Craze roles in the fatigue of polycarbonate

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Unnotched specimens of polycarbonate were deformed to failure in equal tension compression, under load control. Fracture surfaces exhibited two distinctly different crack propagation regimes. In the first zone, the crack moves forward through an already existing craze. Craze ageing at the crack tip is necessary for propagation and several stress cycles are required before the crack tip can move from arrest site to arrest site. In the second zone, the crack tip must form and age its own craze(s) before moving forward. In the initial stage of Zone 2, the crack mobility is still restricted by the age of the craze. Later in this zone, the crack tip is able to create craze and move through it in the same cycle. Static tensile deformation from 90% to 95% of the yield point produced an increase in the low-load fatigue life. This increase is explained on the basis of the mechanics of coarse crazes.

1. Introduction

In recent years the fatigue behaviour of glassy polymers has come under intensive study. In particular, the mechanisms and mechanics of crack propagation have undergone the most progress. It is generally accepted that the precepts of fracture mechanisms, as this is understood in molecularly simple solids, apply here also, at least at sufficiently low stress amplitudes, frequencies, and ambient temperatures (see, e.g., [1] and [2] for reviews). In addition, fracture surface studies have provided detail on the mechanisms involved in the propagation of fatigue cracks. The general conclusion is that cracks form initially in crazes which are themselves created under the cyclic stress conditions. Such cracks then propagate in steps through the craze. The further progress of such a crack, after it reaches the tip of the initial craze, must be of a different type. Only very recently, however, has the nature of this second zone of crack propagation been characterized [3] for the cyclic fracture of notched isotactic polystyrene. A primary concern of the present paper is to demonstrate the nature of the fracture process as it occurs in two distinct zones in another polymer (polycarbonate) and to interpret these microscopic results in terms of a crazing-*Registered trade mark.

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controlled model. In particular, we present new results regarding the interfacial region between the two zones of crack propagation. In addition, data regarding the effects of pre-crazing is presented.

The fatigue behaviour of polycarbonate has come under particularly frequent study. The macroscopic fracture mechanics of their material has been reported several times [4-13]. The fractography of polycarbonate under cyclic loading has also been reported several times [13-19]. It is clear in this large volume of work that at sufficiently mild conditions of stress and frequency the propagation of fatigue cracks in this material can be well characterized macroscopically by fracture mechanics and can be understood microscopically to proceed by the craze-crack coupled mechanism. On this basis polycarbonate was chosen for the present work.

2. Experimental

Lexan* sheet was used throughout this work. Specimens were milled from the sheet in two forms, tensile bars of gauge section $0.31 \text{ cm} \times 1.27 \text{ cm}$ and gauge length 3.81 cm and tension—compression fatigue specimens with dimensions as in Fig. 1. Results were in all important aspects independent of which specimen form was used.

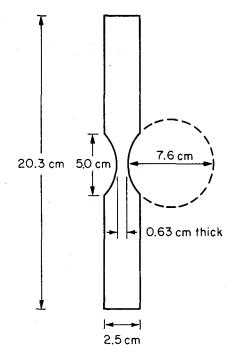


Figure 1 Fatigue specimen dimensions, $\frac{1}{4}$ in sheet.

The tensile bars were subjected to equal tensioncompression cycling at 20 Hz; the other specimens to equal tension-compression at 2 Hz. The load amplitude was controlled in both cases. No significant specimen heating was observed for either type.

3. Results and discussion

3.1. Fractography

Fig. 2 shows a typical fracture surface for the specimens of square cross-section. Two distinctively different zones are found. Zone 1 is comprised of concentric circular fracture surface markings, with no other gross features. In Zone 2 are found feathery, radial markings, as well as a set of basically tangential striae.

The Zone 1 circular markings are the familiar crack-arrest striae reported often in the polymer fatigue literature (see, e.g., [2]). The higher magnification, SEM micrographs of Fig. 3 show that these bands are composed of a region of gross pits, followed by a relatively smoother surface. This fracture surface morphology can be seen in fatigue fracture surfaces of polycarbonate [16], poly(methyl methacrylate) [20, 21], poly (vinyl chloride) [22], and polystyrene [3]. Hertzberg and Manson [1, 22] suggest that the pits are formed by rupture through large voids in the stress-aged craze zone immediately ahead of the crack. Presumably the crack is arrested until the crazed matter beyond its tip becomes sufficiently defective (voidy) to allow for further crack advance. This would be then the mechanism of slow crack growth during fatigure.

