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Striations on polystyrene fracture surfaces formed at elevated temperature

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At low crack velocities fracture in polystyrene occurs by the propagation of a "slot" through the craze layer by a process approximating viscous flow; at higher velocities and higher temperatures there is a tendency for the craze to separate by a process similar to viscous rupture. The two mechanisms may oscillate and the fracture surface then shows clearly defined striations.

1. Introduction

In a previous paper [1] the mechanisms of fracture occurring at different velocities of crack propagation in polystyrene (viscosity-average molecular weight 2 × 10^5) were explained; at room temperature three mechanisms dominate in cleavage fracture, and a fourth appears extensively at room temperature if the fracture is fast (e.g. by bending), and at elevated temperature (e.g. above 80° C). As the crack propagates, two or more of these mechanisms alternate, and a banded surface of fracture arises.

In general, the fracture of amorphous chain-molecule polymers occurs in two stages. First a craze is formed by separation between adjacent molecules or molecule-bundles; the craze is a molecular sponge, the density of which is usually between 30 and 60% of the density of the bulk polymer. Subsequently, either the craze layer is disrupted by viscous sliding between molecule-bundles, or the craze breaks away from the bulk along the craze-bulk boundaries. Where the fracture is extremely fast, it may occur in a practically brittle manner, preceded only by a very thin or practically imperceptible layer of craze.

At low velocities of propagation of the fracture, particularly at the beginning of cleavage, the craze layer parts along its median plane by viscous or viscoelastic flow. It is hardly appropriate to speak of crack propagation in it; what happens is similar to the parting of a layer of oil between two glass plates when these are prized apart. In what follows such a crack in the viscoelastic craze layer will be called a "slot"; its tip is semi-circular or parabolic in shape. The surface of fracture is then smooth apart from the brushmarks formed as the molecule-bundles are laid down at the tip of the propagating slot. At higher velocities the stress for viscous propagation increases and then brittle fracture occurs along the craze boundaries; this is the beginning of fast fracture propagation and the rougher banded surface of fracture is formed. For convenience these regions have been identified as S (slow) and B (banded); where the first change in fracture mechanism occurs is called the transition belt, T, (see, for example, Fig. 4).

The subject of the present paper is a mechanism of craze rupture in polystyrene (viscosity-average molecular weight 2 × 10^5) which occurs extensively at elevated temperatures and which involves disruption of the craze layer by viscous rupture occurring approximately along its median plane. The surface of fracture then has a dull granular appearance when observed in the optical microscope but in the electron microscope, at higher magnification, usually appears quite hairy with the molecule-bundles sticking up from the fracture surface; in contrast, the fracture surface formed by the viscous flow mechanism is smooth and shows brushmarks (Figs. 1, 2 and 5). The details of the texture may vary according to the temperature and the loading history of the craze prior to rupture. The change from propagation of the slot by viscous flow in the craze layer to disruption of the layer by viscous rupture occurs usually as the velocity

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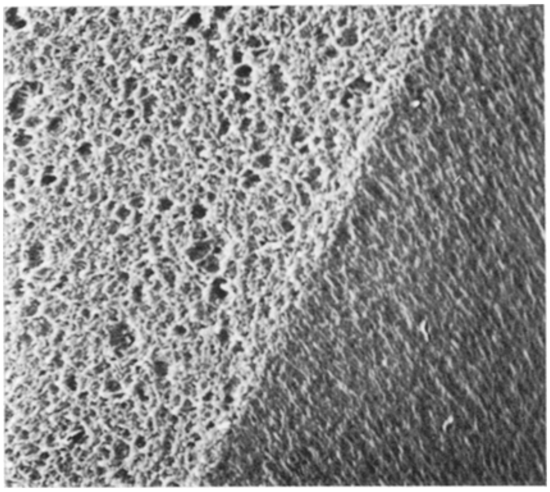

Figure 1 Surface of fracture of polystyrene at room temperature. Transition from parting of the craze layer by viscous flow (right) to separation by viscous rupture (left). Crack propagation from right to left. Scanning EM, × 3800.

of fracture increases. The effect is shown by a layer of a viscous liquid between two glass plates; if the plates are pulled apart quickly, separation does not occur by viscous flow along a single front extending into the layer but by the formation and expansion of many bubbles over an extended area of the layer. In the craze, however, "bubbles" and voids of a few hundred Ångstroms in size are already present even where separation occurs by viscous flow.

