NOTES

Microscopic Aspects of Brittle Failure of Polyethylene at Stress Below the Yield Stress

It has been well known for many years that both ductile and brittle fracture of metals proceed by a hole nucleation and growth mechanism.   Extensive studies presenting the theories, fracture morphology, and fracture criteria have been developed and presented by McClintock and Argon,[1] Tetelman and McEvily,[2] McClintock,[3,4] and Berg.[5,6] Even macroscopically appearing brittle fracture often shows quite extensive plastic deformation and hole nucleation and growth.

Recently, evidence has appeared to show that this mechanism of failure is not unique to metals but also is involved in fracture processes of both glassy and crystalline polymers.

Zhurkov and co-workers[7,8] have used small-angle x-ray and electron spin resonance techniques to show that in polymers such as polypropylene, poly(ethylene terephthalate), nylon 6, poly(vinyl chloride), and poly(vinyl butyral), the polymer undergoes stable, thermally activated cavitation (with holes of ≈ 100 Å) at stresses below the yield stress of the material.   Recently, Doyle et al.[9] have presented the fracture topography of glassy polymers showing various stages of the fracture process in these polymers.   This work also shows cavitation and plasticity as a precursor to failure.

Theories to explain this type of failure in polymers from a generalized failure model have been attempted.   Berg has proposed[6] that his model, which was derived for ductile metals, can be directly applied to fracture processes in glassy and crystalline polymers: "The general conditions given above for fracture of ductile metals by formation of surfaces of unstable void growth should apply as well to those modes of fracture of polymers which are preceded by crazing."   Argon[10] has recently presented a molecular theory for fracture in polymers which takes into account the process of the elastic-plastic expansion of thermally activated pores, followed by craze formation and growth.   Other similar models and theories by Andrews[11] and Gent[12] have provided further insight into this cavitation and failure phenomenon.   Recently, Haward et al.[13] have presented additional experimental results which show that fracture in polystyrene occurs via a hole growth mechanism.   Using energy considerations and a fracture mechanics approach, Haward explains the process of nucleation of voids and the conditions under which these occur.   In particular, he has shown that cavitation stresses (or crazing stresses) are much lower than the yield stresses of the plastics at the use temperatures.

These results serve as a basis for understanding the (macroscopically) brittle fracture behavior of polyethylene, which is accelerated by hostile environments such as detergents and is normally termed "environmental stress cracking" (ESCR).[14]   The phenomenon is such that at low stresses, long times, and in thick specimens, under approximately plane strain conditions, the brittle type of failure occurs.   At high stresses, short times, and in thin specimens, under approximately plane stress conditions, ductile failure occurs.

Recently, it has been demonstrated by Marshall et al.[15,16] that the fracture mechanics approach which has worked so well in metals and glassy polymers is also applicable to environmental stress cracking of polyethylene.

RESULTS

With these concepts of fracture mechanics in mind, we have investigated the fracture of polyethylene under conditions conducive to brittle failure.   Thick, notched samples
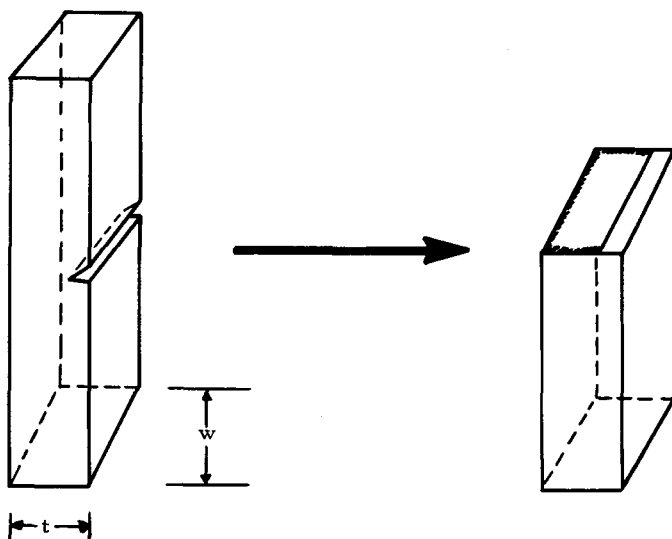
Fig. 1. Sample geometry: t = 0.112 in.; w = 0.188 in.; notch depth = 0.040 in.
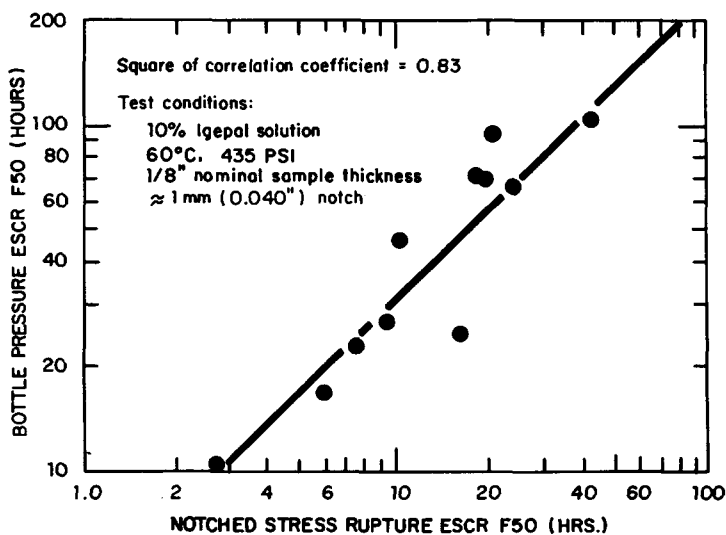

