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A comparison of the morphology of crazes formed in thin films and in bulk specimens of polystyrene

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The microstructure of crazes formed in solvent-cast thin films have been studied by transmission electron microscopy. The results have been compared with the microstructure of crazes determined from the examination of replicas obtained from the fracture surfaces of bulk specimens. The structure of crazes formed in thin films and in the bulk have been shown to be similar with the exception that much finer fibril structures are observed in thin films at large deformations. A model of the microstructure of a craze is presented.

1. Introduction

In a recent paper [1] we described the microstructures of crazes which had been observed in microtomed thin sections of precrazed bulk specimens of polystyrene and in crazes which were formed as a result of straining microtomed thin sections of bulk polystyrene. The experimental procedures were more straightforward than those used by Kambour and Russell [2] who have recently published a paper describing their results of an electron microscope study of crazes formed in polystyrene and rubber modified polystyrene. The basis of their technique was to impregnate the crazes in polystyrene and rubber modified polystyrene with an iodine-sulphur eutectic to act as a reinforcing agent in the preparation of thin films by ultramicrotomy. The use of this procedure is limited in that the reinforcing technique causes ageing of the polymer resulting in a physical deterioration of the crazes. However, the microstructure of the crazes observed in both investigations were similar, although in the former case no degradation occurred as it was not necessary to use reinforcement. It is desirable to consider other procedures for examining the microstructure and failure mechanisms of crazes for a number of reasons. The microtomy procedure is time consuming because of the great care required in the preparation of the thin sections. Microtomed thin sections of bulk material may of course be strained with an electron microscope tensile stage and subsequently examined. However, in this case, it is possible that the microtome knife or chatter marks may result in the premature formation and failure of crazes.

In the investigation which is reported in this paper we have examined the microstructure of crazes formed in solvent-cast thin films which have been strained inside or outside of the electron microscope. It is to be noted that Kargin [3] carried out similar experiments thirteen years ago as part of an investigation directed towards establishing the existence of a domain structure in amorphous polystyrene. The main aim of the present investigation was to determine whether or not the microstructures of crazes formed within thin films were similar to those formed in crazes in bulk specimens and to characterize in more detail the microstructure of crazes in polystyrene.

The microstructure of crazes formed in solvent cast thin films has been compared with the microstructure of crazes formed in the bulk. The latter was determined by the examination of thin films prepared by careful ultramicrotomy [1] and by the examination of replicas of the fracture surfaces.

2. Experimental procedures

A solution of 10% by weight of polystyrene was prepared by refluxing granules of G. P. Carinex (general purpose polystyrene $M_v = 2.03 \times 10^5$) in xylene. Thin films with thicknesses in the range

500 to 1500Å were prepared on clean glass slides by solvent evaporation of the solution. The films were then cut into two different sizes of specimen of dimensions 3 × 3 mm and 30 × 5 mm and were removed from the slides by immersion in deionized water. The small specimens were placed between supporting electron microscope grids and strained in a microstraining device. This will be referred to in future as procedure A. The specimens were strained inside or outside the electron microscope; the former procedure being used for studies of the growth and failure of crazes. The large specimens were placed on a shouldered mylar substrate which was subsequently strained in an Instron tensile machine at room temperature for a selection of cross-head speeds and total deformations. Specimens of dimensions suitable for electron microscopy were cut from the strained films after removal from the mylar substrate by immersion in deionized water (procedure B).

Some specimens were prepared by solvent evaporation from clean glass slides on which several electron microscope grids had been placed prior to coating with the solution (procedure C). In this case the electron microscope grids were embedded in polystyrene. A considerable distortion of the grid occurred on straining and this gave rise to a complex and changing stress system which resulted in the formation of intersecting sets of crazes. It is not possible to establish definitively the dependence of craze density or structure on testing conditions with this type of specimen. However, within a short period of time it is possible to make a preliminary survey of the types of craze microstructure which can arise.

Transmission electron micrographs of replicas were used to examine the fracture surface of a compression moulded bulk polystyrene specimen. The fracture surfaces were replicated using a two-stage replica technique and carbon-platinum shadowing. The observations were restricted to the region of the fracture corresponding to the stage in crack growth associated with the crack propagating alternately between the two craze-matrix interfaces (mackerel pattern [4]). The replicating material was gelatin and the shadowing angle was $\tan^{-1}\sqrt{3}$.

