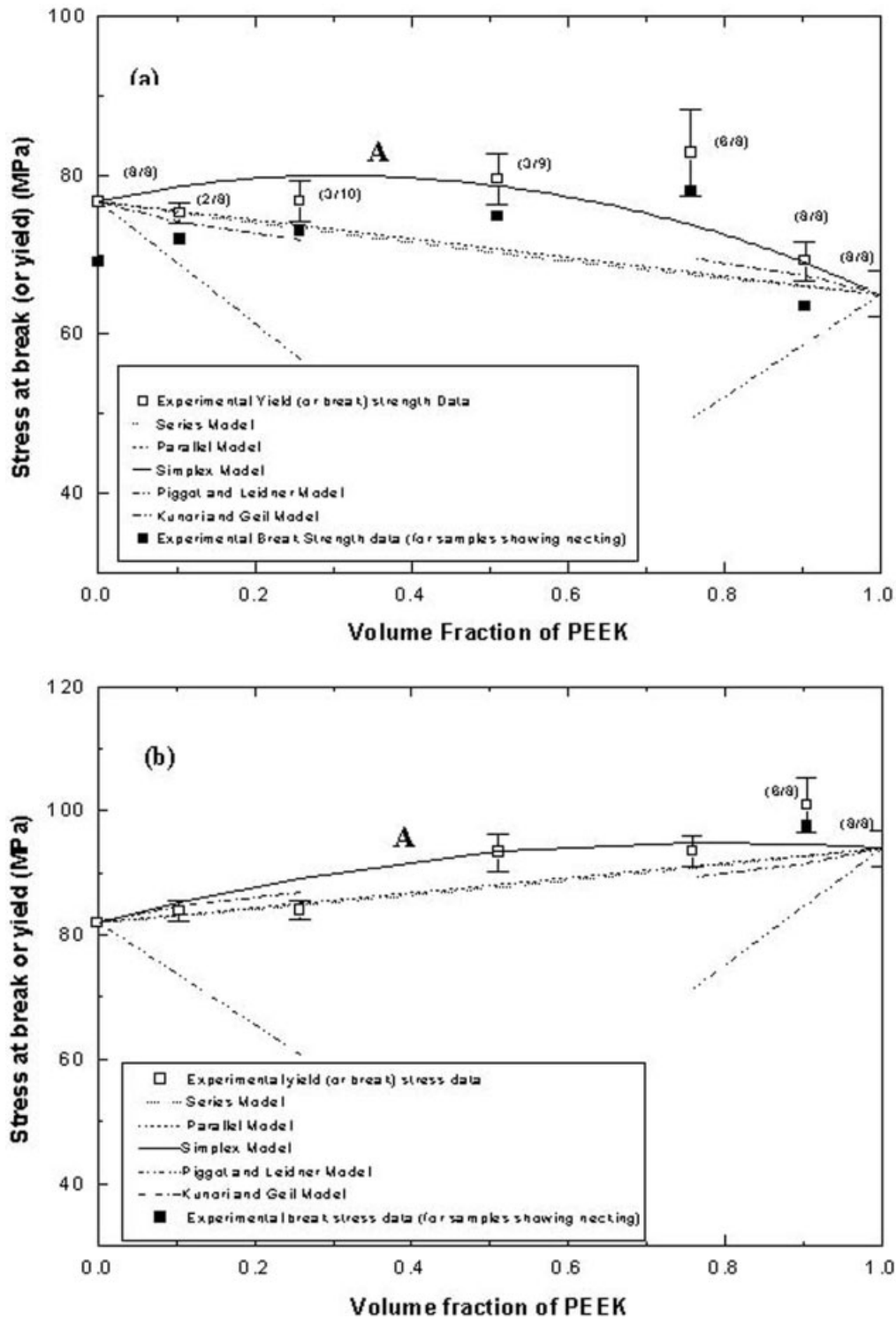


Figure 6 The tensile strength as a function of the volume fraction of PEEK for PEEK/PES blends and a comparison with theoretically predicted variations for (a) quenched, (b) as-molded, and (c) annealed blends. The fraction of total tested specimens that fail in ductile mode is indicated in the parentheses.

