

# An e.s.r. investigation of environmental effects on polymeric materials:

## 2. Polyethylene

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This paper reports results on the effect of various environments, O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, u.v. irradiation, combined with stress on the mechanical degradation of polyethylene. Mechanical strength, toughness, free radical production and changes in molecular weight are reported as functions of the ageing time in these environments and at sustained strains corresponding to as much as 90% of the fracture stress for the oriented material and corresponding to the onset of necking in the unoriented material. The results are compared to those previously reported for nylon and discussed in terms of possible molecular mechanisms active during polymer fracture.

**Keywords** Fracture; environmental degradation; electron spin resonance; molecular weight change; chain scission

### INTRODUCTION

In a previous paper<sup>1</sup> the results of studies on environmental degradation due to agents such as O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, u.v. light, and exhaust gas in combination with mechanical stress were reported on unoriented and oriented nylon. The investigation included studies of tensile strength, toughness, free radical production during failure, molecular weight changes resulting from fracture and the nature of the fracture surface. The effect of environments on mechanical properties of nylon was found to be a very complex phenomenon in which the environmental agents and the applied strains interacted in a synergistic manner in that their combined effects were generally greater than would be anticipated from the sum of their individual effects. In the oriented nylon studied, the fracture phenomena associated with these combined effects was consistent with molecular fracture models incorporating the stress and chemically aided thermal activated scission of load carrying tie chains. In the unoriented nylon different mechanisms appeared to be active during fracture that were not as environmentally dependent. This paper will report the results of similar studies conducted on unoriented and oriented polyethylene (PE).

### EXPERIMENTAL PROCEDURES AND MATERIALS

Two classes of polyethylene (PE) were studied. (1) Oriented high density PE fibres were provided by W. R. Grace and Company. This material had a number average molecular weight of approximately 14500 and a single fibre diameter of 0.030 cm. The preparation of tensile samples has been described in a previous report<sup>1</sup>. The tensile specimen has a cross-sectional area of  $\sim 2.5 \times 10^{-2}$

cm<sup>2</sup> (35 fibres in a tensile bundle) and an effective e.s.r. cavity volume of  $\sim 5 \times 10^2$  cm<sup>3</sup>. (2) Commercial grade linear high density PE rod manufactured by Commercial Plastic Supply Corporation was purchased from a local distributor. These rods were threaded at the end with a reduced area machined in the centre to produce a sample with a cross-sectional area of  $3.2 \times 10^{-1}$  cm<sup>2</sup>.

The environmental agents studied were air, NO<sub>x</sub>, SO<sub>2</sub>, O<sub>3</sub>, and u.v. light (254 nm). The preparation of the agents and the experimental procedures were the same as for the previous study of nylon<sup>1</sup>.

A Varian Associates Model E-3 ESR spectrometer was used to measure free radical production during the final failure process of the oriented PE. This machine is equipped with a servo controlled loading frame that facilitates straining the samples in tension while the central portion is positioned in the spectrometer microwave resonance cavity. Temperature was controlled with a modified Varian variable temperature accessory. From the recorded e.s.r. spectrum of each sample, the free radical concentrations produced during failure were calculated with the aid of a computer and comparison with a standard pitch sample. After the samples were pulled to failure in the e.s.r. spectrometer, the outside surface and fracture surfaces of some of the samples were investigated with the aid of scanning electron and optical microscopes.

The molecular weight changes occurring during failure were determined by viscometry. The dilute solution viscosities of the fractured and unfractured PE fibres with various degradation histories were measured using a *p*-xylene solvent controlled at 105°C ( $\pm 0.1$ °C). The Mark-Houwink equation for these conditions is given by:

$$[\eta] = 1.76 \times 10^{-4} M_v^{0.83} \quad (1)$$

where  $M_v$  is the viscosity molecular weight<sup>2</sup>.

RESULTS AND DISCUSSIONS

Oriented PE fibres

Figure 1 shows the typical e.s.r. spectra for PE fibre samples after loading in air, u.v. light, SO<sub>2</sub>, and NO<sub>x</sub> environments. These spectra are all nearly identical, each exhibit some asymmetry which we attribute, at least in part, to the presence of some 'peroxy radicals'. Experience has shown that even small amounts of oxygen, dissolved in the polymer or cooling medium, result in rapid conversion of the polymer radicals initially produced to peroxy radicals. Figures 2 and 3 show the effect of sustained loading in various environmental agents (air, SO<sub>2</sub>, NO<sub>x</sub> and u.v. light) on the subsequent strength of PE fibres in tension. The breaking stress shown in these Figures was obtained from tensile fracture tests after removal from the particular environment. Results shown in these and subsequent Figures were for samples exposed to the environment under strains corresponding to the following fractions of the ultimate 'short term breaking stress', A, 0%; B, 70%; C, 90%. While strength was degraded slightly in all cases by far the most significant degradation over these periods of time was for the material in NO<sub>x</sub> at '90% sustained strain'. In all cases the

