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# Some Observations by Scanning Electron Microscopy on a New Craze Phenomenon in Bisphenol-A Polycarbonate

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***Dedicated to C. C. Hsiao and J. A. Sauer on the occasion of the 30th anniversary of the publication of their paper: "On Crazing of Linear High Polymers"***

## Summary

A dense pattern of very fine crazes may be observed in unoriented and pre-oriented PC samples drawn to high stresses and strains. Scanning electron microscopy clearly revealed the microstructure of these crazes which are composed of fibrils of considerably larger diameters than those normally observed.

## Introduction

Crazes play an important role in the fracture of glassy polymers, both as sources of fracture toughness and as precursors to cracks (see e.g. RABINOWITZ and BEARDMORE 1972, KAMBOUR 1973, KAUSCH 1978 and KRAMER 1979). In the past valuable information on the craze microstructure, which is of particular importance for a molecular description of fracture, has been obtained by transmission electron microscopy (TEM) (KAMBOUR and HOLM 1969, KAMBOUR and RUSSEL 1971, LAUTERWASSER and KRAMER 1979, DONALD et al. 1980, FARRAR and KRAMER 1980). Despite the problems arising from sample preparation, sample geometry and beam damage TEM has clearly shown that crazes consist of fibrils usually 5-40 nm in diameter.

A new type of craze, initiated at high stresses and strains, has recently been found in bisphenol-A polycarbonate (PC) by DETTENMAIER and KAUSCH (1980) within a temperature range of 120-140 °C at strain rates of 0.28-3.5 %/min. Since these crazes consist of fibrils with relatively large fibril diameter (up to 300 nm) the fibrillar craze microstructure may be observed by scanning electron microscopy (SEM). The use of SEM to observe this craze phenomenon in PC should yield some further insight into the mechanism of crazing in glassy polymers.

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## Experimental

Measurements were carried out on 1 mm thick Makrolon sheets produced by Bayer AG. Crazes were initiated in both unoriented specimens and specimens pre-oriented at a temperature of 160 °C with a strain-rate of 200 %/min. The latter were then drawn parallel to the orientation axis. The degree of orientation was characterized by measuring the optical birefringence at a wavelength of 545 nm. The craze microstructure was usually not directly visible in the SEM. Thus an etching procedure with oxygen ions was employed. The surfaces were coated with gold to reduce the build-up of surface charge.

## Results

Studies were conducted on both unoriented and pre-oriented PC samples, however, this factor did not affect the main characteristics of the craze phenomenon. The drawing conditions of the samples with respect to birefringence $\Delta n$ after pre-orientation, drawing temperature T, strain $\varepsilon$ and strain-rate $\dot{\varepsilon}$ are given in the legends to the figures.

The normal type of craze, described in the literature, may be observed well below the yield point in a stress-strain curve, such as shown in Fig. 1 for unoriented PC.

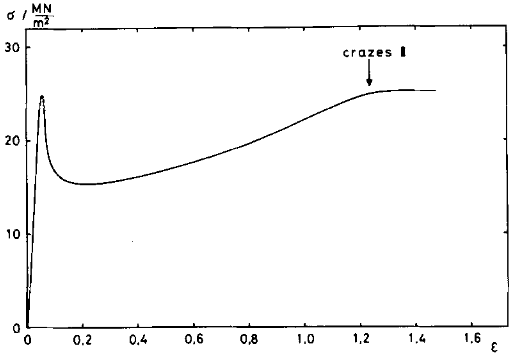


Fig. 1: Engineering stress-strain curve for polycarbonate ($\Delta n$ = 0, T = 129 °C, $\dot{\varepsilon}$ = 3.5 %/min)

These crazes, which we shall call crazes I, are largely separated from each other (Figs. 2a and 3a). Surface defects may frequently be identified as craze initiators. Fig. 3a gives an example for crazes I which were initiated at the surface and which have not grown sufficiently to traverse the whole specimen. Due to the small fibril diameter the microstructure of crazes I is difficult to analyze by SEM. However, some information is available from smallangle X-ray scattering (SAXS). Under the given drawing conditions with respect to temperature, strain-rate and preorientation (see legends to figures) crazes I consist of fibrils 20-40 nm in diameter (DETTENMAIER and KAUSCH 1980).

