Embrittlement and Stress Cracking of Polyethylene by Fuming Nitric Acid

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Synopsis

Oxidative embrittlement and stress cracking of high-density polyethylene has been studied by using fuming nitric acid at 60°C as the oxidative agent. Oxidative stress cracking was found to be insensitive to changes in molecular weight in contrast to environmental stress cracking in a surface-active medium. The oxidative attack was found to be influenced by the surface crystalline texture of the polyethylene. Oriented polyethylene showed an increased resistance to oxidative embrittlement and stress cracking, the mode of failure being dependent upon the prior annealing treatment.

Introduction

Oxidative embrittlement and stress cracking are important factors influencing the application of olefin polymers and have been subject to much research (see, for example, the review article by Howard[1]). The most common oxidizing agent to which polymers are normally exposed is oxygen in the form of oxygen gas or ozone. These are inconvenient for laboratory experiments because of the slow overall rate of attack; this is due to the restricted penetration of the oxidizing agent below the surface which makes the oxidation inhomogeneous and dependent upon sample size. This surface penetration problem is largely eliminated by the use of fuming nitric acid which disintegrates bulk samples rapidly. The disintegration is due to chain scission and digestion of the amorphous regions of the material, leaving behind crystalline debris.[2] This technique was originally developed for morphological studies and is being widely used in this context.[3,4] Because of the speed and homogeneity of the attack of polyethylene by fuming nitric acid, it was used in the present study of oxidative embrittlement, even though this is not the most common environment to which polyethylene is exposed.

The present work originates from the expectation that oxidative embrittlement and stress cracking involving chain scission should be less dependent upon molecular weight than environmental stress cracking in a surface-active medium, where the integrity of the chain is preserved and

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physical separation of adjacent parts of the sample must occur by chain disentanglement, i.e., chains must be dragged out from their original locality. The molecular weight dependence in this latter case is well known.[1]

However, a comparison between the molecular weight dependence of surface active and oxidative agents has not been reported. It was therefore decided to compare the molecular weight dependence of polyethylene to stress cracking in an oxidative medium (fuming nitric acid) with that of a surface-active medium (Teepol, by Shell Chemicals Ltd.).

In the course of this investigation the effects of the oxidative attack were examined microscopically. The salient features are reported as they may be technologically significant.

Experimental

Dumbbell-shaped test specimens 4 mm wide were cut from water-quenched, compression-molded sheets of polyethylene 0.5 mm thick. Four grades of high-density polyethylene of melt flow index 0.2, 0.9, 2.5 and 5 (Rigidex types 2, 9, 25, and 50 respectively) were used. The specimens were placed in a specially designed holder[5] under an applied tensile stress of $1/4$ the yield stress (measured at room temperature). The holder and specimen were then placed either in fuming nitric acid or Teepol at 60°C and the time taken to failure recorded. The specimens were then removed, washed, and examined.

The typical specimens are shown in Figure 1. In both cases a few large cracks, initiated from the cut edge of the specimen, have propagated inwards and led to failure. In the case of treatment in Teepol, Figure 1a, some of the cracks were spanned by drawn fibers and there is an absence of fine surface cracks in contrast to the specimens treated with fuming nitric acid, Figure 1b.

