Microstructure of crazes in solvent-crazed polycarbonate thin films

EDWIN L. THOMAS, SHELDON J. ISRAEL
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, USA

Crazes have been produced in polycarbonate by atomizing acetone over uniaxial stressed solvent cast thin films. Transmission electron microscopy shows that two types of craze orientation exist. Crazes are formed perpendicular to the applied stress direction and at approximately 55° to the applied stress direction. The craze structures observed at 55° to the applied stress direction are suggested to result from cavitation of pre-existing deformation bands. The internal morphology of each type of craze is similar, and the fibre diameter, void size and craze width of each type depends on the amount of craze development. The structure of the craze–matrix interface is, however, different for each type of craze. Necking and work-hardening of the fibres occurs at the normal craze-matrix interface, whereas a rough undrawn interface exists for the angular crazes.

1. Introduction
Under tensile stress and/or exposure to various organic solvents many amorphous polymers develop structures that appear to be fine cracks. These structures, called crazes, differ from cracks in that their interior contains drawn fibres forming an interconnecting network of elongated holes. The oriented polymer fibres form perpendicular to the craze-matrix interface. Fibre and void dimensions are dependent on temperature, environment, and the degree of development of the craze.

Crazes initiate preferentially at the specimen surface and propagate in a plane perpendicular to the primary stress axis. Further deformation causes the craze to widen; the interconnecting fibres are drawn thin and finally fracture, resulting in coalescence of the void regions and ultimate failure of the material.

Previous attempts to study polycarbonate craze structure by electron microscopy have met with limited success [1, 2]. This has been due chiefly to the distortion of the craze structure by microtome sectioning. Use of a reinforcing agent to impregnate and strengthen the craze against the cutting stresses has proven successful with polyphenylene oxide and polystyrene. Unfortunately, the useful impregnants tend to plasticize polycarbonate and the infusion process requires temperatures near the glass

transition, both of which cause deterioration of the craze structure [3].

Recently, the microstructure of polystyrene crazes produced by straining thin (ca. 1000 Å) films has been studied [4, 5]. Good correlation with the crazed structures observed by microtomy of bulk polystyrene crazes indicates the craze microstructures studied in thin film work are representative [4]. With this thin film technique, artifacts produced by volume changes of the solidifying reinforcing agent, difference in cutting resistance of polymer and impregnant, and the knife chatter characteristic of microtomy are avoided. We have employed this thin film technique to study the microstructure of solvent-induced crazes in polycarbonate.

2. Experimental
The polycarbonate specimens were made from General Electric Lexan® bisphenol-A polycarbonate reactor powder (M_v = 40 000) which contains no additives except heat stabilizer. Thin films were solution-cast onto the surface of clean glass microscope slides from a 1 wt % solution of polycarbonate in methylene chloride. The films were then annealed 24 h at 93°C to minimize the solvent content of the polymer film. To remove the film from the microscope slide, cellophane tape was placed on both ends. One end of the slide was then

immersed in a water bath where the tape was used to pull the submerged film away from the slide onto the surface of the water. The microscope slide was then slowly lowered into the water bath allowing surface tension to separate the film from the glass slide.

Crazes were produced by mounting the film in a straining device whose mechanical movement was originally the translation mechanism of an optical microscope stage. A strain of typically 30% was slowly applied, and a fine mist of atomized acetone was then sprayed over the stressed film. Many fine droplets hit the film forming small holes surrounded by a great many crazes. While still in the stressed state, the samples were placed in a vacuum evaporator and backed with a thin layer of carbon. The carbon reinforces the polycarbonate film preventing the crazes from gradually closing as the stress is removed.

The polymer film was then again floated on a water surface where specimens were cut out and mounted for subsequent examination at 100 keV with a RCA-EMU4C transmission electron microscope. Radiation damage was minimized by working at low magnification with low beam intensity. The unstressed film thickness was determined by a metal shadowing technique to be 650 to 850 Å.

Void fractions were determined by printing the transmission micrograph negative at high enlargement and, with the resulting print, cutting out and separating the fibre and void areas. The paper representing each of these areas was weighed and the void fraction calculated. It should be noted that this method actually gives an area fraction but, considering the thinness of the polymer film this method gives a close approximation to the volume fraction.

3. Results and discussion

Application of a crazing agent to a pre-stressed polycarbonate film produces areas of severe deformation. These deformed areas result from a combination of the applied stress, the stresses created by differential swelling due to solvent concentration gradients, stress concentrations due to hole formation and an increase in ease of plastic flow due to plasticization of the upper surface of the polymer film. No apparent crystallization of polycarbonate has been observed and crystallization would not be expected to occur within the limited times of acetone

*No significant number of primary fibres broken.

application to the films [6, 7]. This agrees with Kambour et al. [8] who suggest that crystallization is not the cause of crazing in polycarbonate.

