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The effect of temperature on the deformation and fracture of polystyrene

J. HOARE, D. HULL
Department of Metallurgy and Materials Science, University of Liverpool, UK

Tensile and compression tests have been carried out over a range of temperatures between 78 and 360 K to determine the micromechanisms of deformation and the mode of fracture. In compression, deformation occurred by shear band propagation whereas, in tension, deformation was restricted to crazing followed by fracture. Anomalously low crazing stresses were observed for tests on specimens immersed in liquid nitrogen. Analysis of the mechanism of fracture confirmed previous work relating crazing and fracture and the fracture model has been modified slightly to take account of additional features observed in failure of crazes at high temperatures.

1. Introduction

Several attempts have been made to relate the features found on polymer fracture surfaces to the operative fracture mechanisms (see, for example [1, 2]. From a study of the fracture surfaces of polystyrene fractured at room temperature, Murray and Hull [3–5] and Hull [6] proposed mechanisms for the initiation and growth of cracks in this material.

Bird and co-workers [7] studied the fracture surfaces of injection-moulded polystyrene using high resolution replica techniques. Many of their observations were on a much finer scale than those of Murray and Hull but were complementary to them. More detailed work on the fracture morphology and its relation to craze microstructure has been described recently by Beahan *et al.* [8, 9] and Doyle *et al.* [10].

Little work has been reported on the effect of temperature on the mechanisms and morphology of fracture of polystyrene although the effect of temperature on the crazing and compression behaviour has been reported by a number of workers [11–15]. These studies have, however, been restricted to a small temperature range [11–14] or an unusual specimen shape [15].

The present work set out to study the effect of temperature on the mechanisms of fracture of polystyrene to determine whether or not the models proposed by Murray and Hull could be applied to conditions other than room temperature.

2. Experimental

Rectangular sheets, measuring approximately 100 mm × 100 mm × 3 mm were compression moulded at 453 K from extruded nibs of Shell SB 59 Carinex, $\bar{M}_v = 1.73 \times 10^5$. The sheets were slowly cooled in the press to about 313 to 323 K and then air cooled.

For compression tests, specimens in the form of rectangular prisms measuring approximately 2 mm × 2 mm × 6 mm were prepared from the sheet. All of the faces of the specimens were ground with successively finer grades of silicon carbide paper and finally polished with gamma alumina. Because of the difficulties of avoiding premature failure in the grips tensile specimens were designed which had the shape shown in Fig. 1. The machined faces of specimens were polished using similar procedures to those described above for compression specimens. The tensile specimens were held in angled-channelled grips which were machined to mate with the specimen ends. It was

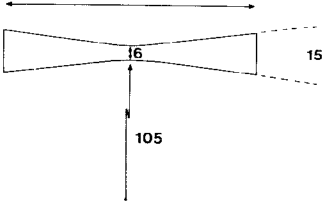

Figure 1 Shape and dimensions of tensile specimens (in mm).

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found that, using this test assembly, premature failure of the specimens at the grips at low testing temperatures could be eliminated almost entirely.

Compression and tensile tests were carried out over the temperature range 78 to 360 K in an Instron machine at a cross-head speed which corresponded to a strain-rate of $1.4 \times 10^{-4} \sec^{-1}$ in the central section of the specimen. Tests at temperatures above room temperature were made in an air oven and tests below room temperature were made in an atomosphere of gaseous nitrogen, with the exception of those at 78 K which were carried out in liquid nitrogen.

The tensile tests were also used to measure the stress required for the onset of crazing. This was determined in an indirect way by examination of fractured specimens. Crazes were found in the thicker sections of the specimen and the crazing stress was calculated from the fracture load and the maximum cross-sectional area of the specimen at which crazes were observed.

3. The effect of temperature on mechanical properties

The effect of test temperature on the upper yield stress in compression and the fracture stress in tension is shown in Fig. 2, together with the results obtained by several other workers. In the range 117 to about 310 K, the compressive yield stress varies linearly with temperature. Compression specimens tested in liquid nitrogen shattered prematurely before yielding.

In general, the compression results are in good agreement with those of other authors and in most cases the small discrepancies evident in Fig. 2 can be accounted for in terms of differences in the type of test, strain-rate and material conditions which are listed in Table I. Thus, a direct comparison of the present results with those of Argon *et al.* [15] would not be appropriate because these authors used notched compression specimens. However, it is clear that the general form of the temperature dependence is identical for the two sets of results. A major discrepancy appears to exist between the present results for upper yield stress and those reported by Rabinowitz and Beardmore [16] for the 0.2% flow stress which show a lower temperature dependence. This could be due to a difference between the temperature dependence of the upper yield stress and the 0.2% flow stress although for a similar study in PMMA, Beardmore [17] reported that the stress–temperature curves for the upper yield stress and the 0.2% flow stress were parallel.

