Deformation of thin films of poly(ether ether ketone)

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(Received 30 October 1991; revised 10 March 1992)

Adaptation of sample preparation methods used previously for amorphous glassy polymers has also allowed us to examine tensile deformation of thin films of poly(ether ether ketone) (PEEK), which is of particular interest given the commercial importance of this polymer. As the preliminary results presented here suggest, this appears to be a promising technique, particularly in view of the possibility of examining such films using transmission electron microscopy. In amorphous PEEK films, the dominant mode of deformation is simple shear at all temperatures below T_g. In semicrystalline PEEK, however, deformation at room temperature is characterized by both shear and crazing. Shear becomes gradually more dominant as the temperature is raised, and replaces crazing altogether above T_g.

(Keywords: poly(ether ether ketone); electron microscopy; deformation; films; crazing; fibrillar shear)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a semicrystalline thermoplastic polymer that has gained considerable currency in recent years as a matrix for advanced composite materials, and in consequence has stimulated a considerable amount of research activity[1]. The additional levels of microstructural complexity present in semicrystalline materials have nevertheless made them less attractive as subjects for fundamental research into deformation mechanisms than intrinsically amorphous polymers. Thus the 'copper grid' technique for transmission electron microscopy (TEM) observation of tensile deformation in thin films, whilst having proven to be a very powerful means of investigation, has, to date, been almost exclusively applied to amorphous polymers and polymer blends[2–8].

Here we report the application of this technique to both amorphous and semicrystalline PEEK films, and preliminary observations of deformation under a variety of conditions. The initial aim for this work was to establish whether the behaviour of PEEK in the amorphous glassy state (as induced by rapid quenching) fits the general pattern found for non-crystallizable amorphous polymers, in which *entanglement* appears to play a crucial role. Such studies of deformation in the amorphous phase of semicrystalline polymers may well be a useful way of bridging the gap between developments in the understanding of intrinsically amorphous and of semicrystalline systems.

Deformation in amorphous polymers

Entanglement refers to the topological constraint on relative chain motion in the glassy state, and is frequently visualized in terms of a notional network of *entanglement points*, of density ν_e, which are the analogue of chemical crosslinks in a rubber. On the basis of rheological data, topologically adjacent entanglement points may be assigned a spatial separation d_e, corresponding to a polymer strand contour length l_e. Under tension, such polymer strands will become extended in the direction of the applied stress, so that deformation is characterized by a fixed maximum extension ratio λ_{max} of the order:

$$\lambda_{max} = l_e/d_e \qquad (1)$$

The evidence for a correlation between λ_{max} and the observed draw ratios, both in craze fibrils and in macroscopic plastic necking in glassy amorphous polymers, is convincing[6].

It is also found that (i) crazing is favoured over simple shear deformation by low entanglement densities and (ii) the extension ratio of craze fibrils is significantly greater than that found for simple shear deformation[6,7]. The key to the understanding of these phenomena appears to be the presence of voids in the craze body. For a void to grow, and hence for a craze to propagate, new surfaces must be created within the material. Hence either a certain number of entangled strands must break, or entanglement must be lost in some other way. This entanglement loss is reflected by the relatively large fibril extension ratios; effectively ν_e, and hence d_e, within the craze body is diminished.

The propagation stress for a craze, σ_{craze}, has been argued to depend on the effective surface tension Γ at the advancing craze void tips, via a surface drawing model[5,6]. Where entanglement loss is mediated by scission, this gives:

$$\sigma_{craze} \sim A\Gamma^{1/2} \sim A(\Gamma_0 + \nu_e d_e U/4)^{1/2} \qquad (2)$$

where Γ_0 is the van der Waals surface energy of the polymer, A is a constant and U is the bond energy. Thus for large ν_e the crazing stress becomes much larger than the shear stress and simple shear deformation dominates. Equation (2) suggests a weak temperature and strain-rate dependence, consistent with the observation of a transition from crazing to shear as the temperature is increased or the strain rate decreased in low-ν_e polymers such as

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0032-3861/93/020305-07

polystyrene (PS; entanglement density $\sim 4 \times 10^{25}\,\mathrm{m}^{-3}$), which craze at room temperature[6].

What this approach fails to account for, however, is the transition from shear to crazing with increasing temperature[4] in thin films of high-ν_e polymers such as poly(ether sulphone) (PES) and polycarbonate (PC) (ν_e in PES is of the order of $30 \times 10^{25}\,\mathrm{m}^{-3}$). Here one must appeal to an alternative mechanism for entanglement loss, namely *disentanglement*. This also requires an alternative view of entanglement to the network model described above, that is, the *tube model*[9,10], in which entanglement is viewed as a non-local tube-like constraint on a given chain, representing its interactions with the surrounding chains.

