

# Effect of strain history on craze microstructure

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Crazes formed under a constant tensile strain in polystyrene (PS) have a dense network of fibrils with an extension ratio  $\lambda \approx 4$ , but a midrib of higher  $\lambda$  forms by drawing fibrils from the craze–matrix interface in the high stress region just behind the craze tip. Stepwise increases in tensile strain during craze growth should thus produce layers of fibrils of different  $\lambda$ , which can be revealed by transmission electron microscopy (TEM) of crazes in stepwise strained PS films. When the time interval between strain increments of 0.5–1% is one minute, TEM images show ‘ridges’ of lower  $\lambda$  fibrils, corresponding to the position of the craze–matrix interface at the time of the strain increments. The ridges appear to be the analogue of the bulge remaining on a macroscopic fibre which has been allowed to stress age by stress relaxation before resuming drawing and imply that rapid stress ageing must occur near the craze–matrix interface so that more material is drawn into the craze in preference to increasing the  $\lambda$  of the existing fibrils.

**Keywords** Structure; microstructure; strain history; craze; transmission electron microscopy; fibrils; tensile strain

## INTRODUCTION

Crazes are formed in glassy polymers under stress as precursors to crack propagation and failure. Unlike cracks, crazes are load-bearing entities because of a network of oriented fibrils which span the craze–matrix interfaces, as revealed by transmission electron microscopy (TEM)<sup>1–3</sup>. The volume fraction  $v_f$  of material within a craze in polystyrene (PS) has been shown to be  $\sim 0.25$  (ref. 2) corresponding to an extension ratio  $\lambda = 4$ . It has been suggested<sup>2,4</sup> that this extension ratio corresponds to a ‘natural draw ratio’ which can be linked to the strain hardening properties of the polymer. In particular, this strain hardening should set in as the polymer chain becomes fully stretched between molecular entanglements (which in this sense act analogously to chemical crosslinks) with the consequence that the maximum extension ratio should depend on the chain contour length between entanglements. This hypothesis has been substantiated by experimental measurements of the extension ratio within crazes for a wide range of glassy polymers<sup>4</sup>.

Transmission electron microscopy of crazes has also revealed that a region of higher  $\lambda$ , the ‘midrib’, exists at the centre of the craze. This feature is thought to be due to surface drawing (the mechanism for craze thickening) under the stress concentration which has been shown to exist at the craze tip<sup>2,5</sup>. This observation suggests that although a characteristic value of the extension ratio may be assigned to each polymer, associated with the chain contour length between entanglements, higher draw ratios may occur when this entanglement network breaks down under a sufficiently high stress permitting chain slippage or scission.

In contrast to this void–fibril network of a craze, an unvoided but drawn region has been shown to form at

crack tips in thin films of polycarbonate. This region is diffuse in unannealed films but becomes highly localized following annealing just below  $T_g$ , the glass transition temperature<sup>6</sup>. Despite the absence of fibrillation, this localized plane stress deformation zone (DZ) has many properties in common with a craze. Furthermore, because its dimensions are typically much larger than a craze ( $\sim 5$ – $10 \mu\text{m}$  wide at the crack tip) optical studies are sufficient to observe its growth. These optical studies of DZ growth are useful since radiation damage in the TEM prevents such growth studies being carried out for crazes. From such growth experiments it has been possible to show that the surface displacement rate  $\dot{w}(x)$  decreases markedly as the local stress decreases. The thickness ratio (defined as the ratio of the original thickness of the film to the final thickness within the zone) which is analogous to the volume fraction  $v_f$  of a craze, is essentially constant at  $\sim 0.7$  throughout the zone, rising towards 1 within a few microns of the zone tip. Immediately at the crack tip the thickness ratio is somewhat lower with a value of  $\sim 0.5$  which rises to the average value of 0.7 within a few microns of the crack tip.