Fig. 2. Log bottle pressure ESCR vs. log notched stress rupture ESCR.

have been used as shown in Figure 1 which at low stresses will approximate plane strain conditions producing macroscopically brittle failure of the type that is typical of ESCR of polyethylene in actual field service in container and pipe applications. We have used this test to predict service life of polyethylene samples for container applications containing hostile environments. The type of correlation which is observed between samples tested by this "notched stress rupture" test and samples tested as actual bottles containing detergent is shown in Figure 2. The notched stress rupture and bottle test ESCR data for the samples included in this correlation are shown in Table I. Also shown are the melt indexes, molecular weights, and densities for all the samples. The

TABLE I
Stress Crack Data and Molecular Parameters

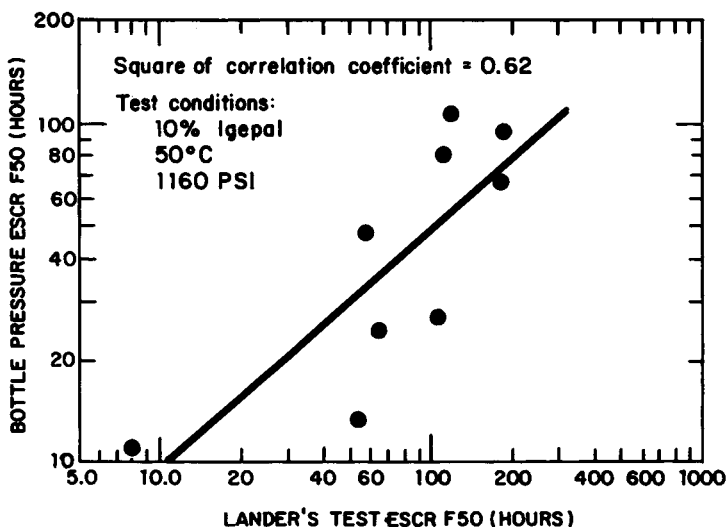| Sample no.	Bottle test ESCR, hr	Notched stress rupture ESCR, hr	Melt index, dg/min	M_w $\times 10^{-5}$	Density, g/cc
1	25.0	16.5	0.41	1.30	0.954
2	27.0	9.6	0.24	1.27	0.946
3	24.0	7.7	0.35	1.77	0.955
4	71.0	19.4	0.11	1.57	0.945
5	11.0	2.7	0.70	0.93	0.960
6	67.5	23.0	0.19	1.21	0.949
7	102.0	42.5	0.15	1.81	0.950
8	94.0	21.0	0.17	1.35	0.950
9	48.0	10.3	0.22	1.34	0.952
10	70.0	20.0	0.39	1.31	0.952
11 (A60-42)	—	3.0	0.40	1.20	0.960
12 (B55-40H)	17.2	6.0	0.44	1.27	0.955

Fig. 3. Log bottle pressure ESCR vs. log Lander's ESCR.

samples vary in melt index from 0.11 to 0.70 decigrams/min and in density from 0.945 to 0.960 g/cc. All are copolymers except two homopolymers, namely, samples 5 and 11 (A60-42), both of which have densities equal to 0.960 g/cc. Both straight reactor product and polymer blends are included in the series. The correlation shown in Figure 2 is much better than any which could be attained from using the more conventional tests such as the Bell Laboratory bent strip test[17] or the Lander's test.[18] As an example, the results for an attempted correlation between the bottle test and the Lander's test is shown in Figure 3. The better correlation obtained with the notched stress rupture test leads us to believe that the failure mode which is imposed by the sample conditions and low stresses more closely approximates the failure conditions of actual in-service applications.