Well above the yield point of the stress-strain curve, at the point marked in Fig. 1, a new type of craze, which we shall call craze II, is observed. Its initiation is preceded by some strain-hardening of the material and is followed by a strain softening mode leading to a flattening out of the engineering stress-strain curve.

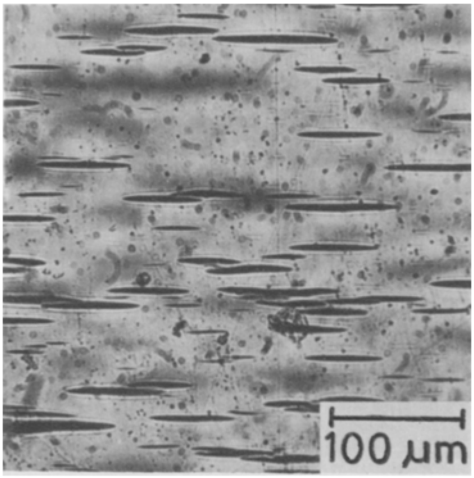


Fig. 2a: Optical micrograph of crazes I ($\Delta n$ = 0.02, T = 119 °C, $\varepsilon$ = 0.42, $\dot{\varepsilon}$ = 0.28 %/min)

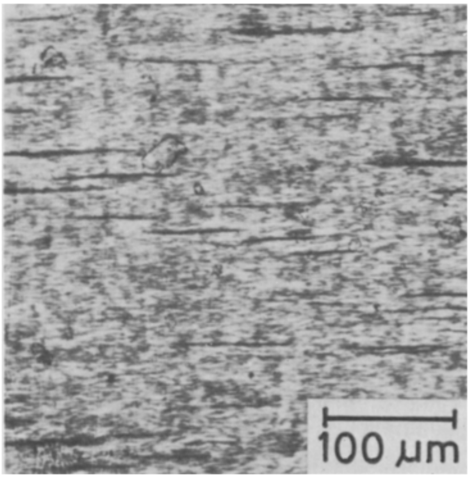


Fig. 2b: Optical micrograph of crazes I and II ($\Delta n$ = 0.02, T = 119 °C, $\varepsilon$ = 0.57, $\dot{\varepsilon}$ = 0.28 %/min)

The marked influence of the initiation and growth of crazes II on the stress-strain curve can easily be understood in view of their large number as revealed by optical and scanning electron microscopy (Figs. 2b and 3b).

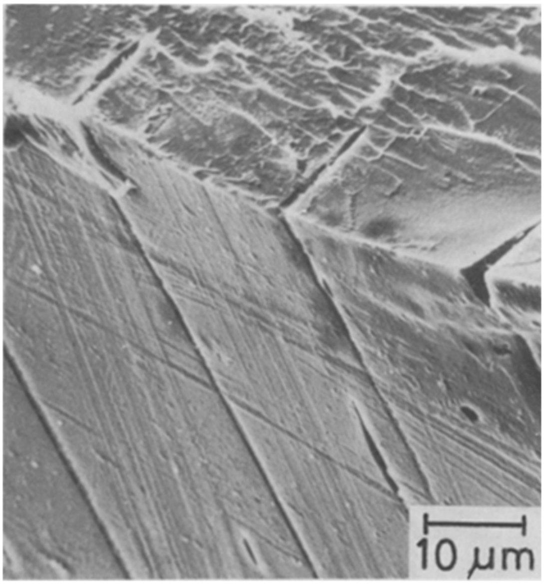


Fig. 3a: Scanning-electron micrograph of crazes I
($\Delta n = 0$, $T = 129$ °C, $\varepsilon = 0.78$, $\dot{\varepsilon} = 3.5$ %/min)