The results of the above tests are shown in Figure 2, where the melt flow index (MFI) is plotted against time to failure. The circles represent the mean value of about six tests, the circle radius being approximately equal to the standard deviation for each set of results. These results are discussed below. Further stress-cracking tests were carried out in fuming nitric acid on polyethylene (Rigidex 50) with a different tensile stress applied to each specimen. The failure times were recorded and are shown in Figure 3. The general appearance and mode of failure was similar to that of the specimens shown in Figure 1b, except for the specimen with the lowest applied stress, and consequently the longest time in contact with nitric acid. This specimen, shown in Figure 4, had developed blisters in addition to the cracks perpendicular to the tensile axis. This observation led to the treatment of polyethylene with fuming nitric acid at 60°C for about 6 hr without an applied stress. The surface of the samples bulged up in places to form blisters as can be seen in Figure 5 (the bulging can be inferred from the incident light illumination). Figures 6 and 7 show a microtomed section, 20 μ thick perpendicular to the surface of the sample,
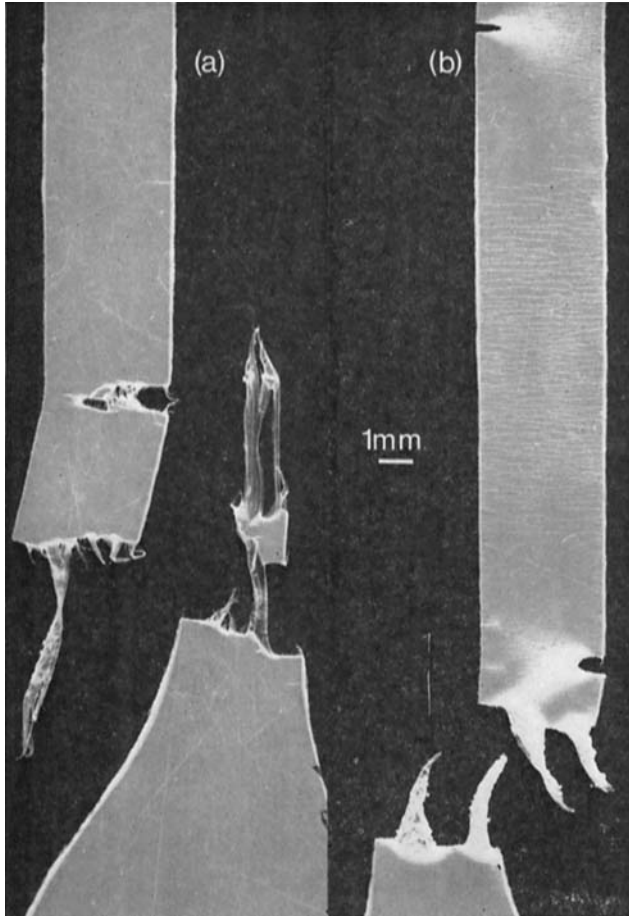
Fig. 1. Failure of specimens of polyethylene (Rigidex 50) by environmental stress cracking (a) in Teepol at 60°C after 20 hr; (b) in fuming nitric acid at 60°C after 2 hr.
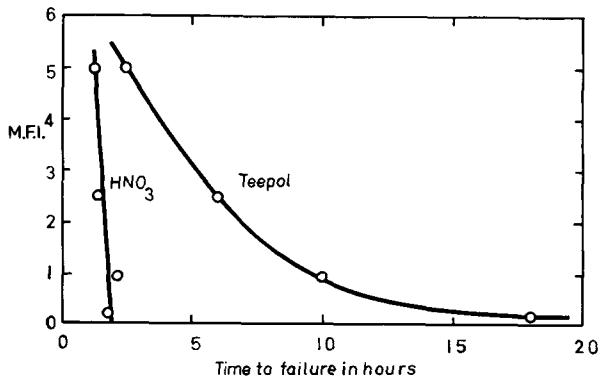

