

Figure 1 Yield stress as a function of temperature for polycrystalline TaC.

The results of this study reveal that ductile behaviour can be accomplished in polycrystalline TaC deformed at strain rates  $\leq 5 \times 10^{-2} \text{ min}^{-1}$  at  $1280^\circ\text{C}$  and above. Analyses of the thermo-mechanical data suggest that deformation occurs in part by dislocation motion controlled by carbon diffusion in contrast to the expected slower diffusing tantalum species; possibly as a

result of the effects of chemistry or structural defects (dislocations or grain boundaries).

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### Low Temperature Crazing in Amorphous Polymers

The phenomenon of crazing in amorphous glassy polymers has been the subject of extensive study for several years [1-3]. The importance of crazes as sites of subsequent crack nucleation and propagation is well established [4-6]. In this capacity, craze morphology is an important parameter of the fracture behaviour. In another publication [6] the morphology of low temperature (ca.  $78^\circ\text{K}$ ) crazes in poly(methyl methacrylate) is reported, with particular emphasis on the relation of craze morphology to crack

nucleation. The important craze parameter in that respect is the surface step resulting from the generation and growth of crazes within the material. The present note is concerned with the general characteristics of low temperature crazes. The observations in PMMA are presented in more detail and some new observations of crazing at low temperatures in polycarbonate and polysulfone are presented.

Tensile specimens of poly(methyl methacrylate) (PMMA) (type II UVA), polycarbonate (PC) (Lexan), and polysulfone (PSF) were tested to fracture over the temperature range  $333$  to  $78^\circ\text{K}$ . At the lower temperatures PMMA fractures in

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an essentially brittle manner on a macro scale, whereas PC and PSF exhibit considerable bulk ductility prior to fracture. Typical stress-strain curves are shown in fig. 1. The specimens were

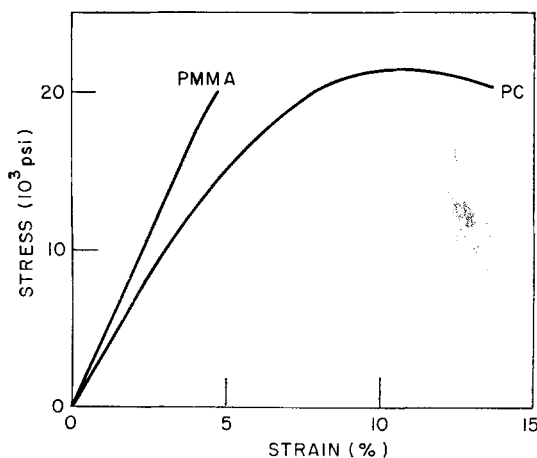


Figure 1 Tensile stress-strain curves for PMMA and PC at 78° K.

examined after fracture by optical microscopy (a) on the original external surface and (b) in cross section. The specimen cross sections were prepared in a manner identical to that in which metallographic cross sections are made. This technique consisted of mounting one half of the fractured specimen in cold setting epoxy to provide a rigid encasement for grinding and polishing. Any commercial material can be used provided it is incompatible with the polymer being mounted; a cold setting epoxy is necessary, however, in order that no thermal annealing takes place in mounting. The mount was then ground on successive emery papers until a cross section close to the centre of the specimen was exposed; final polishing was accomplished on a polishing wheel using Cr<sub>2</sub>O<sub>3</sub> polishing compound. Care was taken throughout these operations to prevent excessive pressure or heating. The longitudinal cross section of the specimen thus prepared is shown schematically in fig. 2. These sections were studied by reflected light microscopy. Since it often proved desirable to make observations in transmitted light as well, the specimen mounts were frequently ground and polished from the other side until only a thin remaining section (~1 mm) was left; this proved adequate for transmitted light studies, but obviously the final thickness can be adjusted to any desired value.

