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Fracture of crazes by the propagation of interfacial stress waves

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Fracture of crazes in glassy polymers can occur by a quasi-brittle separation at the interface between the craze and the adjacent bulk. In some grades of polystyrene this type of fracture can take the form of a very regular pattern, the so-called "mackerel pattern", of parallel or concentric craze strips as fracture alternates from one side of the craze layer to the other. The alternating pattern of fracture is determined by the coupling between stress waves propagating along the craze–bulk boundaries.

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1. Introduction

Fracture of glassy polymers, and at least some semicrystalline polymers, occurs by the formation and rupture of crazes. Several different mechanisms of craze fracture have been described; they are remarkably distinct but general to most glassy polymers. In many of these mechanisms the phenomenology of craze rupture is similar to the processes of separation and rupture of a soft viscoelastic layer of adhesive sandwiched between two planar rigid adherends. A particularly interesting mechanism of craze fracture in polystyrene has been observed and described by Murray and Hull; the fracture surfaces formed from it show what they called the "mackerel pattern" [1]. The latter is formed from the more-or-less brittle fracture of the craze at its interface with the adjacent bulk along narrow continuous strips which lie perpendicular to the direction of fracture propagation and lie alternately on the two craze–bulk interfaces, as is shown schematically in Fig. 1.

This pattern of fracture is observed invariably in some grades of polystyrene, as long as the crack accelerates from some low initial velocity, but it is completely absent under all conditions in other grades of polystyrene. In the work reported here the "mackerel pattern" of fracture has been observed in a low molecular-weight extrusion grade of polymethyl methacrylate as well as in polystyrene, but has not as yet been observed in other glassy polymers. (There are several references to the mackerel pattern in connection with observations of "bands" on the fracture surfaces of other polymers such as polycarbonate, but in these instances the available evidence suggests that the bands should be ascribed to mechanisms [2] other than that of the mackerel bands as originally described by Murray and Hull [1].)

Murray and Hull base their explanation [1] of the phenomenon on the suggestion that the region of the craze layer ahead of an interfacial crack will be under high stress at *both* interfaces and that there is a strong tendency for the crack to jump to the opposite interface, especially when the propagating crack interacts with a stress wave (the Wallner line-effect). The explanation described below is based on the hypothesis that the primary structure of the pattern arises from structural weaknesses or actual interfacial fractures caused by the propagation of stress waves along the craze–bulk interface, as Stoneley waves [3, 4], independently of the propagation of the main fracture. The alternation of the strips of decohesion from one craze–bulk interface to another arises from weak coupling between the disturbances, emitted by some fracture event, propagating along the two interfaces. Energy is periodically localized on one interface of the layer or the other. An analogous effect is observed with the vibrations of two pendula which have a weak

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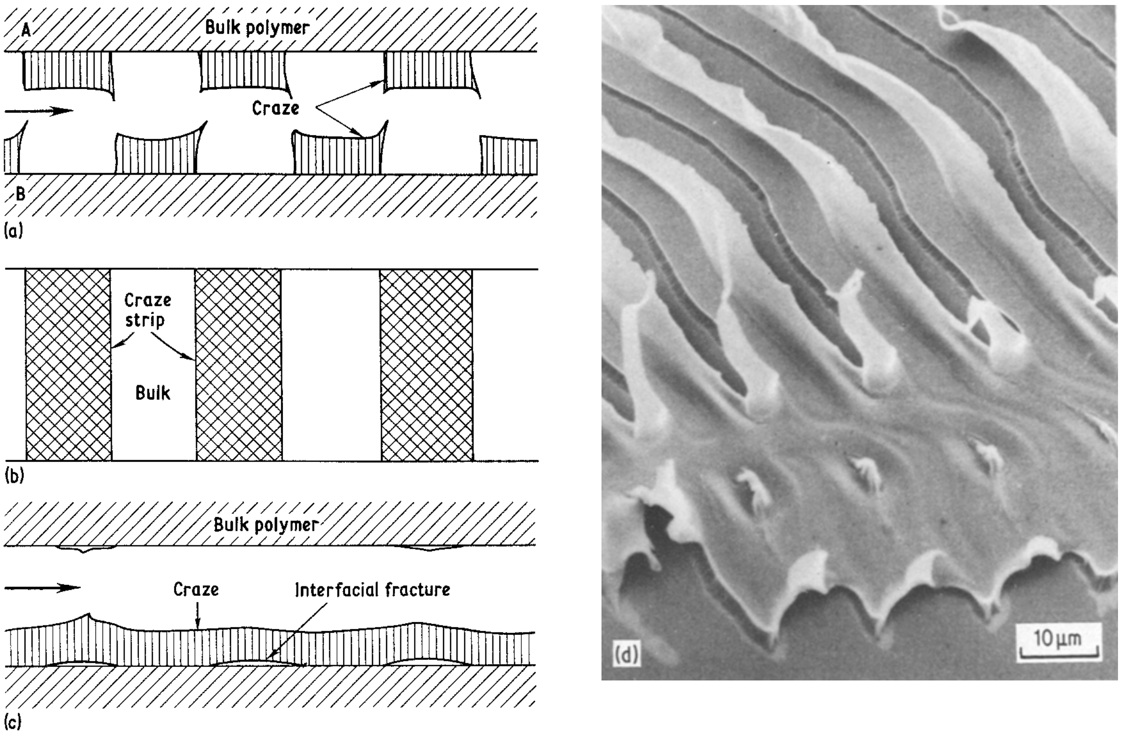

