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High energy radiation effects on ultimate mechanical properties and fractography of nylon 6 fibres

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Nylon 6 fibres were irradiated with up to 60 Mrad of cobalt-60 gamma radiation in air or up to 76 μC of 4.5 MeV cyclotron-accelerated protons in vacuum. The products of the irradiations were then characterized by the resulting changes in ultimate mechanical properties and in fracture morphology when tested at 21° C under selected conditions of fibre moisture content. In general, the results show a progressive deterioration of tensile properties, an increase in torsional brittleness, and a decreasing flex life, with increasing dose, and display some dependence on fibre moisture content. The effects are most pronounced in the first interval of dose; i.e. 10 Mrads gamma irradiation and 12 μC of high energy protons. The rate of deterioration of these mechanical properties generally slows with subsequent dose increases. An annulus/core fracture morphology was found in the gamma-irradiated material which was not in evidence for material irradiated with protons in vacuum. The morphology of the proton-irradiated tensile breaks are characteristic of a brittle material; flex fatigue fracture surfaces were often characterized by step-like formations reminiscent of kink bands. Discussion of the data in terms of radiochemical processes, structure–property relations, and implications for accelerated ageing programs are included.

1. Introduction

Organic polymeric materials in fibre form find application in diverse end uses under extensive environmental conditions. The determination of the serviceable lifetime of the final product, whether it be in a space probe, solar energy applications, or as fabric in clothing, is of obvious importance to the designer. This report provides some information fundamental to the development of a method of accelerated ageing.

We have for some time been exploring the polymer mechanical property changes attendant upon structure modification by chemical or physical means [1–4]. We continue that research programme here, where we present the results of a study of the stability of the ultimate mechanical properties of nylon 6 fibres to two types of high energy radiation, namely cobalt-60 gamma radiation and high energy protons. The results of an earlier study utilizing sunlight will be cited for discussions of accelerated ageing [4].

The products of the irradiations were subjected to a system of interrelated experiments which enables a fairly complete characterization of the ultimate mechanical properties of polymeric fibres tested singly. The experiments are comprised of three mechanical tests – tensile strength, torsional brittleness and flexural fatigue resistance – under selected conditions of fibre temperature and moisture content.

2. Procedures

2.1. Materials

The starting material is nylon 6 filament yarn obtained from two suppliers:

1. Allied Chemical Co., Ltd (660 denier/70 fila-

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0022–2461/84 $03.00 + .12

ments), draw ratio 4.0:1, free of delustrants or additives (1 mg m^{-1} = 9 den).

2. Toyobo Co., Ltd (207 denier/24 filaments), draw ratio 4.6:1, free of delustrants or additives.

2.2. Exposure techniques

2.2.1. Gamma irradiations

Subsequent to a one hour soxhlet methanol extraction, the continuous filament yarn (Toyobo Co., Ltd) was loosely placed in a polyethylene bag and then irradiated in the presence of air at a distance of 25.5 cm from a 163 000 curie cobalt-60 source. The dose rate was 1.0 Mrad per hour for total doses of 10, 20, 30, 40, 50, and 60 Mrads (1 Gy = 0.01 rad). The temperature during the exposure was about 15 to 20° C at a humidity level of about 30% RH.

2.2.2. Charged particle irradiations

The continuous filament yarn (Allied Chemical Co.) was mounted on a 35 mm photograph slide under approximately 6.5 g tension per filament. A 4.5 MeV proton beam from the 76 inch (19.3 m) isochronous cylcotron at the University of California, Davis was collimated to a 7.5 mm square and swept across a sample area of 1.8 cm^2. The beam current was 180 to 200 nanoamperes. The irradiations were done in vacuum, for exposure times ranging from one minute to six minutes. The resulting doses, in terms of total charge on the samples from Faraday cup measurements, were 12, 24, 43, and 76 microcoulombs (μC). An indication of the radiation level of charged particle beam radiation may be obtained from a consideration of power per unit mass (T. A. Cahill, private communication). With the assumption of a thin target, the total dose, D, is given by

$$D = \frac{dE}{dx}\frac{Q}{A} \times 10^5 \text{ rads}$$

where dE/dx is the stopping power of the material, Q is the accumulated charge on the sample during the irradiation, and A is the irradiated area.

If a value for the stopping power is taken to be 90 MeV g^{-1} cm^{-2} for nylon irradiated with 4.5 MeV protons [5], then $D = 5Q$ Mrads.

We report our results in terms of the measured rather than the calculated quantity.

2.3. Product characterization

2.3.1. Tensile and breaking twist angle tests

These tests were performed on a standard table model Instron outfitted with the A cell. Details of the experimental protocols followed, including methods of single fibre manipulation, have been described previously [3]. In the current study, the temperature was maintained at ambient (21° C). For tests conducted in water, the fibre was allowed to soak, under no tension, for a minimum of 30 min prior to insertion into the tester.

