

# Nucleation and propagation of cracks in a polystyrene craze layer

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A mechanism of crack nucleation by ductile rupture in the "mid-rib" layer of polystyrene crazes is described. Progressive failure localized within the mid-rib layer may also be the mechanism of propagation of cracks in polystyrene crazes at low velocities.

## 1. Introduction

Cracks propagate in polystyrene and other glassy polymers by first forming crazes. The latter may be regarded as a partial fracture, i.e., an expanded form of the polymer containing usually less than 50% of polymer [1-3]. The craze has a microstructure of fibrils, of the order of a 10 nm in diameter [3-5], and orientated mostly perpendicular to the plane of the craze. It has been generally assumed that cracks are initiated in stressed crazes by the expansion and coalescence of the interfibrillar voids assisted by the presence of various inclusions, e.g. dirt particles, as these have been engulfed by the growing craze, but the details of the mechanism involved have not been much discussed.

The best known crack nucleation phenomenon in glassy thermoplastics, shown in Fig. 1, is that of the "fracture parabolas". These characteristic markings on the surfaces of fracture arise by the intersection of a plane crack front, propagating through the craze layer which precedes it, with another circular crack front, spreading out from its point of origin within the same craze. This mechanism and the fracture surface morphology which arises from it have been previously described [6]. The defects which initiate advance fractures in polystyrene are usually dirt, lubricant, or catalyst particles [7, 8]. The advance fractures (cracks) are initiated at either of the craze interfaces and frequently far ahead of the main crack tip, although they do not spread much until the main crack is quite close. Because the

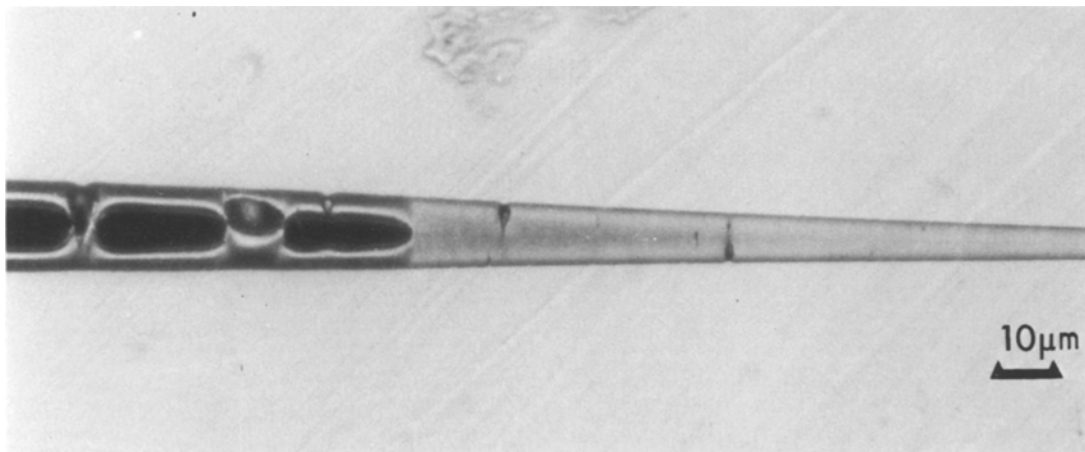
cracks are nucleated at the craze interface, the resulting cavities assume an unsymmetrical shape [6]. This can also be the mechanism for primary crack nucleation in glassy thermoplastics.

Another mechanism of crack nucleation in crazes has been described by Murray and Hull [7-9], which they called the "event" mechanism. The events are cavities, usually irregularly shaped, within the plane of the craze but symmetrical across it. The "events" are associated with the presence of dirt particles [7-9] or localized molecular orientation [10]. Murray and Hull [8] have described this mechanism as the formation and growth of large voids in a thick craze which then coalesce to form a large planar cavity (the event). From the observations described below it is possible to form a more specific and rather different description of this process of crack nucleation and propagation in polystyrene crazes.

