

The effect of film thicknesses on craze microstructure

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Transmission electron microscopy of the fibrillar microstructure of air crazes grown in polystyrene (PS) films thicker than 150 nm, shows this microstructure to consist of fine fibrils 4 to 10 nm in diameter with a mean value of 6 nm, in excellent agreement with recent small angle X-ray scattering measurements on crazes in bulk PS. For films 100 nm and thinner, the crazes have a much coarser microstructure, often resembling a perforated sheet more than a set of discrete fibrils. Where fibrils exist they are much larger in diameter (up to 150 nm) than those in thick film crazes. This change in craze microstructure with decreasing film thickness is attributed to the absence of plastic constraint in the direction of film thickness. Even in much thicker films the absence of plastic constraint at the film surface gives rise to a surface plastic zone producing a surface groove of depth ~ 25 nm which can extend up to 1000 nm ahead of the craze tip. The absence of lateral stresses in these films increases the wavelength of the meniscus instability (the mechanism of craze tip advance and fibril formation) until for a film thickness less than this wavelength a true fibril structure can no longer form.

1. Introduction

Since crazes are important to the fracture of glassy polymers, both as precursors to crack nucleation and as sources of fracture toughness, much effort has been devoted to examining their morphology and fibrillar microstructure. This microstructure (typically with dimensions of the order of tens of nanometers) can be viewed directly by transmission electron microscopy (TEM). Early workers using this technique prepared their specimens by microtoming thin slices from the bulk polymer after crazing, sometimes impregnating the crazes with various low melting eutectics to reinforce them [1, 2, 3]. Since microtoming must be performed on the specimen in an unloaded state, i.e. putting the craze into compression [4], and since impregnation involves exposure of the craze to high temperatures in the presence of potential plasticizing agents (e.g. I_2), it is probable that the craze microstructure is altered by this technique.

Recognizing this problem, Beahan, Bevis and

Hull [3] sought to create crazes directly by stressing thin slices of uncrazed polystyrene (PS) microtomed from the bulk. These crazes could then be viewed directly by TEM. The same authors [5] also produced crazes in thin PS films produced by solvent casting. Unfortunately these films and slices were difficult to stress uniformly and were of uneven thickness. Even so these authors claimed that the microstructure of (1) crazes microtomed from bulk specimens, (2) crazes produced in thin slices, and (3) crazes produced in thin solvent cast films were essentially the same. They measured an average diameter of 25 to 50 nm for the major fibrils (those running normal to the craze surfaces) and one of ~ 10 nm for the minor fibrils running perpendicular to these. However the thin solvent cast films and microtomed slices of this study were 50 to 150 nm thick and therefore comparable with the reported major fibril dimensions.

Lauterwasser and Kramer [6] developed a method for producing PS films of constant thickness. These could be bonded uniformly to ductile