2.3.2. Flexural fatigue

The method of single fibre flex fatigue used is a simple 180° bending of the fibre around a 42 μm diameter mandrel. The details of this test, including a description of the instrument, may be found elsewhere [4, 6]. We have been utilizing two methods of data presentation: arithmetic means and failure diagrams [4, 6]. The arithmetic mean of the flexes at failure gives a crude measure of the central region of the statistical distribution. Failure diagrams are plots of the fraction of the tested fibres which have failed against log number of flexes. In a fatigue test, the mode of failure at shorter lifetimes may be different from that at longer lifetimes and the effect of the experimental milieu may be expected to differ at the two extremes [7]. Central measures could therefore be misleading in discussions of lifetimes of materials. Recognizing the weaknesses of arithmetic means, we have employed, when necessary, failure diagrams as an aid in establishing trends in the data. The failure diagram is a simple, yet effective, method of displaying the dispersion inherent in this type of test; it clearly shows the relative proportion of early and late failures between samples, and the extent of overlap.

2.3.3. Scanning electron microscopy

The method used for the scanning electron microscopy of the fractured fibres is essentially that reported earlier [4].

3. Results and discussion

3.1. Fine structure

Our data is interpreted on the basis of the qualitative aspects of the polymer structure model developed by Prevorsek and co-workers [8]. They postulate two phases of non-crystalline material: an extended chain interfibrillar material, and an amorphous material within the microfibrils, between the lamellar crystallites. The interfibrillar material, though non-crystalline, has a higher degree of order than the amorphous regions, and is

TABLE I Proton radiation effects on the tensile and breaking twist angle (BTA) properties of nylon 6 fibres* (testing temperature 21° C)

Dose (μC)†	Tensile				BTA (degrees)	
	65% RH‡		Wet		65% RH	Wet
	Load (g)	Extension (%)	Load (g)	Extension (%)		
0	58 ± 6	42 ± 6	52 ± 3	43 ± 4	42 ± 1	42 ± 1
12	44 ± 4	30 ± 2	32 ± 4	30 ± 5	49 ± 1	47 ± 2
24	37 ± 5	25 ± 3	28 ± 4	27 ± 3	52 ± 1	52 ± 2
43	36 ± 3	24 ± 3	21 ± 4	21 ± 4	53 ± 6	54 ± 1
76	30 ± 1	23 ± 2	17 ± 4	21 ± 3	54 ± 6	57 ± 2

*Standard deviations for a minimum of 10 samples included with the means.
†μC = microcoulombs.
‡RH = relative humidity.

composed of almost fully extended molecules. The amorphous material, on the other hand, is not of the extended chain configuration. Infrared (IR) analysis of nylon 6 implies the chain folds occur preferentially at the amide group [9]. In addition, for nylon, most of the observable free-radicals produced by high-energy radiation reside at the amide groups [10]. Thus we may expect the crystallite fold surfaces to be replete with these free radicals, i.e. to be localized regions of enhanced radical density. A more homogeneous distribution of radicals among the amide groups in the non-crystalline domains may be expected.

The fate of the free radicals is dependent on many factors. In the amorphous regions they may react with oxygen in a diffusion controlled reaction [10]. Hydrogen bonding of the amide groups of adjacent molecules will provide a steric impediment to crosslinking between juxtaposed radicals [11]. Hence, at crystallite surfaces, chain scission may be favoured over crosslinking, while crosslinks may form in the disordered regions. Radicals extant in the crystalline regions may be perfectly stable [12].

3.2. Proton irradiation

3.2.1. Tensile properties

The tensile strength and elongation at break of proton-irradiated nylon 6 filaments varied inversely with the doses employed in this study (Table I). There was a rapid decline in tensile properties below the 24 μC dose level to about 60% of the original value and a more gradual reduction to a final residual value of about 50% at the 76 μC level. When the tensile testing was performed on wet fibres, the elongation was essentially unchanged from that obtained when testing at 65% relative humidity (RH), irrespective of dose. However, the rupture load was less when the material was tested wet than when it was conditioned at 65% RH, the difference generally increasing with increasing dose. We assert this additional weakening of the material when wet to be a consequence of the interaction of the water with the interchain hydrogen bonds present in the fibres which results in the dissociation of those bonds. The enhancement of this effect with increasing dose is a reflection of the continuing scission of main-chain covalent bonds with concomitant increase in dependence of the fibre strength on the interchain hydrogen bonds. The action of the water in reducing the effectiveness of the hydrogen bonds thus allows the weakened state of the polymer chains to be more evident.

The observed levelling off of the tensile properties at higher doses is presumed to be an effect of radiation-induced interchain covalent crosslinks in the interfibrillar regions, since there is evidence that these extended chain domains are the primary load bearing elements [13–15]. Support for this conjecture is also given by the BTA measurements, as discussed below.

