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Tensile behaviour and fracture toughness of poly(ether ether ketone)/poly(ether imide) blends

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Summary

The bulk tensile behaviour of poly(ether ether ketone) and poly(ether imide) homopolymers and their blends has been investigated, and the temperature and strain rate dependence of the yield stress discussed in terms of simple Eyring rate theory. In fracture mechanics tests, the K_{IC} of PEEK was found to decrease significantly with increasing test speed, whereas the K_{IC} of PEI showed little rate sensitivity. Therefore, although a gradual increase in K_{IC} with increasing PEEK content was observed in the blends at low loading rates, this effect was anticipated to be less pronounced at higher loading rates.

Introduction

The complete miscibility of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) blends in the amorphous state, has made them of considerable interest as model systems for fundamental investigations of the crystallization and diffusion behaviour of PEEK (1-4). There are also practical reasons for blending PEEK with PEI. For PEI, the glass transition temperature (T_g) is about 215 °C whereas for PEEK, $T_g \approx 143$ °C. Since T_g increases with increasing PEI content in amorphous PEEK/PEI blends according to the Fox-Flory equation (1-3, 5), adding PEI to PEEK results in better heat stability than for pure PEEK. Moreover, PEEK/PEI blends should show better chemical resistance than pure PEI owing to the outstanding solvent and environmental stability of PEEK. An equally important question is that of the mechanical properties. The room temperature (RT) mechanical properties have previously been described by Harris (5), and we have also reported on certain aspects of microdeformation in the blends over a range of temperatures (T), using thin film techniques (6). In what follows we discuss the temperature and rate dependence of the tensile behaviour and the fracture toughness of bulk PEEK/PEI samples.

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Experimental

The starting materials were commercially available Victrex PEEK 450G (ICI) and PEI Ultem 1000 (GE Plastics). Blend compositions in wt% PEEK/wt% PEI of 20/80, 40/60 and 60/40 were prepared as described previously (6). Dog bone-shaped tensile bars with dimensions width x thickness x gauge length = 10 x 3 x 60 mm^3 were moulded using an Arburg Allrounder 270C injection moulding machine. Differential scanning calorimetry (DSC) indicated all the blends to be amorphous after moulding, whereas the degree of crystallinity of the PEEK tensile bars was never less than about 25 wt%, regardless of the moulding conditions. Tensile tests were carried out between RT and T_g - 20 K at a crosshead speed of 30 mm min^{-1} (corresponding to a global strain rate ($\dot{\varepsilon}$) of approximately 5×10^{-3} s^{-1}) with a Schenk universal tensile test machine. To investigate the effect of $\dot{\varepsilon}$ at RT we used a servo-hydraulic Schenk high speed tensile test machine. For crosshead speeds greater than 10 mms^{-1} a damping system (7) was employed to minimize perturbations due to the dynamic effects generally associated with high speed testing.

For fracture toughness testing, three-point bend specimens with width (W) x thickness x length = 10 x 3 x 44 mm^3 were cut from the gauge length of the injection moulded tensile bars. A pre-crack was introduced by sliding a fresh razor blade over the tip of a machined notch. The crack length, *a*, was about 5 mm giving $a/W \approx 0.5$. Fracture tests were performed on a Zwick universal tensile test machine at a crosshead speed of 2.5 mms^{-1}. The maximum in the load-deflection curve was used to calculate the critical stress intensity factor, K_{IC}, for crack initiation. For pure PEI and PEEK, rate dependent tests using compact-tension (CT) specimens were carried out on the servo-hydraulic Schenk high speed tensile tester at crosshead speeds of between 1 and 4000 mms^{-1}, again using the damping system at high speeds. The PEI specimens were cut from 3 mm thick compression moulded sheets and the PEEK specimens were cut from 12 mm thick injection moulded plaques. The degree of crystallinity in these latter was again about 25 wt%. The pre-crack was introduced as for the three-point bend samples, with $a/W \approx 0.5$.