Examples of the low temperature mode of crazing as seen on the original surface of a PMMA specimen are shown in figs. 3a and b and can be

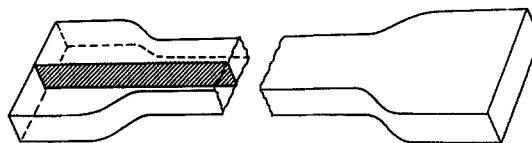
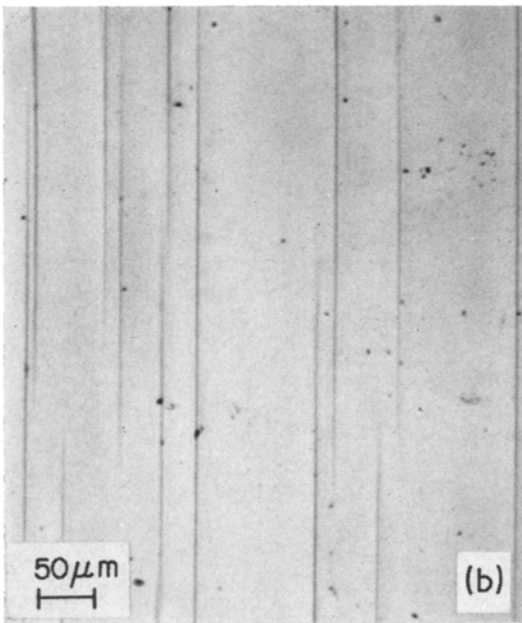
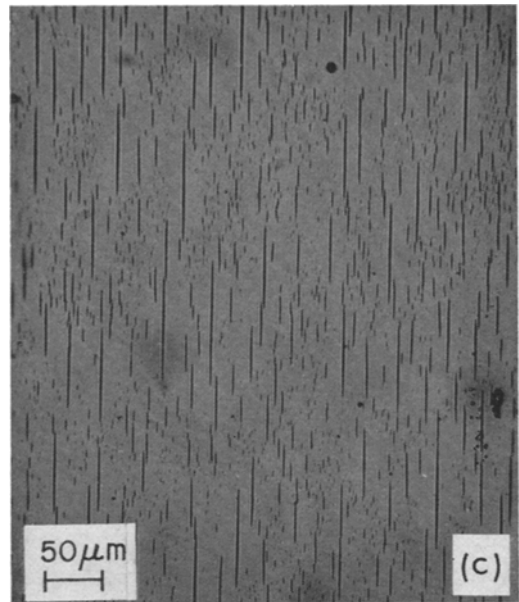
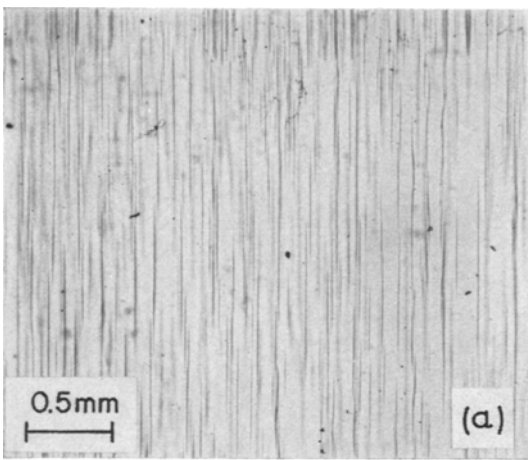


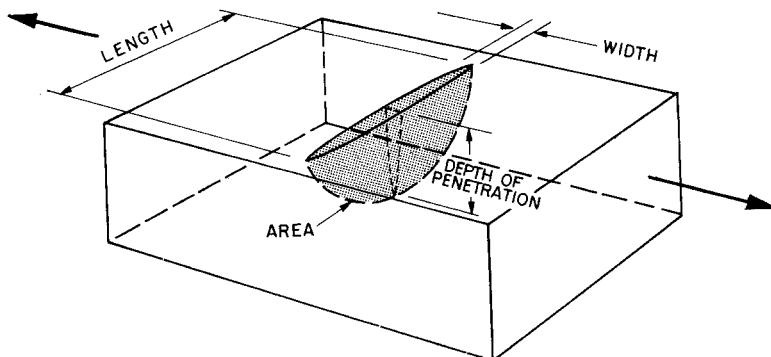
Figure 2 Schematic representation of the specimen cross-section (shaded area) exposed by grinding and polishing