The typical fractography of semicrystalline polymers (see, for instance, [16–18]) can be observed in the scanning electron micrographs (SEM) of tensile fracture surfaces of our samples. A "V-notch", or ductile fracture, begins at an initiation site. This region of subcritical crack propagation velocity is adjacent to the region of abrupt, or brittle, failure (Fig. 1). We did not observe a well-defined distinction between a sample fracture air-dry and one fractured wet. A distinction between the tensile fracture morphology of non-irradiated as compared to irradiated nylon was detected in that the slow crack propagation region in the degraded samples is more nearly

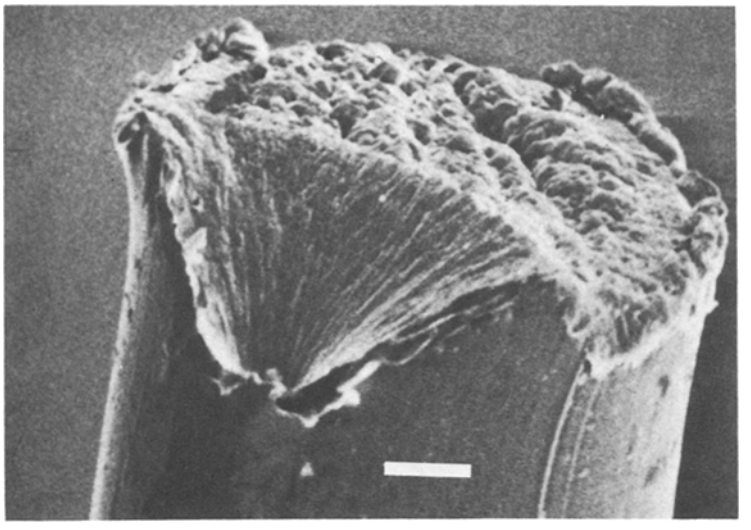

Figure 1 SEM of tensile fracture of nylon 6 control for proton-irradiation test series; fractured in air (5 μm bar).

perpendicular to the fibre axis than in the unexposed samples, i.e. the V-notch narrows with increasing dose (cf. Figs. 1, 2 and 3). A fracture plane perpendicular to the fibre axis is a morphology characteristic of brittle materials, such as glass fibres [16]. In our material, embrittlement is likely the result of radiation-induced crosslinks, in conjunction with a general degradation owing to chain scission.

3.2.2. Breaking twist angle

The BTA-determined brittleness of the materials was found to increase with dose, with a levelling tendency evident after the 24 μC level when tested in air (Table I). In contrast, there appears to be a trend for the BTA of the wet-tested irradiated material to continue to increase beyond that at the 24 μC level.

Crosslinking of polymers can be caused by high energy radiation, particularly when irradiated in vacuum [19], and would result in embrittlement of the samples. Our data indicates that crosslinking increases with increasing dose, and is made evident by the dissociation of the interchain hydrogen bonds by the water.

Water is normally expected to act as a plasticizer when present in hydrophilic polymers. However, this expectation can be contradicted in certain experimental arrangements. At low temperatures, for example, increasing the water content produces an increase in modulus [20]. In many mechanical tests, such as tests of brittleness, stress concentration can be a key factor. In our opinion the labile network of hydrogen bonds overlying the covalent bond structure of the molecular chains and any extant crosslinks can

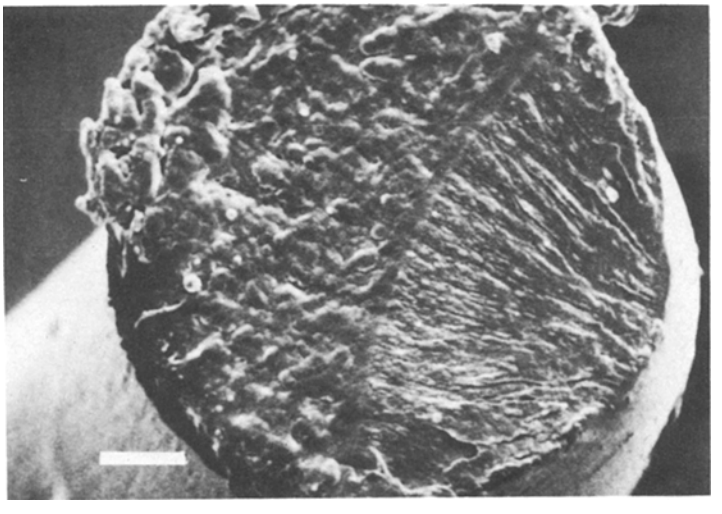

Figure 2 SEM of tensile fracture of nylon 6 fibre at 12 μC proton-irradiation dose; fractured in air (5 μm bar).

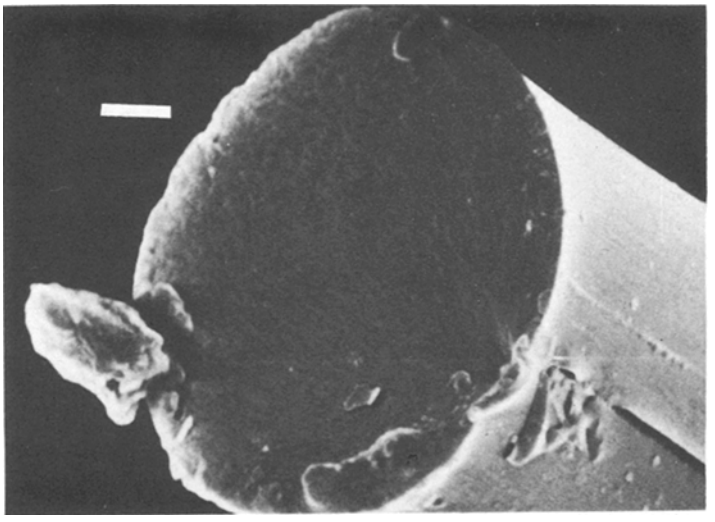

Figure 3 SEM of tensile fracture of nylon 6 fibre at 76 μC proton-irradiation dose, fractured in air (5 μm bar).

serve to distribute the stresses resulting from the deformation, thus preventing the build-up of local stresses to a critical level. If these hydrogen bonds are dissociated by sorbed water, and the material has an enhanced level of crosslinking, local stresses can conceivably attain a critical level and cause the formation and subsequent catastrophic propagation of a crack. We believe this is a credible explanation for the increased brittleness of the irradiated nylon samples when tested wet over that of their counterparts tested at 65% RH.

