

Thermal and Mechanical Characterization of Partially Miscible Blends of Poly(ether ether ketone) and Polyethersulfone

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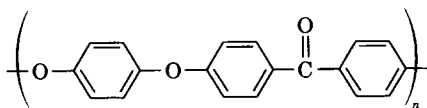
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SYNOPSIS

The miscibility behavior of poly(ether ether ketone) (PEEK) and polyethersulfone was studied by differential scanning calorimetry (glass transition temperature) and tensile properties: Young's modulus and ultimate tensile strength. A single glass transition temperature was observed over the entire composition range. The glass transition temperature of blends, however, did not follow any of the theoretical equations. Utracki and Jukes equation was used with $K = 11$ to fit the experimental data that indicate partial miscibility. Up to 30 wt % PEEK, the blends showed amorphous behavior with the glass transition temperature very close to that of polyethersulfone. Because of partial miscibility, blends showed mechanical compatibility. Both the modulus and strength increased significantly with an increasing concentration of PEEK in the blends, reaching a maximum around 40%. Electron microscopic results revealed phase separation but strong adhesion between the phases.

INTRODUCTION

The research and development of a tough high-temperature and low-density thermoplastic is the area in which the polymer industry has seen lot of activity in recent years.¹⁻³ These materials are sought mainly as an alternative for metals in the structural 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). This polymer has exceptional toughness, strength, and rigidity as well as excellent chemical and radiation resistance.^{4,5} The repeat unit of PEEK is



Its glass transition temperature (T_g) is 143°C and its melting point (T_m) is 334°C, which allow an estimated continuous working temperature of 250°C with mechanical properties retained over 300°C.⁶ It is a crystallizable polymer, and crystallinity may vary from 0 to 40% depending on sample history.⁷ The physical properties can be greatly influenced by the processing conditions. The crystallinity imparts excellent resistance to a wide range of liquids. PEEK can be used for thousands of hours in steam or high-pressure water without significant property degradation. Because of all these properties, considerable attention has been given to PEEK as a high-performance thermoplastic as well as a matrix for advanced composites.⁸⁻¹² Despite the advantages noted above, it is unlikely that PEEK will replace metals, ceramics, or other engineering thermoplastics in the near future. PEEK has a share of disadvantages of its own: It is not soluble in any of commercial solvents, synthesis methods are quite tedious, and it is manufactured in relatively low quantity and often by very costly procedures, which limit severely its applications. Blends of PEEK with

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other less expensive engineering thermoplastics could be an attractive alternative.

Polymer blending is a proven tool to obtain new types of materials with a wide diversity of properties intermediate between those of the pure components along with economic advantages. As these materials can be developed by simply melt-mixing the homopolymers and because of the high productivity and design flexibility offered, the polymer blends are increasingly replacing commodity polymers in engineering applications.^{13,14} Most of the polymer blends reported in the literature are two-phase systems, the morphology of which depends on the arrangement of the phases and their interphases.¹⁵ In the case of semicrystalline-amorphous polymer blends, the crystallization, which, in turn, controls the mechanical properties, takes place during the molding cycle. The blending of semicrystalline engineering thermoplastics such as PEEK with an amorphous and relatively less expensive polymer such as polyethersulfone (PES) could not only reduce the cost of finished products but also would facilitate development of a new material with possibly combined characteristics of both the PEEK and PES.

In the present paper, we have analyzed blends of PEEK/PES. Mechanical and thermal methods are used to characterize the blends.

EXPERIMENTAL

The PEEK used was provided by ICI Chemicals (grade 380G) with a molecular weight of 3.2×10^5 . PES was also manufactured by ICI Chemicals (grade 4100) and its molecular weight was 37,200.

The PES and PEEK resins were dried overnight at 100°C. Blends were prepared by mixing the two resins in a Brabender Plasticorder at 355°C and 60 rpm. A small amount of (0.1 g/100 g PES) of an antioxidant, irganox 1010, was added to prevent degradation. The components were mixed for at least 10 min to assure homogeneous distribution. The samples were then compression-molded in a press at 50 MPa and 355°C. The mold was then cooled at room temperature, keeping the pressure constant.

