Environmental stress cracking and morphology of polyethylene

S. Bandyopadhyay and H. R. Brown
Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia
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Studies have been made of the fracture surfaces of high density polyethylene which failed by environmental stress cracking at very low stress. The failure appears to be almost entirely brittle, contrary to the evidence of plastic deformation and void formation reported by other workers. The failure occurred either in an interlamellar manner within a spherulite, or, when the lamellae matched poorly across an interspherulitic boundary, by cracking along that boundary. Because of the brittle nature of the failure, the fracture surface provides information on spherulite morphology in bulk crystallized material.

INTRODUCTION

It is well known that in environmental stress cracking (e.s.c.) of polyethylene, the failure is brittle at low stresses, but rather ductile at higher stresses. While the e.s.c. phenomenon has been studied extensively by a number of workers, the amount of information from fracture surface studies is rather limited. Isaksen *et al.*[1] showed from optical microscopy that the cracks in e.s.c. tests originated at the boundaries between deformed and undeformed materials. From optical microscopic observations Haas and MacRae[2] found that cracking occurred at the centres of spherulites and also on the boundaries. Marshall *et al.*[3], presented a low magnification scanning electron micrograph of a fracture surface of a medium density polyethylene where they observed the presence of plastically deformed regions. Hannon[4] carried out scanning electron microscopic work on the fracture surface of e.s.c. failed samples and showed that there was nucleation and growth of voids and the material in between the voids deformed plastically. Haward and Owen[5] presented high magnification scanning electron micrographs of e.s.c. fracture surfaces of high density polyethylene (HDPE) and showed the presence of fibrillation and voids.

The present authors[6] observed the presence of fibrils on the fracture surfaces of different grades of low density polyethylene which, at higher magnification, showed the evidence of interlamellar failure. This paper describes the extension of that work to the examination of surfaces formed by fracturing HDPE in a detergent at low stress.

EXPERIMENTAL

The material chosen for this study was a medium molecular weight HDPE, GA 7260 supplied in particle form by Hoechst Australia Ltd. It has a density of 0.961 gm/cm^3. The material was formed into sheets by compression moulding at 180°C then fast cooling to room temperature. A cooling rate of 1°C/sec was used above 100°C. Single edge notch e.s.c. specimens were cut from the sheet one month after moulding. The notch tip was sharpened with a razor blade and the test was carried out in a dead weight load apparatus at a stress of about 0.79 MPa. The stress cracking agent was a 10% (v/v) solution of Igepal Co–630 in water held at 24.5° ± 0.5°C. The thickness of the specimen was 1.5 mm.

The crack propagation was initially very slow and the total time to failure was about 1200 h.

One fracture surface of the failed specimen was subsequently sputter coated with gold then studied in a Cambridge Scanning Electron Microscope S4–10. Two-stage replicas were made from the other fracture surface and also studied in the *SEM*. In all the scanning electron micrographs presented below the direction of crack propagation is from left to right.

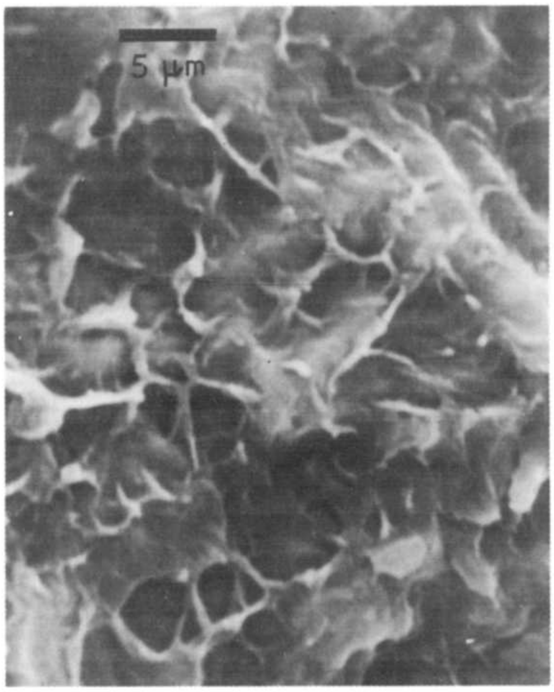

Figure 1 Fracture surface showing formation of voids in the immediate vicinity of the razor cut. Scale, 5 μm