During the course of this work, the fracture surfaces were investigated by means of scanning electron microscopy. The fracture surfaces of three different samples are
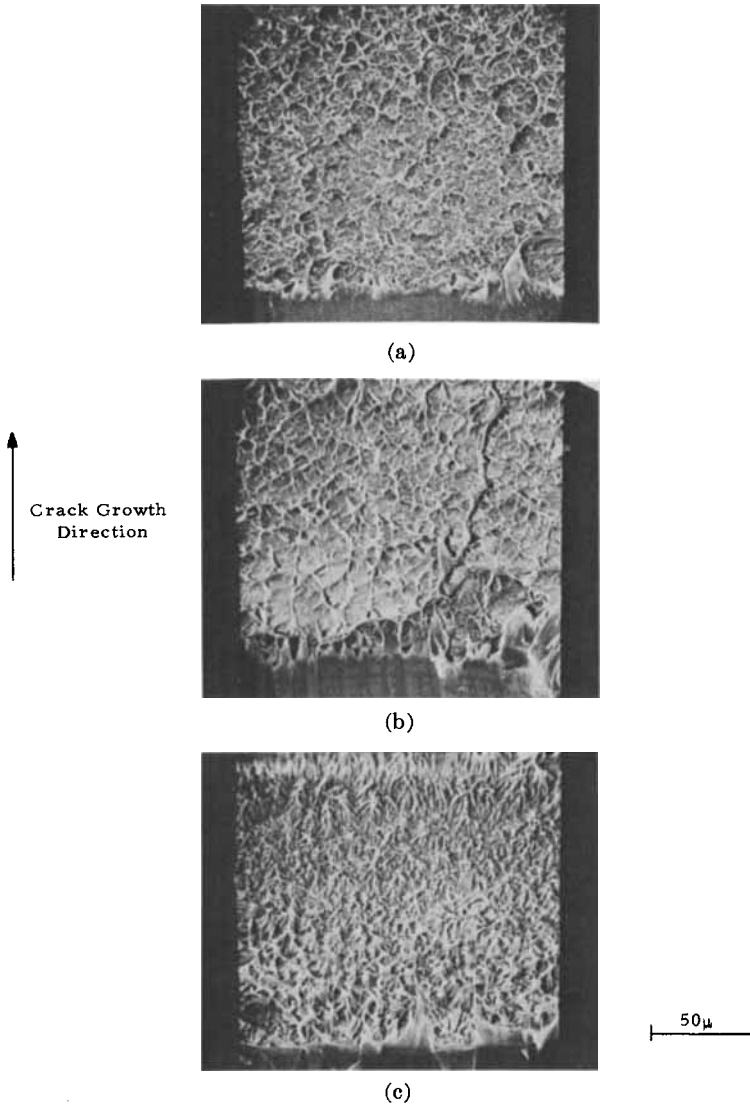
(a)

Crack Growth
Direction

(b)

(c)

50μ

Fig. 4. (a) Fracture surface of polyethylene homopolymer (A60-42) at 60°C in 10% Igepal solution; (b) fracture surface of polyethylene copolymer (B55-40H) at 60°C in 10% Igepal solution; (c) fracture surface of polyethylene copolymer (B55-40H) at 60°C in water.

shown in Figure 4.   It can be seen from the pictures that in each case, whereas the fracture was macroscopically brittle, the failure proceeded by a void nucleation and growth process with considerable ductile deformation between the voids.   Three micrographs are shown: Figure 4a is the fracture surface of a polyethylene homopolymer (Fortiflex A60-42) under nominal stress of 435 psi at 60°C in 10% Igepal; Figure 4b is a polyethylene copolymer (Fortiflex B55-40H) under the same conditions of stress and environment; and Figure 4c is the same copolymer (B55-40H) under the same stress and loading conditions but tested in pure water environment at 60°C.   As can be seen from the data in

Table I, the copolymer (B55-40H) and homopolymer (A60-42) have roughly the same melt indexes and molecular weights. They differ only in that the B55-40H has a certain amount of hexene comonomer (roughly 1.0 comonomer units per 1000 chain carbon atoms) randomly distributed throughout the polymer. This leads to a lower density for this sample (0.955 g/cc) and a lower crystallinity.

In general, it is well known that polyethylene copolymers withstand environmental stress cracking better than homopolymers, particularly in detergent solutions. This observation holds true for the samples shown in Figure 4. The average time to failure for the copolymer (B55-40H) under the test conditions in detergent solution being approximately 6 hr compared with 3 hr for the homopolymer. The striking differences in the fracture surfaces of these samples correlate with their relative time to failure in the particular test. It is seen that many more holes are nucleated in the copolymer (Fig. 4b) and the amount of plastic deformation (the ridges in the photograph) is much greater than in the homopolymer sample (Fig. 4a). Making a rough estimate of the number of voids nucleated in a 50-micron × 50-micron area close to the notched (smooth) edge of the sample, one obtains approximately 0.4 voids per 100 square microns for the homopolymer sample (Fig. 4a), compared with approximately 1.8 voids per 100 square microns for the copolymer (Fig. 4b). Fracture differences are also apparent when comparing the copolymer tested in a 10% Igepal solution (Fig. 4b) with the same polymer (B55-40H) under the same conditions of stress and temperature in pure deionized water (Fig. 4c). The times to failure averaged approximately 6 hr for the copolymer in the detergent solution and 17 hr in pure water. In the micrographs it is seen that many more voids are nucleated, and the amount of plastic deformation which took place is much greater in the water-tested sample than in that tested in Igepal solution. A rough estimate gives approximately 3.4 voids per 100 square microns when tested in water, compared with 1.8 voids per 100 square microns when tested in Igepal solution.