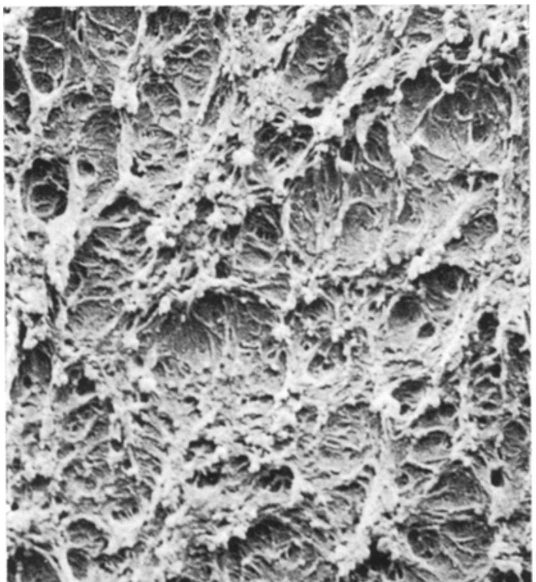

Figure 2 "Hairy" surface of fracture of polystyrene at room temperature. Scanning EM, × 7300.

2. Disruption of the craze layer by viscous rupture

On the fracture surfaces of polystyrene specimens broken in tension at strain rates below 1.3 × 10^{-6} sec^{-1} at room temperature, Murray and Hull [2] have observed a narrow strip between the regions S and T which had a coarse "granular" surface texture consisting of a high density of small cavities. Similar observations have been reported by Bird *et al.* [3] who described the surface as a "coarser non-directional stipple" between the areas of "slow and fast fracture". In the scanning electron micrograph (scanning EM) shown in Fig. 3 the surface, S, is smooth and shows brushmarks, the area, T, which shows a graininess, is part of the transition belt where the craze layer has been stripped away from the

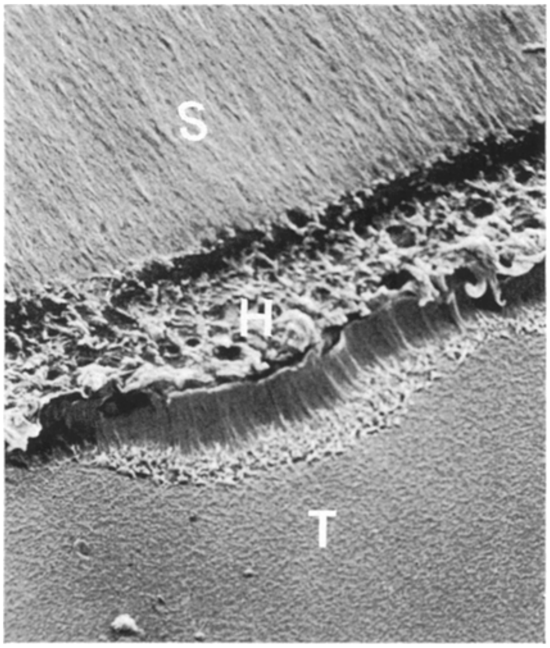

Figure 3 Surface of fracture of polystyrene. Upper left: Smooth brush-marked surface, S, formed by crack propagation near the median plane of the craze; lower right: granular surface, T, where the craze layer has pulled away from the adjacent bulk by fracture along the craze-bulk boundary; area H: irregular "hairy" surface formed by viscous rupture. Crack propagation from left to right. Scanning EM, × 4100.

adjacent bulk; between S and T is a darker band H, more or less co-planar with S, with a quite irregular surface. The surfaces of the area H and T may both be described as granular depending upon the scale of observation; however, the surface, T, is smoother and the graininess less pronounced even in the electron microscope. The area, H appears granular in the optical microscope but it is usually distinctly "hairy" a, higher magnification in the electron microscope, sometimes with distinct holes or cavities (e.g. Fig. 1) in it. It is unlikely that the difference between these two regions is merely that fracture occurs either along the median plane of the craze layer or along its boundary with the bulk; the fracture mechanisms are probably quite different.

