JOURNAL OF MATERIALS SCIENCE 17 (1982) 1739–1744

Interaction of crazes with pre-existing shear bands in glassy polymers

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Shear bands have been grown in bulk specimens of P_3O(poly 2,6 diphenyl 1,4 phenylene oxide) and in thin films of two blends of polystyrene with poly(xylenyl ether). The subsequent interaction of crazes with these shear bands has been characterized by transmission electron microscopy. For the case of shear bands grown under the plane stress conditions of thin films, it is found that the bands act as preferential sites for craze nucleation. A fairly regularly-spaced array of short crazes grows within the shear bands and these crazes may thicken sufficiently to coalesce. When the crazes reach the end of the shear band they emerge and propagate into the unoriented polymer matrix. Within the shear band the craze growth direction does not lie normal to the tensile axis, but is rotated due to the molecular orientation of the shear band. The direction of craze growth is also affected under the plane strain conditions of bulk specimens. In this case the craze is diverted along the shear band before re-emerging into the matrix. Measurements of the craze fibril extension ratio, λ, within the shear band show an increase over typical values obtained outside the shear band in the same polymer. This high value of λ leads to an increased likelihood of craze break-down and crack nucleation within the shear band.

1. Introduction

Although for many polymers crazes and shear bands form under differing stress conditions, there are cases where both modes of plastic deformation may occur simultaneously [1, 2]. In such a regime, the possibility exists that interactions between crazes and shear bands may occur. Kambour [3] and Bucknall [4] have discussed the different forms such interactions may take. One possibility is that shear bands may be nucleated from the tip of a growing craze, causing arrest of craze advance. This type of craze–shear band interaction has been inferred from several studies [5–8] and its development has been directly observed by growth experiments with an optical microscope [9]. Similarly, a growing craze may meet a pre-existing craze and also be arrested [5, 10, 11].

However, if a growing craze intersects a pre-existing shear band two further possibilities may arise. The craze path may be diverted from its normal trajectory so that the craze propagates some way inside the shear band before re-emerging into the undeformed matrix. This type of interaction has been observed by Kambour [3]. Alternatively, the shear band may act as a preferential site for craze initiation, because of the altered stress field and/or molecular orientation within the band.

The effect of pre-orientation on the crazing behaviour of glassy polymers has been considered by Beardmore and Rabinowitz [12] and Farrar

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0022–2461/82/061739–06$03.22/0

and Kramer [13]. Both the crazing stress [12] and the craze fibril volume-fraction, v_f, [13] have been shown to be higher for the case of parallel tensile and orientation axes, compared with either an isotropic sample or a sample oriented perpendicular to the tensile axis. Furthermore, Beardmore and Rabinowitz [12] have shown that the direction of craze growth need no longer be normal to the tensile axis, as suggested by the principal stress criterion of Sternstein and Ongchin [14]. Instead the direction of propagation may be governed by the principal strain axis which, in the case of anisotropic specimens will not coincide with the principal stress axis.

These conclusions are relevant to the case of a craze, initially growing normal to the tensile axis, intersecting a pre-existing shear band; the orientation within the shear band will affect the subsequent craze growth. Since, for many commercial toughened plastics such as ABS and Noryl ® resins, both crazes and shear bands may grow simultaneously, it is important to understand the nature of the craze–shear band interactions and their contributions to the overall toughness of the polymer. In this paper the results of a transmission electron microscopy study of the craze–shear band interactions are presented.

2. Experimental procedure

In this study three different polymers and two different sample preparation techniques have been investigated. Samples of poly(2,6 diphenyl-1, 4 phenylene oxide)(P_3O), approximately 100 μm thick, were bent to produce a low level of applied strain. These samples (corresponding to a state of plane strain) were subsequently immersed in liquid sulphur at 125° C to produce crazes filled with a reinforcing impregnant [3]. Examination by light microscopy revealed not only the formation of crazes, but also thin bi-refringent bands oriented at approximately 45° to the tensile axis, which were interpreted to be shear bands. Thin sections, about 80 nm thick, were microtomed from the specimens and carbon backed (during which process the impregnant evaporated). These sections were examined in the TEM, permitting characterization of the craze–shear band interaction.

