

Surface Morphology of Polystyrene Fractured in Liquids. II

B. L. EARL,* *Yarsley Research Laboratories Limited,
Chessington, Surrey*, M. CROOK, *Polytechnic of the South Bank,
London, S.E.1.*, R. J. LONERAGAN, J. H. T. JOHNS, and
J. MARKHAM, *The Royal Armament Research and
Development Establishment, Fort Halstead, Kent, United Kingdom*

Synopsis

Polystyrene has been fractured in tension at two temperatures in *n*-heptane and *n*-propanol and the fracture surfaces studied by optical and scanning electron microscopy. The test temperatures were selected such as to be approximately 20°C above and below the temperatures at which it was expected¹ that a glass-to-rubber transition would occur in the solvent-penetrated craze material. It was found that features of the fracture process and also structure of the fracture surfaces were different at the two temperatures. These changes have been interpreted in terms of a T_g occurring in the craze material.

INTRODUCTION

In a previous paper,² we described early studies of the morphology of surfaces produced by fracture of polystyrene by flexure at normal temperature after moistening the surface with alcohol. Concurrently with that work, the minimum strain to craze polystyrene in alcohols and *n*-heptane was measured as a function of temperature, and it was found that this correlated with the softening effects of these liquids.¹ The results from the latter experiments suggested that a glass-to-rubber transition was occurring in the polystyrene craze at about 12.5°C in *n*-heptane and 45–46°C in methanol, ethanol, and *n*-propanol. It was expected that this transition would have an effect upon craze fracture properties and the morphology of the surface produced, and therefore fracture surfaces produced above and below this temperature have been studied.

EXPERIMENTAL

The polystyrene used was Carinex GP (Shell Chemicals Limited suspension polymer, $\bar{M}_w = 2.3 \times 10^5$, $\bar{M}_n = 1.05 \times 10^5$; data supplied by Shell Carrington Plastics Laboratory). This was compression molded at 200°C

* Present address: I.A.C.E., Sherborne House, Sherborne, Nr. Cheltenham, Glos., United Kingdom.

into sheets 1.1 ± 0.1 mm thick from which dumbbell test pieces approximating to BS.903 Type E were prepared by bandsawing, filing to a template, and finishing the cut edges with fine emery paper. Care was taken, throughout the test piece preparation, to avoid scratching the molded surface. Before test, the dumbbells were annealed for 2 hr at 87°C followed by cooling to room temperature over about 10 hr.

The liquids used in the tests were methanol, ethanol, *n*-propanol, and *n*-heptane and were all of laboratory reagent quality.

Dead load tests were carried out in *n*-heptane at -10°C and 35°C and in *n*-propanol at 23°C and 65°C , i.e., approximately 20°C above and below the expected transition temperature of polystyrene craze in each liquid. A limited number of tests were also made using methanol and ethanol at 23°C and 65°C . For each test, the sample was thermally equilibrated in air at the test temperature before applying the load and then immediately immersed in the test fluid. After fracture, the surfaces were examined by optical microscope and were then dried of solvent under vacuum at room temperature at least overnight. They were subsequently gold-palladium coated and examined in a Stereoscan Mark I scanning electron microscope.

RESULTS AND DISCUSSION

The structures observed were quite different depending upon whether the test temperature was above or below the anticipated transition temperature of the solvent craze. These two temperature regions will therefore be described separately.

Morphology Below the Craze Transition Temperature

The results to be described are related to data which were discussed previously.² In our previous work, samples were fractured by flexing at room temperature after moistening with an alcohol; the temperature and environment was therefore exactly the same as in one series of the present experiments (23°C in *n*-propanol). The surface features differ somewhat in the two experiments because of the different fracture modes, however, which lead to different stress sequences on the craze and at the craze tip. In the tension tests, if the craze has appreciable strength (as is the case below the transition temperature), it may not fracture immediately it forms because the stress concentration moves with the craze tip,³ and there may not be sufficient stress remaining in the craze to fracture it. It is therefore possible to obtain a stable craze in a test piece under tension.

In flexure, the situation is different; movement of the craze tip causes further stress to be applied to the craze. Hence, in the flexure test, the crack tip tends to follow the craze tip, and the stress at the tip continuously increases as the craze extends. Thus, different fracture characteristics and slightly different surface features were observed in the two tests.