Figure 1 (a to c) Schematic diagram of "mackerel" craze fracture patterns, (a) side-view of craze layer with strips lying alternately on each surface of fracture, (b) surface of fracture A from (a) above, and (c) continuous fracture along one craze–bulk boundary with alternating strips of decohesion at the underlying craze–bulk interface. (d) Scanning electron micrograph of a mackerel pattern on the surface of fracture of polystyrene; the upper part of the micrograph shows alternating strip pattern and the lower part shows periodic subsurface decohesion pattern.

spring connecting their masses or, for another example, with the vertical and torsional oscillatory modes of a mass suspended from a spring [5]. The amplitude of each component or mode periodically increases and decreases.

2. Observations and discussion

At low crack velocities fracture of polystyrene occurs by the formation and rupture of a craze by a viscous flow mechanism localized at about its median plane. At some critical crack velocity the mechanism of failure changes to a quasi-brittle fracture at the boundary between the craze and the adjacent bulk [6]. This change in mechanism usually initiates, for example, the fast, unstable crack propagation in a tensile test. In polystyrene, the craze boundary fracture usually occurs approximately randomly at both interfaces causing fragments of the craze layer to lie on one surface of fracture or the other, giving an irregular patchwork pattern. However, in some particular polymer grades this region is dominated by the very regular mackerel pattern. Figs. 2 to 5 show micrographs of typical mackerel patterns in polystyrene and polymethyl methacrylate.

The bands appear to emanate from a region on the surface of fracture which, in all cases so far observed, is always of the same nature: a small region of viscous rupture which lies between the smooth (slow) viscous-flow craze-rupture surface and the brittle craze-boundary fracture. This zone, V, which appears stippled in the optical microscope (Figs 2 and 6), marks the beginning of fast fracture and occurs, most probably, by rapid, ductile fracture or "ripping" along the "mid-rib"-layer in the craze [7]. Surrounding this source there is always a region of craze boundary fracture but which is unbanded. The bands themselves are of two main types. In the first and the more usual type the strips of craze lie alternately on each fracture surface. In the second type, the craze lies more-or-less completely on one surface of fracture but there are alternating strips which are debonded from bulk polymer lying beneath, see Fig. 1d.

