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Methanol crazing of coarse shear bands in polystyrene

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A specimen with coarse shear bands produced at stress concentrations by compression was immersed in methanol to observe craze formation. Thin crazes were initiated at shear bands and joined together while propagating to form thick crazes. Crazes were formed only on the tension side of shear bands with the craze planes perpendicular to the shear bands. When a craze propagated through a shear band, each displaced the other at intersections. Some secondary shear bands were transformed partly into crazes resulting in about a factor of ten increase in thickness. This transformation was achieved by a tensile deformation of fibrous sheets in the shear band with simultaneous production of fine fibres.

1. Introduction

Shear bands are considered as craze stoppers either by blocking the path of a propagating craze or by nucleating at craze tips. In his 1973 review, Kambour [1] showed a sketch of several possible craze–shear band interactions inferred from previous results of other investigators [2–4]. If a craze is not stopped by a shear band it can be diverted by producing a step in the craze plane and continuing its propagation through the shear band. This step formation was clearly shown by Donald *et al.* [5] who also showed crazing inside shear bands. On the other hand, a shear band can propagate through a craze and also shear it [6]. The craze–shear band interactions were considered by Bucknell *et al.* [7] as the main reason for the increased creep resistance of rubber toughened polymers.

To study some craze–shear band interactions, a shear banded specimen was immersed in methanol to form crazes. In this way it could be certain that the crazes were formed after the shear bands. Furthermore, since there was no external stress applied during crazing, the change of shear banding was almost zero when the specimen was immersed in methanol, so that all the shear bands were formed before the crazes. In addition, the distribution of crazes will give an indication of the intensity and direction of internal stresses in the shear banded specimens [8].

2. Experimental details

2.1. Materials and specimen preparation

An atactic polystyrene sheet 6.3 mm thick was obtained from the Westlake Company. It was the same material as that used in our previous studies [9–14]. Blocks cut from the sheet were first annealed at 115° C for 20 h. They were then furnace cooled to room temperature over a period of about 6 h. The annealed blocks were cut into rectangular pieces by a milling machine. Some pieces were 25 mm × 10 mm and had a 60° notch cut out at the middle of one of the long sides. Others were 15 mm × 9 mm and had a 1.1 mm hole drilled at one of the corners. All specimens were polished to a 0.05 μm alumina finish. They were annealed again at 98° C for 16 h to reduce the residual stresses.

2.2. Compression and methanol crazing

Specimens were compressed in an Instron at a strain rate of about 0.1 $\sec^{-1}$. Coarse shear bands initiated from either the notch or the hole would propagate towards the other side of the specimen

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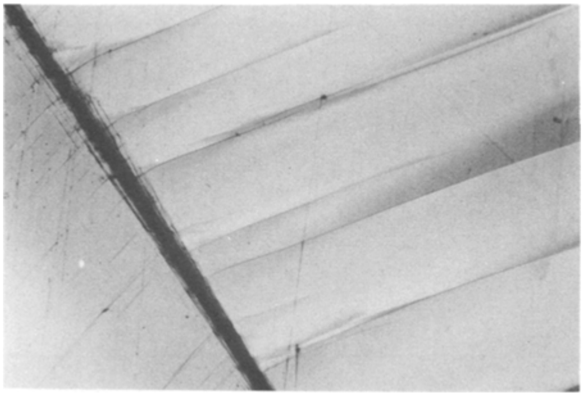

Figure 1 Crazes developed from one side of a shear band.

in the form of a packet. After the packet had extended all the way to the other side of the specimen, a large scale shear motion would complete the formation of a well developed thick band. By using the crosshead control dials, the compression could be stopped at different stages. However, the thickness of the coarse band could not be controlled [14–16].

The crazes were produced by immersing the deformed specimen in liquid methanol. Methanol was chosen as the crazing agent because of its ability to reveal small stresses in polystyrene. After immersion, the specimens were removed from methanol and dried in air for 2 h before observation in the microscope.