## 2. Results and discussion

Fig. 1 shows a part of the wedge-shaped layer of craze which precedes a cleavage crack propagating in a block of polystyrene (viscosity-average molecular weight,  $M_v = 2 \times 10^5$ ) which is viewed at the side surface from a direction perpendicular to the direction of crack propagation and in the plane of the crack. Several crack nuclei, of the type which produce the unsymmetrical advance fractures, (the fracture parabolas mentioned above) can be seen. Fig. 2 shows a sequence of photomicrographs of the same crack-craze wedge viewed in monochromatic light through the block

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*Figure 1* Crack propagating in a craze layer in polystyrene and showing several advance fractures initiated at the craze-bulk boundaries. Taken using reflected light of  $\lambda = 546$  nm.

from a direction perpendicular to the plane of the crack; in this sequence the crack has propagated about  $200\ \mu\text{m}$  over a period of three hours ( $\dot{c} \approx 2 \times 10^{-6}\ \text{cm sec}^{-1}$ ). Within the craze wedge a crack has been nucleated which appears to be identical to an “event” as described by Murray and Hull. It can be seen that during the propagation of the main crack front, R–R, the edge of the craze, E–E, moves forward a similar distance. This latter effect is not apparent in Figs 4, 5, and 6 of [8], which is otherwise similar to Fig. 2 above, probably because the crack was unloaded and then reloaded during their experiment. Under such circumstances the continued growth of the craze tip is seldom exactly coplanar with that of the craze growth prior to unloading, in which case it may not reflect the incident light. It was observed that the nucleation of the crack occurred very rapidly over an area, which in this case was roughly  $15\ \mu\text{m}$  in diameter, just behind the leading edge of the craze layer where it is still thin (less than a quarter of a micrometre thick). Observations of the growth of other “events” showed that crack nucleation invariably occurred in about the same location with respect to the craze edge. In contrast, the fracture parabola nucleation mechanism has been observed to initiate randomly along the whole length of the craze wedge. This suggests that the nucleation of the event is specifically associated with some aspect of the growth of the craze adjacent to the craze tip. It probably begins in the so-called “mid-rib” of the craze, the characteristic median layer, roughly  $50\ \text{nm}$  thick in polystyrene crazes, which arises from

the craze nucleation and growth process at and just behind the craze tip. The microstructure of the “mid-rib” is slightly different from that which results when the craze spreads sideways into the adjacent bulk further behind the craze tip [3]. Additional support for this interpretation is shown in Fig. 3 which shows the nucleation of an event where the craze, seen at the side surface of the specimen, propagates across a circular patch of a residue of adhesive from the protective masking paper which covered the extruded sheet; this is also an example of an “environmental” fracture. The morphology of the resulting surface of fracture, Fig. 4, is identical to the “edge event” described by Murray and Hull. The initiation of a crack at the edge of the craze layer is due, however, not to an edge suction effect in a fully developed thick craze, as has been suggested, but to the nucleation of a crack by the premature rupture of a very thin craze before it has expanded beyond the mid-rib stage in exactly the same way as events nucleated away from the edge of the specimen. Edge events could be initiated by rubbing the surface of the specimen with a soft cloth; surface imperfections are the most probable cause of edge events. If the embryonic craze tip layer strain-hardens sufficiently, then conversion of more bulk polymer to craze can occur at the boundaries of the layer, and the craze layer thickens by drawing in more bulk polymer; if the layer strain-softens, the embryonic craze layer widens by stretching the polymer fibrils within it until ductile rupture occurs by the continuous reduction in density. This is the origin of the “event” and explains why there is no

