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Morphology and intersections of crazes in polystyrene films

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Craze network with interconnecting crazes was produced in thin (~ 60 nm) polystyrene films by using a spherical stretching method. For 30% and 45% radial strain, the average mesh size, defined as the square root of average non-crazed areas enclosed by crazes, decreased from about 28 μm to 4.6 and 2.7 μm, respectively, as the molecular weight increased from 46 900 to 1 350 000. At a molecular weight of about 10^6, the interactions between crazes became evident by the split and change of directions at the end of their propagation. Two types of intersection appeared to exist in parallel. The first type showed void formation at the intersections with no apparent fibril displacement effect. The second type showed that the fibrils at the intersection of two perpendicular crazes reoriented to a new direction which seemed to be determined by the relative displacements of the two crazes at the intersections. This observation suggests that the craze fibrils can be displaced and further stretched by a second crazing process.

1. Introduction

It is known that plastic deformation of amorphous polymers usually generates localized shear bands and crazes. One way to understand the deformation process is to study the mutual interactions in shear bands, crazes and between them. In the case of shear bands, two sets of intersection bands with constant intersection angles can be produced in a rectangular polystyrene specimen by a simple uniaxial compression or consecutive compressions along two mutually perpendicular axes [1–3]. On the other hand, the interactions between shear bands and crazes have been studied in both thin films and bulk specimens by a number of investigators. Kambour [4] observed the diversion of crazes by a pre-existing shear band in poly (2, 6-diphenyl–1, 4-phenylene oxide) under tension and proposed several possible shear band–craze interactions from the results of other investigators [5, 7]. Donald *et al.* [8] showed that the direction of propagation of crazes was diverted by shear bands in a bent and crazed specimen. A craze can also be displaced by a propagating shear band as noted by Harris and Ward [9]. The morphology of shear to craze transition as a function of temperature and blend composition was studied in thin polymer films [10]. By immersing a shear banded specimen in methanol, a regular craze pattern can occur and interact with pre-existing shear bands in bulk polystyrenes [11]. Bucknall *et al.* [12] considered craze-shear band interactions as the main reason for the increased creep resistance of rubber toughened polymers.

No extensive study on the interactions between crazes, appears to have been done so far. Since crazes only respond to tensile stresses, to produce craze intersections, a deformation procedure to include two tensile stresses of different directions seems necessary. King and Kramer [13] demonstrated craze intersections by consecutively applying two perpendicular tensile stresses in 0.4 to 0.6 μm thick polystyrene films. They found void formation at the intersections could act as nuclei for cracks to develop. In this communication, a new deformation method is used to study craze interactions in thin films. Polystyrene films of about 60 nm thick were stretched spherically in the radial direction. The multi-directional tensile

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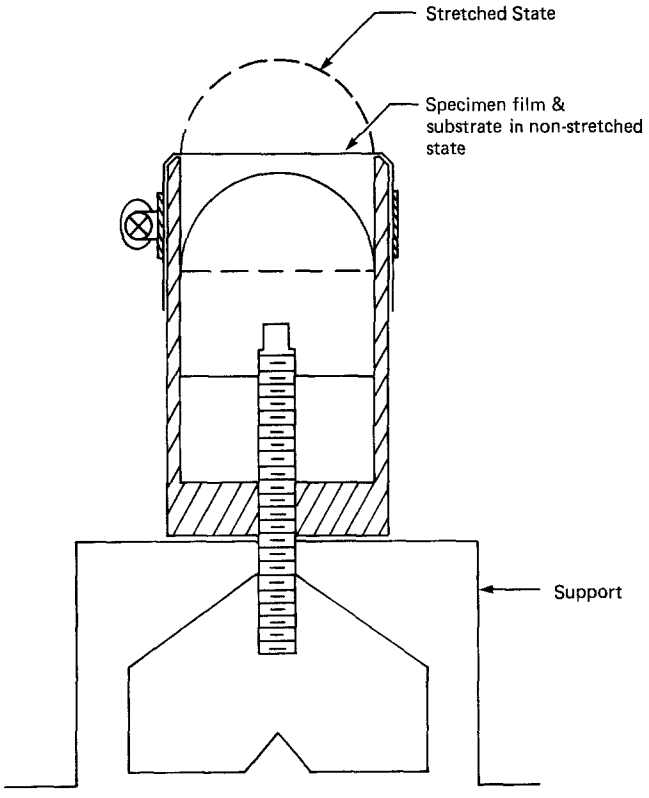


Figure 1 A schematic representation of the spherical stretcher showing initial non-stretched (solid line) and final stretched (dotted line) states.

stresses should be able to generate crazes in different directions and produce intersections between them, although specimens are subjected to a certain extent of bending during stretching. Furthermore, the distribution of crazes in spherically stretched films should reveal any possible heterogeneities of the craze yielding process. The results on these and others are presented here.

