JOURNAL OF MATERIALS SCIENCE 11 (1976) 1624–1630

Microstructural control of fatigue-crack growth in a brittle, two-phase polymer

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Fatigue-crack propagation in a brittle, two-phase polymer important in bioengineering applications has been studied. It was found that the polymeric microstructure, although based on PMMA, enhances the fatigue-crack growth resistance of the composite polymer, in comparison with pure PMMA. This enhanced behaviour derives from several micromechanisms, i.e. (1) crack front pinning by constituent particles, (2) a reduction of the intrinsic PMMA crack growth rate within the partially polymerized MMA matrix, and (3) crack-tip wandering and energy absorption through microcrack nucleation at matrix voids lying within the path of the crack.

1. Introduction

The application of polymers formed by the mixing of polymeric powders and liquid monomers is increasing, particularly in the fields of dentistry and orthopaedic surgery. Little has been known previously concerning the resistance of these materials to subcritical crack growth, although static crack growth and fatigue are recognized as important factors in their failure in bioengineering applications. Recently, the slow (static load) crack-growth behaviour of such materials was established by Beaumont and Young [1] in terms of crack velocity versus stress intensity relationships. Earlier, Kusy and Turner [2] had investigated tensile strength properties. In these studies, it was found that the peculiar microstructures of these materials were responsible for distinct variations in both crack velocity and tensile strength, in comparison with the pure forms of their polymeric components.

General classes of metals such as aluminium or steel alloys, despite wide-ranging microstructural differences, usually show rather minor variations in their fatigue-crack growth rates [3]. Polymers, on the other hand, are known to exhibit order of magnitude ranges in crack growth rates which are attributable to macroscopic mechanical property differences [4]. Consequently, it seemed reasonable to expect that fatigue crack growth in brittle, two-phase polymers might be related to the details of their composite-like microstructure. Owing to its engineering importance and previously well characterized structure, the acrylic cement studied by Beaumont and Young [1] was chosen for the present investigation.

2. Experimental

2.1. Specimen preparation

The material that was used in this study was a commercially available acrylic bone cement (Surgical Simplex P*), which is supplied in the form of a PMMA powder and MMA liquid monomer. The cured polymer will hereafter be referred to as SP. The components were stirred together (in a PMMA:MMA ratio of 2:1) for 4 min, forming a dough-like mass. Upon mixing of the powder and liquid, an exothermic polymeric reaction occurs; as the reaction progresses, a hard, brittle complex is formed, the mechanical properties of which are controlled by manual kneading during the setting period. Kneading of selected batches

*North Hill Plastics, Ltd, London, UK.

was carried out for either 30 or 90 sec, at a temperature of 19 ± 1° C.

During actual orthopaedic use of such materials various fluids are often entrapped in the polymer. In order to evaluate the effect of such entrapment, half of each batch was exposed to 10 ml whole blood during the kneading process. As will be shown, the presence of a fluid tends to be accommodated in the polymer by the formation during kneading of a dispersion of microvoids throughout the partially polymerized MMA matrix. These voids seem to be important as mechanical rather than chemical entities, so that the material exposed to the fluid is hereafter referred to as void-filled SP (non-void-filled material will be termed simply SP or pure SP). Results similar to those obtained would have been expected from exposure to many other liquids, including water.

At the completion of the kneading process, each batch was cast into a slab form using an aluminium extrusion mould, in which each specimen was cold-cured for 2 h. From these slabs, pin-loaded, single-edge-notched fatigue specimens were machined. Specimens were 3.1 cm wide by 0.4 cm thick, notched to a depth of 0.3 cm. Pre-fatigue microcracks were introduced at the base of each notch with a razor blade.

2.2. Specimen microstructure

Simplex P is a porous, composite polymeric material, composed of pure PMMA spheres embedded within a matrix of recently polymerized monomer [2]. The spheres derive from the solid PMMA granules introduced during the mixing–kneading process, and range from 10 to 40 μm diameter, with an average spacing of a few μm. Large (approximately 150 μm diameter) air spaces also exist within the matrix, with an average spacing of about 300 μm.