As seen in Fig. 2, the transition between Zones 1 and 2 is characterized by a set of radiallydirected fingers and by a less regular set of coarse

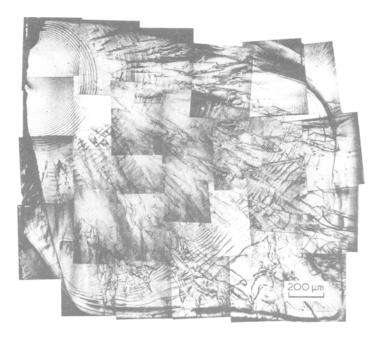


Figure 2 Optical micrograph of fatigue fracture surface.

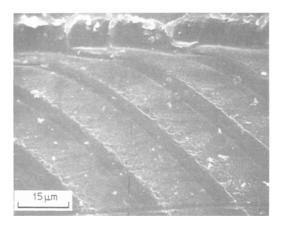


Figure 3 Scanning electron micrograph of striae in Zone 1.

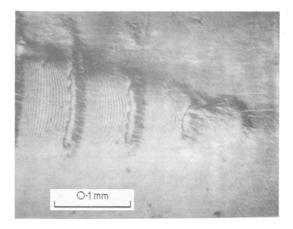


Figure 4 Segments of coarse bands in early stage of Zone 2.

tangential bands. The tangential bands continue the periodicity increase from Zone 1. However, the coarse banding in Zone 2 is segmented; the bands are no longer continuous along their length. Fig. 4 shows, in larger magnification, segments of

the coarse bands. These bands are characterized now by a very fibrous appearance. Further, between the bands exist a set of much finer striae. The distance between the very fine striae decreases with distance from the crack source. Optical and SEM micrographs of the fine striae far into Zone 2 are seen in Fig. 5. That the striae are observed in the SEM indicates that they are true surface features and cannot be explained as interference fringes. In the well-developed region of Zone 2, where measurements can be made, there is a oneto-one correlation between number of striae and number of cycles; the fine Zone 2 striae somehow mark where the crack front stopped at the end of each cycle. These single-cycle arrest lines are often observed to be held up, as in Fig. 6 (arrows), at out of plane projections of the coarse bands. To a considerable extent, these observations run parallel to those on polystyrene, reported by Skibo *et al.* [3].

The several microscopic observations are consistent with a simple model of crack initiation and growth. The model runs as follows:

(a) At some time in the course of loading and unloading, a craze develops at the surface and propagates inward.

(b) During this period, whatever craze exists is itself under the applied alternating stress. As Doyle [23, 24] has shown, the rupture of a craze is a viscous process; the fibrils slowly pull apart, like taffy (toffee-like). As a result, the combination of stress amplitude and application time results in a locally voidy craze. The void volume would be largest where the combination of stress amplitude and application times is closest to the level needed for stress rupture (failure by creep). This would be a specific example of the general process of "linear

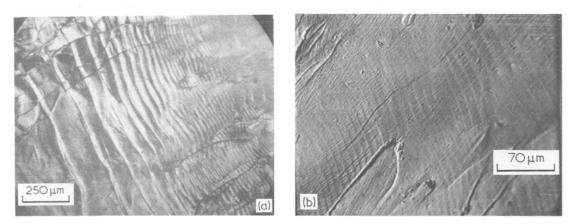


Figure 5 Late stage of Zone 2: (a) light micrograph, (b) scanning electron micrograph (different area).

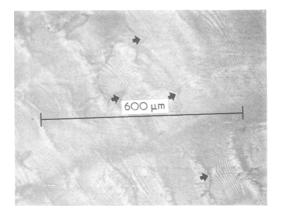


Figure 6 Arrest lines held up at out-of-plane projections, optical micrograph.

damage" [25-28]. In this stage of fatigue, the largest void volume would exist at the craze initiation site at the surface.

(c) When the void volume at the craze initiation site reaches a critical value, a crack forms within the craze. The crack propagates inward during one tensile stress half cycle until the stress level is no longer sufficient to rupture the partially-voided craze and the crack tip is arrested.

