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Thin film and bulk deformation behaviour of poly(ether ether ketone)/poly(ether imide) blends

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The deformation behaviour of amorphous thin films of poly(ether ether ketone) (PEEK)/poly(ether imide) (PEI) blends was investigated over a wide temperature range by optical and transmission electron microscopy. All the materials showed localized shear deformation at temperatures well below T_g. In pure PEI and in blends with up to 60 wt% PEEK content, a transition from shear deformation to disentanglement crazing occurred as the temperature was raised. However, this transition was absent in PEEK, which deformed by shear over the whole temperature range, and similar behaviour was found for PEI/80 wt% PEEK. It is argued that at high PEEK content disentanglement crazing is suppressed by strain-induced crystallization and some evidence for crystalline order in deformed regions of initially amorphous PEEK thin films was obtained by electron diffraction. The thin film deformation behaviour of the blends was also shown to be consistent with their bulk deformation behaviour, a high temperature ductile–brittle transition being observed at low PEEK content in tensile tests.

1. Introduction

Poly(ether imide) (PEI) is an amorphous thermoplastic with high strength and stiffness, good ductility, and a glass transition temperature (T_g) of about 215 °C. The chemical resistance of PEI is inferior to that of poly(ether ether ketone) (PEEK), but it has the advantage of being relatively inexpensive [1]. By blending PEEK and PEI, one might therefore hope to obtain a high-performance chemically-resistant material at reduced cost. Indeed, PEEK/PEI blends have been the subject of several fundamental investigations dealing with basic mechanical properties, miscibility, morphology and the crystallization behaviour of the PEEK component in the blends [2–7]. It has been shown that PEEK and PEI are fully miscible in the amorphous state, the T_g dependence on composition obeying the Fox equation, which predicts a slight negative deviation from linearity [2–5]. Therefore, adding PEI to PEEK has the additional advantage of raising the T_g with respect to that of PEEK ($T_g \approx 143\,^{\circ}\mathrm{C}$), and hence of shifting the drop in mechanical performance associated with the glass transition to higher temperatures.

In this paper, we examine the temperature-dependent deformation behaviour of amorphous PEEK/PEI thin films by optical and transmission electron microscopy (TEM) using the technique of Lauterwasser and Kramer [8], which has proven to be a useful tool in the evaluation of the microdeformation behaviour of amorphous and semicrystalline polymers as well as polymer blends [8–10]. Recently, Plummer and Kausch [11] reported on the deformation behaviour of amorphous and semicrystalline PEEK thin films. In amorphous PEEK, they observed no change in mechanism in the temperature range from room temperature to T_g, deformation being characterized by the occurrence of homogeneous shear deformation zones (DZs) throughout. This is unusual in that amorphous polymers which show DZs at room temperature generally undergo a transition to crazing as the temperature is raised towards T_g, accounted for in terms of the increased chain mobility as will be discussed below. Since suppression of high temperature mobility by strain induced crystallinity was invoked to explain the behaviour of PEEK [11], it is of interest to investigate how the behaviour of PEEK thin films is altered by the presence of the non-crystallizable component, PEI. We also compare the thin film deformation behaviour of the blends with the bulk deformation behaviour in tensile tests in the same temperature range.

2. Experimental procedure

2.1. Blend preparation

The starting materials for this study were Victrex PEEK 450G obtained from ICI, and PEI Ultem 1000

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obtained from GE Plastics. The reported molecular weights of the materials are $M_w \approx 39\,\mathrm{kg\,mol^{-1}}$, $M_n \approx 14\,\mathrm{kg\,mol^{-1}}$ for PEEK and $M_w \approx 30\,\mathrm{kg\,mol^{-1}}$, $M_n \approx 12\,\mathrm{kg\,mol^{-1}}$ for PEI, respectively [5, 6]. The blends were prepared by melt extrusion on a corotating Leistritz twin-screw laboratory extruder. The melt temperature was about 380 °C for all the materials. Prior to blending, the materials were dried overnight at 120 °C in a circulating air oven. The extruded melt strand was quenched into cold water and subsequently chopped into pellets. Four blends with following composition in wt % were prepared: PEEK/PEI (20/80, 40/60, 60/40, 80/20).