2. Experimental details

2.1. Materials and testing method

Atactic polystyrenes used in this study were obtained from The Dow Chemical Company. They were free of additives and had narrow molecular weight distributions. Six different polystyrenes with the weight average molecular weight ranging from 46 900 to 1 350 000 were used as listed in Table I.

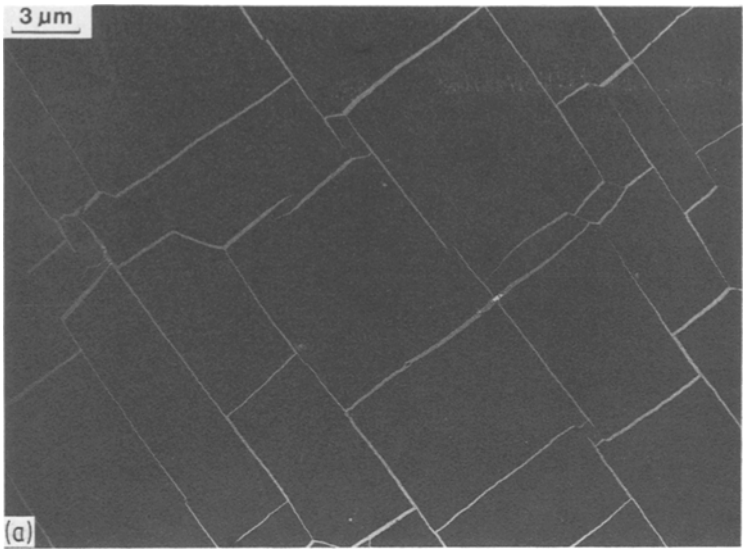
A spherical stretcher was designed and constructed for the deformation of thin films as shown schematically in Fig. 1. It was composed of a bullet-shaped Teflon* piston and installed in a cylindrical brass housing 2 in. long. The end of the piston was precisely machined to a hemisphere with a diameter 1 in. A substrate with coated film specimens to be studied was fastened flat to the end of the housing with a hose clamp. When the threaded brass rod was operated by the attached wing nut, it could move the piston forward and push the spherical portion into the film; the film was then stretched radially into a hemispherical shape. The multidirectional forces generated during stretching would initiate crazes in the thin specimen film.

0.3% dilute solutions were prepared by dissolving 0.15 g polystyrenes in 50 ml xylene. 10 μl of the solutions were cast on 1.1 mil† thick Mylar* films fastened on the spherical stretcher by using a 10 μl glass syringe. The cast solutions were spread uniformly on the 1 in. diameter film area as defined by the stretcher and were dried in air

TABLE I

M_w	M_w/M_n
46 900	1.08
110 000	1.07
242 000	1.11
491 000	1.21
961 000	1.59
1 350 000	1.70

*Trademark of E.I. du Pont de Nemours & Co.
†1 mil $\equiv 2.5400 \times 10^{-5}$ m.



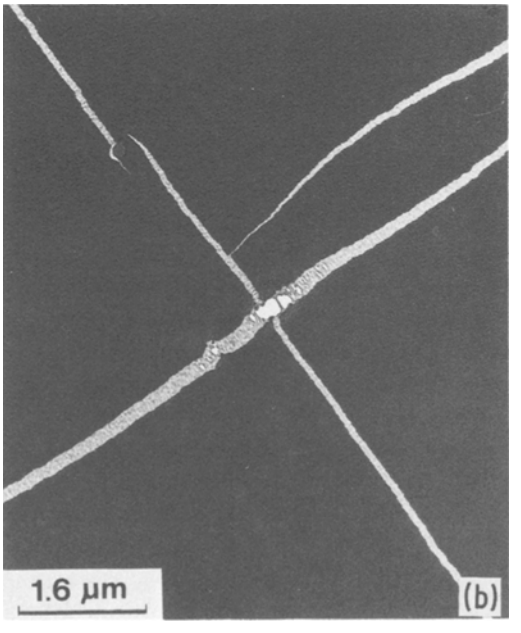


Figure 2 (a) Morphology of craze network developed in a specimen with molecular weight M_w = 961 000 at 30% strain. (b) A magnified view of a craze intersection from (a).

for 30 min. The whole assembly was then annealed in vacuum at 105° C for 3 h and was air cooled to room temperature. The thickness of the specimen as prepared was about 60 nm.