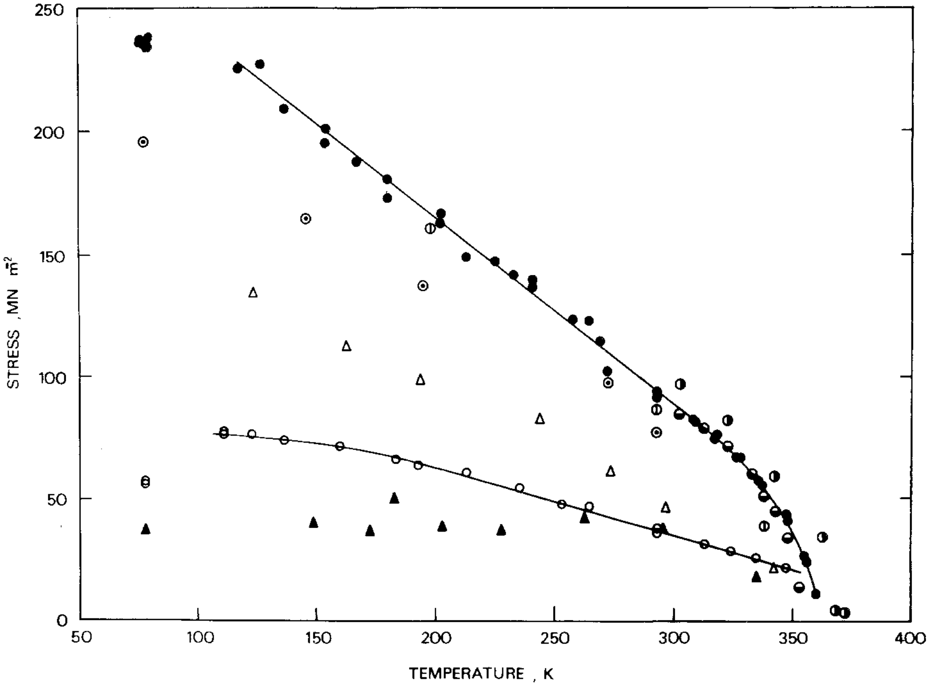


Figure 2 Temperature dependence of upper yield stress in compression and fracture stress in tension for SB 59 Carinex (denoted by curves) compared with the results of other workers (see Table I for details). •, compressive yield stress (this work); ○, tensile fracture stress (this work); ◑ ⊖ ⦶ and ⊙ refer to compressive yield stresses recorded in [12, 13] [14] and [15] respectively; △, 0.2% flow stress in compression [16]; ▲, tensile fracture stress [16].

TABLE I Details of strain-rate, material, test method and thermal history for compression tests on polystyrene

Reference	$\dot{\epsilon}$ (sec^{-1})	Material	Test method	Thermal history
This work	1.4×10^{-4}	SB 59 Carinex	Simple compression, rectangular specimens	Compression moulded at 180° C, cooled slowly in press to < 60° C
Haward *et al.* [14]	10^{-4}	G.P. Carinex	Simple compression, rectangular specimens	Well annealed
Binder and Müller [12]	2×10^{-3}	?	Simple compression, cylindrical specimens	?
Bowden and Raha [13]	3.6×10^{-4}	G.P. Carinex	Plane-strain compression	Well annealed
Argon *et al.* [15]	3.1×10^{-3}	?	Simple compression, notched specimen	Well annealed
Rabinowitz and Beardmore [16]	?	?	Simple compression, 0.2% flow stress	?

The variation of the fracture stress and crazing stress with temperature is shown in Fig. 3. For the purposes of this work the stress required to nucleate deeply penetrating crazes is used for the crazing stress. Fine surface crazes which have been shown to have little or no effect on the fracture process [5] are formed at lower stresses. Above 230 K both the crazing stress and the fracture stress vary linearly with temperature, whereas below this temperature the gradients of both plots decrease progressively. Specimens tested in liquid nitrogen were anomalous in that they crazed and fractured at much lower stresses than specimens tested at 110 K.

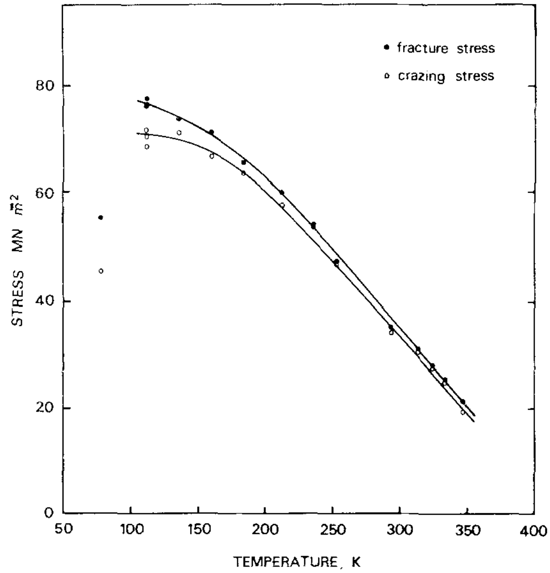


Figure 3 Temperature dependence of crazing and fracture stresses.