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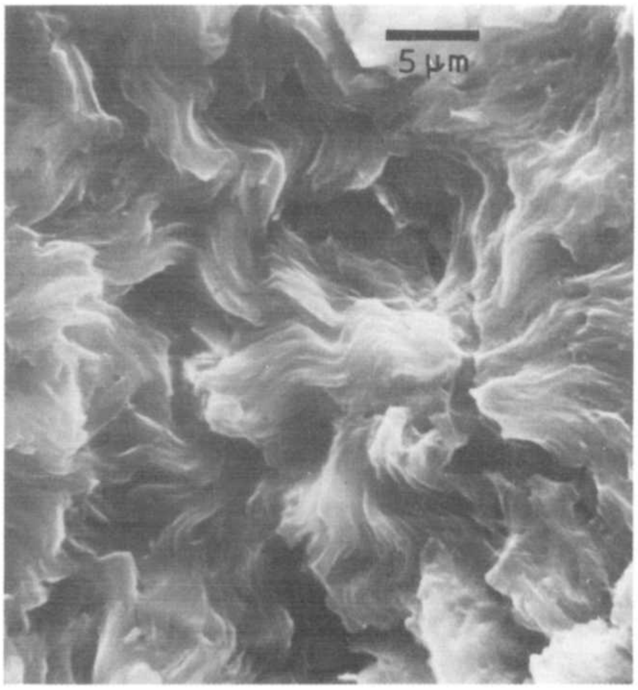

Figure 2 Fracture surface giving impression of plastic deformation. Scale 5 µm

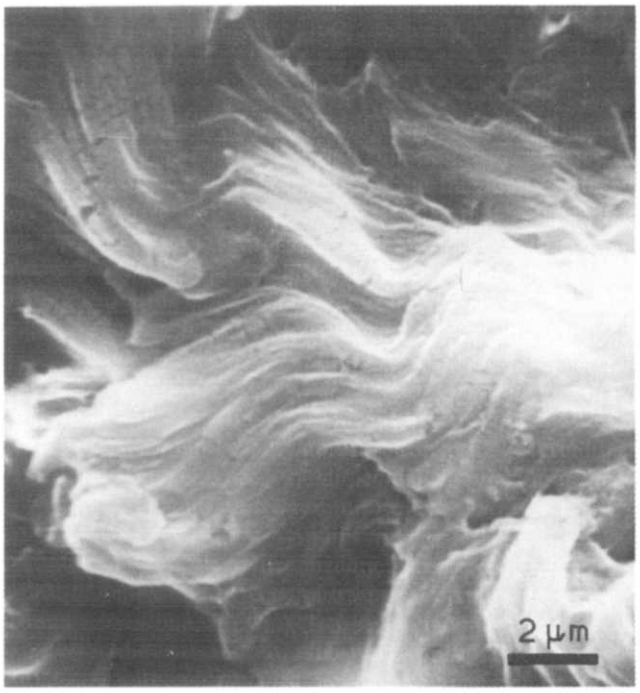

Figure 3 Central portion of *Figure 2*, indicating presence of banded lamellae. The fine cracks are those of the coating. Scale 2 µm

DISCUSSION

The fracture surface was apparently brittle and showed no contraction in thickness. Further, the optical microscopic observation did not give indication of fibrillation ahead of the crack tip as was observed for the low density polyethylenes.