2.2. Mechanical stretching and replicas for electron microscopy

The specimens were stretched to predetermined radial strains by slowly operating the stretcher over a 2 min interval. A 5 mm diameter circle was marked around the centre of the hemispherical Teflon piston to serve as the gauge area within which the craze morphology was studied. Both 30% and 45% radial strains were determined based on the gauge area and were also marked circumferentially on the piston as an indication of stretching levels. The deformation was completed when a marker on the substrate moved radially from the innermost circle to the desired strain marks. After stretching, the specimen was coated with a thin layer of platinum and backed with a layer of carbon in a vacuum evaporator while it was in the stretched state. The shadowing angle was 45° and the distance between the specimen and the evaporation source was about 10 cm. A drop of polyacrylic acid water solution was then put on the top of the coated specimen within the pre-marked 5 mm diameter area. After it was dried for 6 h, the replica was peeled off using tweezers and was floated on water to remove PAA. It was then picked up on a copper grid for observation in a JEM-100B electron microscope.

3. Results and discussion

3.1. Morphology and interactions of crazes

A preliminary study indicated that crazes would not be developed for strains lower than 10%, a minimum of 10 to 15% strain seems to be necessary to initiate crazes. Fig. 2a shows the craze pattern developed in a specimen with M_w = 961 000 at 30% strain. It is seen that crazes developed in a

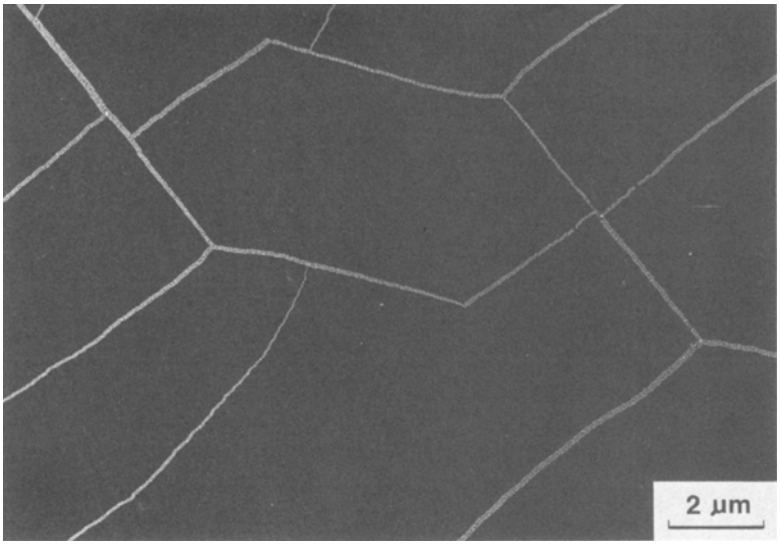


Figure 3 Irregular craze network developed in areas outside the centre of stretching.

spherically stretched polystyrene film form a structurally reticulate network. The network is composed of two sets of mutually perpendicular crazes interconnected with each other. They are equally abundant in both directions and distributed uniformly within the area examined. The thicknesses of the crazes are usually in the range 0.03 to 0.3 μm and are more or less uniform thoughout the length of propagation. It is likely that when a craze meets another craze oriented perpendicularly, this craze is either stopped by the perpendicular one or propagates across it forming an intersection. A magnified view of an intersection is shown in Fig. 2b. It is clear that a void is produced at the intersection with no effect on the directions of propagation of the two intersecting crazes. The average non-crazed areas enclosed by crazes are an indication of the density of the crazes constituting the network. The mesh size, as defined by the square root of the area enclosed by the crazes, varies from less than 1 μm to about 8 μm with an average of 4.5 μm within an area of 2500 μm^2 examined. In areas away from the centre of stretching, the network structure becomes irregular in shape as shown in Fig. 3. The thickness of the crazes seems to be unchanged. The average mesh size of the network, however, increases to 6.3 μm in an area of 2500 μm^2 examined indicating that the local strain decreases. In areas further away from the centre, uniaxial crazes are seen to distribute uniformly in the circumferential directions and are evenly spaced as shown in Fig. 4. They are usually wavy with variable thicknesses and seem to split, and terminate freely inside the specimen.

As in the case of uniaxial deformation, crazes developed in the spherically stretched film can also terminate freely as seen in Fig. 2. The thickness of a craze decreases gradually to zero when approaching the end of propagation. Several types of craze interactions have been observed. As in the case of uniaxial stretching, when two parallel and close-by crazes terminate inside a specimen, both change their direction of propagation and seem to attract each other at their ends as shown in Fig. 2a. An interesting and prevailing observation is that the direction of propagation of a craze seems to be affected by the ending of a perpendicular craze so that it changes the direction of propagation to join the end of the other craze as shown in Fig. 5a. The new direction makes an angle of about 45° with the original one. However, the craze resumes its original propagation direction after leaving the junction. It is noted that the fibrils inside the craze are all in the same direction even though the propagation direction changes as shown schematically in Fig. 5b. Another type of interaction behaviour is shown in Fig. 6. When four orthogonal crazes terminate and meet in the same area, splits and change of directions in all the crazes occur. These observations indicate that the propagation and termination behaviour of a craze is strongly affected by the local stress fields generated by other crazes in the film.