(d) When the pre-formed craze directly ahead of the crack reaches the critical damage level, the crack will again move forward, until again its stress level is insufficient for craze rupture. This process repeats itself over and over until the crack tip comes near the tip of the existing craze. At this point, the fracture surface would consist of the concentric bands characteristic of stage (a).

(e) Stage 2 begins. The crack tip now has very little craze ahead of itself and must create new craze in order to propagate. As Sternstein has shown [29–32], crazes propagate when a critical stress state is attained. For the case of plane strain, with principal stresses σ_1 , σ_2 in the plane of stress, the criterion for propagation is

$$|\sigma_1 - \sigma_2| - \frac{A(T)}{(\sigma_1 + \sigma_2)} \ge -B(T) \qquad (1)$$

where A(T) and B(T) are positive constants dependent on material, chemical environment, temperature, and strain rate. At the tip of a plane strain tensile crack, the stresses σ_1 and σ_2 are equal in magnitude. The craze propagates in the plane normal to the larger of the two plane principal stresses. If σ_1 and σ_2 are equal in magnitude, and the sum $(\sigma_1 + \sigma_2)$ great enough, the craze can still propagate, in random direction. The state of strain at a crack tip is complex. The maximum principal stresses lie at the tip, in the crack plane and normal to it. They are of equal magnitude. At directions out of the crack plane, the stress bias $(\sigma_1 - \sigma_2)$ becomes finite and the left side of Equation 1 becomes larger than for the case of the crack plane itself. Thus one should expect crazes originating at the tip of a crack to initially run out of the plane of the crack. Bevis and Hull [33] recognized this and showed that indeed crazes originating at the tip of the crack in glassy polystyrene are curvilinear and follow trajectories initially out of the crack plane, curving gradually back into the crack plane as they propagate away from it.

Such new crazes, formed ahead of a fatigue crack, can follow initial trajectories in either direction ("up" or "down") relative to the original crack. If crazing initiates at more than one site along the crack tip, one should expect to find crazes going both up and down. Most probably, the fingers projecting into Zone 2 from the boundary of Zone 1 represent crazes which originally went in opposing orientations.

(f) The fatigue crack front follows the fronts of the new crazes. The gross bands in Zone 2, found only near the Zone 1 limit, most probably indicate sites where the crack tip has again caught up with the craze tip. At each such site, the crack must again await a critical void volume level before it can propagate. However, the stress level at the crack tip is now sufficiently large to permit some propagation at each cycle through the voidy craze. The evidence for this is the very fine striae between the broad, out-of-plane rupture bands. These striae become more closely spaced as they approach the next broad band, indicating that the level of ageing in the craze becomes lower with distance into the craze.

(g) Ultimately the stress level at the crack tip becomes sufficiently high to create its own craze and to propagate to its tip all in the same cycle. This is the condition in the well-developed region of Zone 2 (Figs. 2 and 5). The striae in this region exhibit a rounded region, presumably the out-ofplane craze trajectory as the craze begins to move forward at the beginning of each cycle, followed by the expected flat region.

3.2. Effects of prior crazing on fatigue life

It was noted that in the course of the fatigue deformation the cyclic stress strain behaviour

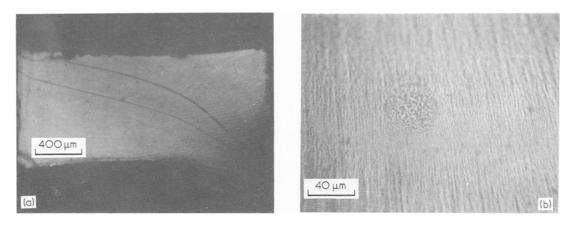


Figure 7 Craze discs in pre-cycled constant-strain-rate fracture surface. (b) is an enlargement of one of the discs in (a).

changed. As the number of cycles increased, the material appeared softer; that is, the initial slope of the cyclic tensile stress-strain response decreased. Such cyclic softening is common in glassy polymers (see, e.g., [2, 19, 34]). For both polycarbonate and polystyrene the shape of the cyclic stress-strain curve becomes similar to those observed by Kambour and Kopp [35] and by Hull [36] for highly crazed material. Indeed, very fine crazes (not observable by surface examination) were detected prior to crack formation in our polycarbonate specimens. These very fine crazes were made visible in cyclically loaded materials by stopping the cyclic deformation and then reloading at constant strain rate to fracture. On the fracture surface, small discs of crazed material could be observed, as in Fig. 7. Along the side surfaces, small cracks with lateral dimensions similar to those of the craze discs could also be seen. These craze discs were never seen in material fractured without prior cyclic loading.