Exposure to a non-reactive liquid during kneading further complicates the microstructure. Fluid inclusions easily shear during the kneading process, and are dispersed as tiny, sharp-edged voids (2 to 10 μm maximum dimension) throughout the

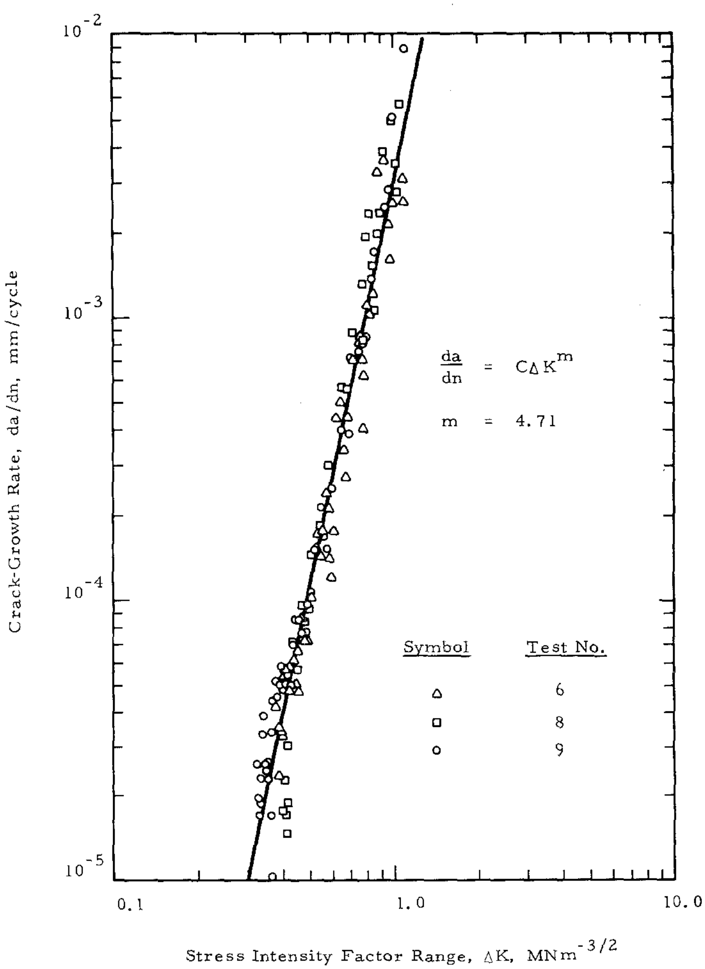


Figure 1 Fatigue crack propagation in Simplex P, 90 sec kneading time.