Results and Discussion

The yield stress (σ_y) is given in Figures 1(a) and 1(b) as a function of $\dot{\varepsilon}$ and T respectively (averages of 2 to 4 experimental values). In the blends, σ_y was generally found to decrease with increasing PEEK content, the highest values being observed for pure PEI. The semicrystalline PEEK samples showed σ_y comparable with PEEK/PEI (40/60). Although shear yielding was the dominant deformation mechanism in the range of T considered here, some crazing was observed in PEI and the blends at T > 80 °C, even if this had little apparent effect on the overall ductility (it was only when T exceeded T_g - 15 K that crazing became dominant in the bulk samples, leading to semi-brittle fracture (6)).

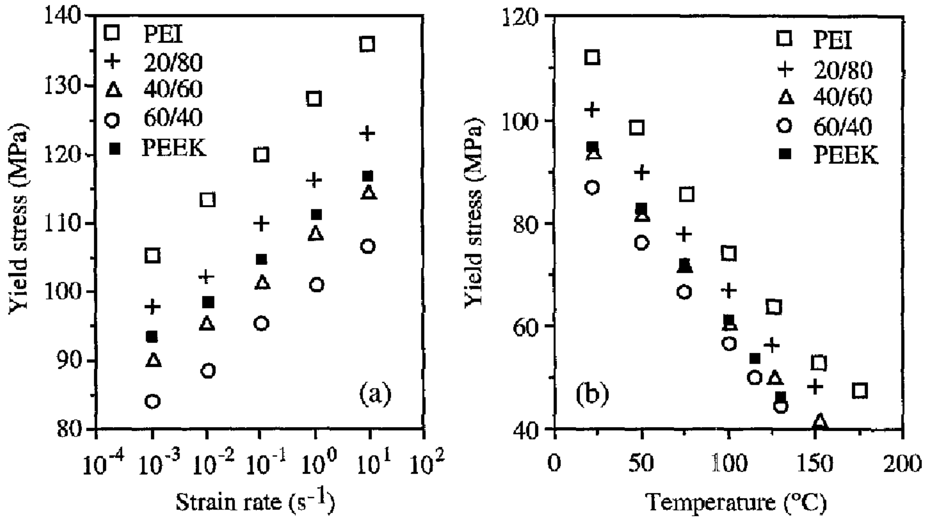

Figure 1: σ_y as a function of (a) strain rate and (b) temperature.

	strain rate dependent tensile tests		temperature dependent tensile tests	
	activation volume (nm^3)	correlation coefficient of linear regression	activation energy ($kJmol^{-1}$)	correlation coefficient of linear regression
PEI	1.22	0.999	176	0.996
20/80	1.43	0.997	196	0.998
40/60	1.50	0.999	193	0.999
60/40	1.60	0.998	196	1.000
PEEK	1.56	0.999	213	0.999

Table 1: Activation volume and activation enthalpy for the yield process.

In all the materials, σ_y increased linearly with $\ln(\dot{\varepsilon})$ (Figure 1(a)) and decreased linearly with increasing T (Figure 1(b)), consistent with the Eyring theory of thermally activated rate processes in its basic form (8-10). Assuming sufficiently high stresses, the corresponding Arrhenius equation for the yield stress, σ_y, is,

$$\frac{\sigma_y}{T} = \frac{\Delta G}{vT} + \frac{R}{v}\ln\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \quad (1),$$

where ΔG and v are the activation energy per mol and the activation volume respectively (assumed here to be independent of T), R is the molar gas constant and $\dot{\varepsilon}_0$ is a constant.

ΔG and v were determined by fitting the σ_y data to equation (1), as summarized in Table 1, along with the correlation coefficients of the linear fits. As shown in Figure 2, v increased with PEEK content. By assuming simple linear mixing rule v was predicted to be about 1.85 nm^3 in amorphous PEEK, which compares with a value of 1.56 nm^3 obtained for the semicrystalline PEEK samples. Little variation was found in ΔG, which was approximately 195 $kJmol^{-1}$ for the blends, although PEI and semicrystalline PEEK showed somewhat lower and higher ΔG respectively.

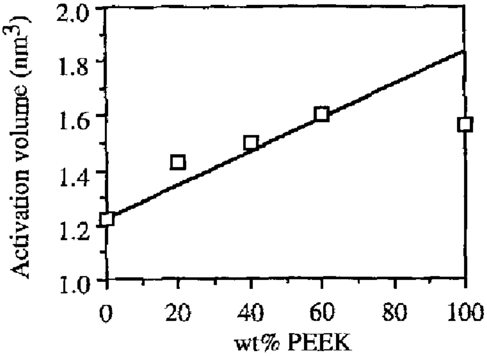

Figure 2: Activation volume as a function of composition.