2.2. Thin film preparation and testing

Following the procedure of Lauterwasser and Kramer [8], thin films of about 0.5 μm in thickness were prepared by drawing glass slides at a constant rate out of a polymer solution. The PEI was dissolved at 80 °C in *N*,*N*-dimethylacetamide. Pure PEEK and all the blends were dissolved at 60 °C in 2, 3, 4, 5, 6-pentafluorophenol. After drying, the films were floated off the glass slides on a water bath and picked up on annealed copper grids. Bonding of the films to the grids involved a short exposure to the solvent vapour, which also served to remove any wrinkles remaining in the films. After bonding, the films were dried overnight at 120 °C in a vacuum oven, and then strained in tension in a Polymer Laboratories Minimat™ miniature tensile tester equipped with an environmental chamber. The applied strain rate was about $6.5 \times 10^{-4}\,\mathrm{s^{-1}}$ and the test temperature was varied between room temperature (22 °C) and T_g in each case. The deformed films were observed by optical microscopy and finally, individual grid squares from selected samples were removed for examination by TEM (Philips EM 300, at an acceleration voltage of 100 keV).

2.3. Bulk tensile tests

Dumb-bell-shaped tensile bars with dimensions width × thickness × gauge length = $10 \times 3 \times 60\,\mathrm{mm^3}$ were injection moulded using an Arburg Allrounder 270 C injection-moulding machine. The mould temperature was 180 °C for PEEK and 140 °C for PEI and the blends. Prior to moulding, all the materials were dried at 120 °C for 12 h in a circulating air oven. The mixture PEEK/PEI (80/20) could not be moulded owing to feed problems, which precluded automatic injection moulding, and consequently no samples of this composition were available. The tensile bars of the three other blends were amorphous after moulding, as confirmed by differential scanning calorimetry (DSC) measurements. The PEEK tensile bars had a semicrystalline structure with a degree of crystallinity of about 25% (determined by DSC). Owing to its high crystallization rate it was impossible to prepare amorphous bulk samples of PEEK by injection moulding, ruling out direct comparison of the deformation behaviour of amorphous thin films and amorphous bulk samples. Tensile tests were carried out on a Schenk universal tensile testing machine equipped with an environmental chamber, at a crosshead speed of 30 mm min^{-1} (corresponding to a strain rate of $5 \times 10^{-3}\,\mathrm{s^{-1}}$) between room temperature and the respective T_gs. After deformation, the tensile bars were examined by optical microscopy.

3. Results and discussion

3.1. Thin film deformation behaviour

At room temperature all the materials were observed to deform by simple shear, in the form of DZs [10, 12, 13]. These were visible as regions of more or less localized ductile necking down of film thickness [11], analogous to the formation and propagation of a neck during tensile yielding in bulk samples. Like crazes, DZs run perpendicular to the tensile axis, but unlike crazes, which show a characteristic fibrillar structure, DZs consist of uniformly drawn material. Fig. 1 shows DZs observed in a film of the mixture PEEK/PEI (20/80), tested at room temperature.

As the temperature was raised, PEI and the blends containing up to 80 wt % PEEK content underwent a change in the deformation behaviour. In the temperature range between 70 and 100 °C, the DZs became smaller and more diffuse, and short crazes began to occur. In some cases the craze tips were blunted by diffuse shear bands. These ran either directly ahead of the craze tip or at an angle to the craze trajectory. Similar shear blunting has been observed in polystyrene–poly(phenylene oxide) (PS/PPO) blends and polystyrene–acrylonitrile (PSAN) [12]. Furthermore, DZs were present that showed craze-like features in the interior. Fig. 2 shows such a hybrid DZ in a film of PEEK/PEI (80/20), deformed at 140 °C. The interface with the undrawn material was relatively diffuse, and the lighter, more highly drawn regions in the interior were believed to result from localized fibrillation [13]. Such structures occurred in PEI and in all of the blends, but were most widespread in PEEK/PEI (80/20). Indeed, no natural crazes were observed in