Figure 7(c,d) shows the variations of the elongation at yield (or break) for as-molded and annealed blends, which are more or less similar to those for quenched blends, although the ductility of these blends is far lower.

Further discussion and correlation with morphology

Generally, miscible polymer blends give rise to synergism or linear behavior in the fracture properties,^{39,50} partially miscible blends give values close to line-

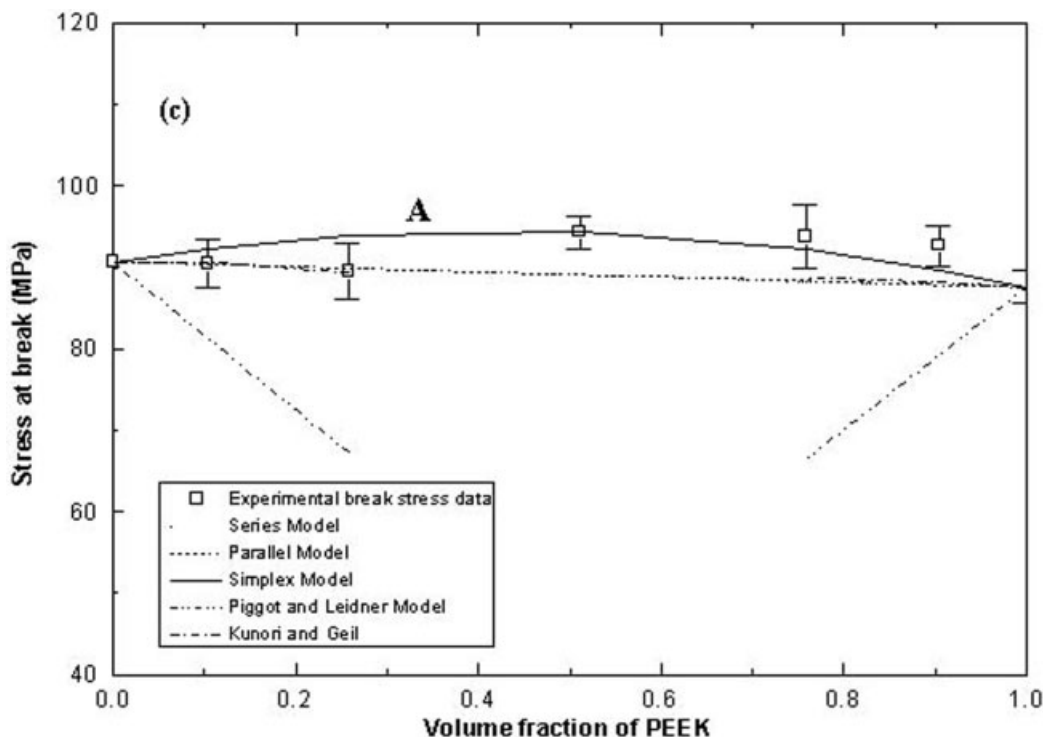


Figure 6 (Continued from the previous page)

arity,⁵¹ and immiscible blends give values well below linearity.^{52,53} We reported previously that PEEK/PES forms an immiscible blend system with a low level of miscibility. Hence, the mechanical properties obtained here are quite unusual for these kinds of blends. Although similar behavior has been reported previously for some blend systems, no proper explanation has yet been given for these exceptional properties.

Before going on to further discussion and explanations, we attempt to correlate the above tensile properties with the morphology of the blends. Figure 8(a–d) shows the morphology of the tensile fractured surface of as-molded PEEK/PES blends with different compositions. Because the morphologies of the annealed compositions are almost similar, these micrographs have not been shown here for reasons of brevity.