The dependence of σ_y on blend composition is shown in Figure 3(a) for different $\dot{\varepsilon}$ and in Figure 3(b) for different T. As also shown in Figure 3, in all the amorphous materials, σ_y could be described using the following rule of mixtures for a given $\dot{\varepsilon}$ and T:

$$\frac{1}{\sigma_y} = \frac{w_{PEI}}{\sigma_{y,PEI}} + \frac{w_{PEEK}}{\sigma_{y,PEEK}} \qquad (2),$$

where w_{PEI} and w_{PEEK} are the weight fractions of PEI and PEEK and $\sigma_{y,PEI}$ and $\sigma_{y,PEEK}$ are the yield stresses of the amorphous starting materials. The following general expression for a property P of a mixture as a function of the properties P_1, P_2 of the starting materials and their molar fractions ϕ_1 and ϕ_2, has recently been proposed by Furukawa (11)

$$P^m = \Phi_1 P_1^m + \Phi_2 P_2^m \qquad (3).$$

Equation (2), which reflects a slight negative deviation from linearity as shown in Figures 3(a) and 3(b), may be obtained from equation (3) by setting m = -1 and P = σ_y. For the semicrystalline PEEK tensile bars somewhat higher yield stress values were obtained than those required to fit equation (2) to the blend data as may be seen by comparing the fitted curves and the data points corresponding to 100 wt% PEEK in Figure 3. No directly measured values of $\sigma_{y,PEEK}$ were obtained, because we were unable to obtain sufficiently large amorphous PEEK samples by either injection or compression moulding. Some data are available for amorphous PEEK films (thickness ≈ 100-200 μm), where σ_y is found to vary between 55 and 80 MPa depending on test conditions and extent of physical ageing (12-14), but in such cases the stress state may differ considerably from that in bulk samples, making interpretation difficult.

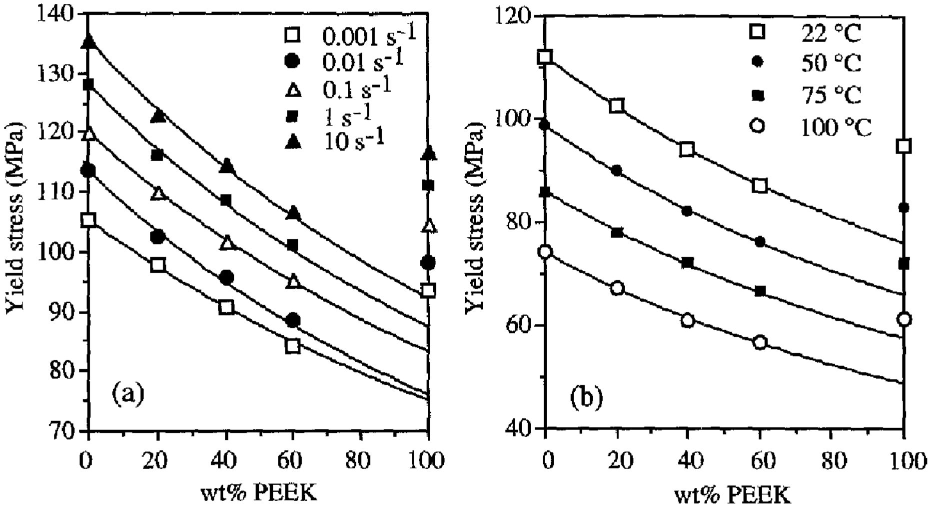

Figure 3: Yield stress as a function of composition for (a) different $\dot{\varepsilon}$ and (b) different T. The curves are the result of fitting equation (2) to the data by adjusting $\sigma_{y,PEEK}$.