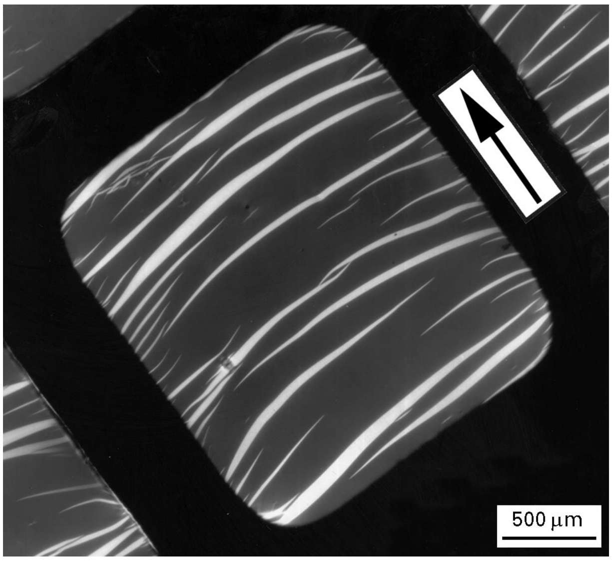

Figure 1 Optical micrograph of DZs in a film of PEEK/PEI (20/80), tested at room temperature (tensile axis as indicated).

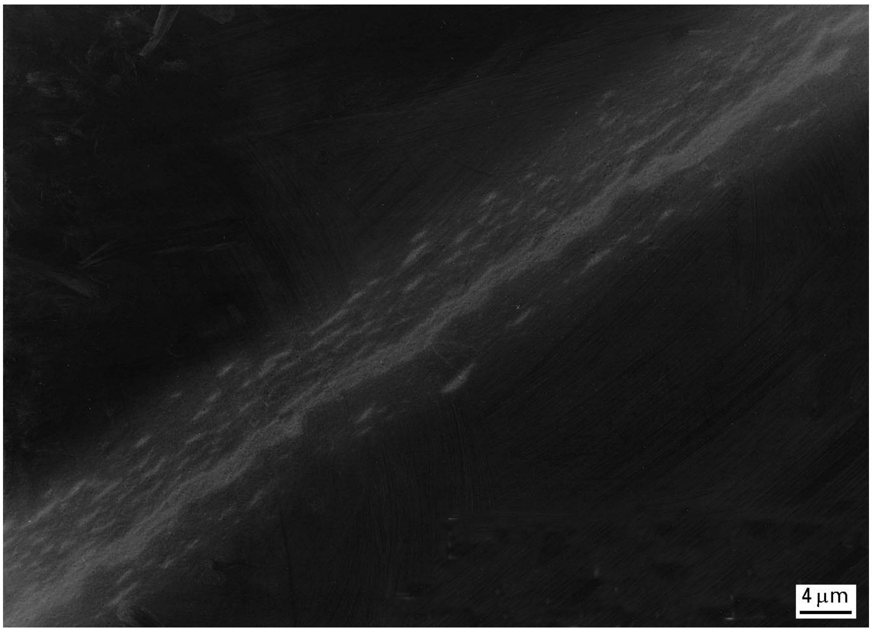

Figure 2 TEM micrograph of a hybrid DZ in a film of PEEK/PEI (80/20), deformed at 140 °C.

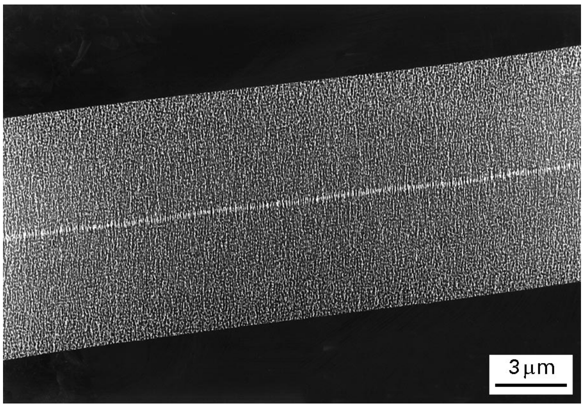

Figure 3 TEM micrograph of a craze in a film of PEEK/PEI (20/80), tested at 180 °C.

PEEK/PEI (80/20), under the present experimental conditions. In PEI and the blends with up to 60 wt % PEEK content, on the other hand, DZs were completely replaced by crazing close to T_g, the fibrillated craze structure being clearly visible in the TEM (Fig. 3). Finally, in amorphous PEEK thin films no change in the deformation behaviour was observed with increasing temperature. DZs were present in the whole temperature range up to T_g, in accordance with the previous study on PEEK thin films, referred to in the introduction [11]. Fig. 4 summarizes these results in the form of a deformation map in which the observed deformation mechanisms are shown as a function of temperature and blend composition.