Mechanical measurements were performed by an Instron Tensile Tester at room temperature, and the strain rate was kept at 10 mm/min. For thermal analysis, a DuPont differential scanning calorimeter 9900 was used. Indium was a standard for temperature calibration. The melting temperature was taken as the peak of the melting endotherm and the glass transition temperature was the midpoint of

the step change in the thermogram. The determination of both temperatures was within $\pm 2^\circ\text{C}$. The heating rate was $10^\circ\text{C}/\text{min}$ and the scan was done between 25 and 380°C .

RESULTS AND DISCUSSION

Glass transition temperature (T_g) was used to determine the miscibility between PEEK and PES. T_g is the second-order transition existing between glass and liquid supercooled below its melting point.¹⁶ In polymers, the glass transition is related to cooperative segmental motion.¹⁷ Boyer¹⁸ suggested that T_g involves 50–100 backbone chain carbon atoms, i.e., a domain with diameter $d_d = 2.3$ nm. The use of T_g in the determination of polymer–polymer miscibility is based on the premise that a single T_g indicates that the domain size is below d_d ($2 \leq d_d \leq 15$ nm). It is worth mentioning here that a single T_g is not a true measure of miscibility but only of the state of dispersion. The exact correlation among phase equilibria, miscibility under processing conditions, and T_g is quite difficult to comprehend.¹⁷ T_g is a good tool for obtaining information and approximation about the miscibility phenomenon. In the present study, we have used T_g values of the blends to understand the dispersion of phases and to have some idea of miscibility without going into molecular-level details.

Figures 1 and 2 show the DSC thermogram of PEEK and PES. The PEEK sample shows the characteristics of a semicrystalline PEEK. There is a broad T_g step with the midpoint at 151°C . The glass transition of amorphous PEEK occurs at about 140°C , some 10°C lower than that of semicrystalline PEEK, and occurs with a sharp relaxation peak.^{4,7} The melting point of PEEK is shown by a well-defined endothermic peak with a maximum T_m at 345°C . The DSC curve of PES is a typical of an amorphous polymer with a sharp T_g step with the midpoint at 229°C .

Figure 3 is a representative DSC thermogram of 50/50, PEEK/PES blend. Similar curves were found for other compositions and the data are summarized in Table I. It is seen that blends exhibit a single glass transition temperature for the entire composition examined. A plot of T_g vs. PES composition is shown in Figure 4. If we take a single glass transition temperature for each blend as a criterion for miscibility,^{19,20} we may conclude with a safe approximation that these blends may be miscible.