To study craze–shear band interactions under plane stress conditions, thin films of two blends of polystyrene (PS) with poly(xylenyl ether) (PXE) [also known as poly(2,6 dimethyl–1,4 phenylene oxide)] with compositions of 90 and 50 vol% PS, respectively, were examined. These films, about 0.7 μm in thickness, were prepared by drawing glass slides from chloroform solutions. The films were floated off on a water bath and picked up on copper grids which had been precoated with a thin film of the same blend. Bonding of the film to the grid was accomplished by a short exposure to chloroform vapour. The film was then left to dry overnight to permit excess solvent to evaporate. The blend containing 50 vol% PXE was then annealed for 1.5 h at 100° C to enhance crazing relative to the formation of diffuse deformation zones [9]. Both blends were strained in tension and suitable grid squares were cut out for observation in the TEM, a Siemens 102 microscope operating at 125 keV. Further details of this specimen preparation technique are discussed by Lauterwasser and Kramer [14].

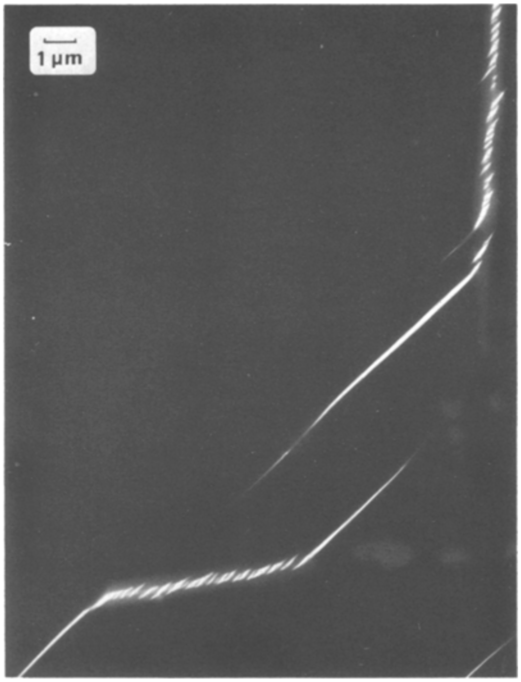

Figure 1 Crazes and two shear bands in a 90 vol% PS: PXE blend.

3. Results

Shear bands in polymers form along directions inclined at angles of 45 to 58° to the tensile axis [15, 16], whereas crazes in unoriented polymers grow normal to the tensile axis. Fig. 1 shows the interaction of crazes with two shear bands symmetrically inclined to the tensile axis in a PS:PXE blend of 90 vol% PS. The profound effect of the

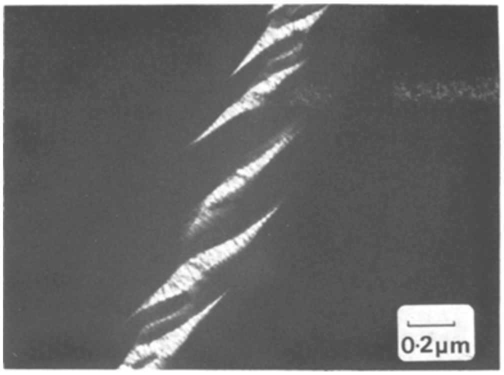

Figure 2 Close-up of part of Fig. 1 showing rotation of fibrils for crazes within a shear band.

shear band upon the growth of the crazes is immediately apparent. Crazes were nucleated within the original shear band and propagated along it until emerging into the matrix at its ends. A rather regular array of many short crazes is formed within the shear band in this process, laterally displaced one from another. The normal craze growth direction of these crazes within the shear band is rotated by about 15° towards the plane of the shear band, relative to the growth direction outside (at 90° to the tensile axis). Their shape is distinctive, being wide relative to their length, as compared with the thin and slowly tapering form of a craze outside.