Fig. 2 is particularly interesting in that several

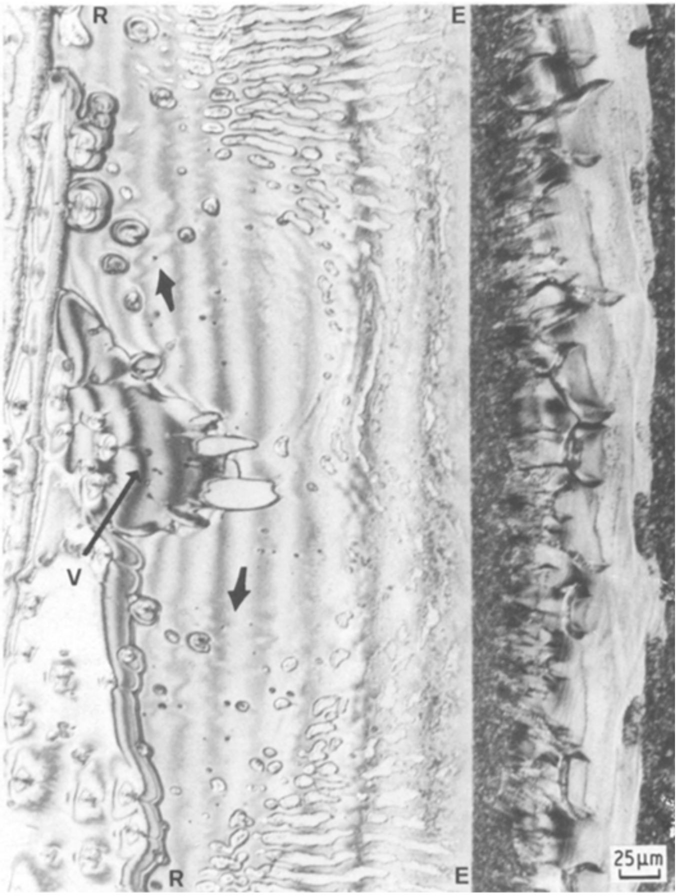

Figure 2 Mackerel pattern in the surface of an oriented polystyrene (see [7]) in the region of the craze wedge detachment. R–R is the rear of the craze wedge, E–E is its edge. V is the region of viscous rupture which is the source of the wave disturbance. Arrows mark region where displaced interference fringes indicate distortion of the craze–bulk interface. Optical micrograph, λ = 546 nm.

progressive stages of interfacial decohesion are evident. In the continuous area of detached craze, before the mackerel bands begin, there is some deformation of the craze layer and/or the lower craze–bulk boundary, judging by the distortion of the optical interference fringes in the craze layer (arrows). From the contrast of the interference fringes, however, there seems to be no sharp discontinuity at the craze boundary compar-

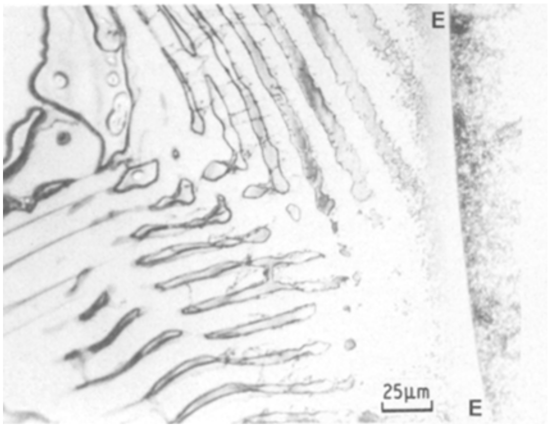

Figure 3 Intersection of mackerel bands propagating from two different sources. Optical micrograph, λ = 546 nm.

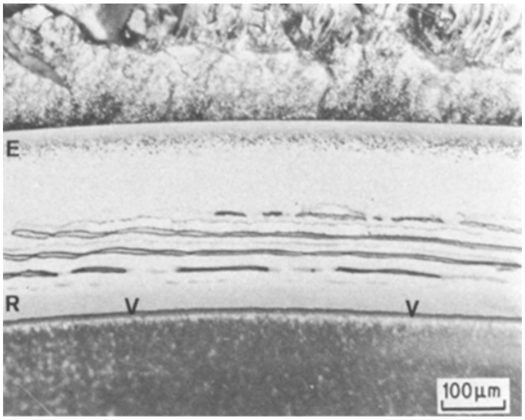

Figure 4 Mackerel bands initiated from a linear source, a narrow band, V–V, of viscous craze rupture between the region of slow separation of the craze by viscous flow and the brittle craze wedge detachment mechanism. Optical micrograph, λ = 546 nm.