In discussing the phase morphology of polymer blends, the phase inversion point prediction is useful. Jordhamo et al.⁵⁴ developed an empirical model based on the melt-viscosity ratio and volume fraction for predicting the phase-inversion region of immiscible polymer blends. According to the model, phase inversion occurs when the following equation holds:

$$(\eta_m/\eta_d)(\phi_d/\phi_m) = 1 \quad (12)$$

The quantities η_m and η_d represent the viscosities of the respective matrix and dispersed phases whereas ϕ_d and ϕ_m represent the respective matrix and dis-

persed volume fractions of the phases. Miles and Zurek⁵⁵ emphasized that the condition for cocontinuity should be expressed by the viscosity ratio at the shear rate prevailing in the mixing device used to prepare the blends. Jordhamo et al.⁵⁴ showed that this simple equation describes the experimentally observed phase inversion point for polystyrene/polybutadiene blends. Ho et al.⁵⁶ suggested a modified version of eq. (12):

$$(\phi_d/\phi_m) = 1.22(\eta_m/\eta_d)^{0.29} \quad (13)$$

Recently, Kitayama et al.⁵⁷ found that for uncompatibilized polyamide/styrene-acrylonitrile blends, both of the above equations failed to correctly predict the phase inversion point; they proposed the following equation:

$$(\phi_d/\phi_m) = 0.887(\eta_m/\eta_d)^{0.29} \quad (14)$$

Considering that the processing history given in the extruder is erased during the compression molding process, the phase inversion point prediction can be done at 1 s^{-1} , which is the shear rate normally observed in the latter process. Complex viscosity values⁵⁸ were used instead of shear viscosity, assuming that the samples follow the Cox–Merz rule.⁵⁹ Applying the above models, eq. (12) predicts the phase inversion point for a 95/5 PEEK/PES composition, whereas eqs. (13) and (14) predict the phase inversion