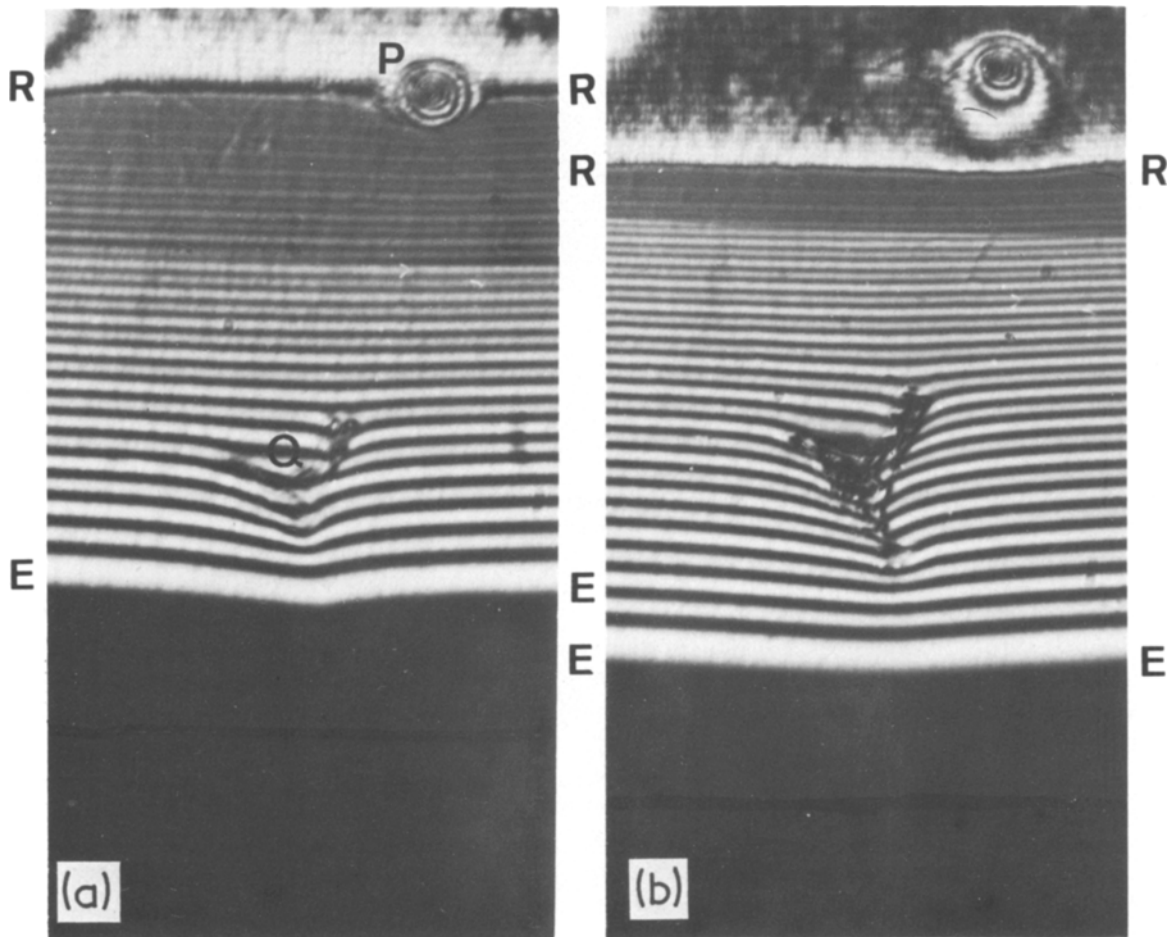


Figure 2 A series of micrographs, taken at different times showing the craze wedge preceding the tip, R, of a cleavage crack in polystyrene. An advance fracture and an event are shown at P and Q respectively. Taken using reflected monochromatic light of  $\lambda = 546 \text{ nm}$ .

visible optical interference effect at its centre; the residual craze layer (the ruptured mid-rib layer) would be only 10 nm or so thick on each surface and the corresponding interference colour would be white. It is interesting to note in Fig. 4 that a band, roughly  $1 \mu\text{m}$  wide, at the very edge, A, of the "edge event" and adjacent to the surface of the plate, shows a surface of fracture noticeably coarser than that further away from the surface at the centre of the event. The rupture of the craze fibrils evident in side view in Fig. 3 is not exactly representative of the event *nucleation* process in the bulk. This, no doubt, is due to the loss of constraint at the free surface; for this reason it seems likely that the conditions for nucleation of events may not be easily reproduced in the thin films ( $< 1 \mu\text{m}$  thick) usually used in transmission electron microscopy.

In view of the connection between crack

nucleation in a craze and the mid-rib layer, it is of interest to determine whether the latter is of importance in the propagation of the crack through a thick craze (e.g.  $10 \mu\text{m}$  under stress). The resistance to crack propagation depends upon the constitutive properties and the microstructure of the craze layer, and in this regard it is important to know whether the process of straining to rupture occurs uniformly across the full thickness of the craze or whether it is confined mostly to the mid-rib layer.