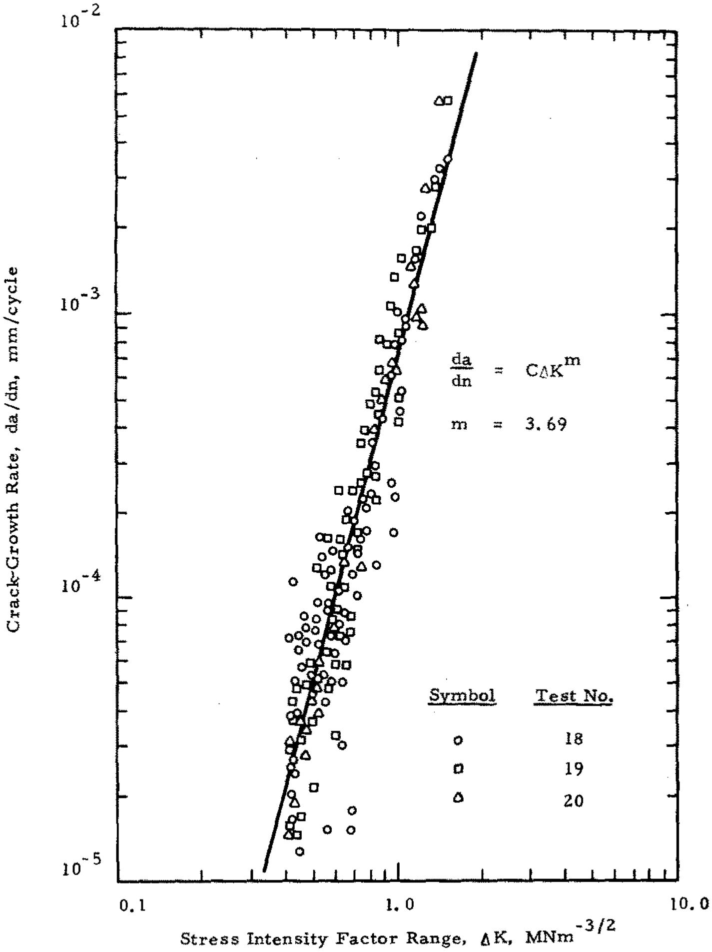


Figure 2 Fatigue-crack propagation in void-filled Simplex P, 90 sec kneading time.

matrix. Dispersion of the voids is most efficient for longer kneading times; average spacing of these voids is approximately 25 μm.

2.3. Testing

Specimens were tested in zero-tension, sinusoidal constant amplitude load cycling in a closed-loop, servo-controlled hydraulic test machine. Tests were carried out in a laboratory environment, and at a cyclic frequency of 5 Hz. Crack growth, which commenced almost at once from the razor notch, was monitored incrementally with a 100x travelling microscope. Following completion of a test, specimens were broken open for fractographic study in the SEM. The latter was facilitated by vacuum coating the fracture surfaces with a thin layer of palladium.

3. Results

Typical crack growth rate (da/dn) versus stress intensity (ΔK^*) data for SP are shown in Fig. 1. Within the crack growth rate regime studied, the da/dn versus ΔK relationship is quite log-linear, and for this material, as well as the other non-void-filled specimens, the data exhibit little scatter. The void-filled material, on the other hand, consistently produced considerable scatter in the microscopic crack growth rate (Fig. 2), although the average macroscopic rate again was linear. For both materials, then, the Paris and Erdogan relationship [6]

$$da/dn = C\Delta K^m \quad (1)$$

was obeyed, where C and m are constants, in agreement with results for PMMA and other pure polymers [3, 4].

The results of all of the tests are summarized in Fig. 3, with each line representing the combined data from three separate, duplicate tests, as shown in Figs. 1 and 2. It appears that differences in

*Stress intensities were calculated according to the relationship of Brown and Srawley [5] for single-edge-notch specimens.

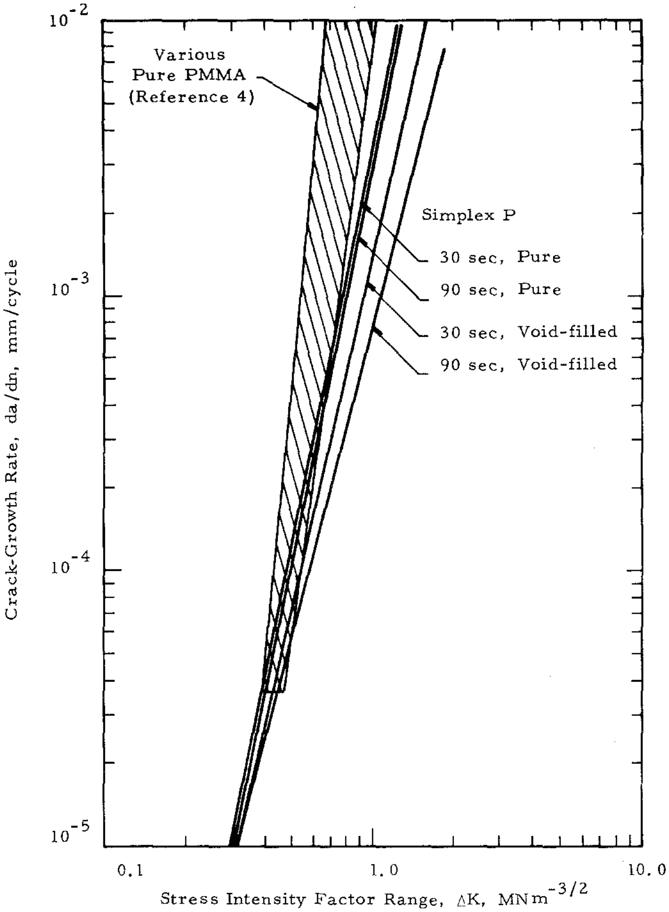


Figure 3 Fatigue-crack propagation in Simplex P and in pure PMMA.

crack-growth rates exist from the very early stages of crack propagation, and that all of the SP-based polymers possess fatigue-crack growth resistance superior to that of pure PMMA [4]. Although kneading time proved to be an insignificant parameter in affecting the rate of crack growth in non-void-filled SP, the crack-growth rate in the void-filled material was influenced, with the longer kneading time material possessing the slowest rate; both void-filled batches were superior to the non-void-filled polymers in their crack-growth resistance.