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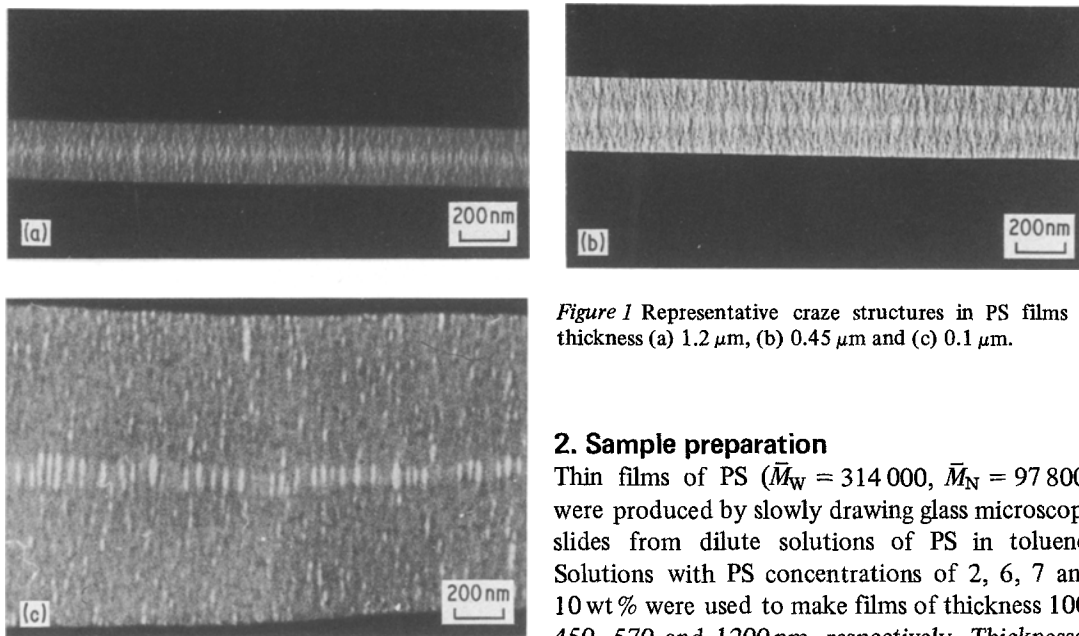


Figure 1 Representative craze structures in PS films of thickness (a) 1.2 μm , (b) 0.45 μm and (c) 0.1 μm .

copper grids which could then be strained to produce a state of uniform stress in the film overlying each grid square. For a craze in a 750 nm thick film they estimated somewhat smaller fibril diameters than those of Beahan *et al.* However, in films of this thickness many fibrils superimpose in the image making it difficult to resolve individual fibrils, and so this estimate cannot be very precise. Recently Donald and Kramer [7] tilted crazes in the TEM, permitting the individual fibrils to be identified. An average fibril diameter of ~ 6 nm for crazes in PS films 190 to 500 nm thick was measured, a value which is in agreement with that found from small angle X-ray scattering measurements on air crazes in bulk specimens of PS by Brown and Kramer [8]. This large discrepancy between the various studies can be at least partially rationalized if the fibril diameters were a function of PS film thickness, becoming larger for thinner films. If so, it is important to determine above what thickness the thin film craze microstructure becomes characteristic of crazes in bulk samples. In this paper we demonstrate that such a film thickness effect on craze fibril microstructure does exist. In the following paper [9] we show that these differences in the fibril microstructure are at least partially produced by the changes in the micromechanics of craze thickening by fibril drawing from the craze surfaces in thin versus thick films.

2. Sample preparation

Thin films of PS ($\bar{M}_W = 314\,000$, $\bar{M}_N = 97\,800$) were produced by slowly drawing glass microscope slides from dilute solutions of PS in toluene. Solutions with PS concentrations of 2, 6, 7 and 10 wt % were used to make films of thickness 100, 450, 570 and 1200 nm, respectively. Thicknesses were measured by an interference microscope to within 30 nm. Thin films of monodisperse PS ($\bar{M}_W = 200\,000$, $\bar{M}_W/\bar{M}_N = 1.03$ from Pressure Chemical Co.) with thicknesses of 190 and 240 nm were also produced. These films were then floated off on the surface of a water bath and were picked up on ductile copper grids, the grid bars of which have been previously coated with a thin film of PS. These films were uniformly bonded to the grid by a short exposure to toluene vapour. The grids were subsequently strained uniaxially to produce isolated crazes in grid squares which could then be cut away from the rest of the grid. The plastically deformed copper held the PS film under stress, so that the crazes in each grid square could be examined without removing the stress on the craze. This method of preparation is discussed in detail by Lauterwasser and Kramer [6]. Crazes have also been grown from "cracks" (actually diamond pyramid indenter marks) in a number of films. These crazes will be discussed further in the following paper [9], but their microstructures are essentially the same as those reported here. The thinner samples were examined using a Siemens 102 TEM operating at 125 kV, whilst the thickest film was examined in a JEM 200 TEM operating at 200 kV.