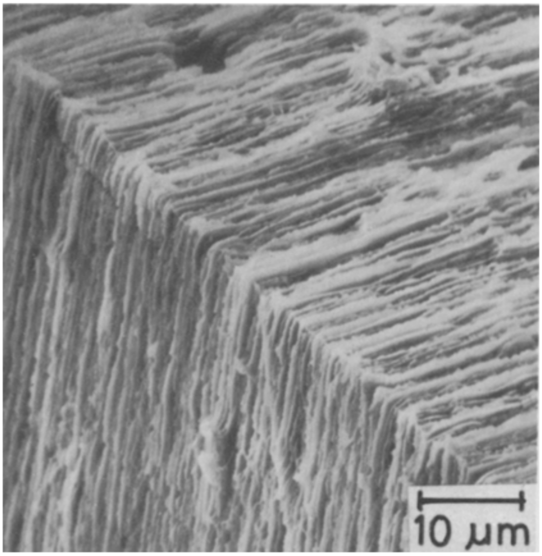
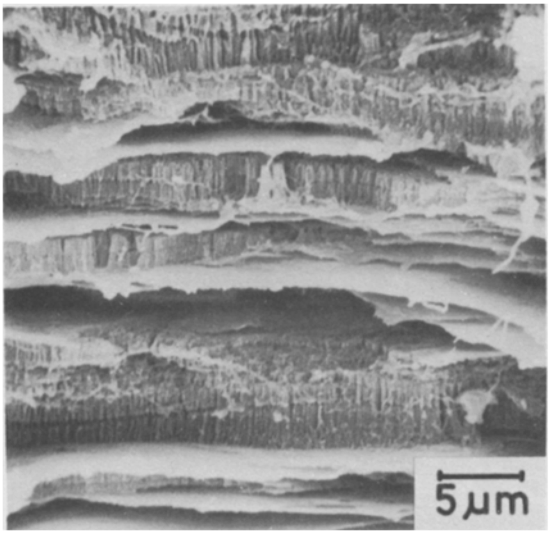
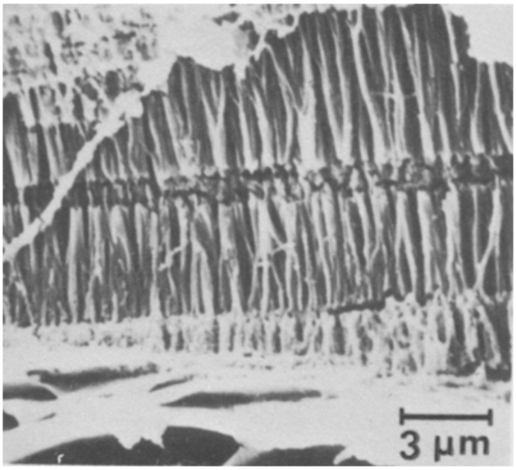


Fig. 3b: Scanning-electron micrograph of crazes II
($\Delta n = 0$, $T = 129$ °C, $\varepsilon = 1.48$, $\dot{\varepsilon} = 3.5$ %/min)

In Fig. 2b both types of crazes can clearly be identified, the large and isolated crazes I (also shown in Fig. 2a for a smaller elongation) and the dense pattern of very fine crazes II. The latter type usually leads to the phenomenon of stress-whitening.



Figs. 4a and b: Fibrillar microstructure of crazes II
($\Delta n = 0.02$, $T = 129$ °C,
$\varepsilon = 0.53$, $\dot{\varepsilon} = 0.28$ %/min)



The microstructure of crazes II is shown in Fig. 4. These micrographs were taken from a sample crazed and afterwards fractured in liquid nitrogen parallel to the draw axis. The same procedure was applied to uncrazed specimens to confirm that the observed structure was not initiated by the fracture process. After etching with oxygen ions the fracture surfaces revealed a well pronounced fibrillar microstructure. From these micrographs fibril diameters of 100-300 nm have been determined.