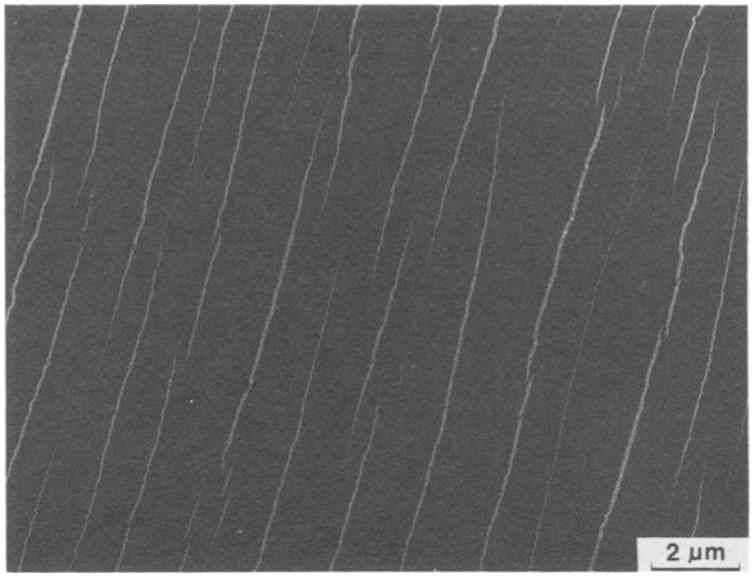


Figure 4 Uniaxial crazes developed circumferentially in areas further away from the centre of stretching.

3.2. Intersections of crazes

Since the craze network developed by spherical stretching is composed of two sets of mutually perpendicular crazes, it is likely that these crazes could initiate somewhere and propagate away from it along different directions. The intersections between crazes are thus developed when some crazes meet other pre-existing crazes during their propagation. As noted before, a strong voiding effect is usually generated at the intersections. An example of intersections for a specimen of $M_w = 1350000$ ($\epsilon = 30\%$) is shown in Fig. 7. The long craze seems to have propagated across three crazes oriented in the perpendicular direction and finally have stopped at the fourth one. The craze seems to have felt some resistance at each intersection so that the thickness gradually decreases. The direction of propagation, however, does not seem to be affected by the intersection processes. The three intersected crazes do not seem to have been displaced either. Furthermore, it is clear that these intersections developed voids with no further deformation of the fibrils at the intersections. The fibrillar microstructure inside an intersection is shown in detail in Fig. 8 for another specimen stretched at about 40% strain. In contrast to the development of two directional fibrils at the intersections produced in a biaxially-

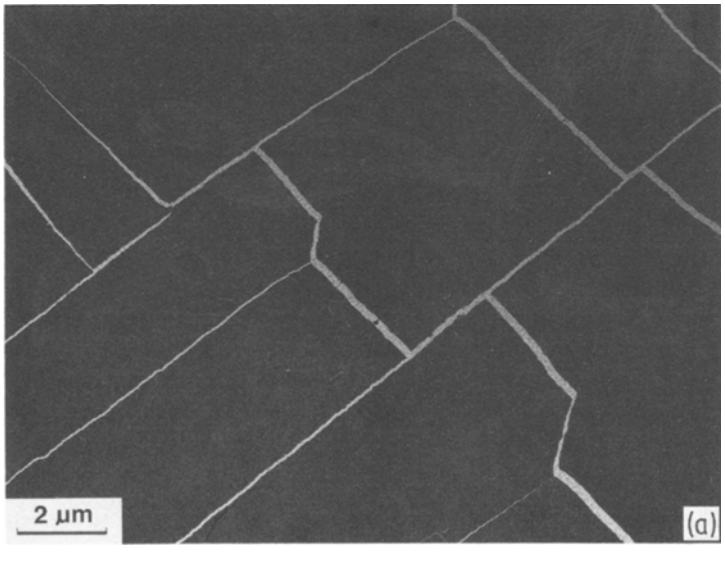


Figure 5 (a) Interactions between a craze and the ending of a nearly perpendicular craze showing the change of propagation directions of the former. (b) Schematic drawing showing the uni-directional arrangement of the fibrils inside a craze upon interaction by the ending of another craze.