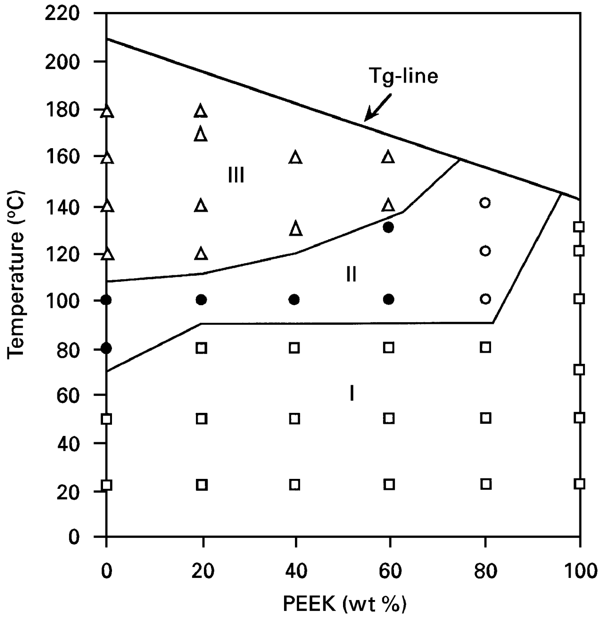

Figure 4 Deformation map for PEEK/PEI thin films: regimes I, II and III correspond to DZs, mixed deformation and crazing, respectively. (□) DZs; (△) crazes; (●) DZs + crazes + hybrid DZs; (○) DZs + hybrid DZs

3.1.1. The role of entanglements

It is now well established that the competition between DZs and crazes in thin films is strongly influenced by the entanglement network structure of the polymer in question [9, 10, 12–14]. Amorphous polymers in the glassy state are frequently modelled as a network of entangled polymer coils with physical entanglement points, whose characteristic features are the density of entanglement points in space, ν_e, the mean molecular weight between two adjacent network points, M_e, the distance between two adjacent network points, d_e, and the mean contour length, l_e, of the polymer strand linking two network points. M_e and ν_e can be derived from rheological data by using the theory of rubber elasticity [10], assuming the entanglement points to correspond to chemical crosslinks in a rubber. The theoretical maximum extension ratio $\lambda_{\max}$ of a stretched polymer strand between two network points is given by

$$\lambda_{\max} = \frac{l_e}{d_e} \sim \left(\frac{M_e}{C_\infty M_0}\right)^{1/2} \tag{1}$$

where M_0 is the mean molecular weight per bond, C_∞ is the characteristic ratio and assuming a Gaussian conformation for the entangled strands. Strong correlation has been found between measured λ in DZs and crazes in thin films and estimated $\lambda_{\max}$, with $\lambda_{DZ} \sim 0.6\lambda_{\max}$ [9, 10, 12–14].

During crazing a certain number of entanglements must be lost in order to allow the craze voids to propagate [9, 10]. This "geometrically necessary" entanglement loss can occur either by chain scission (scission crazing) or disentanglement (disentanglement crazing). For temperatures well below T_g it is assumed that entanglement loss is only possible by chain scission, because the chain mobility is too low to permit disentanglement. Kramer [10] showed the craze propagation stress σ_{craze} to depend on ν_e under these conditions, according to

$$\sigma_{\text{craze}} \propto \left(\Gamma_0 + \frac{\nu_e d_e U}{4}\right)^{1/2} \tag{2}$$

where Γ_0 is the van der Waals surface energy of the polymer and U is the bond energy. In thin films of high ν_e polymers such as polycarbonate (PC, $\nu_e = 29 \times 10^{25}\ \text{m}^{-3}$), σ_{craze} is usually higher than the shear stress at room temperature and therefore shear DZs are the dominant deformation mechanism. In low ν_e polymers, such as polystyrene (PS, $\nu_e = 4 \times 10^{25}\ \text{m}^{-3}$), on the other hand, entanglements contribute relatively little to σ_{craze}, and hence scission crazing dominates at room temperature [10]. However, even high ν_e amorphous polymer thin films are observed to show a transition from DZs to crazing with increasing temperature, as the chain mobility becomes sufficient for disentanglement to contribute to entanglement loss during craze void formation [9, 10, 15–17]. This transition is favoured by low molecular weights and low strain rates, consistent with the notion of disentanglement as a frictional process involving entire chains [9, 15–17].