The deviation from linearity in Fig. 3 is associated with a change in the amount of crazing which precedes fracture. As will be reported later, below 235 K crazes spread completely across the specimen and craze yielding [18] occurs, whereas above this temperature, failure occurs before the crazes have spread across the section. The position of this transition will depend on a number of factors including the rate of growth of the crazes, the rate of craze nucleation, the concentration of crazes and the ease of cavity and crack formation and growth within a craze. It appears that these factors can be affected by material parameters such as molecular weight and molecular weight distribution. Thus, in a previous paper [18] it has been shown that in HR Carinex polystyrene, craze yielding occurs at room temperature indicating that the transition is above room temperature. The position of this transition may account for the different fracture stress results reported by Rabinowitz and Beardmore [16] which are shown in Fig. 2. They observed a temperature independent fracture stress up to 290 K. Between 290 and 340 K the results are in reasonable agreement with those reported here.

Anomalously low fracture stresses at 78 K have been observed by Brown and Parrish [19, 20] for a variety of polymers, both crystalline and amorphous, and also by Olf and Peterlin for polypropylene [21]. Brown and Parrish [20] suggested that this was due to the adsorption of liquid nitrogen into the polymer surfaces which in turn reduced the surface energy of the material. Olf and Peterlin [21], however, argued that the nitrogen was acting as a plasticizer at temperatures close to its boiling point. Large amounts of crazing were observed in polymethylmethacrylate, polyethylene terephthalate, polycarbonate and polypropylene [19, 21]. Fig. 3 shows that crazing precedes fracture at all temperatures and that the crazing stress in liquid nitrogen is unusually low. Thus, the major effect of the liquid nitrogen appears to be one of reducing the crazing stress which in turn governs the fracture stress.

Measurements of the proportion of the fracture surface area occupied by the mirror region, which is a measure of the area in which the crack propagates through pre-formed craze [3], were made on tensile specimens. The results are shown in Fig. 4. The mirror area decreased from 40% of the fracture surface area at 350 K to a minimum of 15% at about 308 K and then rose to a maximum at 100% at 235 K.

The extent of the mirror area is a measure of both the ease of growth of the crazes and the ease of crack nucleation and growth within the craze. Below 235 K, the crazes grew completely across the section of the specimen before significant crack growth had occurred within the craze. As the temperature was increased above 235 K cracks nucleated and propagated within crazes before complete craze growth had occurred.

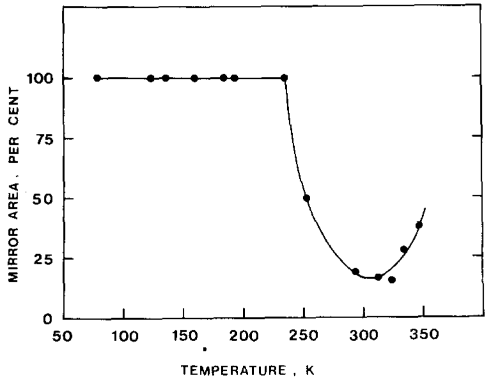


Figure 4 Variation of the fracture surface area occupied by "mirror" with temperature.

The shape of the curve in Fig. 4 suggests that there are two competing effects. The increase in the mirror size above 308 K is due to the growth of the craze during crack growth, an effect which tends to increase with increasing temperature. The rise below 308 K indicates that most of the craze growth occurs before crack nucleation has occurred, suggesting that nucleation of cracks becomes more difficult as the temperature is decreased.

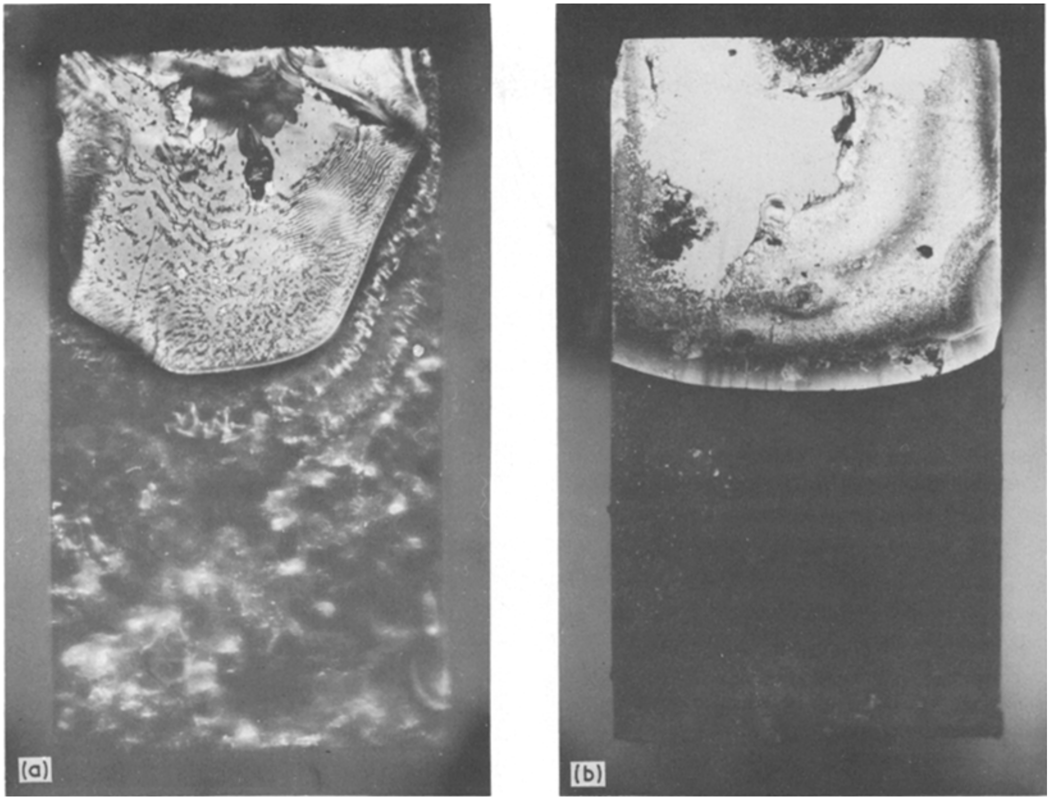
The mode of deformation during compression varied with temperature in a similar way to that reported by Bowden and Raha [13]. In the temperature range 117 to 273 K all specimens deformed by the nucleation and propagation of micro shear bands. Above 273 K, the deformation was located in zones of shear which became progressively more diffuse with increasing temperature. At 356 K and above, the specimens deformed homogeneously and no zones of shear could be detected.