The interference pattern shown in Fig. 2 shows bright fringes of alternating intensity due to the presence of the mid-rib layer [11]. The ratio,  $\phi$ , of the intensities of adjacent bright fringes is given by

$$\sin \alpha = P \left( \frac{1 - \phi^{1/2}}{1 + \phi^{1/2}} \right), \quad (1)$$

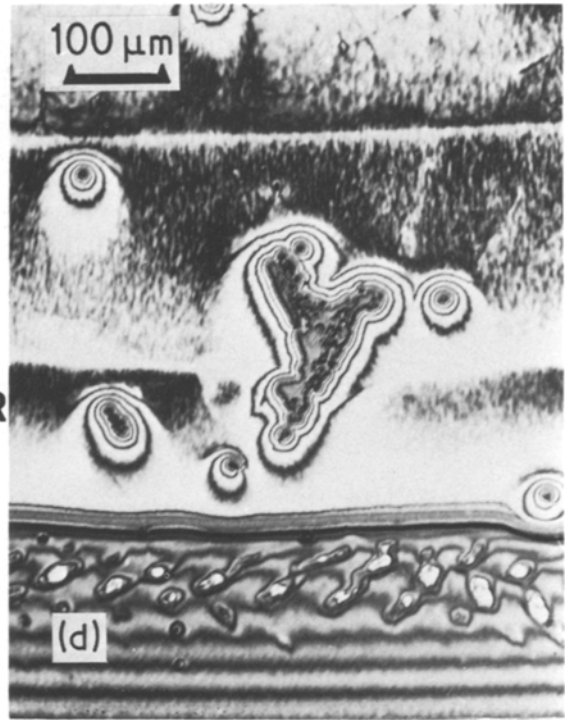
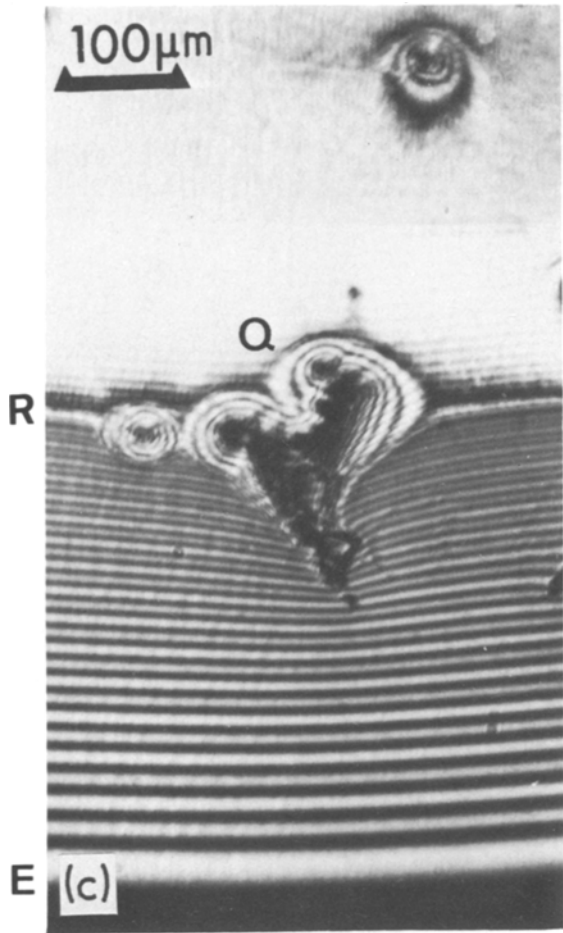


Figure 2 (Continued).