It is helpful in attempting to rationalize the preceding behaviour to consider the results obtained by scanning electron fractography of the fatigue fracture surfaces. In Fig. 4 it can be seen that the fatigue fracture process in SP has occurred through striation formation, whose spacing is in general agreement with the macroscopic crack growth rate, and that the crack has traversed the PMMA spheres in a "transgranular" fashion. However, the matrix-sphere boundary does serve as a barrier to growth, as shown by the reduction in matrix striation spacing as the crack approaches a sphere (arrow, Fig. 4). In fact, the crack frequently is pinned at a boundary for a number of cycles, and will bow

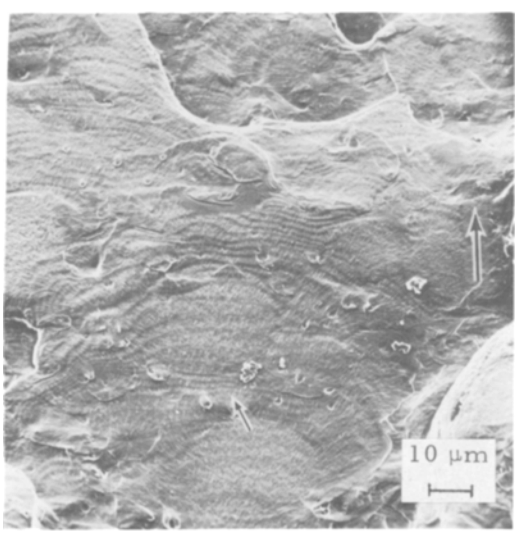


Figure 4 Fracture surface showing relation between incremental crack growth and sphere–matrix boundary (arrow). Large arrow indicates crack-growth direction.

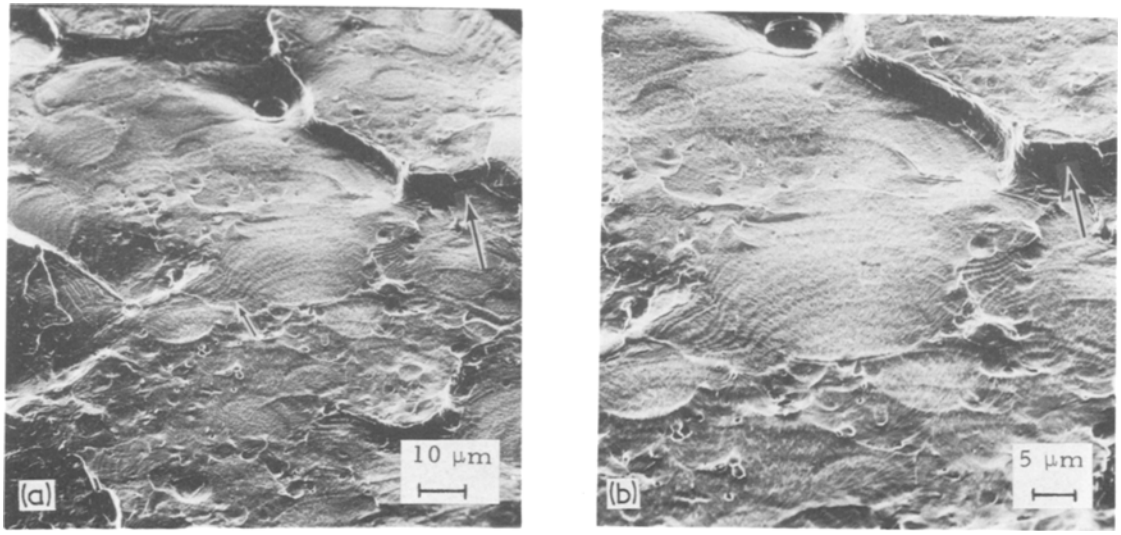


Figure 5 Fracture surface showing relative incremental crack growth in spheres and in matrix. Large arrow indicates crack-growth direction. (a) Typical striation pattern (arrow). (b) View of centre of (a) at increased magnification.