During high-temperature disentanglement crazing in PES and PC, chains are 'pulled' out of their tubes as the voids advance, which has led to the adoption of the term *forced reptation* to describe this mechanism for disentanglement[11]. The frictional forces opposing forced reptation will increase strongly with the molecular weight M of the chains in question, consistent with the observed M dependence of high-temperature crazing in PES and PC[4].

In samples cut from commercially available amorphous PEEK sheet (Stabar™ K200 from ICI), we have observed extension ratios of approximately 2 during room-temperature tensile necking, which suggests a similar entanglement density to PES and PC. This is reasonable in view of the structural similarities of all three materials. For PES, a clear transition from shear to crazing has been observed in thin films for a range of M_w, occurring at approximately 100°C below T_g (218°C) for $M_w = 47\,000$ and a strain rate of $10^{-2}\,\mathrm{s}^{-1}$. The grade of PEEK used here, supplied by ICI Ltd, has a molecular weight average M_w of the order of 50 000. One might therefore reasonably expect to observe a transition from shear to crazing in amorphous PEEK as the temperature is raised towards its T_g of approximately 144°C.

Deformation in semicrystalline polymers

The phenomenology of both crazing and shear in semicrystalline polymers is widely documented, and qualitative explanations have been advanced both for crazing below T_g and for coarse fibrillation above T_g[12–18] (also referred to as crazing in the literature).

It is certainly reasonable that coarse fibrillation should occur during cold drawing (above T_g) of polymers following break-up of the crystalline lamellae, and similar effects may occur during the latter stages of plastic deformation below T_g[12,14]. However, below T_g, the size and spacing of fibrils in crazes in certain semicrystalline polymers are found to be similar to those observed in amorphous polymers[13,19,20]. This implies that the morphology of the former is not strongly influenced by the presence of the lamellae. Moreover, since the magnitude of the observed fibril spacings in amorphous polymers is accounted for by the surface drawing model on which equation (2) is based[5], one might expect the basic mechanism for crazing to apply in both cases. There is strong evidence from previous use of the copper grid technique to investigate deformation in amorphous and semicrystalline isotactic polystyrene (iPS) that entanglement network concepts remain highly relevant to crazing below T_g in this latter[20].

EXPERIMENTAL

The basic experimental method involves the solution casting of a uniform thin film of about 0.5 μm in thickness by drawing a glass slide from a suitable solution of the polymer in question at a constant rate. The film left behind on the glass slide after evaporation of the solvent is then floated off on a water bath and picked up on an annealed copper grid that has been previously coated with the same polymer. A short exposure to the solvent vapour then serves to bond the film to the copper grid, and to remove any wrinkles. The copper grid acts as a support to the film during deformation, and prevents craze closure during subsequent mounting of individual grid squares for TEM observation[2–8].

For PS, which formed the basis of much initial work[6], the procedure is straightforward, since many room-temperature solvents are available, and subsequent refinements of the technique have mainly involved filtering of the solutions to prevent contamination by dust particles[21], and in the case of materials such as PES, casting at slightly elevated temperatures owing to the absence of a suitable room-temperature solvent[4].

PEEK presents additional difficulties. First, the lowest-temperature solvent for PEEK available is 1-chloronaphthalene, which is nevertheless ineffective below its boiling point of 230°C (other solvents we are aware of either require impractically high dissolution temperatures, or, in the case of concentrated sulphuric acid, chemically alter the polymer). However, it was found to be possible to obtain uniform films by drawing a glass slide from the boiling solution. To ensure complete evaporation of the solvent, the films were held at just below 230°C for up to an hour under vacuum.

Secondly, exposure to the solvent vapour above its boiling point being impracticable, it was necessary to melt the films in order to bond them to the copper grids (at just over 350°C, the position of the main d.s.c. melting peak). For amorphous polymers the analogous method of heating to just above T_g presents little problem since the films remain relatively stable for short exposures at temperature, but in the case of PEEK above its melting point, this is no longer the case. Attempts to bond films of the order of 0.5 μm in thickness in this way resulted in immediate disintegration of the film, and it was necessary to increase the film thickness to over 1 μm to obtain satisfactory results.

In producing amorphous films the problem remains, regardless of the bonding technique, since it is necessary to remelt the films to destroy their crystallinity. The procedure used here was to heat to 400°C and then quickly to transfer the film plus copper grid to a cold aluminium block. The main difficulty was not so much in obtaining a sufficiently rapid cooling rate, but in the initial melting stage, since melting had to be sufficiently protracted to ensure a fully amorphous state, but sufficiently short to avoid structural or chemical degradation of the film.