When the dumbbells were fractured in tension at temperatures below the anticipated transition, the types of surface feature observed varied as

the applied stress was increased. At the lowest stress which would cause fracture, the surfaces were almost featureless under the optical microscope (stress 3.2 MN/m^2 in *n*-heptane, $\sim 10^4$ sec to break; 5.0 MN/m^2 in *n*-propanol, $\sim 10^5$ sec to break). Under the scanning electron microscope, the fracture surfaces had a slightly irregular cellular structure (Fig. 1) which was similar over the entire surface.

As the fracture stress was increased, the surface became more complex, with the appearance of secondary fractures and regions with features identical to slow and fast fracture surfaces produced in air at the test temperatures.^{2,4} At the highest stresses used (15.5 MN/m^2 in *n*-heptane, 6.5 sec to break; 17 MN/m^2 in *n*-propanol, 15 sec to break), the surface had a shattered appearance under the optical microscope because of the large number of facets which it comprised. Upon examining these samples in the scanning electron microscope, it was found that the fracture surfaces were composed mainly of three types of structure, two of which appeared to be due to stress acting in the presence of solvent and the third being a dry-fracture type of slow crack region. Sometimes the other two typical dry-fracture regions corresponding to fast fracture⁴ were also seen.

A sample fractured in the below-transition temperature range at an intermediate stress is shown in Figure 2. (This sample was broken at 23°C in *n*-propanol with an applied tension of 9.0 MN/m^2 .) Both the fracture surfaces are shown in Figure 2a, and each of these contains three

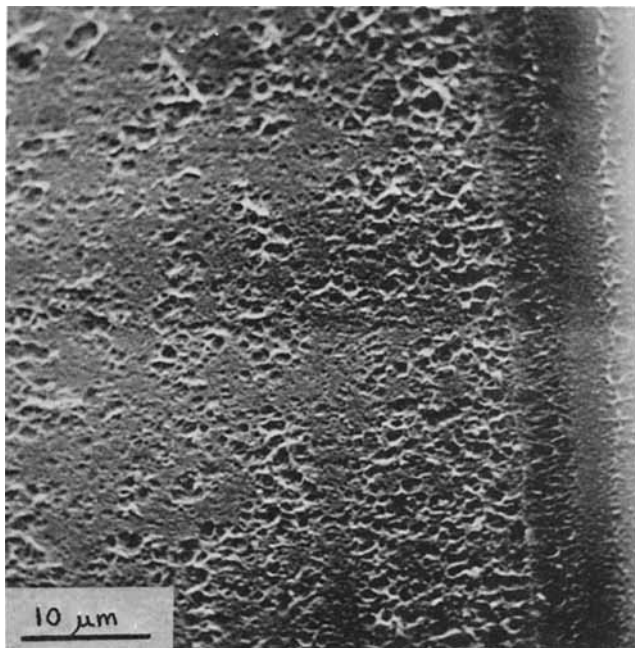
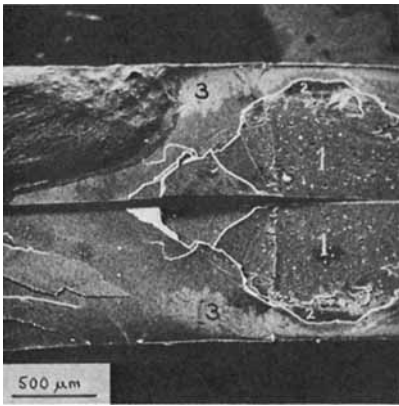
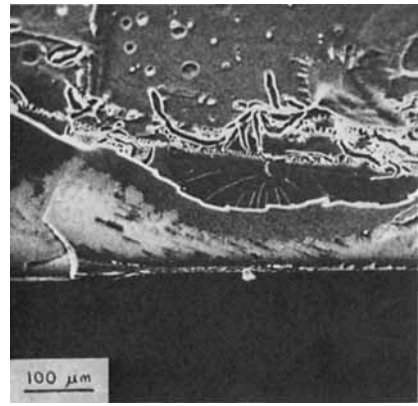


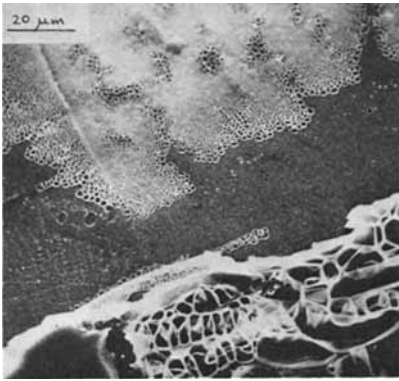
Fig. 1. Polystyrene broken in methanol showing structure typical of low-stress fracture in a low-temperature test (applied stress 7.2 MN/m^2 , 5×10^3 sec to break at 23°C).