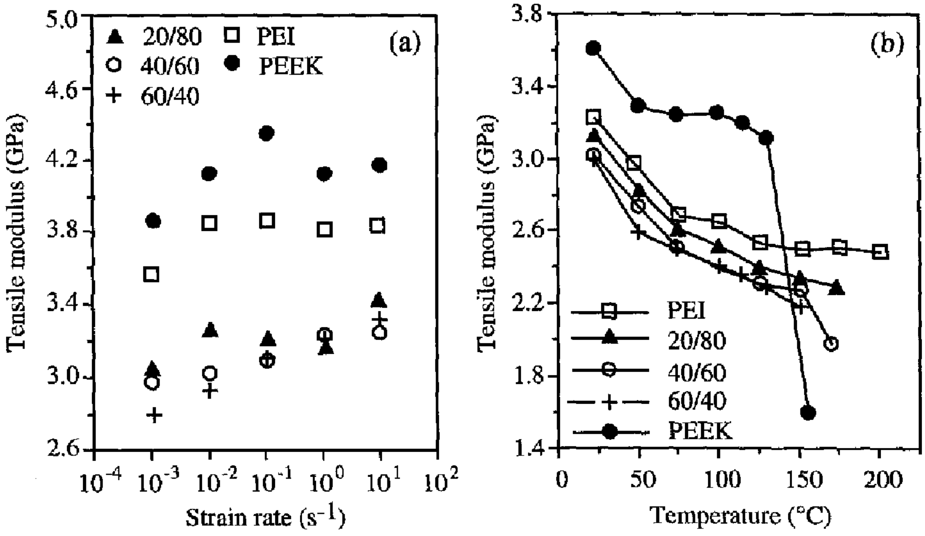

Figure 4: Tensile modulus as a function of (a) $\dot{\varepsilon}$ and (b) T.

Setting P = T_g and m = -1 in equation (3) gives the Fox-Flory equation for the dependence of T_g on composition, which is known to describe the evolution of T_g in PEEK/PEI blends (1-3, 5). Lu *et al.* (15) have argued the Fox-Flory equation to be valid for miscible blends with weak energetic interactions and hence with a small negative interaction parameter χ. In PEEK/PEI blends, Chen *et al.* (16) estimate χ to be -0.4 at 400 °C from equilibrium melting point depression for PEEK/PEI blends, which may be considered small in terms of the approach of Lu *et al.*, providing some basis for the use of equation (2) for yielding.

The variation of the tensile modulus (E) as a function of $\dot{\varepsilon}$ is shown in Figure 4(a). In each case, E increased slightly with $\dot{\varepsilon}$, although the rate dependence differed somewhat for the various materials. For example, in PEI, E did not vary with $\dot{\varepsilon}$ beyond 0.01 s^{-1}, whereas the blends PEEK/PEI (40/60) and (60/40) showed a progressive increase over the range of $\dot{\varepsilon}$ investigated here. E is shown as a function of T in Figure 4(b). Well below Tg, semicrystalline PEEK showed the highest E, but E dropped significantly for T > 145 °C. Although E was less than that of PEEK in PEI and the blends up to 140 °C, the stiffness levels were substantially maintained up to relatively high T as a consequence of the higher T_g. The slight decrease in E between 22 °C and 75 °C, depending on composition, is attributable to secondary relaxation processes and is also reflected by the dynamic storage modulus G' (17). It is clear from Figures 4(a) and 4(b) that equation (2) does not describe the composition dependence of E for different T and $\dot{\varepsilon}$.

Figure 5(a) shows the rate dependence of K_{IC} in PEEK and PEI. Instead of the crosshead velocity the loading condition was characterized in terms of the crack-tip loading rate dK/dt, calculated from the force-time gradient dP/dt prior to crack initiation according to (18)

$$K_{IC} = f\,\frac{P_c}{BW^{1/2}} \qquad \text{and} \qquad \frac{dK}{dt} = \frac{f}{BW^{1/2}}\,\frac{dP}{dt} \qquad (4),$$

where f is a geometric factor, B is the sample thickness and P_c is the load at crack initiation which corresponded to the maximum in the force-time curve. dK/dt reflects the strain rate which, unlike in conventional tensile tests, cannot be determined directly in CT tests. After initiation, unstable crack propagation was observed for all the samples.