From such results one suspects that, as with crazes, the extension ratio will be a function of the local stress. If this conclusion is correct, stepwise increments in strain should lead to layers within the craze or DZ with different values of  $\lambda$ , corresponding to growth under the various levels of the applied stress. In this paper the results of such sequential straining experiments will be presented for thin films of polystyrene and annealed polycarbonate.

## EXPERIMENTAL

Thin films of PS were produced by drawing glass microscope slides from a solution of PS dissolved in

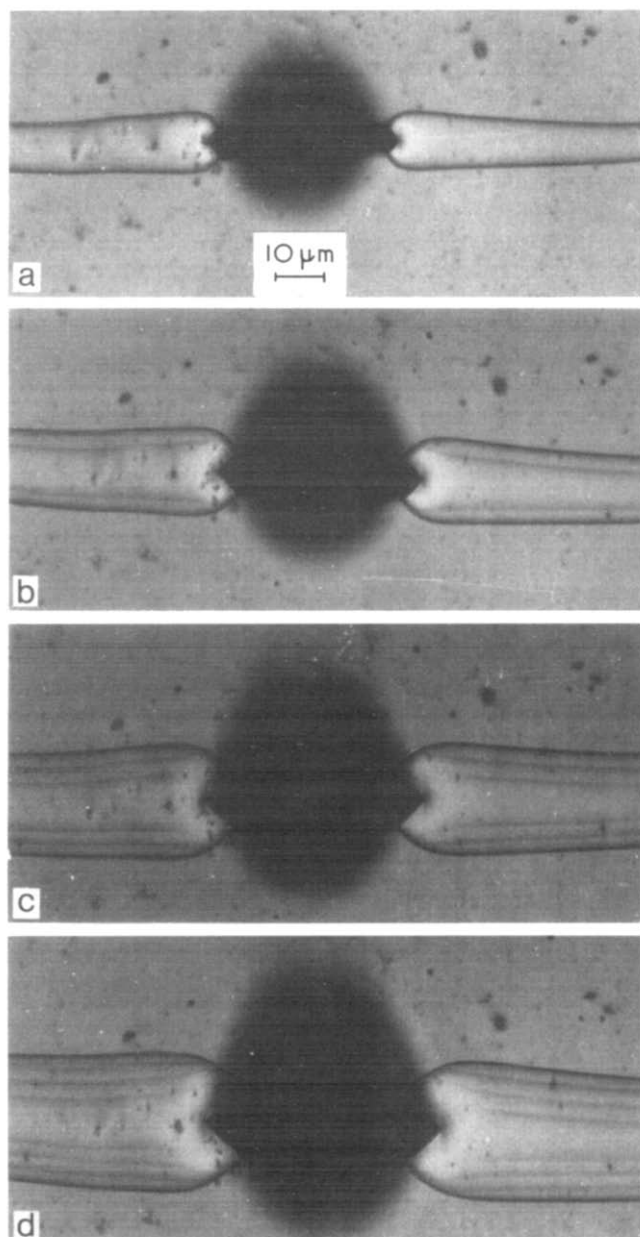


Figure 1 (a) A deformation zone (DZ) at a crack tip in annealed polycarbonate.  $\epsilon = 3.5\%$ . (b–d) Appearance of the DZ as  $\epsilon$  is increased stepwise by 1% at one minute intervals

toluene. The PS, which was kindly supplied by Dr Robert Bubeck of the Dow Chemical Company, had  $\bar{M}_w = 264\,000$ ,  $\bar{M}_n = 110\,000$ , and contained no mineral oil. For the PC films, GE Lexan™ grade 130 ( $\bar{M}_w = 39\,000$ ,  $\bar{M}_n = 15\,700$ ) resin, supplied by Dr Roger Kambour of GE, was dissolved in methylene chloride and glass slides were drawn from this solution. The subsequent steps in specimen preparation were identical for the two polymers. The films (with thicknesses in the range 0.5–1  $\mu\text{m}$ ) were floated off onto the surface of a water bath and picked up on annealed copper grids, the grid bars of which had been precoated with a thin film of the appropriate polymer (PS and PC respectively). The films were bonded to the grids by a short exposure to the solvent vapour (toluene and methylene chloride respectively) and then placed in vacuum overnight to remove excess solvent. This method of preparation has been described in detail by Lauterwasser and Kramer<sup>2</sup>.