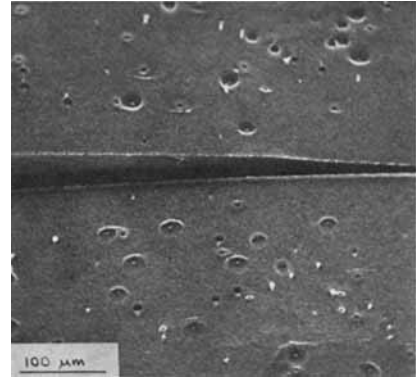
(a)



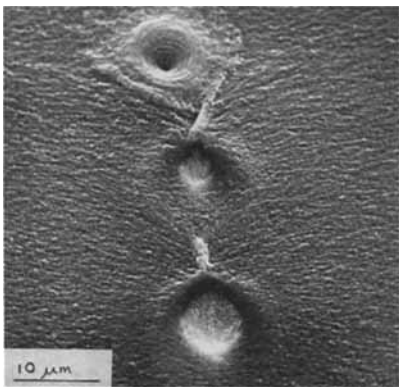
(b)



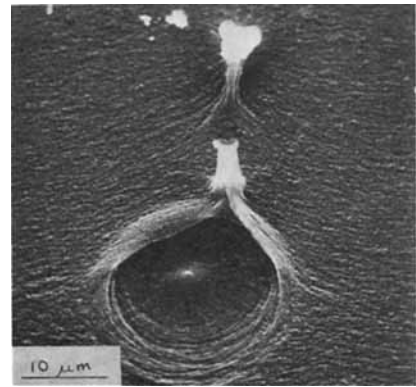
(c)



(d)



(e)



(f)

Fig. 2. Polystyrene fractured in *n*-propanol at 23°C. (Applied tension 9.0 MN/m², 152 sec to break): (a) both surfaces; (b), (c) and (d) detail from (a). The areas in the matching micrographs (e) and (f) are from the left side of (d).

principal regions, marked 1 to 3 in the micrograph. (The dark area near the upper left is graphite used to improve conduction away of surface charge.)

In region 1 of Figure 2a, the presence of secondary fractures suggests that crack growth was slow; and the ductile appearance of the surface, Figure 2f, indicates that the craze through which the crack grew had been plasticized by the alcohol. The wrinkled surface could have developed during evaporation of the propanol. The corresponding secondary fractures on the two matching fracture surfaces frequently do not match well (Figs. 2d, e, and f). Sometimes a tube-like feature corresponds to a saucer-shaped depression on the other face. We believe that these features form in the manner shown in Figure 3.

Region 2 of Figure 2a is typical of a slow crack growth region on a dry-fracture surface, i.e., it is due to fracture ahead of the solvent front, a phenomenon which has been reported previously on samples fractured in alcohol.²

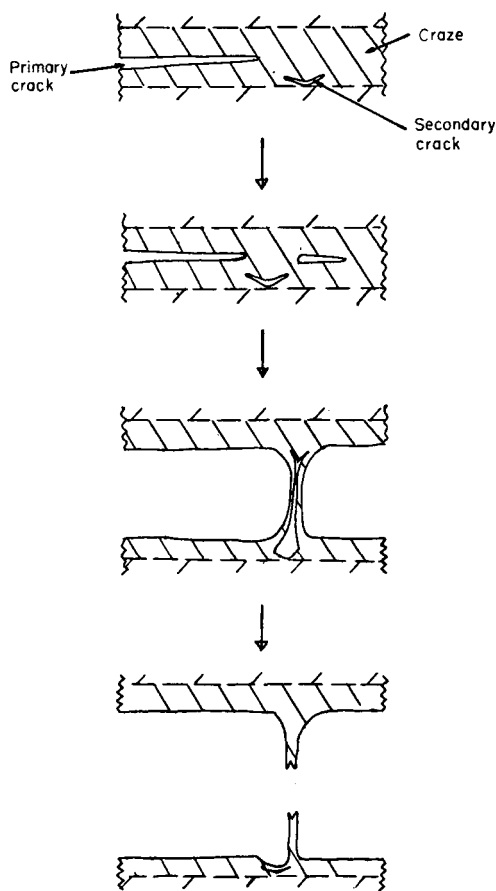


Fig. 3. Formation of a secondary fracture in solvent craze.

