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

1. Nylon

M. Igarashi and K. L. DeVries
College of Engineering, Department of Mechanical and Industrial Engineering, Salt Lake City, Utah 84112, *USA*

(Received 6 *July* 1982*; revised* 22 *August* 1982*)*

Mechanical degradation on nylon with time resulting from the effects of various environments combined with strain on nylon are reported. The environments studied were air, O_3, SO_2, NO_x, automotive exhaust gas and ultraviolet light. Stress and these oxidizing agents were found to act in a synergistic way to decrease the strength of oriented nylon. Residual strength and number of free radicals formed during final fracture are given as a function of environment, magnitude of the applied strain, and time. While they had much less influence on strength in spherulitic nylon, exposure to sustained strains in these environments resulted in a significant decrease in toughness. The differences in response to the stimuli suggest different mechanisms are responsible for load carrying capability for oriented and spherulitic nylon, and as a consequence, the failure mechanisms differ in the two classes of nylon. It is suggested that in oriented systems tensile strength is due, at least in part, to tie chains that can break under the combined influences of stress, chemical attach and thermal activation. Slip and/or other failure mechanisms active in nonoriented nylon proved to be not as environmentally sensitive.

Keywords Nylon; mechanical properties; degradation; environmental effects

INTRODUCTION

An important property of polymers is their ability to withstand environmental attack. In the early 1960's studies were begun on the degradation of polymers due to u.v.-light, electron beams and radiation (-rays). Many of these studies[1-7] were conducted with the aid of Electron Spin Spectroscopy (e.s.r.). Studies of degradation caused by weathering (heat, light, ozone and humidity) and toxic gases (NO_2 and SO_2) were also initiated by several researchers in the 1960's[8-11]. Such studies take on a significant meaning when practical applications of polymers are considered. Failure due to these environmental effects causes serious problems especially as the use of polymers as structural load bearing members increases. Many of these studies, however, did not give much consideration to polymer morphology and the effects of these environments combined with those of loading and deformation.

The object of this study was to observe the effects of environmental agents such as O_3, NO_x, SO_2, u.v.-light and automobile exhaust gases in combination with stress and strain on polymers. An attempt has been made to elucidate the molecular mechanisms active during degradation. This study included measurements of tensile strength, toughness, free radical production, changes in molecular weight, as well as optical and scanning electron microscope studies of the fracture surfaces of polymers exposed to stress in various environments.

EXPERIMENTAL

Materials

Oriented and unoriented semi-crystalline nylon (highly drawn fibre and unoriented rod) were used in this study in order to make a comparison between the environmental stress characteristics of these physically different classes of polymers.

(1) Nylon-6 fibres (tire yarn) were provided by Dr. D. Prevorsek of Allied Chemical Company. This material has a number average molecular weight of approximately 25000 and a single filament diameter of 0.0028 cm with 202 filaments in each yarn. Tensile samples consisted of a bundle of these fibres prepared in such a way as to give as uniform stress as possible and so that fracture would occur in the e.s.r. cavity. A tensile sample was prepared by winding the yarn on a jig to the desired length and number of yarns. Epoxy collars were then applied forming a loop at each end. After the epoxy had cured for 24 h at room temperature, four strands were cut and removed from the centre portion of the sample of 17 strands. This procedure provided a 'quasi dog-bone' type sample which fractured near the centre of the sample. All samples were 11 inches in total length with approximately 1.4 inches between bonded regions. The 13 strands remaining in the sample centre provided a cross-sectional area of 1.6×10^{-2} cm^2 for an effective e.s.r. cavity volume of approximately 2×10^{-2} cm^3.

(2) Commercial grade $\frac{1}{4}$inch diameter nylon-6,6 rod

0032-2861/83/060769-14$3.00

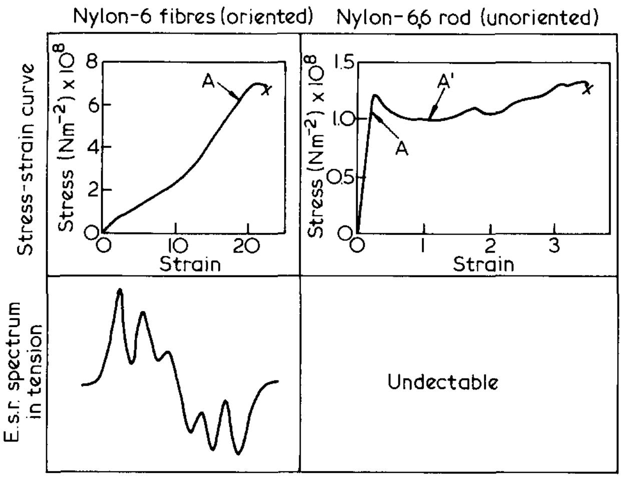

Figure 1 Stress and strain curves and e.s.r. spectrum of the nylon samples (control)

obtained from Commercial Plastics and Supply Corporation was purchased from a local distributor. Tensile samples were prepared by machining the diameter at the centre of the rod to 0.42 cm. Both ends were threaded to fit into tensile grips.

All of the nylon samples were kept in a desiccator at room temperature (23° ± 1°C) with a relative humidity of 5–7% for a week before testing. The stress–strain curves and the e.s.r. spectrum at fracture for untreated (control) samples in tension are shown in *Figure 1*. For environmental testing samples were loaded to points such as A or A′ and were held at essentially fixed strain while being exposed to various environments as explained in the next section.

Environmental agents

The environmental agents used in the study were air, NO_x, SO_2, O_3, u.v.-light and automobile exhaust gas. A small loading frame (see *Figure 2*) was constructed which would maintain an essentially constant strain on the nylon-6 fibre samples over extended periods of time. The test samples were loaded in the frame with the aid of an Instron testing machine and placed in a sealed chamber in which a predetermined environment could be maintained (NO_x, SO_2 and exhaust gas) or passed through with the desired flow rate (O_3). Periodically, samples were removed from the environmental chamber and unloaded. They were then loaded in tension to failure with either an Instron or a servo controlled tension machine. For the samples tested in air, O_3, SO_2, NO_x, u.v.-light and exhaust gas, the load was maintained at room temperature (23° ± 1°C). In addition, a series of tests were conducted at 81° ± 2°C in order to compare the damage in the glassy and the 'leathery' states. The initial loads applied to the samples varied from that corresponding to a load of 60% of what it could take to fracture the sample in a control test to 90% of this breaking load. As stated above, the loading frame would maintain a constant strain in the sample corresponding to these initial loads. After removal from the environmental chamber, a final tensile fracture test was conducted in the e.s.r. spectrometer cavity at a strain rate of 0.1% strain s^{-1}. *Figure 2* shows a schematic diagram of the loading frame and load measurement apparatus.

Commercial grade SO_2 gas was used at a concentration of 12% by volume in the chamber. NO_x gas was produced by the reaction between copper and concentrated nitric acid HNO_3,

$$Cu + 4HNO_3 \rightarrow Cu(NO)_3 + 2NO_2 + 2H_2O \qquad (1)$$

At room temperature, however, nitrogen dioxide, NO_2, is partially converted into dinitrogen tetroxide N_2O_4 which is reasonably stable, and one would assume that a mixture of NO_2 and N_2O_4 would generally be present,

$$2NO_2 \rightleftarrows N_2O_4 \qquad (2)$$

These two chemical substances behave primarily as oxidizing agents with polymers, but the reactivity of these substances are different. NO_2 is generally thought to be more reactive than N_2O_4. The concentration of NO_x gas was varied from 0.58% to 2.5% by volume. Ozone was produced by passing air over two ultraviolet lamps (GE G4S11). The apparatus and a determination of the O_3 concentration are described in detail elsewhere[12]. For the studies reported here the O_3 concentration was 0.236 mole%. Exhaust gas was collected from the exhaust pipe of an automobile (Subaru 1400 cc DL 1975). A vinyl tube one foot long was connected between the chamber and the exhaust pipe, and the exhaust gas was pumped through the chamber for 20 min and the chamber was sealed for the remainder of the test. During collection of the exhaust gas, the engine (4 cylinder) was run at about 700 rev/min at normal temperature and under no load. Irradiation of the samples by u.v.-light (Ultra-Violet Products, Inc. Model UVS-11, 254 nm) was carried out in the following manner without use of the environmental chamber. After the samples were put under constant strain in the loading frame, they were placed such that the centre section of nylon samples was exposed to u.v.-light. The distance between the samples and the u.v.-lamp was varied between 5 and 10 cm. This would correspond to a radiation level of ~300 $\mu W\,cm^{-2}$.

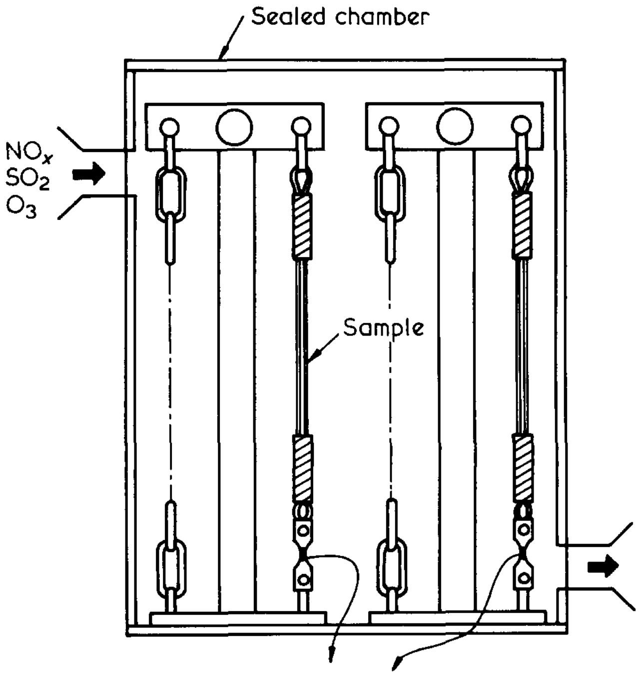

Figure 2 Loading frame and load measurement apparatus

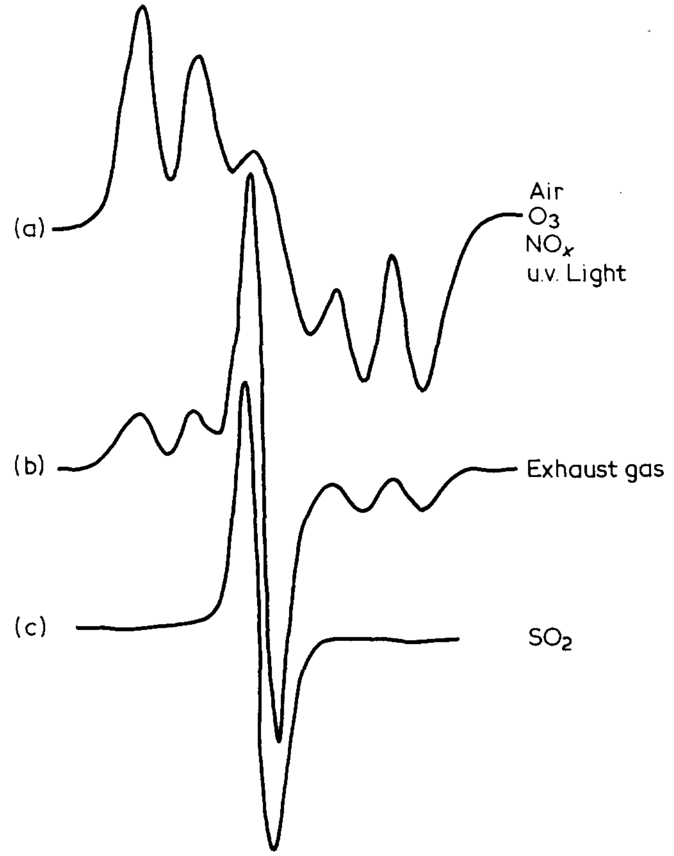

Figure 3 E.s.r. spectra resulting from pulling in tension of nylon-6 fibres degraded in various environments. The relative sizes of the spectra were chosen for convenience

E.s.r. measurements

The e.s.r. spectrometer used in this study was a Varian Associate Model E-3. 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. All temperature e.s.r. measurements were made at room temperature (23° ± 1°C). From the recorded e.s.r. spectrum of each sample, the free radical concentrations produced during the final failure process 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 and fracture surfaces of some of the samples were viewed with the aid of scanning electron and optical microscopes.