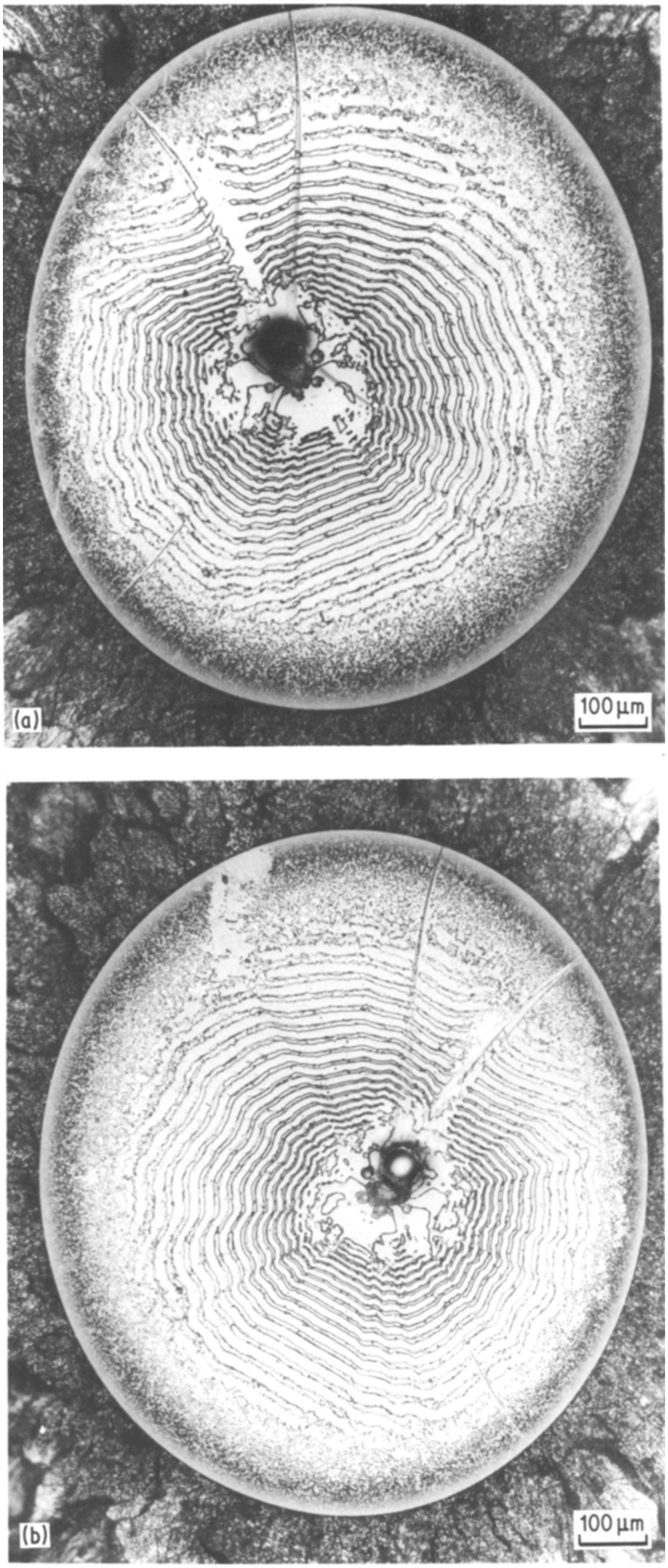

Figure 5 (a and b) Mackeral bands in a fractured craze in a polymethylmethacrylate extruded rod fractured in tension. Matching surface of fracture. Optical micrograph, $\lambda = 546$ nm.

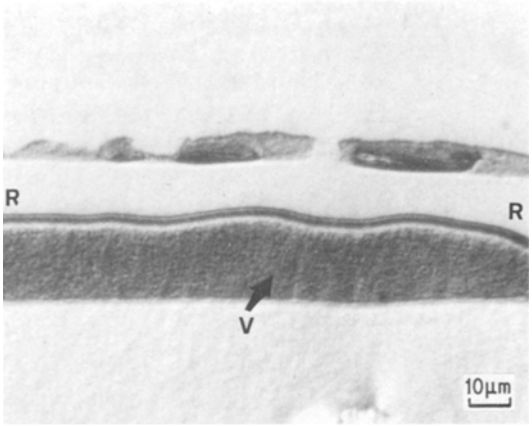

Figure 6 Higher magnification of the viscous rupture strip V–V in Fig. 4. Optical micrograph, Nomarski interference contrast.

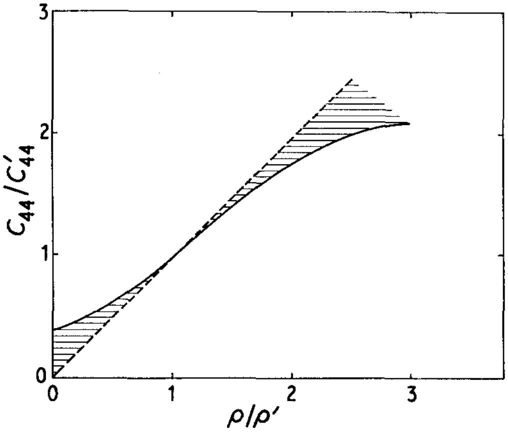

Figure 8 Range of existence of Stoneley waves (shaded area); after J. G. Scholte, reproduced from [4]. C_{44}, shear modulus; ρ, density.

able to complete fracture, The periodicity of these rings coincides with the spacing of the bands.