Having prepared amorphous samples, crystallinity could then be induced in a relatively controlled fashion by suitable heat treatment above T_g. The fact that such heat treatments resulted in soluble films showing the fine pseudo-spherulitic structures typical of this grade of PEEK in the as-received state suggested minimal cross-linking and degradation of the films during preparation. *Figure 1* shows a micrograph of a film that had been

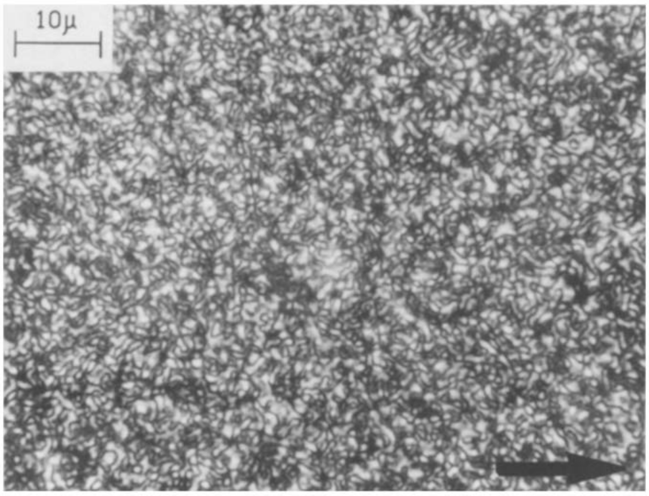

Figure 1 Optical micrograph under crossed polarizers of a PEEK film crystallized from the amorphous state at 300°C (analyser direction indicated by arrow)

crystallized from the amorphous state by holding it at 300°C for 5 min.

In order to obtain coarse spherulitic structures, a further preparation stage was entailed, based on the observation that heating the films to 400°C resulted in spherulites on a scale of several micrometres on isothermal crystallization just below the melting point. To achieve this without damaging the films, the samples were placed face down on single salt crystals (NaCl), that is with the film in full contact with the surface of the crystal. The salt ensured sufficient mechanical support to the molten film to prevent damage both during heating to 400°C and during subsequent isothermal crystallization. After cooling to room temperature, the salt, at this stage bonded to the film, was dissolved away by immersion in water. *Figure 2* shows a film that had been prepared in this way, as well as the microstructure at an intermediate stage of crystallization, during which the spherulites were most clearly visible.

The films, mounted on the copper grids, were finally physically aged overnight *in vacuo* at 110°C, that is, below T_g, following a procedure adopted for PES and PC[4]. In these latter, physical ageing increases the yield stress without affecting the crazing stress, whence crazing should be promoted. Observations of embrittlement of physically aged PEEK are suggestive of a similar effect[22].

Deformation was carried out using a Zwick 1484 tensile test machine furnished with an environmental chamber. Since direct observation was not possible during deformation, the copper grids were all strained to approximately 5%, which was generally sufficient to ensure the onset of irreversible deformation mechanisms such as crazing. Subsequent to deformation, individual grid squares were cut from the grids for TEM observation. The constraints imposed by the sample preparation technique meant that the resulting samples were somewhat thicker than is ideal for TEM, and problems with sample transparency were compounded in the presence of crystallites. Although deformation could be imaged, the samples were not suitable for electron diffraction.

RESULTS AND DISCUSSION

Deformation of the amorphous films

Deformation of the amorphous films was carried out between ambient temperature and T_g, and in the first series of tests, at a strain rate of approximately $2\times10^{-2}\,s^{-1}$. Viewed under crossed polarizers, crack-like regions of localized shear deformation, resulting in local necking down of the film thickness, are visible. Such features are known as *deformation zones* (DZs) and are characteristic of shear deformation in thin films, being the analogue of macroscopic ductile necking in bulk samples[4,23].

TEM shows these regions to contain no fibrillation, and no visible evidence of strain-induced crystallization (*Figure 3*). Nevertheless, one cannot *a priori* dismiss the possibility of crystallization having occurred to a limited degree, and an increase in crystallinity of up to 6% may occur on drawing bulk amorphous samples (from differential scanning calorimetry (d.s.c.)[24]).

As the temperature was raised, no apparent change in behaviour was found. DZs were observed at all temperatures below T_g at the usual strain rate of $2\times10^{-2}\,s^{-1}$ and indeed reducing the strain rate by three decades did not induce a transition to crazing, even at temperatures close to T_g. Although the DZs remain clearly visible under such conditions, they are somewhat more diffuse than for low temperatures/high strain rates, as expected given the general phenomenology of DZs in other materials and also the general tendency for shear necks in bulk samples to become more diffuse as the temperature is increased[4,23].