In the vicinity of the razor blade cut there was a very small region where the fracture surface showed voids (*Figure 1*) similar to those shown by Haward and Owen[5]. Elsewhere, the fracture surface was quite different. *Figure 2* shows a fracture surface which gives an initial impression of plastic deformation, but a magnfiication of the central portion as shown in *Figure 3* shows similarity with the banded lamellar structure of HDPE as shown by Grubb and Keller[7] and others[8,9]. This suggests that one could observe a banded structure of the spherulite by more careful investigation. *Figure 4* shows the banded structure of a spherulite. The

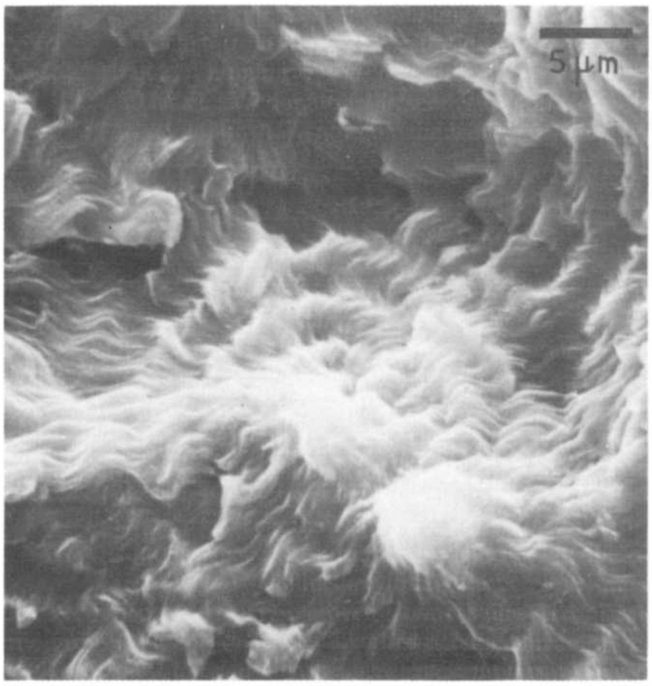

Figure 4 Fracture surface showing banded spherulite structure revealed by interlamellar crack propagation. The electron beam makes an angle of 60° with the specimen surface. Scale, 5 µm

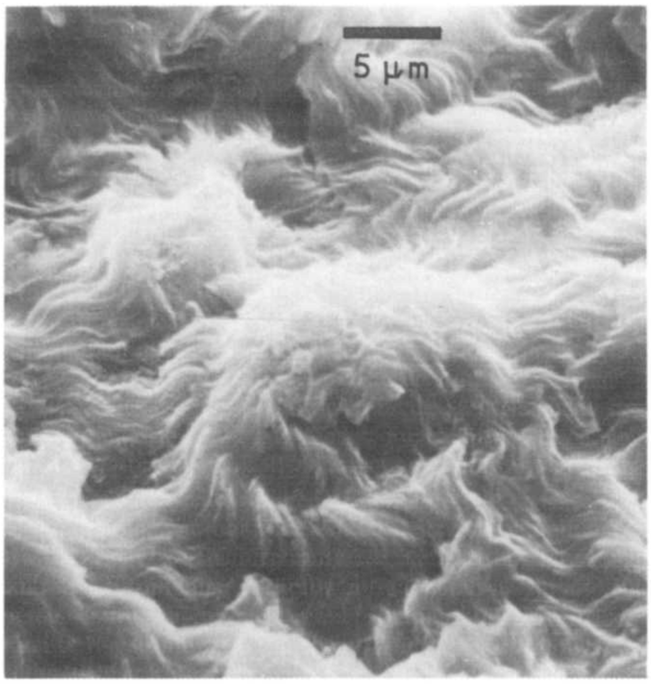

Figure 5 Interlamellar crack propagation in a spherulite whose centre lies above the approaching crack. The electron beam makes an angle of 60° with the specimen surface. Scale, 5 µm