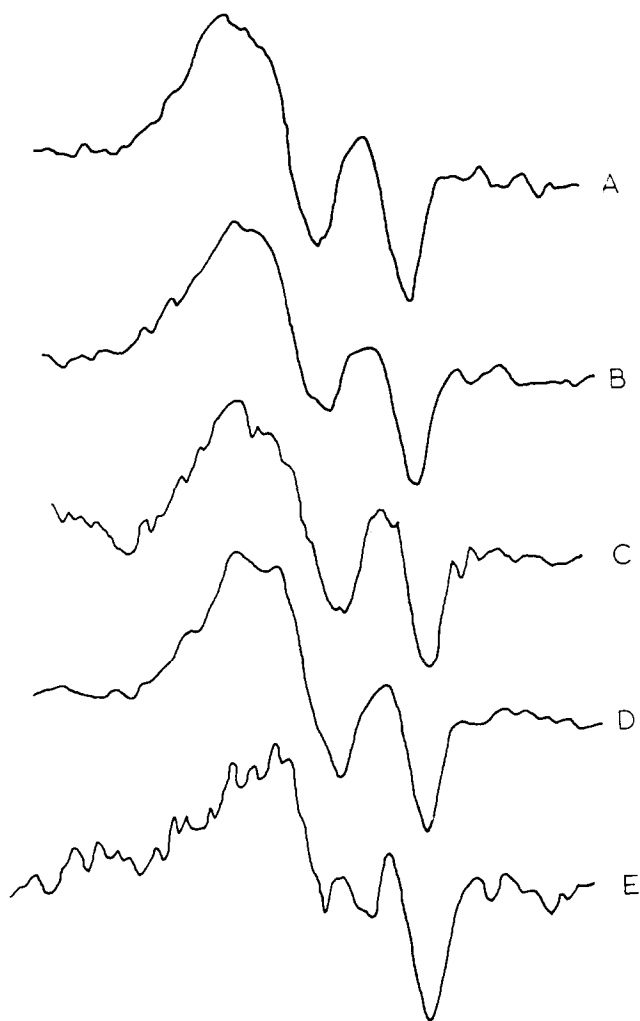


Figure 1 E.s.r. spectra resulting from tensile fracture of PE fibres degraded in various environments, (A) control sample in tension test, (B) air, (C) NO<sub>x</sub>, (D) u.v. light, (E) SO<sub>2</sub>. Samples were maintained at a strain corresponding to 70% of the ultimate stress while in the given environment for 6 days before the final fracture test except the sample exposed to NO<sub>x</sub> (which was held for 20 h)

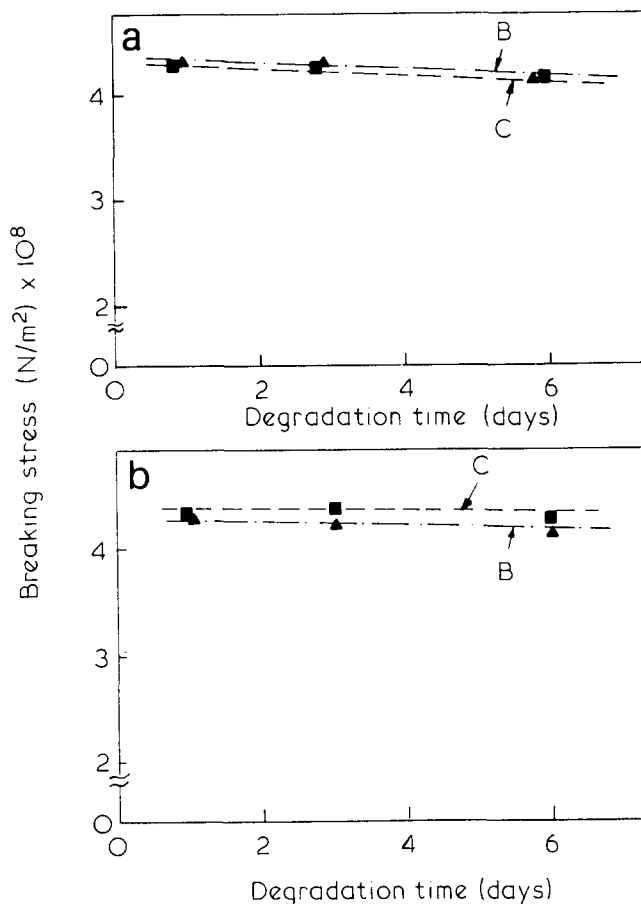


Figure 2 Degradation in strength as a function of time for PE fibres in various environments, (a) air, (b) u.v. light (B and C are as explained in the text)