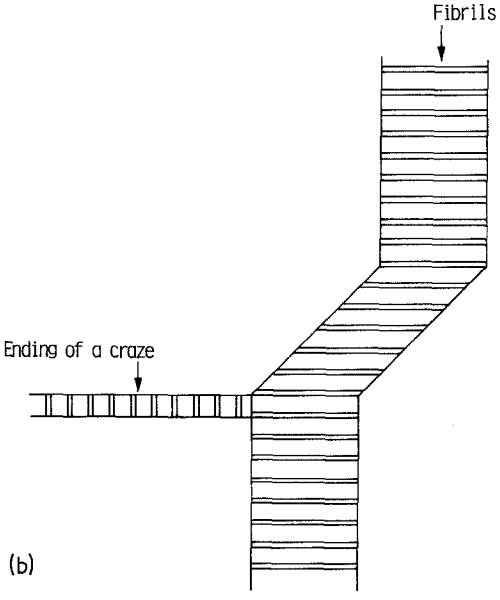


Figure 5 Continued.

stretched thick film [13], the intersections produced here show multidirectional fibrils with large voids developed between them. The void formation in this case, however, seems to involve much smaller amount of fibril breakdown.

A careful examination indicates that there seems to be another type of intersection appearing parallel in high molecular weight specimens. As shown in Fig. 9 for a specimen of M_w = 1350000 at 45% strain, when the horizontal craze met a pre-existing craze oriented perpendicular to it, the new craze seems to have propagated along the pre-existing craze for a certain distance and finally left the intersection resuming its original propagation. It eventually stopped by another perpendicular craze. The craze fibrils at the intersection reorient to a new direction which seems to be determined by the relative displacements of the two crazes at the intersection. Furthermore, the fact that the thickness of the craze at the intersection increases seems to indicate that the fibrils inside the pre-existing craze are further stretched and elongated by the intersection action. This further stretching effect is indicated by the fact that the boundaries of the craze at the intersection are in line with the external boundaries of the intersected craze on each side of the intersection, suggesting little or no fibre pull-out is involved in the intersection processes. The intersection also involves little or no fibril breakdowns due to the stretching in the lateral direction as usually occurs. The decrease of

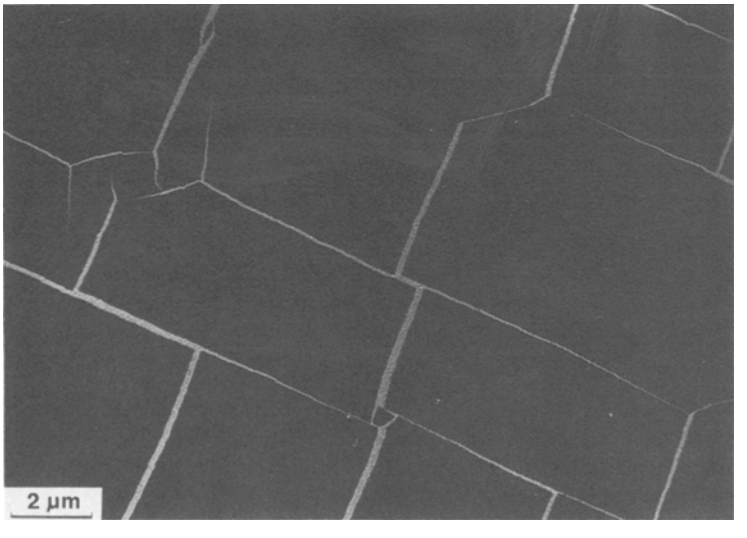


Figure 6 Morphology of craze end interactions showing split and/or change of directions in the meeting crazes.

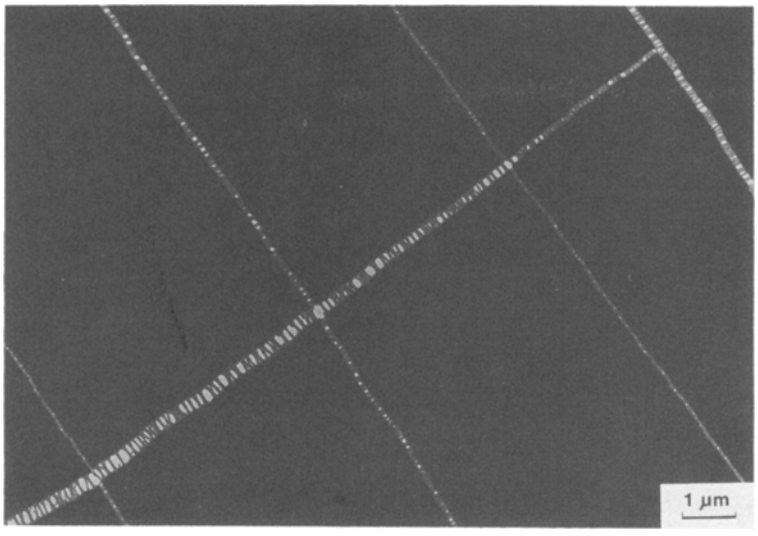


Figure 7 Intersections of crazes developed in a specimen with molecular weight M_w = 1 350 000 at 30% strain.