The crazes develop normal to the applied stress direction (see Fig. 1) and their internal microstructure depends markedly on the local strain. Initially, a craze forms as a narrow, ribbon-like band where the thickness of the bulk polymer film has decreased. The uniformly thin bands can appear either as very long constant width regions (Fig. 2a) or tapered regions (Fig. 3). The lateral edges of this "thin" region are well defined and the internal craze microstructure appears at high magnification as diffuse regions of varying thickness.
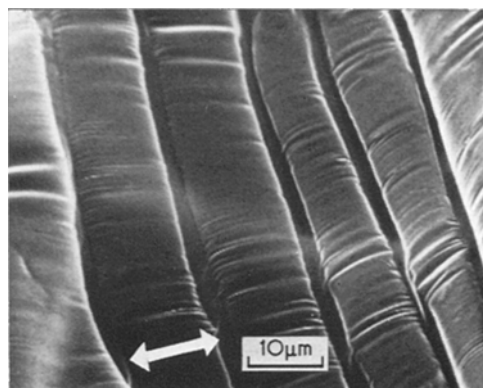

Figure 1 Scanning electron micrograph of crazes formed normal to stress direction in acetone-treated film. The direction of the applied stress is indicated by an arrow on all micrographs.

As the strain is increased, very small spheroidal void regions begin to appear simultaneously with a network of fibrous polymer (Fig. 2b). With increased strain the voids become oval in shape as the fibres grow narrow and more distinct (Fig. 2c). At this stage, some extremely thin fibres are visible (Fig. 2c) which cross the voids approximately perpendicular to the primary fibre axis. These interconnecting fibres range from 200 to 450 Å but the greatest portion have diameters of about 220 Å. Further strain causes the fibres and void regions to become long and narrow and the small perpendicular fibres to break and retract.

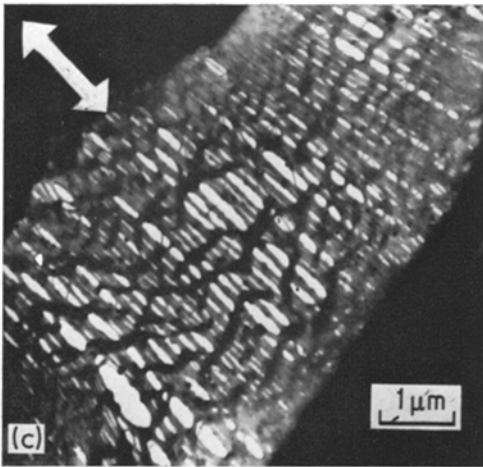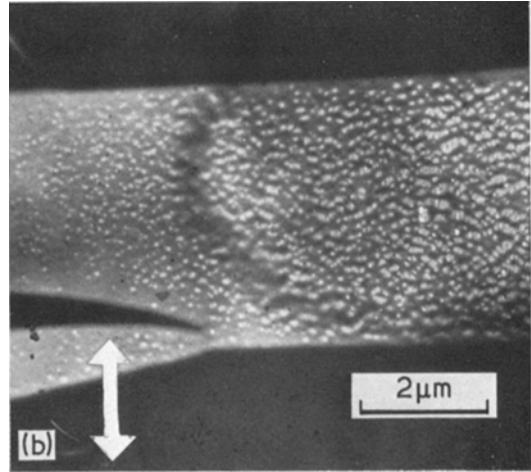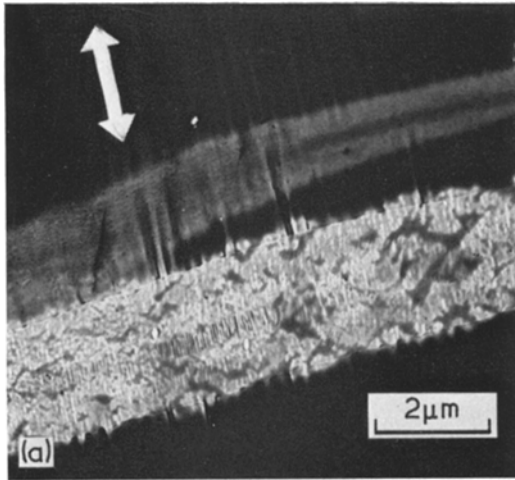Typical fibre diameters in mature* craze

Figure 2 Bright-field transmission electron micrographs showing growth history of thin film crazes. Bright regions are due to high transmittance of thinner areas. (a) Immature normal crazes. The upper craze contains no distinct voids or fibres whereas the lower craze, at a higher state of strain contains a developing void and fibre structure. (b) Immature normal craze containing 100 to 300 Å voids. (c) A more mature normal craze containing distinct fibres and elongated voids. Also note the cross fibres of about 220 Å diameter.

regions are approximately 750 Å. The smallest fibres observed which were found in considerable number measured about 220 Å in diameter. The dimension of the small fibres agrees well with those noted by Hull [4] and Kambour and Holik [3]. Another investigation [9] has reported fibre diameters as small as 30 Å in polycarbonate.