Region 3 is largely featureless, even at high magnification in the scanning electron microscope, but contains areas of coarse cellular structure which are believed to form under conditions of high solvent content and low stress.² This is based upon the theory⁵ that during craze formation a greater or smaller number of voids form depending upon the stress acting. If the crazing stress is small, only few voids form, and these become relatively large.

It is possible tentatively to suggest a series of events leading to the morphology shown in Figure 2; crazes probably grew concurrently in the two large regions (1 and 3) until their stress fields interfered. Region 1, which contains secondary fractures, is considered to be the first of these regions to have fractured. This crack probably grew slowly until near the boundary with region 3 and then stopped. Because of the low stress and ready availability of propanol ahead of this crack, a number of large voids formed (shown near the middle of Fig. 2b). A dry fracture then initiated at the center of region 2 and grew radially.

The stress causing the growth of the craze in region 3 decreased as the craze in region 1 was approached. Near to the boundary with regions 1 and 2 and the free surface, the cellular structure is seen to have coarsened (Fig. 2c). This suggests a reduction in stress, slowing down of craze formation, and excess of propanol, all of which appear reasonable. The dark band across the middle of Figure 2c corresponds to the pitted structure which we have suggested² is formed by relaxation of a "supersaturated" craze. Region 3 probably fractured by fast crack growth since the surface exhibits relatively little evidence of ductility.

Morphology Above the Craze Transition Temperature

Tests in the temperature range above the expected T_c of the craze material differed from the low-temperature tests in that a different morphology resulted and also in that the types of surface feature produced were independent of the applied stress. Similar features were observed on fracture surfaces after tests in *n*-heptane at $35 \pm 1^\circ\text{C}$ at 4.6 MN/m^2 (2.8 sec to break) to 1.7 MN/m^2 (13 sec to break) and in *n*-propanol at $65 \pm 2^\circ\text{C}$ at 5.5 MN/m^2 (8.1 sec to break) to 1.8 MN/m^2 (15 secs to break). Below these lower stress limits, frequently the samples did not break. It will be apparent from these figures that fracture occurred after a shorter time than in the low-temperature tests.

Figure 4 is a typical optical micrograph showing both fracture surfaces. On each surface, the triangle between the center and the right edge corresponds to dry fracture, and the features in this region are identical to what are observed after fracture of polystyrene in air at this temperature (65°C). The remainder of the surface is formed from solvent crazes which have grown inward from the upper and lower edges.

The series of micrographs of another surface in Figure 5 shows the structure increasing in coarseness and the craze increasing in thickness from the

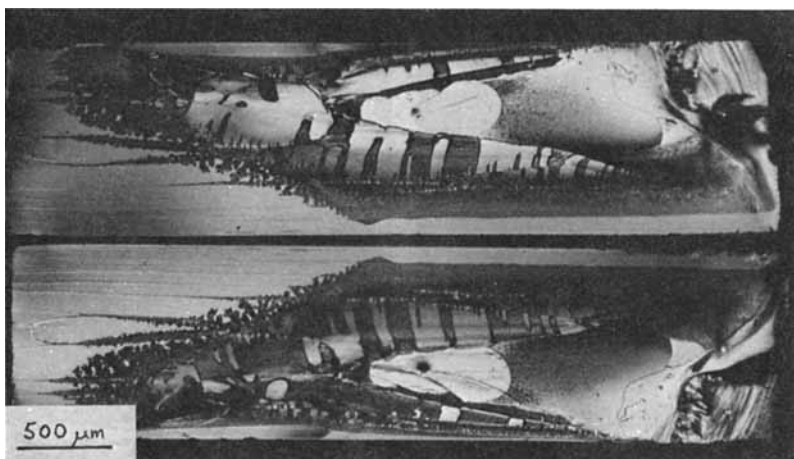


Fig. 4. Optical micrograph of both surfaces of a polystyrene sample broken in *n*-propanol at 65°C. The triangular region extending from the right edge to the center of the test piece corresponds in structure to dry-fracture. The remainder of the surface is formed by fracture through a solvent craze (applied tension 2.4 MN/m², 13 sec to break).

edge of the sample to the solvent front. Figure 5d shows detail of the stretched porous craze structure near the solvent front.