In distinction to the tensile tests, the fracture plane of the twist-broken fibres is generally not perpendicular to the fibre axis (Figs, 4, 5 and 6). There remains, however, evidence of an initiation site and ductile and brittle crack propagation behaviour similar to the tensile tests. There did not appear to be any striking difference between the BTA fracture surface of water- and air-tested samples.

3.2.3. Flex tests

Irrespective of load and RH there was a rapid drop in flex life at the lowest dose used (12 μC), and a subsequent slow decline as the dose increased, with exceptions as noted below (Table II). Tensile fatigue damage in nylon 6 fibres occurs in the disordered regions; the primary element sustaining damage is the interfibrillar material, by repeated sliding of the microfibrils [21]. Bending fatigue may be presumed to proceed, in part, by a similar mechanism. Degradation of the interfibrillar material will therefore have a marked influence on fatigue life. The bending moment, however, will also introduce a distortion in the intrafibrillar amorphous domains as the microfibrils bend. Thus, in bending fatigue, degradation by chain scission within the microfibrils at the crystallite surfaces will also contribute to the observed flex behaviour.

The single exception to the monotonic decrease in flex life was when the test conditions were 65% RH with a 2.9 g load. (The apparent exception when tested at 4.8 g load and 30% RH was deemed insignificant after a critical analysis of the experimental results [6].) In that instance, there was an increase in mean flex life at 43 μC which held steady at 76 μC. The experiment was conducted many more times under these conditions than under the others and the points are reasonably stable to replication, in that the failure diagrams (Fig. 7) showing the results of several independent tests of the fatigue life of these samples, thoroughly overlap. A possible explanation of the data may lie in the nature of flex fatigue damage and in the synergism between the mechanical con-

TABLE II Effect of proton radiation on the flex life of nylon 6 fibres conditioned at 30% RH or 65% RH at 21°C, with selected applied loads. Mean flex lives (×1000)

Dose (μC)*	30% RH†		65% RH	
	2.9 g	4.8 g	2.9 g	4.8 g
0	–	5.9	185	68.8
12	11.3	3.6	27.2	6.8
24	4.5	0.97	21.6	4.4
43	3.1	9.4	72.8	2.7
76	0.6	5.3	65.4	0.11

*μC = microcoulombs.
†RH = relative humidity.

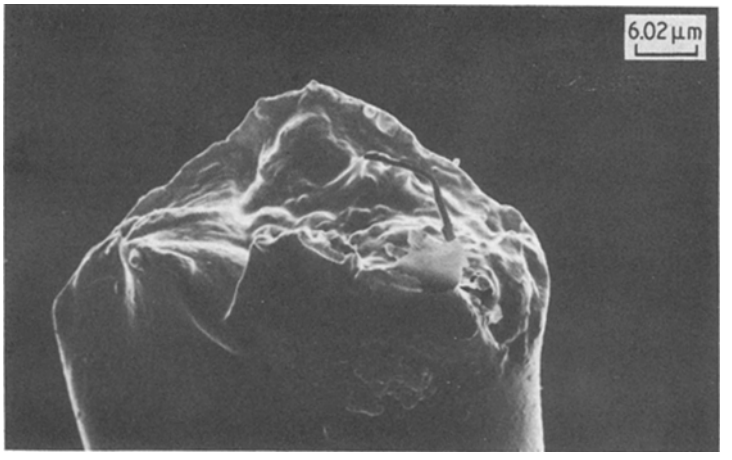

Figure 4 SEM of BTA fracture of nylon 6 control for proton-irradiation test series; fractured in air (6 µm bar).

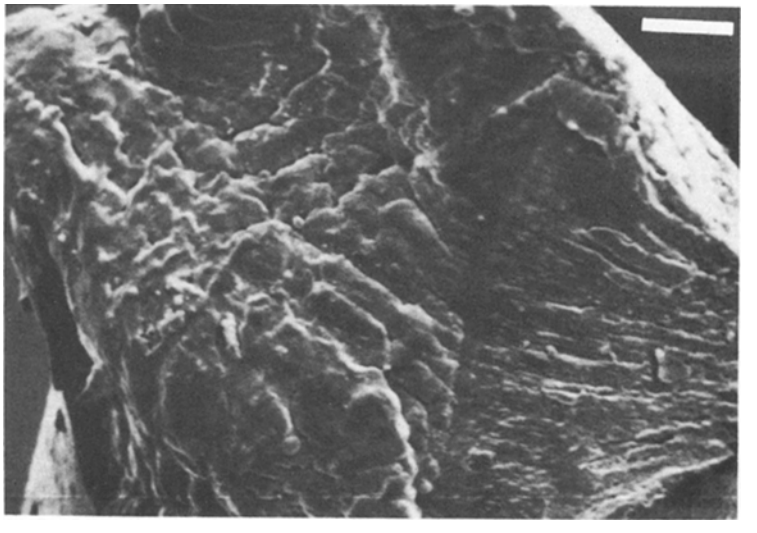

Figure 5 SEM of BTA fracture of nylon 6 fibre at 12 µC proton-irradiation dose; fractured in air (5 µm bar).