compared to the high temperature crazes shown in fig. 3c. In general, the low temperature craze mode is much longer than its high temperature counterpart. The number of crazes per cm<sup>2</sup> is much lower at cryogenic temperatures than at room temperature. However, individual low temperature crazes are much longer than the high temperature variety and the total craze area may be similar or even higher at low temperatures. A schematic drawing of a craze defining the terms used in the text is shown in fig. 4. The low temperature crazes as revealed in cross section are shown in figs. 5a and b and, again for comparison, in fig. 5c several high temperature crazes are seen in cross section. The important difference between the two craze modes is that at low temperature the crazes penetrate considerable distances into the specimen, while the high temperature crazes remain essentially at the surface. Auxiliary studies indicate that the low temperature crazes are considerably narrower, i.e. accommodate less total strain. The crazes can penetrate into the bulk of the specimen so that crazes from opposite surfaces overlap in the centre of the specimen (see figs. 5a and 6). It appears that the crazes overlap with no interaction. Sections through tapered specimens indicate that the depth of penetration and the areal extent of the crazes are directly proportional to the applied stress level. The crazes initiate at the surface at a fixed stress level [6] and grow into the interior as the stress is increased. The specimen in fig. 6 had a continuously varying gauge width so that a known stress gradient could be applied in a tensile test. The cross section in fig. 6b shows clearly how the depth of craze penetration varies with stress level.

Similar observations in polycarbonate indicate that the general morphology of low temperature crazes is the same as in PMMA, but that the greater bulk ductility of PC at these temperatures



*Figure 3* Crazes formed in PMMA as seen on the original specimen surface: (a) crazes formed at 78° K imaged with transmitted light; (b) higher magnification of (a) viewed in reflected light; (c) crazes formed prior to necking at 330° K imaged with transmitted light. Stress axis horizontal.



*Figure 4* Schematic representation of a craze. The various descriptive craze parameters used in the text are defined.