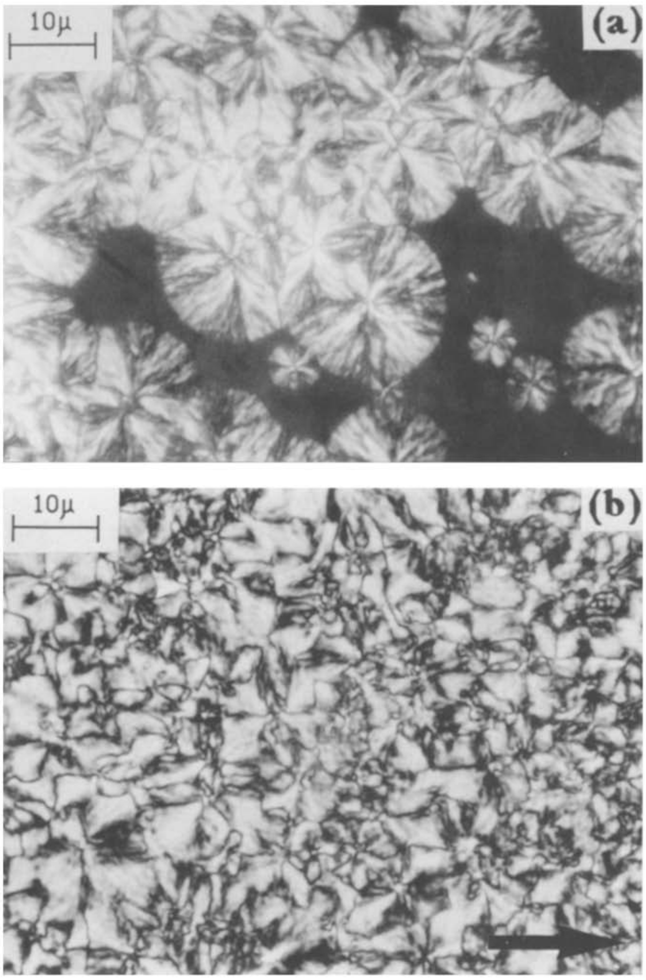

Figure 2 Optical micrograph under crossed polarizers of a spherulitic PEEK film: (a) during crystallization; (b) after completion of crystallization (analyser direction indicated by arrow)

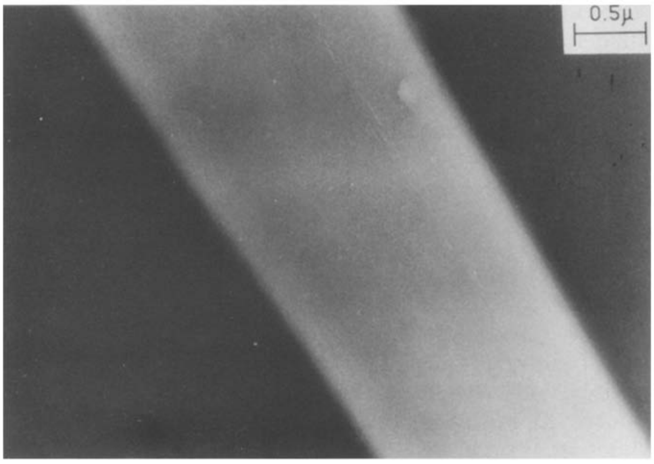

Figure 3 TEM of DZ in an amorphous film deformed at room temperature

Deformation of semicrystalline films

Deformation of the semicrystalline films with microstructures as shown in *Figure 1* was again carried out at $2 \times 10^{-2}\,s^{-1}$, and in this case the temperature range was increased to 200°C, that is, well above T_g. *Figure 4* shows optical micrographs of films deformed at room temperature. Most striking is the continued presence of DZs, as shown in *Figure 4a*. In contrast with the amorphous case, these DZs show a faint texture under crossed polarizers, from which it is clear that, in spite of the induced orientational birefringence, the initial crystallite structure of the undeformed material is not totally destroyed on deformation (indeed, overall increases in crystallinity for bulk samples of this grade may occur for typical initial levels of about 30%[24]). *Figure 4b* shows a different region of the film in *Figure 4a*, without crossed polarizers. Here a second type of deformation is visible (no longer being masked by the birefringence contrast), consisting of many fine crack-like defects running perpendicular to the tensile axis, similar in optical appearance to crazes in thin films of amorphous polymers.