Fig. 2. Dependence of time to failure upon melt flow index (MFI) for polyethylene subjected to stress cracking in either fuming nitric acid or Teepol.
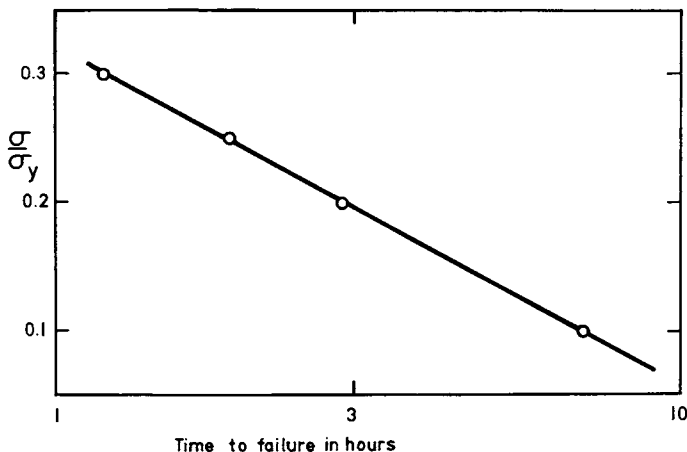
Fig. 3. Dependence of time to failure upon applied stress for polyethylene (Rigidex 50) subjected to stress cracking in fuming nitric acid at 60°C. The stress σ is expressed as a fraction of the yield stress σ_y.
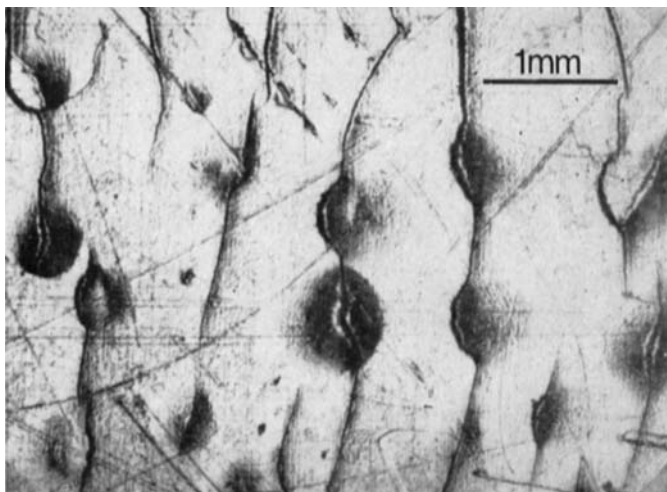

Fig. 4. Specimen subjected to low stress ($^1/_{10}$ yield stress) in fuming nitric acid at 60°C for 6 hr showing blisters and cracks.

from which it can be seen that part of the surface layer, about 50 μ thick, has broken away from the material below and bulged up to form the blister thereby cracking the upper surface.

To investigate the role played by the surface of the polyethylene (Rigidex 50), a number of specimens were prepared from which the original surface layer was removed. This was done by repeatedly cutting off thin layers of polyethylene, with a microtome moving parallel to the surface, until a depth of about 200 μ was reached. These specimens were then subjected to stress-cracking tests, with an applied stress of $^1/_4$ the yield stress in either fuming nitric acid or Teepol. The times to failure were not
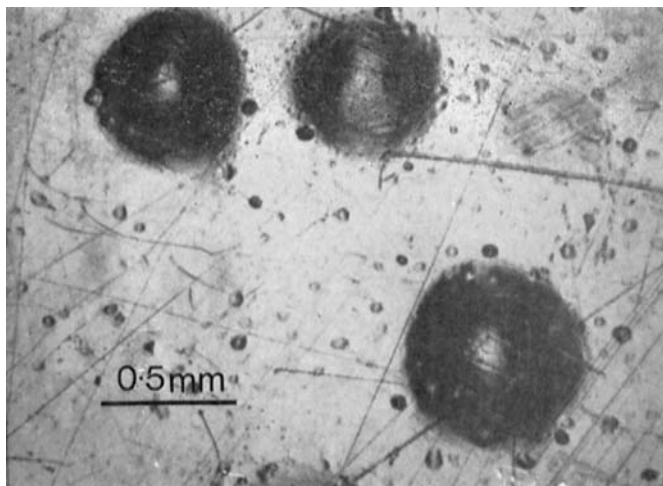
Fig. 5. Specimen subjected to fuming nitric acid at 60°C for 6 hr with no applied stress showing blistered surface. The specimen was illuminated by incident light.
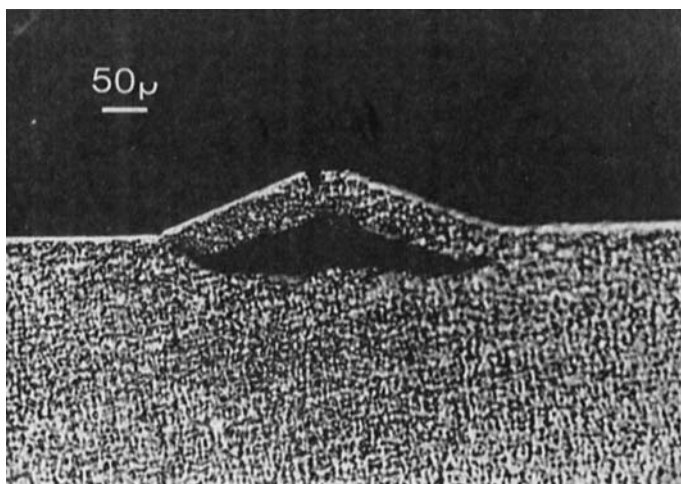