around a PMMA particle until at some critical bowing angle, the local crack front snaps across the boundary to form a thumbnail-shaped crack within the sphere (see Fig. 5a). The possibility of such crack front pinning has been previously suggested, and verified in brittle ceramic materials, by Lange [7]. Once having passed the boundary, the crack grows significantly faster within the pure PMMA spheres than in the matrix, as evidenced by wider striation spacings within the PMMA. Note especially in Fig. 5b the manner in which the crack assumes a curved shape, with the local leading portion lying within the spheres, arcing back to the boundary where growth is retarded due to the reduced incremental growth per cycle which prevails in the matrix. Two factors then, (1) the matrix-sphere interfacial barrier and (2) the lower intrinsic growth rate in the MMA matrix, serve to account for the enhanced fatigue resistance of SP relative to pure PMMA.

Exposure to a fluid during kneading further increases fatigue resistance, but for different reasons. As a major fatigue crack grows in the void-filled SP, many small microcracks are nucleated at the dispersed voids, causing the crack front to wander, on a microscopic scale, as it turns to join these small cracks. This effect is shown in Figs. 6 and 7, with the material etched in concentrated nitric acid fumes to highlight the microstructure. The erratic microscopic behaviour of

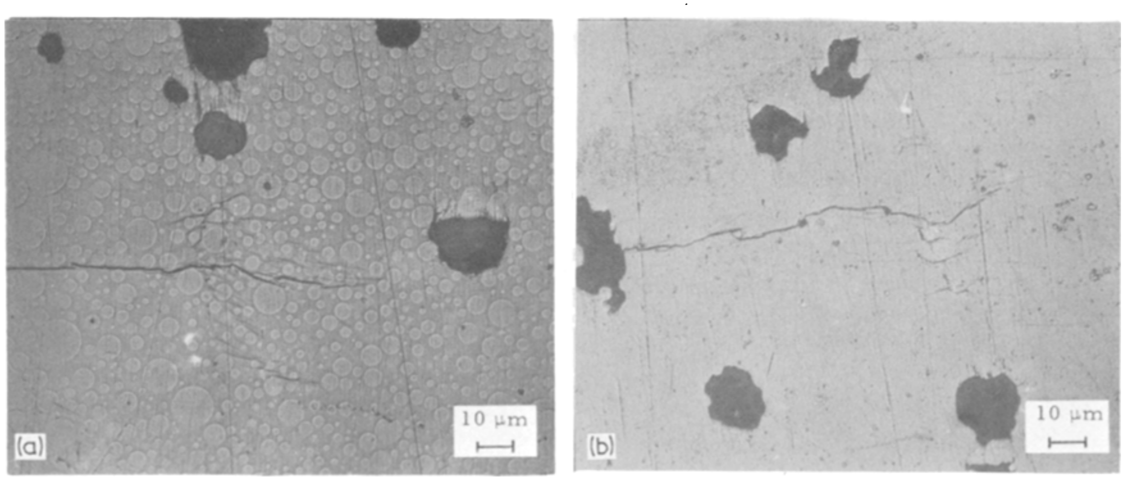


Figure 6 Side view of crack paths. (a) Simplex P, 90 sec kneading time, etched to show PMMA spheres. Large holes are air spaces. (b) Void-filled Simplex P, 90 sec kneading time. Small pits are voids, large holes are air spaces.