Viscometry

Dilute solution viscosities of fractured nylon-6 fibres with various degradation histories were measured with Cannon-Fenske Routine Viscometers. The flow times varied from 72–101 s corresponding to relative viscosities $[\eta]$ in the range 1.05–1.30 dl g^{-1}. The solution temperature was controlled at 25°C ± 0.5°C using a water bath. An 85% formic acid solvent was used. The Mark–Houwink equation for these conditions is given by:

$$[\eta] = 2.26 \times 10^{-4} M_v^{0.82} \qquad (3)$$

where M_v is the viscosity average molecular weight[13].

EXPERIMENTAL RESULTS

Environmental effects on oriented nylon fibres

Typical e.s.r. spectra for nylon-6 samples after loading in air, O_3, SO_2, NO_x, u.v.-light and exhaust gas environments are shown in *Figure 3*. As seen in *Figures 3b* and *c* the spectra for the samples degraded in SO_2 and exhaust gas differ drastically from the 5-line spectrum resulting from degradation in the other environments. The observed SO_2 and exhaust gas spectra appear to be essentially singlets. The singlet signal shown in *Figure 3b* was recorded during final fracture after exposure to the exhaust gas for more than two days. Samples kept in the exhaust environment for a day or less, however, exhibited 5-line spectra similar to the spectrum shown in *Figure 3a*. However, the sharp singlet signal produced by exposure to SO_2 as seen in *Figure 3c* is independent of degradation time (at least in the time scale of from a few hours to a few days).

An interesting characteristic of the reaction of SO_2 with nylon fibres is that the reaction was found to be relatively reversible. That is the samples degraded in an SO_2 environment with or without applied strain recovered, with time, their free radical concentrations at failure, the original line shapes of their e.s.r. spectra, and a large part

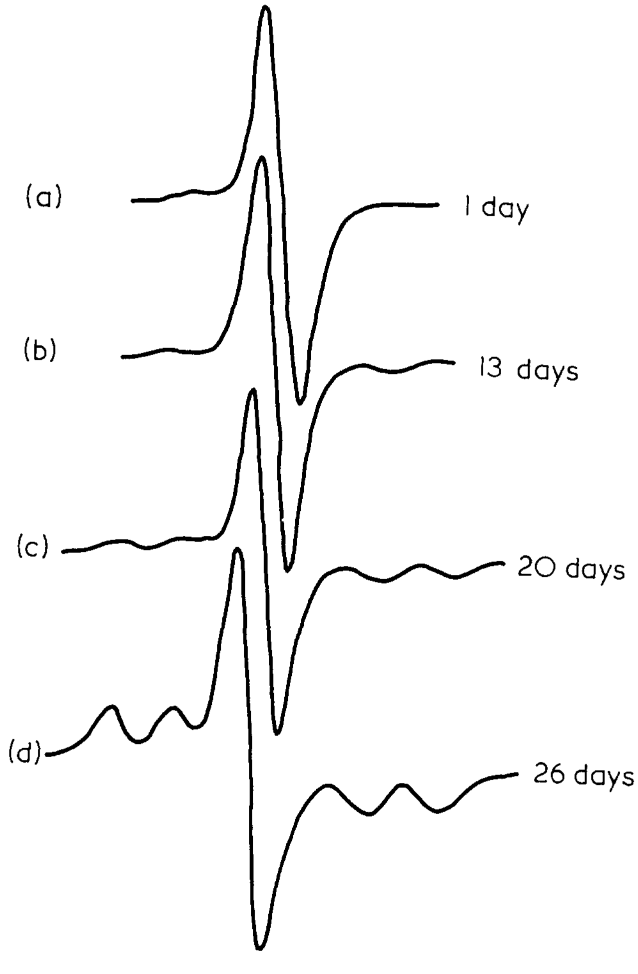

Figure 4 E.s.r. spectra of nylon samples observed in annealing tests after the samples were degraded in an SO_2 environment at room temperature. Annealing was conducted at room temperature in air for annealing times indicated by the curves

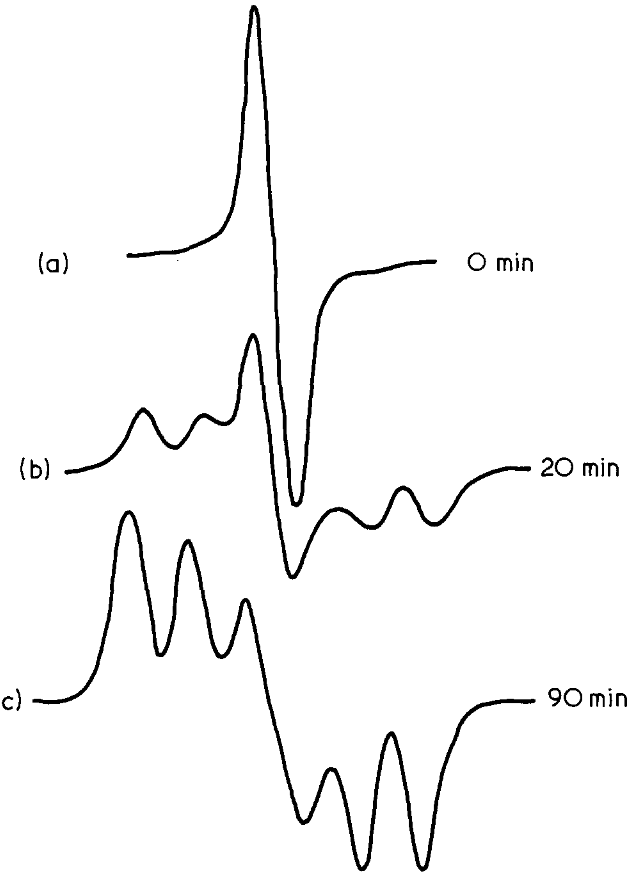

Figure 5 E.s.r. spectra of nylon-6 samples observed in annealing test after the samples were degraded in an SO_2 environment at room temperature. Annealing was conducted at 82° ± 1°C in air with various annealing times as indicated

of their strength. After the nylon-6 fibre samples were exposed to the SO_2 environment at room temperature for a period of time ranging from 3 to 4 days, the samples were placed in air at two different temperatures (room temperature and $82° \pm 2°C$). The samples were then stretched in tension and their e.s.r. spectra and free radical concentrations were measured. *Figures 4* and *5* show the e.s.r. spectra obtained. The spectra in *Figure 4* are for the samples annealed at room temperature for four different annealing times: (a) 1 day, (b) 13 days, (c) 20 days and (d) 26 days. The spectra in *Figure 5* are for the samples annealed at $82° \pm 1°C$ with annealing times: (a) 0 min, (b) 20 min and (c) 90 min. The e.s.r. spectra of the annealed samples changed from the sharp singlet to the 5-line spectrum. When samples were annealed at high temperature, for a few hours, their e.s.r. spectra assumed the same shape as those obtained during tests on samples not exposed to sustained stress in the environment hereafter referred to as the control tests. This observation lends strong support to the hypothesized reversible reaction of SO_2 with nylon[14,15]. However, SO_2 can also cause irreversible reactions such as bond rupture, when combined with an external strain. This is demonstrated from the observation that under the combined effects of an SO_2 environment and strain, a degradation in strength and a decrease in the free radical concentrations were observed.

Figure 6 shows the maximum breaking stress and strain measured during the final fracture test after exposure to SO_2 and then annealing for various times at the two different temperatures mentioned previously. Note that the stresses and strains shown in *Figure 6* are normalized, i.e., the maximum breaking stress and strain measured with various annealing times are divided by the maximum breaking stress and strain obtained in the control tension tests. It is observed that both the final stress and strain at failure are comparable to the virgin control material. It is interesting to note from this Figure that the samples kept in an SO_2 environment with an applied load corresponding to 70% of the maximum breaking load recovered their original breaking strain more slowly than the unloaded samples. However, this phenomenon was not observed for the breaking stress.

It is generally accepted that the radical observed during fracture in nylon at room temperature is not the primary radical produced by chain scission but rather a secondary radical resulting from proton migration from the original radical. The primary radicals are thought to be $R\text{-}CH_2\text{-}\dot{C}H_2$ and $R\text{-}\dot{C}H_2$[12]. The conversion of the primary radical to the secondary one might differ for the control sample from those exposed to SO_2 gas if SO_2 or H_2SO_3 were present along the nylon chains. The

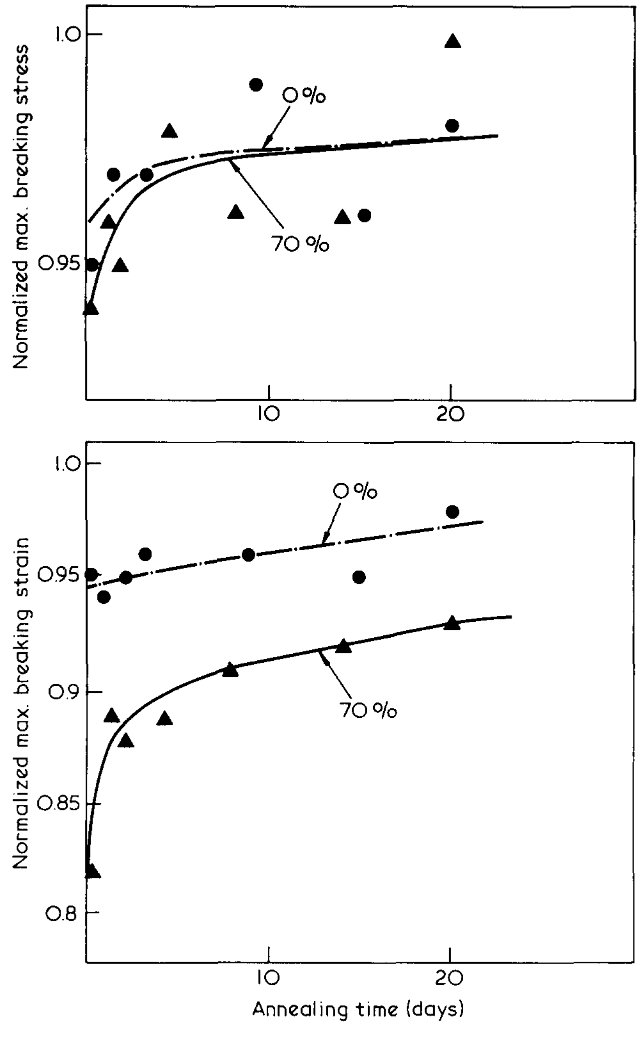

Figure 6 Normalized maximum breaking stress and strain measured during final fracture after exposure to SO_2 and then annealed at room temperature. Initial loads applied to nylon-6 samples during exposure to SO_2 were 0% and 70% of the maximum breaking load