In many crazes a midrib, similar to that observed for crazes I by TEM (BEAHAN et al. 1972, LAUTERWASSER and KRAMER 1979) can clearly be identified. LAUTERWASSER and KRAMER (1979) attributed the presence of the midrib to the fact that the central part of the fibril is formed at the craze tip under higher stresses than those occurring during craze growth. According to the meniscus instability theory, as applied to craze growth by ARGON and SALAMA (1977), higher stresses should give rise to the formation of fibrils with smaller diameters. Further investigation either by SEM or TEM may lead to a more detailed characterization of the midrib.

A more quantitative description of the craze microstructure and a proof for the reliability of the SEM technique can be given by SAXS. This method is also more appropriate to analyze the effect of parameters such as temperature, strain-rate and pre-orientation on the craze microstructure. Such a comprehensive analysis is beyond the scope of this paper. However, a few remarks concerning the effect of pre-orientation may be of interest. SAXS experiments, performed by DETTENMAIER and KAUSCH (1980), showed that the fibril diameter of crazes II strongly increases with increasing pre-orientation of the samples. Depending on the drawing conditions it is even possible that the craze II phenomenon is only observed above a certain pre-orientation of the samples (DETTENMAIER and KAUSCH 1980). In this case pre-orientation plays a dual role: it decreases the growth-rate of crazes I and leads to a craze I microstructure that is more resistant to crack propagation. Without pre-orientation cracks propagate in crazes I before the sample reaches the condition for craze II initiation. In that case, however, the running crack can build up the stress concentration necessary for craze II initiation, and the dense pattern of crazes II is observed in a zone close to the fracture surface.

## Discussion

In discussing the crazing of PC two previously reportet phenomena may be of interest. ARGON and HANNOOSH (1977) observed in polystyrene (PS), which was free of surface and volume defects, a phenomenon which they called intrinsic crazing. At high stresses the samples yielded and stress-whitened by the formation of closely-spaced crazes throughout the total volume. Unfortunately, no information on the microstructure of these crazes is available. The normal type of craze, which is observed in PS, is attributed to premature crazing initiated at surface grooves or trapped foreign particles. In studying instabilities of the deformation process during cold-drawing of polyethylenterephthalate, isotactic polypropylene and polyamid-6, PAKULA and FISCHER (1980) observed at high stresses craze-like structures which they called macro-crazes. Both phenomena and that of crazes II in PC are basically intrinsic phenomena, i.e. at high stresses intrinsic local fluctuations are sufficient to serve as craze nuclei. On this basis the large number of crazes II, as compared to crazes I, can easily be understood. However, one still has to account for the fact that crazes I and II consist of fibrils with different diameters. The possibility cannot be excluded that crazes II are initiated by the activation of intra- or intermolecular processes (change in chain conformation, chain rupture or disintegration of entanglements) leading to a deformation mode that does not occur during craze I initiation. However, even if it is assumed that the same deformation mode is responsible for the initiation of craze I and craze II the microstructure of both types of crazes may be different. In fact, at craze I initiation the sample is usually in a much earlier state of deformation than at craze II initiation. Crazes II are produced in samples which have been oriented significantly by the deformation process. The corresponding birefringence was found to be $45 \cdot 10^{-3}$ at the moment of craze II initiation.

The fibrillation process in crazes II starts, therefore, from a considerably higher level of orientation (draw ratio $\lambda_o$). Consequently, it has to be expected that the relative extension $\lambda/\lambda_o$ will be smaller. According to Equ. 3 in the preceding paper (KAUSCH and DETTENMAIER 1980) this can lead to an increase in d. The question as to whether the orientation of the matrix alone accounts for the observed large fibril diameter of crazes II can only be answered by further investigations.

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