Figures 5a and *5b* show TEM micrographs of a DZ, and the craze-like features in *Figure 4b* respectively. The structure within the DZ (*Figure 4a*) is highly inhomogeneous, with regions of high crystallinity interspersed with more highly drawn amorphous regions. Also visible is a faint banded texture perpendicular to the tensile axis, which resembles what is referred to in the literature as a 'string of pearl' structure, that is, the break-up of the crystalline lamellae into blocks, separated by more highly drawn material[12–18]. Although the texture of these DZs has a generally fibrillar appearance, it is difficult to distinguish true voids.

The deformation shown in *Figures 4b* and *5b*, and at higher magnification in *Figure 5c*, on the other hand, shows a far clearer void/fibril structure, with an apparent fibril spacing of the order of 40 nm. This is typical of crazes in amorphous polymers (although with somewhat irregular boundaries and less coherent fibrillar structures, corresponding to the inhomogeneity of the surrounding material).

There appears little change in the optical appearance of the DZs in the semicrystalline samples with increasing temperature, even beyond T_g, although the DZs become gradually more diffuse above 160°C. Changes are apparent in the crazing behaviour, however. The density of crazing decreases with temperature, and the individual crazes appear longer than those observed at room temperature. Eventually, within approximately 40°C of T_g crazing is replaced entirely by shear deformation in the majority of the grid squares (some residual crazing persists in isolated grid squares to within 20°C of T_g but there is little doubt as to the overall tendency). No crazing is seen above T_g.

Spherulitic films

DZs in the coarse spherulitic films (*Figure 6a*) show much less well defined boundaries than for either the amorphous or the non-spherulitic semicrystalline films, and a marked tendency towards branching. From the optical micrographs, initial deformation appears to take place predominantly along the spherulite diameters perpendicular to the tensile axis, as in the regions to the left of the main DZ in *Figure 6a*. As the TEM micrograph in *Figure 6b* shows, localized shear can also occur in interspherulitic regions (in this case, at the point of intersection of three adjacent spherulites). However, it is clear that, unlike in certain other semicrystalline thermoplastics, the interspherulitic boundaries do not represent regions of particular mechanical weakness in PEEK[25].

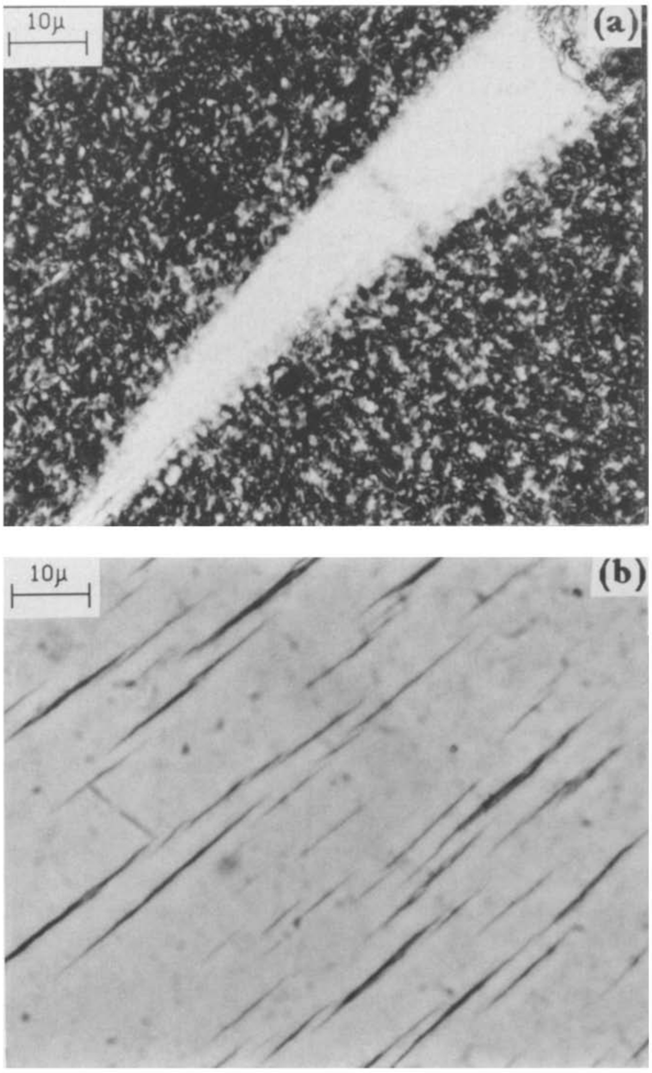

Figure 4 Optical micrographs of deformation in a crystalline film at room temperature: (a) DZ under crossed polarizers; (b) crazing in a region not containing a DZ, viewed without crossed polarizers