A crack was then introduced into the film by utilizing

the intense electron beam of a JEOL 733 superprobe, as described by Donald and Kramer<sup>6</sup>. This method produces a thin slot of 'burnt' material in the centre of each grid square within which a high degree of chain scission has occurred. The remaining parts of the film are not irradiated. Suitable operating conditions were (a) a specimen current of 130 nA at 30 keV and a magnification of 1200 for PS, and (b) 30 nA specimen current at 25 keV and a magnification of 2000 for PC. For these studies it is necessary to introduce a crack to act as a stress concentrator for craze initiation, so that the position of the first craze to form can be controlled, permitting the time and strain at which craze growth is initiated to be well characterized by observation of the crack tip in an optical microscope. Furthermore, this first craze to form can subsequently be distinguished, in the TEM, from the other crazes that form as higher levels of strain are applied. Following the introduction of this crack, the PC films were annealed for 1 h at 132°C.

The whole copper grid and film was then strained whilst observed with an optical microscope. As soon as the craze/DZ initiated at the crack tip the strain and time were recorded. Successive increments of strain were applied at one minute intervals as described in the following section. Following the completion of the strain increments, those squares that had been observed optically were cut out (the copper grid bars maintaining the applied strain) and examined in the TEM (a Siemens 102 microscope operating at 125 kV).

## RESULTS AND DISCUSSION

Although it is possible to verify, via optical microscopy, that the successive increments of strain are producing craze growth (both in length and width) in PS, the details of the resulting fine structure will clearly be beyond the limits of resolution of light microscopy. This is not the case for deformation zones in PC. Thus the experimental results from optical microscopy on PC DZ growth will be presented first, and then the TEM results for both PC and PS will be discussed and compared.

Figure 1a shows the appearance of a DZ at a crack tip in annealed PC, formed under the application of 3.5% strain. The characteristic 'flame' shape of the zone, with its well defined edges, is clearly seen. As successive 1% increments in strain are applied at 1 min intervals (Figures 1b–d) various features can be observed in the micrographs. The

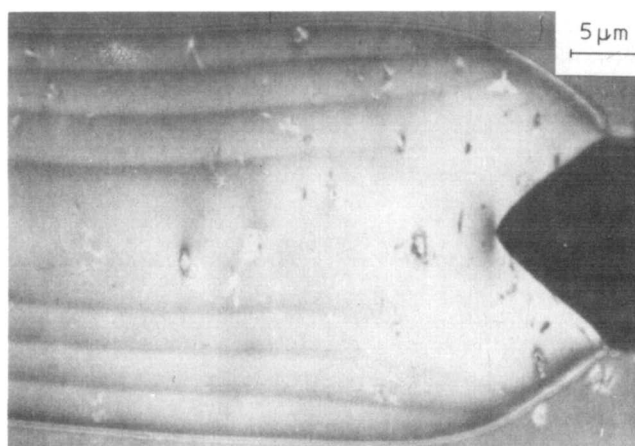


Figure 1e Appearance of the DZ at  $\epsilon = 5.5\%$ , viewed in monochromatic light

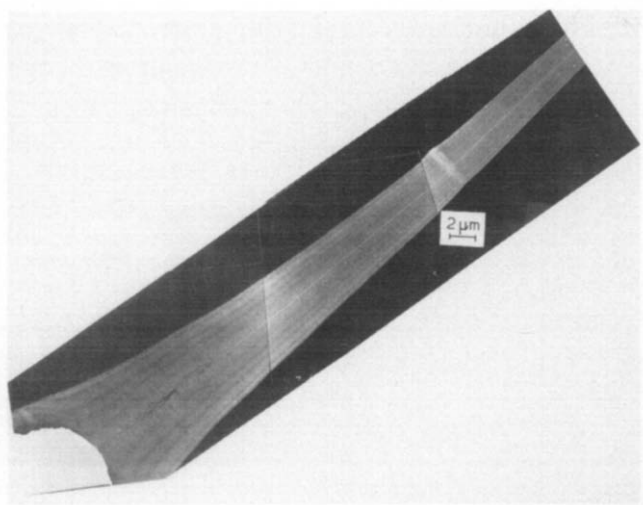


Figure 2 TEM image of a craze in PS, strained in five stages at one minute intervals