3. Experimental results and discussion

Representative areas of crazes in the three film thicknesses (1.2, 0.45 and 0.1 μm) are shown in Fig. 1. These areas are in the thicker region

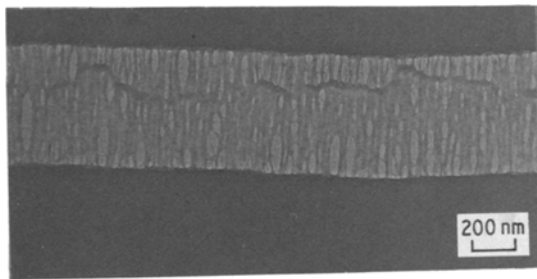


Figure 2 Craze in a PS film 0.1 μm thick, showing unfibrillated matter in the middle of the craze.

of the craze well behind the craze tip. In the two thicker films, the fibril structure is similar, consisting of a dense network of fine fibrils with a region (the “midrib”) of lower volume fraction v_f along the centre line of the craze. Because the films are thick, many fibrils superimpose in the image and it is not possible to resolve the individual fibrils very easily, making accurate measurements of the fibril diameter difficult. However, by tilting the specimen in the TEM about an axis lying approximately parallel to the craze, it is possible to reveal the separate layers of fibrils and hence to identify individual fibrils [7]. Using this technique we measured fibril diameters of 4 to 10 nm in the two thicker films, with a mean value of 6 nm.

From Fig. 1c it is clear that the fibril structure of the craze in the thinnest film differs markedly from those observed in the thicker films. Indeed in places it is hard to identify a true fibril structure since the craze structure more nearly resembles perforated sheets. The smallest fibril diameters observed are ≥ 10 nm and measured values extend up to 150 nm for the perforated sheet structure.

Although some crazes in the thin film showed a well-defined midrib region (Fig. 1c), others showed an undulating region of unfibrillated material running along the middle of the craze, as shown in Fig. 2. This structure, which is never observed in crazes in thicker films, originates from the altered craze tip structure and mechanism of craze tip advance in the thinnest films. To understand this change in structure, it is helpful first to consider the craze tip advance mechanism in thick films.

Two mechanisms have been previously proposed for craze tip advance: (1) that small, isolated voids nucleate ahead of the craze tip which then expand until they become interconnected [10, 11], or (2) that the Taylor meniscus in-

stability [12] operates at the tip causing it to break up into a series of void “fingers” which extend ahead of the craze, the fibrils being formed at the web between “fingers” [13]. Stereo-transmission electron microscopy [7] shows conclusively that craze tips in polystyrene advance by the meniscus instability mechanism. Consider a craze with the x -direction in the direction of craze advance, the z -direction along the craze front (in the film thickness direction), and the y -direction normal to the craze. The meniscus instability is driven by the gradient $d\sigma_h/dx$ of negative pressure ahead of the craze tip. A sinusoidal perturbation (amplitude ζ and wavelength Λ) of the meniscus (craze front) can only grow if the extra negative pressure $\delta\sigma_h = (d\sigma_h/dx)\zeta$ at the front exceeds that needed to create the new surface area. This condition sets a lower limit for the wavelength of the perturbation (smaller wavelengths cannot grow) of

$$\Lambda_m = 2\pi \left(\frac{\Gamma}{d\sigma_h/dx} \right)^{\frac{1}{2}}. \quad (1)$$

The fastest growing wavelength of the instability Λ_c is just $\sqrt{3}\Lambda_m$ [14, 15]. For polystyrene crazes the computed Λ_c is 20 to 30 nm, in good agreement with the spacings between fibrils observed in thick films by stereo TEM [7] and those deduced from small angle X-ray scattering from crazes in bulk PS [8].