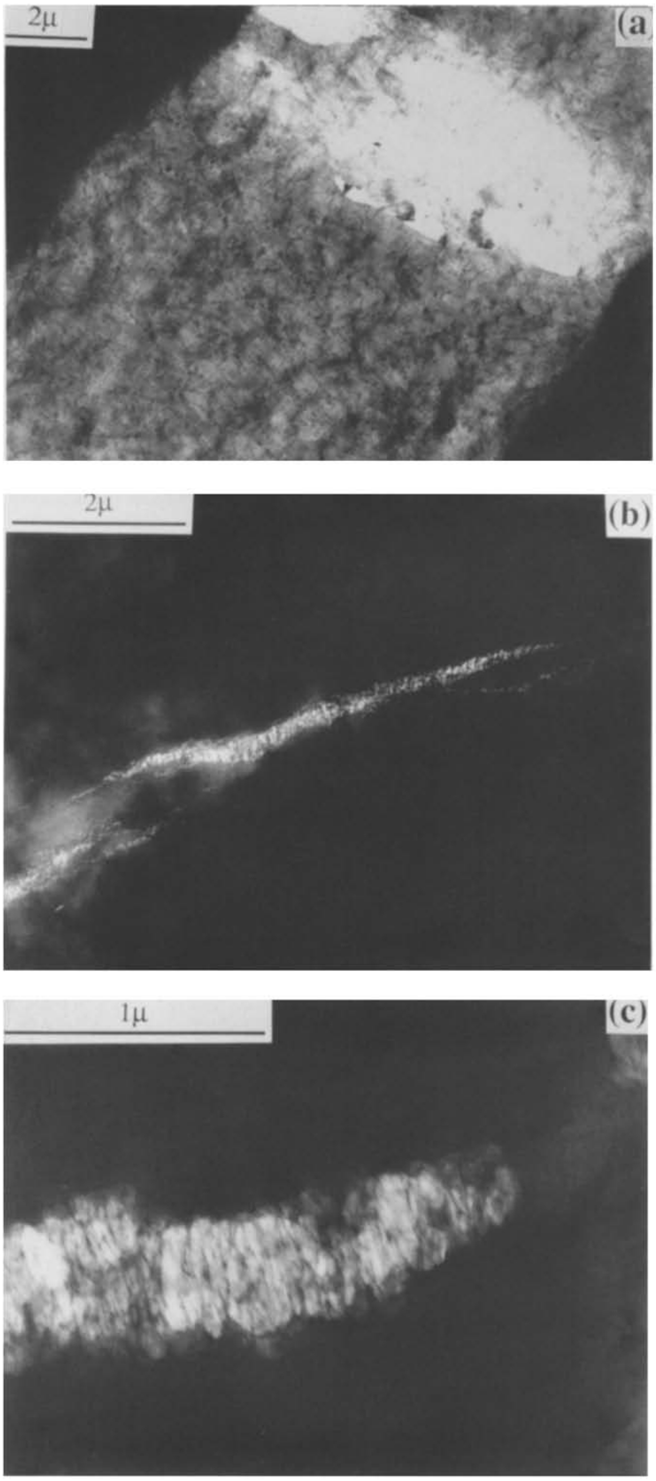

Figure 5 TEM micrographs of the same film as in *Figure 4*: (a) DZ; (b, c) crazing

It is clearly seen that traces of the spherulitic morphology persist within the DZ, and, indeed, it appears that the spherulite diameters perpendicular to the tensile axis remain relatively intact, with large deformation being localized to regions of the spherulites where the spherulite arms lie along, or at low angles to, the tensile axis. Further, the boundaries between regions of low and high deformation in adjacent spherulites appear well defined, running at an angle of between 30° and 40° to the tensile axis, as in *Figure 6c*.

The chain orientation in the crystalline regions is generally radial in PEEK spherulites. Although yielding of the amorphous material between the spherulite arms is easiest where it is in series with the crystalline material, that is, where the spherulite arms are perpendicular to the tensile axis, the crystallites themselves are presumably unfavourably oriented for further deformation in such regions. Thus, on initial work hardening, deformation will transfer to regions where the spherulite arms lie along the tensile axis, and hence the chain orientation in the crystalline material is perpendicular to the tensile direction. In such regions, as with the DZs in the non-spherulitic semicrystalline films, there is a banded structure perpendicular to the tensile axis corresponding to break-up of the crystalline lamellae (*Figure 6d*).

It proved difficult to image crazes and the structure of the surrounding undeformed spherulites simultaneously, the former tending to break down at beam intensities sufficient to show the latter in films of this thickness. Small crazes were, however, found below T_g, nucleating predominantly in intraspherulitic regions, and growing along the spherulite diameters perpendicular to the tensile axis (which present a continuous path of amorphous interlamellar material to a craze propagating in this direction). However, these crazes were much less widespread than in the non-spherulitic films, and restricted to individual spherulites, presumably because the discontinuous change in crystallite orientation between spherulites means that paths favourable to craze propagation are generally discontinuous at the spherulite boundaries. Similar phenomena have been described for crazing in polypropylene (PP) below T_g (ref. 12).