2.3. Scanning electron microscopy

Dried specimens were coated with a thin layer of gold by using Technics Hummer II sputtering equipment at a voltage of 10 V and by using a 4 min sputtering time. The coated specimens were examined in a Coates and Welter model HPS-70B field emission scanning electron microscope with a tilt angle of about 45°. Pictures with large depth of focal field were taken.

3. Results and discussion

3.1. Crazing at coarse bands

Fig. 1 shows the crazes developed from the coarse bands (optical microscopy). The shorter the time elapse after the compression of the specimen (or the production of the coarse band) and before the immersion of the specimen into methanol, and the longer the period of immersion, the more numerous and longer were the crazes. The growth of the crazes was fastest in the first 30 min of immersion. Obviously both nucleation and growth of crazes increased with the internal stresses inside the specimen.

Fig. 2a shows the situation after 15 days immersion in methanol. It is seen that the crazes always appear on one side of the coarse band, namely, the tension side (see Fig 3). In addition to these crazes, there are some near the side surfaces as a result of bending caused by the shear movements near the notch (see Fig. 3). These shear movements also caused severe local bending which produced a region of tension next to the notch. In addition these are curved crazes distributed inside the specimen as magnified in Fig. 2b.

The stress distribution around the coarse bands is schematically illustrated in Fig. 3 by using a dislocation model for the shear bands which started at the notch and terminated inside. The situation is different when the thick bands are fully developed and extended all the way to the other side of the specimen [14]. When such a specimen was immersed in methanol, little or no crazes were found around the thick bands, apparently due to a lack of tensile stresses.

3.2. Interaction between coarse shear bands and crazes

Fig. 4a shows the initiation of crazes within the coarse band packets. The direction of propagation of the packet is indicated by an arrow. Fine or thin crazes seem to join together to become a thick craze. Unlike shear bands the striations (fibres) inside a craze are perpendicular to the craze plane. Crazes are then crack-like openings with normal displacements. As a result, when a craze propagates through a shear band, the shear band is displaced parallel to the fibre directions in the craze. This is seen more clearly in Figs. 4b and c which are enlargements of Fig. 4a. It is seen also in Fig. 4c that the crazes seem to initiate at the striations (fibrous sheets [13]) inside shear