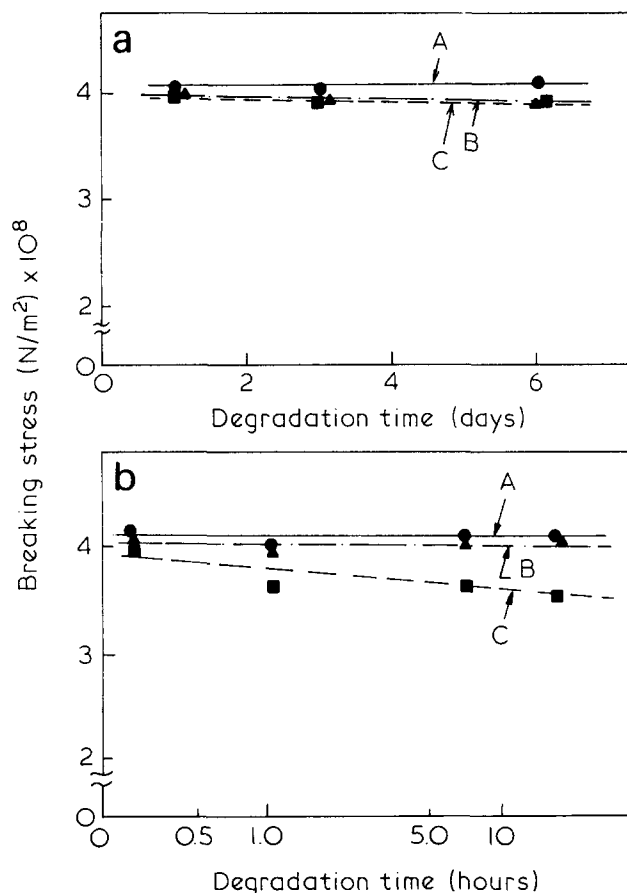


Figure 3 Degradation in strength as a function of time for PE fibres in various environments, (a) SO<sub>2</sub>, (b) NO<sub>x</sub> (A, B, and C are as explained in the text)

combined degradational effects of strain and the environments were significantly less than that previously reported for oriented nylon<sup>1</sup>. The free radical concentration produced during subsequent fracture tests after exposure to four different environments under strain are shown in Figures 4 and 5. With the exception of the samples exposed to NO<sub>x</sub>, the number of free radicals produced during the final fracture tests decreases almost linearly as a function of degradation time (note a semi-log plot was used for NO<sub>x</sub>). This feature was generally similar to that previously reported for nylon<sup>1</sup> except the amount of molecular degradation was significantly less for PE.

The combined effects of the environment and strain also have an effect on the microscopic appearances of the fracture surfaces and exposed side surfaces of the degraded PE fibres. Figures 6-8 show scanning electron micrographs of some of these samples. The photomicrographs of Figure 6 show the fracture surfaces of a standard sample (pulled to failure in tension). In this case the surfaces are relatively clean and unmarked. The micrographs of Figure 7 are of fracture surfaces for a PE sample exposed to an SO<sub>2</sub> environment, (a) at no load for one day, and (b) 90% strain for six days at room temperature. The appearance of the fracture surfaces is almost identical to those of the control. Figure 8 is for fracture surfaces of the samples exposed to an NO<sub>x</sub>

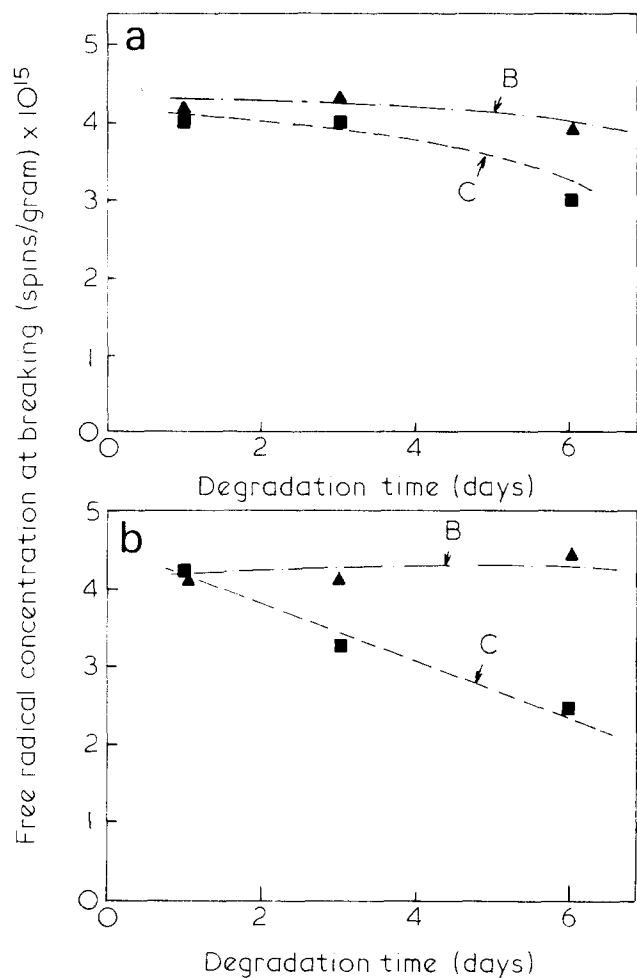


Figure 4 Free radical concentrations produced during fracture after exposure to various environments under strain as a function of degradation time, (a) air, (b) u.v. light (B and C are as explained in the text)