Closer examination (see Fig. 2) of the crazes contained within the shear band shows that the altered direction of propagation is reflected in a rotation of the fibril orientation within the craze so that it always lies normal to the local direction of the craze–shear band interface, as is observed for crazes in isotropic material.

Although the crazes within the shear band of Figs 1 and 2 are isolated one from another, in other cases these crazes may thicken sufficiently to coalesce, forming a continuous craze within the shear band whose edges now lie parallel to the shear band–matrix edge itself. Such a coalesced set of crazes is shown in Fig. 3. That this wide craze has formed by coalescence of many initially distinct crazes can be inferred from close examination of the coalesced structure. Fig. 3 shows that islands of undrawn material remain at the centre of the final craze. These islands form where lateral coalescence was not completed before interaction and coalescence of neighbouring craze tips had occured. Thus, the edges of the islands correspond to the edges of the originally isolated crazes. The craze fibrils spanning such islands lie normal to the island edges, as would be anticipated from the arguments presented above for the isolated crazes. However as the coalescence proceeds the instantaneous direction of craze thickening is determined by the direction of the craze–shear band interface at that time and, thus, the direction of the fibrils rotates until it lies normal to the shear band edge.

The total effect of the craze–shear band interaction in this case is to cause the formation of a continuous craze apparently propagating along the shear band and subsequently emerging, reminiscent of the craze diversion originally observed by Kambour [3]. This similarity of behaviour under conditions of plane stress and plane strain is also demonstrated in Fig. 4, which was obtained in a P_3O specimen deformed under plane strain. In this case the growing craze intersects with the shear band and is diverted along it before re-emerging into the matrix. For this craze, the fibril orientation within the shear band is not strictly normal to the craze–shear band interface, as was observed under plane stress conditions. This change may partly be due to compressive stresses produced during microtomy and the removal of the external stress during this process,

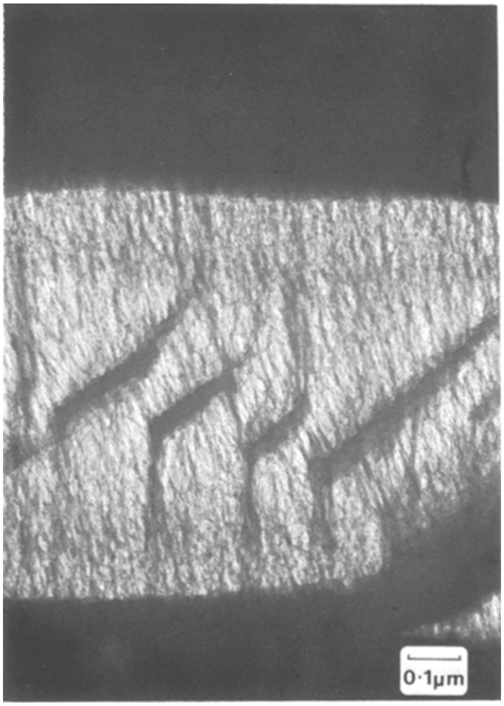

Figure 3 Coalescence of crazes within a shear band.

but may also reflect differences in the shear bands produced under plane stress and plane strain conditions.

4. Discussion

From the micrographs presented here, it is apparent that under plane stress conditions the shear bands act as preferential sites for craze initiation. To understand why this is so, it is necessary to consider the stress fields within the shear band, and to examine the nature of the shear band itself. The TEM image of the craze and shear band contains information on mass–thickness. That the shear band itself appears lighter than the undeformed matrix is evidence that local thinning, as well as orientation, occurs under plane stress conditions. Bowden and Raha [17] reported a similar observation for shear bands formed in the bulk (i.e., under plane strain conditions), observed by TEM following microtomy, concluding that the shear bands were either thinner or less dense than the undeformed matrix.