4. Fracture surface observations

The fracture surfaces of the tensile specimens were examined using both optical and scanning electron microscopy. The most obvious change in fracture surface was the proportion of the fracture surface occupied by mirror area (Fig. 4). Three typical fracture surfaces are shown in Fig. 5. Fig. 5a and b represent the extremes in behaviour which were found in the range where the fracture stress varied linearly with temperature. Differences in the initiation regions and in the rest of the mirror areas are apparent. Fig. 5c shows the fracture surface of a specimen, tested in liquid nitrogen, which had craze-yielded prior to fracture. The 100% mirror area is typical of a craze yielded specimen and, with the exception that the initiation region is away from the specimen surface, Fig. 5c is representative of all specimens fractured below 235 K. These large changes in fracture surface appearance were accompanied by changes on a finer scale. In discussing the various features of the fracture surfaces, the nomenclature introduced by Murray and Hull [3–6] will be used; thus the crack initiation occurs in zone A, crack propagation along the craze-matrix interfaces occurs in zone B and hackle fracture occurs in zone C.

The fracture surface morphology varies over the entire temperature range. Between 253 and 350 K two general types of morphology in the mirror region can be distinguished. At the higher temperatures, the mirror region exhibits a two zone initiation region which will be referred to as A and A′ and mackerel pattern (Fig. 5a), while at the lower end of the range the mirror region contains a single zone initiation region and the remainder of the mirror region is covered by patch pattern (Fig. 5b). The two zone initiation region is shown in more detail in Fig. 6.

The extent of zone A′ (Fig. 6), decreases with decreasing temperature and at 265 K it is less



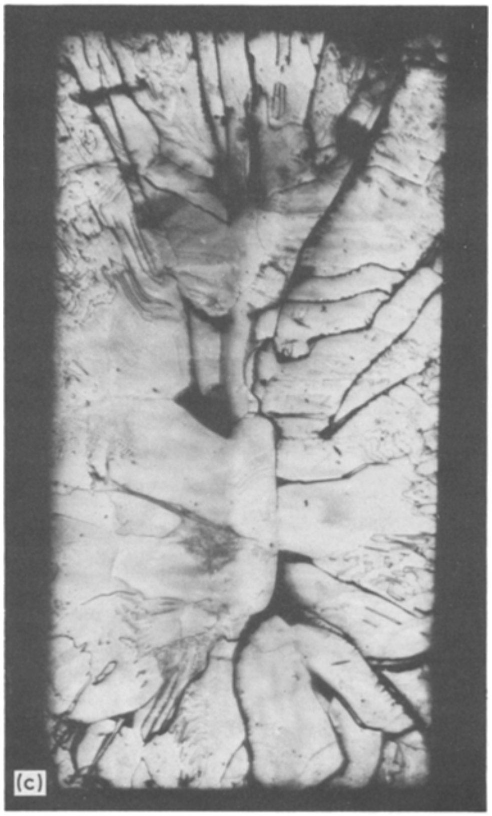


Figure 5 Typical fracture surfaces illustrating the effect of temperature on fracture surface morphology, (a) 347 K, (b) 253 K, (c) 78 K.

regular and may occur in "islands" away from the main slow growth region. Examination of the initiation regions by scanning electron microscopy (Fig. 7) confirms the existence of two zones, which have different surface textures. The texture shown in Fig. 8 is typical of the outer zone A′, of the initiation region. The fracture surface has a fine granular appearance which is formed from broken fibrils aligned normal to the surface. The

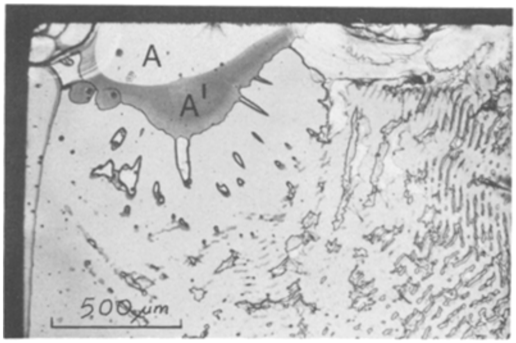


Figure 6 Optical micrograph of a two zone fracture initiation region in a specimen tested at 335 K.