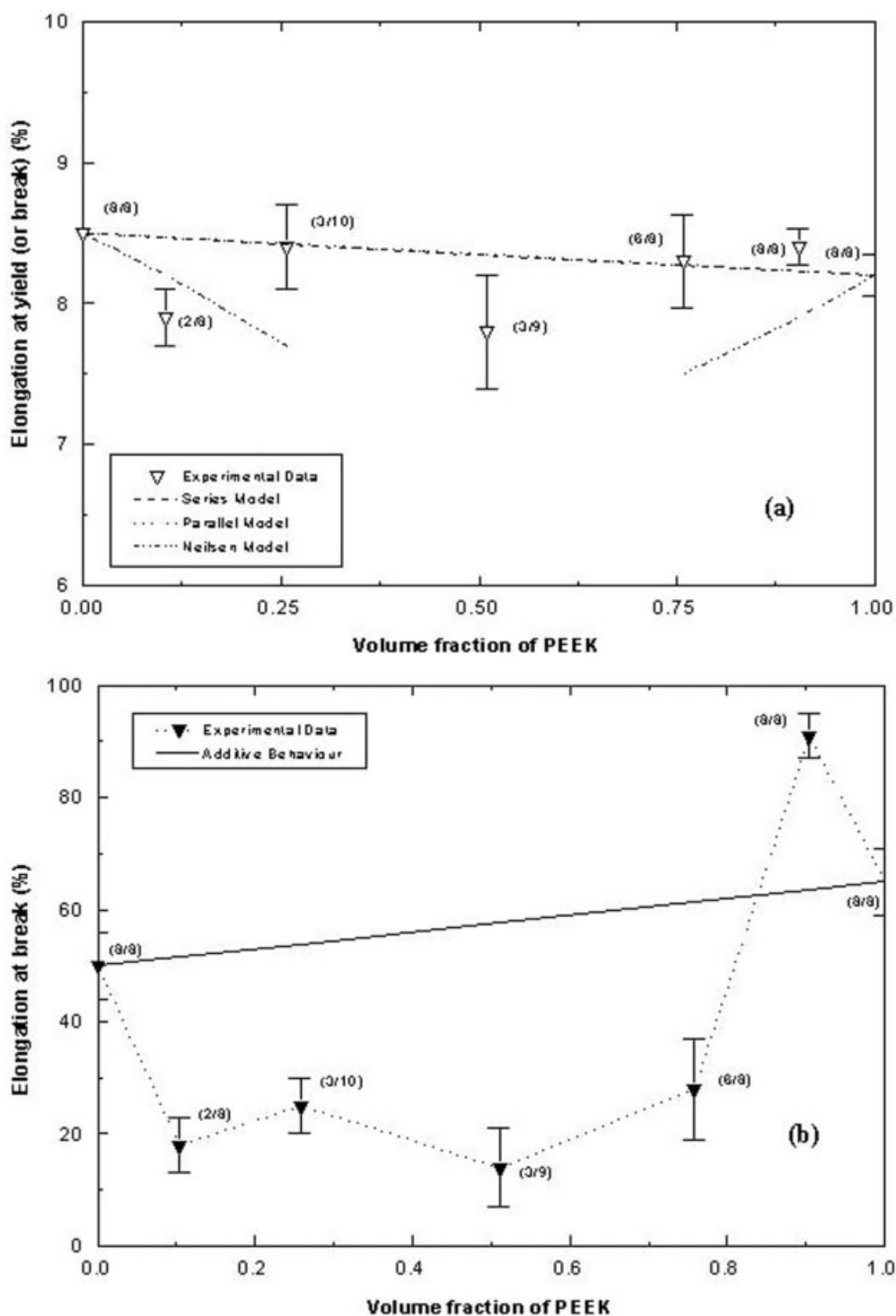


Figure 7 The percent elongation at break (yield) as a function of the volume fraction of PEEK for PEEK/PES blends: (a) quenched with elongation at yield for break for specimens showing brittle failure, (b) quenched with elongation at break for specimens showing ductile failure, (c) as-molded, and (c) annealed. The fraction of total tested specimens that fail in ductile mode is indicated in the parentheses.

point for around a 75/25 PEEK/PES composition, which is more in agreement with the morphology observed, as discussed below.

Figure 8(a) shows the morphology of the 75/25 as-molded PEEK/PES blend. As can be seen, because

the composition is very close to the phase inversion point, a cocontinuous type of morphology is visible and no disperse phase can be clearly observed. The remarkable mechanical properties observed at this composition may be because of its cocontinuous mor-