In a few instances mackerel bands arising from two different sources are observed which, where they meet, appear to cross (see Fig. 3), but this intersection only persists where the two sets of bands meet; usually they do not pass through each other. This is because, once one pattern of strips involving complete interfacial separation is established, the propagation of another across it is bound to be affected by the presence of the first. The wave amplitude of the second disturbance is diminished by interference from the discontinuities formed by the passage of the first wave. Where only "partially fractured" bands occur, and craze–bulk continuity still exists, crossing patterns are more persistent (see Fig. 7) on the final surfaces of fracture.

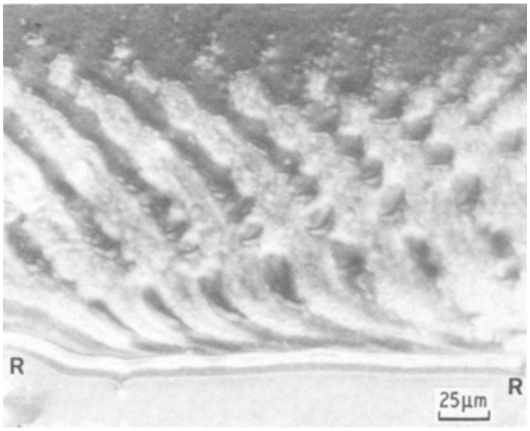

Figure 7 Intersecting sets of mackerel bands where the detached craze wedge lies completely on one surface of fracture. Optical micrograph, Nomarski interference contrast.

3. Coupled interfacial waves

Where interfacial (Stoneley) waves can exist at the boundaries of an embedded layer of finite thickness, the field pattern of the upper interfacial disturbance has a small residual amplitude at the lower interface and vice versa. The two waves interact so that the symmetric and antisymmetric modes have different phase velocities [4]. At the point of initiation of a disturbance the two waves are in phase so that

$$A_{\mathrm{L}} = A \exp(-i\beta_{\mathrm{L}}z) \tag{1}$$

and

$$A_{\mathrm{F}} = A \exp(-i\beta_{\mathrm{F}}z), \tag{2}$$

where β is the propagation constant for the wave travelling in the z-direction parallel to the layer and the subscripts L and F refer to the symmetric and antisymmetric modes, respectively. The waves will not be in phase again until a distance, L, from the origin, equal to

$$(\beta_{\mathrm{F}} - \beta_{\mathrm{L}})L = 2\pi, \tag{3}$$

so that the energy is continuously transferred back and forth from one interface to the other as the disturbance propagates outwards from its point of origination. The propagating disturbance is localized at the interface to give Stoneley waves only under certain conditions (see Fig. 8) of the material properties of the two media. That this is satisfied is difficult to establish in the case of a

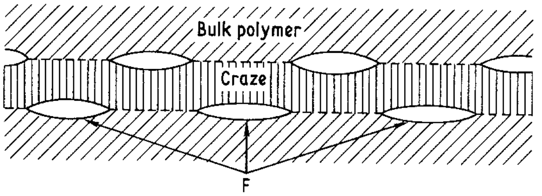

Figure 9 Regions (F) of structural alteration on alternating sides of the craze layer after passage of coupled interfacial stress waves (schematic diagram).

craze layer embedded in bulk glassy polymer since the constitutive properties of the craze are not well established, in addition to the further complication of its anisotropy. However, in view of the known large reduction in density and modulus from the bulk during craze formation, the craze–bulk interface would well satisfy the conditions in the lower quadrant of Fig. 8.

The propagation of the interfacial stress-wave superposes a transient stress increment on the quasi-static stress distribution at the craze–bulk boundary at positions lying alternately on one interface then on the opposite interface as the disturbance propagates. This will produce modifications (including complete fracture) in either the existing craze structure adjacent to the interface, or more likely will produce new craze growth with modified microstructure distributed around the source of the stress-wave pulse in the same pattern. This effect may leave only a distributed pattern of modified craze structure in separate strips and it need not imply a continuous fracture path at this stage. This is the main difference from previous explanations of the mackerel pattern. If the primary crack now propagates through such a modified craze layer (see Fig. 9) it is clear how the different fracture morphologies sketched in Fig. 1 could arise.

