thicker. Obviously this does not result from bulk transport of complete plates but by a process of plate elimination as shown in Fig. 3. Certain plates are consumed by their immediate neighbours, a process being initiated by local perturbations. This mode of growth does require some variation in the plate thicknesses, possibly of a greater degree than existed originally, but the degree of variation is not sufficiently great to conflict with the observations.

Acknowledgement

This research was sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation.

References

1. J. W. CAHN, *Acta Met.* **9** (1961) 795.
2. *Idem, ibid* **10** (1962) 179.
3. S. AGARWAL and H. HERMAN, *Scripta Met.* 7 (1973) 503.

Received 8 November 1974
and accepted 28 January 1975

R. O. WILLIAMS
Metals and Ceramics Division,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee, USA

The effect of voids on the brittle failure of polystyrene

Owing to the technological importance of high impact polymers, there has been much work on the role of small elastic particles in modifying the properties of thermoplastics [1, 2]. The work described here, which was largely incidental to a study of hole growth in polymers [3] has been useful in examining a limiting case of this problem, that of a thermoplastic containing voids.

Spherical voids, 0.20 mm radius and occupying a volume fraction of 0.189, were produced in 4 mm thick sheets of polystyrene by degrading the material by an annealing treatment of 30 min in air at 393 K. The number average molecular weight as determined by the conventional G.P.C. techniques was found to be 68 000 compared with a number average molecular weight of 72 700 before degradation. The similarity of these molecular weights suggests that large quantities of monomer or dimer were not being produced, and this is borne out by the fact that the observations of monomer production have generally been made at temperatures between 580 and 775 K [4, 5]. A likely process is the production of steam from absorbed water vapour or the degradation of excess catalyst which remains in the polymer. Such reactions would not significantly change the molecular weight, which is an important factor in determining the strength of polymers. The effect of this variable has been investigated by Vincent [6]; and using his data it may be concluded that molecular weight changes such as occur in the present case have a negligible effect on the fracture of polystyrene. It is thus proposed to attribute any difference in the behaviour of the degraded and undegraded material to the effect of the voids in the latter.

At room temperature polystyrene is a hard brittle solid which at the strain rate used in the work (6.6×10^{-4} sec^{-1}) behaves in an approximately elastic manner up to fracture. The introduction of small spherical cavities by degradation produces sites of stress concentration to which the analyses by Southwell and Gough [7] and also Goodier [8] may be applied. Using the usual cylindrical co-ordinate system with the notation of Southwell and Gough in which a uniaxial stress is applied along the Z axis, the greatest stress concentration occurs on the equator of the void where $\sigma_{ZZ} = 2\ 1/16\sigma^{\infty}$, $\sigma_{rr} = 0$, and $\sigma_{\theta\theta} = 3/16\sigma^{\infty}$ (taking Poisson's ratio as 1/3 and σ^{∞} as the applied stress). It is at this point that the crazes are nucleated and begin to grow radially as shown in Fig. 1. Owing to the concentration of stress, craze nucleation occurs at significantly lower overall applied stresses than in the undegraded material. Despite this fact, the fracture stress of the undegraded material is comparable with the original. In fact, if the average stress on the matrix is considered and the fracture stress of the degraded material raised by a factor of $(1 - f)^{-1}$ where f is the volume fraction of holes, its fracture stress becomes significantly greater than that of the undegraded specimens as shown in Fig. 2.

Examination of the fracture surface showed the usual features which have been discussed by Hull and Murray [9], and Fig. 3a emphasizes the

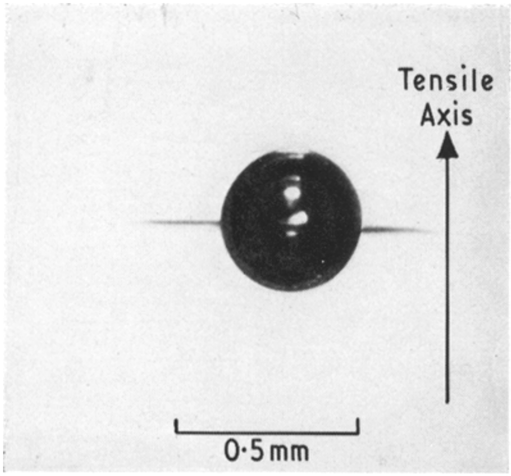

Figure 1 Craze nucleation at the equator of a void under tension.