Test pieces broken at 35°C in *n*-heptane had a similar appearance under the optical microscope to the pieces broken at 65°C in propanol, but under the scanning electron microscope the craze layer was seen to be thinner. Figures 6a and b are comparable to Figures 5b and d, respectively, with regard to position on the fracture surface.

Referring back to Figure 4, we believe the sequence of events occurring during fracture, within the temperature range in which the solvent craze is expected to be rubbery, is as follows: Under the influence of the stress and the plasticizing effect of the liquid, crazes grow inward from points on the test piece surface. If these crazes are composed of rubbery polymer, they will not be load bearing, and the average stress in the uncrazed cross section will increase as the crazes grow inward until the dry-crazing stress is exceeded. At this point, fracture initiates in the uncrazed cross section and is immediately followed by rapid fracture through the solvent craze. The sequence is indicated by the fact that in the dry-fracture regions there are always zones of slow and fast fracture, but in the solvent fracture regions the structure always suggests fast crack growth. Evidence for fast fracture in the solvent region is provided by the craze material having been thrown into folds (Fig. 6b) and by overlapping crack growth on two planes within a single craze which we have observed many times (e.g., Fig. 5d).

It might be expected that the stress at the tip of a nonload-bearing craze would increase as the craze grew so as to cause accelerating craze growth and an increasingly fine-cell structure; but in practice the reverse of this is