3. Results and discussion

The crazes which were observed in the examination of many thin films prepared and strained in the ways described in Section 2 were up to 4 μm wide. In general it appeared that narrower crazes exhibited a coarser fibril microstructure. This general morphological feature is illustrated in Fig. 1 which shows three intersecting crazes which formed in a complex stress system associated with testing procedure C. In all three crazes a fibril structure is present and in the regions away from the craze intersection the fibrils are normal to the well defined craze-matrix interface. This micrograph demonstrates that craze-craze intersections and the resultant morphologies may be examined *in situ* in the electron microscope. The narrow craze (X) in Fig. 1 has a coarse microstructure consisting of fibrils with diameters in the range 250 to 400Å

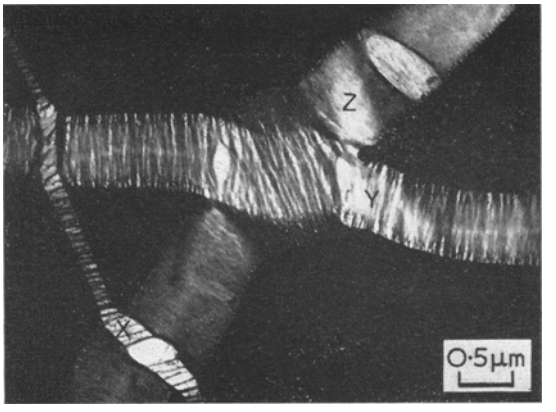

Figure 1 Transmission electron micrograph of a strained solvent-cast thin film showing the relationship between fibril morphology and craze width.

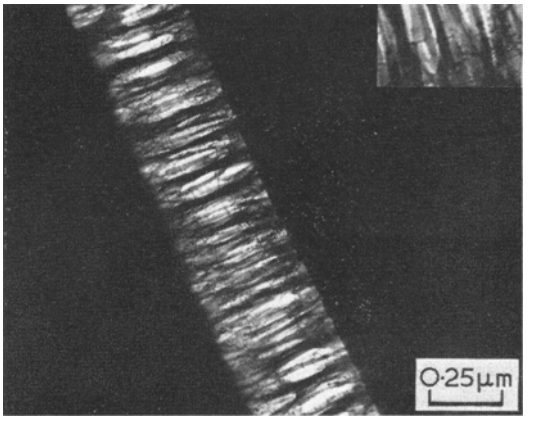

Figure 2 Transmission electron micrograph of a narrow craze formed in a "thick" solvent-cast thin film of polystyrene. The inset shows a higher magnification micrograph the minor fibrils with diameters in the range 30 to 60 Å which join the major fibrils.

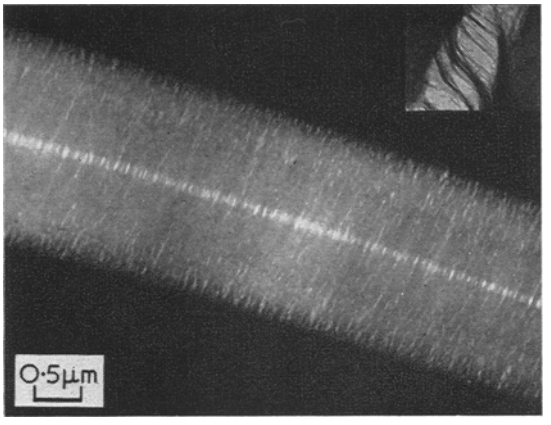

Figure 3 Transmission electron micrograph of a wide craze showing a finer fibril structure which has formed within the craze and which is oriented normal to the craze-matrix interface. The inset shows the finer fibrillar structure in more detail which is more readily observed in fractured crazes. The less dense mid-rib region of the craze which occurs in all crazes is much more apparent in this example.

and this is typical of this type of craze morphology. Craze Y in Fig. 1 is wider than craze X and has a finer microstructure than X but the microstructure is significantly coarser than the microstructure of the widest craze Z. The diameters of the fibrils within craze Z are in the range 30 to 60Å. Fig. 1 also shows that in the wider crazes the microstructure at the centre of the craze and at the craze-matrix interface is coarser than in the remainder of the craze. The difference in contrast at the centre of crazes is more apparent in thick specimens as illustrated in the narrow craze in Fig. 2. The decrease in coarseness of the fibril structure with increasing craze width and the occurrence of a coarser fibril structure at the craze matrix interface suggests strongly that the fine fibrils arise as a result of the thickening of the crazes.