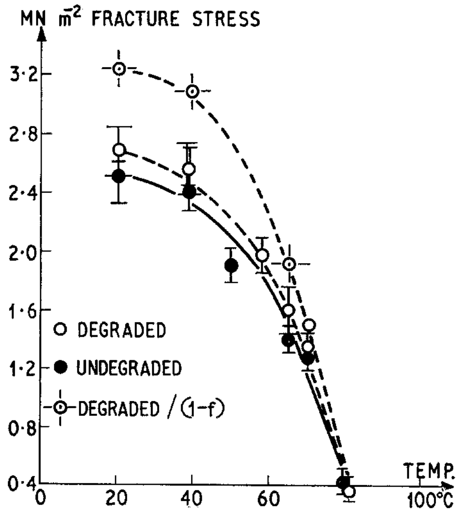

Figure 2 Fracture stress of degraded and undegraded polystyrene.

symmetrical circular manner in which the craze growth and crack propagation manner occur in the undegraded material. In contrast the degraded material frequently showed configurations similar to the one shown in Fig. 3b. In this case, fracture has started by the stable growth of a craze from the void in the lower right corner of the micrograph. However, the symmetrical growth of the craze has been interrupted by meeting the second void which it has been forced to bow around. Similarly, when unstable crack propagation occurred the "hackle" marks also suggest that the crack has been temporarily arrested at the void possibly because the structure of craze has not reached an advanced stage.

In the particular case shown in Fig. 3b a craze has approached a void along a plane which in the present notation is defined by $Z = A$ (A being the void radius). The stress σ_{ZZ} acting across this particular plane and other parallel planes is shown in Fig. 4a. As the radius of the void is very much larger than the craze tip radius, it is reasonable to assume that these stresses are not unduly disturbed by the approaching craze, and that the stress σ_{ZZ} just in front of the craze is a factor which determines whether or not the craze continues to grow. Thus a craze approaches a void on the planes indicated in Fig. 4 it moves into a region of decreasing tensile stress in which

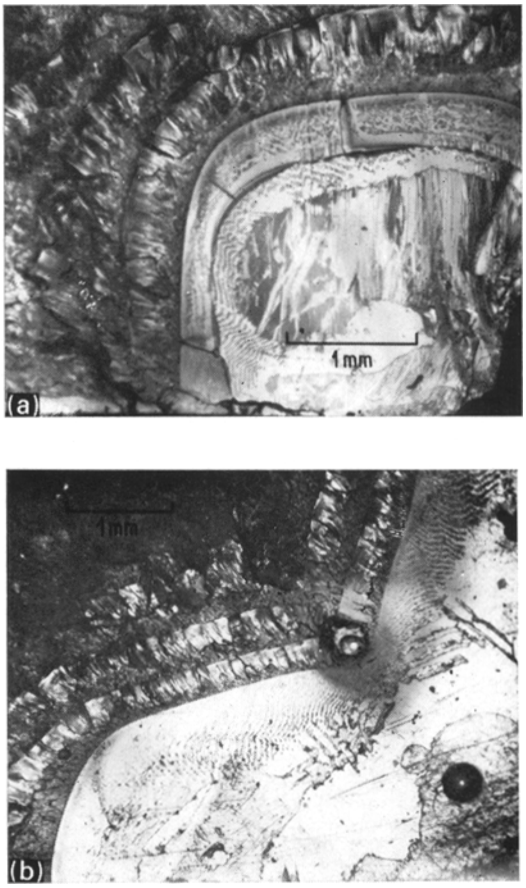

Figure 3 (a) Fracture surface of undegraded polystyrene tested at 293 K showing symmetrical craze growth. (b) Fracture surface of degraded polystyrene tested at 333 K showing the effect of voids in inhibiting craze growth.