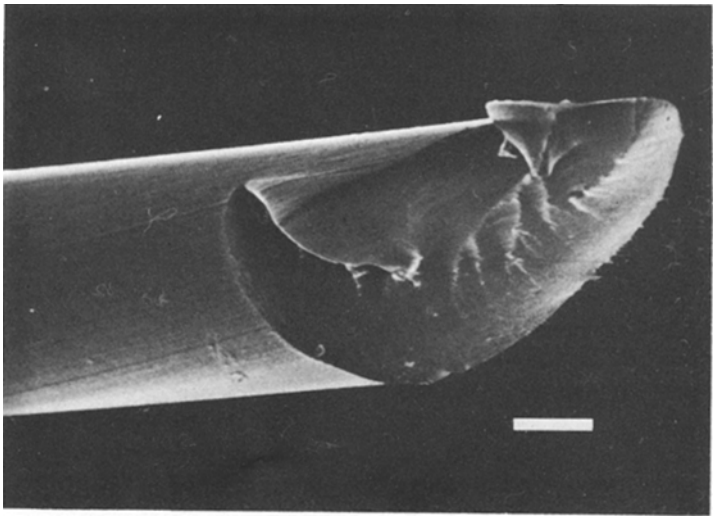

Figure 6 SEM of BTA fracture of nylon 6 fibre at 76 µC proton-irradiation dose; fractured in water (10 µm bar).

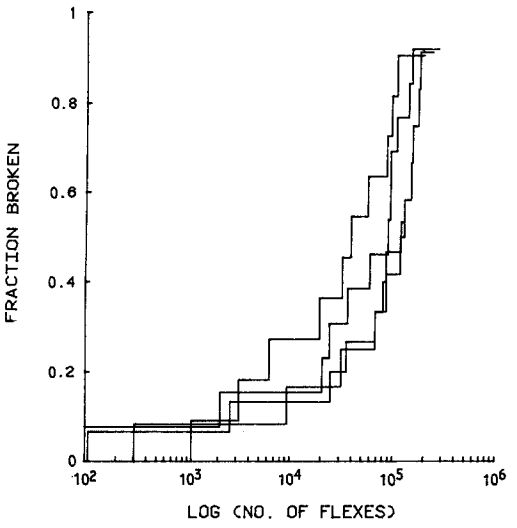

Figure 7 Failure diagram for 43 μC proton-irradiation, tested at 2.9 g, 65% RH, showing overlap of four separate runs.

ditioning caused by the increased number of flexes afforded by the lower load and the enhanced lability of the hydrogen bond structures at the higher humidity. Narisawa *et al.* [21] claims an orientation phenomenon occurs in the early stages of (tensile) fatigue, which adds to the life of the material. In our view, an analogous mechanical ageing process can occur in flexural fatigue. A lighter load will permit a longer flex life, thus allowing more time for the orientation to occur.

The specificity with doses of this anomaly may be a result of the competition between radiation-induced crosslinking and chain scission. Nylon 6 fibres will rupture in the proton beam if the dose is high enough; the appearance of the fracture surface (Fig. 8) is smooth, with none of the texture shown in the ordinary tensile fractures (e.g. Fig. 3). Thus, chain scission may predominate over crosslinking at the higher radiation doses. The load under which the fibres were held during the irradiations could enable the crosslinks formed to impart a permanent set to the material. Subsequent testing under light load allows a long flex time during which mechanical ageing can occur. This ageing, combined with a high moisture content which facilitates the rearrangement of interchain hydrogen bonds, could accommodate this set. Thus internal stresses would be reduced and a longer-than- expected flex life achieved.

A possibly related phenomenon is observed in the influence of RH on the flex behaviour as displayed in the failure diagrams (Fig. 9). At the 2.9 g load, there is a general shifting of the fractional failure line toward larger values of flex life when tested at the higher humidity. This condition also obtains at the 4.8 g load until the dose reaches the 43 μC level whereupon the trend dramatically reverses and the higher humidity conditions no longer enhance the flex fatigue properties, but actually result in a shorter flex life. Apparently, the higher load (4.8 g) does not allow for sufficient time of flexing for mechanical conditioning processes to relax internal (set) stresses and the material fails because of the increased level of chain scission present in those materials which had been irradiated more intensively.