The void content by area fraction analysis of high magnification photomicrographs of mature craze regions was found to be approximately

40%. This correlates well with the results of Kambour [1], who measured the void fraction of a mature polycarbonate craze by saturating the "sponge-like" void network with alcohol and comparing the resulting refractive index with that of bulk polymer. He concluded that the void fraction ranged from 45 to 50%.

Mature craze widths were found to be typically about 5 μm. At higher strain the long narrow fibres break and retract to form small globular structures ranging from 500 to 2400 Å in diameter (Fig. 3).

As well as the long straight crazes observed, craze structures are also found with the craze-matrix interface at angles of about 55° to the applied stress direction (Fig. 4). The internal microstructure of this type of "angular" craze
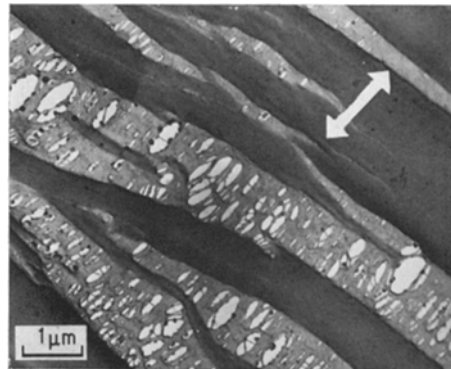

Figure 3 Normal crazes of varying degrees of development. Note that the tips of the crazes are uniformly thinned and do not contain a distinct void and fibre structure. The dark globular structures are from broken retracted fibres in regions near large voids.
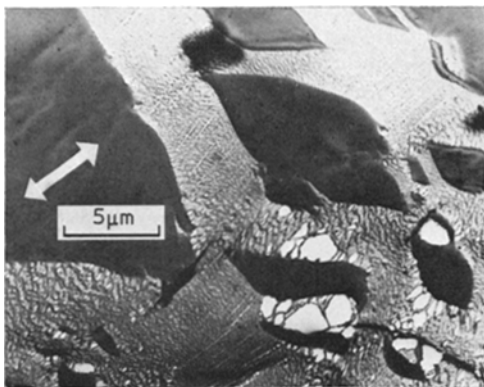
Figure 4 Angular crazes containing diamond-shaped island structures of undeformed polymer. Pre-existing intersecting deformation bands have cavitated and deformed leaving diamond-shaped regions.
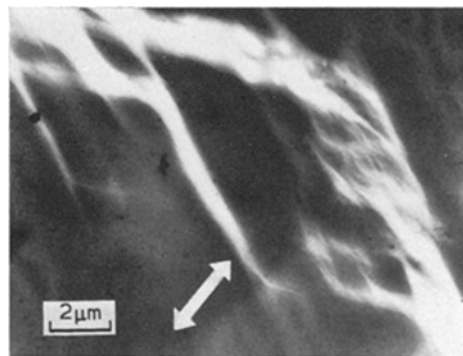

Figure 5 Bright-field transmission electron micrograph of deformation bands in a uniaxially stressed film of polycarbonate.
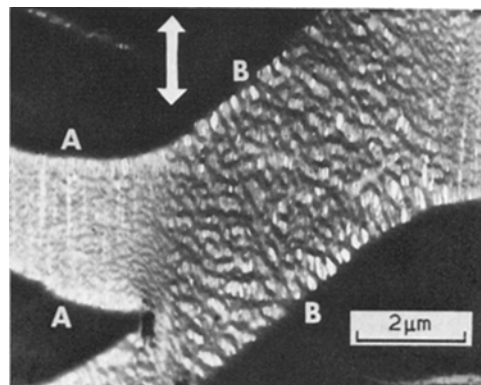

Figure 6 High magnification micrograph showing drawn fibres at normal craze-matrix interface (region A) and large, undrawn fibres at angular craze-matrix interface (region B).

is similar to that found for normal crazes at similar strains.

Two interesting aspects of these angular crazes are the large diamond-shaped islands of undeformed polymer contained within the craze and the rougher craze-matrix interface. We believe these structures are caused by cavitation and deformation of pre-existing deformation bands.