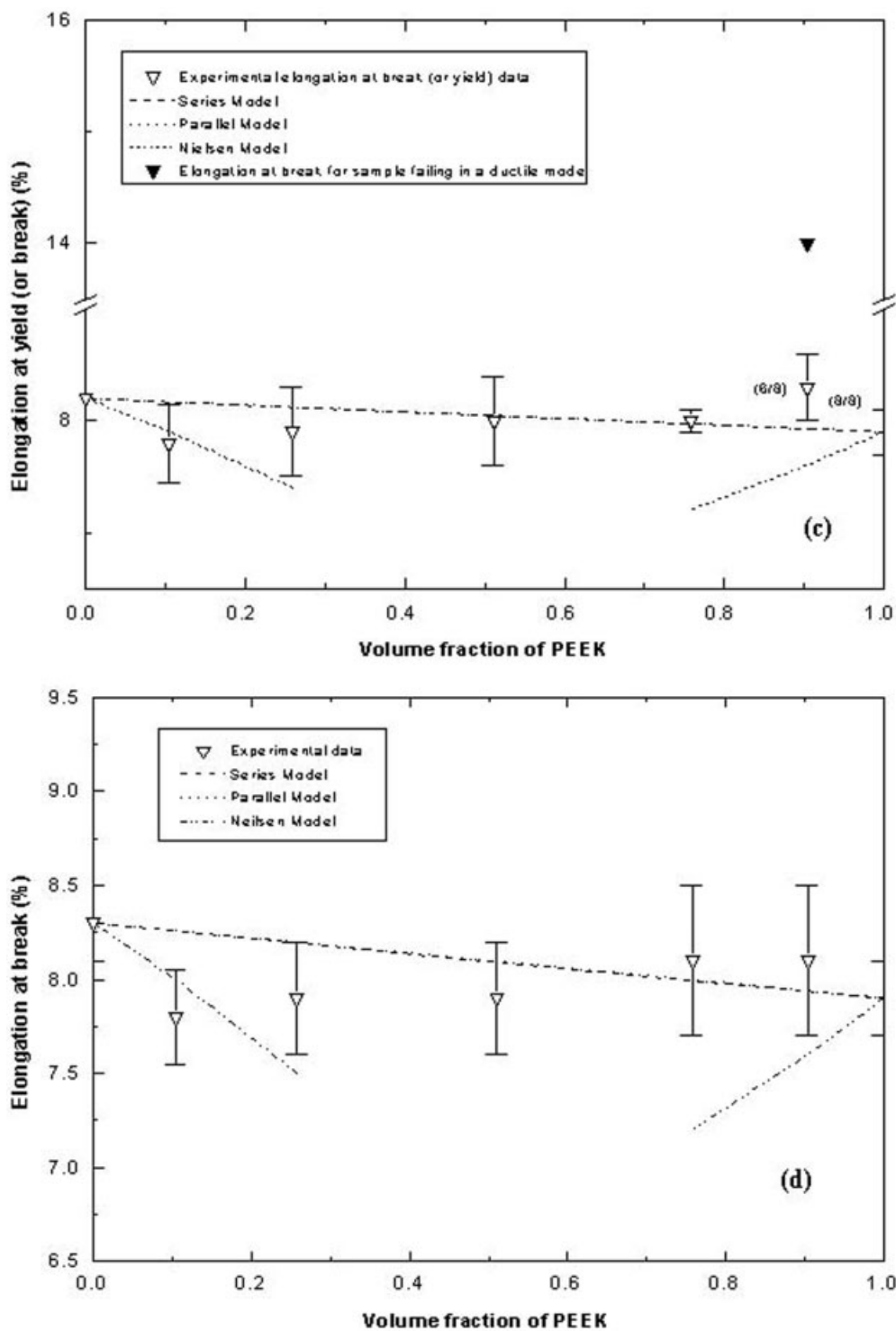


Figure 7 (Continued from the previous page)

phology. As the PES weight fraction in the blend is further increased, the cocontinuous morphology changes to a clear two-phase morphology. Figure 8(b) shows the morphology of a 50/50 PEEK/PES blend. An unusual composite droplet type of morphology can be observed. This type of structure consists of a matrix phase, a dispersed phase, and dispersed drop-

lets within the dispersed phase. The overall structure is highly reminiscent of some rubber-based blends where low molecular weight polystyrene remains dissolved in the dispersed rubber particles.⁶⁰ Although this type of morphology has been reported previously for thermoplastic blends,⁶¹ the controlling mechanism in these cases is clearly different from that in rubber-