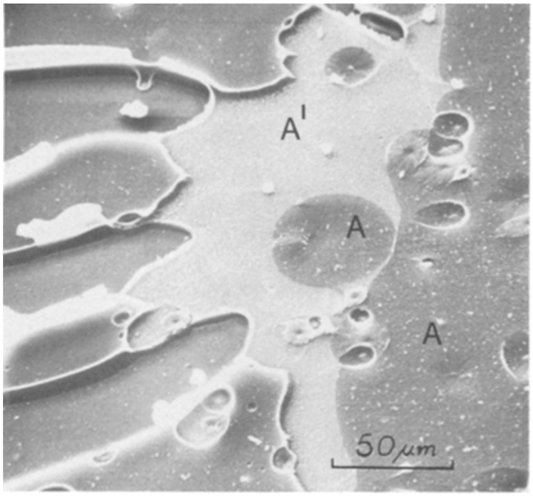


Figure 7 Scanning electron micrograph showing the different textures associated with zones A and A′ (Fig. 6) in a specimen tested at 293 K. The step like features are associated with the crack propagating along the surfaces of the craze.

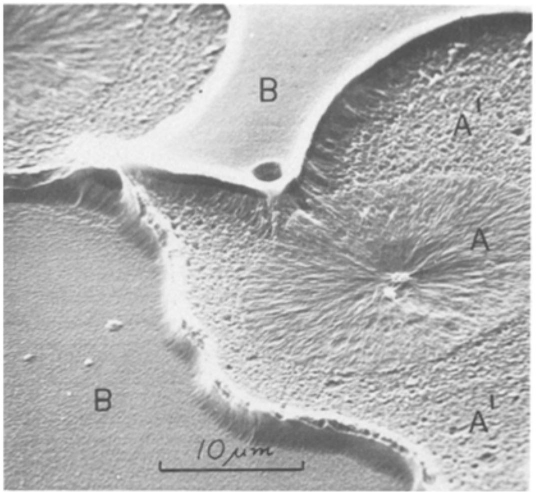


Figure 8 Scanning electron micrograph showing parts of the granular fracture initiation zone A′ and a secondary fracture produced by zone A type failure. Specimen fractured at 265 K.

region also contains a circular secondary fracture feature with a texture corresponding to inner zone A in which the broken fibrils radiate outwards from the nucleation site and areas B where the crack has propagated along the craze surface. Fig. 9 shows a small area typical of the inner initiation region. The texture is again fibrillar with the fibrils aligned in the direction of crack propagation. The familiar hyperbolic secondary fracture features are observed in this region.

Examination of the boundary between zones A and A′ reveals that there is no height difference between them, see Fig. 7. The location of these zones within the craze may be deduced from Fig. 8. The granular surface lies mid-way between two levels on the fracture surface which are identified with the original craze-matrix interfaces. Thus, the surface texture is formed by crack motion through the fibrillar craze material, such that the mass of broken fibrils behind the crack front tend to retract and lie parallel to the direction of crack propagation. The texture in the granular zone A′ is not aligned indicating that the fibrils will be approximately normal to the fracture surface. This suggests that fracture separation is zone A′ has occurred by the simultaneous ductile fracture of all the fibrils along the centre of the craze. Isolated regions of granular texture also occur in association with secondary slow growth fracture features which have nucleated ahead of the main crack and expanded radially in the central place of the craze.

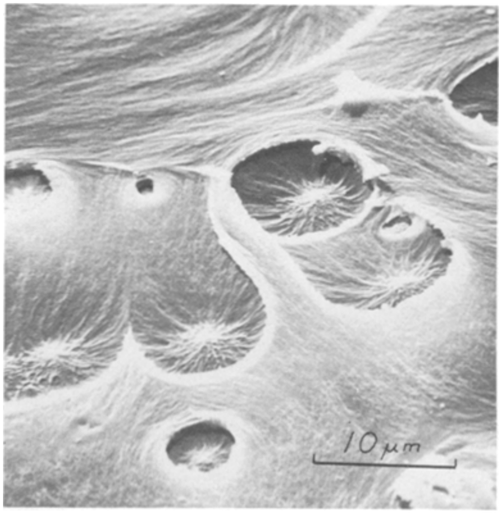


Figure 9 Scanning electron micrograph of a part of initiation zone A. Specimen fractured at 265 K.

Further crack propagation outside regions A and A′ occurs along the craze surface in an oscillatory manner. Two types of pattern called patch [3] and mackerel [4] have been observed. As the temperature of fracture is reduced the proportion of mirror area covered by mackerel pattern decreased and is replaced by patch.