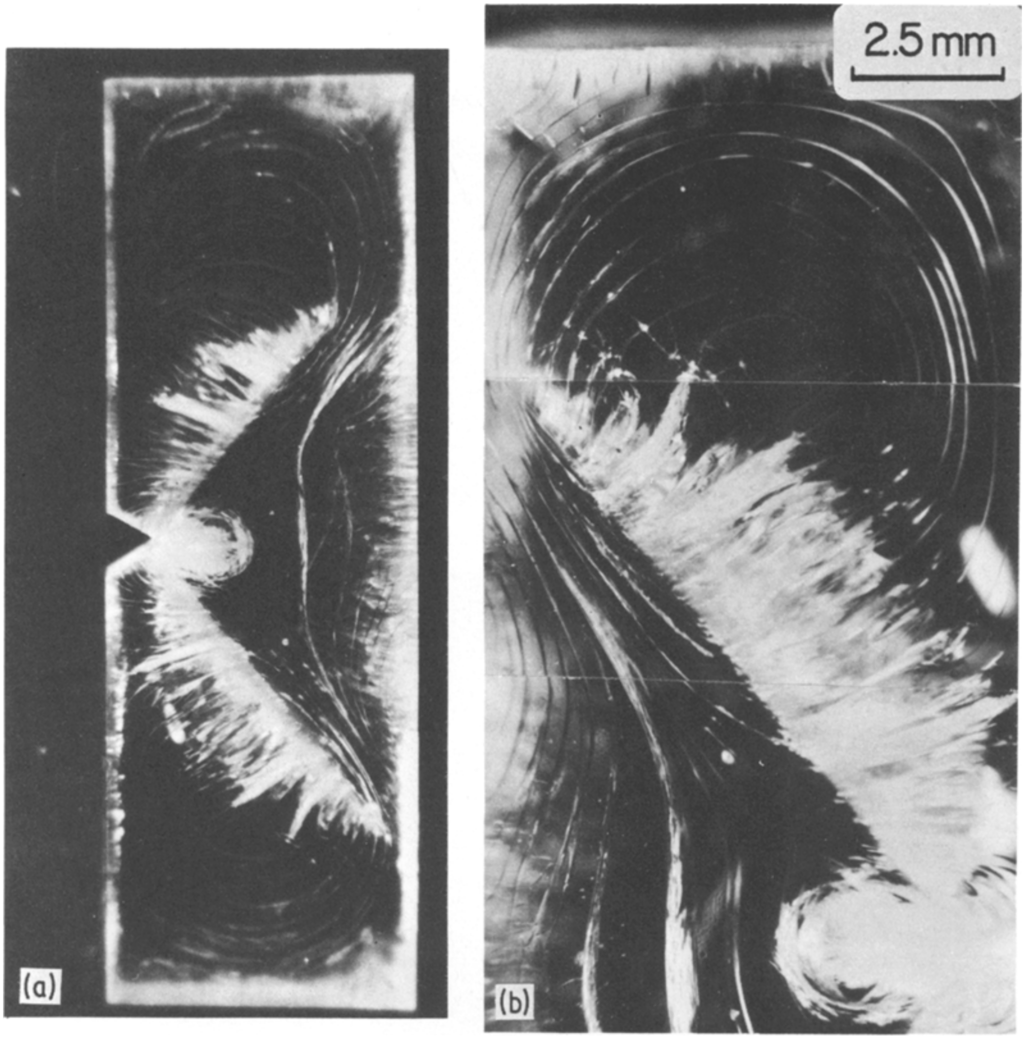

Figure 2 (a) Craze pattern after 15 days in methanol. (b) Curved crazes developed between the shear band and specimen surfaces.

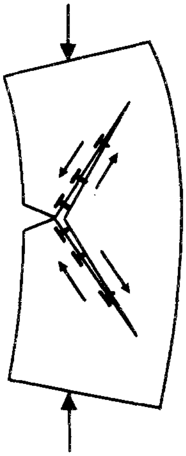

Figure 3 Stress distribution around shear bands by using a dislocation model. The effect of bending is exaggerated.

bands. After initiation, the craze seems to propagate away from the shear band in a direction perpendicular to the shear band. When a craze propagates through a shear band, it seems to go along the striation directions. As a result the craze is displaced by the intersected shear band and at the same time the shear band is displaced by the intersecting craze.

3.3. Crazing of coarse shear bands

Since the crazing direction is perpendicular to the shear bands (90°) it is close to the direction of the second set of shear bands (79°) which are part of the band packet. Sometimes the second set of shear bands can open up as shear band crazes, previously reported [13], by using a tensile