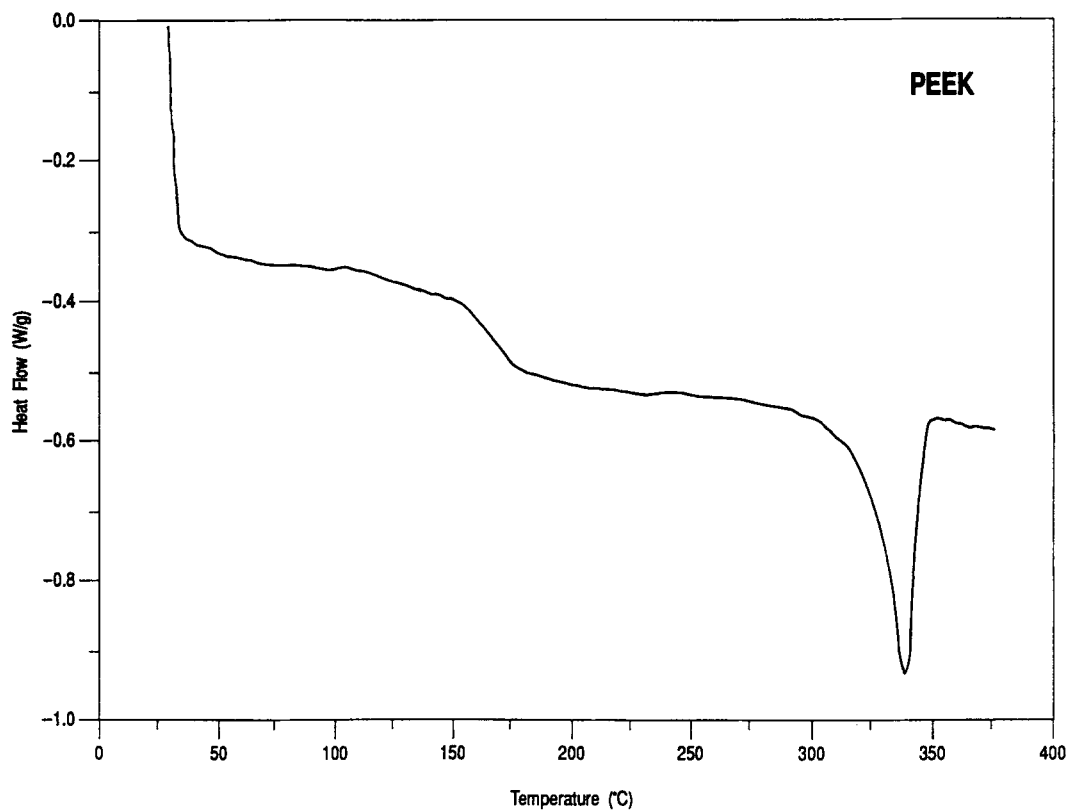


Figure 1 Differential scanning calorimetric heating scan at 10°C/min for PEEK.

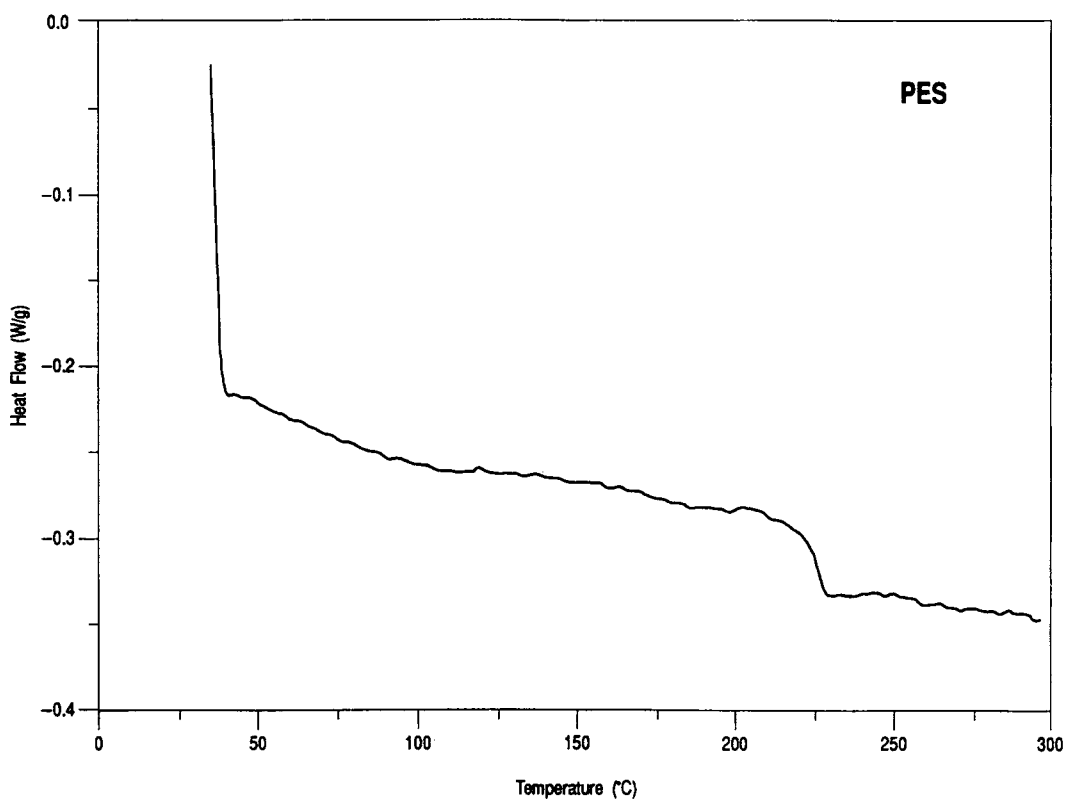


Figure 2 Differential scanning calorimetric heating scan at 10°C/min for PES.