The observation of granular zone A′ fracture which was first reported briefly by Murray and Hull [5] means that the detailed model of fracture described by Beahan *et al.* [9] requires some modification for these higher temperature frac-

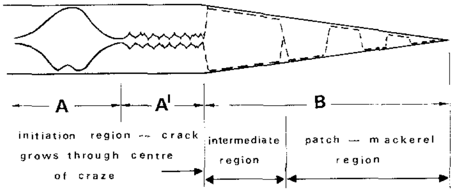


Figure 10 Model of fracture including the granular zone A$'$ which occurs in specimens fractured at high temperature. This is a modification of the model described elsewhere [9].

tures. The modified model is illustrated in Fig. 10. In every other respect the observations reported here are consistent with the original model.

Fig. 5b illustrates the fracture surface of a specimen tested at 253 K. The initiation zone, shown in more detail in Fig. 11, consists of a single zone of tightly packed features which are similar to secondary fracture features. Many of these are circular particularly at the outer extremities of the region. A scanning electron microscope view of this zone is shown in Fig. 12 and a matching pair of micrographs from opposite fracture surfaces is shown in Fig. 13. The fracture surface texture in this region is similar to that described previously for the inner zone A in specimens fractured at higher temperatures (Fig. 9). Fracture appears to nucleate at a large number of sites in the craze close to the edge of the specimen and the initial crack results from linking up of the cavities by a slow growth type process in the centre of the craze. There is a change in the mode of crack propagation indicated by line X – X$'$ in Fig. 12 and more clearly in the matching photographs in

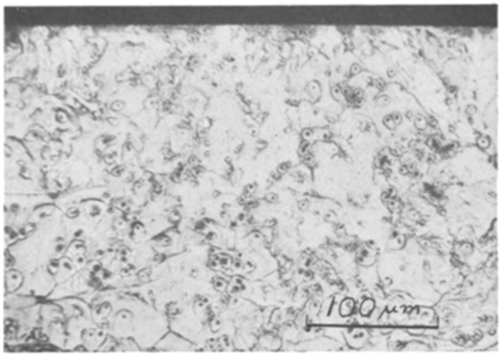


Figure 11 Optical micrograph of part of initiation zone in a specimen fractured at 253 K.

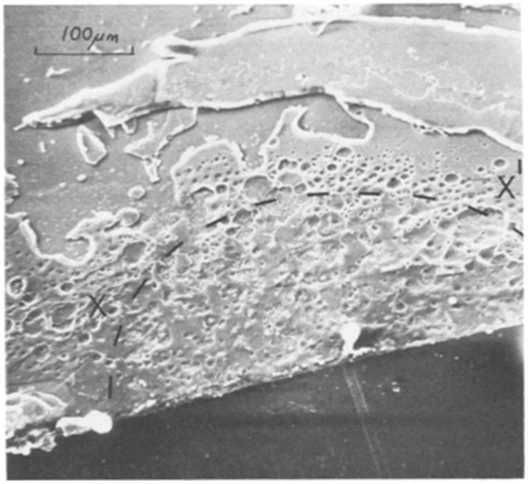


Figure 12 Scanning electron micrograph of the initiation zone showing transition to crack propagation along craze surface. Specimen fractured at 253 K.

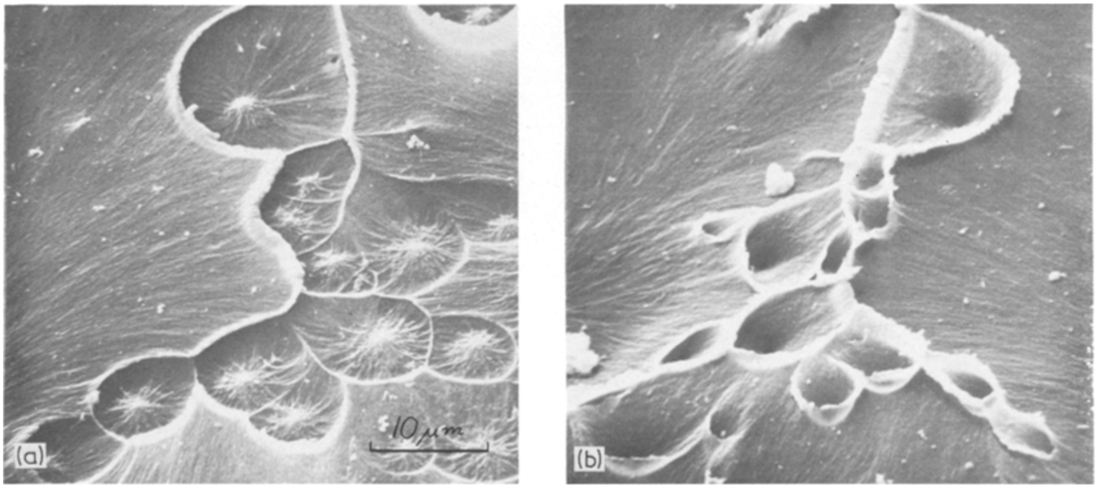


Figure 13 Scanning electron micrographs of matching features on opposite fracture surfaces from the initiation zone. Specimen fractured at 253 K.