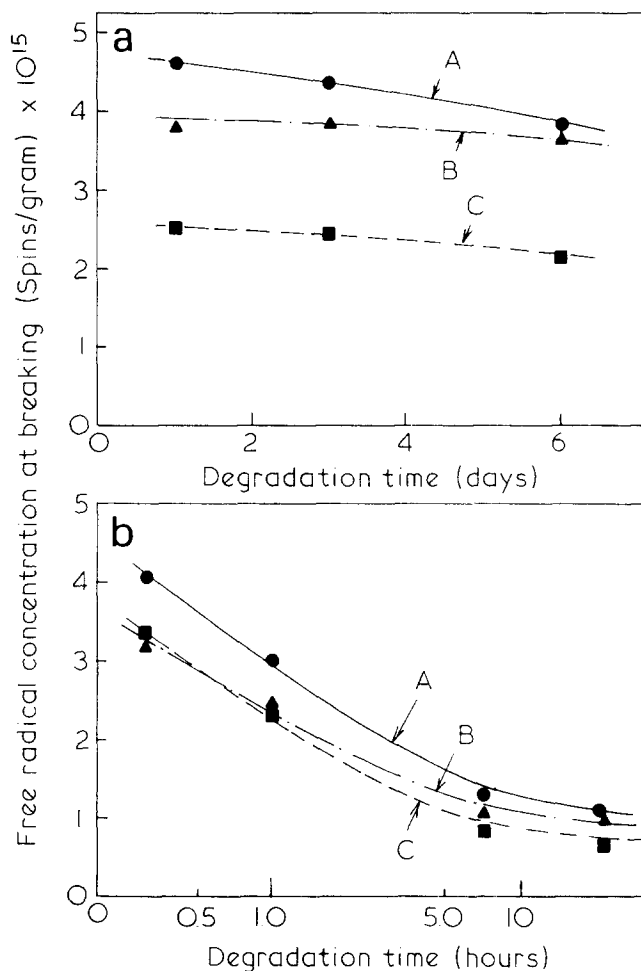


Figure 5 Free radical concentrations produced during fracture after exposure to various environments under strain as a function of degradation time, (a) SO<sub>2</sub>, (b) NO<sub>x</sub>, (A, B, and C are as explained in the text)

environment (a) at 70% strain for 20 min, and (b) at 90% strain for 20 h at room temperature. The sample held at 90% strain for 20 h has a quite different fracture surface from that of the control. The fracture surface of the damaged samples is rougher than the control and the perimeter surface exhibits several microcracks (Figure 8a). The fracture surface in Figure 8b indicates a splitting into a relatively long tip with what might be characterized as 'hand-nail' fracture elements along the split surface.

As a compliment to e.s.r. in the determination of the number of ruptured bonds after failure, viscometry techniques were used to make measurements of the molecular weight change resulting from sample fracture. The number of ruptured bonds  $[Q]$  determined in this way was then compared with the number of free radicals  $[N]$  produced during the final fracture process. The equation to obtain  $[Q]$  is given by<sup>3</sup>,

$$[Q] = \left( \frac{\zeta N_a}{\bar{M}_{n0}} \right) \left( \frac{\bar{M}_{n0}}{\bar{M}_n} - 1 \right) \quad (2)$$

where  $\zeta$  is the sample density,  $N_a$  is Avagadro's number, and  $\bar{M}_{n0}$  and  $\bar{M}_n$  are the measured number average molecular weights for the undeformed and deformed samples, respectively. This equation assumes random chain scission. Since PE has a relatively broad molecular