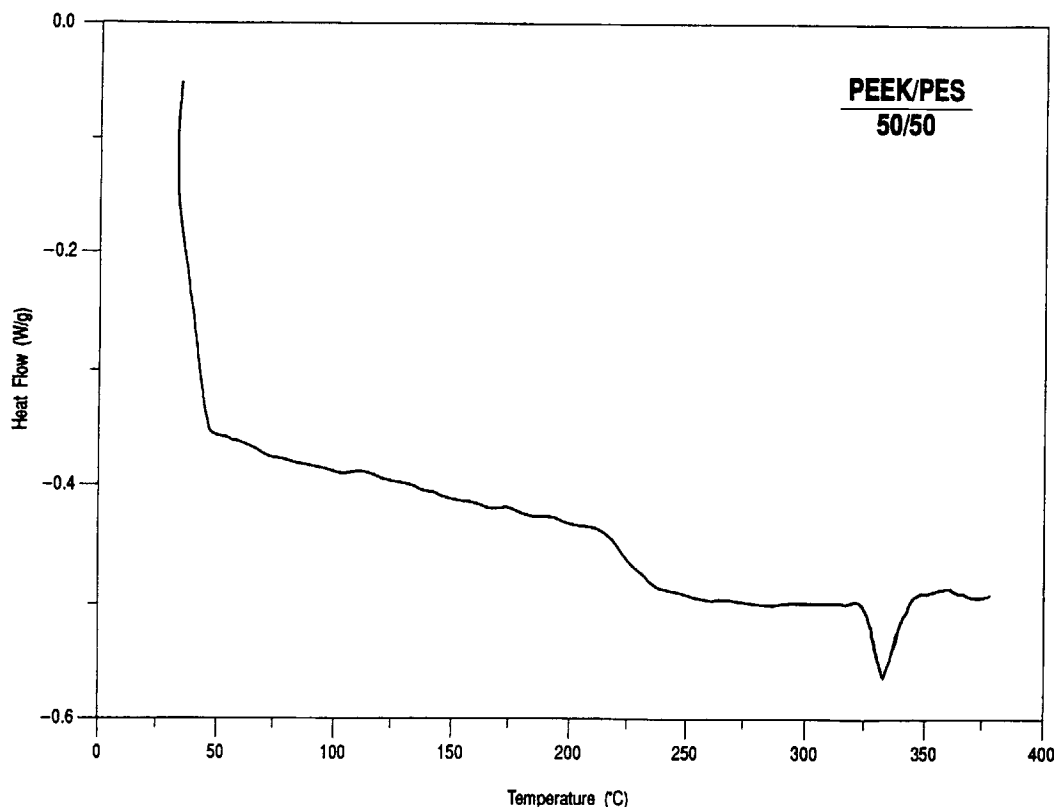


Figure 3 A representative DSC thermogram for the 50/50 PEEK/PES blend.

There are several equations relating T_g to the composition. Among these equations, the most frequently used is the Gordon-Taylor equation²¹ reduced by Wood²²:

$$\sum_i W_i \Delta C_{pi} (T_{gi} - T_g) = 0 \quad (1)$$

where W_i and T_{gi} are, respectively, weight fraction and glass transition temperature of polymer i in the blend. For a two-component system, this equation can be written as

$$W_1 (T_{g1} - T_g) + KW_2 (T_{g2} - T_g) = 0 \quad (2)$$

where K is an empirical parameter and measures the miscibility. Utracki and Jukes²³ more recently proposed another equation:

$$(\ln T_g) / T_g = \sum_i (W_i \ln T_{gi}) / T_{gi} \quad (3)$$

The Utracki and Jukes equation was found to follow T_g vs. weight fraction dependencies for miscible blends such as poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene as well as plasticized sys-

tems such as poly(vinyl chloride)/di-2-ethylhexyl phthalate.¹⁷ For partially miscible blends, they introduced an empirical parameter describing the deviation from the assumed negligibility of entropy of mixing. For a two-component system, the Utracki and Jukes equation becomes

$$W_1 \ln(T_g / T_{g1}) + K_2 \ln(T_g / T_{g2}) = 0 \quad (4)$$

Table I Thermal Data of PEEK/PES Blends

% PES	% Crystallinity	T_m (°C)	T_g (°C)
0	42.0	342	151
10	40.0	339	191
20	37.0	335	200
30	33.0	330	210
40	30.0	331	215
50	28.0	327	221
60	27.0	325	220
70	0.0	—	226
80	0.0	—	227
90	0.0	—	—
100	0.0	—	229