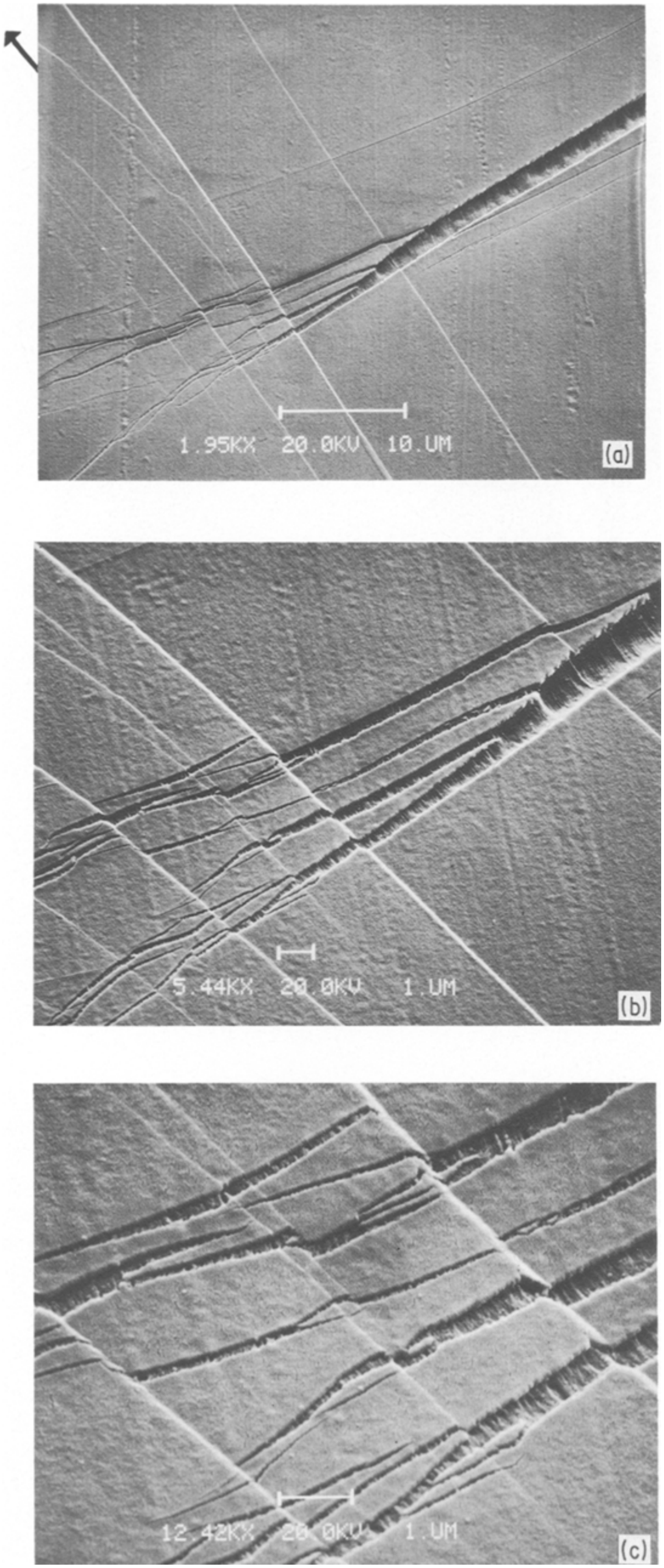

Figure 4 (a) Initiation of crazes within a coarse band packet which was propagating in the direction of arrow. (b) Enlarged view of Fig. 4a showing the coarse band displacement in the direction of craze fibres. (c) Enlarged view of Fig. 4a showing the initiation of crazes between the coarse band fibrous sheets.