A more detailed description of the microstructure of crazes formed in polystyrene was obtained by using specimen preparation procedures A and B. Procedure A was used to establish the fibril microstructure in more detail and procedure B was used to establish the dependence of microstructure on such factors as the strain-rate in testing and of the total deformation of the thin films. Procedure B did not in general give as much fine detail of the microstructure as procedure A and this was attributed to the extensive handling of the thin films with the former procedure.

In the craze in Fig. 2 produced by procedure A the major fibrils have diameters in the range 200 to 300Å with a spacing at the centre of the craze approximately 700Å and they are approximately normal to the craze-matrix interface. The major fibrils are connected to each other by minor fibrils with diameters of less than 100Å. The minor fibrils tend to be oriented normal to the major fibrils (see inset). A wide craze produced by procedure A having a very fine microstructure is shown in Fig. 3. The inset shows the fine 30 to 60Å fibril structure which becomes more apparent in fractured crazes.

Some insight into the origin of the coarser fibril structure in the centre of both wide and narrow crazes can be seen in Figs. 4a and b which show a craze of the narrow type before and after fracture. The fibril structure at the centre of the craze is inherited from the very narrow band of voids which comprise the tip of the craze and which define the areal extent of the craze prior to thickening. This central region of the craze is often associated with fracture as illustrated by Figs. 4a and b which show that fracture occurred along the centre of the craze. There is strong evidence from optical and scanning electron microscopy studies [5] that the fracture initiation region within crazes in bulk specimens is associated with this central region.

To establish that the fibril structure of crazes formed in thin films becomes finer with the progressive thickening of crazes it is necessary to produce crazes of a variable thickness. In this situation there should be a gradual transition of the coarse to the fine fibril structure with increasing craze thickness. The use of procedure B for specimen preparation enabled this requirement to be satisfied in a very straightforward way. When mylar films are drawn uniaxially they develop ridges which are parallel to the tensile axis. In procedure B the solvent-cast films were removed from the glass slides and were then attached to a mylar substrate by simply placing the films on the substrate. In many cases the films do not adhere strongly to the substrate and allow the substrate to form the ridged structure referred to above. When the ridges in the mylar developed the polystyrene film separated from the substrate in the vicinity of the ridges. In the remainder of the specimen there was sufficiently strong adherence of the film to the substrate for the polystyrene to undergo the applied uniaxial strain. As a consequence of the removal of the constraints imposed by the

mylar substrate in the vicinity of the ridges the thickness of the crazes in these regions was greater than that in the remainder of the specimen. This feature is illustrated by the optical micrograph of Fig. 5.

A series of experiments were carried out under the conditions referred to above for a range of strain-rates and total deformations. The density and widths of crazes which formed in thin films of the same initial thickness increased and decreased respectively with increasing strain-rate. There was no increase in the density of crazes with increasing total deformation. The widths of the crazes increased with increasing deformation. Sections of thin polystyrene films were examined with an electron microscope and some typical examples of the microstructure of crazes formed under different conditions are shown in Figs. 6 and 7. Fig. 6 is an electron micrograph of a craze formed at a strain-rate of 6.66×10^{-3} min^{-1} for a total deformation of 50 %. At low strain-rates the craze increases in thickness by the drawing of further matrix material and to some extent by an increase in the orientation of the fibrils. The micrograph of Fig. 7 shows the microstructure of a craze formed at a strain-rate of 1.66×10^{-1} min^{-1} after a total deformation of 66 %. There is a gradual transition from the coarse to the fine microstructure with increase in the thickness of the craze in the vicinity of the