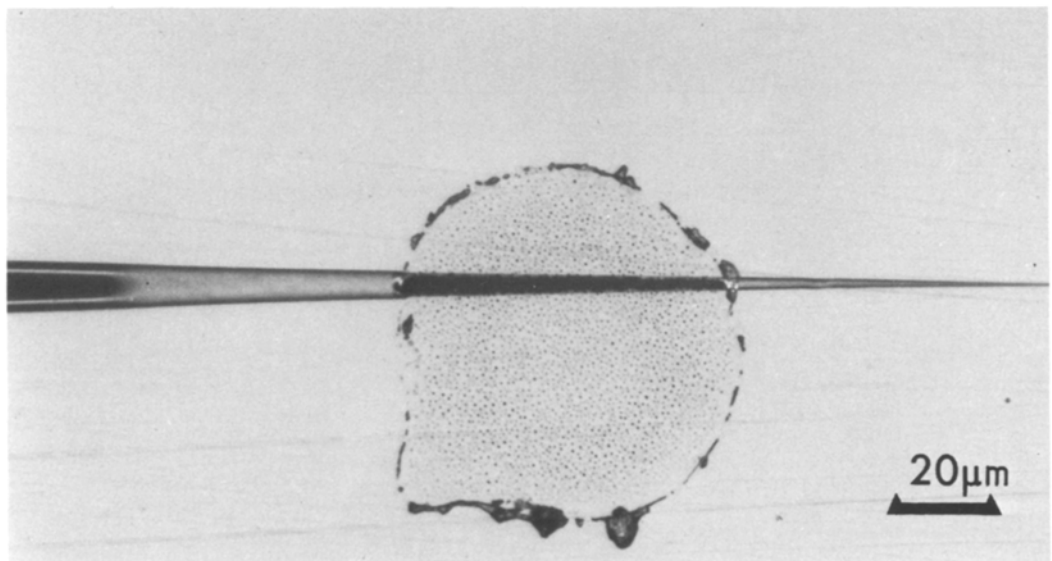


Figure 3 An “event” nucleated in a craze at the surface of a polystyrene specimen. The circular patch is a residue of adhesive from the sheet of masking paper which covered the extruded sheet of plastic. Taken using reflected light of  $\lambda = 546 \text{ nm}$ .

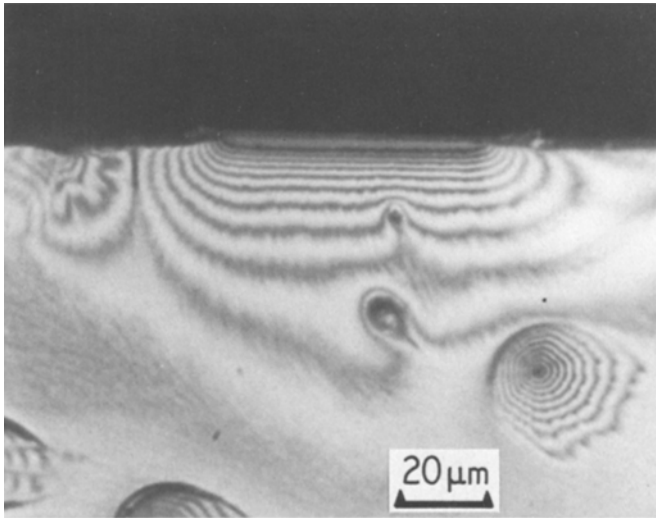


Figure 4 Edge of the surface of fracture of the specimen shown in Fig. 3 showing the edge event. Taken using reflected monochromatic light of  $\lambda = 546$  nm.

where  $\alpha$  is the phase difference of light reflected from the boundaries of the median layer, and  $P$  is the ratio of the reflection coefficients,  $a_1/a_2$ , at the bulk-craze and craze-“mid-rib” interfaces, respectively. The craze layer is actually wedge-shaped, but, as shown by Verheulpen-Heymans [12], the angles of incidence are so small along the craze wedge that negligible error is introduced by using plane layer theory. The variation of  $\phi$  along the craze, shown in Fig. 5, was obtained from a microdensitometer trace across an interferogram similar to Fig. 2. The results of trans-

mission electron microscopy (TEM) by Kramer *et al.* [3] and by Beahan [5] show that the mid-rib layer is about 60 nm thick; its boundaries are much less sharply defined than the craze-bulk interface. From quantitative TEM, Kramer has estimated the mid-rib to have a polymer volume-fraction of about 0.17; that of the craze wedge itself varies from about 0.2 to 0.3. These results were obtained on narrow crazes ( $\sim 0.5 \mu\text{m}$ ) in thin ( $< 1 \mu\text{m}$ ) films and are probably characteristic of the microstructure of the craze wedge near its tip.