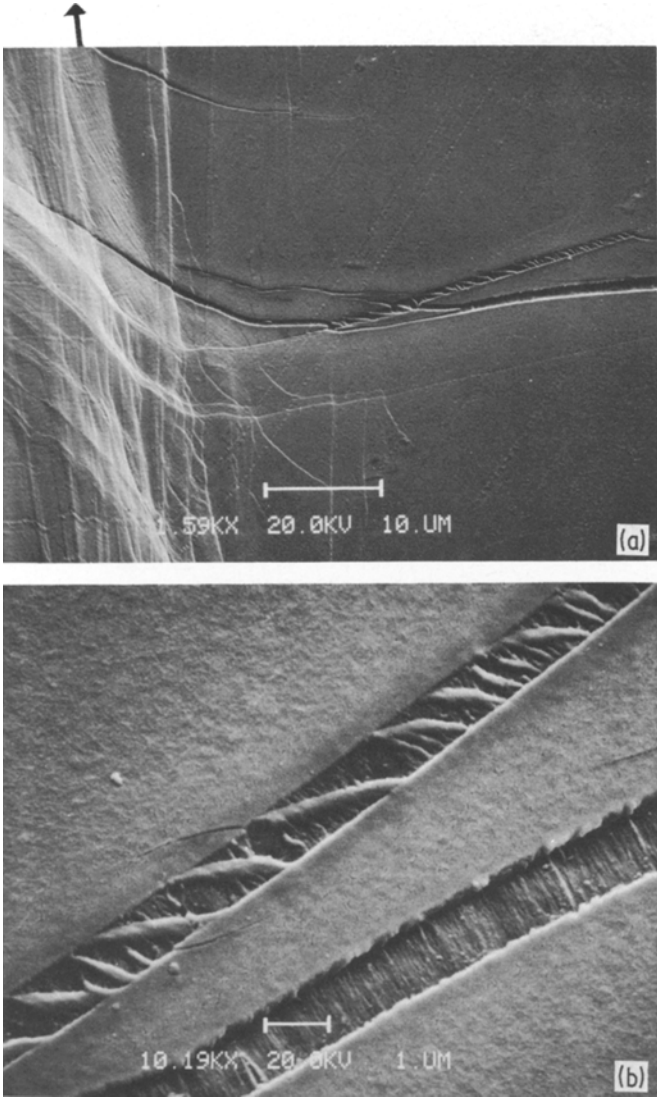

Figure 5 (a) A shear band craze and a normal craze developed in different directions near a band packet. (b) Enlarged view of Fig. 5a showing the difference in structure of the two crazes.

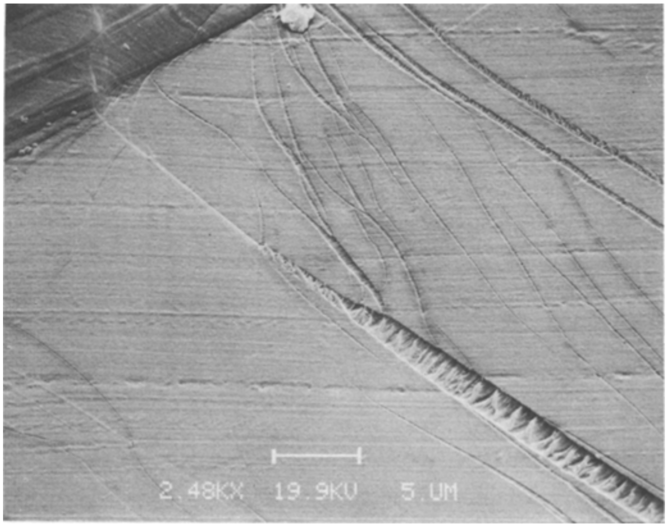

Figure 6 The partial transformation of a shear band into a shear band craze.

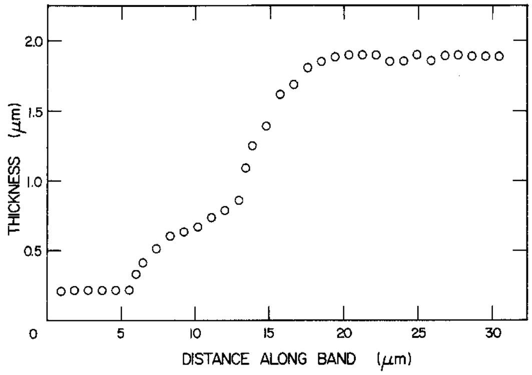

Figure 7 The thickness variations along the partially transformed shear band of Fig. 6.

stress. Here the structure is different, as shown in Figs. 5a and b. Fig. 5a shows a band packet whose direction is indicated by an arrow. A normal craze is seen to propagate perpendicular to the band packet. Next to it is seen a shear band craze which orients at 79° from the band packet so that the angle between the two crazes is about 10°. As seen in Fig. 5b the shear band craze has two kinds of striations in it. One is perpendicular to the craze plane (fibres) and its appearance is similar to those in the normal craze. The other orients at some angle from the shear band (fibrous sheets) and its appearance resembles the shear band crazes opened up by a tensile stress [13].