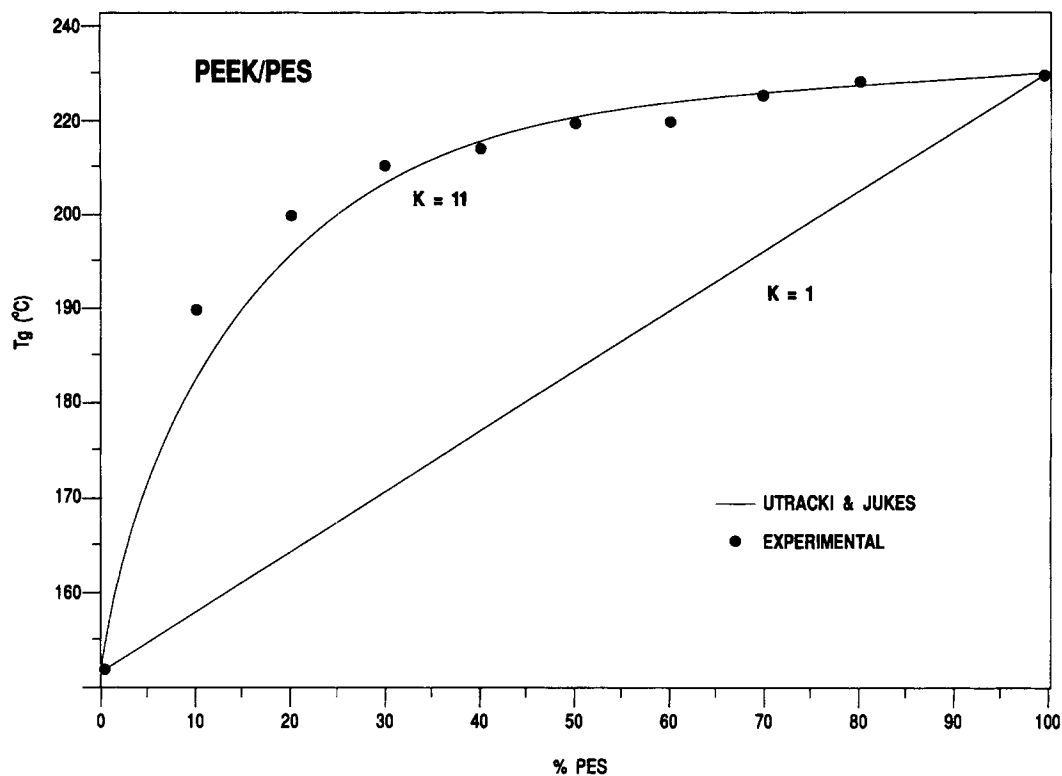


Figure 4 Glass transition temperature vs. weight percent of PES in the blends using the Utracki-Jukes equation.

For our PEEK/PES, we chose both eqs. (3) and (4). For eq. (4), by selecting a K value equal to 11, there was a perfect fit of experimental and theoretical values, which proposes that PEEK/PES blends are partially miscible. This partial miscibility between PEEK and PES may be the result of the slightly exothermic heat of mixing caused by some specific interactions between the two polymers.²⁴ It could also be suggested that the miscibility in PEEK/PES stems from the interaction of the carbonyl group of PEEK and highly polarizable aromatic sulfonate structure of PES.

Figures 5 and 6 show the tensile modulus and ultimate strength of PEEK/PES as a function of PEEK concentration. It is seen that both the modulus and strength increase significantly with increasing concentration of PEEK, reaches a maximum around 40%, and then drops to the values predicted by the rule of mixing. This synergistic effect is most probably due to the partial miscibility of PEEK/PES systems.

Miscible polymer/polymer blends form single-phase materials as a result of the presence of a specific interaction between two polymers.²⁵ It is expected that the mechanical properties of the miscible

blends will follow or exceed the values predicted by the rule of mixing. In certain cases, the mechanical properties will be even greater at certain blend compositions than will the corresponding properties of either polymers in the unblended state. Specific interactions between blend components cause volume contractions on mixing and a loss in free volume of the blend, leading to higher modulus and strength values than predicted by the rule of mixing.

Immiscible polymeric blends form multiphase materials and exhibit poor mechanical properties as a result of poor adhesion between phases. Mechanical properties of immiscible blends normally fall below those predicted by the rule of mixing. Partly miscible blends (or immiscible but compatible blends) represent an intermediate situation in terms of phase dispersion between those of miscible and immiscible blends. Partly miscible blends also show separate phases; however, under proper phase dispersion and mixing conditions, partly miscible blends often exhibit mechanical properties that follow closely the rule of mixing or even show some synergism in modulus or tensile strength.