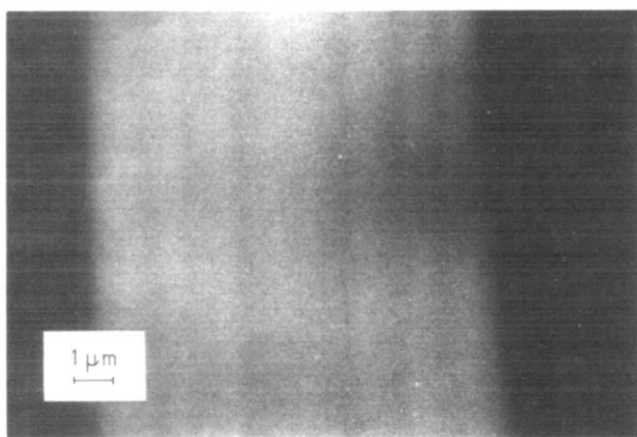


Figure 3 TEM image of the DZ shown in Figure 1

zone thickens substantially with each strain increment, but a line demarcating the position of the outer edge of the zone at the time the strain was increased remains clearly visible everywhere except in the immediate vicinity of the crack tip. Thus in Figure 1d three lines inside the zone are visible corresponding to the zone edge at  $\epsilon = 3.5\%$ ,  $4.5\%$  and  $5.5\%$  respectively. Viewed in monochromatic light (Figure 1e) these lines are even more apparent. Figure 1e also shows the characteristic diamond shape assumed by the crack as it propagates into the oriented polymer within the zone<sup>6</sup>; this behaviour is similar to crack propagation in cold-drawn polymer<sup>7,8</sup>.

As stated previously, the fine scale of the craze microstructure in PS requires the use of TEM for its observation, and this implies that only the final microstructure of a multiple straining experiment can be examined, and not its evolution. Figure 2 shows the appearance of a craze that has been strained in five successive steps ( $\epsilon = 1 \rightarrow 1.5 \rightarrow 2 \rightarrow 2.5 \rightarrow 3\%$ ) at 1 min intervals. As with the PC films, lines demarcating the position of the yielded-unchanged (craze-matrix) interface at the time the strain was increased are clearly visible. In this case it is clear that these lines correspond to regions of less highly drawn material (greater mass thickness).

That this is also the case for the PC film cannot be immediately inferred from the optical micrograph taken with monochromatic light, but observation of the DZ in the TEM shows that the dark lines observed optically do correspond to regions of lower  $\lambda$  (Figure 3).

Although Figure 2 (and to a lesser extent Figure 3) shows these lines clearly, microdensitometry across the craze shows that the absolute change in  $\lambda$  is small. The value of  $\lambda$  can be obtained from:

$$\frac{1}{\lambda} = v_f = 1 - \frac{\ln(\phi_{\text{craze}}/\phi_{\text{film}})}{\ln(\phi_{\text{hole}}/\phi_{\text{film}})}$$

where  $\phi_{\text{craze}}$ ,  $\phi_{\text{film}}$  and  $\phi_{\text{hole}}$  are the optical densities of the craze, film and a hole in the film as measured via microdensitometry of the electron image plate, after ref. 2. The visibility of these demarcation lines in the image is enhanced by defocussing the image, although this does not alter the  $v_f$ 's measured by microdensitometry. This visual enhancement is thought to be due to a reduction in the contribution of phase contrast from the voids, which aids the visual interpretation of the image without actually affecting the mass thickness contrast.