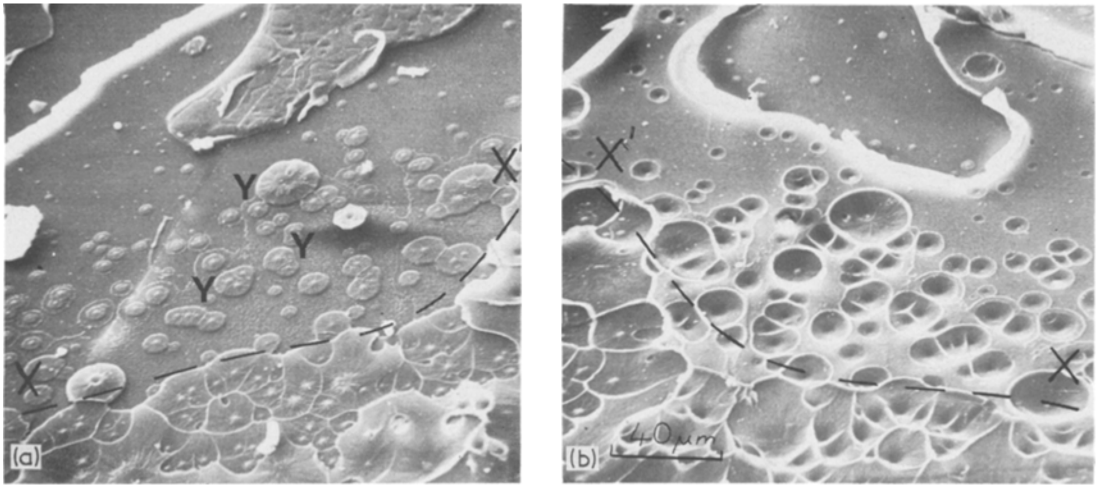


Figure 14 Scanning electron micrographs of matching features on opposite fracture surfaces from the edge of the initiation zone showing the transition to crack propagation along the craze surface. Specimens fractured at 253 K.

Fig. 14. The main path of crack propagation is along the craze matrix interface but there are regions e.g. Y in Fig. 14, where the interface crack has intersected circular slow growth cracks.

Below 253 K the fracture surface is entirely mirror as expected for craze yielded material. Fracture nucleates within the craze and propagates across the specimen entirely through preformed crazes. The dark lines in Fig. 5c indicate where the crack has jumped from one craze matrix interface to another parallel to it. In most specimens fracture nucleated at the edge except in those tested at 78 K in liquid nitrogen. The mechanism of crack nucleation was similar to fracture at 253 K as illustrated in Fig. 15 for fracture at 160 K. Outside the nucleation region the surface is covered with patch or mackerel.

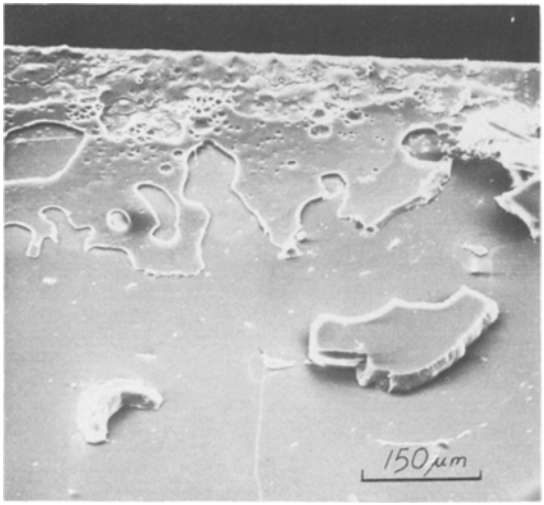


Figure 15 Scanning electron micrograph of nucleation region in a specimen fractured at 160 K.

A typical initiation region in a specimen fractured at 78 K is shown in Fig. 16. It consists of small clusters of impinging circular features. A scanning micrograph (Fig. 17) of part of the initiation region indicates that primary initiation has occurred in the centre of the craze and subsequent propagation has occurred along the craze surface. On some fracture surfaces there is evidence that the craze layer has been stripped off from both fracture surfaces and has been washed away by the liquid nitrogen. Isolated patches of craze confirm that crack propagation occurred in an oscillating manner.

5. Discussion and conclusions

This work has confirmed and expanded previous studies on the effect of temperature on the deformation mechanisms in polystyrene. The most

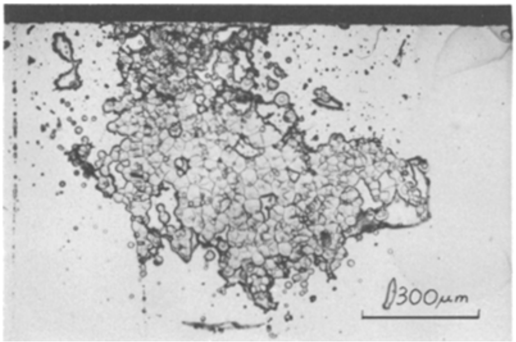


Figure 16 Optical micrograph of nucleation region in a specimen fractured at 78 K in liquid nitrogen.