Fig. 6. Section (20 μ thick) of blistered surface of polyethylene sheet.

substantially different from the times to failure shown in Figure 2 for normal specimens. The appearance and mode of failure of the specimens subjected to Teepol was very similar to that shown in Figure 1a. However, the appearance of the specimen treated with fuming nitric acid differed from that shown in Figure 1b, in that there were fewer fine surface cracks although the mode of failure was the same.

Specimens from which the surface layers had been removed were also subjected to fuming nitric acid without a stress applied to them. No blisters formed, but after about 20 hr treatment the specimens became brittle and fragmented.

Some specimens of oriented polyethylene (Rigidex 50) were obtained by cutting out dumbbell-shaped samples, from sheets of polyethylene that
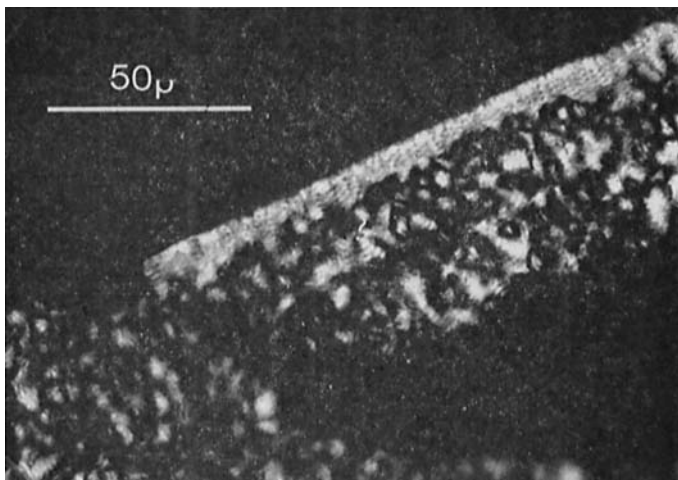
Fig. 7. Section (20 μ thick) of blistered surface of polyethylene sheet showing the same feature as Figure 6 at greater magnification in polarized light.

had been cold drawn (draw ratio about 8) with their long axis parallel to the draw direction. These specimens were subjected to stress cracking tests in either Teepol or fuming nitric acid at 60°C, with an applied stress of $1/4$ the yield stress of the drawn material at room temperature.

In Teepol the failure time was greater than 50 hr while in fuming nitric acid the failure time was about 20 hr (the failure times for undrawn polyethylene were 2.4 and 1.2 hr, respectively). The specimens were initially milky in appearance due to stress whitening during the drawing process. However, the milkiness cleared in those specimens subjected to fuming nitric acid while there was no change in appearance in those specimens subjected to Teepol.

Specimens of oriented polyethylene (Rigidex 50) were also treated with either Teepol or fuming nitric acid at 60°C without any applied stress. No effects were observed in Teepol but in fuming nitric acid cracks parallel to the draw direction developed after about 20 hr, as can be seen in Figure 8. No blisters formed on the surface of the specimens, in contrast to specimens of undrawn material.

Samples of polyethylene (Rigidex 50) with a single preferred texture* were also treated to fuming nitric acid at 60°C without an applied stress. No surface blisters formed, but cracks developed perpendicular to the draw direction as can be seen in Figure 9.