Comparison with crazing in amorphous polymers

The observation that thin films of amorphous PEEK show no evidence of disentanglement crazing for conditions under which it is expected for similar, but non-crystallizable polymers, may be linked to strain-induced crystallization. During craze propagation, a region of highly strain softened and deformed polymer exists ahead of the advancing void tips, in which, in the case of disentanglement crazing, chains are gradually being pulled out of their tubes. Indeed, it is likely that as the void tips advance, there will be a build-up of highly stretched mobile chains in this region, and thus locally a strong tendency for crystallization to occur. Such crystallization may then act to 'pin' the chains in their tubes, and hence render continued disentanglement progressively more difficult. (The analogous effect of chemical crosslinking has been observed in PES, where it has been found to suppress disentanglement crazing in the high-T regime[26].) Selected-area electron diffraction has been used to provide direct evidence for strain-induced crystallization during room-temperature scission crazing at low strain rates in amorphous iPS[27], and this at approximately 80°C below T_g in a material that crystallizes relatively slowly, even at 180°C, where the rate of crystallization reaches a maximum.

The absence of scission crazing in the amorphous films is likely to be a consequence of the high entanglement density in PEEK, as discussed in the introduction. Crazes are seen, however, in the amorphous phase in *bulk* samples of PEEK subject to room-temperature tensile deformation. The reason appears to be that in bulk samples there is a high degree of constraint on the lateral contractions resulting from homogeneous drawing, re-