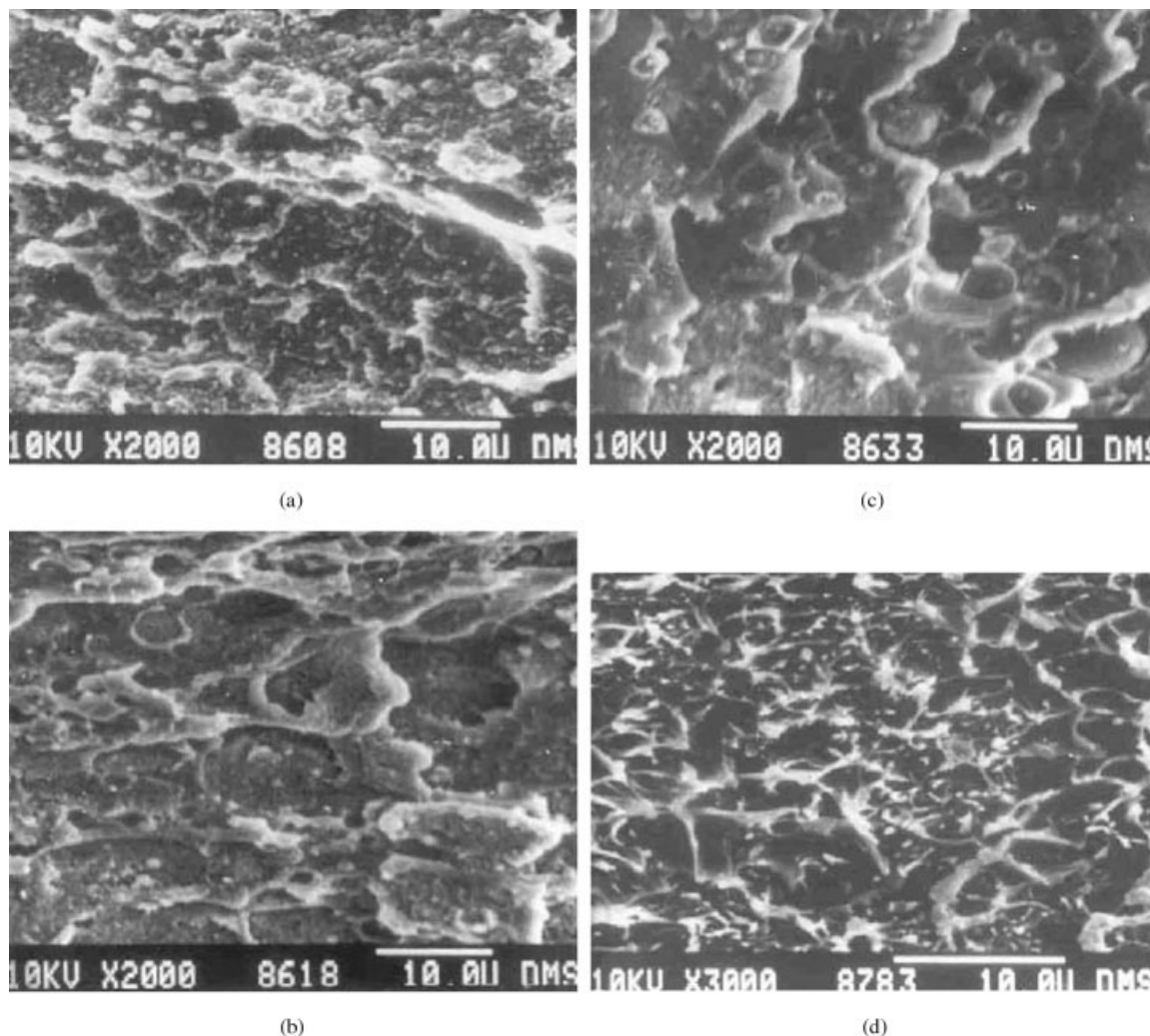


Figure 8 Scanning electron microscopy photographs of the tensile fractured surfaces of as-molded PEEK/PES (a) 75/25, (b) 50/50, (c) 25/75, and (d) 10/90 blends.

based blends because both constituents of the blend in these studies are immiscible high polymers. Van Oene⁶² has demonstrated that an elastic material can tend to encapsulate one of low elasticity in order to lower the overall surface free energy. Because PEEK is more elastic in nature than PES, the former has a tendency to preferentially encapsulate the latter (hence the observed morphology). The mechanism is still not clear. Nevertheless, this type of morphology does lead to excellent mechanical properties and is corroborated by the tensile data. Figure 8(c) shows the distribution of PEEK in the PES matrix with phase dimensions on the order of 2–10 μm in the 25/75 PEEK/PES blend. The hole that is present shows the debonding or dewetting of the PEEK dispersed phase during fracture. The surface of the holes is seldom clear and rough surfaces usually appear. The matrix deformation is also appreciable, which shows the very high adhesion level that exists at the surface and the existence of some continuity of the matrix through the

interphase. The nearly additive tensile properties in this composition are in agreement with the observed morphology. Figure 8(d) shows a micrograph of the 10/90 PEEK/PES blend. Again the roughness and shape of the dewetting zones and the matrix deformation clearly show the strong interphase adhesion in this system.

Figure 9(a–d) shows the cross-sectional view of the tensile fractured surface of different compositions of quenched PEEK/PES blends. The fracture surfaces of quenched PEEK/PES blends show typical ductile failure morphology. Oriented peaks, fibrils, and bands at right angles to the direction of fracture propagation can be distinguished as characteristic features of extreme ductile failure. The dispersed phase also exhibits a permanent deformation along with the matrix, having a rodlike morphology in the matrix except in the 75/25 PEEK/PES blend. It seems this composition is very close to a phase inversion composition, and thus no second phase could be observed on the frac-