Considering the fibrous structure of crazes, it seemed possible that large concentrations of gross crazes could be used to raise the fatigue life at low stress amplitudes. The reasoning is as follows: Fig. 8 shows, schematically, stress—strain curves for non-crazed and crazed material. The effect of the craze is to lower the effective initial modulus, without significantly decreasing the higher stress level response (except that fracture should occur at a lower stress level). The effect of numerous gross crazes should act, at low stress levels, as a soft second phase. This hypothesis was tested by loading polycarbonate fatigue specimens from 90% to 95% of the macroscopic yield stress prior to cyclic deformation. The specimens were held at this stress level for 1 hour in order to stabilize the craze material. The specimens were subsequently cycled to failure and an S-N curve obtained. Fig. 9 shows S-N curves for virgin and for tensiledeformed material. At high stress amplitudes, where the craze fibrils become highly extended, the fatigue life is reduced. At low-stress amplitudes, the presence of the coarse crazes initially present produces an increase in the fatigue life.

4. Summary

Fatigue fracture surfaces of polycarbonate cycled in equal tension and compression at relatively low stress levels were observed using optical microscopy. Two distinct zones were observed, as well as a transition region between the two zones. In the first zone, the crack propagated sporadically, with many cycles between arrest lines. In the second zone, in its well-developed state, the crack propagated at each cycle. The transition region showed elements of both types of behaviour, as well as the onset of long crazes running parallel to

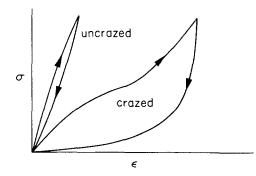


Figure 8 Schematic stress-strain curves for material with and without gross crazes.

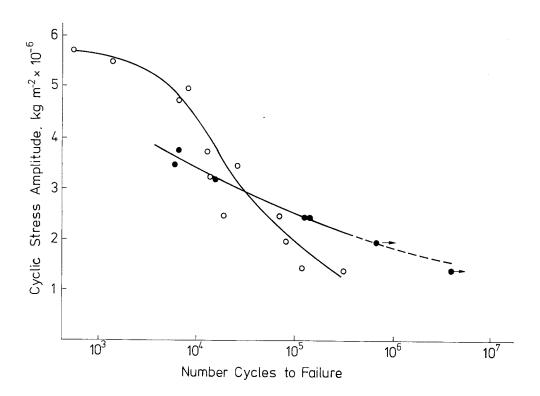


Figure 9 S-N curves for as-received (\circ) and prestressed (\bullet) material.

the crack propagation direction. On this basis, fatigue crack propagation in this material was described in terms of a model in which cracks move only through existing crazes with a sufficiently large pore structure. In the first zone, the time between crack jumps is occupied with craze damaging. The second zone begins when the crack tip catches up with the craze tip. In Zone 2, the crack must form new craze in order to propagate. In the well-developed region of stage 2, craze formation and ageing can occur during the same tensile stroke. In the early portions of Zone 2, the stress level is insufficient to both create and age the craze in the same stroke.

Experiments were reported, in which cyclic deformation was stopped prior to crack formation, and the material then loaded to failure at constant strain rate. Crazes which could not be seen prior to reloading were visible in the fracture surface. S-N curves of material which had been statically loaded nearly to the yield stress before cyclic deformation were also reported. An increase in fatigue life at low stress levels was observed. This increase in fatigue life was attributed to a softening effect of the gross crazes formed during the static loading.