Clearly, as a film of PS is made thinner and thinner there will be a thickness t below which the meniscus instability cannot operate. The minimum wavelength Λ_m for the instability is clearly a lower limit for t , but other factors combine to increase this limit. The most important effect is due to the loss of plastic constraint in the deforming polymer at the craze tip as t is made smaller and smaller. The lack of constraint means that only a small lateral stress σ_{zz} develops in the film thickness direction; in the limit of a very thin film σ_{zz} is zero and a state of plane stress exists. This in turn means that the hydrostatic stress and its gradient $(d\sigma_h/dx)$ will be decreased; from Equation 1 the smaller value of $(d\sigma_h/dx)$ for the thin film means a larger Λ_m than for a thick film.

Even in a thick film the polymer at the film surface has little plastic constraint – the relative ease of plastic deformation produces a localized surface plastic zone and resultant surface groove which may extend as much as 1000 nm ahead of the craze tip [7]. These surface grooves, one for

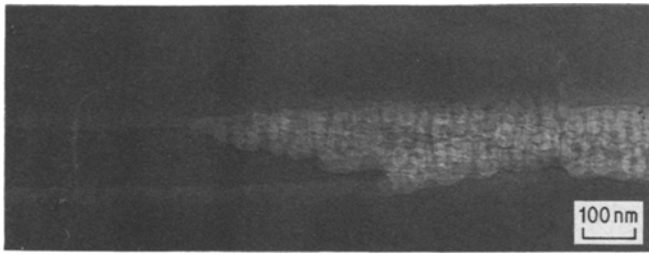


Figure 3 Surface grooves running ahead of a craze tip in a monodisperse PS film (0.24 μm thick) tilted through 15° .

each surface, can be easily seen on tilted TEM images of craze tips, such as Fig. 3, as lines of lower polymer mass thickness. These grooves are straight and parallel extensions of the craze edges. Stereo TEM leaves no doubt that they are surface features. By measuring the optical densities of the grooves on the micrographs with a microdensitometer, using the method of Lauterwasser and Kramer [6], it is possible to show that the typical depth of the groove (in the z -direction) is ~ 25 nm [7].

Since the surface grooves are already 25 nm deep at the craze tip it is logical to anticipate that fibrils will not be formed in the immediate vicinity of the two free surfaces behind the craze tip even in the thicker films. By tilting the craze in the TEM through large angles it is possible to see that indeed the fibrils do not extend throughout the film thickness. A schematic drawing of a craze with no fibrils near the free surfaces giving rise to a "surface step" is shown in Fig. 4a and its projection, as would be seen in the electron microscope is shown in Fig. 4b. Fig. 4c shows an image of a craze tilted through 25° which demonstrates the effect. The "inner" edges of the craze image do not show any signs of the vaulted structure associated with fibril drawing. The edges correspond to the intersections of one surface of the craze (craze-bulk interface) with the top surface of the film and the other surface of the craze with the bottom surface of the film. The "outer" edges are less well defined due to the thickness of uncrazed polymer through which they are being viewed. This lack of definition prevents the easy detection of the surface step at the outer edge in thick films. Similar surface steps were reported previously for solvent crazes [16].

Further confirmation that the fibrils do not fill the entire film thickness comes from quantitative stereoanalysis, after the method of Minter and Piller [17], of two micrographs of the same area of the craze tilted through relatively large

angles ($\geq 15^\circ$ to ensure reasonable accuracy). The method allows one to compute the z -co-ordinates (depth in the film) of the topmost and bottommost layers of fibrils. The thickness of the fibrillated region thus determined is always ~ 90 nm less than the thickness of the film (as measured with the optical interference microscope). These results show that for crazes in films 200 nm or more thick, the fibrils in regions well behind the craze tips start only ~ 45 nm below the true surface of the film. This result suggests that the relatively shallow 25 nm surface groove ahead of the craze tip deepens as the craze thickens (as the fibrils are drawn from the craze surface [6]).