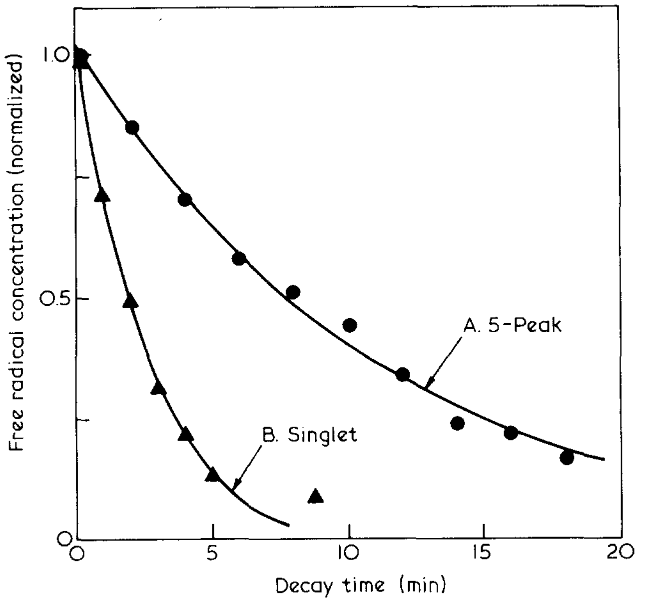

Figure 7 Decay of free radical concentration with time and stress in the e.s.r. cavity at room temperature

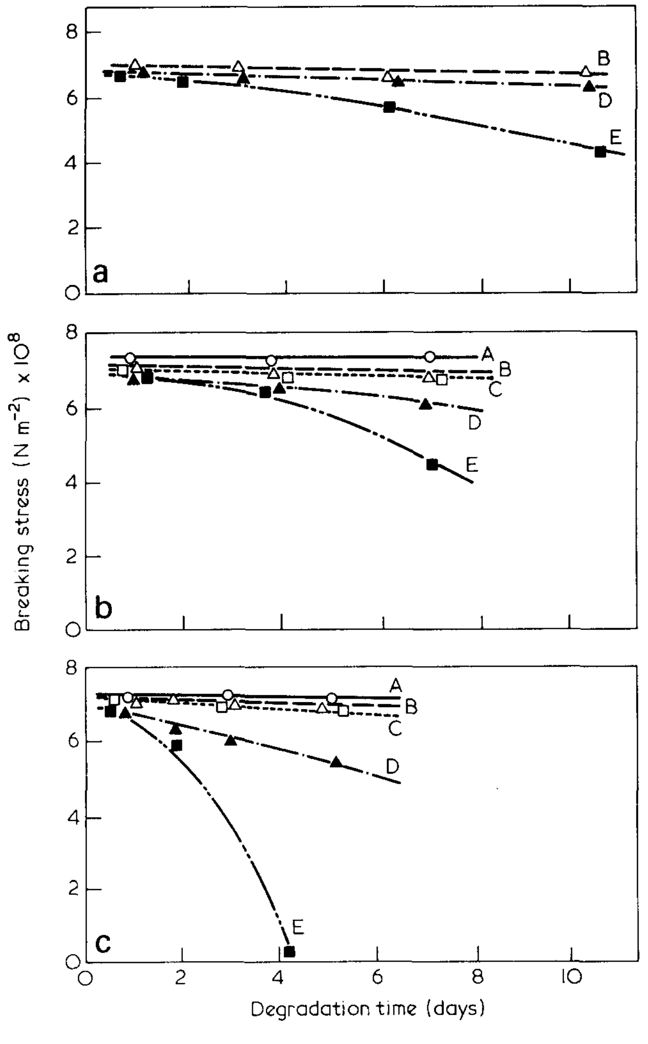

Figure 8 Degradation in strength as a function of time for nylon-6 fibres in various environments. All of the tests were conducted at room temperature. Capital letters designate sustained strains corresponding to the ultimate short term breaking loads A, 0%; B, 60%; C, 70%; D, 80%; E, 90%

secondary radicals produced in the presence of SO_2 or H_2SO_3 have three prominent features: (1) the e.s.r. spectrum is a singlet with its free radical concentration significantly less (between a factor of three and an order of magnitude) than that of the 5-peak spectrum. We were unable to determine exactly how much less because of the very rapid decay rate of free radicals for the singlet spectrum (approximately five times) compared to that for the 5-peak spectrum. This comparison is shown in *Figure 7*. It is very difficult to record the e.s.r. spectrum immediately after pulling the sample in tension. It takes approximately one minute to complete the scanning of the spectrum. During this time significant decay may have already occurred. Nevertheless, it is possible to roughly estimate the initial concentration of radicals by using the decay curve shown in *Figure 7*. The slope of the curve for the SO_2 near zero time is so steep that the exact intercept could be in error by as much as factor 3. (2) The singlet spectrum may arise from the SO_2 radical-ion as proposed by several researchers[16–18]. They have reported that the e.s.r. spectrum of SO_2 shows a strong, sharp singlet signal with very weak satellite signals ($g = 2.005 \pm 0.003$, line width = 9–15 G). (3) By annealing the samples at elevated temperatures, the e.s.r. spectrum changes from a sharp singlet signal back to the 5-peak spectrum usually associated with nylon. It appears that SO_2 and/or H_2SO_3 are driven from the nylon chains during the annealing process by what appears to be a thermally activated process.

Figures 8 and *9* show the effect of sustained strain in various environments on the subsequent strength of nylon-6 fibres in tension (the environments are as indicated in the Figure captions). The breaking stresses of the samples given in the Figures were obtained from load to fracture tests subsequent to removal from their respective environments. Note that in these Figures and all subsequent Figures the curves designated by the capital letters were for samples exposed to the environments under strains corresponding to the following fractions of the ultimate short term breaking load: A, 0%; B, 60%; C, 70%; D, 80%; E, 90%. *Figures 8a, b* and *c* show that samples exposed to air, u.v.-light and exhaust gas environments at strains corresponding to less than 70% of the short term ultimate load exhibited almost insignificant decreases in residual strength. Above this strain, exposure to all these environments resulted in marked decreases in the residual strength of the material. *Figure 9a* shows similar results in an ozone rich environment (a concentration of 0.236 mole% in the environmental chamber). The degree of deterioration was a somewhat stronger function of strain than for air. In *Figure 9b* the combined effects of strain and SO_2 on deterioration in strength are shown. The rate of deterioration is similar to, but more rapid than, that observed in air. The concentration of SO_2 for the tests in *Figure 9b* was 12% by volume. *Figure 9c* shows a similar plot for the combined effect of sustained strain and NO_x on strength. The degradation took place very rapidly (within hours) as compared with other agents. All these tests were conducted at room temperature ($23° \pm 1°C$).

Very rapid deterioration occurred at room temperature in the NO_x environment. Similar experiments were conducted at a higher temperature with the results shown in *Figure 10*. This Figure shows the residual strength of fibres held at the strains indicated by the letters (as

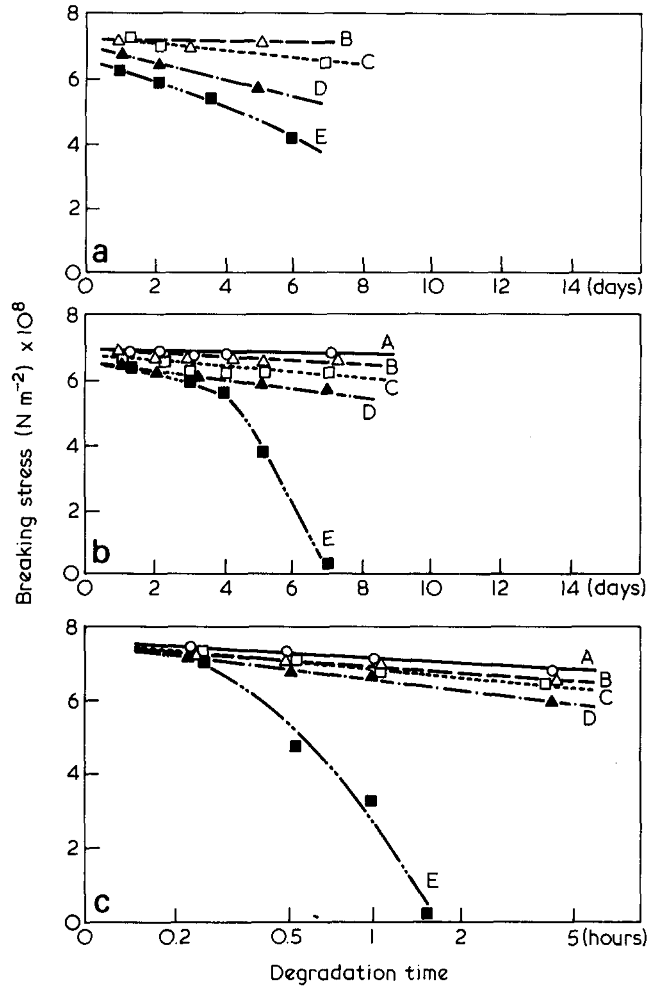

Figure 9 Degradation in strength as a function of time for nylon-6 fibres in various environments: (a) O_3, (b) SO_2, (c) NO_2 (concentration 2.58% by volume). (See *Figure 8* for explanation of capital letters)

explained in the last paragraph) in NO_x at 81° ±2°C for varying periods of time. At strains greater than 80% and high NO_x concentrations the destruction of the sample was almost immediate. Hence no breaking stress is recorded for these strains in *Figure 10c*. The decrease in strength is much more rapid at elevated temperature than for the experiments conducted at room temperature as clearly demonstrated in *Figures 9* and *10*.

Figures 11 and *12* show the free radical concentrations produced during fracture after combined exposure to strain and six different environments. The net number of free radicals produced decreases approximately linearly on a log–log plot in the case of NO_x, and on a semi-log plot in the cases of the other environments. The rate of decrease of free radical production at fracture was much more rapid for those samples that were held at the highest strains in the environment.

In the control fracture tests of nylon-6 at room temperature in air typically 10^{17} to 10^{18} free radicals/gram are detected by e.s.r.[12,19]. If one assumes a two to one correspondence between the free radicals produced and the number of chain scissions, e.s.r. provides a quantitative means of measuring the extent of molecular degradation.

Figure 13 shows the relationship between the relative change in breaking stress and the decrease in the number of free radicals produced during fracture subsequent to a stress-ageing period in the environmental chamber. In this Figure N_0 is the number of free radicals that would result from fracturing at 'zero time' in the environment, obtained by extrapolation from *Figures 11a* and *12*. σ_0 is the corresponding breaking stress obtained from control fracture tests. N_i is the number of free radicals at fracture obtained from *Figures 11a* and *12*. σ_i is the corresponding breaking stress obtained from *Figures 8a*, *9a*, *9b* and *10a*. Simply stated the term $(N_0-N_i)/N_0$ is the fractional decrease in the number of free radicals produced at fracture due to the combined effects of stress and environment relative to the number of free radicals produced during a standard fracture test. If the quantity $(N_0-N_i)/N_0$ is equal to zero, it would imply no molecular destruction due to the environmental stressing. However, if this quantity were one, it would imply destruction of all the load supporting chains prior to the final fracture tests. The fact that the curve of *Figure 13* is reasonably linear might be interpreted as evidence for the hypothesis that the strength of oriented nylon is dependent on the number of load carrying chains and the load distribution among these load carrying tie chains.