Beahan *et al.* [8] have remarked that secondary fracture features are not observed in the region of the surface of fracture where the mackerel pattern appears. This is related to the nature of the initiation and growth of the advance fractures. Those of the unsymmetric type [6] are initiated randomly as narrow channels anywhere along the craze–wedge boundary and propagate at right-angles to the plane of the craze layer. However, they do not swell-out to large cavities until the main crack front is quite close (a distance of a few times the craze thickness). Since the mackerel pattern itself does not begin for some distance from the position of the main crack front at the moment of the brittle craze-boundary fracture transition this excludes the region which would contain the expanded advance fractures from the region of the mackeral bands. The advance fractures are much smaller and are not visisble because they are embedded in the full thickness of the craze layers which are the bands.

Advance fractures of the symmetric type, which Murray and Hull called "events" [9], are initiated in the median plane of the craze and grow to a larger size than the unsymmetric advance fractures for similar positions along the craze

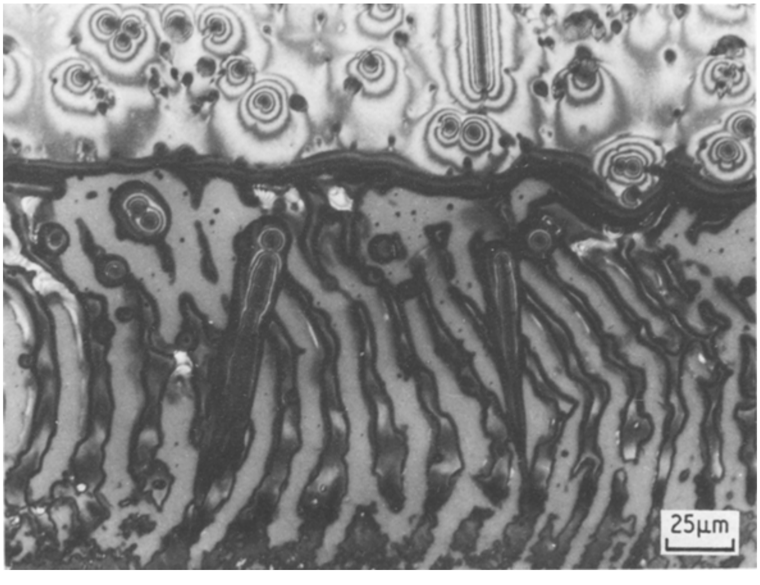

Figure 10 Mackerel bands and advance fractures in an oriented polystyrene. Optical micrograph, $\lambda = 546$ nm.

wedge. The "event"-type of advance fractures can coexist with the mackerel pattern, as can be seen in Fig. 10.

An additional feature of the mackerel pattern mentioned by Murray and Hull and which has also been observed in the present work is the increase in band spacing on the surface of fracture with the radial distance from the source of the stress waves. This effect is observed independently of any changes in the thickness of the layer which would itself be expected to change the spacing through the change in the strength of the coupling between the interfaces. The increasing band-width could arise from the non-linear strain softening in the bulk polymer which, at the craze–bulk boundary, is at the crazing stress. As the wave disturbance propagates away from its source of initiation its strain amplitude must decrease. If the effective elastic modulus is thus increased at smaller wave amplitudes then the phase velocity should also increase. This is consistent with the observation [1] that the band spacing remains approximately constant with increasing distance from the source for fractures at 77 K where more-nearly linear elastic behaviour would be expected.

References

1. J. J. MURRAY and D. HULL, *J. Polymer Sci. A-2* 8 (1970) 583.
2. M. J. DOYLE, *J. Mater. Sci.* **10** (1975) 159.
3. R. STONELEY, *Proc. Roy. Soc.* **A106** (1924) 416.
4. B. A. AULD, "Acoustic Fields and Waves in Solids", Vol. 2 (Wiley-Interscience, New York, 1973) chap. 10.
5. N. FEATHER, "The physics of Vibration and Waves", (Edinburgh University Press, Edinburgh, 1961) chap. 3.
6. M. J. DOYLE, A. MARANCI, E. OROWAN and S. T. STORK, *Proc. Roy. Soc.* **A329** (1972) 137.
7. M. J. DOYLE, *J. Polymer Sci. Polymer Phys. Ed.* **13** (1975) 127.
8. P. BEAHAN, M. BEVIS and D. HULL, *Proc. Roy. Soc.* **A343** (1975) 525.
9. J. MURRAY and D. HULL, *Polymer* **10** (1969) 451.

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