The results in Figures 5 and 6 indicate that PEEK/PES blends are compatible and also that

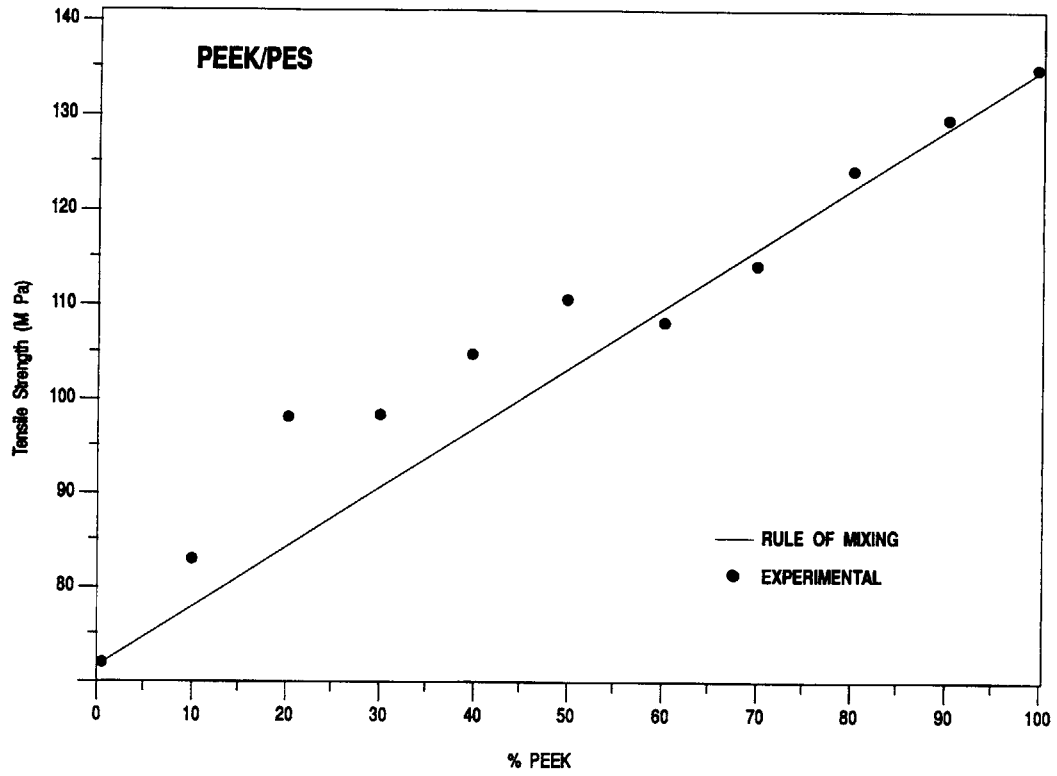


Figure 5 Young's modulus vs. weight percent of PEEK in the blends at 25°C.