As a complement to the e.s.r. studies of free radicals (bond scission) a study was undertaken of the viscosity average molecular weight change resulting during fracture of the material. With the assumption that random chain scissions occur and that the most probable

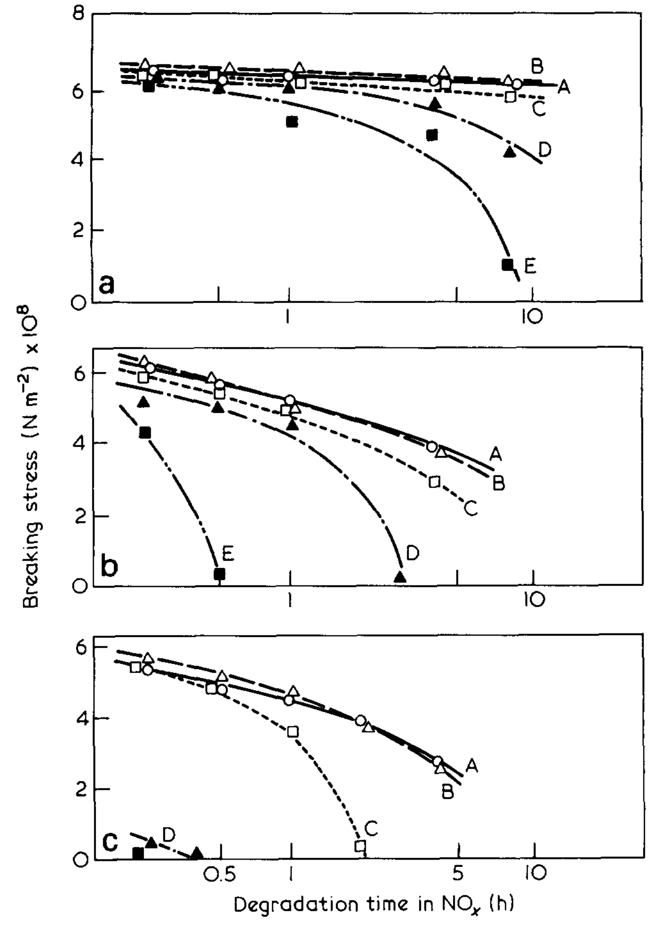

Figure 10 Degradation in strength as a function of time for nylon-6 fibres in three different concentrations of NO_x at 81° ± 2°C. Final fracture was at room temperature: (a) 0.86%, (b) 2.58%, (c) 5.16%. (See *Figure 8* for explanation of capital letters)

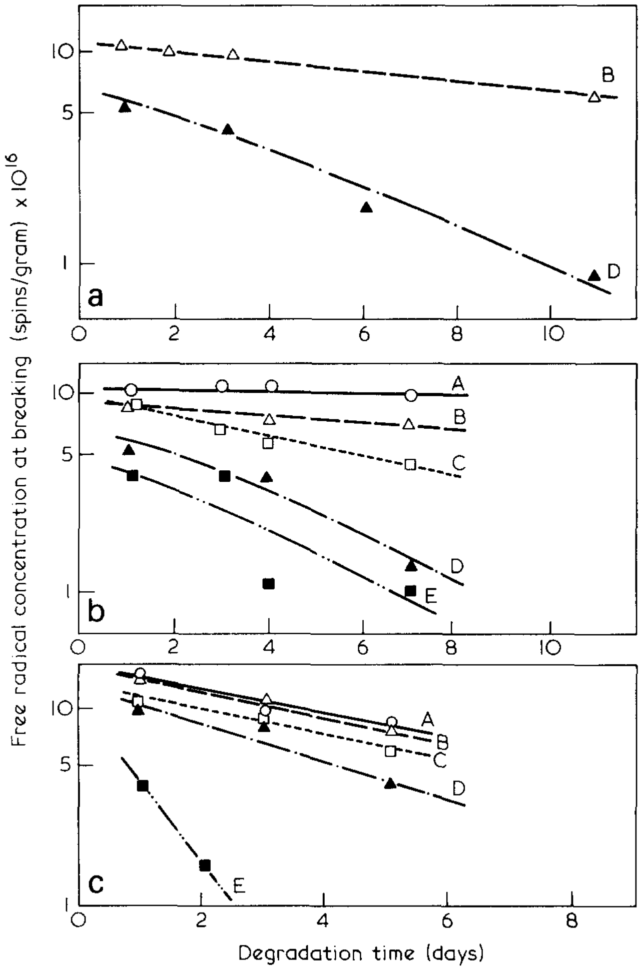

Figure 11 Free radical concentration produced during fracture after exposure to various environments: (a) air, (b) u.v.-light, (c) exhaust gas, under strain as a function of degradation time. (See ***Figure 8*** for explanation of capital letters)

distribution takes place during the random chain scissions, it is possible to calculate the number of ruptured bonds $[Q]$ required to produce a given viscosity change[20]. The equations used to calculate chain rupture concentrations $[Q]$ under this assumption are:

$$[Q] = (\rho N_a/[M_{n0}])([M_{n0}]/[M_n] - 1)$$

$$[M_n] = [M_v]([(a+1)\Gamma(a+1)]^a) \qquad (4)$$

where ρ is the sample density, N_a is Avagadro's number, $[M_{n0}]$ and $[M_n]$ are the number average molecular weight in the undegraded and degraded samples, respectively, and a is the exponent in the Mark–Houwink equation (3).

The number of free radicals $[N]$ measured with e.s.r. were then compared to the number of ruptured bonds $[Q]$ as determined by viscometry. The results are shown in *Table 1*. The sample fractured in a control tension test had viscosity molecular weight $[M_v] = 3.54 \times 10^4$, while the $[M_v]$ of an undeformed control sample was 3.88×10^4. That is, a 9% decrease in $[M_v]$ was observed during fracture in our experiments. Note that the method of sample preparation in these experiments may affect the measured $[M_v]$: Arev and his co-workers[21] reported a very large decrease (up to 40%) in $[M_v]$ for polycaproamide samples in their experiments. They used injection-moulded specimens by which we assume they were largely unoriented. They reportedly measured $[M_v]$ for material taken near the fracture in the sample. This appears to be a very large change in $[M_v]$, which we have been unable to reproduce. They found no decrease in $[M_v]$ in the undeformed part of the same specimen. Crist and his coworkers[20] studied changes in $[M_v]$ for nylon-6 fibres in which their sample material was taken from the deformed sample, since they were interested in the amount of chain rupture throughout the bulk of the sample. In our experiments, the samples were prepared in two ways. In the first method, the fractured samples were cut to about 1 cm in length from the tip of one fracture end, and by the other to about 0.5 cm length. We found no discernible difference in the $[M_v]$ measured in the samples prepared by these two different methods.

It is noteworthy that the ratio $[Q]/[N]$ becomes large as the sustained strain increases in the various environments as seen in *Table 1*. Superficially this is what one might expect, since $[Q]$ is a measure of the total chain scission from the start of testing while $[N]$ is only a measure of the number of scissions between termination of the sustained loading and final fracture. Hence, $[Q]$

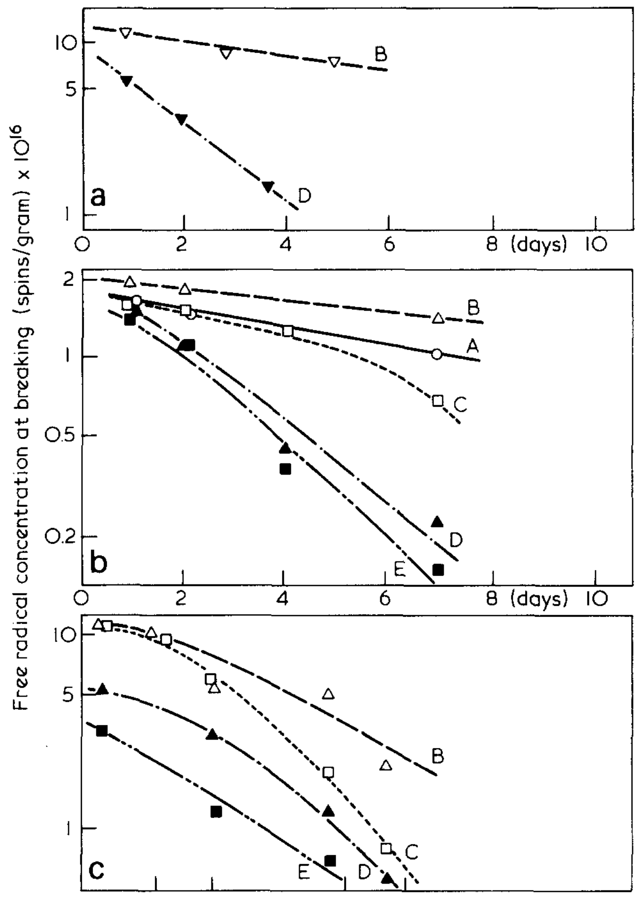

Figure 12 Free radical concentration produced during fracture after exposure to various environments: (a) O_3, (b) SO_2 (12% by volume), (c) NO_2 (0.86% by volume), under strain as a function of degradation time. (See ***Figure 8*** for explanation of capital letters)

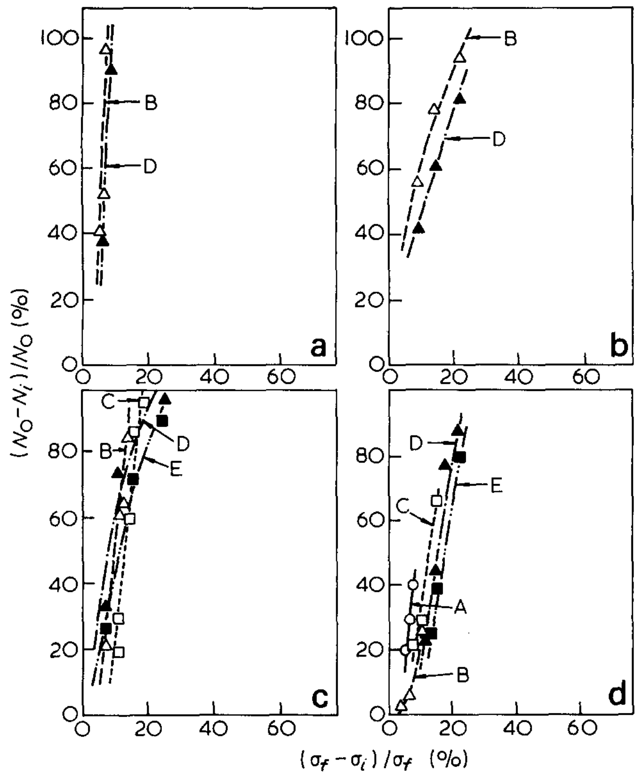

Figure 13 Observed relationship between breaking stress and free radical production during fracture. N_0 is the number of free radicals produced in a control test. N_i is the same for samples loaded while exposed to the indicated environment. σ_0 is breaking strength in a control test. σ_i is the same but after exposure to various environments: (a) air, (b) O_3, (c) NO_2 (concentration 0.86% by volume), (d) SO_2 (concentration 12% by volume). (See *Figure 8* for explanation of capital letters)

includes [*N*] as well as the degradation that occurred previous to the final fracture test. Such phenomenon would be consistent with a tie chain model of strength. For the air environment, however, there was almost no difference between the value [*Q*] for the control test and that for the sustained loading test. In other words, sustained straining in the air environment did not significantly affect the number of load carrying bonds, consistent with the fact that it had little effect on residual strength.