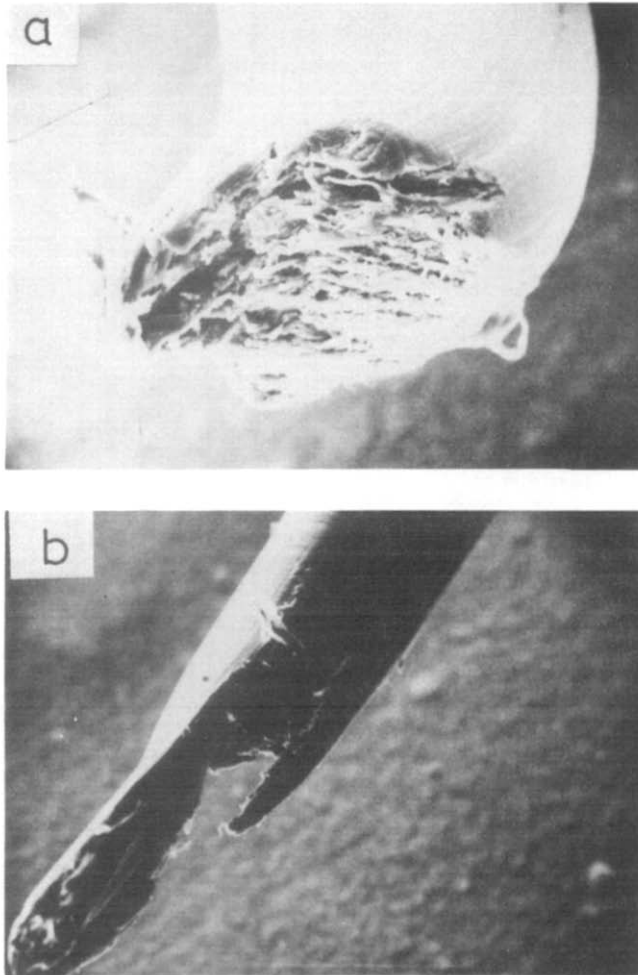


Figure 6 SEM of tensile fracture surface for a control sample (a) 230x, (b) 115x

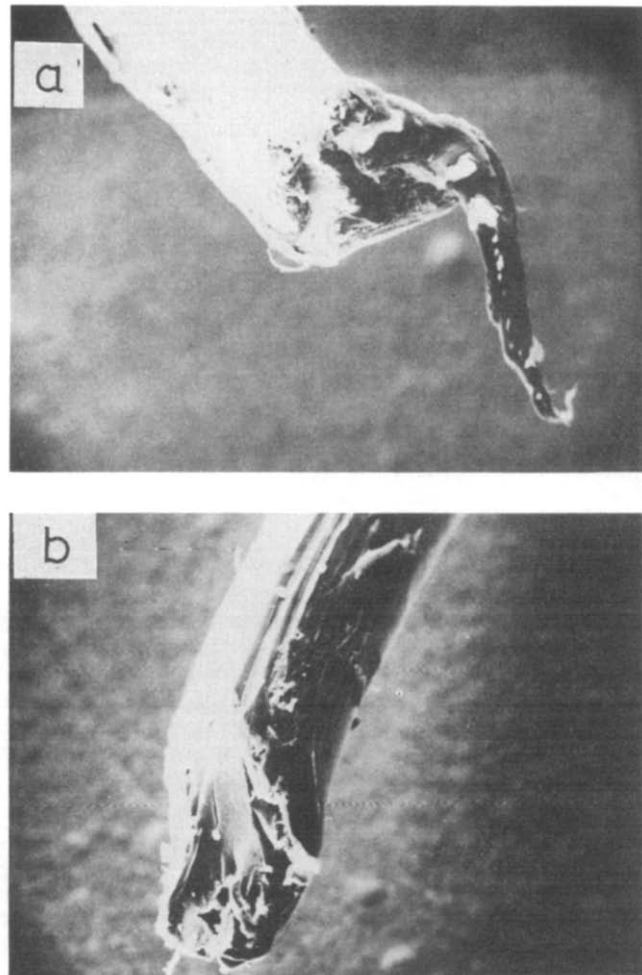


Figure 7 Fracture surfaces of PE fibres under strain exposed to an  $\text{SO}_2$  environment. Samples were held at (a) no load for 1 day, (b) 90% strain for 6 days at room temperature. Magnification: (a) 115x, (b) 115x

weight distribution, Scott<sup>3,4</sup> has shown that the ratio  $\bar{M}_n/\bar{M}_{n0}$  may be expressed as

$$\bar{M}_n\bar{M}_{n0} = 1 - \frac{3\bar{M}_{n0}}{\bar{M}_{z0}} \left(1 - \frac{\bar{M}_w}{\bar{M}_{w0}}\right) \quad (3)$$

where  $\bar{M}_{z0}$  is the z-average molecular weight of the control sample (undeformed), and  $\bar{M}_{w0}$  is the weight average molecular weight of the control sample. From gel permeation chromatography (g.p.c.)\* it was determined that  $\bar{M}_{n0}/\bar{M}_{z0}$  is  $4.96 \times 10^{-2}$  (14600/293500). Since the control sample's viscosity average molecular weight,  $\bar{M}_{v0}$ , and weight average molecular weight,  $\bar{M}_{w0}$ , are 61 500 and 76600, respectively, we replace  $\bar{M}_w/\bar{M}_{w0}$  in equation (3) by the measured  $\bar{M}_v/\bar{M}_{v0}$  for this particular polymer.

The results of the viscosity average molecular weight measurement are summarized in Table 1. The sample which fractured in a control test (pulling in tension) had a viscosity average molecular weight  $[\bar{M}_v] = 5.40 \times 10^4$ , while the  $[\bar{M}_v]$  of an undeformed control sample was  $5.77 \times 10^4$ . This represents a 6.4% decrease in  $[\bar{M}_v]$ .