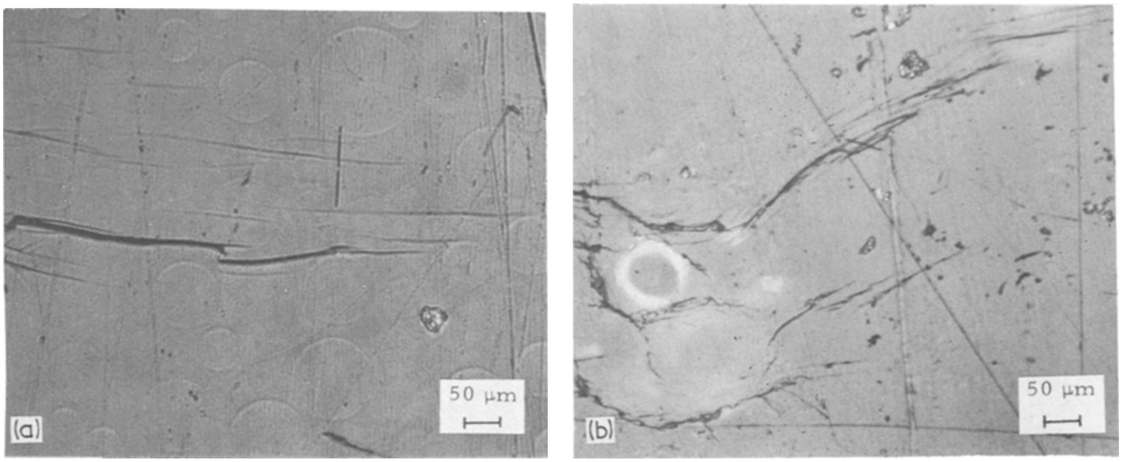


Figure 7 Side view of crack tip. (a) Simplex P, 90 sec kneading time. Crack runs straight. (b) Void-filled Simplex P, 90 sec kneading time. Crack tip changes direction erratically.

the void-filled material, as contrasted with that of pure SP, is especially evident in Fig. 7. This behaviour causes a net reduction in the average macroscopic crack growth rate, while increasing the scatter of the microscopic growth rate. Similar microscopic wandering of the crack front along weak PMMA–MMA interplanar boundaries was observed by Beaumont and Young [1] during slow crack growth in SP, which tends to reduce the rate of static crack growth. In the present case, however, interparticulate debonding was not a factor in either SP or the void-filled SP, and the lower crack growth rates in the latter material apparently must be ascribed solely to the beneficial presence of the voids. It is possible that an additional factor in the reduced da/dn in void-filled SP is the reduction in primary crack driving force due to energy given to nucleation of secondary microcracks at the voids.

There remains to establish the reason for the maximum fatigue-crack growth resistance of the void-filled SP kneaded for 90 sec. Consideration of Fig. 8 provides a possible explanation. After only 30 sec kneading, the fluid is still somewhat concentrated, producing a (macroscopic) streaky, mottled appearance (Fig. 8b), while after 90 sec (Fig. 8c) the fluid and void distributions are reasonably homogeneous. The finer and more homogeneous the void distribution, the greater is the opportunity for a maximum number of voids to interact on each load cycle with the stress field of a propagating fatigue crack and cause it to deviate from its path in order to link up with void-nucleated microcracks, as shown in Fig. 7b.

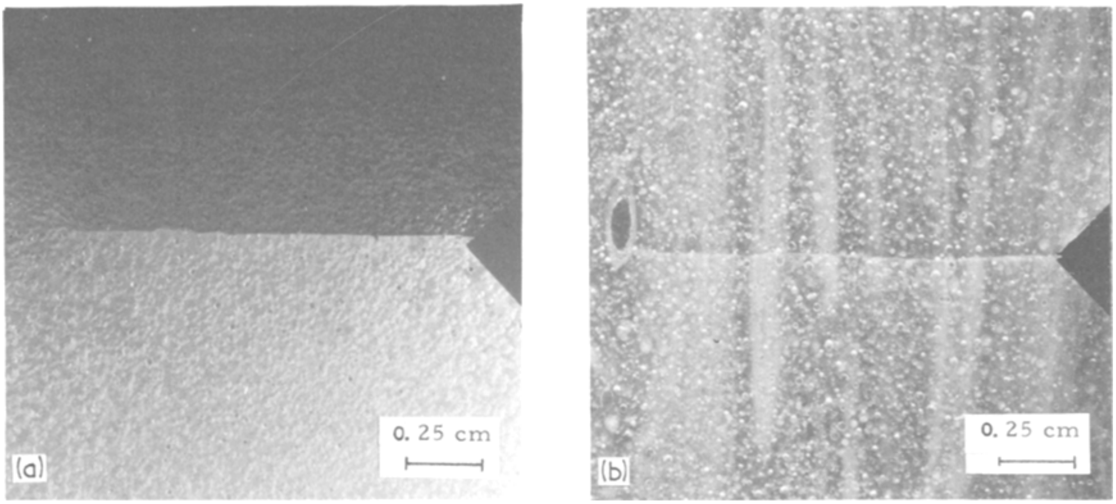
From Fig. 3, it is apparent that if the proposed mechanism through which microvoids influence the crack path is correct, then it must be operative at quite low stress intensities, since the crack-growth rate versus ΔK curves for the various SP microstructures begin to diverge at around $\Delta K = 0.3\,\text{MN m}^{-3/2}$. For the mechanism to be reasonable, the mean spacing between microvoids must be less than the size of the plastic zone associated with the crack tip. This parameter can be calculated according to the Dugdale relationship, which Marshall *et al.* [8] have shown is a reasonable approximation to the crazed yield zone at the tip of a crack in PMMA. The length r_p of this zone is given by [8]