Sustained straining in the SO_2 environment had a small effect on [*Q*] when compared with that caused by an NO_x environment. This may be due to the quasi-reversible reaction of SO_2 gas with nylon-6 samples, especially the samples that were not stretched during exposure to the environment. We view this as evidence that the basic reaction of SO_2 is not chain scission. Were it a chain scission reaction the reversibility or annealing would be difficult to explain. The above results and observations appear to support the idea of the strength in the highly oriented polymers as being in large part dependent on the presence of load carrying tie chains.

An interesting question that has arisen before and continues to bother the authors is the exact reason for the difference between the number of ruptured bonds determined by e.s.r. and viscometry. As reported by this lab previously as well as Crist[20], the ratio [*Q*]/[*N*] for the sample fractured during the control test is about 10/1. While we cannot as yet give a definitive answer; several plausible explanations for this observation do come to mind. They include: (1) the very rapid decay of primary free radicals; (2) the occurrence of chain reactions in which one orignally stressed induced radical reacts with

Table 1 Decrease in viscosity molecular weight and chain rupture by e.s.r. and viscometry

Samples (Nylon-6)	$[M_v]$	Decrease in $[M_v]$ %	[*N*] Spins/cm^3	[*Q*] Rupture/cm^3	[*Q*]/[*N*]
1 Control	3.88×10^4	–	–	–	–
2 Fracture control in tension	3.53×10^4	9.0	1.1×10^{17}	1.1×10^{18}	10
3 Air for 3 days					
1. at 60% of S max	3.50×10^4	9.9	1.1×10^{17}	7.2×10^{17}	6.5
2. at 70% of S max	3.35×10^4	13.8	1.7×10^{17}	1.1×10^{18}	6.2
3. at 80% of S max	3.45×10^4	11.1	1.1×10^{17}	8.3×10^{17}	7.5
4. at 90% of S max	3.57×10^4	8.1	0.8×10^{17}	5.8×10^{17}	7.3
4 O_3 for 6 days					
1. at 60% of S max	3.28×10^4	15.5	5.1×10^{16}	2.1×10^{18}	40
2. at 70% of S max	3.16×10^4	18.6	6.5×10^{16}	2.6×10^{18}	40
3. at 80% of S max	3.35×10^4	13.7	3.9×10^{16}	1.8×10^{18}	46
4. at 90% of S max	3.38×10^4	12.9	3.8×10^{16}	1.7×10^{18}	45
5 NO_2 for 0.2 h					
1. at 60% of S max	2.78×10^4	28.4	5.0×10^{16}	4.5×10^{18}	90
2. at 70% of S max	2.64×10^4	32.0	3.0×10^{16}	5.3×10^{18}	180
3. at 80% of S max	2.51×10^4	35.3	1.9×10^{16}	6.2×10^{18}	330
4. at 90% of S max	2.52×10^4	35.1	1.8×10^{16}	6.1×10^{18}	340
6 SO_2 for 1 day					
1. at 60% of S max	3.53×10^4	9.0	$\sim 5.0 \times 10^{16}$	1.1×10^{18}	22
2. at 70% of S max	3.41×10^4	12.1	$\sim 4.0 \times 10^{16}$	1.6×10^{18}	41
3. at 80% of S max	3.44×10^4	11.3	$\sim 3.0 \times 10^{16}$	1.4×10^{18}	47
4. at 90% of S max	3.48×10^4	10.3	$\sim 2.4 \times 10^{16}$	1.3×10^{18}	54
7 SO_2 for 7 days					
1. at 60% of S max	3.46×10^4	10.8	$\sim 6.0 \times 10^{16}$	1.4×10^{18}	20
2. at 70% of S max	3.43×10^4	11.6	$\sim 3.3 \times 10^{16}$	1.5×10^{18}	45
3. at 80% of S max	3.12×10^4	19.6	$\sim 1.2 \times 10^{16}$	2.8×10^{18}	233
4. at 90% of S max	3.31×10^4	14.7	$\sim 0.8 \times 10^{16}$	1.9×10^{18}	253

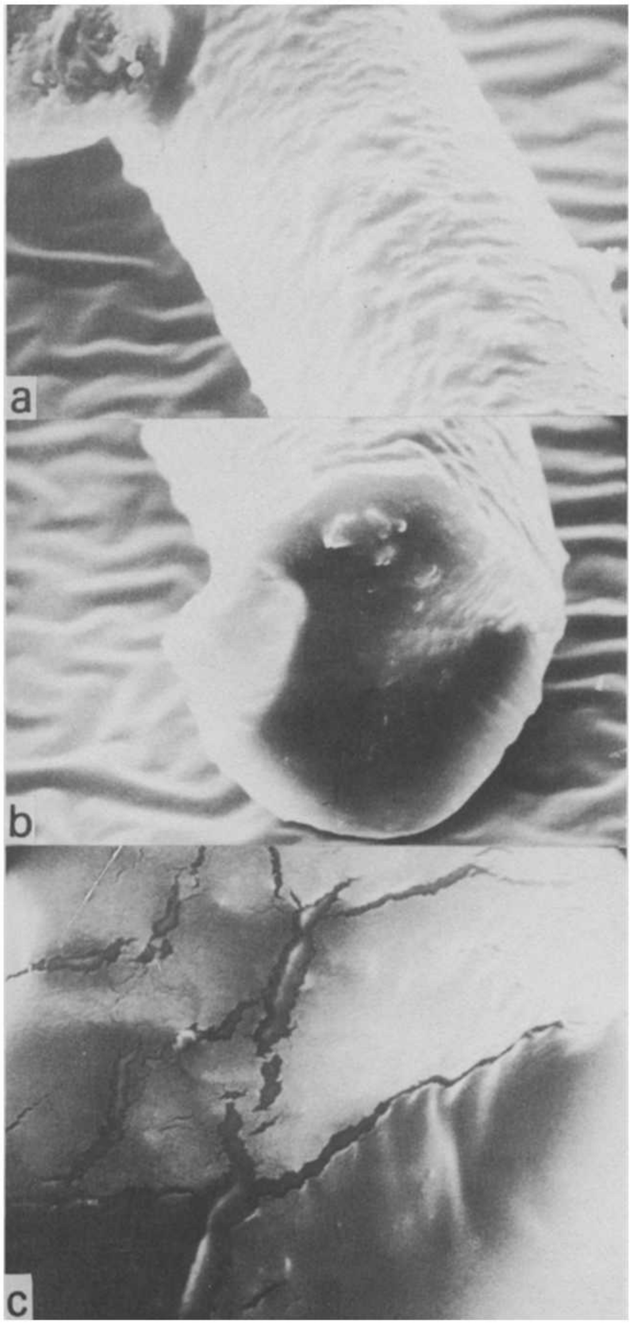

Figure 14 Fracture surface of a nylon filament exposed to an SO_2 environment. Sample was held at 90% strain for 4 days at room temperature. Magnification: (a) 2300 x, (b) 2300 x, (c) 5700 x. (Note the fibres in *Figures 14* through *20* have a diameter of 25 μ)

neighbouring bonds to produce scission without additional radicals, with a length of propagation equal to 10; (3) non-random chain scission, e.g. higher probability of rupture in longer chains. The rupture of these larger chains would result in a greater viscosity change per scission than that predicted by a random chain scission assumption. That is a few broken long chains would produce the same apparent viscosity change as a great many short ones.

The combined effects of the environment and strain also have a pronounced effect on the samples appearance as manifest in microscopic pictures of the fracture surfaces and sides of the degraded nylon filaments. *Figures 14* through *20* show scanning electron micrographs of some of the samples. In each of these Figures, (*a*) is a micrograph of the fibre surface, while (*b*) and (*c*) show fracture surfaces at the indicated magnifications after exposure to the environment and strains designated for the periods given in the captions. *Figure 14* shows the fracture surface of a nylon-6 filament which was exposed to SO_2 for four days at 90% of the maximum breaking strain and then fractured. The extent of surface degradation for this case might be illustrated by comparison with the relatively smooth surface of the standard sample shown in *Figure 15*. *Figure 16* shows fracture surfaces which were obtained in the same environment as *Figure 14* except at a lower sustained strain. *Figure 17* shows fracture surfaces of the sample exposed to the same environment at 90% of the maximum breaking strain but held at this strain for only one day. The reader will note the marked difference in surface degradation for these different loads and degradation times, including a strong synergistic effect between environment and strain on extent of surface degradation. *Figures 18* and *19* show fracture surfaces of samples which were exposed to an NO_2 environments for similar time periods but at different strain levels. In this case the appearances of the perimeter surfaces are similar but there is a fairly pronounced difference in the fracture

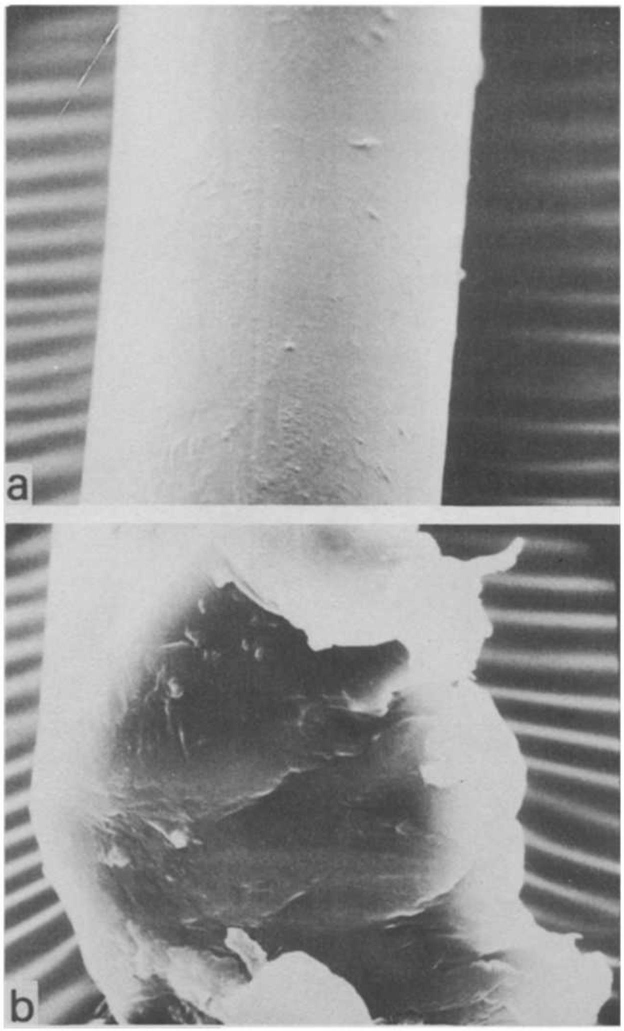

Figure 15 (a) Nylon filament control. Surface is clean and undamaged. (b) Surface produced by cutting with scissors. Magnification: (a) 2300 x, (b) 2300 x