fibril density in the intersection could be due to the further stretching effect of fibrils. A schematic drawing showing this mechanism is shown in Fig. 10. The deformation of the fibrils at the intersections is assisted by both the internal stresses of the existing craze and the tensile stress of the intersecting craze so that the total thickness of the craze increases and the fibrils are oriented and elongated. It is noted that each individual fibril is further stretched or sheared along its new direction similar to the tensile fracture processes of shear bands as reported [14]. To accommodate the thickening effect, a slight displacement of the fibrils along the intersecting craze could occur outside the intersection. The extent, however, is small.

Although the thickening of a craze is determined by the tensile displacement caused by the internal stresses at intersections, the length of propagation of the intersecting craze along a pre-existing craze seems to be arbitrary. An example of two intersections for a specimen with M_w = 961 000 at 30% strain is shown in Fig. 11. The thick craze seems to have propagated a relatively longer distance along the first intersected craze than that on the second intersected craze, before resuming the same and the original propagation. The displacement and reorientation effects of the fibrils at the intersections do not seem to be affected by the size of the intersection. A clear appearance of both effects is seen at both intersections. These observations seem to indicate that the craze fibrils can be further deformed along the original fibril axis by a second crazing process.

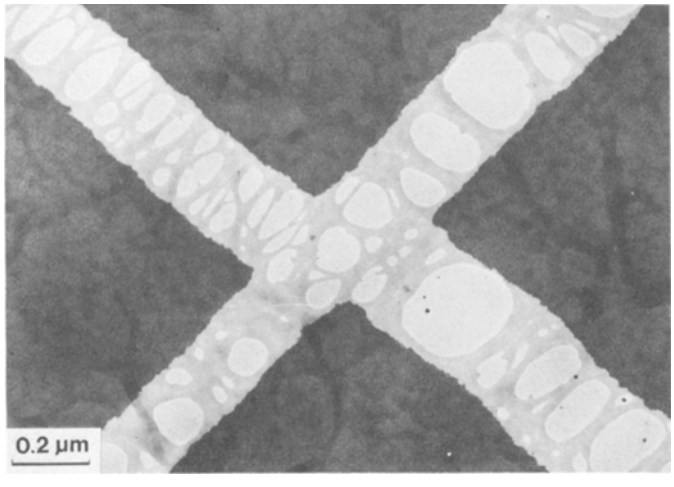


Figure 8 Fibrillar microstructure inside an intersection for a specimen stretched at 40% strain.

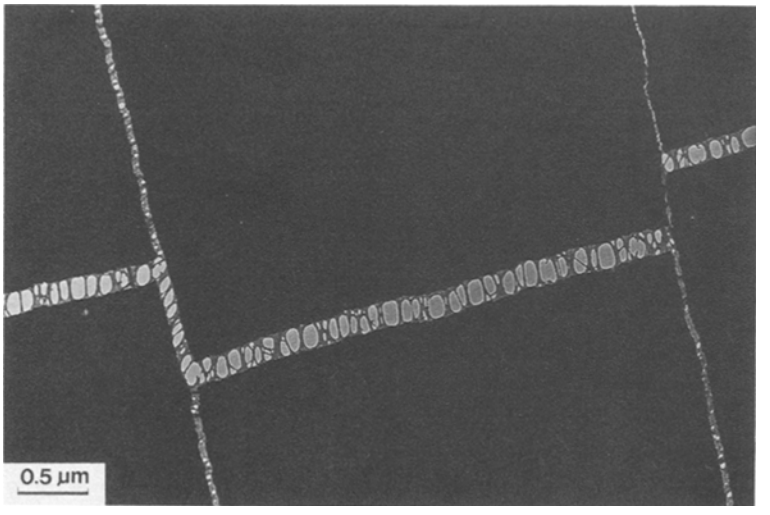


Figure 9 Intersection between two mutually perpendicular crazes showing the fibril reorientation and displacement effects of the craze.

