electron transfer again predominates, suggesting that this result is general for all isocyanates; it is noteworthy that although carbon dioxide and isocyanates have similar cumulative bonds, they react with sodium naphthalene in entirely different ways.

REFERENCES

1 Shashoua, V. E. *J. Amer. Chem. Soc.* 1959, **81**, 3156
2 Berger, M. N. *J. Macromol. Sci., Revs. Macromol. Chem.* 1973, **C9(2)**, 269
3 Iwakura, Y., Uno, K. and Kobayashi, N. *J. Polym. Sci. A-2*, 1966, **4**, 1013
4 Devries, K. A. *Rec. Trav. Chim.* 1942, **61**, 223
5 Ulrich, H. and Sayigh, A. A. R. *J. Org. Chem.* 1965, **30**, 2781
6 Morton, M., Rembaum, A. and Bostick, E. E. *J. Polym. Sci.* 1958, **32**, 530
7 Richards, D. H. and Szwarc, M. *Trans. Faraday Soc.* 1959, **55**, 1644
8 Walker, J. F. and Scott, N. D. *J. Amer. Chem. Soc.* 1938, **60**, 951
9 Mita, I., Yabe, S., Imai, I. and Kambe, H. *Makromol. Chem.* 1970, **137**, 133
10 Tsuzuki, R. and Iwakura, Y. *J. Org. Chem.* 1965, **30**, 1665

Letter

Deformation of PMMA samples containing a stress-raising flaw

It is well established that yield in glassy amorphous polymers occurs either by craze formation or shear deformation. Extensive reviews of work on the conditions for craze and shear yielding have been made by Kambour[1] and Bowden[2] respectively. Crazing and shear deformation can occur independently and exclusively, or simultaneously, depending on the test conditions in general, but in particular on the nature of the local stress field.

We are examining the deformation of polymeric glasses in uniaxial compression with samples containing a centrally positioned stress-raising flaw. Previously published work by Bevan[3] has shown that whilst crazing requires a state of hydrostatic tension, such states can exist locally when a specimen with a suitable flaw is deformed nominally in compression, or when it is unloaded after compressive yielding. The present investigation deals with aspects of shear band deformation, craze and crack formation not reported previously.

Experimental

PMMA (ICI 'Perspex') samples of nominal dimensions 20 x 20 x 6 mm containing a centrally-drilled 2 mm diameter hole were annealed, between smooth aluminium plates, in air at 95°C for more than 1 h and then cooled to room temperature at a rate of about 10°C/h. Samples were subsequently subjected to applied uniaxial compression at ambient temperature between the dies of an Instron machine. Tests were conducted at a strain rate of $4.2 \times 10^{-4} s^{-1}$. The results reported here were obtained with no lubricant at the interfaces, but separate tests using Teflon tape showed the same deformation characteristics.

The onset of residual birefringence in the samples was determined from a large number of interrupted compressive tests where samples subjected to various strains were rapidly unloaded and viewed in an adjacent polariscope.

Some tests were done on samples with differing surface conditions of the hole. These were obtained by varying the drilling conditions and also by polishing the internal hole surface with a cylindrical roll of 600 grade emery paper. The same deformation features are observed irrespective of the surface conditions of the hole. The results reported here were obtained on unpolished holes.

Results

The nominal stress–nominal strain graph obtained for our samples shows a departure from linearity at 2.8% ϵ and exhibits a load maximum at 9.5% ϵ, similar to results reproduced by Bowden[2] for PMMA in uniaxial compression. Diffuse shear zones were distinguished from birefringence observations. These zones propagate symmetrically from the hole across the sample at an angle of about 50° to the compressive axis and appear to reach the edges of the sample as the stress–strain graph becomes non-linear. Samples unloaded at this point showed no residual birefringence several hours later. Remnant birefringence was associated with the initiation and growth of 'broad diffuse shear bands'. These shear bands initiated at the hole at about 6% ϵ within the established shear zones. The bands subsequently propagated through the zones and were observed to reach the sample edge at about the load maximum. Specimens showed a slight thickening along the shear bands due to the surface of the shear band bulging outwards symmetrically from the surface about the band propagation direction. This type of 'broad diffuse shear band' is quite different to the sharply defined shear bands observed in polystyrene[4,5] and polycarbonate[6].

When samples were unloaded some of them were observed to contain three mutually perpendicular discontinuities, which are either craze- or crack-like in nature. These were designated C_L, C_B and C_U as shown schematically in *Figure 1*. C_L and C_U have been reported previously[3]. C_L formed during loading at strains of between 6 and 8%. C_B, which we have called a 'butterfly' discontinuity, also occurred during loading at a strain of about 9 or 9.5%. The unloading discontinuity C_U was always present on samples unloaded from about 7%. Each type of loading feature can occur on either or both sides of the hole and we have observed samples containing only C_L, only C_B, and both types simultaneously.

The initiation and propagation of C_L, C_U and C_B have been observed with an optical microscope. C_L and C_B appear to initiate as crazes, rather than cracks, but rapidly break down into cracks. The initiation of 'craze' C_L is often followed by its propagation as a crack, signified by an audible click.