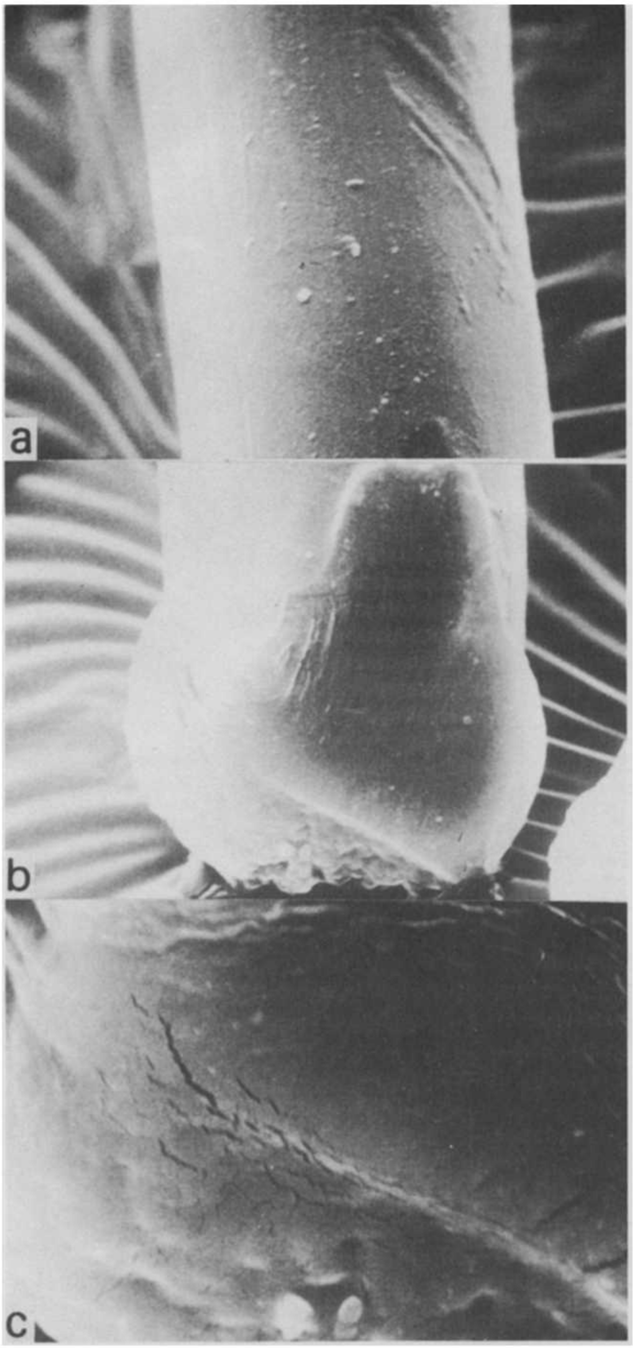

Figure 16 Fracture surface of a nylon filament exposed to an SO_2 environment. Sample was held at 70% strain for 4 days at room temperature. Magnification: (a) 2400 x, (b) 2400 x, (c) 5800 x

surfaces. The sample exposed to 90% strain (*Figure 18*) failed in a more brittle manner with much less apparent elastic spring back than did the sample held at 70% strain (*Figure 19*). The failure surface of this latter sample is similar to samples that have failed under strain without the aid of environmental attack[22,23]. *Figure 20* is a fracture surface produced from a sample that was subjected to an O_3 environment at room temperature, at 90% strain for six days. The peripheral surface of the fibre does not exhibit the blistered appearance produced by SO_2, (shown in *Figure 15*) but a number of microcracks are visible.

Hearle and his coworkers[22,23] studied the fracture surfaces of nylon produced by tensile failure, and reported 'typical configurations' for such fracture surfaces. The micrographs of nylon samples in this study exposed to the relatively inactive agents (air, O_3, u.v.-light) are similar to those reported by these investigators. For the samples which were exposed to more active degrading agents (NO_x, SO_2, exhaust gas) the fracture surfaces were relatively flat, with small cupped regions (assumed to be a crack propagating region) and exhibited considerable microcracking.

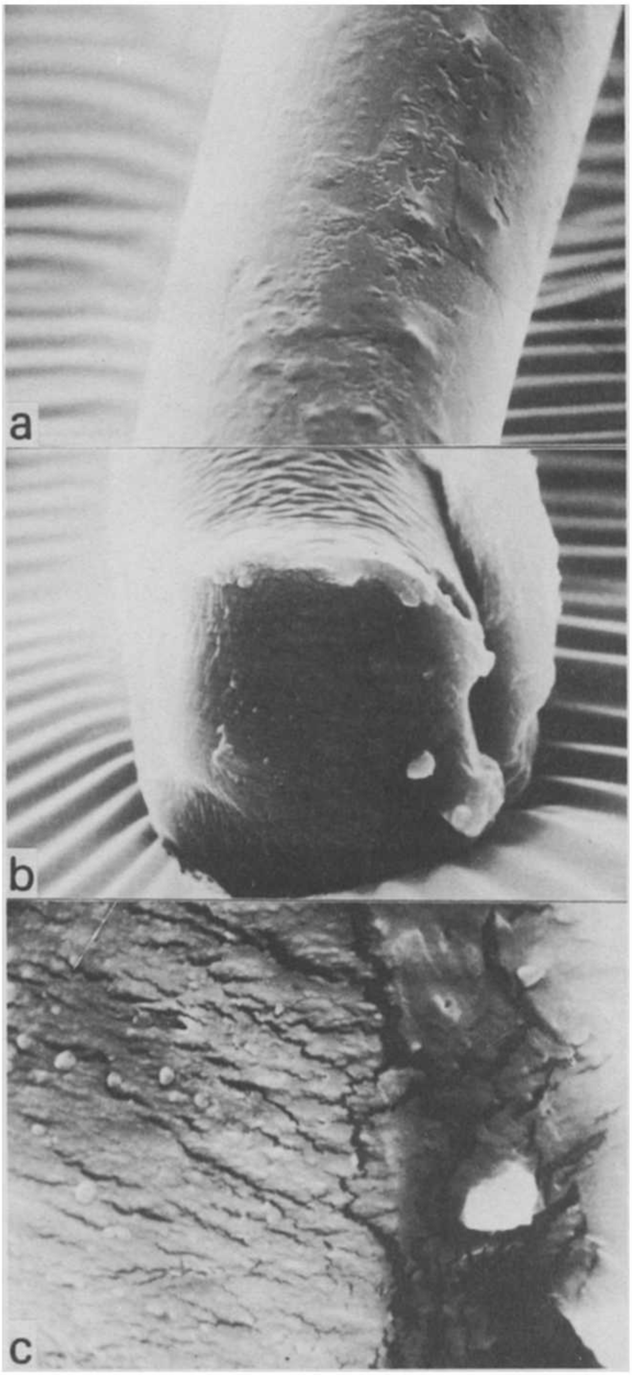

Figure 17 Fracture surface of a nylon filament exposed to an SO_2 environment. Sample was held at 90% strain for 1 day at room temperature. Magnification: (a) 2400 x, (b) 2400 x, (c) 6000 x

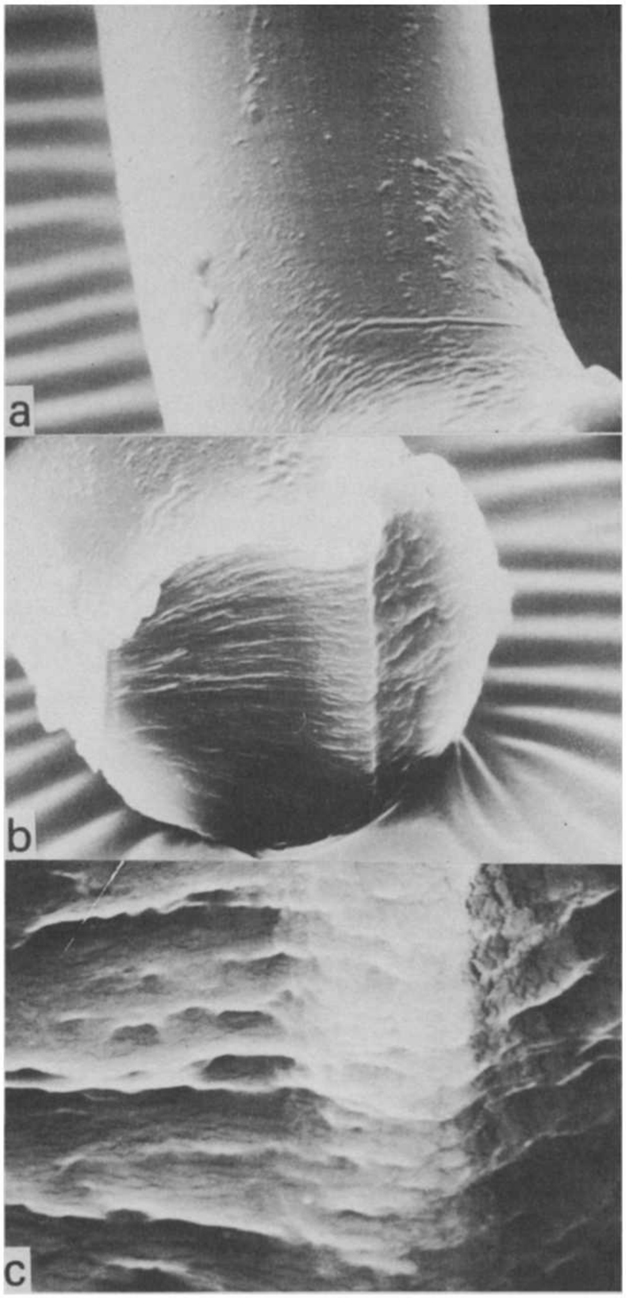

Figure 18 Fracture surface of a nylon filament exposed to an NO_2 environment at a concentration of 2.58% (by volume). Sample was held at 90% strain for 2 h at room temperature. Magnification: (a) 2600 x, (b) 2600 x, (c) 6500 x

Environmental effects on unoriented nylon

Experiments similar to those for highly oriented nylon-6 fibres were conducted on unoriented nylon rods to compare the combined effects of environment and stress on these physically and morphologically different forms of chemically similar materials. The samples were again tested in environments of air, O_3, SO_2, NO_x and u.v.-light. During exposure to the environment the nylon-6,6 rods were loaded to one of the following levels: (1) no load, (2) 90% of the yield stress and (3) the load corresponding to the strain which first visibly initiated necking. The authors were unable to observe significant numbers of free radicals in unoriented polymers employed in this study apparently because the number of chain scissions was below the threshold sensitivity of the spectrometer ($\sim 10^{14}$ spins/gram).