As viewed in the SEM, the morphology of the flex fatigue fractures of the proton-irradiated

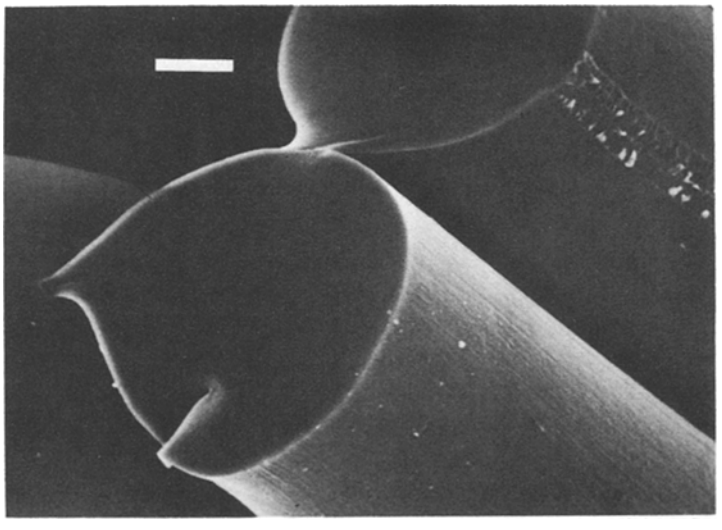

Figure 8 SEM of In-beam Fracture of proton-irradiated nylon 6 fibres (10 μm bar).

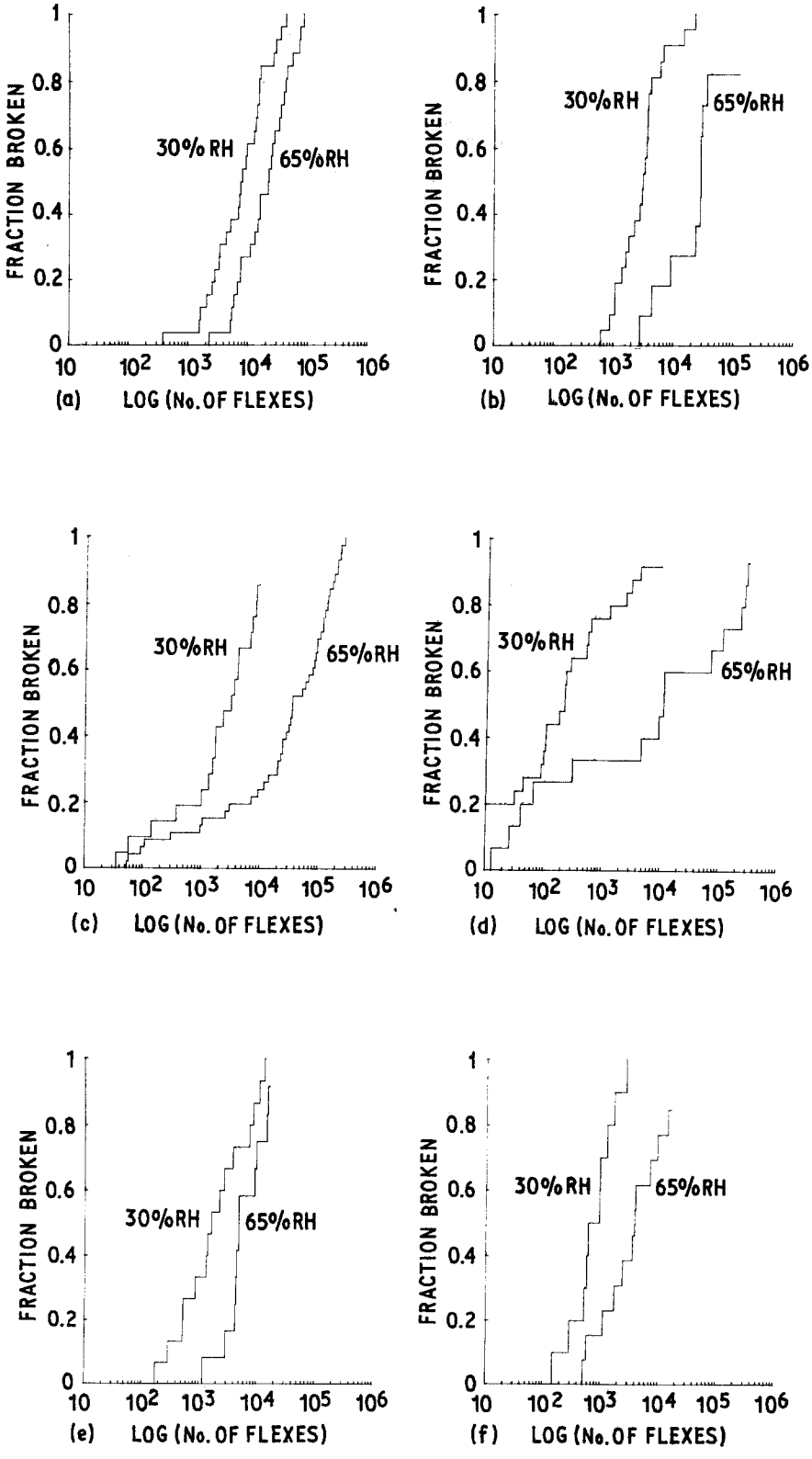

Figure 9 Failure diagrams for proton-irradiated nylon 6 fibres, tested at 21° C and 30% RH or 65% RH; (a–d) 2.9 g load. (a) 12 μC dose; (b) 24 μC dose; (c) 43 μC dose; (d) 76 μC dose. (e–h) 4.8 g load. (e) 12 μC dose; (f) 24 μC dose; (g) 43 μC dose; (h) 76 μC dose.