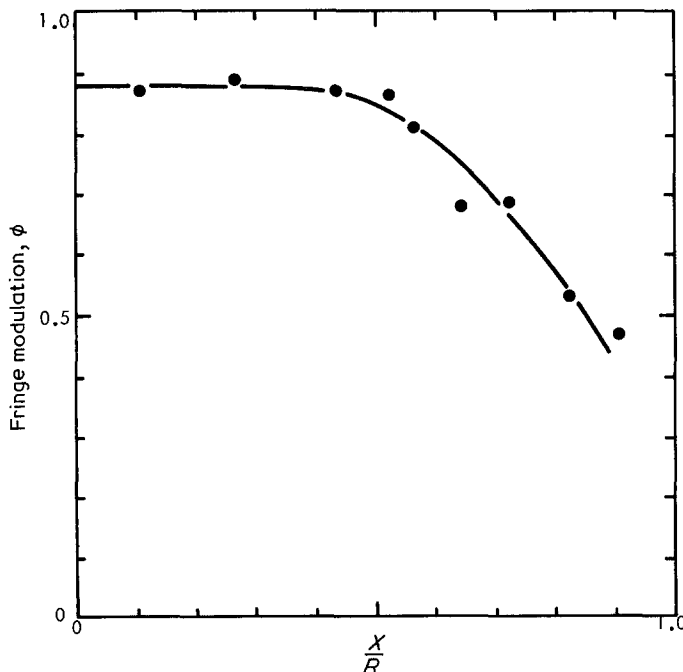


Figure 5 Variation of the fringe modulation,  $\phi$ , along the length of the craze.  $R$  is the full length of the craze; the craze tip is at  $X = 0$ .

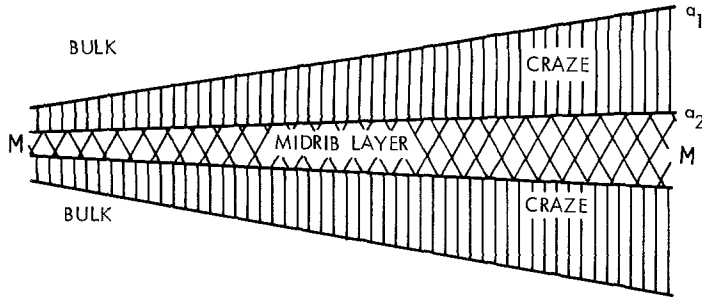


Figure 6 Schematic diagram of the craze wedge. The median or mid-rib layer is M-M.

In Equation 1 above

$$\alpha = \frac{2\pi}{\lambda} n_3 d_3, \quad (2)$$

where  $n_3$  and  $d_3$  are the refractive index and thickness of the median layer, respectively (see Fig. 6). It is assumed that the median layer is formed by a given layer of bulk polymer of thickness  $d_{b3}$  which would be related to the size of the craze tip plastic zone and which will remain constant (see below) along the craze wedge; i.e., the median layer may stretch, which reduces its density, without the adjacent craze transforming into the median layer structure. In view of the rather large changes in density and refractive index which occur during formation and rupture of the craze, a simple relationship between the volume-fraction of polymer,  $v_c$ , and refractive index,  $n_c$ , which neglects the bi-refringence effects, can be used without serious error:

$$n_c = 1 + v_c(n_b - 1), \quad (3)$$

where  $n_c$  is the refractive index of the craze layer and  $n_b$ , which is, 1.60, is the refractive index of the bulk polymer. The reflection coefficient for normally incident light polarized perpendicular to the plane of incidence is given by

$$a_{12} = \frac{n_1 - n_2}{n_1 + n_2}, \quad (4)$$

so that the ratio of the reflection coefficients at the bulk-craze and craze-mid-rib interfaces is given by

$$P = \frac{(n_b - n_c)(n_c + n_3)}{(n_b + n_c)(n_c - n_3)}. \quad (5)$$

The refractive index of bulk polystyrene is 1.60 and assuming for the moment that the refractive index of the craze layer [2, 13] remains constant at  $n_c = 1.16$  then:

$$P = 0.16 \left( \frac{1.16 + n_3}{1.16 - n_3} \right). \quad (6)$$

According to Kramer, the volume-fraction of polymer,  $v_3$ , in the mid-rib layer of crazes about 1  $\mu\text{m}$  wide is approximately 0.17, corresponding to a refractive index of 1.11. If  $v_3$  decreases towards the crack tip and  $v_2$  remains constant, then from Equation 3 the numerator in Equation 6 remains approximately constant and:

$$P \approx \left( \frac{0.6}{v_2 - v_3} \right). \quad (7)$$

Also from Equations 2 and 3:

$$\alpha = \frac{2\pi}{\lambda} d_{b3} \left( 0.6 + \frac{1}{v_3} \right). \quad (8)$$