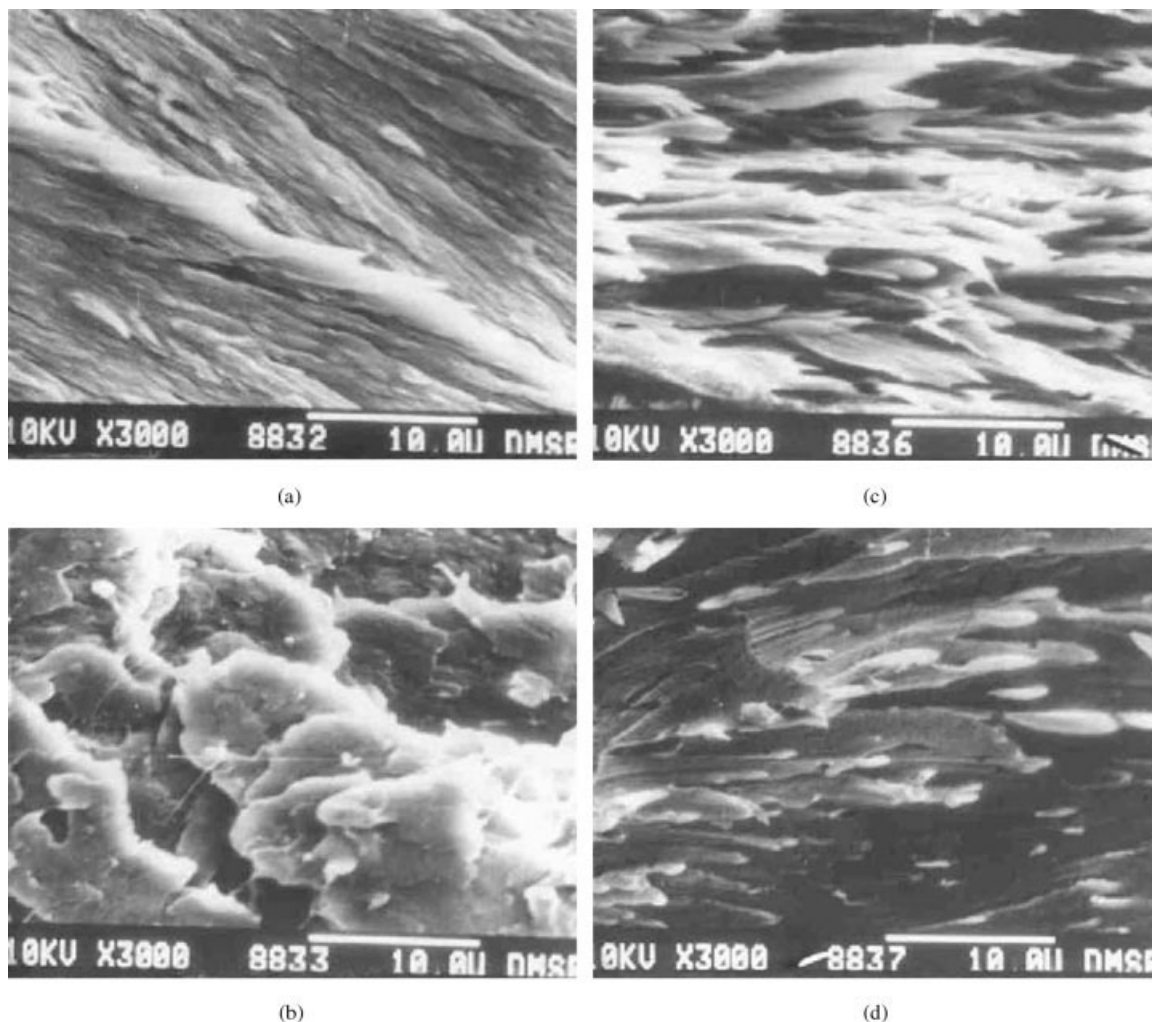


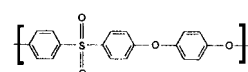
Figure 9 Scanning electron microscopy photographs of the tensile fractured surfaces of quenched PEEK/PES (a) 90/10, (b) 75/25, (c) 50/50, and (d) 25/75 blends.

ture surface. In all other compositions, where a rodlike morphology is seen, no holes or dewetting appear in the fracture surface and all the rods are clearly deformed and broken. This experimental evidence shows the exceptional adhesion level existing between the two phases. This breaking out of the dispersed phase in all cases without any sign of dewetting allows an effective incorporation of the properties of the dispersed and matrix phase into those of the blend. The 50/50 PEEK/PES blend is also close to phase inversion composition and exhibits a partially cocontinuous morphology with a highly cohesive fracture surface. The 25/75 PEEK/PES blend, in which the dispersed phase morphology is much more visible, exhibits a fracture with low plastic deformation. The mechanical properties of quenched PEEK/PES blends are also in agreement with the observed morphology.