The observed breaking stress and Young's modulus on nylon-6,6 samples under the combined degradation effects were nearly constant irrespective of how the samples were tested in various environments with varying sustained loads. For example, nylon-6,6 rods maintained for a week at strains up to 90% of the strain at ultimate load in a NO_x environment showed almost no degradation in strength or change in modulus. This is in marked contrast to the response of oriented nylon and is

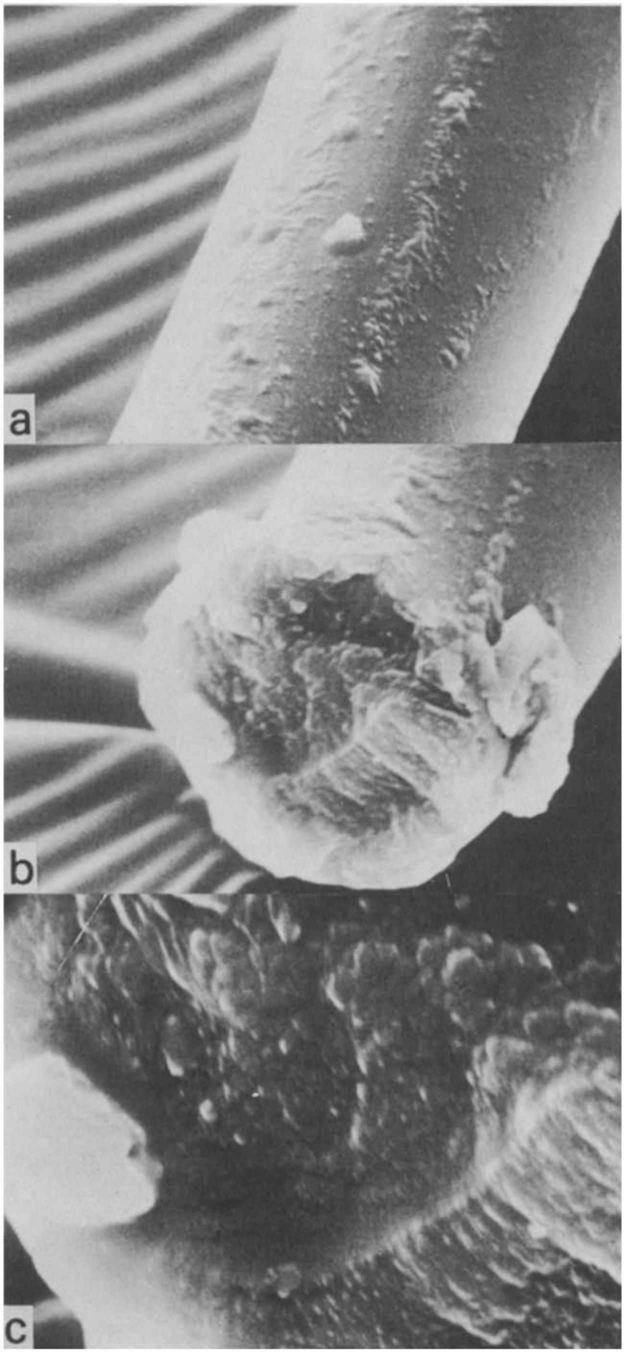

Figure 19 Fracture surface of a nylon filament exposed to an NO_2 environment at a concentration of 2.58%. Sample was held at 70% for 1 h at 81° ± 2°C. Magnification: (a) 2300 x, (b) 2300 x, (c) 5700 x

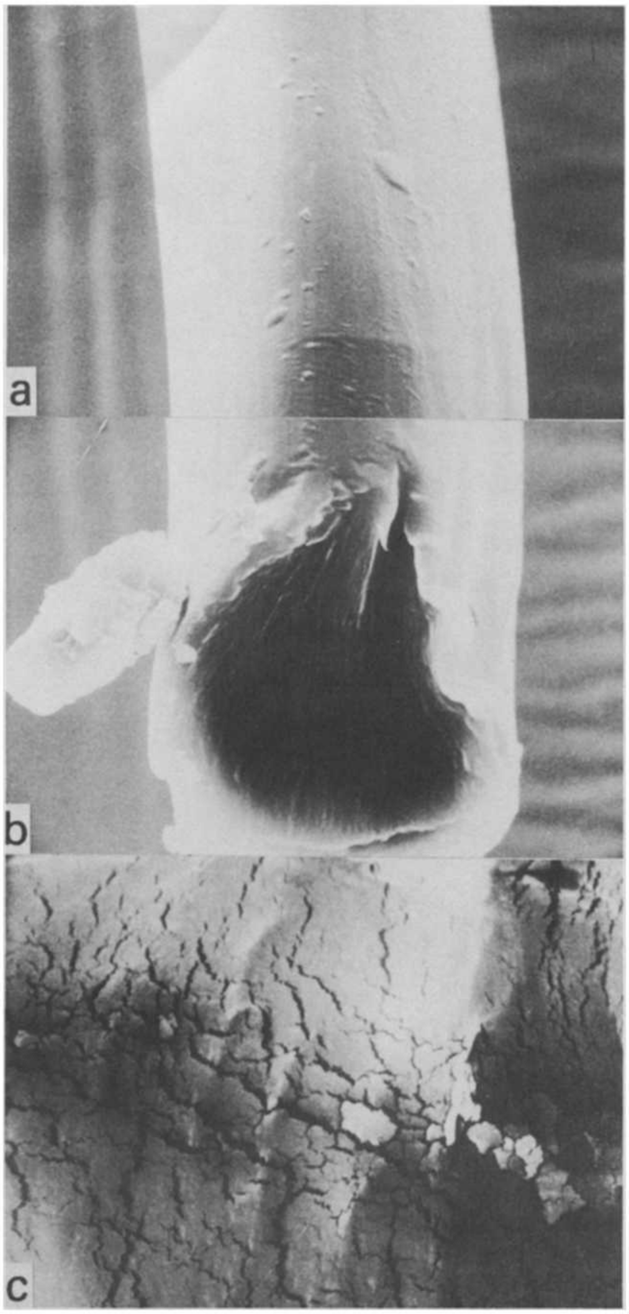

Figure 20 Fracture surface of a nylon filament exposed to an O_3 environment at concentration of 0.1% mol. Sample was held at 90% strain for 6 days at room temperature. Magnification: (a) 2300 x, (b) 2300 x, (c) 5700 x

what might be expected if the high strength of the oriented material is dependent on tie chains bridging amorphous regions between crystallites while failure in the non-oriented material is involved more with slip, breaking of secondary bonds etc. In the former case scission of the tie chains apparently results from stress and chemically aided thermal activation processes while the slip mechanisms or whatever processes are responsible for failure in the second case are apparently not very sensitive to the chemical agents.

Toughness can be defined as the strain energy $[W]$ to failure obtained from the area under the load *versus* elongation curve. Measurements of toughness yielded more definitive information on the combined effects of environment and applied load on the unoriented materials. The toughness is given as:

$$W=\int_{0}^{\Delta l} P(l)\mathrm{d}l \tag{5}$$

where $P(l)$ is the load as a function of elongation, l is the enlongation, and Δl is the elongation at failure. *Figure 21* shows a plot of $[W]$ for nylon-6,6 for various applied loadings *versus* degradation time in various environments.

The samples loaded to 90% of the yield stress and with a load corresponding to the occurrence of necking during exposure to an environment exhibited a decrease in toughness with degradation time. The amount of degradation was dependent on the environment and time of exposure. In this study, u.v.-light caused the most severe decrease in toughness and this was comparatively independent of the time of loading for the necked samples held a day or more. This saturation can probably be attributed to the fact that after a day the surface layer is degraded to a very low strength but still acts to shield the

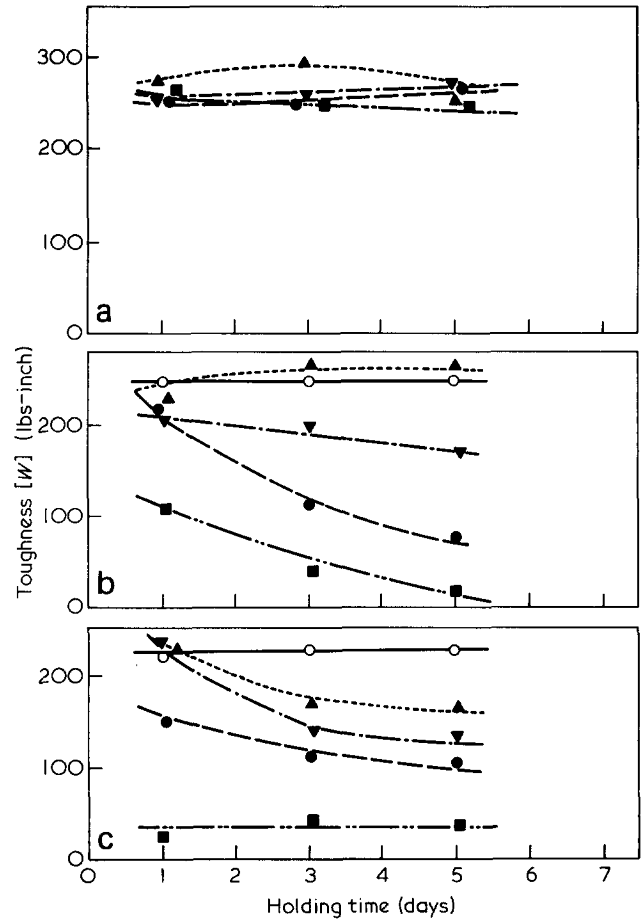

Figure 21 Degradation in toughness $[w]$ as a function of degradation time for nylon-6,6 rods exposed to various environments with three different sustained loads: (a) no load, (b) 90% of the yield stress, (c) the load corresponding to occurrence of necking. (–O–O–) air; (—●–●—) O_3; (---▲---▲---) SO_2; (–·–▼–·▼–·–) NO_x; (–··–■··–■··–) u.v.-light

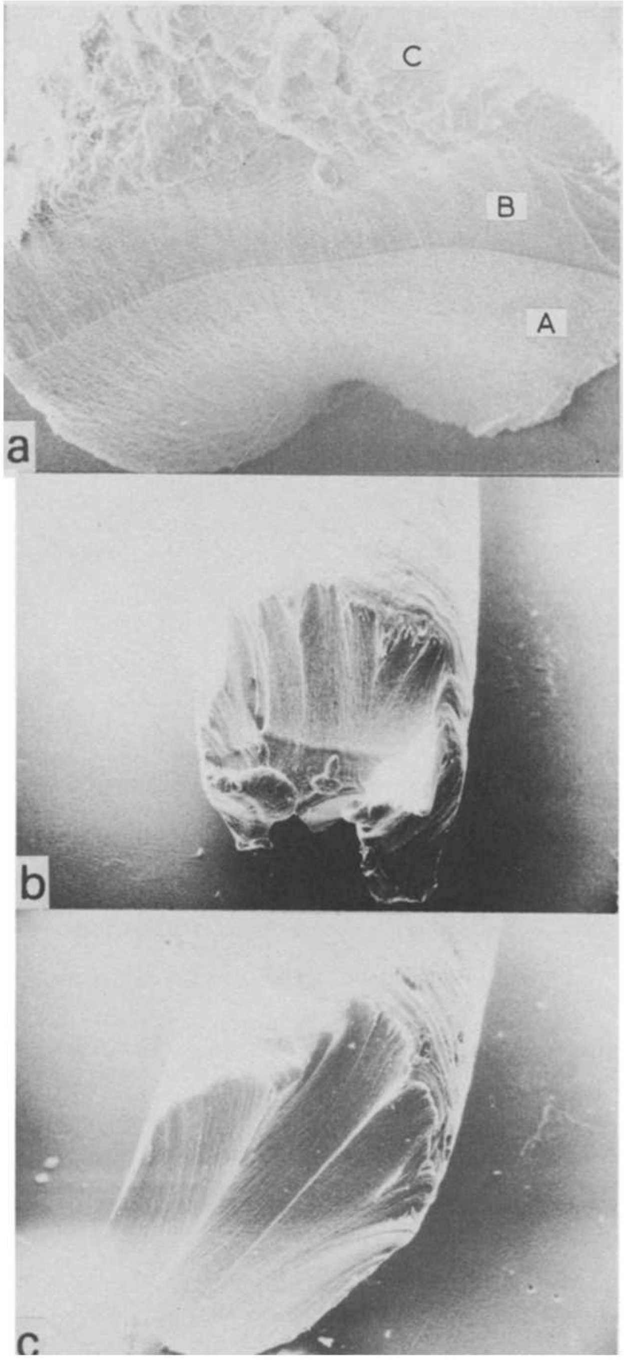

Figure 22 Fracture surfaces of nylon-6,6 rods exposed to (a) SO_2, (b) O_3, and (c) u.v.-light. Samples were kept in those environments with a load corresponding to the occurrence of necking at room temperature. Magnification: (a) 50 x, (b) 21 x, (c) 21 x

internal material from the u.v. light. There was no decrease in $[W]$ for the samples exposed to the various environments in the absences of the sustained loadings.