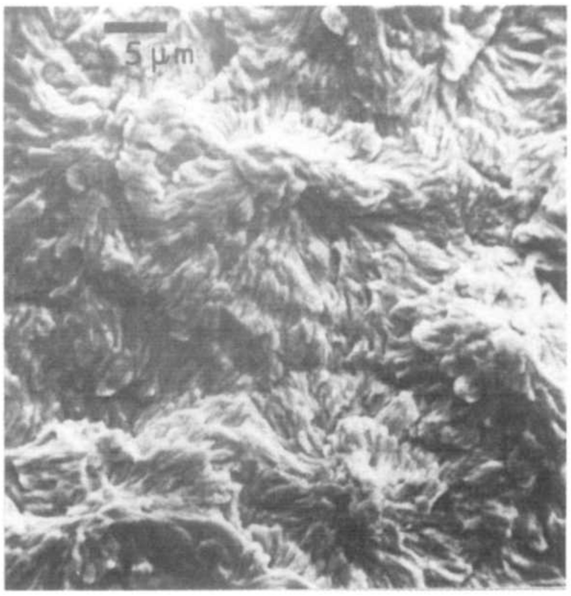

Figure 6 Fracture surface from a two-stage replica showing banded spherulites. Scale, 5 µm

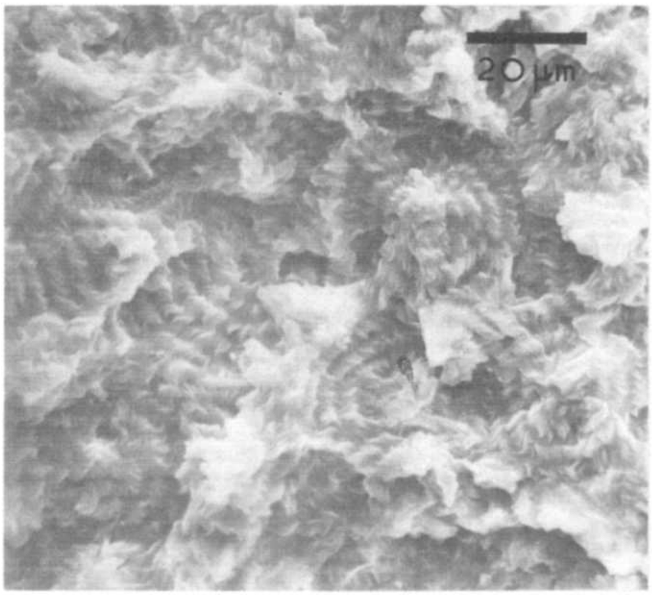

Figure 7 Fracture surface showing matching interface. Scale, 20 µm

contrast of the bands may have been enhanced by the mechanism suggested by Grubb and Keller[7] but their existence on the fracture surface demonstrates that the failure was brittle and not by a ductile, void growth mechanism. This also suggests an interlamellar mode of failure. *Figure 5* shows the banded structure of a spherulite whose centre appears to be above the general crack surface. Further, the fracture surface observed from a two-stage replica as shown in *Figure 6* shows that the banded spherulitic structure is a feature of the original fracture surface.

When a crack meets a spherulite, the spherulite centre can lie on or above (or below) the crack plane. In the former case, the crack can split the spherulite between the lamellae in the diametrical plane as is observed in *Figure 4*, but when a crack meets a spherulite whose centre lies above its plane, there may be three possible paths for the propagating crack: (i) follow the interlamellar region up to the spherulite centre and continue down to the other edge leaving a conical section of the spherulite on the fracture surface as observed in *Figure 5*; (ii) cut through the spherulite keeping within the one plane – this was not observed; (iii) follow the spherulite edge, thus cracking the interspherulitic boundaries. Case (iii) will not occur when the direction of lamellae in two adjacent spherulities match on the crack plane. The fact that the crack can travel smoothly across matching interfaces is shown in *Figure 7*. The band spacing agrees with that observed by optical microscopy.

When the crack front encounters interfaces across which there is poor or little matching of the lamellae, the easier modes of propagation are obstructed and interspherulitic cracking occurs, as shown in *Figure 8* in which a number of spherulites are involved. This picture shows that the crack cuts through the edge of one spherulite and the crackfront drastically changes its direction. However, across the matching interface of two spherulites in the background (shown by arrow), the crack propagation is still smooth.

The above pictures also provide information about the morphology of spherulites in three dimensions. This is possible because the low stress e.s.c. failure is brittle and the morphology has been retained undeformed. The depth of focus of the scanning electron microscope is sufficient to give the information.