The exact nature of this thinning can be examined using the microdensitometry technique developed by Lauterwasser and Kramer [14]. By measuring the optical densities on the image plate of the shear band, ϕ_{SB}, the film, ϕ_{film}, and of a hole through the film, ϕ_{hole}, the thickness ratio, v_f, (equal to the ratio of the thickness within the shear band to the thickness of the undeformed film) at any point within the shear band can be determined from

$$v_f = 1 - \frac{\ln(\phi_{SB}/\phi_{film})}{\ln(\phi_{hole}/\phi_{film})}. \qquad (1)$$

From such an analysis it is found that the thickness ratio decreases gradually from 1 in the matrix to 0.5 in the shear band over a distance of about 1 μm at the shear-band edge. For a given level of

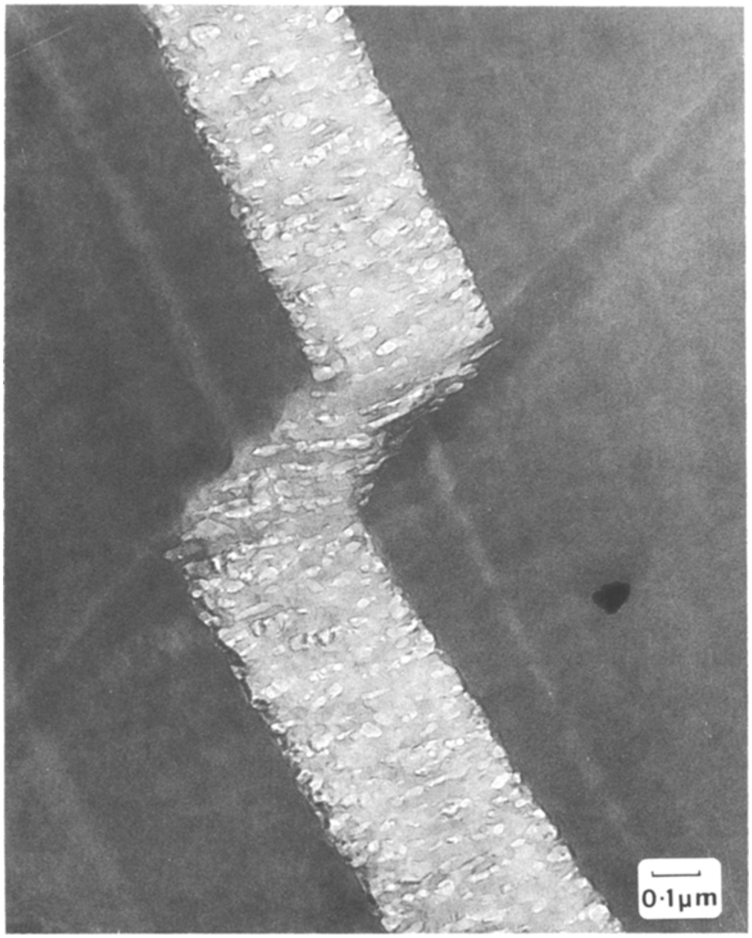

Figure 4 Craze diversion when a craze intersects a pre-existing shear band; plane strain conditions in a P_3O specimen.

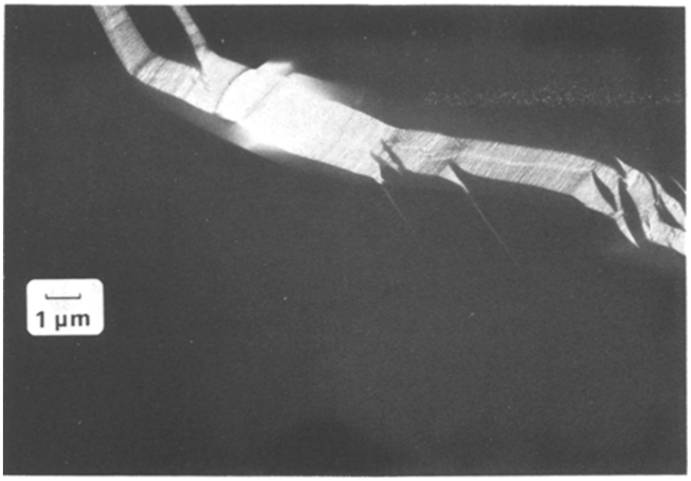

Figure 5 Shear band–craze interaction leading to crack formation.

applied stress, σ_∞, this thinning leads to a local increase in the stress within the shear band

$$\sigma_{SB} = \sigma_\infty / v_f. \qquad (2)$$

This increase makes it more favourable for crazes to be nucleated at the centre of the shear band.