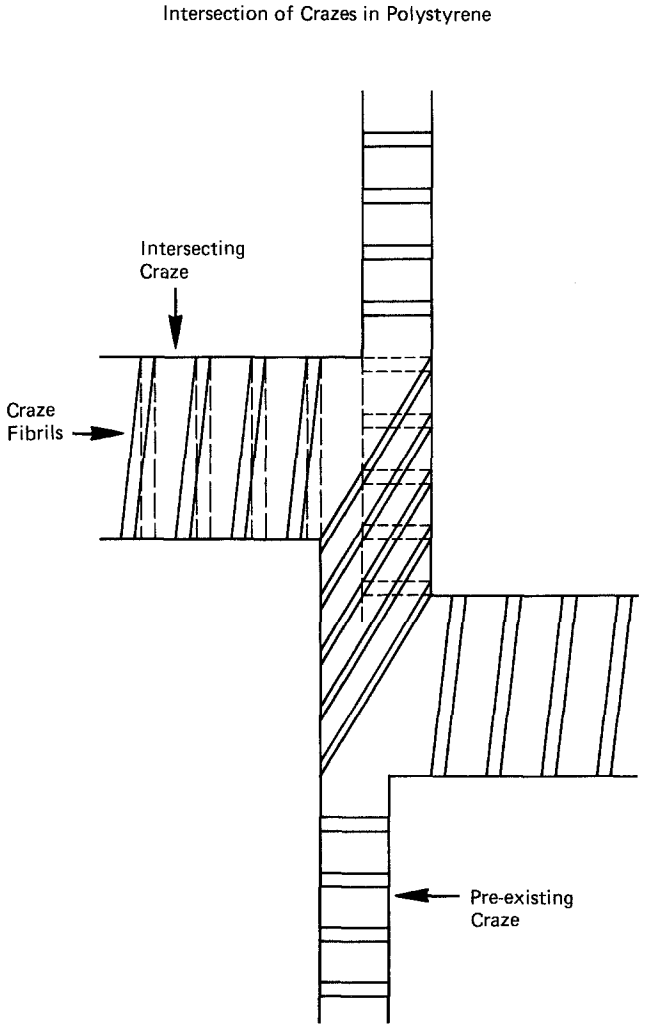


Figure 10 Schematic representation showing the thickening of a pre-existing craze and the reorientation of fibrils at the intersection.

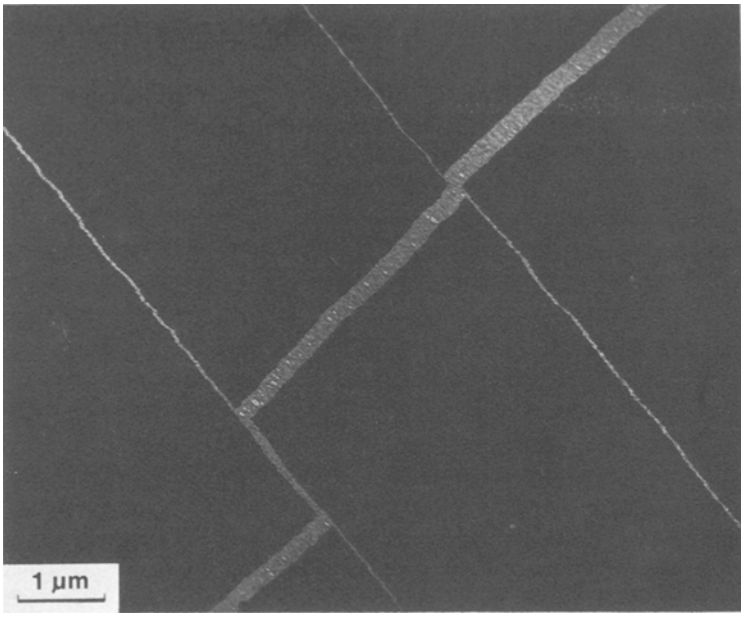


Figure 11 Another example showing the intersections in a specimen with $M_w = 961\,000$ at 30% strain.

3.3. Effects of molecular weight and strain on craze network morphology

So far the craze interaction and intersection behaviour were observed in high molecular weight polystyrenes, i.e. polystyrenes with weight average molecular weight $M_w = 961\,000$ and 1350 000. To see how molecular weight affects the craze morphology, an extensive study was done with the chosen materials listed in Table I. Fig. 12 shows a plot of the average mesh size as a function of molecular weight. The measurements were done on electron micrographs within an area of 2500 μm^2. At 30% strain, the mesh size decreases at the beginning when the molecular weight increases from 46 000 to 491 000. A plateau with an average mesh size of about 4.6 μm appears as the molecular weight is larger than about 2×10^5. The average mesh size seems to increase to 6.6 μm as the molecular weight reaches about 10^6. It is found that specimens of $M_w = 46\,900$ do not give stable craze network; localized craze rupture or gross failure developed instead. Crazes in specimens with molecular weight lower than 491 000 can still form an interconnected network consisting of two mutually perpendicular sets. However, they are relatively wavy and, in addition, the intersection usually generates voids caused by fibril ruptures with no evidence of reorientation and displacement effects.