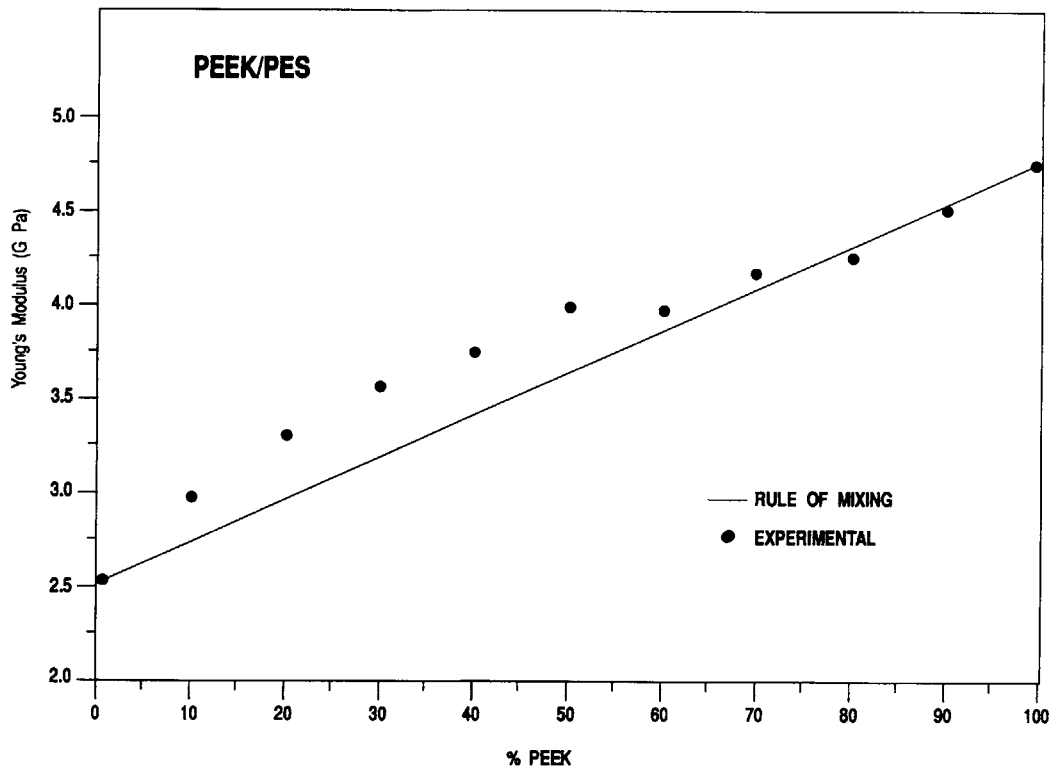


Figure 6 Tensile strength vs. weight percent of PEEK in the blends at 25°C.

there must be some sort of interaction present between the polymers. Another reason that could explain the maximum at 40% PEEK composition in the blends is that PES is amorphous and PEEK is substantially a crystalline polymer. The blends containing up to 40% PEEK are amorphous, and beyond this concentration, semicrystalline. As the development of crystallinity is usually associated with a decrease in toughness,^{26,27} Young's modulus and ultimate strength decrease once PEEK concentration increases beyond 40%, approaching the values predicted by the rule of mixing. The positive deviation from the rule of mixing suggests that there is enough interaction between the components to retard its internal mobility significantly.

Figure 7 represents a micrograph obtained from scanning electron microscopy (SEM) measurements at 2000 \times of 20% PEEK/80% PES film fractured under liquid nitrogen. It shows the spherical domains of PEEK 100–300 nm in size. Such domains result from phase separation. Even though a clear phase separation is seen, the PEEK domains are well distributed in the PES matrix, indicating that the mixing is good. Figure 7 also shows a good adhesion between the two distinct phases. This adhesion or interaction is responsible for partial miscibility between the two polymers.

CONCLUDING REMARKS

Poly(ether ether ketone) and polyethersulfone form semimiscible blends at all proportions. This partial miscibility, we believe, arises from the similarity in the structure of the two polymers. A detailed study

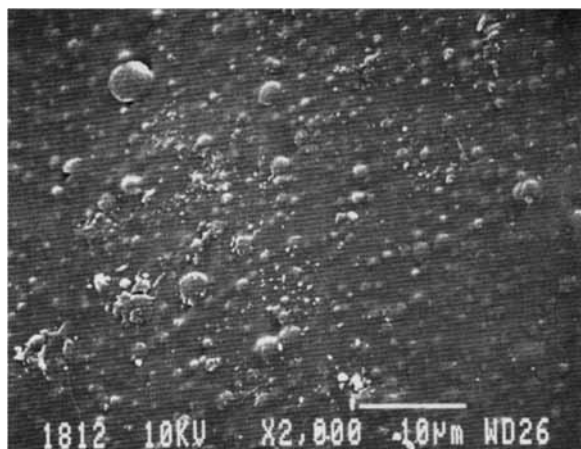


Figure 7 Scanning electron micrograph at 2000 \times for 20/80 PEEK/PES blend, fractured under liquid nitrogen.

of this miscibility is the subject of future study. Thermal analysis showed a single T_g for the blends with quite higher values than predicted by most of the theoretical equations. Blends containing 40% PEEK were crystallizable; the development of crystallinity did not show much effect on the value of the glass transition temperature. Because of the partial miscibility, blends are mechanically compatible. Both the modulus and strength increased significantly with increasing concentration of PEEK in the blends, reached a maximum around 40% PEEK concentration, and then dropped to the values predicted by the rule of mixing.

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