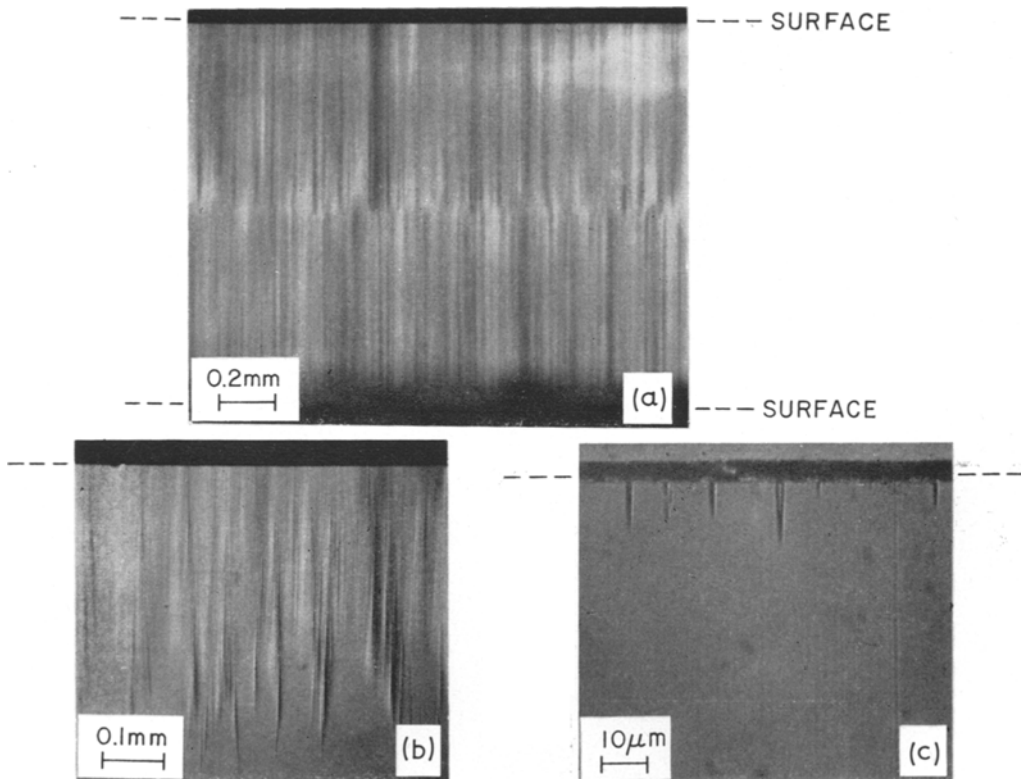


Figure 5 Cross sections through PMMA specimens: (a) crazes formed at 78° K imaged with reflected light – note the overlapping of crazes penetrating from opposite surfaces at the centre of the specimen; (b) crazes formed at 120° K as viewed in transmitted light; (c) crazes formed at 333° K imaged with reflected light. Note the changes in magnification. Stress axis horizontal.

is reflected in the width of the craze. In fig. 7 the crazes formed at 78° K in PC are shown both on the original external surface (7a and b) and in cross section (7c and d). The low temperature crazes in PC cannot be compared with crazes formed at high temperatures, because PC does not craze under the action of an applied stress alone at temperatures above about 150° K. The low temperature crazes in PC penetrate a considerable depth into the sample and develop to appreciable areas, but are much wider than their PMMA counterparts. The dependence of the depth of craze penetration on stress in PC is shown qualitatively in fig. 7c, where the cross section includes the shoulder of a specimen (see fig. 2) and consequently represents an unknown, but monotonically varying spectrum of stress.

The generality of this type of low temperature crazing as a mode of deformation in amorphous glassy polymers is further demonstrated by observations made on polysulfone. PSF shows much the same behaviour as PC at low temperatures. Fig. 8 shows the crazes formed in PSF at

78° K both on the original surface (8a and b) and in cross section (8c and d). A similar crazing mode has also been observed in polystyrene at about 200° K [7].

Craze growth, at any temperature, can be described in terms of two parameters – (a) the areal extent of the craze, as defined by length and depth of penetration and, (b) the width of the craze. The driving force for growth is the stress acting at the growth front, i.e. the applied stress and the stress concentration factor associated with the deformed zone in the vicinity of the advancing craze. The observations in figs. 6 and 7c show that areal craze growth is an increasing function of the applied stress at constant temperature. Specimens examined after being deformed to different peak stresses also showed that areal growth is continuous beyond the critical craze initiation stress and that the rate of growth is roughly in phase with the rate of strain ( $10^{-4} \text{ sec}^{-1}$ ) during the tensile test; the crazes at the mid-section in fig. 6 grew to their present size in the time during which the stress at the mid-