Because of the absence of constraint at the surface of the film, it might be expected that the first layer of fibrils formed near each surface would differ from those in the centre of the film. In films with thicknesses near the lower limit of the "thick" film range, i.e. for thicknesses of ~ 200 nm, this different type of fibril structure can be seen, as in Fig. 5 at A where a "skin" of more continuous matter is visible. That this skin occurs at the top and bottom of the craze is confirmed by examination of stereopairs. In thicker films this surface layer is presumably still present, but the increased number of underlying layers of fibrils precludes its observation. Both these surface layers and the minor fibrils (first discussed by Beahan, Bevis and Hull [5]) contribute to the total v_f of the craze. A further discussion of the effect the absence of lateral constraint has on the craze thickening mechanism will be given in the following paper [9].

From the results on surface grooves in the thicker films one can rationalize what happens in the thinner films. In a 100 nm thick film, the presence of two surface grooves of depth 25 nm at the craze tip would leave only a 50 nm thickness of polymer between them for craze formation. As argued above, the critical wavelength Λ_c for the meniscus instability increases from its 20 to

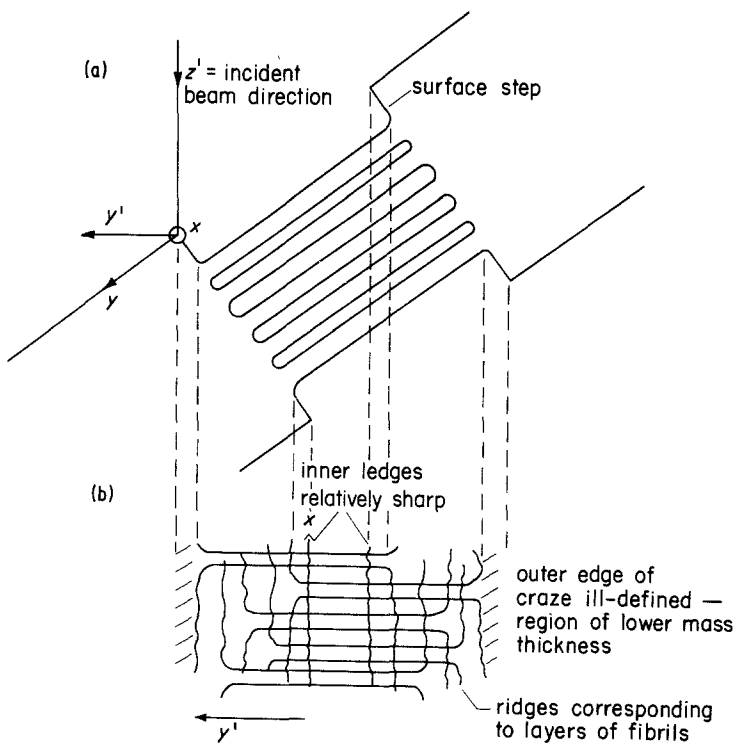
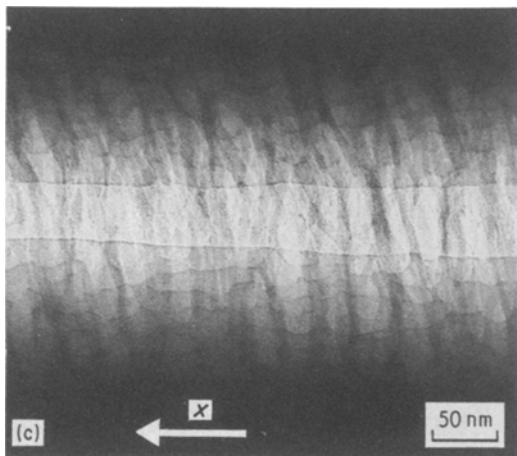


Figure 4 (a) Schematic drawing of the "surface step" at the intersection of the craze with the film surface, (b) schematic drawing of the projection of this craze as viewed in the electron microscope and (c) micrograph of a craze tilted through 25° , showing the absence of fibrils at the film surface. Arrow shows direction of craze advance.