If a strain of 30% is applied to polycarbonate at room temperature without the presence of a crazing agent, many fine deformation bands are produced (see Fig. 5). These bands lie along the direction of least plastic work (55° to the applied tensile stress direction for very thin films [10]). The bands measure tens of microns in length and from a few microns to less than 1000 Å in breadth. After such a deformation band has formed the critical stress or strain for craze initiation is lowered due to molecular orientation within the band. Upon plasticization by the crazing agent of the still stressed film the deformation bands cavitate and form angular crazes. Such an explanation also accounts for the absence of deformation bands in the solvent crazed specimens as well as the angular orientation of crazes. The diamond-shaped islands of undeformed polymer are left as a result of the cavitation of surrounding, intersecting deformation bands.

The boundary between a normal craze and the undeformed material is sharp and well defined. For mature crazes a thinner region develops at this interface (see region A, Fig. 6).

It appears that the fibres in this region have undergone necking. In contrast to this normal craze-matrix interface behaviour, the angular craze-matrix interface appears rougher and is not thinned (see region B, in Fig. 6). It is also interesting to note that angular crazes are often tens of microns wide, two to three times wider than the normal crazes. This is possibly due to a different mechanism of craze thickening for each type of craze orientation. The thickening of normal crazes appears to occur by drawing of fibres within the craze. The rough, angular craze–matrix interface with larger craze width, and greater internal fibre diameter suggests that craze width growth occurs by advancement of the elongated void region into the polymer

matrix. This type of easy crazing of pre-existing deformation bands perhaps explains the origin of the occasional large ~ (0.1 mm wide) crazes observed in methanol-crazed polycarbonate and the report of "shear" crazes in oriented poly (ethylene terephthalate) [12].

The crazes we observed in acetone treated thin films are unlike the crazes observed by microtomy of bulk crazed material in that immature crazes in thin films do not always contain a distinct void and fibre structure. Rather thin film crazes can initially exist as a uniform region of drawn polymer and only after increased strain does this uniform region cavitate and form the typical void and fibre structure (see for example the tapered crazes in Fig. 3). This difference in behaviour is probably due to the lack of plastic constraint in the thickness direction of thin specimens. In bulk specimens plastic constraint causes a triaxial state of stress to exist at the growing craze tip. This triaxial state of stress will both decrease the ease of plastic (shear) flow and promote the formation of voids.

4. Conclusions

By atomizing a fine mist of acetone over a thin, pre-stressed polycarbonate film, many crazes are produced at room temperature. Crazes are found both normal and at approximately 55° to the applied stress direction. The crazes oriented at about 55° to the applied stress direction are suggested to be due to cavitation and deformation of pre-existing deformation bands.

The craze morphology in thin films differs from that of bulk specimens in that due to a lack of plastic constraint, thin film crazes form initially as thin regions of uniformly drawn polymer. With increasing strain a distinct void and fibre structure develops.

The fibre diameter and void size were found to be a function of the degree of craze development. In mature crazes the fibres are typically 750 Å in diameter with numerous 220 Å cross fibres. The smallest detectable voids are 50 Å spheres. The void fraction in mature crazes was determined by area fraction analysis to be approximately 40%.

The craze-matrix interface is sharp and well defined for normal crazes. The maximum width of normal crazes is determined by necking and work-hardening of fibres at the normal craze-matrix interface. The angular craze-matrix interface consists of large, undrawn fibres. The width of angular crazes is typically two to three times larger tha normal crazes due to widening via advance of the elongated void region into the polymer matrix.

Acknowledgement

References

1. R. P. KAMBOUR, *Polymer* 5 (1964) 143.
2. R. P. KAMBOUR and R. R. RUSSELL, *ibid* 12 (1971) 237.
3. R. P. KAMBOUR and A. S. HOLIK, *J. Polymer Sci. A-2* 7 (1969) 1393.
4. D. HULL, in "Deformation and Fracture of High Polymers", edited by H. H. Kausch, J. A. Hassel, R. I. Jaffee (Plenum Press, New York, 1973).
5. S. T. WELLINGHOFF and E. BAER, *A. P. S. Bulletin* 19 (1974) 377.
6. G. A. BERNIER and R. P. KAMBOUR, *Macromolecules* 1 (1968) 393.
7. G. W. MILLER, S. A. D. VISSER and A. S. MORECRAFT, *Poly. Engr. Sci.* 11 (1971) 73.
8. R. P. KAMBOUR, C. L. GURNER and E. E. RAMAGOSA, *Macromolecules* 7 (1974) 248.
9. P. BEAHAN, M. BEVIS and D. HULL, *Polymer* 14 (1973) 96.
10. A. NADAI, "Theory of Flow and Fracture of Solids" (McGraw Hill, New York, 1950).
11. R. KAMBOUR, *J. Polymer Sci. Macromol. Revs.* 7 (1973) 1.
12. J. S. HARRIS and I. M. WARD, *J. Mater. Sci.* 5 (1970) 573.