At low loading rates PEEK showed an exceptionally high K_{IC} of about 6.8 $MPam^{1/2}$. With increasing test speed K_{IC} dropped progressively to 2.5 - 3 $MPam^{1/2}$. Unlike PEEK, PEI showed only a moderate decrease in K_{IC} with increasing dK/dt. At low loading rates K_{IC} was about 3.5 $MPam^{1/2}$ which is significantly lower than that of PEEK in the corresponding dK/dt range. Assuming additive behaviour of the fracture toughness properties of the homopolymers these results suggested that the blends should display intermediate toughness at low loading rates. To verify this, three-point bending tests were performed at a relatively low loading rate (crosshead speed = 2.5 mms^{-1}). The results are shown in Figure 5(b). To a first approximation, the K_{IC} of the amorphous blends increased linearly up to 60 wt% PEEK and by interpolating to 100 wt% PEEK, a K_{IC} value for amorphous PEEK of the order of 5 MPam$^{1/2}$ was obtained. The values for PEI ($K_{IC} \approx 3.5$ MPam$^{1/2}$) and for the semicrystalline PEEK samples ($K_{IC} \approx 6.3$ MPam$^{1/2}$) were in good agreement with those obtained from the CT tests in the corresponding dK/dt range which was about 15 MPam$^{1/2}$s^{-1} for the three-point bending tests (see Figure 5(a)). For all the three-point bending samples stable-unstable or stable crack propagation was observed, and in most cases the load-deflection curves displayed some non-linearity prior to the load maximum, resulting from energy consuming damage processes at the crack tip prior to crack initiation. Thus, K_{IC} calculated from the maximum in the load-time curve represented a critical stress state ahead of the crack tip which lead to marked material damage and to stable or stable-unstable crack propagation. However, in view of the good correlation between the K_{IC} values for PEI and PEEK from the rate dependent tests and the three-point bending tests we believe the K_{IC} values for the blends shown in Figure 5(b) to be reliable and suitable for comparison. The results suggest that the gradual increase in K_{IC} with increasing PEEK content found for low loading rates should progressively vanish at high loading rates. Therefore, the blends should display similar fracture toughness under impact conditions to the starting materials.

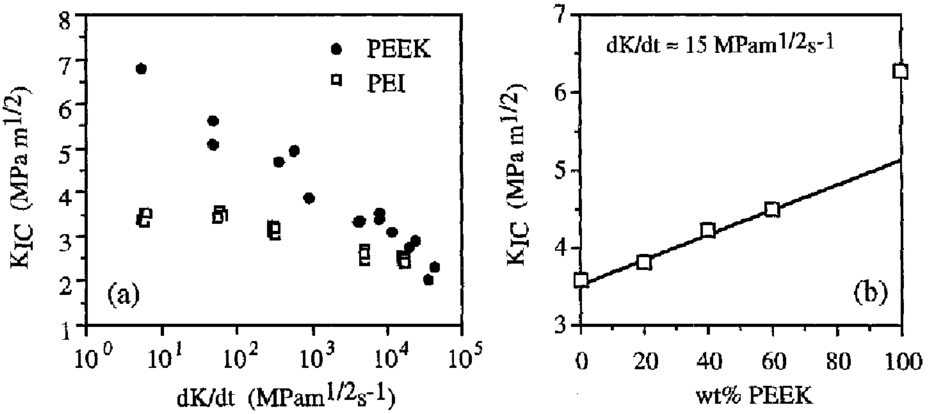

Figure 5: K_{IC} as a function of (a) the crack tip opening rate and (b) blend composition.

Conclusions

In this work we have investigated some important mechanical properties of bulk samples of amorphous PEEK/PEI blends. The main results are as follows:

- $\sigma_y(\dot{\varepsilon},T)$ could be described by an Eyring expression for the present range of experimental conditions. A rule of mixtures was proposed for the composition dependence of the yield stress of the amorphous blends, whose mathematical form is the same as that of the Fox-Flory equation for the dependence of T_g on blend composition. More theoretical work needs to be done to verify the validity of the proposed equation in terms of the energetic interactions between the two blend components.

- For T > 150 °C, PEI and the blends showed greater stiffness and strength than pure PEEK. This increase in performance, which is attributable to the shift of T_g to higher T with increasing PEI content, is worth bearing in mind when considering potential applications of PEEK/PEI blends.
- The fracture toughness of the blends increased with increasing PEEK content at low loading rates. The K_{IC} of PEEK was very rate sensitive whereas the K_{IC} of PEI showed only a moderate decrease with increasing test speed.

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