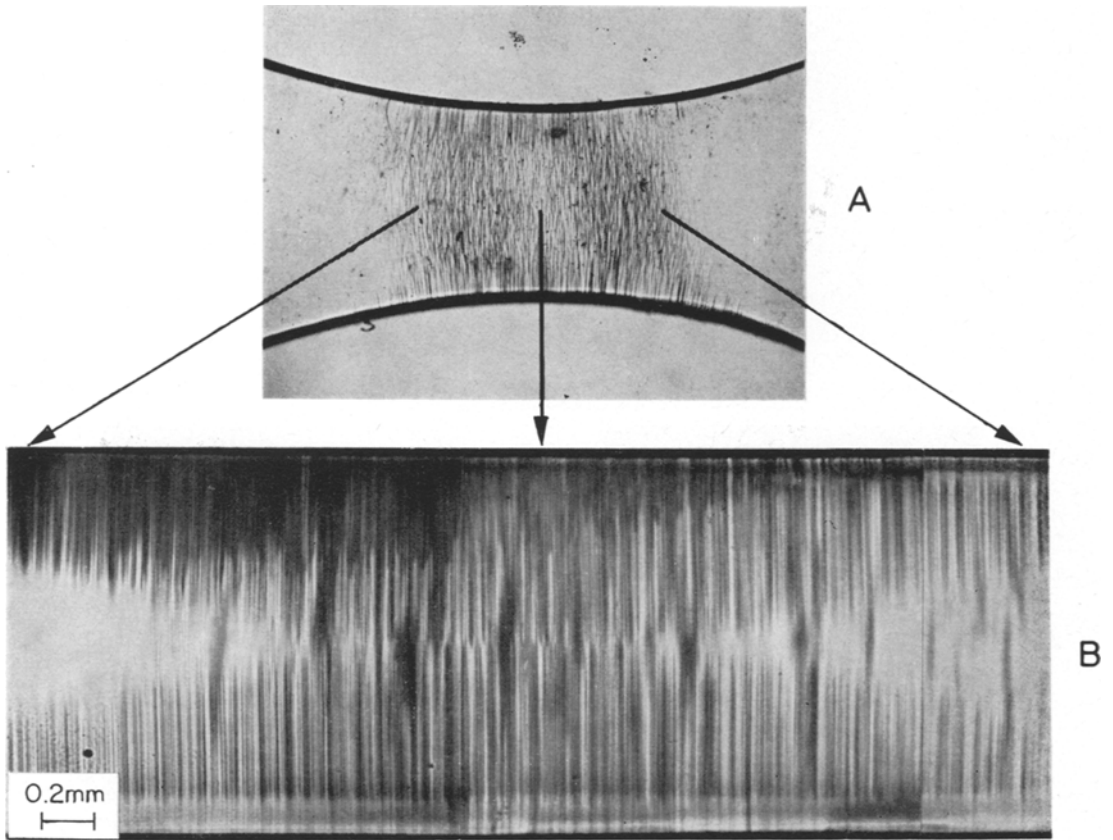
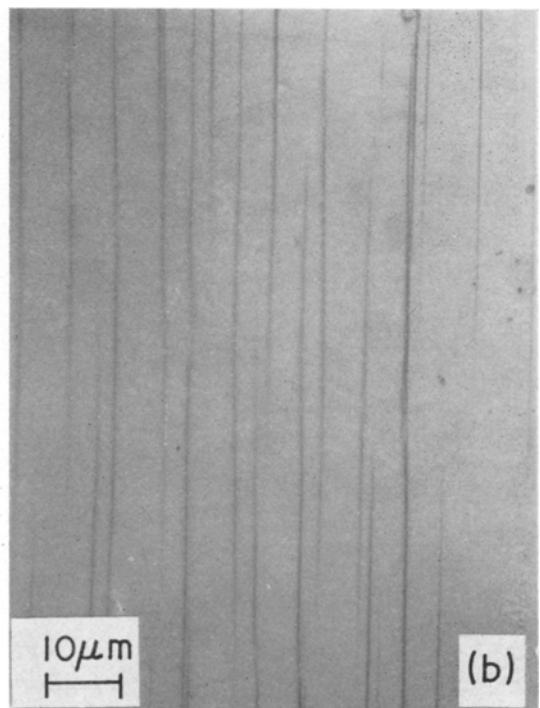


Figure 6 Crazes formed at 78° K in a PMMA specimen with a continuously varying gauge width, viewed in transmitted light: (a) original external surface; (b) cross section. Note the depth of craze penetration decreases with decreasing stress. Stress axis horizontal.