DISCUSSION AND CONCLUSIONS

There is a great deal of discussion in the literature concerning the factors which are important in the brittle fracture process. However, several features appear to be common to most of the models[6,10,13]: (1) the development of microvoids in the sample; (2) the rate at which the voids grow and coalesce, and (3) the amount of plasticity and degree of strain hardening of the material around the voids, supporting the spongy matrix formed. The voids are apparently stress activated and caused at least in part by bond rupture as demonstrated by the work of Zhurkov et al.[7,8] The rate at which these voids grow seems to be related to the stress strain relationships of the polymer at and following the yield point, and the energy available from the formation of new surface (and the rupture of chains) which goes into the creation of new voids (as explained by Haward[13] and Andrews[11]). Finally, plastic deformation and strain hardening of the sample occur, which resists further nucleation of voids and tends to stabilize the crazes or cracks.[6,13]

On the molecular level, these results are best explained in terms of the "tie molecule" or "intercrystalline links" concept of polymer morphology. These intercrystalline links have been shown experimentally in polyethylene by Keith et al.,[19] who also investigated how molecular weight affected the concentration and length of links obtained. The increase in intercrystalline links with comonomer content in a polyethylene copolymer was investigated using thermodynamic arguments by Richardson, Flory, and Jackson,[20] and the increase with molecular weight was investigated by Mandelkern et al.[21] using similar arguments. Other more subtle factors, related to the molecular weight distribution, seem to be important but have not been well documented. A detailed model of the intercrystalline links concept and how the physical properties of the polymer are related to them was presented by Cumberbirch and Mack.[22,23]

Our observations of the effects of comonomer content and stress crack agent upon the brittle fracture behavior of polyethylene can be explained in terms of the above molecu-

lar models.   The larger number of tie molecules in the copolymer samples is related to the greater interfacial free energy during crystallization in the copolymer samples.   Essentially, the comonomer units prefer not to crystallize with the ethylene units, leave the crystallite, traverse an "amorphous" region, and eventually enter another crystallite where the free-energy match is more favorable.   This is the source of the increased amount of intercrystalline links (and lower densities) in the copolymer samples.   When the samples are stressed, these intercrystalline links bear the stress concentrations and fracture, causing the microvoids to form.   The load is then transferred to the surrounding chains which deform, strain harden, and bear the load.   These chains then either stabilize the crack or fracture, thus repeating the process.

In the copolymer sample, there are more voids and a greater number of tie molecules.   Hence, the load can be distributed more uniformly and more chains are available for plastic deformation and strain hardening, causing increased resistance to the void growth process.   It is felt that this is why in the copolymer sample more voids are seen and a larger amount of extended, yielded material is observed than in the homopolymer; and also why the failure times are so much longer in the copolymers than in the homopolymers.   The manner in which the detergent acts to decrease failure time is still unknown.   However, it is almost certain that it penetrates into the intercrystalline regions and the voids, since the detergent molecule is too large to enter the crystallites.   Having entered these microvoids, the detergent apparently serves to aid in the void growth process and to reduce the amount of plastic deformation and strain hardening around the voids, as seen in Figure 4.

These results and the attendant photomicrographs support the thesis that brittle fracture of polyethylene under conditions of relatively plane strain conditions at low stresses (whether in a hostile environment or not) proceeds by a mechanism of hole nucleation, hole growth, and finally followed by the viscoplastic deformation (yielding) of the molecules surrounding the voids.

In addition, by confining the mode of failure to brittle fracture under plane strain conditions at relatively low stresses, one approximates much more closely the type of failure observed in polyethylene samples in containers in actual field service.   This failure is almost totally brittle (macroscopically), and electron micrographs of the fracture surfaces of these samples show the failure to be by the same hole growth mechanism.   The more conventional tests used to predict such failure, such as the bent strip test or the Lander's test, confound this brittle mode of failure with a ductile mode and confound the state of stress in the sample.   It is for these reasons that the notched stress rupture test proposed here predicts in-service failure better than the conventional tests.

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