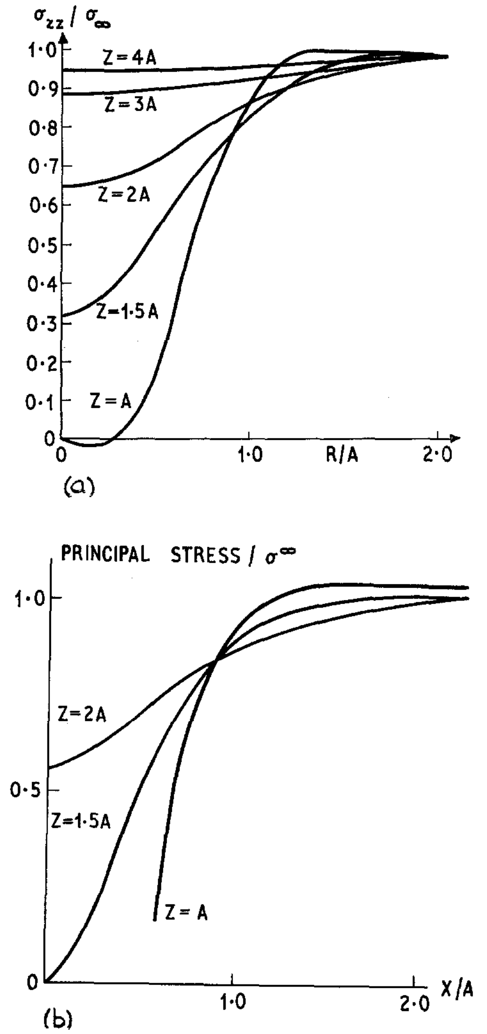

Figure 4 (a) Axial stress σ_{ZZ} normalized with respect to the applied stress σ^∞ as a function of distance from the void using cylindrical co-ordinates. (b) The major principal stress across the minor principal stress trajectories, which start at $Z = A$, $1.5A$, and $2A$, distant from the void.

it must eventually stop. The particular craze shown in Fig. 3b stopped at $R = A$ where the stress starts to drop severely. On this basis, there are regions extending for two or three radii above and below voids where the stress field inhibits craze growth. Similarly the further growth of crazes which break into the void surface is expected to be inhibited by the change in geometry. Both of these effects limit craze growth and account for the high fracture stress of degraded polystyrene.

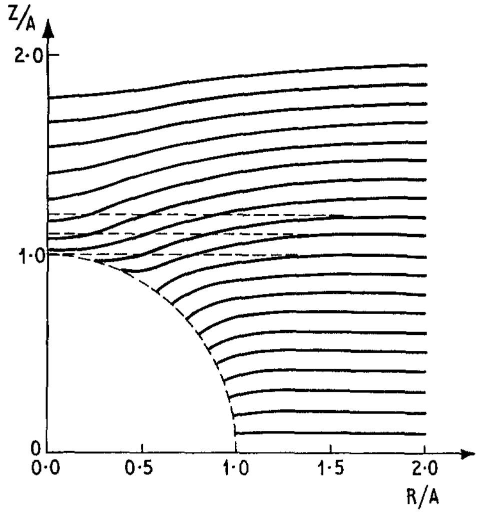

Figure 5 Principal stress trajectories around a spherical void computed from the anslysis of Southwell and Gough [7].

Examination of the mirror area in Fig. 3b showed that it was not planar in the vicinity of the void. In fact, in view of the observation of Sternstein *et al.* [10] that crazes grow along the trajectories of minor principal stress, the craze, and following crack path in the vicinity of a void would be expected to be those shown in Fig. 5, and the fracture surfaces which have been observed experimentally are consistent with these trajectories. It is then more reasonable to take the size of the major principal stress in front of the craze as a criterion of craze growth rather than σ_{ZZ}. This is plotted along the minor principal stress trajectories indicated in Fig. 4b. However, at the points at which crazes have been observed to halt (such as $R = A, Z = A$ in Fig. 3b, this introduces a small change but does not alter the trend of the results. Both the major principal stress and the hydrostatic stress component which may also effect craze growth decrease in the regions above and below the void.