Discussion

From the results shown in Figure 2 it can be seen that the resistance to stress cracking increases very rapidly with reduction in melt flow index

* Single texture polyethylene is obtained by cold drawing, rolling and annealing polyethylene sheet to produce a preferred texture in which the axes abc of the orthorhombic unit cell are aligned with the principal axes of the sheet.[6]
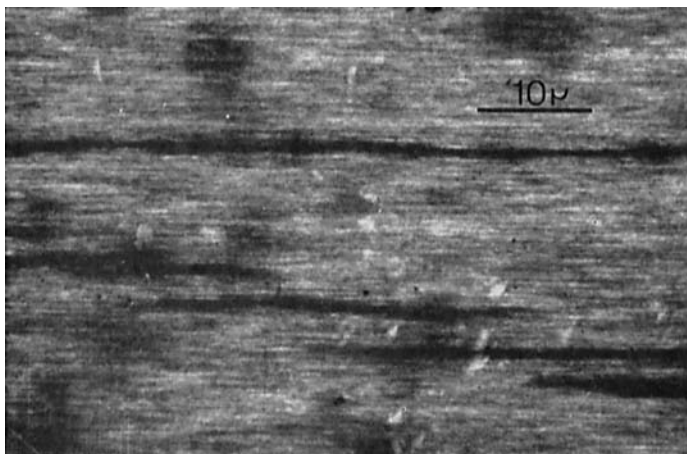
Fig. 8. Surface of specimen of oriented polyethylene sheet after treatment with fuming nitric acid at 60°C for 20 hr showing cracks parallel to the draw direction (the draw direction is parallel to the length marker).

Fig. 9. Surface of specimen of polyethylene sheet after treatment with fuming nitric acid at 60°C for 5 hr showing cracks perpendicular to the draw direction (the draw direction is parallel to the length marker).

for a surface-active medium (Teepol). This behavior conforms with that frequently reported in the literature.[1] However, for an environment of fuming nitric acid the resistance to stress cracking increases only very slightly with decrease in melt flow index. These results are consistent with the idea that stress cracking in Teepol occurs by a process of chain disentanglement and is thus molecular weight-dependent, while cracking in the presence of fuming nitric acid occurs by chain scission, and is thus insensitive to changes of molecular weight. This result is contrary to the suggestion by Howard[1] that the effect of molecular weight on oxidative stress cracking is the same as on environmental stress cracking.

The majority of cracks, in the Teepol-treated specimens, were initiated from the cut edge and were spanned by fibrils of material drawn out from either side of the crack. This is consistent with the suggested process of chain disentanglement.

The cracks in fuming nitric acid treated specimens were of two types. Those initiated from the cut edge, which led to failure, and fine cracks in the wide surface of the specimens. None of the cracks were spanned by fibrils which is consistent with the suggested process of chain scission. The occurrence of fine cracks was dependent upon the state of the surface and is discussed below.

The time to failure for specimens in fuming nitric acid was found to increase with decreasing applied stress as shown by the data in Figure 3, with a linear relationship between stress and time (log scale). For the case of environmental stress cracking of high-density polyethylene in Igepal, Lander[7] has reported a similar dependence.

The occurrence of blisters on the surface of specimens subjected to a minimum of about 6 hr fuming nitric acid treatment (Figs. 4 and 5) with or without an applied stress has not been previously reported.

As these blisters did not form in material from which the surface layer had previously been removed it is suggested that the surface morphology is responsible for the blistering.

In fact, as seen from Figures 6 and 7, the surface layer is distinct: it possesses a so called columnar or transcrystallized structure which results from crystallization originating from very closely spaced nuclei along the surface. This confines crystal growth to a direction normal to the surface, the resulting overall texture being the same as that along a spherulite radius.[8-11] Such nucleated crystallization from the surface is expected to arise in molded objects which have been cooled by water quenching from the exterior. The columnar growth is expected to meet spherulites growing from homogeneously dispersed nuclei within the bulk of the material at a depth depending on the temperature gradient.

Nevertheless, it is seen from Figures 6 and 7 that the blistering layer is thicker than the columnar skin. We propose to explain the two observed facts, namely that the columnar skin is definitely required for the blistering and yet the detaching layer is thicker than the skin, in the following way.