For PEI a value of $\nu_e = 26 \times 10^{25}\ \text{m}^{-3}$ is given by Wu [18], which is comparable with that of PC, providing an immediate rationalization for the observation of DZs in PEI thin films at room temperature. Similarly, λ_{DZ} of PEI as calculated by optical densitometry of the electron image plates, following the method of Lauterwasser and Kramer [8], was approximately 1.6, which is reasonable given Equation 1, and the structural similarities between PEI and PC, for which λ_{DZ} is also reported to be 1.6 [16]. The entanglement density of PEEK is unknown, but we found $\lambda_{DZ} \sim 1.5$ in the amorphous PEEK thin films deformed at room temperature, and little evolution with PEEK content in the blends, from which we conclude that ν_e in PEEK is of the same order as that in PEI. Thus DZs dominated at room temperature in all the blend compositions investigated.

Although there is at present no way of predicting the transition temperature for the onset of disentanglement crazing, the molecular weights of all the polymers considered here were relatively low, falling well within the range of molecular weights for which this transition has been observed in thin films of other amorphous high ν_e polymers, occurring typically over a range of temperatures starting at about $T_g - 100$ K, depending on the polymer and test conditions [16]. The behaviour of pure PEI was therefore as anticipated on this basis, with the onset of disentanglement being observed at $T_g = 130$ K (see Fig. 4). For the blends, however, the onset temperature for disentanglement crazing is shifted to higher temperatures with increasing PEEK content, although the T_g decreases (see Fig. 4). This suggests that the disentanglement process was progressively hindered and even prevented as the PEEK content was raised.

Although strain induced crystallization at temperatures close to T_g has been advanced as an explanation for the lack of disentanglement crazing in PEEK itself [11], there is currently no direct evidence for strain-induced crystallization in DZs in PEEK thin films (strain-induced crystallization has been observed just below T_g in crazes in isotactic polystyrene (iPS) thin films [19, 20] where it was also associated with suppression of disentanglement effects). However, by using somewhat thinner films ($< 0.2\ \mu\text{m}$) we were able to obtain selected area electron diffraction (SAED) patterns from the interior of PEEK DZs formed at temperatures close to T_g, such as shown in Fig. 5a, which are a direct indication of the presence of a disordered form of the orthorhombic phase, which would presumably represent a thermodynamic barrier to chain disentanglement during plastic deformation. As the PEEK content was reduced in blends and/or as the test temperature was reduced, the diffraction patterns became fully diffuse and the hkl reflections schematically indicated in Fig. 5b vanished. It is well known that crystallization can occur in PEI/PEEK blends, but that the crystallization rate at a given temperature and the final degree of crystallinity fall off rapidly with increasing PEI content [4]. Therefore, it would seem that the extent to which strain-induced crystallization is both present and effective in suppressing disentanglement below T_g is linked to the crystallization kinetics, under quiescent conditions. It is pertinent therefore that PC, which is generally considered to be a fully amorphous polymer, and which shows a transition to disentanglement crazing some 120 K below its T_g, does show some tendency to crystallize in the melt, but at very much slower rates than either of iPS and PEEK. Indeed, there is even evidence for disentanglement crazing in thin films of PC which have been crystallized by exposure to solvent vapour [21].

3.2. Bulk deformation behaviour

We now consider the phenomenology of bulk tensile deformation in those PEEK/PEI blends, for which amorphous tensile bars were available (the mechanical properties will be discussed in more quantitative