Direct observation of the propagation of cleavage fractures with the optical microscope confirmed that the propagation of fracture by the viscous rupture mechanism occurs at a high velocity as has been previously proposed [3]. Occasionally a slowly moving cleavage crack (velocity about 0.1 cm sec^{-1}) at room temperature would suddenly jump forwards to a new position giving an audible click sound; the resulting fracture surface showed a belt of the hairy texture with no trace of the brushmarks evident on the fracture surface both preceding the belt and after it where the crack slowed down. The velocity of fracture propagation by viscous rupture is probably at least an order of magnitude faster than the highest velocity observed for the viscous flow (brushmark) mechanism; the reason being that the disruption of the layer occurs in the former case by localized flow starting at many points simultaneously over a wide belt of the craze layer. The higher fracture velocity in this area is also indicated by the observation that where the advance fractures occur in the hairy belt they are circular [3] for the same reason that they are circular in the transition belt, T [1]. The advance fracture initiated in the craze layer ahead of the propagating viscous slot spreads out slowly from its point of origin along a roughly circular front until it is intersected by the main crack front; if the two fronts propagate at comparable velocities they intersect along a curved line (usually, parabolic, hyperbolic or ensiform depending on the relative velocities) [4]; if the main crack propagates fast enough the line of intersection is a circle.

Bird *et al.* [3] have suggested that the hairy rupture surface arises during the transition from the slow viscous mechanism to the very fast splitting along the craze boundary: the fast crack may run ahead at certain points along its front, spread sideways and then backwards to join up with slower lagging segments of the crack front and so encircle portions of the craze layer. Islands of unbroken craze would then be pulled apart "in a somewhat different manner" because presumably, of their somewhat atypical loading configuration. Although the hairy fracture surface often occurs between the areas S and T, bounded on one side by the brushmark surface and on the other by the fast craze-bulk boundary fracture surface, this is not always the case. As was mentioned previously, in some cleavage experiments the transition from viscous flow to viscous rupture occurs without any possibility of involvement of the fast craze boundary splitting of the transition belt T. The transition from viscous flow to the hairy rupture mechanism is a velocity effect. After the band of hairy fracture is formed the fracture mechanism may revert back to the viscous flow mechanism. This behaviour is even more pronounced at higher temperatures where the fracture surfaces of polystyrene broken by fast bending (by hand) frequently show a regular sequence of alternating smooth brushmarked (slow) and hairy (fast) bands.

3. Bands of "hairy" fracture at elevated temperature

Fig. 4 shows part of the fracture surface of a specimen of polystyrene broken in fast bending at 90°C; the photograph was taken in reflected monochromatic light ($\lambda = 5460$ Å). The dark bands H are fracture surfaces formed by viscous rupture of the craze layer; the lighter bands show brushmarks and are formed by the viscous flow mechanism. The bands are shown at higher magnification in Fig. 5. To the right in the photograph in Fig. 4 is an area, B, of the "fracture bands" of both the "shattering" type and of the "single craze wedge" type [1]; preceding the first band of shattering is the transition belt T. The oblique lines L are moulding defects; they are the boundaries between the pellets from which the specimen was compression moulded [5, 6]. The light and dark stripes lying along the direction of crack propagation in the area, S, arise from a difference in the order of optical interference where the propagating slot parts the craze layer into

Figure 4 Surface of fracture of polystyrene formed at 90°C. Area S: slow crack propagation near median plane of craze; area T: transition belt where craze wedge breaks off along craze-bulk boundary; area B: field of banding, fast propagation; area H: alternating bands formed by viscous flow (light) and viscous rupture (dark). Composite photomicrograph; reflected light, $\lambda = 546$ nm, × 80.

slightly different thicknesses on each fracture surface; the phenomenon is well known on the fracture surfaces of cast polymethylmethacrylate [7] and shows that under some conditions the craze layer is weaker slightly away from its median plane.

The bands all lie perpendicular to the direction of crack propagation and mark the successive positions of the crack front at the moment that the mechanism of fracture changes. In Fig. 4 the width of the bands of viscous rupture decreases away from the middle of the specimen and the bands disappear before reaching the edge of the fracture surface. Also, the boundary which marks the change in mechanism from viscous rupture to viscous flow (deceleration of the fracture) is normally more bowed out in the direction of crack propagation than that marking the beginning of the belt of viscous rupture (acceleration of the fracture).