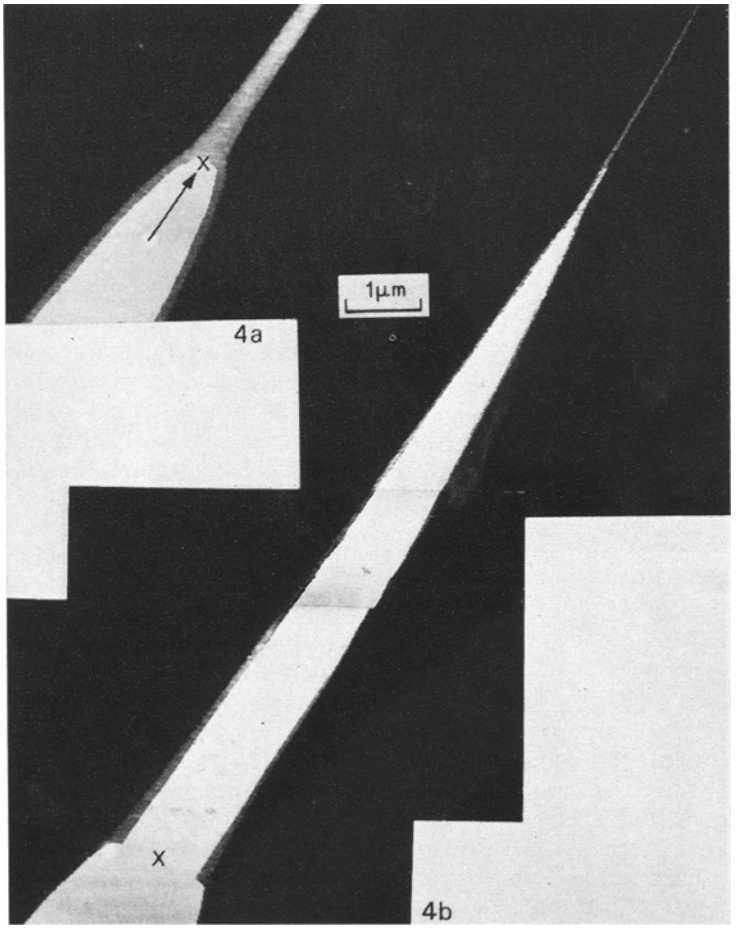

Figure 4 (*a*) *and* (*b*) Transmission electron micrographs showing a narrow craze before and after fracture. The region X in (a) corresponds to the region X in (b). Fracture which occurs in *in situ* tensile experiments often occurs along the central region of the craze indicated by the arrow in (a). The origin of the less dense region at the centre of this craze is associated with the very narrow band of voids which form at the tip of the craze as shown in (b).

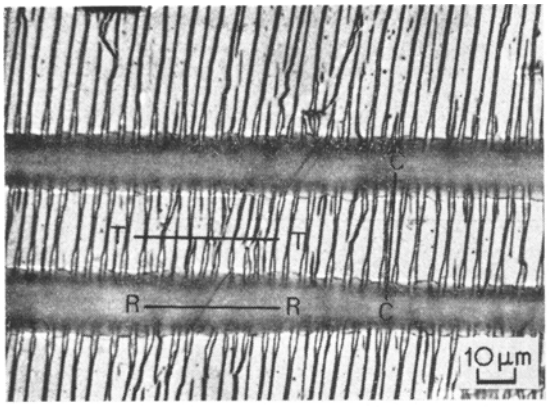

Figure 5 An optical micrograph showing the array of crazes C–C which formed normal to the applied stress axis T – T. In the vicinity of ridges R – R of the mylar substrate which develop parallel to the tensile axis the crazes are noticeably wider. This occurs when the thin polystyrene film lifts from the supporting substrate. In the vicinity of the ridges, the crazes are out of focus.

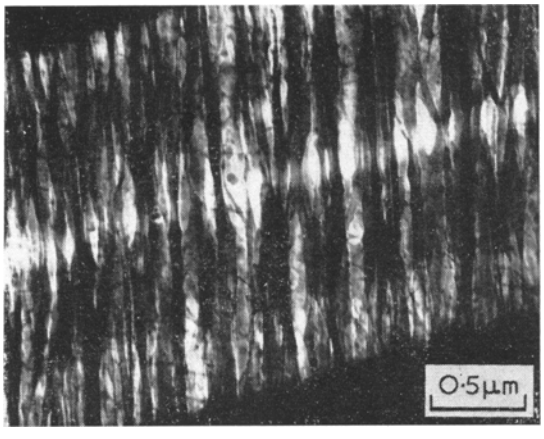

Figure 6 Transmission electron micrograph of a craze formed at a strain-rate of 6.66×10^{-3} min^{-1} at a total deformation of 50%.

mylar ridge. The micrograph shows that the fine microstructure of crazes in thin films was associated with the progressive thickening of crazes. The results obtained from a large number of observations indicate that the fine microstructure occurs at narrower craze widths with increasing strain-rate.