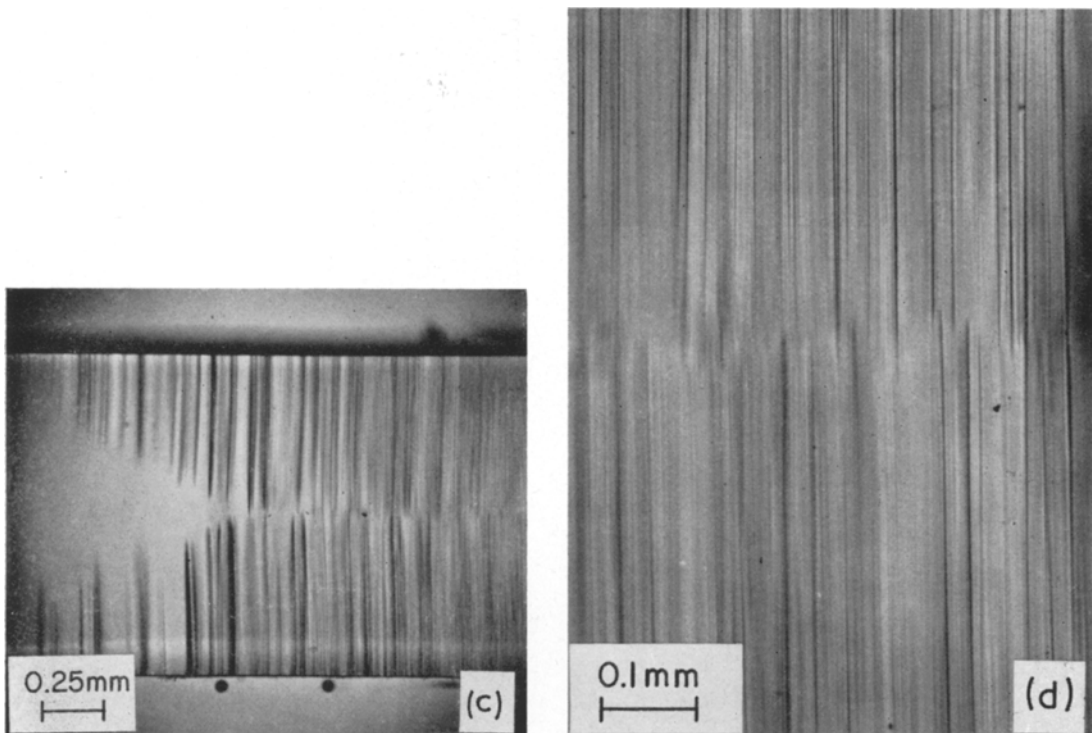


Figure 7 Crazes formed in PC at 78° K. The original external surface is imaged with reflected light (a) and (b), and cross sections (c) and (d) are imaged with transmitted light. Stress axis horizontal.

section increased from the initiation level to its final value. The low temperature craze is a macroscopic defect in that it is a sheet of deformed material, the area of which is a significant fraction of the specimen cross-sectional area (fig. 4). We suggest that the large craze area at 78° K reflects both the high flow stress and the inability of the material to significantly blunt the advancing craze tip. The effect of stress level has been described above. The effect of relaxation at the craze tip is illustrated in figs 5a and b. Over the range 78 to 120° K the stress range for craze growth in PMMA remains fairly constant [6]. However, the increased ductility induced by the same increase in temperature is manifest in the shorter (i.e. reduction in area) crazes at 120° K. At high temperature (fig. 5c) the stress level is reduced by a factor of two in comparison to 78° K; the lower stress level combined with the large increase in bulk ductility in going from 78 to 333° K results in the formation of crazes in which the area of an individual craze is an insignificant fraction of the area of a large low temperature craze.

The same factors, stress and ductility, also determine the development of craze width. A

qualitative comparison between PMMA and PC at 78° K reveals that the stress level is approximately the same (fig. 1), but that the greater ductility in PC results in a wider craze. The trend with temperature is not as clear (fig. 3) since the stress is decreasing and the ductility increasing. It would appear, however, that the material ductility is the dominant factor in determining the craze width since the width increases monotonically with increasing temperature.

These preliminary data point out the large modifications in craze morphology which can occur. Obviously, since crazes play such an important role in the deformation and fracture process in amorphous polymers, the changes in craze morphology noted here suggest that the study of the fracture process under one given condition will not be representative of other conditions. The authors are currently examining the formation and growth kinetics of these low temperature crazes in more detail.