The change in viscosity (total chain scission  $[Q]$ ) was smaller for the strained PE samples exposed to the various

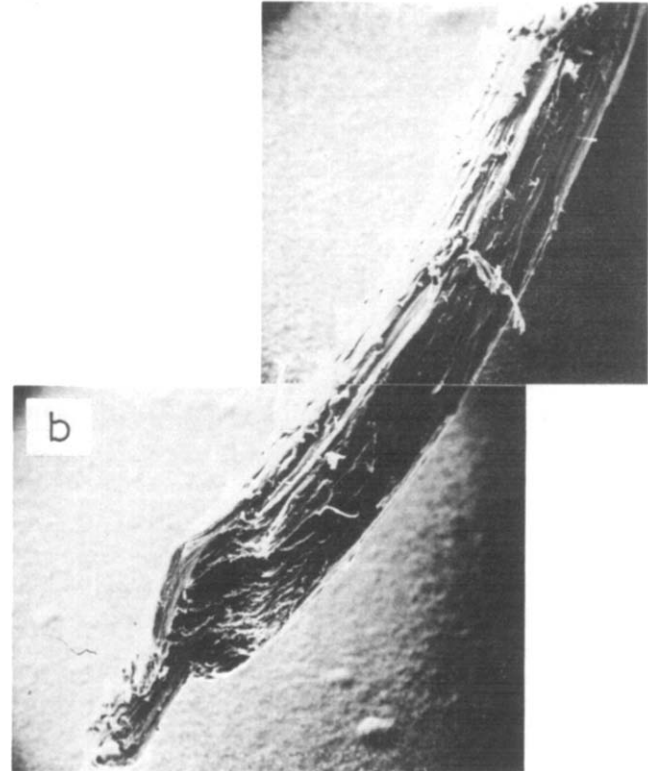
environments than it was for nylon. That is,  $[Q]$  remains in the range  $\approx 4 \times 10^{17}$  for both the control and environmentally aged materials. This agrees with the results of measurements of breaking strength and number of free radicals  $[N]$  produced at final fracture (refer to Figures 2-5) which also exhibited relatively small changes.

$[Q]$  is a measure of all the chain scission from the start of testing, while  $[N]$  is a measure only of the number of free radicals produced (chain scission) between the termination of the sustained loading and the final fracture. If one assumes some bonds are broken due to the initial applied load, some bonds are broken under the combined effect of an environment during the sustained loading and others are broken during the final fracture test then it is reasonable to represent the total chain scission as

$$[Q] = [N] + [I] + [C] \quad (4)$$

where  $[I]$  and  $[C]$  indicate the number of scissions by the initial applied strain and that due to the combined effect of the sustained strain and environment, respectively. To obtain  $[C]$ , additional molecular weight measurements were conducted. After the PE samples were exposed to a given environment and strain history, and before these were pulled in tension to failure in the final fracture test, the viscosity molecular weight was measured. This

\* Courtesy of L. Pike and W. G. Baird, Cryovac Division of W. R. Grace Co.



**Figure 8** Fracture surfaces of PE fibres under strain exposed in an  $\text{NO}_x$  environment. Samples were held at (a) 70% strain for 20 min, and (b) 90% strain for 20 h at room temperature. Magnification: (a) 220x, (b) 110x

measurement should provide an indication of  $[I]$  plus  $[C]$ . These results are shown in *Table 2*. It will be noted that the decrease in  $[\bar{M}_v]$  for the samples exposed to various environments under strain are almost the same as of those shown in *Table 1*. That is, the term  $[C]$  is very nearly zero and apparently nearly all chain scission occurs either during the initial loading or the final fracture test. It will be noted that the magnitude of  $[Q]$  from these studies is in basic agreement with the results reported by Crist *et al.*<sup>3</sup>.

The ratio  $[Q]/[N]$  for the standard samples provides a comparison between the number of chain scissions calculated from viscometric molecular weight measurements and that determined from the free radical concentration. This ratio has typically been greater than  $1^{1,3,6}$ . Several reasons have been proposed to explain this

difference including: (1) free radical chain reactions occur in which additional chains are broken without the formation of additional free radicals, (2) the chain scission is non random, with a tendency for longer chains to rupture, resulting in a greater viscosity change for a given amount of chain scission than equation (2) would indicate, and (3) that initial rapid free radical decay results in an  $[N]$  measured by e.s.r. lower than the actual number of chain scissions.

For nylon fibres tested in the standard tensile test  $[Q]/[N]$  was of the order of  $10^1$ . The PE fibres in this

**Table 1** Decrease in viscosity molecular weight and chain ruptures by e.s.r. and viscometry for samples loaded to the indicated strains in the indicated environments