The effect of formation of isolated blisters is reminiscent of local expansion of surface material. The function of the surface layer would be therefore to make the penetration inhomogeneous. Now, it is known that diffusion in a columnar structure is highly anisotropic; it is fastest parallel to the columnar axis which corresponds to liquid penetration along the lamellar interfaces.[10,12] In addition, sporadic elongated gaps parallel to the columnar axis can also be expected in view of the known occurrence of radial cracks in spherulites. Strong local variations in the columnar structure could therefore be anticipated which would produce variations in penetration. Where penetration is higher than elsewhere local expansion of the material beneath the skin will result, in addition to the expansion of the columnar skin itself (the liquid plus the unremoved reaction products

would be expected to expand the polyethylene). As local expansion in the lateral direction will be opposed by the surrounding less swollen material detachment in the form of observed blisters would result.

Removal of the surface layers did not reduce the overall rate of oxidative attack but did result in more homogeneous attack. This is shown by the fact that the time for embrittlement and fragmentation with no stress applied was about the same for both types of material, although no blisters formed in material from which the surface layer had been removed. Further, the times to failure for oxidative stress cracking were about the same for both types of material due mainly to the fact that the cracks, leading to failure, were initiated from the cut edge of the specimens and not the surface. In addition, the occurrence of fine cracks was much reduced in material from which the surface layer had been removed.

The increase in resistance to environmental stress cracking in oriented polyethylene found in the present work is in agreement with other workers.[13,14] However, the increase in resistance to stress cracking in fuming nitric acid of oriented polyethylene has not previously been reported.*

In the absence of an applied stress, oriented polyethylene was more resistant than unoriented material to attack by fuming nitric acid, as shown by the increase in the time for embrittlement and fragmentation. This is in agreement with previous observations by Hay and Keller[16] and with the general observation by Peterlin[17] of a reduction in accessibility of drawn polyethylene due to its lower entropy state. The acid attack caused cracks to propagate parallel to the draw direction as shown in Figure 8. This is the same direction in which cracks readily propagate when oriented polyethylene undergoes brittle fracture as shown by Keller and Rider.[18] Both cracking processes are thought to be due to the highly anisotropic tensile strength of the material which also gives rise to the fibrous texture, characteristic of oriented linear polyethylene.

In the case of oriented polyethylene with a single preferred texture subjected to fuming nitric acid treatment in the absence of applied stress, cracks propagate perpendicular to the draw direction, as can be seen in Figure 9. Annealing is known to develop a transverse texture in the morphology of drawn polyethylene as revealed by electron microscopy[19] and by low-angle x-ray diffraction.[20] Accordingly, the transverse cracks in Figure 9 are most probably due to the annealing treatment that the material received rather than its single preferred texture. This transverse cracking† is in agreement with the observations by Hay and Keller[16] on drawn and annealed high-density polyethylene (draw ratio about 5).

* Rider[15] has shown that partially drawn specimens subjected to stress cracking in fuming nitric acid preferentially crack in the drawn region adjacent to the neck.

† Transverse cracks have been reported in unannealed drawn polyethylene by Hay and Keller.[21] However, it was found out subsequently that the material used was an ethylene–3% propylene copolymer (Rigidex type 3). Undoubtedly it must have been the greater susceptibility to nitric acid, due to the side groups, which produced the transverse cracks.

In conclusion the main feature of the present work is that it confirms our expectation that oxidative embrittlement and stress cracking of high-density polyethylene involving chain scission is insensitive to changes in molecular weight. This contrasts to the highly molecular weight-dependent environmental stress cracking of polyethylene in a surface-active medium which depends upon the disentanglement and the pulling out of uncut molecules.

The commencement of the oxidative attack is much influenced by the crystalline texture of the surface, as shown by the formation of blisters in compression-molded polyethylene that had been water-quenched.

The increased resistance of oriented material to oxidative attack and the modes of crack formation are consistent with expectations from the morphology.

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