Because of the plane stress conditions, these shear bands may have slightly different properties from shear bands generated in bulk specimens. In particular, in thick sections the constraint of the surrounding material will not permit the local thinning observed in thin films, although the work of Bowden and Raha [17] suggests local dilatation does occur. The consequence of this inhomogeneity can be seen in the present work. Crazes never emerge from a shear band except at its ends, indicating that growth into the thicker, unoriented regions outside the shear band is less easy than nucleation of a new craze in the shear band. However, the dominating effect under plane strain conditions is the diversion of the craze path, and preferential craze nucleation is less likely to occur.

Similar preferential craze nucleation has been observed by other workers, although not recognized as such. Brady and Yeh [18] generated shear bands by straining thin films of PS. On re-stressing in a direction normal to the original tensile axis, TEM of replicas revealed a fibrillar structure within the shear bands. Brady and Yeh [18] interpreted this as demonstrating the fibrous nature of the shear bands. The results presented here indicate that, on the contrary, crazes were being observed that had nucleated preferentially within the pre-existing shear bands.

Figs 1 and 2 show clearly that the crazes nucleated within the shear band grow along a direction inclined at 75° to the tensile axis, with the orientation of fibrils being normal to this direction. Similar to the interpretation of Beardmore and Rabinowitz [12] of their macroscopic observations, this rotation suggests that growth is not being governed by the principal tensile stress. Due to the orientation within the shear band the principal stress and principal strain no longer coincide and the results presented here are consistent with the suggestion that it is the latter that is controlling craze growth and thickening [12].

Since the craze is growing within an oriented region, it might be anticipated that the extension ratio of the craze within the shear band would be different from that for a craze in the unoriented matrix. This idea can be tested using the microdensitometry technique described above and in Equation 1, noting that crazing is a constant volume process and therefore, that

$$\lambda = 1/v_f. \qquad (3)$$

Typical values for λ in unoriented PS:PXE blends have been tabulated by Donald and Kramer [18], average values of 3.45 and 3.1 being obtained for 90 and 50 vol% blends, respectively. Values for λ of 10 (90 vol% blend) and 8.3 (50 vol% blend) are obtained for crazes within shear bands, which are very much higher than the unoriented values (approximately three times as high). Farrar and Kramer [13] found a five-fold increase in λ for crazes in PS grown normal to the orientation axis relative to the crazes grown in isotropic PS. For the case under consideration here, there is a finite angle (estimated to be about 30°) between the orientation axis and the craze plane and, thus, such a five-fold increase in λ is not to be expected. Nevertheless, the markedly higher values of λ measured within the shear band are entirely consistent with their ideas.

Such high values of λ for crazes within shear bands will lead to high fibril true stresses and therefore increase the likelihood of premature craze break-down. By analogy with Equation 2, the fibril true stress, σ_t, will be given by

$$\sigma_t = S\lambda, \tag{4}$$

where S is the craze surface stress. That crazes within shear bands do act as sites for premature craze break-down can be seen in Fig. 5. Crazes in the isotropic matrix in the same specimen showed no equivalent signs of failure. It has been noted previously that voiding may be initiated at two intersecting crazes [11]. These results demonstrated that craze–shear band interactions are similarly damaging. Consequently, when both crazing and shear bands may occur, although both contribute to the impact toughness of the material, as the number density of both increases so does the probability of a damaging interaction occurring. This damage will set a limit to the volume of material that can deform plastically before a critical crack nucleus is initiated.

Acknowledgements

The financial support of the US Army Research Office, Durham for the Cornell portion of this research is gratefully acknowledged. This research also benefited greatly from the use of the facilities of the Cornell Materials Science Center which is funded by the National Science Foundation.

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Received 30 September
and accepted 9 November 1981