$$r_p = \frac{\pi}{8}\left(\frac{K}{\sigma_y}\right)^2, \tag{2}$$

where σ_y is the yield strength and K the maximum stress intensity. For pure SP, σ_y is $40\,\text{MN m}^{-2}$, so that for the point of divergence of the da/dn versus ΔK curves, i.e. $\Delta K = K = 0.3\,\text{MN m}^{-3/2}$, r_p is calculated to be $22\,\mu\text{m}$. This value is in good agreement with the average microvoid spacing of approximately $25\,\mu\text{m}$, and as anticipated, would obviously exceed the mean void spacing at higher ΔK values.

4. Conclusions

The results of these tests indicate that a variety of micromechanisms exist whereby the fatigue-crack growth resistance of amorphous composite polymers may be altered. It should be possible to control cyclic crack growth in composite



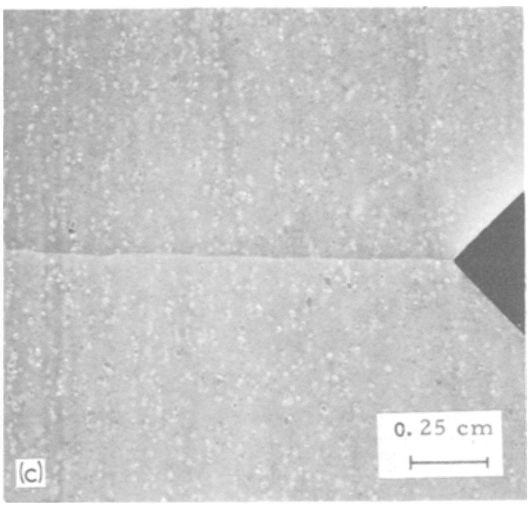


Figure 8 Edge view of fatigue fracture plane. Pebbly structure composed of air spaces. (a) Simplex P, 90 sec kneading time. (b) Void-filled Simplex P, 30 sec kneading time. Voids inhomogeneously distributed. (c) Void-filled Simplex P, 90 sec kneading time. Voids uniformly distributed.

polymers through the mechanical properties, size, and spacing of included polymeric particles, as well as through manipulation of the mechanical properties of the matrix and its void content, i.e. void size, spacing, and morphology. However, the effect of these particular variables upon strength, slow crack growth, and fracture toughness is not yet known in a systematic way, and must also be taken into account, since optimization of one property may well be achieved at the cost of reducing others. For example, although the presence of microvoids enhances the resistance of SP to fatigue-crack growth, it would be surprising if resistance to crack initiation were improved; in fact, the opposite effect might well be the case.

Acknowledgements
We are grateful to Howmedica, Inc, for the donation of the Simplex P material used in the experiments. In addition, we gratefully acknowledge the financial support of the Orthopaedic Research and Education Foundation and the University of Texas Health Science Center at San Antonio. Finally, we wish to acknowledge an unknown reviewer who pointed out to us a significant error in our original draft of this paper.

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Received 31 December 1975 and accepted 18 February 1976.