Despite a fairly isotropic morphology, cohesive fracture, and remarkable adhesion observed by scanning electron microscopy, the synergistic behavior is significant in small strain properties over almost the whole

composition range and in large strain properties in PEEK-rich compositions. This synergism in the mechanical properties was not observed previously by Eguiazabal et al.,¹⁶⁻¹⁸ who also extensively studied this blend system. In fact, in as-molded compression molded blends, they observed that the break stress values have a significant negative deviation from the additive behavior, reaching almost 30 MPa with a 50/50 composition. Similarly, the elongation at break of as-molded blends was well below the additive behavior. In our previous work on the compatibility behavior of these blends,²³ we gave three reasons for the difference in the results obtained in our system:

1. a different grade of poly(ether sulfone), which contains a repeating unit that is more identical to the PEEK structure shown below:



2. a lower molecular weight PES than that by previous workers (Eguiazabal et al. used a PES with $M_w = 97,000$); and
3. a different melt blending technique.

Although we are not sure how responsible the third reason could be for the significant deviation of our results from others because the compression molding technique used after blending erases the previous processing history and hence the morphology of the blends. But as has been discussed by Arzak et al.,¹⁶ the wide variation in compatibility results obtained by different workers does suggest that the method and characteristics of blending play a definitive role in the phase behavior and composition obtained in this system. As for the first reason, Harris and Robeson²⁰ have shown how the structural difference in PES results in significant variations in the compatibility and mechanical properties of PEEK/PES blends.

Several reasons have been assigned for the synergism in the mechanical properties found in some blends, despite their immiscibility:

1. the fairly oriented morphology because it is well known that in oriented blends a certain miscibility level is not a necessary condition to reach an acceptable mechanical performance,⁴⁷
2. the largely aromatic character of the blend components,^{16,17,63}
3. the relatively similar chemical structure of both components,
4. the possibility of preferential surface adsorption and hence surface enrichment,⁶⁴ and
5. the enthalpic interaction and related polymer-polymer adhesion between the phases.⁶⁵

Statistical thermodynamic theories predict that varying degrees of interdiffusion of polymer segments will occur in the interfacial layer as required to minimize the interfacial energy and the degree to which this can occur depends primarily on the enthalpic interaction between the phases.

Extensive studies of the morphology and interface of these immiscible blends are needed to arrive at a definite reason for their unusual synergistic mechanical properties. However, the results obtained here and previously by other workers do signify that complete miscibility, modification of the interface, or addition of a compatibilizer is not the only way to obtain a mechanically compatible blend.

CONCLUSIONS

Blends of PEEK and PES, despite their limited miscibility, show excellent mechanical properties. Synergistic behavior in the tensile modulus and tensile strength was observed with a maximum at around

50–75 wt % PEEK in the blend. This synergistic behavior in the tensile modulus and strength is consistent with a similar increase in density at these compositions and signifies the importance of the packing density in determining these properties in polymers. The elongation at yield (break) decreases in the blends but it shows an unexpected synergistic behavior in the PEEK-rich compositions, especially at 90 wt % PEEK in the blend. Specimens with different thermal histories show almost similar variations in their mechanical properties. The scanning electron microscopy observation of the morphology indicates a cohesive fracture and remarkable adhesion between the phases, but it cannot fully account for the synergistic behavior in the mechanical properties. A comparison with theoretical predictions based on some composite equations shows how these models fail to predict the experimental data in a multiphase blend with components having moduli ratios near to one and showing a synergistic variation in the mechanical properties. However, a simplex equation provides a reasonable fit to the experimental data and proves its usefulness in predicting the mechanical properties of polyblends with synergistic behavior.

The excellent mechanical properties, especially of PEEK-rich compositions, is worthy of further investigation to clarify whether this improvement is maintained with variations in temperature and different test conditions. Further, the synergistic behavior in the mechanical properties in some immiscible blend systems like the present one needs some extensive research efforts of their blend morphology and interface to arrive at some definite explanations.

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