The dependence of mesh size on molecular weight changes as the strain increases from 30% to 45%. At the higher strain, the average mesh size seems to decrease more rapidly as the molecular weight increases. A more steady plateau of the average mesh size of about 2.7 μm is seen to develop between 242 000 and 1350 000. A quantitative measurement of the thicknesses of 100 crazes in a specimen with $M_w = 1350\,000$ indicates that the average craze thickness is $0.162 \pm 0.12\,\mu m$ which is about the same as that of 30% strain. This suggests that increase of the strain from 30% to 45% results in an increase of the number of crazes constituting the network rather than the thickness of crazes.

4. Summary and conclusions

1. A craze network with two sets of mutually perpendicular crazes are produced in thin (~ 60 nm) polystyrene films by using a spherical stretching method. The crazes are equally abundant in both directions and distributed uniformly in an area of about 20 mm^2 examined. At 30% and 45% radial strain, the thickness of the crazes is in the range of 0.03 to 0.3 μm. They seem to interact with each other as indicated by the split and change of direction at the end of their propagation in the vicinity of other crazes.

2. Two types of craze intersections are observed in specimens with molecular weight $M_w = 961\,000$ and 1350 000. The first type shows the formation of voids, which seems to result from multidirectional stretching of fibrils or fibril ruptures at the

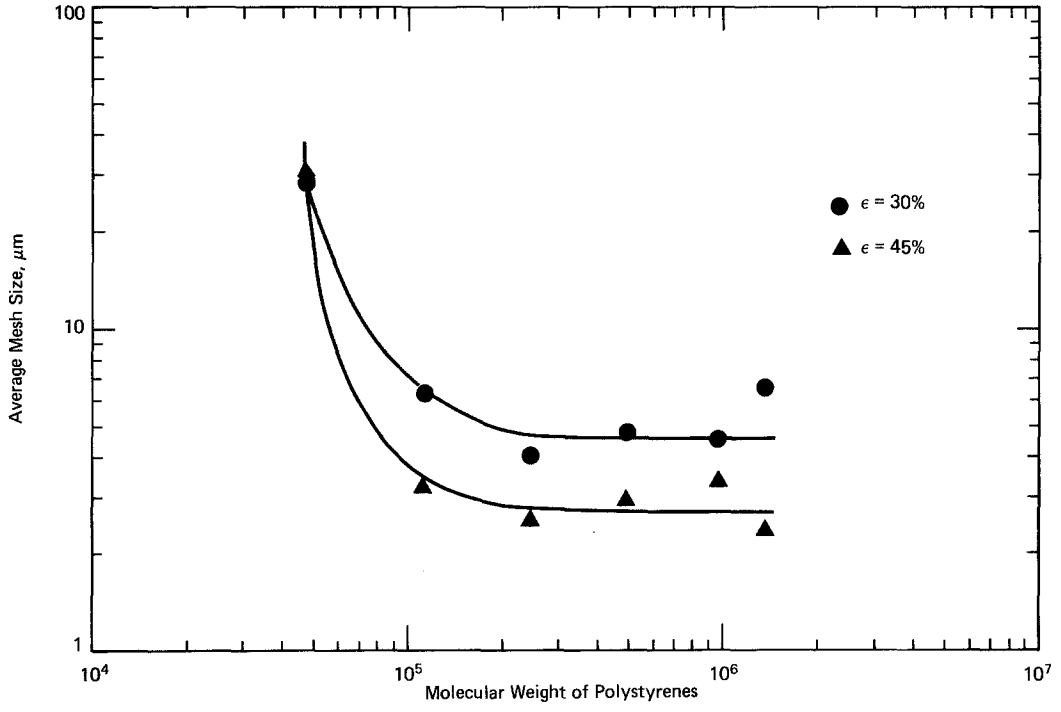


Figure 12 Plots of average mesh size as a function of molecular weight for both 30% and 45% strains.

intersections, with no apparent fibril displacement effect. The second type is that the intersections appear to show fibril reorientation and thickening effects which seem to result from the further stretching of fibrils caused by the action of internal stresses of the existing craze and the tensile stresses of the intersecting craze. This observation suggests that craze fibrils can be further stretched and elongated along the original fibril axis by a second crazing process.

3. At 30% strain, the mesh size, defined as the square root of the non-crazed area enclosed by crazes, decreases drastically as the molecular weight increases from 46 900 to 242 000. An average mesh size of about 4.6 μm is observed as the molecular weight increases from 242 000 to 961 000. At 45% strain, the average mesh size decreases to 2.7 μm as molecular weight increases from 242 000 to 1350 000. The average thickness of the crazes is about the same at both strains. The increase in strain seems to result mainly in an increase in the number of crazes.

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