Scanning electron microscope studies of sections of

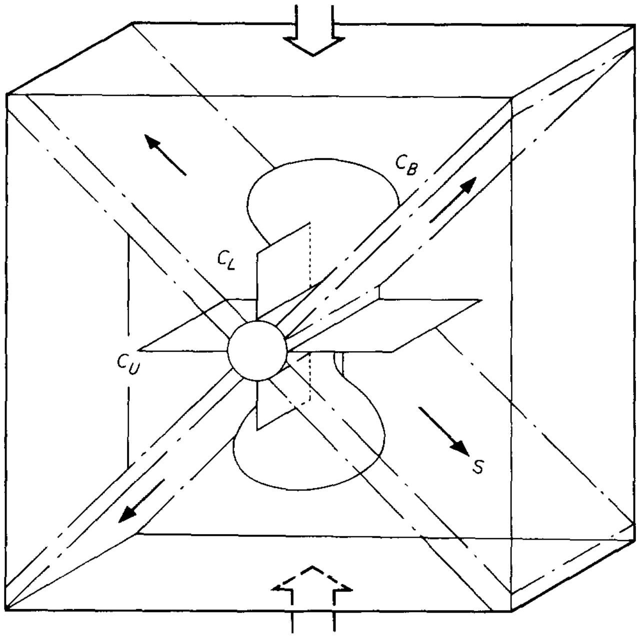

Figure 1 Schematic representation of sample subjected to applied compression showing shear bands (*S*), with arrows, showing directions of propagation, and orthogonal discontinuities C_L, C_B and C_U

samples tested some days previously show both craze and crack features. C_L and C_U are certainly ostensibly cracks at this time, whereas C_B sections indicate a crack near the hole surface which merges into craze as the periphery of the butterfly wing is approached.

Figure 2 shows all three types of crack orientation in a sample deformed to 9.5% ϵ. Only one wing of the butterfly craze/crack C_B has formed in this case.

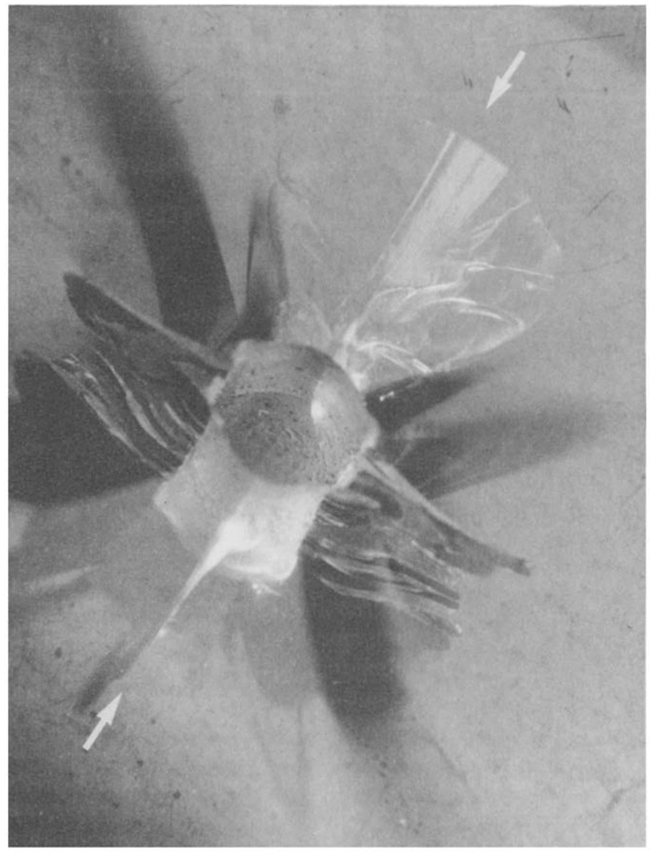

Figure 2 Orthogonal crack orientations in an unloaded sample. The photograph has been taken at an oblique angle to reveal all deformation features simultaneously. The arrows indicate the applied stress direction. Magnification about 20X

DISCUSSION

Kramer[5] has subjected notched bars of polystyrene to uniaxial compression and reported the presence of a diffuse shear zone and a localized packet of fine shear bands. He showed that general yield (corresponding to a load maximum) occurred when the shear zone reached the opposite side of the sample to the notch, at which stage the shear band packet had traversed about a third of the way across the sample. In contrast, with PMMA samples with a central hole, the propagation of the shear zone from the hole to the sample edge appeared to correspond to a departure in linearity of the stress–strain curve, and general yield to the propagation of the 'shear band' to the sample edge.

Camwell and Hull[4] have reported that fine shear bands, produced in polystyrene under compression, can interact to form a craze which eventually breaks down to a crack. More recently, disc-shaped crazes have been observed in polycarbonate[6], where crazes nucleate within the material near the tip of a plastic zone of fine shear bands. In both these cases the plane of the initiated craze bisects the angle between the planes of interacting shear bands. In contrast, the butterfly discontinuity, C_B in *Figure 1*, has formed perpendicular to the shear bands with its plane parallel to the shear band propagation directions.

The formation of C_B can be explained in terms of plastic constraint. As stated above, the broad diffuse shear bands we have observed form a local bulge (as opposed to a neck in a flat sheet tensile sample) along the edge of the shear band. This thickening of the shear bands in a direction parallel to the hole axis produces a high hydrostatic stress on the plane on which C_B eventually nucleates. In other words, the butterfly craze has initiated, due to plastic constraint, on a plane subjected to hydrostatic tension developed in order to maintain continuity of displacement at the 'elastic–plastic' boundaries.

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References

1 Kambour, R. P. *J. Polym. Sci. (D)* 1973, **7**, 1
2 Bowden, P. B. 'The Physics of Glassy Polymers' (Ed R. N. Haward) Applied Science, London, 1973, Ch 5, pp 279–339
3 Bevan, L. *J. Mater. Sci.* 1978, **13**, 216
4 Camwell, L. and Hull, D. *Phil. Mag.* 1973, **27**, 1135
5 Kramer, E. J. *J. Macromol. Sci. (B)* 1974, **10**, 191
6 Ishikawa, M., Narisawa, I. and Ogawa, H. *J. Polym. Sci.* 1977, **15**, 1791