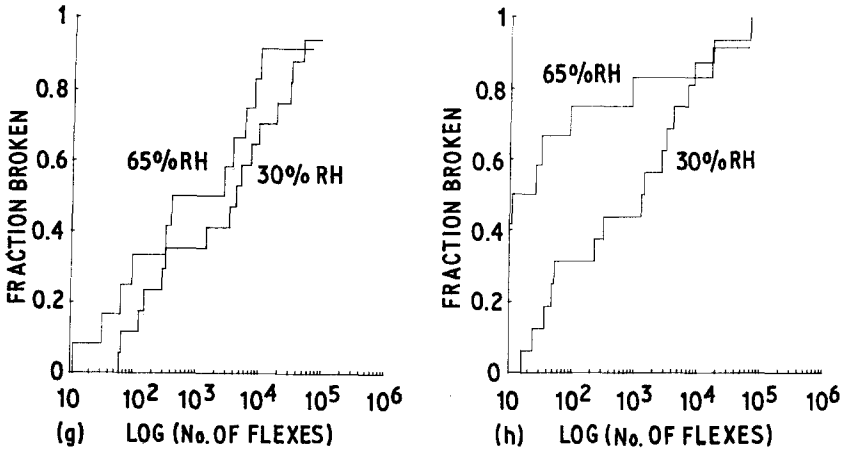

Figure 9 Continued.

material undergoes a progressive modification from a striated, oblique fracture plane for the unexposed material to a relatively smooth, transverse fracture surface when exposed to 76 μC (Figs. 10 and 11). The influence of load and of moisture content was not distinct. One very interesting feature observed in many of the micrographs was the presence of steps on the fracture surfaces (Figs. 12a and b). The nature of this structure resembles that of a kink band formation in polyester under compressive loading ([18] p. 227). In our work, these could be the result of the flexural compression of the material. A contributory factor could derive from morphological changes induced by the irradiation treatments. Using a model such as Prevorsek *et al.*'s [8] to describe the fine structure of the fibre, a step-like fracture morphology may then be a consequence of crystallite faces serving as cleavage planes with some degree of crosslinking in the non-crystalline matrix.

3.3. Gamma irradiation

3.3.1. Tensile properties

Irradiation of nylon 6 with cobalt-60 gamma radiation to the 10 Mrad level reduced the fibre tensile strength and elongation at break (Table III) by about 50%, irrespective of whether the test was conducted in air (65% RH) or in water. A further, more gradual reduction in tensile strength, was attendant upon increased dose, the fibre strength reducing to 15% of its original value at the 60 Mrad dose level. The elongation at break, for samples tested in air, remained essentially constant with doses between 10 and 40 Mrad, whereafter it steadily declined to about 35% of its original value at a 60 Mrad dose. In contrast, when samples were tested wet the extensions at break were essentially constant for all doses.

It can be observed in the SEM of irradiated fibres tensile tested in air (Figs. 13 and 14) that two distinct morphological states exist in gamma

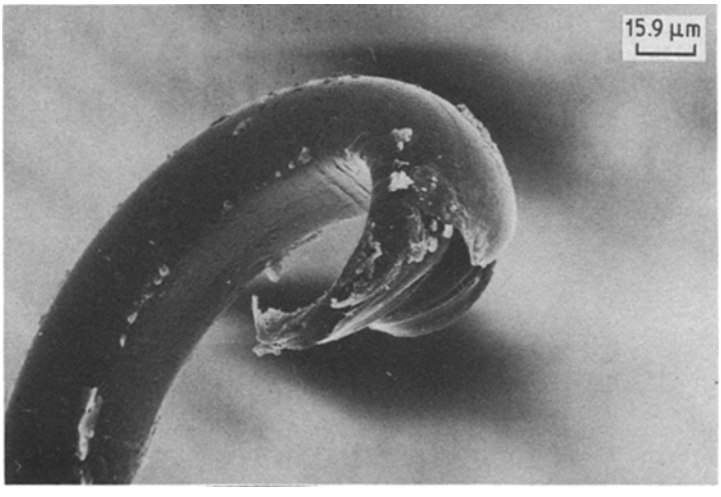

Figure 10 SEM of flex fatigue failure of control for proton-irradiation test series; tested at 2.9 g, 65% RH (16 μm bar).