To understand these results, it is useful to reconsider some previous work on macroscopic fibres. In an investigation of stress ageing effects on necks in nylon-6,10, Kramer<sup>9</sup> has shown that at ageing stresses just below the 'propagation stress' the neck continues to propagate but at reduced velocity. When the higher propagation stress is reapplied a delay time is observed before neck propagation at the higher velocity is resumed. This delay time can be related to the appearance of a second yield point<sup>9</sup>, which appears upon resumption of constant rate extension of a drawing fibre, after a period of stress relaxation (caused by stopping the crosshead of the testing machine). A 'bulge' is left behind at the position of the neck edge when neck propagation is reinitiated. This 'bulge' was first observed by Richards<sup>10</sup> in nylon-6,10, and an example is shown in Figure 4 for a nylon-6,6 monofilament.

The growth of deformation zones or crazes under constant strain is equivalent to neck propagation in a fibre under stress relaxation conditions. In this case the 'bulge' is apparent as the ridge of lower extension ratio, and corresponds to the region of polymer which has been stress aged. When the level of applied strain is increased the introduction of a second yield point has the net effect that it is easier for fresh material away from the neck edge to draw in preference to the aged material at the interface.

Because of the rapid stress ageing of the polymer, and

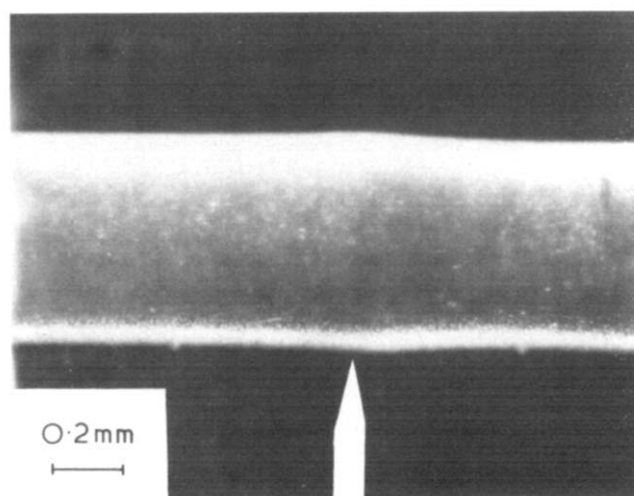


Figure 4 Optical micrograph of a 'bulge' in a stress aged neck in a nylon-6,6 monofilament

because the average stress  $\langle S_c \rangle$  on the zone or craze surface drops with time<sup>6</sup>, these experiments do not permit a ready correlation between the applied stress and the extension ratio of the fibrils. The local value of the surface stress due to the superposition of the stepwise increase in strain and a dropping  $\langle S_c \rangle$  cannot readily be computed. Microdensitometry of the craze shown in *Figure 2* suggests that the value of  $\lambda$  for each successive layer (aside from the midrib) is approximately constant; similar results are found for the DZ in *Figure 1*. This suggests that for these particular combinations of the magnitude of strain increase and the time interval between increments, the net effect on the local surface stress is small. Under different experimental conditions more distinct variations in  $\lambda$  might be observed. The dominating feature of these microstructures is clearly the lower  $\lambda$  of the locally stress aged material and not the  $\lambda$  versus  $\langle S_c \rangle$  response of the virgin polymer.

It might be anticipated that stepwise increments of strain would lead to higher values of  $\lambda$  and hence to rapid craze breakdown and fracture. However, these experiments demonstrate clearly that the combined effects of surface drawing and stress ageing result in a response of the polymer that is non-damaging. Fresh material is drawn into the craze at essentially constant  $\lambda$  and the craze thickens without weakening. This behaviour is in contrast to that following the application, in a single step, of a strain of 3% to a PS sample. In this case many of the

crazes formed fracture, presumably because the surface drawing cannot occur sufficiently rapidly to relax the stress at the centre of the craze.

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