In the thin films prepared by methods A and B the onset of crazing occurred at approximately 1% strain which is comparable with the behaviour of bulk polystyrene. However, for the range of strain-rates investigated the transition

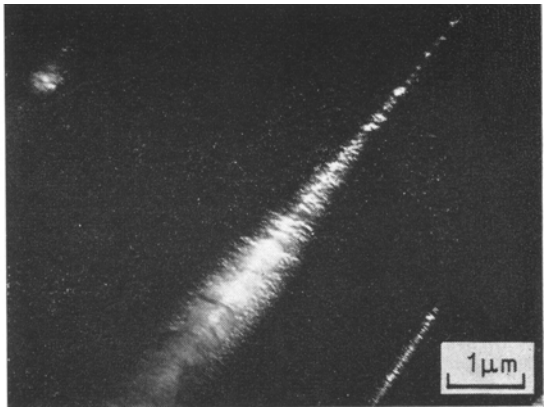

Figure 7 Transmission electron micrograph of a craze formed at a strain-rate of 1.66×10^{-1} min^{-1} at a total deformation of 66%. The transition from coarse to fine fibril structure is clearly shown.

from the coarse to the fine fibril microstructure in specimens of type B always occurred well in excess of the strain to fracture observed in bulk specimens. The formation of crazes which exhibit a fine fibril structure would therefore be unlikely to occur in thick specimens.

The electron microscopy studies that have been made to date support the model of a craze represented by the schematic diagram in Fig. 8. For convenience the angle of the tip of the craze has been exaggerated in this diagram.

Replica studies which are described below together with additional studies [8] show that the craze microstructures that are observed in the bulk fall into regions b and c of Fig. 8. The major fibril diameter in these regions does not vary widely and is in the range 250 to 500Å. The fine fibrils which are normal to the craze matrix interface in region d of the craze form by the breakdown of the major fibrils, which is represented schematically in Fig. 8 by the transition of structure c to structure d.

A comparison of the micrographs presented in this paper with those published previously [1] shows that the microstructure of crazes formed in bulk specimens and the microstructure of "coarse" crazes formed in thin films are very similar. There are close similarities between the results presented in this paper and those described by Kambour and Russell [2].

Further confirmation of the similarity between the structure of crazes formed in thin films and in the bulk may be obtained from replica studies of the fracture surfaces of polystyrene. The fracture of glassy polymers has been shown to be

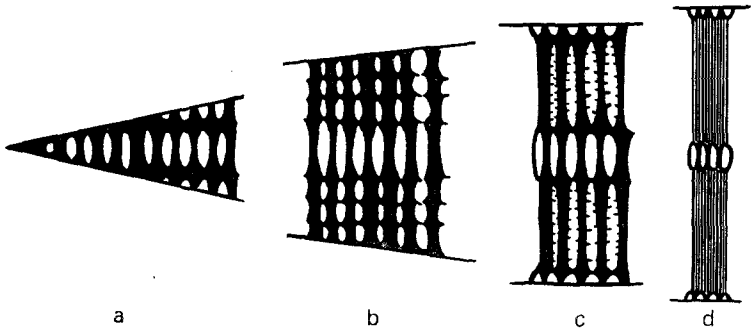

Figure 8 Schematic diagram of the variation in microstructure of a craze in polystyrene with increasing craze width. In this diagram the angle at the tip of the craze is exaggerated and the craze width of region d in relation to region c would be greater than that shown.

closely associated with the formation and failure of crazes [5]. It is therefore to be expected that fibrils with diameters of several hundred Angstroms should be present on the fracture surfaces of polystyrene. Replica studies by Bird *et al* [6] and by Haward and Brough [7] have shown the existence of fibril structures on the fracture surfaces of polystyrene. These observations have been confirmed in a more detailed study of polystyrene fracture surfaces [8] using the replica technique described in Section 2. An optical micrograph of a fracture surface of a polystyrene specimen is shown in Fig. 9. An illustration of the fibril structure on this fracture surface is shown in Fig. 10 which is a replica of region b of the Mackerel pattern. The band X on the fracture surface exhibits a distinct fibril structure which can be seen more clearly in the

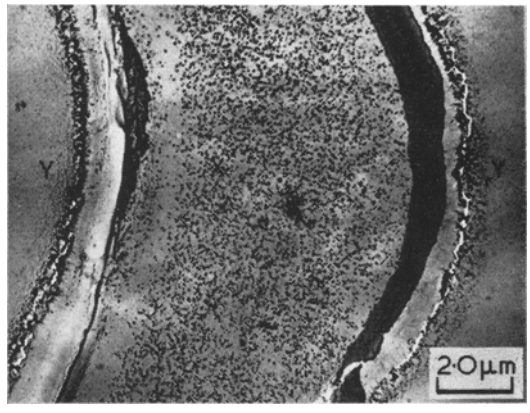

Figure 10 Transmission electron micrograph of a replica taken from the mackerel region shown in Fig. 9. The mackerel band X shows well defined fibrils whereas the two adjacent regions Y show a less pronounced fibrillar structure. The fibril dimensions compare very well with the dimensions of the major fibrils in Fig. 2.