30 nm value in thick films to much larger values in the thinner films due to the lack of lateral constraint (which decreases $d\sigma_h/dx$). Consequently, not even one void finger can form; the single 50 nm sheet between the surface grooves simply draws further to produce the perforated sheet structure seen in Fig. 1c. In this case the craze tapers uniformly as seen in Fig. 6a, and Fig. 6b shows the mature structure of such a craze.

Ahead of the continuous perforated sheet structure a few "isolated voids" (really isolated holes through the film thickness) may be seen. However, these are a natural consequence of the

intermittent coalescence of the two surface grooves ahead of the tip, and hence do not correspond to the isolated void mechanism envisaged by Gent [10] and Argon [11]. On the contrary, they can be seen to give rise to the anomalous perforated sheet structure rather than the typical fibrillar microstructure observed in all but these thinnest films. As has already been demonstrated by Donald and Kramer [7], and argued on theoretical grounds by Argon and Salama [13], the meniscus instability mechanism operates for craze tip advance, and this observation of "isolated voids" only occurs in films too thin for the mechanism to be operative.

A second type of craze tip in thin films has also been seen; an example is shown in Fig. 7, viewed at normal incidence. The tip breaks up and appears to stop and start several times before the fibril/perforated sheet structure disappears completely. In this case three lines of lower mass thickness run ahead of the craze tip. Where fibrillation does occur two of these surface grooves are involved and the third continues to run alongside the fibrillated zone.

When a craze tip in a thick film is viewed at normal incidence, the two surface grooves superimpose. Here three such grooves are visible, demonstrating significant lateral separation (in the y -direction); it can also be seen that the grooves

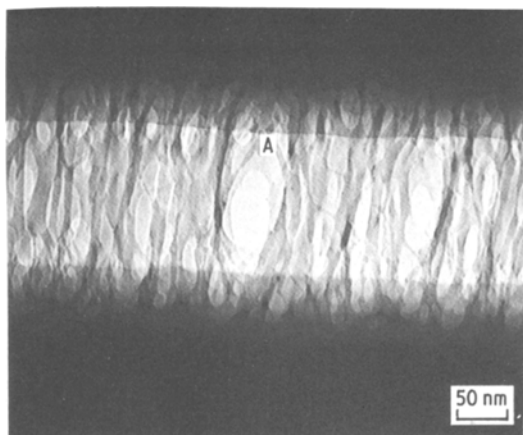


Figure 5 A craze in a film 200 nm thick, showing a “skin” at A.

are much less straight than those in thicker films. Examination of stereopairs of such tips shows that the two outer grooves lie in one surface of the film (“top” surface) whilst the middle groove lies in the other (“bottom”). This “bottom” groove appears to interact first with one of the upper grooves and then the other, causing the craze to move from side to side. Evidently the absence of lateral constraint in thin films can lead to multiple surface grooves, and also weaker coupling between them, than in the thicker films where only one groove at each surface is ever observed.

As the craze thickens the two portions of the craze originating from the two “upper” grooves may come together over much of their length, but occasionally partly drawn strips of polymer from between the two upper surface grooves become surrounded by “mature” fibrillated/perforated sheet crazed material. Such a partly drawn strip is the undulating line of higher mass thickness clearly visible in Fig. 2. Nevertheless, despite this change in tip structure, it can be seen from Fig. 2 that the perforated sheet structure surrounding the partly drawn strip is essentially the same as

that generated (Fig. 6b) by an unbifurcated craze tip (Fig. 6a). It is not clear what determines whether the tip has double or multiple surface grooves but, aside from the presence or absence of this partially drawn strip in the centre of the craze, it is obvious that the craze structure for the two cases is the same. It seems probable that the difference arises from inhomogeneities in the polymer film where the craze nucleates and propagates; these inhomogeneities must be very local since both types of tip were observed in the same grid square.