Similar features to those described above can be seen almost all over the fracture surface but at different places they are observed with different angles with respect to the beam. *Figures 9* and *10* illustrate how much the angle can affect the observation of the banded structure. In this case a difference of 5° in the angle has caused considerable change in the appearance of the same spherulite, but there are also places where the structure can be observed over a wider range of angles. The reason for this may be as follows. From previous observations it is reasonable to presume that the

Figure 8 Interspherulitic crack propagation; also showing a smooth crack propagation across a matching interface (shown by arrow). Scale, 10 µm

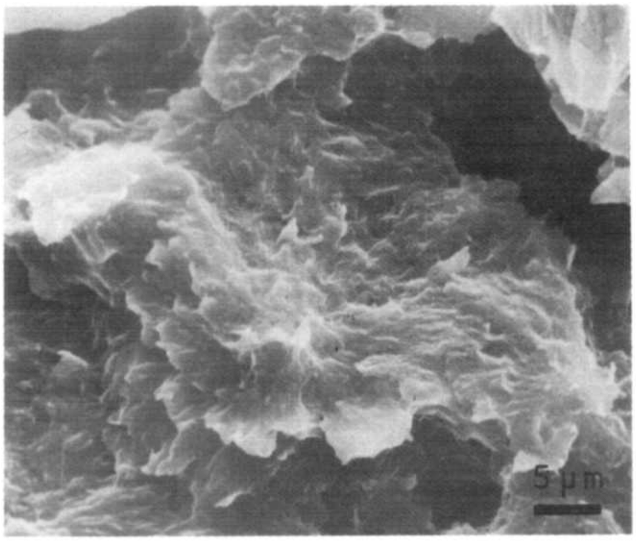

Figure 9 A view of a spherulite when the electron beam makes an angle of 60° with the specimen surface. Scale, 5 µm

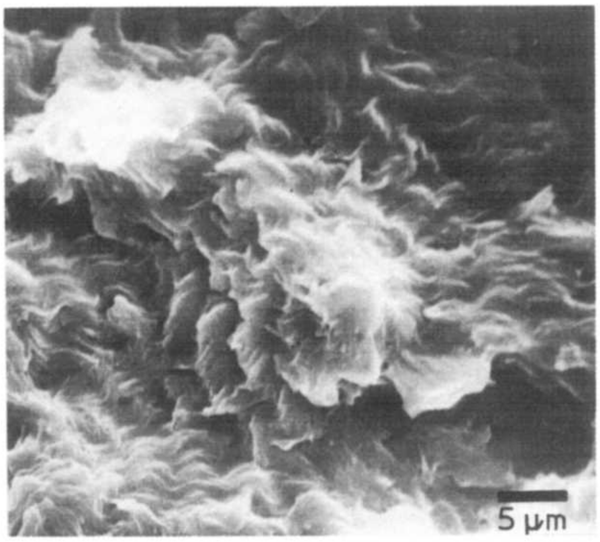

Figure 10 The same spherulite as *Figure 9* when the electron beam makes an angle of 65° with the specimen surface. Scale, 5 µm

crack front changes its direction from place to place, particularly when it meets poorly matching interfaces. Consequently the plane along which subsequent interlamellar failure will take place depends on the direction of the crack front at that instant. This effect will be studied in more detail in the future.

The only exception to this brittle failure mode is observed, apart from in the immediate vicinity of the initial razor cut, near the specimen edges. Over a region of up to about 30 µm from each side there is evidence of voids and drawing within the individual spherulites.

CONCLUSIONS

From the results of tests carried out on a compression moulded HDPE under conditions of very slow crack propagation at very low stress, the following conclusions are reached.

(1) Low stress environmental stress crack failure of high density polyethylene is brittle in nature.

(2) The failure within an individual spherulite is interlamellar and the mode of crack propagation within the spherulite depends on the position of the spherulite centre with respect to the crack front.

(3) The crack propagation across a matching interface is smooth without any change in direction. On the other hand, when the crack front meets poorly matching interfaces, interspherulitic cracking can occur.

(4) The brittle failure in low stress environmental stress cracking of high density polyethylene provides information about the spherulite morphology.

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