Figure 22 shows the fracture surfaces of nylon-6,6 rods exposed to SO_2, O_3 and u.v.-light with sustained load from three to five days. There is a definite difference between the fracture surfaces of samples exposed to SO_2 and those exposed to u.v.-light. The former (*Figure 22a*) exhibits a fracture surface very similar to that of samples broke in simple tension (control), which is characterized by (1) a crack initiation region, A; (2) a smooth cupped region, B; and (3) rough areas, C. The general aspects of the fracture surface of the nylon samples in the simple tension test has been characterized and described by Hearle and Cross[22], and Ogata *et al.*[24] Our results do differ slightly from these descriptions (*Figure 22c*), i.e., the surface does not have a rough area and has several smooth regions rather than only one such region. Furthermore, on the peripheral surface of these samples several open cracks were observed.

CONCLUSIONS

The study has demonstrated that the environmental effects on the mechanical properties of polymers are very complex phenomena. Moreover, the combined effects of the various environmental agents and applied strains interact in a synergistic way and are greater than the sum of their individual effects.

The environmental effects on polymer samples (unoriented and oriented) investigated in this study may be summarized as follows. Of the environmental agents studied, NO_x caused the most severe damage to highly oriented polymers (nylon-6 fibres) in terms of both a reduction in the breaking strength and a decrease in the free radical concentration measured during the final fracture test. The degradation was found to be accelerated by an increase in the applied strain, degradation time and temperature. Environmental effects on unoriented polymers (nylon-6,6 rods), differ from those for oriented polymers. No significant degradation in strength was observed for the unoriented material with or without applied strain. The reason for this difference is attributed to the large differences in the morphology of the two classes of polymer.

The fracture phenomena associated with the combined effects of environmental agents and strain on the oriented polymers are consistent with models proposed by several investigators, including Peterlin, Kausch, Lloyd and others[25-27]. Such models allow us to explain the degradation phenomena caused by environmental agents in oriented semi-crystalline polymers in terms of the thermally activated scission of these chains aided by both stress and the chemical environment. When a load is applied to a highly oriented polymer, the load bearing chains which bridge the amorphous regions are highly stressed and apparently play a dominant role in the load carrying ability or strength of these materials. Some of these highly stressed tie chains apparently fail due to the combined effect of the environment and stress-aided thermal activation. This results in a decrease in the number of molecular load bearing elements and hence the material's strength as well as the number of bonds that need to be broken in subsequent fracture tests. The extent of degradation depends on the reactivity of the chemical environment, the 'stress' experienced by the molecule, the time of exposure, and the type of polymer.

In the unoriented systems, however, strength is more likely to be dependent on secondary forces which are apparently not as sensitive to the environmental agents studied.

The toughness $[W]$, defined as the total strain energy absorbed up to failure, yielded useful information on the combined effects of environment and applied stress on unoriented polymers. In unoriented nylon samples with a sustained load, u.v.-light caused the most severe degradation in toughness. There was, however, no decrease in $[W]$ for the unoriented nylon samples exposed to various environments without a sustained load.

As discussed previously a singlet e.s.r. spectrum resulted after pulling nylon-6 fibres in an SO_2 environment. The singlet spectrum is thought to arise from the SO_2 ion-radical. However, nylon-6 fibres degraded by agents other than SO_2 yielded a 5-line spectrum very similar to the spectrum of the control material. The other notable characteristic of the reaction of SO_2 with nylon-6 fibres is that the reaction was found to be in large part reversible, i.e. the samples degraded in an SO_2 environment with or without applied stress recovered much of their strength and associated free radical production after a thermal annealing process.

The e.s.r. spectra recorded during fracture of the SO_2 treated material indicates about an order of magnitude fewer free radicals produced during fracture than for the virgin nylon with the 5-line spectra. Because of the very rapid decay associated with this singlet spectra it is very difficult to ascertain exactly how much of this difference should be attributed to the difference in decay kinetics and how much to actual differences in bond rupture. It does appear clear, however, that somewhat fewer free radicals (ruptured bonds) are required for fracture with SO_2 present than when it does when absent from the material.

Measurements of molecular weight changes resulting from degradation provided additional insight into the combined effects of environment and strain on the oriented polymers. The chain rupture concentration $[Q]$ of the fractured nylon-6 fibre samples after exposure to various environments was calculated from measurements of the viscosity molecular weight $[M_v]$ changes. This assumes that random chain scission occurs and that the 'most probable distribution' takes place during random chain scission. The number of free radicals $[N]$ obtained by e.s.r. was compared with $[Q]$. The results, shown in *Table 1*, may be summarized as follows. (1) The nylon-6 fibre samples exposed to NO_x showed a comparatively large $[Q]$, indicating that severe degradation occurred and that the exposure to this agent resulted in a comparatively large number of broken chains. This agrees with the e.s.r. observations where a larger decrease in the number of free radicals produced during fracture was observed as shown in *Figure 13c*. (2) The effect of the degradation time on the value of $[N]$ and $[Q]$ for the samples exposed to SO_2 for one and seven days is shown in *Table 1*. In general $[N]$ decreases with stress and to a lesser extent with time while $[Q]$ increases with both factors. (3) The nylon fibres fractured in control tension tests showed about a 9% decrease in $[M_v]$ and $[Q]/[N]$ ratio equal to approximately 10. The differences between $[Q]$ and $[N]$ may imply (a) very rapid decay of primary radicals, (b) the existence of chain reactions in which free radicals react with neighbouring chains to produce broken bonds without free additional free radical production, or (c) non-random chain scission, e.g. longer chains ruptured with high probability. The authors feel that the correct explanation is most likely a combination of these three. (4) $[Q]/[N]$ increased with increased sustained load, i.e., in the samples exposed to one of the environments while under strain, many tie chains were gradually fractured due to thermally and chemically thermal activated chain scission.

Models of fibre structure generally picture the fibre as being very inhomogeneous, made up of microfibrils oriented in the fibre direction. These microfibrils themselves are usually viewed as having a sandwich structure of highly crystalline regions separated by less crystalline (amorphous) regions bridged by tie chains. In this study the picture is further complicated by the fact that we are working with bundles of yard in which the individual fibres might differ slightly in properties, length etc. As a consequence of these factors, the bonds in the material may be nonuniformly stressed. As scission occurs in the more highly stressed chains, their load must be redistributed among the remaining chains. The possibility that the environmental agents that aid in the chain rupture might also be nonuniformly distributed in the polymer structure serves to further complicate the kinetics of chain scission. The fact that the ratio $[Q]/[N]$ increases with sustained load is evidence that in the presence of aggressive environments and stress more chain scission occurs than with rupture under stress alone.

ACKNOWLEDGEMENTS

This study was sponsored by the National Science Foundation Polymer Program No. DMR 79-2590.

REFERENCES

1 Lawton, E. J., Balwith, J. S. and Powell, R. S. *J. Chem. Phys.* 1960, **33** (**2**), 395
2 Kashiwagi, M. *J. Chem. Phys.* 1962, **36** (**3**), 575
3 Kashiwagi, M. *J. Polym. Sci.: Part A* 1963, **1**, 189
4 Graves, C. T. and Ormerod, M. C. *Polymer* 1962, **4**, 81
5 Shinohara, Y. and Ballantine, D. *J. Chem. Phys.* 1962, **11**, 3042
6 Ohnishi, S., Ikeda, Y., Kashiwagi, M. and Nitta, I. *Polymer* 1961, **2**, 119
7 Ohnoshi, S., Sugimoto, S. and Nitta, I. *J. Chem. Phys.* 1963, **39** (**10**), 2647
8 Ross, J. H. 'Fibres', (Eds. D. V. Rosato and R. T. Schwarts), John Wiley and Sons Ind., 1968
9 Kuri, Z. and Ueda, H. *J. Polym. Sci.* 1961, **1**, 349
10 Kuri, Z., Ueda, H. and Shida, S. *J. Chem. Phys.* 1960, **2**, 371
11 Ogihara, T., Tsuchiya, S. and Kuratani, K. *J. Chem. Phys.* 1964, **6**, 978
12 Igarashi, M. *Ph.D. Thesis* Mechanical Engineering, University of Utah, 1982
13 Elias, H. G. and Schumacher, R. *Macromol. Chem.* 1964, **76**, 23
14 Zeronian, S. H., Alger, K. W. and Omaya, S. T. *Textile Res. J.* 1973, **43**, 228
15 Ueda, H., Kuri, Z. and Shida, S. *J. Polym. Sci.: Part A* 1963, **1**, 3537
16 McCain, D. C. *J. Chem. Phys.* 1970, **53**, 1297
17 Suzuki, I. and Abe, R. *J. Phys. Soc. Jpn.* 1971, **30**, 586
18 Burlamacchi, L. *Mol. Phys.* 1969, **16** (**4**), 369
19 Lloyd, B. A., DeVries, K. L. and Williams, M. L. *J. Polym. Sci., A-2* 1972, **10**, 1415
14 Zeronian, S. H., Alger, K. W. and Omaya, S. T. *Textile Res. J.* 1973, **43**, 228
15 Ueda, H., Kuri, Z. and Shida, S. *J. Polym. Sci.: Part A* 1963, **1**, 3537
16 McCain, D. C. *J. Chem. Phys.* 1970, **53**, 1297
17 Suzuki, I. and Abe, R. *J. Phys. Soc. Jpn.* 1971, **30**, 586
18 Burlamacchi, L. *Mol. Phys.* 1969, **16** (**4**), 369
19 Lloyd, B. A., DeVries, K. L. and Williams, M. L. *J. Polym. Sci.* 1972, **10**, 1415
20 Stockel, T. M., Blasius, J. and Crist, B. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 485
21 Arev, A. M., Zaslavskii, N. N. and Dolzhenkova, N. G. *Mekhanika Polimerov* 1968, **3**, 562
22 Hearle, J. W. S. and Cross, P. M. *J. Mat. Sci.* 1970, **5**, 507
23 Hearle, J. W. S. and Lomas, B., *J. Appl. Polym. Sci.* 1977, **21**, 1103
24 Ogata, N., Dougasaki, S. and Yoshida, K. *J. Appl. Polym. Sci.* 1979, **24**, 837
25 Peterlin, A. *Intl. J. Fract.* 1975, **11**, 761
26 Kaush, H. 'Polymer Fracture', Springer, Berlin, 1978
27 Lloyd, B. A., DeVries, K. L. and Williams, M. L. *Rheo Acta* 1975, **11**, 352