The transition from the thin film craze microstructure just described to the typical well-defined fibrillar craze microstructure of the thicker films appears to occur for film thicknesses of ~ 150 nm. In the light of the previous discussion of the meniscus instability mechanism, a transition at this thickness seems very reasonable since in this case there is ~ 100 nm of polymer between the two surface grooves at the craze tip, permitting the growth of several void fingers and hence the formation of the familiar fibril structure.

4. Comparison with previous experiments

It is of interest to compare these results with those of previously published studies. Beahan, Bevis and Hull [3] tried to compare crazes formed in thin microtomed sections with those formed in bulk specimens, thin sections of which were subsequently microtomed for examination by TEM. Their published micrographs are all similar in appearance to Figs 1c and 6b, i.e. to crazes in our thinnest films. Because the observed microstructure appeared to be the same for the two types of specimens they claimed that craze structure was independent of film thickness. However when their specimen preparation is studied in detail, it becomes apparent that the specimens crazed prior to microtoming showed no readily identifiable structure until the thin sections were

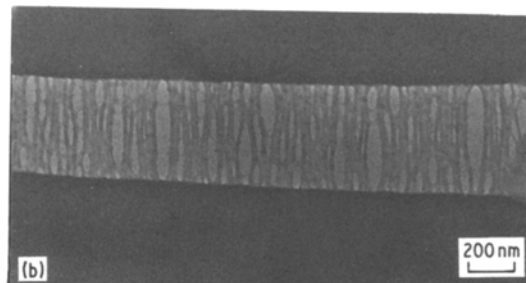
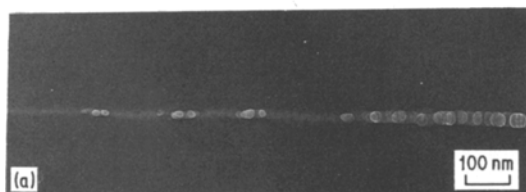


Figure 6 (a) Craze tip tapering uniformly in a $0.1 \mu\text{m}$ thick film and (b) mature craze structure formed behind such a tip.

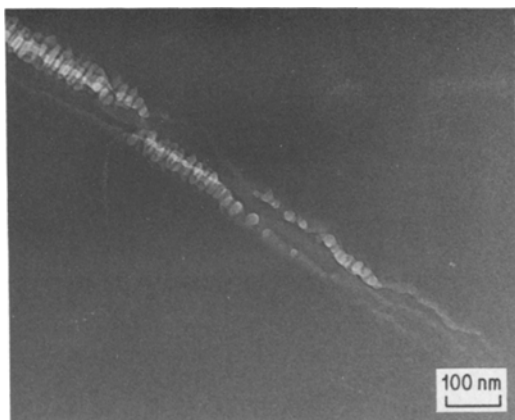


Figure 7 Bifurcated craze tip in a 0.1 μm thick film.

re-strained by deforming the microscope grids. Hence it seems likely that the published micrographs are actually of crazes formed in the thin sections and are not truly representative of crazes in "bulk" samples.

These same authors [5] also studied crazes in solvent cast films that supposedly had thicknesses between 50 and 150 nm. Most of their micrographs of crazes formed in these specimens more closely resemble the structures observed here in thicker films (Fig. 1a and b). Since the actual thicknesses of the films of which the published micrographs were taken were not measured, a detailed comparison with our results is impossible. It is clear that their crazes were produced in inhomogeneous stress fields since intersecting crazes were observed. This complex stress state, together with the non-uniform film thickness known to be produced by their method of solvent casting, may account for the apparent change in fibril structure they observed on craze thickening. They reported that thicker (wider) regions of the craze had a finer fibril structure than thinner (more narrow) regions just behind the craze tip. We find no such change in fibril size with craze thickness and in fact can infer the opposite is true,

that the fibrils just behind the craze tip are more highly drawn than those in the mature portion of the craze [9].

Acknowledgements

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