| Samples              | $[\bar{M}_v]$     | Decrease in $[\bar{M}_v]$ % | $[Q]$ Rupture/cm <sup>3</sup> | $[N]$ Spins/cm <sup>3</sup> | $\frac{[Q]}{[N]}$ |
|----------------------|-------------------|-----------------------------|-------------------------------|-----------------------------|-------------------|
| 1 Original material  | $5.8 \times 10^4$ | —                           | —                             | —                           | —                 |
| 2 Fracture (control) | $5.4 \times 10^4$ | 6.4                         | $3.9 \times 10^{17}$          | $4.5 \times 10^{15}$        | 87                |
| 3 U.v. light         |                   |                             |                               |                             |                   |
| 1 day, 70%           | $5.4 \times 10^4$ | 6.4                         | $3.9 \times 10^{17}$          | $4.2 \times 10^{15}$        | 93                |
| 1 day, 90%           | $5.4 \times 10^4$ | 6.4                         | $3.9 \times 10^{17}$          | $4.2 \times 10^{15}$        | 93                |
| 6 day, 70%           | $5.5 \times 10^4$ | 3.5                         | $2.6 \times 10^{17}$          | $4.3 \times 10^{15}$        | 60                |
| 6 day, 90%           | $5.4 \times 10^4$ | 6.4                         | $3.9 \times 10^{17}$          | $2.5 \times 10^{15}$        | 156               |
| 4 $\text{SO}_2$      |                   |                             |                               |                             |                   |
| 1 day, 70%           | $5.7 \times 10^4$ | 2.1                         | $1.3 \times 10^{17}$          | $3.8 \times 10^{15}$        | 34                |
| 1 day, 90%           | $5.6 \times 10^4$ | 3.0                         | $1.8 \times 10^{17}$          | $2.5 \times 10^{15}$        | 72                |
| 6 day, 70%           | $5.6 \times 10^4$ | 2.4                         | $1.5 \times 10^{17}$          | $3.7 \times 10^{15}$        | 41                |
| 6 day, 90%           | $5.7 \times 10^4$ | 1.0                         | $0.6 \times 10^{17}$          | $2.3 \times 10^{15}$        | 26                |
| 5 $\text{NO}_x$      |                   |                             |                               |                             |                   |
| 20 min, 70%          | $5.5 \times 10^4$ | 4.2                         | $2.5 \times 10^{17}$          | $3.3 \times 10^{15}$        | 76                |
| 20 min, 90%          | $5.4 \times 10^4$ | 3.8                         | $2.3 \times 10^{17}$          | $3.2 \times 10^{15}$        | 72                |
| 20 h, 70%            | $5.4 \times 10^4$ | 6.8                         | $4.1 \times 10^{17}$          | $1.1 \times 10^{15}$        | 372               |
| 20 h, 90%            | $5.5 \times 10^4$ | 4.2                         | $2.5 \times 10^{17}$          | $0.8 \times 10^{15}$        | 313               |

**Table 2** Decrease in viscosity molecular weight and the calculated chain ruptures by viscosity for samples strained in the indicated environments but not pulled to failure

| Samples |                   | $[\bar{M}_v]$     | Decrease in $[\bar{M}_v]$ % | $[Q]$ Rupture/cm <sup>3</sup> |
|---------|-------------------|-------------------|-----------------------------|-------------------------------|
| 1       | Original material | $5.8 \times 10^4$ | —                           | —                             |
| 2       | U.v. light        |                   |                             |                               |
|         | 6 day, 0%         | $5.7 \times 10^4$ | 1.0                         | $0.7 \times 10^{17}$          |
|         | 6 day, 90%        | $5.3 \times 10^4$ | 6.6                         | $4.7 \times 10^{17}$          |
| 3       | SO <sub>2</sub>   |                   |                             |                               |
|         | 3 day, 0%         | $5.6 \times 10^4$ | 2.0                         | $1.4 \times 10^{17}$          |
|         | 3 day, 90%        | $5.2 \times 10^4$ | 9.0                         | $6.5 \times 10^{17}$          |
| 4       | NO <sub>x</sub>   |                   |                             |                               |
|         | 20 h, 0%          | $5.7 \times 10^4$ | 1.0                         | $0.7 \times 10^{17}$          |
|         | 20 h, 90%         | $5.4 \times 10^4$ | 6.0                         | $3.8 \times 10^{17}$          |

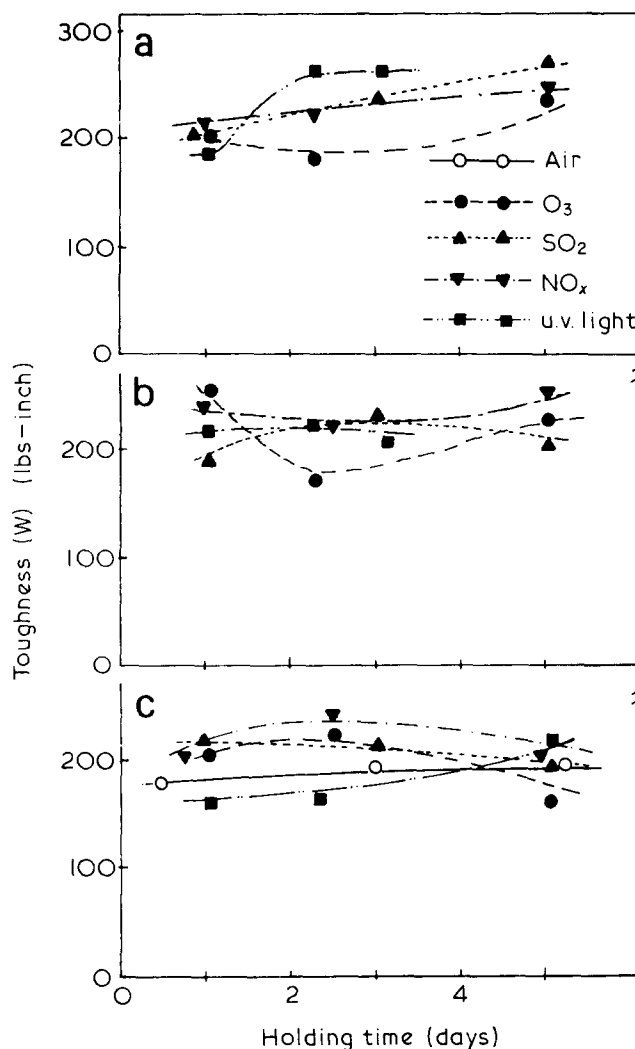
study yielded an apparent  $[Q]/[N]$  of nearly 100. Possible reasons for this difference are the same as those outlined in the last paragraph. In the case of PE the third reason is likely more significant. Davis and Chaing<sup>7,8</sup> have reported significant increases in the apparent number of free radicals produced under certain circumstances during fracture of PE and PET when oxygen was used as a free radical stabilizer. Under these conditions, they report about an order of magnitude more free radicals were observed than were obtained in tests conducted similar to those in the current study. They attributed this difference to a rapid initial free radical decay. If this is true it would indicate the ratio  $[Q]/[N]$  for PE should be roughly the same as for nylon.