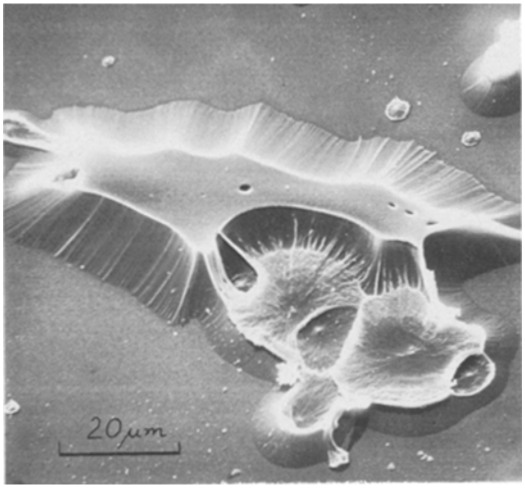


Figure 17 Scanning electron micrograph of part of the edge of nucleation region of a specimen fractured at 78 K in liquid nitrogen.

significant mechanisms in the range 78 to 360 K are shear band propagation in compression and crazing in tension. There is a marked difference in the temperature dependence of these two processes and it is clear that in uniaxial tensile tests crazing precedes shear deformation at all temperatures below 360 K in this material.

The close relationship between crazing and fracture, which was first established in polystyrene at 293 K, has been demonstrated over the whole temperature range used. There are small differences in the fracture process within the craze at different temperatures but these do not affect the main conclusions that fracture nucleation occurs within a preformed craze and that subsequent crack propagation occurs along craze matrix interfaces.

The most significant differences in fracture behaviour relate to the mechanisms of craze breakdown in the nucleation stage. At high temperatures a few isolated cavities form and grow considerably through the centre of the craze before coalescing to form a crack. Alternatively, the crack starts at the edge of the specimen and grows through the centre of the craze. Only a small number of secondary fractures are formed. In contrast, at low temperatures, nucleation is associated with a high density of nuclei and large numbers of secondary fractures develop. A similar effect was observed by Murray and Hull [5] on specimens tested at different strain-rates at 293 K. In this case the increase in number of cavities formed in the nucleation stage which occurred as the strain-rate increased was attributed to the higher stresses involved in crazing at the higher strain-rates which will determine the critical nucleus size for cavitation. A similar explanation can be used for the effect of temperature since there is a significant increase in crazing stress with decreasing temperature.

It is also possible that the microfibril structure within the craze will vary with temperature and strain-rate. Following Beahan *et al.* [9] a change in microstructure is likely to affect the mechanism of craze breakdown. However, microstructure studies of crazes have so far been restricted to 293 K. There is evidence from recent work [22] that craze microstructure of polystyrene is affected by molecular weight, degree of cross-linking and additives and these in turn affect craze

The ease of crazing and fracture of specimens immersed in liquid nitrogen confirms much recent work on this effect and emphasizes once more the important effect of crazing in determining fracture behaviour.

Acknowledgement

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References

1. J. P. BERRY, *J. Polymer Sci. C* 3 (1963) 91.
2. R. J. BIRD, J. MANN, G. POGANY and G. ROONEY, *Polymer* 7 (1966) 307.
3. J. MURRAY and D. HULL, *ibid* **10** (1969) 451.
4. *Idem, J. Polymer Sci, A-2* 8 (1970) 583.
5. *Idem, ibid* 8 (1970) 1521.
6. D. HULL, *J. Mater. Sci.* 5 (1970) 357.
7. R. J. BIRD, G. ROONEY and J. MANN, *Polymer* **12** (1971) 742.
8. P. BEAHAN, M. BEVIS and D. HULL, *J. Mater. Sci.* 8 (1972) 162.
9. *Idem, Proc. Roy. Soc. A* **343** (1975) 525.
10. M. J. DOYLE, A. MARANCI, E. OROWAN and S. T. STORK, *Proc. Roy. Soc. A* **329** (1972) 137.
11. R. N. HAWARD, B. M. MURPHY and E. F. T. WHITE, "Fracture, 1969", (Chapman and Hall, London, 1969) p. 519.
12. G. BINDER and F. H. MÜLLER, *Kolloid Z.* **177** (1961) 129.
13. P. B. BOWDEN and S. RAHA, *Phil. Mag.* **22** (1970) 413.
14. R. N. HAWARD, B. M. MURPHY and E. F. T. WHITE, *J. Polymer Sci. A-2* 9 (1971) 801.
15. A. S. ARGON, R. D. ANDREWS, J. A. GODRICK and W. WHITNEY, *J. Appl. Phys.* 39 (1968) 1899.
16. S. RABINOWITZ and P. BEARDMORE, *CRC Crit. Revs. Macromol. Sci.* January (1972) p. 1.
17. P. BEARDMORE, *Phil. Mag.* **19** (1969) 389.

18. J. HOARE and D. HULL, *ibid* **26** (1972) 443.
19. M. PARRISH and N. BROWN, *Nature, Phys. Sci.* **237** (1972) 122.
20. N. BROWN and M. PARRISH, *J. Polymer Sci. Polymer Letters* **10** (1972) 777.
21. H. G. OLF and A. PETERLIN, *Polymer* **14** (1973) 78.
22. D. L. G. LAINCHBURY and M. BEVIS, to be published.

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