The transition from a shear band to a shear band craze is seen in Fig. 6. While the thickness of the shear band may be only 0.2 μm, the thickness of the shear band craze can be as large as 1.9 μm, almost a factor of 10 increase in thickness. However, the thickness of the shear band craze seems to reach some limit. Before it reaches such a limit, some fibres are inclined at an angle with respect to the craze plane while others are perpendicular to the same. After it reaches the limit, all the fibres seem to become perpendicular to the craze plane. This observation suggests that crazing is a localized normal strain deformation process. Such a process is assisted in this experiment by both a crazing agent (methanol) and the internal residual tensile stresses introduced by the shear bands.

The change in thickness of a shear band when it gradually changes into a shear band craze is measured along the length of the shear band as shown in Fig. 7. It seems to have two stages. In each stage the change is initially fast and then levels off to a limit. It probably takes a certain swelling pressure of methanol before a shear band can open up into a craze of a certain thickness. Then another critical swelling pressure is needed to open up further into a new thickness. Further studies are needed to explore these possibilities.

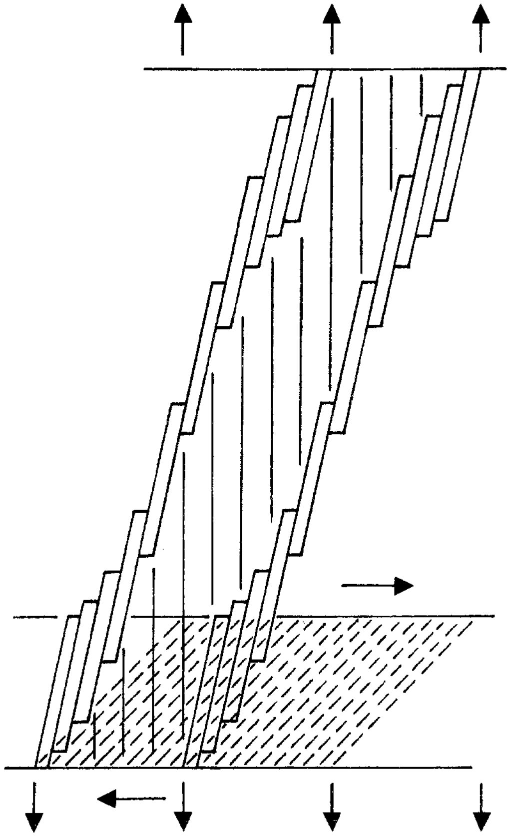

Figure 8 Schematic representation of the crazing of a shear band.

The change of a shear band into a shear band craze is schematically illustrated in Fig. 8. The deformation of fibrous sheets is assisted by both internal tensile stresses and the swelling pressure of methanol. Without methanol, the separation of fibrous sheets upon deformation takes place without fine fibres between them [13]. With methanol, the space between fibrous sheets is filled with fine fibres. Furthermore, with methanol even the fibrous sheets are transformed into fine fibres in the later stages of craze formation.

4. Summary and conclusions

1. Craze formation at and around shear bands due to the use of methanol seems to initiate at shear band striations (fibrous sheets) and propagate along planes of tensile stress. Numerous and

long crazes are formed if the time between deformation and immersion in methanol is short and the time of immersion is long.

2. When a craze intersects a shear band, it displaces the shear band in the direction of craze fibres which are perpendicular to the craze plane. At the same time the craze propagates along the striation directions (fibrous sheets) of the shear band. So each is displaced by the other at intersections.

3. A shear band can become a craze by opening up and deforming the fibrous sheets in a direction perpendicular to the shear band. This is caused by both tensile stresses and the swelling pressure of methanol. It seems to take a certain critical swelling pressure to open up to a certain thickness. The action of methanol is to produce fine fibres between the fibrous sheets during their deformation and to facilitate the deformation of fibrous sheets by disintegrating them into fine fibres.

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