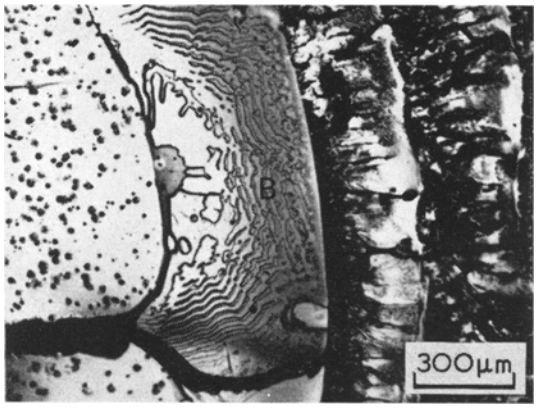

Figure 9 Optical micrograph showing the initiation, mackerel and hackle regions of a bulk polystyrene fracture surface.

enlargement shown in Fig. 11. The fracture surface is parallel to the craze-matrix interface and the ends of the broken fibrils that can be seen on the electron micrograph are 250 to 500Å in diameter. The distribution of fibrils and their dimensions are therefore very similar to the craze microstructure shown in Fig. 2 which formed in a relatively thick "thin" film. The whole of the mackerel pattern exhibited a fibril structure. Regions of pronounced fibrils (X) alternate with regions (Y) showing less well defined fibrils. This morphology is consistent with the description of the Mackerel pattern given by Murray and Hull [4]. They proposed that the crack in the Mackerel region of a craze propagates from one surface of the craze to

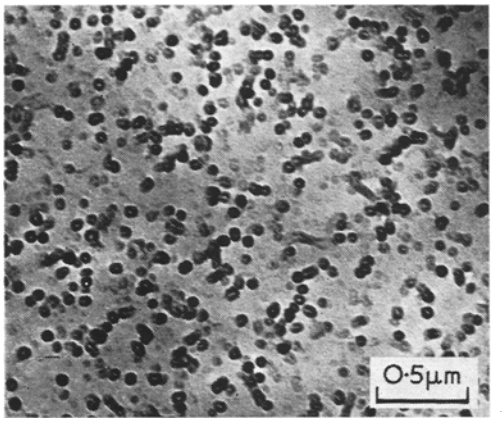

Figure 11 Transmission electron micrograph of the band X in Fig. 10 taken at a higher magnification.

another. This mode of propagation would expose on alternate regions of the Mackerel pattern arrays of short and pronounced fibres respectively. Opposite sides of the fracture surface would likewise exhibit pronounced and short fibres respectively. This morphology is illustrated very clearly by Fig. 5 of a previous paper [1], and replicas of the fracture surfaces shown in this figure would compare very closely with regions X and Y of Fig. 10.

4. Conclusions

This paper has shown that it is possible to produce crazes in solvent-cast thin films which are comparable with those of the bulk, and to examine the microstructure of these crazes without the use of reinforcement techniques. Thin films thus provide a way of studying the formation, growth and failure of crazes in polymeric materials by *in situ* experiments in the electron microscope. The effect of heat-treatment testing conditions and environment on crazing and subsequent failure processes may also be studied directly with this technique. Differences in the physical or mechanical properties of thin films and bulk specimens must however be taken into account in the interpretation of results.

Fibrils of 250 to 500Å in diameter are the predominant common feature of the microstructures of crazes in cast thin films and in bulk specimens. At large total deformations however the microstructure of crazes in thin films changes from coarse to fine fibrils of less than 100 Å in diameter which also feature as cross fibrils in narrow crazes. The fine fibrils become apparent in the progressive thickening of crazes which at large deformations causes the major fibrils to break down.

The fine fibrils have not been observed on the fracture surfaces of bulk specimens. This is attributed to the loss in resolution associated with the replica technique. Subtle differences in fibril morphology on fracture surfaces have been identified showing that the more general application of the replica technique could lead to a more detailed understanding of the fracture process.

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