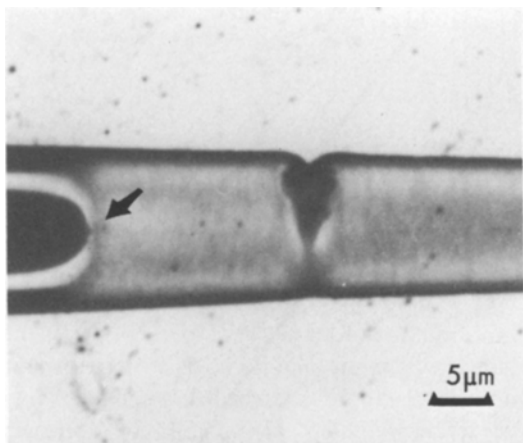
Again using the data of Kramer, the thickness of the mid-rib layer (under stress) is about 60 nm near the tip of the craze wedge and the volume-fraction of polymer,  $v_3$ , is 0.17 giving an equivalent bulk layer thickness,  $d_{b3}$ , of approximately 10 nm.

From Equations 1, 7 and 8 the interference fringe modulation,  $\phi$ , calculated from chosen values of  $v_3$ , is shown in Table I.

It is likely that the assumption of a constant craze density,  $v_2$ , is not exactly correct. What little data that is available on fully developed crazes in bulk specimens indicates that the density is fairly constant over most of the craze length and decreases near ( $0.8 < X/R < 1.0$ ) the crack tip [13]. The inclusion of this effect in the above analysis would diminish the change in  $\phi$ . In the extreme case, if the density of the mid-rib layer remains constant

TABLE I Dependence of fringe modulation,  $\phi$ , on the volume-fraction of the mid-rib layer,  $v_3$ , with  $d_{b3} = 10$  nm,  $\lambda = 543.6$  nm and  $v_2 = 0.26$

$v_3$	$\phi$
0.20	0.80
0.16	0.60
0.12	0.45
0.10	0.37
0.08	0.30
0.06	0.27
0.04	0.80



**Figure 7** Crack tip in a polystyrene craze layer. Taken using reflected light of  $\lambda = 546$  nm.

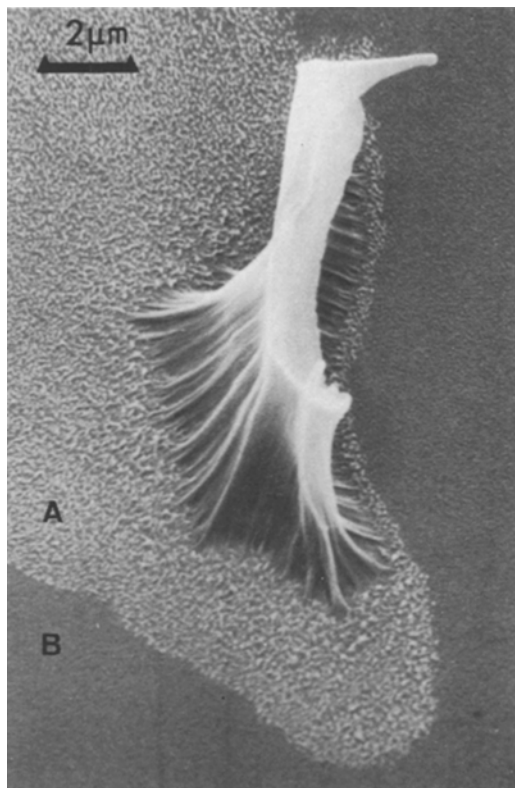
and that of the adjacent craze layer ( $v_2$ ) decreases, then  $\phi$  would tend to 1 as the density reached that of the mid-rib layer. As can be seen from Fig. 5, the value of  $\phi$  decreases monotonically from the craze tip towards the crack tip. The major effect, then, must be the expansion of the mid-rib layer for which the estimates in Table I are likely to be conservative.

The fact that the rupture of the craze layer may be mostly localized to the mid-rib layer is supported by inspection of the crack tip region shown in Fig. 1 and at higher magnification in Fig. 7. The existence of the mid-rib is revealed by the dark line (clearly seen on the negative but not on this print) in the centre of the craze layer and the smooth parabolic curve of the crack tip is interrupted by a small, sharp notch at its tip. Examination of the surfaces of fracture show that what is observed in side view in Fig. 7 is the rupture of a thin film and cannot be exactly the same as the conditions further inside the specimen. However, in view of the optical effects discussed above, the localization of the craze failure process seems to be similar.