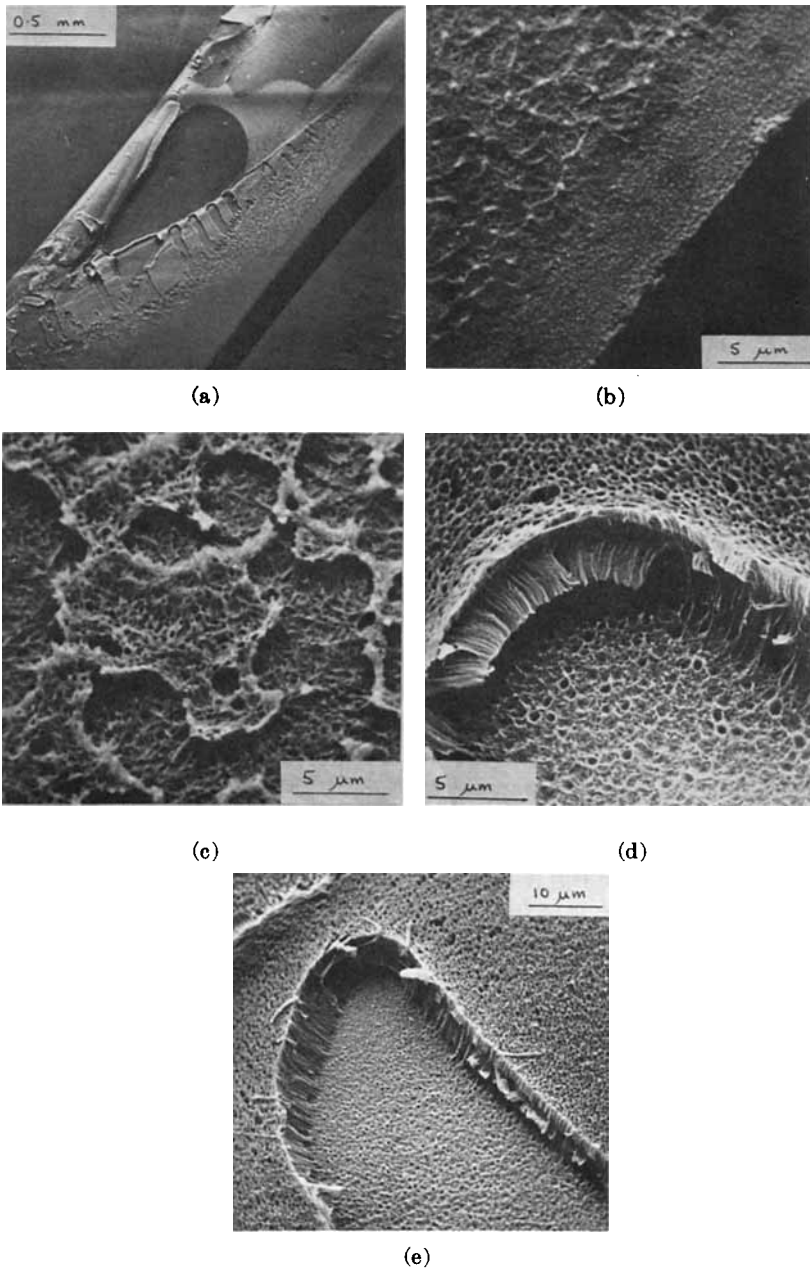


Fig. 5. Polystyrene surface after fracture in *n*-propanol at 65°C (2.9 MN/m², 13 sec to break): (a) general view; (b), (c), (d) and (e) detail of regions progressively further from the molded surface; (b) shows the intersection of fracture surface with the molded surface; (e) shows the tip of the solvent craze and a triangle of dry-fracture surface in the top left corner.

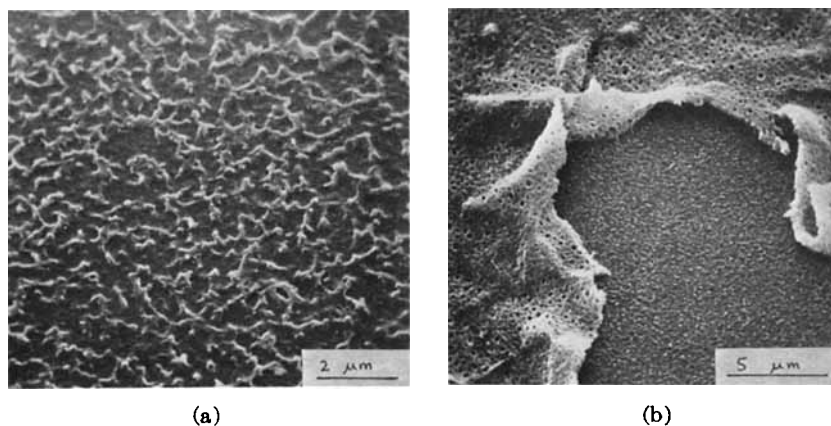


Fig. 6. Detail from a fracture surface of a polystyrene test piece broken in *n*-heptane at 35°C (3.3 MN/m², 3 sec to break): (a) and (b) are approximately comparable with Fig. 5(b) and 5(d) with regard to position on the fracture surface. The overall appearance of the surface was similar to 5(a) at low magnification, excepting for minor differences in the dry-fracture regions due to the lower test temperature.

observed. The craze tends to slow and the craze cell size tends to increase as the craze area extends. There appears to be a reducing stress concentration at the craze tip due to an increasing craze tip diameter, as is shown in the series of micrographs in Figure 5 (where the effect is seen as an increase in craze thickness toward the craze tip). This progressive thickening of the craze tip is not really understood but is believed to be associated with relaxation of the solvent-penetrated polymer ahead of the craze tip.

The authors are grateful to Mr. L. W. Turner for valuable discussions. This work was supported by the Ministry of Defence Procurement Executive.

References

1. B. L. Earl, Ph.D. Thesis, Polytechnic of the South Bank; B. L. Earl, R. J. Loneragan, J. H. T. Johns, and M. Crook, *Polym. Eng. Sci.*, in press.
2. B. L. Earl, R. J. Loneragan, J. Markham, and M. Crook, *J. Appl. Polym. Sci.*, **18**, 245 (1974).
3. E. H. Andrews and L. Bevan, *Polymer*, **13**, 337 (1972).
4. J. Murray and D. Hull, *J. Polym. Sci. A-2*, **8**, 583 (1970).
5. A. N. Gent, *J. Mater. Sci.*, **5**, 925 (1970).

Received June 22, 1973