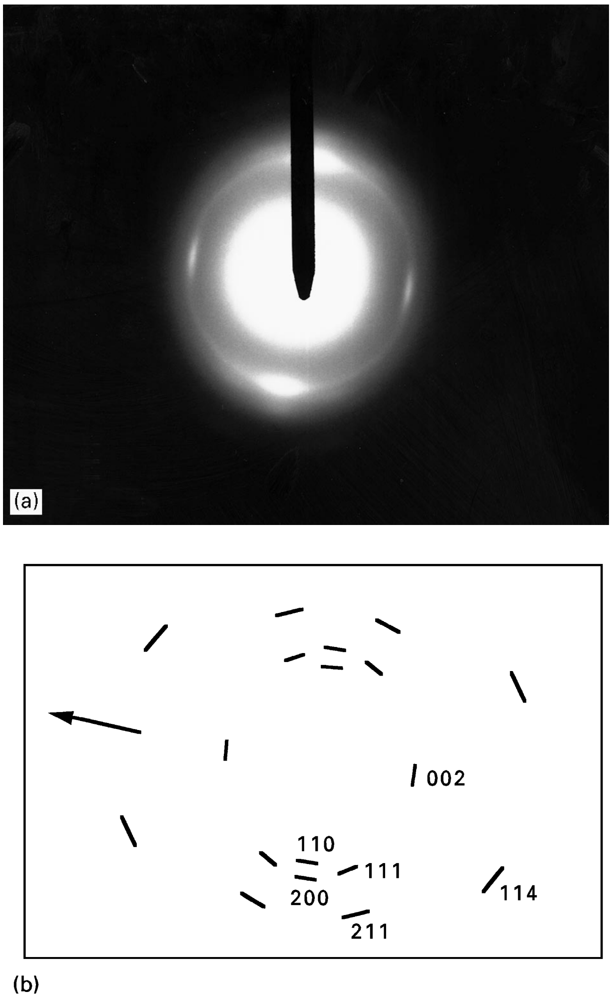

Figure 5 (a) SAED from a DZ in a PEEK film, deformed at 120 °C; (b) schematic representation of all the *h k l* reflections visible in the negative from which (a) was taken (tensile axis as indicated).

detail elsewhere [22]). In each case we observed a ductile–brittle transition just below T_g, leading to semi-brittle fracture. This transition was coincident with the onset of widespread crazing, as reflected by stress-whitening. Fig. 6 shows crazes close to the point of fracture of a tensile bar of PEEK/PEI (60/40), tested at 150 °C. Moreover, optical microscopy indicated crazes to be present at much lower temperatures, even if they were sufficiently stable for the global behaviour to be ductile (Fig. 7).

The optical observations are again summarized as a deformation map in Fig. 8. Between room temperature and about 60–80 °C the tensile bars showed ductile necking (regime I), and no crazes could be detected. Regime II in Fig. 8 is a mixed mode regime in which necking and crazing appeared simultaneously. Crazes were detected in the drawn, as well as in the undrawn, regions of the tensile bars, although they tended to be restricted to close to the sample surface. The transition temperatures from regime I to regime II in Fig. 8 correspond well with the transition temperatures from the shear deformation to the mixed mode regime of the thin films in Fig. 4, bearing in mind the different applied strain rate and of course the difference in the stress state between bulk samples and

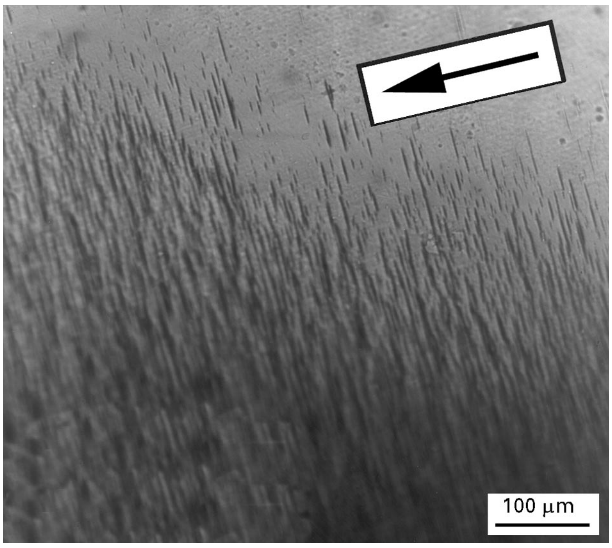

Figure 6 Optical micrograph of crazes close to the fracture point of a PEEK/PEI (60/40) tensile bar, tested at 150 °C (tensile axis as indicated).