Recently, in connection with the earlier characterization of craze fracture as a viscous process [6], Haward *et al.* have discussed the feasibility of a viscous separation as opposed to a chain scission mechanism with respect to the probability of the polymer chain molecules spanning the two boundaries of the craze [14]. Busse *et al.* [15] proposed that fracture of polystyrene occurred by a viscous mechanism, while more recently, Shunkevich *et al.* [16], on the basis of chemical

kinetics studies based on infra-red spectroscopy observations, concluded that molecular scission determines fracture life.

The layer of bulk polymer from which the mid-rib layer is formed is about 10 nm. From the calculations of Haward *et al.* [14] it follows that for a  $M_v = 200\,000$  about 50% of the polymer chains must bridge the layer with their ends embedded in the adjacent layers of bulk material. Even in this case, some of these molecules could be pulled from the bulk without molecular rupture because the intermolecular frictional forces are much weaker than the carbon-carbon covalent bonds within the chain molecule. However, the observed average craze fibril stress is only 200 MPa [17], well over an order of magnitude below the likely carbon-carbon bond strength [18]. A very rough calculation shows that at this stress level an embedded chain end of more than a few nanometers length cannot be pulled out from the bulk. It seems likely then that the mid-rib layer contains a large fraction of bridging molecules which cannot be pulled out from the bulk by a visco-plastic mechanism. This may explain why the developing craze layer passes through a critical state of growth when it is still thin (compared to its maximum thickness). At first, when the layer is just a few tens of nanometers thick, the fibrils and the bridging chain molecules may not be very highly oriented nor very uniformly stressed. A few critically stressed bridging molecules (or fibrils) may rupture, causing the stress on adjacent fibrils to increase which then also rupture. The process is analogous to that observed in unidirectional composites where there exists a critical volume-fraction of reinforcing fibres below which the composite may be weaker than the unreinforced matrix [19]; the bridging molecules correspond to the reinforcing fibres, the other molecules to a plastic matrix. In regions of localized orientation, such as might arise during moulding for example, the number of bridging molecules across the embryonic craze layer may be less than the critical concentration and thus craze fracture occurs immediately. If the embryonic craze does not break, the craze boundary can continue to advance against the secondary bonding forces between the chain molecules, by plastic cavitation in the adjacent bulk. As the craze widens, the number of bridging molecules decreases and the fibrils become more highly oriented. Resistance to rupture within the craze



*Figure 8* A scanning electron micrograph showing the surface of fracture of polystyrene with the transition belt. Material of a coarse “granular” texture, A, surrounds a highly deformed patch of craze matter, and a smooth “brittle” fracture surface, B, is beyond.

is then determined by the molecules in the fibrils sliding apart against intermolecular forces and persistent entanglements. Within the craze, the continuous reduction in load bearing cross-sectional area arising from the fibril flow must eventually overcome orientation hardening of the fibrils, and the craze stress, as opposed to the fibril true stress, must decrease and the spread of the craze further into the bulk must stop. From the observations described above, it seems that this process may be mostly localized in the mid-rib layer. Some molecular fracture is inevitable when the craze is first formed, as implied by the analysis of Haward *et al.* [14].

On a related subject, Haward *et al.* have discussed the possibility of viscous rupture where the craze separates along its interface with the adjacent bulk. It is important to recognize that two distinctly different craze boundary fracture mechanisms can be inferred from observations of fracture surfaces. In that to which Haward *et al.*

refer, rupture occurs close to the craze interface, but clearly within the craze layer; the roots of the broken craze fibrils are easily seen. This mechanism has been observed in the transmission electron microscopy of polystyrene films ([3], Fig. 16; [5], Fig. 14). However, the more usual form of craze boundary fracture observed on fracture surfaces of bulk specimens shows a much finer scale graininess on both the “bulk” surface and the “top” of the detached craze layer itself ([6], Fig. 10). There is no evidence of the fibrillar craze matter at all; the fracture must occur below the craze boundary, slightly into the bulk. An illustration of the two mechanisms is shown in Fig. 8, which is a scanning electron micrograph of the “transition belt” [6] on the surface of fracture of polystyrene; remnants of the “roots” of craze fibrils are seen at A but not on the adjacent area B. In our observations the fibrillar boundary rupture invariably occurs in surrounding regions where the fracture has switched from one craze interface to the other; e.g., around “mackerel” bands [9] as in Fig. 8, or around advance fractures. The most likely explanation, suggested by Kramer [3], is that the fibrillar boundary fracture results from a local variation in craze microstructure due to a transient increase in the craze boundary stress.

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