References

- 1. J. A. MANSON and R. W. HERTZBERG, Crit. Rev. Macromol. Sci. 1 (1973) 433.
- J. M. SCHULTZ, in "Treatise on Materials Science and Technology, Vol. 10B: Properties of Solid Polymeric Materials", edited by J. M. Schultz (Academic Press, New York, 1977).
- 3. M. D. SKIBO, R. W. HERTZBERG, and J. A. MANSON, J. Mater. Sci. 11 (1976) 479.
- 4. B. MUCKHERGEE, L. E. CULVER, and D. J. BURNS, *Exp. Mech.* 9 (1969) 90.
- 5. R. W. HERTZBERG, H. NORDBERG, and J. A. MANSON, *J. Mater. Sci.* 5 (1970) 521.
- S. ARAD, J. C. RADON, and L. E. CULVER, Polymer Eng. Sci. 12 (1972) 193.
- T. KUROBE and H. WAKASHINA, Proceedings at the 15th Japan Congress Materials Research, (The Society of Materials Science, Kyoto, 1972) p. 137.
- R. W. HERZBERG, J. A. MANSON, and W. C. WU, ASTM STP 536 (1973) pp. 391–403.
- 9. J. A. MANSON, R. W. HERTZBERG, S. L. KIM, and W. C. WU, ACS Polymer Preprints (Fall, 1974).
- 10. J. C. RADON, J. Polymer Sci., Polymer Chem. Ed. (1975) 383.
- 11. J. C. RADON and L. E. CULVER Polymer 16 (1975) 539.
- 12. J. C. RADON, P. CHAUHAN, and L. E. CULVER, Colloid Polymer Sci. 254 (1976) 382.
- M. D. SKIBO, R. W. HERTZBERG, J. A. MANSON, and S. L. KIM, J. Mater. Sci. 12 (1977) 531.

- 14. A. J. MCEVILY, Jr, R. C. BOETTNER, and T. L. JOHNSON, in "Fatigue – An Interdisciplinary Approach", edited by J. J. Burke, N. L. Reed, and V. Weiss, (Syracuse Univ. Press, Syracuse, New York, 1964) p. 95.
- 15. M. HIGUCHI and H. ISHII, Rep. Res. Inst. Appl. Mech. 16 (1968) 69.
- 16. G. JACOBY and Ch. KRAMER, *Rheol. Acta* 7 (1968) 23.
- 17. T. KUROBE and H. WAKASHINA, J. Soc. Mater. Sci. Japan 21 (1972) 800.
- 18. P. BEARDMORE and S. RABINOWITZ, J. Mater. Sci. 7 (1972) 720.
- 19. Idem, ibid. 9 (1974) 81.
- 20. C. E. FELTNER, J. Appl. Phys. 38 (1967) 3576.
- 21. S. RABINOWITZ, A. R. KRAUSE, and P. BEARDMORE, J. Mater. Sci. 8 (1973) 11.
- 22. R. W. HERTZBERG and J. A. MANSON, J. Mater. Sci. 8 (1973) 1554.
- M. J. DOYLE, A. MARANCI, E. OROWAN, and S. T. STORK, *Proc. Roy. Soc. Lond.* A239 (1972) 137.
- 24. M. J. DOYLE, J. Mater. Sci. 10 (1975) 300.
- 25. J. BAILEY, Glass Ind. 20 (1939) 21, 59, 95, 143.
- 26. V. R. REGEL and A. M. LEKSOVSKII, Mekh. Polim. 5 (1969) 70.

- 27. P. P. OLDYREV and V. P. TAMUZH, Mekh. Polim. 7 (1971) 654.
- 28. W. G. KNAUSS, Appl. Mech. Rev. 26 (1973) 1.
- 29. S. S. STERNSTEIN, L. ONGCHIN, and A. SILVERMAN, *Appl. Polym. Symp.* 7 (1968) 175.
- 30. S. S. STERNSTEIN and L. ONGCHIN, ACS Polym. Preprints 10 (1969) 1117.
- 31. S. S. STERNSTEIN and F. A. MYERS, J. Macromol. Sci.-Phys. B8 (1973) 539.
- 32. S. S. STERNSTEIN, in "Treatise on Materials Science and Technology, Vol. 10B: Properties of Solid Polymeric Materials", edited by J. M. Schultz (Academic Press, New York, 1977).
- 33. M. BEVIS and D. HULL, J. Mater. Sci. 5 (1970) 983.
- 34. J. MINDEL and N. BROWN, J. Mater. Sci. 9 (1974) 1661.
- R. P. KAMBOUR and R. W. KOPP, J. Polymer Sci. A-27 (1969) 183.
- D. HULL, in "Deformation and Fracture of High Polymers", edited by H. H. Kausch, J. A. Hassel, and R. I. Jaffee (Plenum Press, New York, 1973).

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