In the "hackle" region which results from unstable crack growth, voids also deviate cracks from a planar path and, as before, cracks which would not be expected to intersect voids do so, as shown in Fig. 6. In this case, the fracture surface, which at several radii from the void is planar and can be described by $Z = 1.35\ A$, is deviated until it breaks into the void surface. Although the trajectories of the principal planes cannot entirely account for the effect, they may be instrumental in bringing the crack closer to the void. However, voids do not appear to signifi-

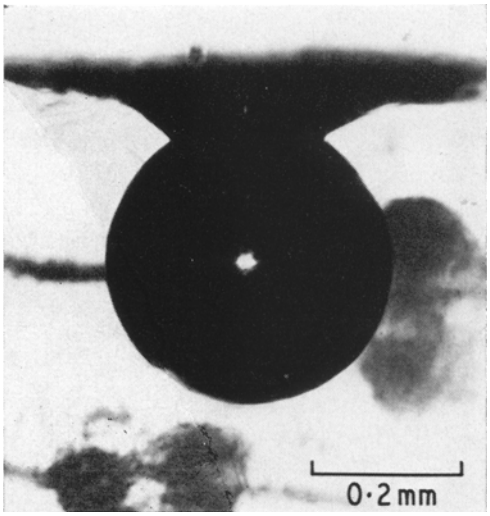

Figure 6 A transmitted light micrograph showing the way in which planar cracks are deviated in the presence of voids.

cantly retard the rapidly moving cracks characteristic of the "hackle" region. The "slip-stick" marks on the surface indicate that the crack may bow slightly at voids as shown in Fig. 7 but there is a great deal of scatter on these observations, and the major feature of crack-void interactions in this region is the long steps in the fracture surface left trailing behind voids after a crack has passed.

Similar effects to those described here may also be expected in thermoplastics containing particles whose elastic modulus is less than that of the matrix. In particular, the low stress region above and below low modulus particles may have an effect on the properties of more technologically important particle modified materials than the one described here.

References

1. G. B. BUCKNELL, *British Plastics* **40** (1967) 84.

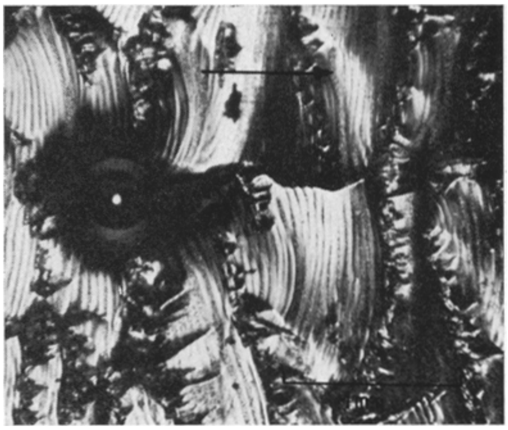

Figure 7 Fracture surface showing the interaction of a moving crack with a void. The direction of crack propagation is indicated by the arrow.

2. L. E. NIELSEN, "Mechanical Properties of Polymers" (Reinhold, New York, 1962).
3. J. W. HANCOCK, University of Glasgow, Internal Report (1974).
4. S. L. MADORSKY and S. STRASS, *J. Res. Nat. Bur. Stand.* **40** (1948) 417.
5. P. BRADT, V. H. DIEBLER and F. MOHLER, *ibid* **50** (1953) 201.
6. P. I. VINCENT, *Polymer* **1** (1960) 425.
7. R. V. SOUTHWELL and H. J. GOUGH, *Phil. Mag.* **1** (1926) 79.
8. J. N. GOODIER, *J. Appl. Mech. Trans. ASME* **55** A–39 (1933).
9. J. MURRAY and D. HULL, *J. Mater. Sci.* **6** (1971) 1277.
10. S. STERNSTEIN, L. ONGCHIN and A. SILVERMAN, Appl. Polymer Symp. Vol. **7** (Interscience, New York, 1969) p. 175.

Received 22 November 1974
and accepted 24 January 1975

JOHN HANCOCK
Department of Mechanical Engineering,
University of Glasgow, UK

The structure of the high pressure phase in cis*-polyisoprene*

In studies of the crystallization of polymers under high pressure, two new crystalline forms have been reported, one in *cis*-polyisoprene [1, 2] and one in polyethylene [3-5]. The morphological form of both species is similar, being ellipsoidal (oblate or prolate) although the species in polyethylene are up to a thousand times larger than those in *cis*-polyisoprene (Fig. 1). Precise identification of these phases is difficult since in neither case may the phase be maintained at atmospheric pressure and room temperature. With *cis*-polyisoprene we have recently succeeded, by quenching to 0°C before releasing the pressure, in producing a stable specimen. The specimens, which as detailed previously [1, 2] were in the form of thin films supported by electron microscope grids, were stored in liquid nitrogen prior to performing the electron microscopy. Electron diffraction