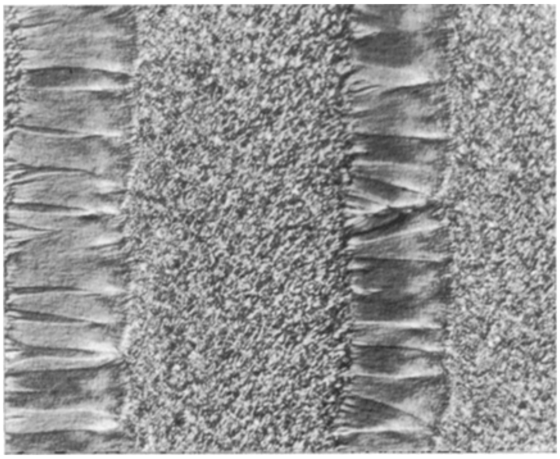

Figure 5 Bands in area H (see Fig. 4). Surface of fracture silver coated; Nomarski interference, reflected light, $\lambda = 546$ nm, × 500. Crack propagation from left to right.

Evidently, the initiation of the viscous rupture process in the craze layer is enhanced by the state of stress at the middle of the crack front. Because of the Poisson's effect the stress is highest at the centre of the propagating crack front and the dilatational component of the stress state is highest at the centre and just ahead of the crack front.

4. Discussion

That the viscous flow mechanism of fracture propagation in the craze layer changes to viscous rupture at higher velocities is not unexpected. As has been previously mentioned the same effect is observed when two glass plates separated by a thin layer of a viscous liquid are peeled apart; at low peeling velocities separation can occur by viscous flow, but at higher velocity formation and expansion of bubbles ahead of the "crack tip" leads to viscous rupture by the thinning and rupture of the segments of liquid between the bubbles. The fracture may be fast because it starts simultaneously at many points along and ahead of the fracture front.

The surface of fracture shown in Fig. 4 shows, however, an alternation of the viscous flow and viscous rupture mechanisms; evidently, the fracture must slow down after each band formed by viscous rupture and reverts back to the slower viscous flow process. At the relatively low speeds involved (10 cm sec^{-1}) inertia effects would not be important. Furthermore, if the width of the transition belt, T, is an indication of the length of the craze wedge ahead of the propagating crack (which appears to be the case at room temperature at least), then the width of the bands is probably less than the length of the craze wedge; the viscous rupture mechanism is not sustained long enough to propagate through the entire craze layer ahead of the viscous slot.

The craze has a much lower density than the bulk; it contains an interconnecting network of voids a few hundred Ångstroms in size [8-11]. In unbroken crazes in bulk polystyrene the void content of the craze at room temperature is about 40% [12]. During the process of fracture the craze layer ahead of the propagating slot is considerably stretched and the void content probably increases mostly by the expansion of the existing voids in the craze rather than by the nucleation of new voids. This would apply even at low fracture velocities where the viscous flow mechanism occurs. On stretching, the craze wedge changes from an open celled sponge at its edge to a highly oriented reticulated foam; an expanded network of molecule-bundles. After fracture the ruptured craze layer which remains on the surface of fracture has a void content of 70% or more [13].

From Fig. 1 it appears that the craze layer in the viscous rupture region contains voids of about 0.5 μm in size as previously has been reported by Murray and Hull [2] and by Bird *et al.* [3] in their observations of the "coarse granular" regions. The mechanism of fracture changes from viscous flow to viscous rupture when, at some critical stage, the void structure in the craze layer just ahead of the slot starts to expand at an accelerated rate by the rupture of the strings in the network. The process has been called "void coalescence" by Murray and Hull. Further opening of the walls of the crack necessary for continued propagation of fracture is then accommodated by expansion of the bubbles in the craze layer without further propagation of the viscous slot. At first the expansion of the bubbles can reduce the load bearing capacity of the craze layer at that point and spread the region of high stress forward into the craze layer where more bubbles are formed. In a simple liquid the walls between the bubbles rapidly thin out and rupture; in the case of a high polymer, however, the thinning action causes orientation of the molecules within the segments which may therefore still carry significant load. At high temperature the strings may pull out to relatively high elongation before rupture. As the belt of viscous rupture extends forward, it can still carry a significant load but one which is distributed over an increasingly large area in the fracture belt. Eventually the stress ahead of the viscous rupture belt falls below the critical level required for rapid expansion of the voids in the craze layer and the viscous rupture mechanism cannot be sustained. After it is initiated rapidly over a belt ahead of the viscous flow slot the fracture is slowed down and reverts back to the flow mechanism. As the slot extends further under the applied stress it accelerates, a new belt of viscous rupture is initiated and the process is repeated.

Acknowledgements

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