#### Unoriented PE

Experiments similar to those on the oriented PE fibres were conducted on unoriented PE tensile samples in rod form. In nylon the effects of stress combined with chemical degradation were found to be very different for these two forms of chemically similar materials. The unoriented PE samples were tested in environments of O<sub>3</sub>, SO<sub>2</sub>, NO<sub>x</sub>, and u.v. light loaded at strains corresponding to the following loads (1) no load, (2) 90% of the initial yield stress, and (3) the loading corresponding to the strain at which necking first became apparent. After ageing under stress in the various environments, measurements were made of modulus, breaking stress and toughness,  $[w]$  (defined as the total strain energy to failure and obtained from the area under plots of load *versus* elongation). None of these physical properties appeared to be significantly effected by the ageing under stress in any of the environments for periods up to one week. As an illustration of this, Figure 9 shows  $[W]$  *versus* degradation time in the various environments. It should be noted that we were unable to obtain meaningful e.s.r. spectra for the unoriented PE for either the control material or for material environmentally aged under stress. This is an indication that the amount of chain scission was in sufficient and/or the rate of decay so rapid that a free radical concentration above the threshold sensitivity of the spectrometer ( $< 10^{14}$  spin/cc) was never produced.

#### DISCUSSION AND CONCLUSIONS

In a previous study<sup>1</sup> it was concluded that experimental observations associated with environmental stress



**Figure 9** Degradation in toughness  $[w]$  as a function of holding time for PE rods exposed to various environments with three different sustained loads: (a) no load, (b) 90% of the yield stress, (c) the load corresponding to occurrence of necking

degradations supported the concept that the basic mechanisms responsible for tensile strength in oriented and unoriented nylon are fundamentally different. Tensile failure in the former case is dependent on stress and chemically aided thermally activated scission of load bearing tie molecules between crystalline regions and/or microfibrils. In spherulitic nylon, on the other hand, tensile failure is apparently associated with slippage or other processes that are not as environmentally sensitive.

Marked contrasts were observed between the combined effects of stress and environmental attack on PE and that reported previously for nylon. For oriented nylon the combined effects of the various environmental agents and applied strain interact in a synergistic way in which their combined effect on strength is generally greater than would be anticipated from the sum of their individual effects. For oriented PE, this effect also appeared to be present but is not nearly as significant. PE fibres exhibited a relatively strong resistance to environmental attack under strain as manifest by changes in strength and evidence of molecular degradation. The strength of the PE fibres was only slightly reduced (as compared with nylon) as were the number of free radicals produced during the fracture test and the change in

molecular weight for samples strained in the various atmospheres for several days. These observations imply that less chain scission occurs in PE fibres under the described test conditions than previously observed in nylon. It appears reasonable, on the basis of these observations, to conclude that oriented PE exhibits a combination of the characteristics of oriented nylon (strength governed by environmental-stress sensitive factors such as rupture of the molecules) and spherulitic nylon (strength controlled by slip or other less environmentally sensitive factors). Nylon, of course, has hydrogen bonding that would help prevent slippage, chain pullout, etc. In PE fibres such strong bonding between macromolecules is not present and slippage could result in stress relaxation of and about tie chains. This could serve to reduce the molecular 'stresses' to the point that for some tie chains the effect of stress, combined with that of the chemical environment, and thermal activation are insufficient to cause scission before slip or pull out occur.

Unoriented PE exhibited more resistance to environmental stress degradation than did comparable nylon material. It experienced significantly less decrease in toughness than that previously reported for nylon. This might again be due to the fact that the inherent strength of PE is so much less than that of nylon. As a consequence, it

might be that stress relaxation processes prevent the production of large enough local stresses to combine with chemical attack and produce degradation of the material.

#### ACKNOWLEDGEMENTS

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