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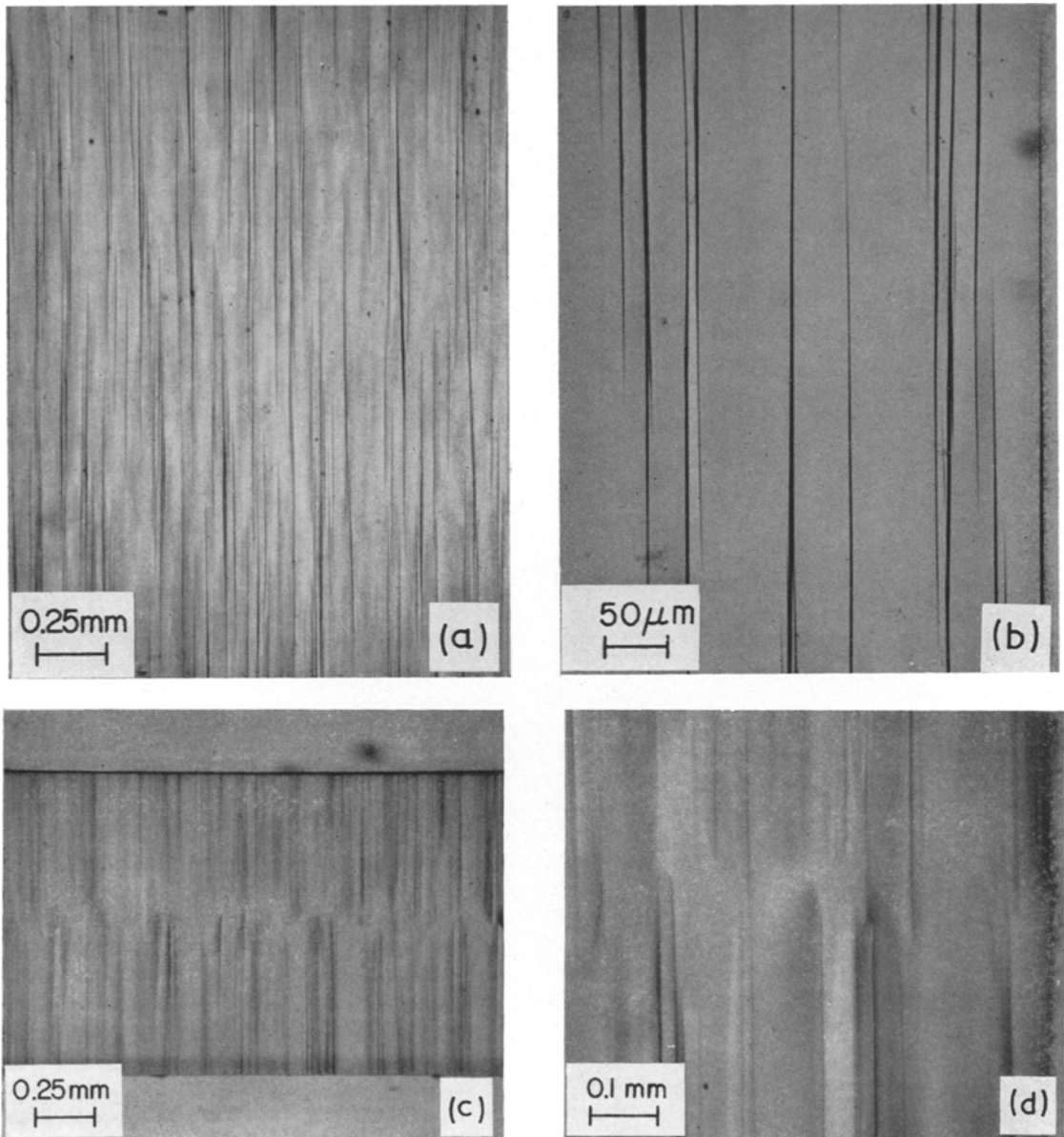


Figure 8 Crazes formed in PSF at 78° K. The original external surface is imaged with reflected light (a) and (b), and cross sections (c) and (d) are imaged with transmitted light. Stress axis horizontal.

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