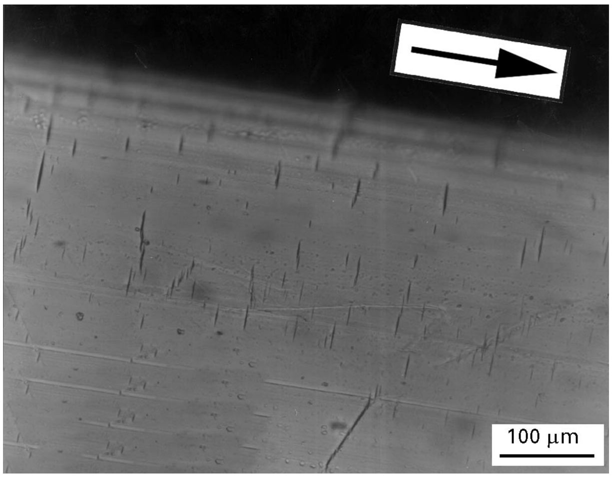

Figure 7 Optical micrograph of surface crazes in a PEI tensile bar, tested at 75 °C (tensile axis as indicated).

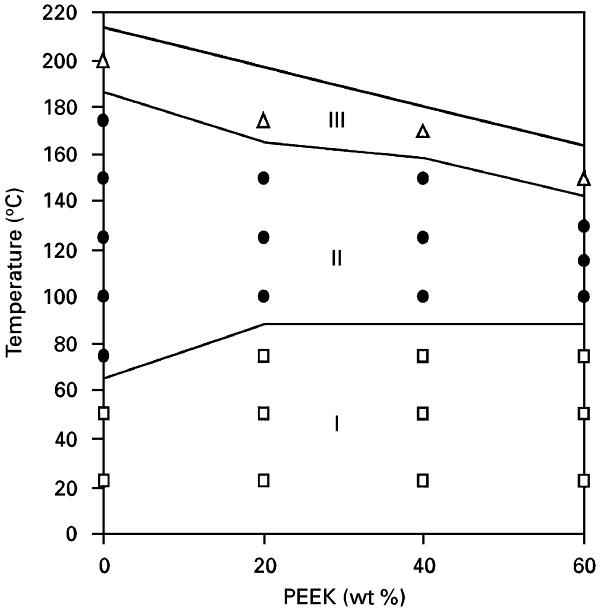

Figure 8 Deformation map for PEI and PEEK/PEI tensile bars. (□) necking; (●) necking and crazing; (△) fracture.

thin films. In regime III in Fig. 8, all the samples failed by fracture following widespread crazing and we assume a rough correspondence with regime III in Fig. 4, although there were some signs of limited ductile necking at the point of fracture in the bulk samples. On the other hand, there was no ductile–brittle transition in the semicrystalline PEEK tensile bars at high temperature, ductile necking being observed in the whole temperature range up to T_g. The absence of such a transition may also be attributable to strain-induced crystallization, as in amorphous PEEK thin films. Although the PEEK tensile bars showed extensive ductile necking, the occurrence of scission crazing at temperatures well below T_g cannot be excluded, especially under plane strain conditions and highly triaxial stress states where shear yielding is suppressed. Indeed, Narisawa [23] has reported crazing in notched three-point bend specimens of PEEK well below T_g.

4. Conclusions

The temperature-dependent deformation behaviour of amorphous PEEK/PEI thin films was investigated and compared with the bulk deformation behaviour. The main results of the study are:

1. Thin films of all the blends and the pure polymers deformed by simple shear at temperatures well below the respective T_g. Shear was also the prevailing deformation mechanism at low temperatures in bulk tensile bars of PEI and in the blends up to 60 wt % PEEK content.
2. In thin films of pure PEI and of the blends containing up to 60 wt % PEEK, a transition from shear to disentanglement crazing was observed as the temperature was raised towards T_g. Such transitions occurred also in bulk tensile bars of these materials leading to fracture of the samples close to T_g.
3. Despite structural similarities with the other materials, amorphous thin films of PEEK deformed by simple shear at all temperatures between room temperature and T_g. Similar behaviour was found in PEEK/PEI (80/20). It is argued that the absence of disentanglement crazing in these materials is the result of strain-induced crystallization of PEEK preventing the disentanglement of polymer chains. From SAED, evidence for crystalline order in deformed regions of initially amorphous PEEK thin films was obtained. Strain-induced crystallization may also be the reason for the absence of a ductile-brittle transition at high temperatures in semicrystalline bulk tensile bars of PEEK.

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