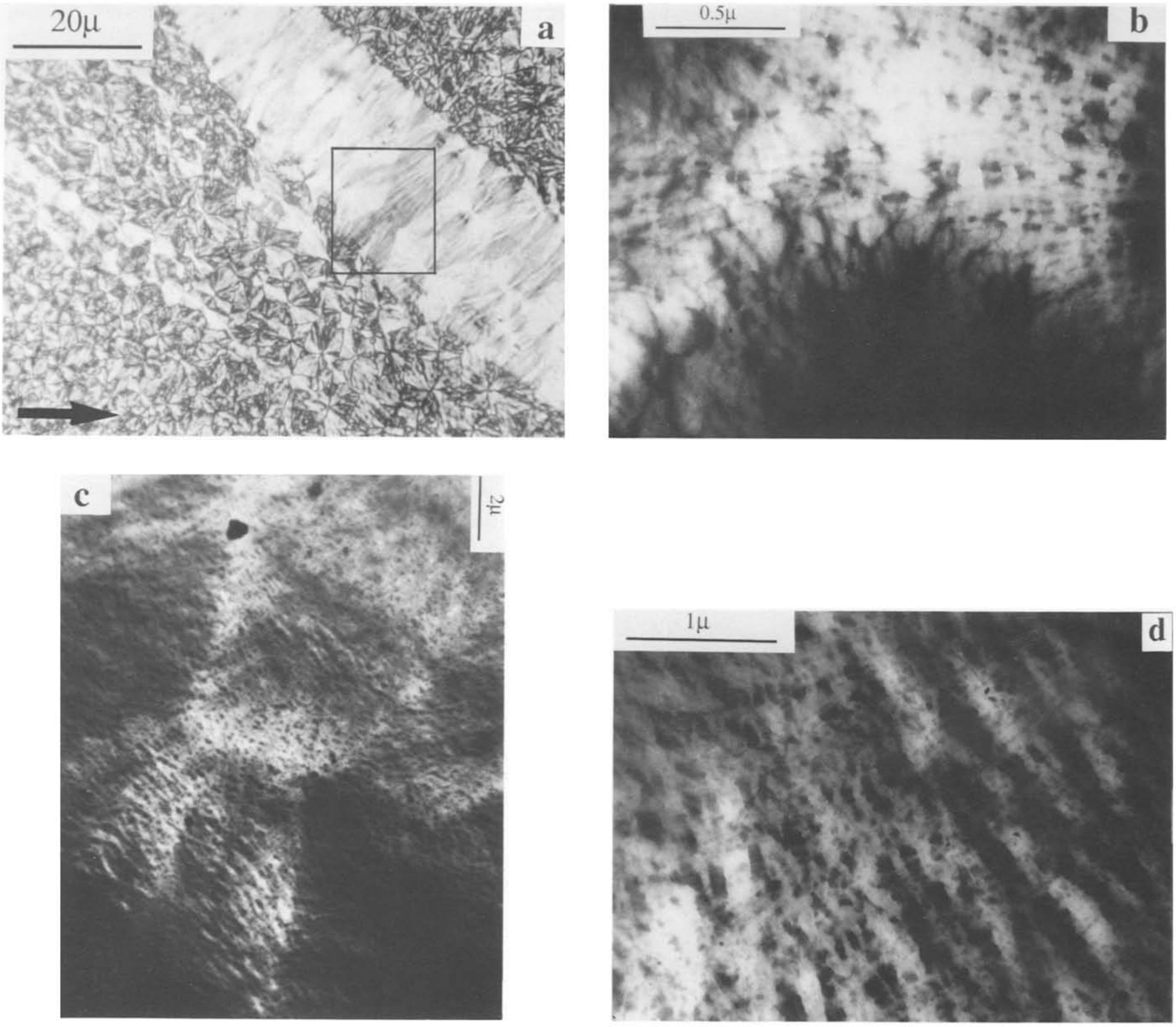

Figure 6 Deformation in a spherulitic film: (a) optical micrograph under crossed polarizers of a DZ (analyser direction indicated by arrow); (b) TEM of localized shear deformation between three spherulites; (c) TEM of the outlined region of the DZ in (a); (d) TEM at higher magnification of banded region of (c)

sulting in an increase in the hydrostatic tension at the expense of the shear stress driving the deformation. On the other hand, the presence of voids in the craze body means that crazing can result in local axial deformation without the need for lateral contraction. Thus a transition from shear to crazing can result from increased sample thickness. Earlier investigations of amorphous PEEK suggested this to occur at film thicknesses of the order of $10\,\mu m$[28].

Qualitative models for crazing in semicrystalline thermoplastics in the literature have been based on the idea of coalescence of micro-voiding, arising from stress concentrations subsequent to break-up of the crystalline lamellae[12]. This mechanism would seem most appropriate to what is referred to here as a DZ and which has been termed *fibrillar shear* by More and Donald[29,30] (although from the present TEM observations it is difficult to confirm whether true voiding is in fact present in such structures). Consistent with our observations of PEEK, More and Donald did not find fibrillar shear to be a precursor to crazing in (semicrystalline) nylon films, whilst admitting the possibility of the coexistence of the two types of deformation under certain conditions (as with DZs and crazes in amorphous polymers). Further, crazing was only present in salted nylon films, this being accounted for in terms of a stiffening of the molecules in these latter, resulting in an increase in the yield stress, favouring scission crazing at ambient temperature[29,30].

In the present case, we believe that the appearance of crazing in the semicrystalline films is linked to changes in the degree of constraint on shear deformation in the presence of crystallites, and that the crazing mechanism is again one of scission crazing, similar to that in amorphous polymers. Whilst strain-induced crystallization may affect disentanglement, it seems less likely to be an important factor in scission crazing, and certainly the phenomenology of the crazing seen in the crystalline films is consistent with the scission mechanism as outlined in the introduction. That is, the competition between crazing and shear is strongest at room temperature, with a tendency for shear to dominate closer to T_g. A gradual transition to shear with increasing temperature is also suggested by the results of Narisawa and Ishikawa[13] for fracture tests on semicrystalline PEEK below T_g. In other cases, where ν_e is low, scission crazing should occur in both the amorphous and the semicrystalline state below T_g, as is the case for amorphous and semicrystalline iPS[19,20].

CONCLUSIONS

A method for the examination of deformation in thin films of PEEK has shown that the shear to disentanglement crazing transition shown by amorphous polymers of similar entanglement density is absent from amorphous quenched films of PEEK, shear being observed at all temperatures. It is suggested that this might be due to strain-induced crystallization disfavouring craze propagation owing to its effective pinning of the chains in their tubes. In semicrystalline films of PEEK crazing is observed to coexist with shear deformation below T_g, but this is argued to be scission crazing, locally favoured over simple shear deformation by the altered constraints in the presence of crystallites.

It is as well to emphasize the clear distinction made here between the two types of deformation in the semicrystalline films of PEEK, since it has not always been clearly made in the literature, owing to the general fibrillar appearance of highly drawn structures in semicrystalline polymers. Nevertheless, it is important to recognize that the crazing mechanisms described in the introduction are unlikely to be directly relevant to fibrillar or quasi-fibrillar structures that result from the break-up of crystalline lamellae during shear, for which the term *fibrillar shear* has recently been suggested[29,30].

The technique itself offers promise for future work, as regards both PEEK and semicrystalline films in general.

ACKNOWLEDGEMENTS

We acknowledge many useful discussions with P.-Y. Jar, A. P. More and A. M. Donald. CJGP is supported by the Swiss Committee for the Encouragement of Scientific Research (CERS).

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