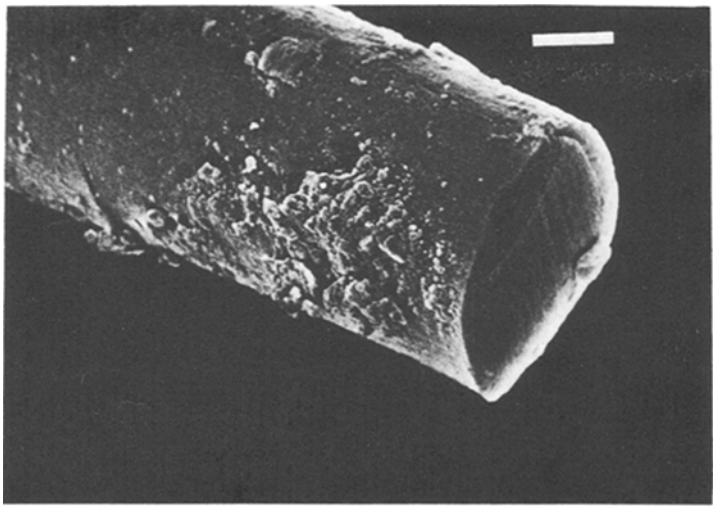

Figure 11 SEM of flex fatigue failure of nylon 6 fibre at 76 μC proton-irradiation dose, tested at 2.9 g, 30% RH (10 μm bar).

irradiated nylon 6 fibres. SEM of this type of gamma-irradiated specimens do not appear to have been published previously. At all doses, there is a core concentric with a double annulus of a material with a very different fracture morphology. Morphological differences within the annulus, though not so dominant, may derive from the fibre skin. The fracture initiation site is apparently a circle circumscribing the fibre; the fracture surface is approximately perpendicular to the fibre axis, as compared with the typical ductile crack fracture of unirradiated nylon 6 (Fig. 1). In general, the annulus morphology consists of radial splitting with rays originating at the core surface and terminating near the fibre surface. The ray termini seem to be a constant distance from the fibre edge, possibly the thickness of the skin on the fibre. The ray origins, on the other hand, vary with dose; i.e. the core becomes smaller with increasing dose. The fracture morphology of the skin and of the core are similar. The appearance of the skin in the irradiated materials may be described as small curds and that of the core as larger curds, approaching gentle undulations.

The presence of these two primary states of the irradiated nylon is found in the fractures of all the mechanical tests performed here; there is, however, a distinction seen between the wet-tested and air-tested samples. It appears from the fractography of wet-tested samples that dissociation can occur at the annulus-core boundary. It can be observed in Fig. 15 that the skin is quite thin in relation to the rest of the fibre, as it separates from the core.

Radiation-induced photo-oxidation reactions are purported to result in the formation of oxygen bridges (ether linkages) as crosslinks [19]. In the case of diffusion with irreversible reaction, as for the oxygen/free-radical reaction, a sharp boundary

TABLE III Gamma radiation effects on the tensile and breaking twist angle (BTA) properties of nylon 6 fibres* (testing temperature 21°C)

Dose (Mrad)	Tensile				BTA (degrees)	
	65% RH†		Wet		65% RH	Wet
	load, g	exten, %	load, g	exten, %		
0	70 ± 3	48 ± 8	63 ± 4	44 ± 6	39 ± 3	40 ± 2
10	34 ± 5	21 ± 2	28 ± 4	18 ± 2	52 ± 1	42 ± 2
20	29 ± 2	22 ± 2	26 ± 2	20 ± 1	51 ± 1	44 ± 2
30	24 ± 2	19 ± 1	27 ± 3	21 ± 3	52 ± 1	46 ± 3
40	18 ± 3	22 ± 4	15 ± 1	20 ± 2	51 ± 1	49 ± 3
50	10 ± 1	11 ± 2	12 ± 1	19 ± 2	52 ± 1	54 ± 2
60	10 ± 1	15 ± 3	12 ± 1	18 ± 2	51 ± 1	54 ± 1

*Standard deviations for a minimum of 10 samples included with the means.
†RH = relative humidity.

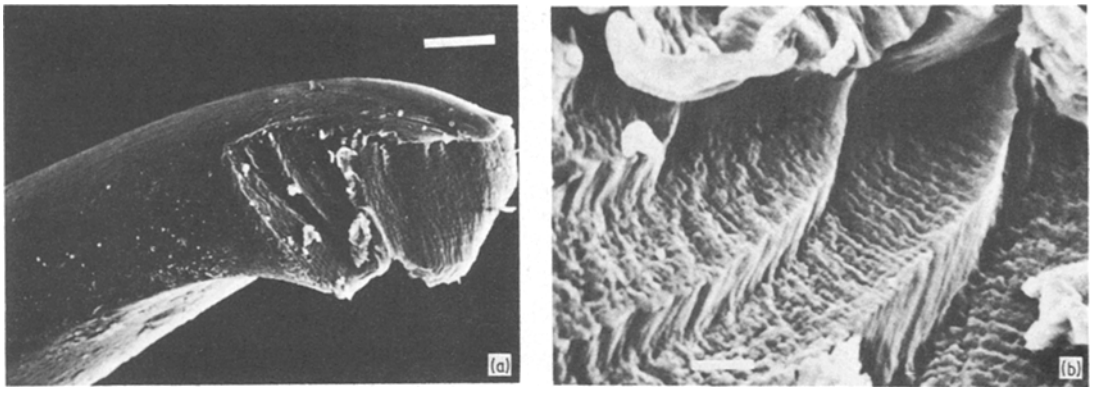

Figure 12 SEM of flex fatigue failure of nylon 6 fibre at 24 μC proton-irradiation dose, tested at 2.9 g, 65% RH. (a) 10 μm bar, and (b) 2 μm bar.

would be expected when the concentration of reactive sites in the polymer is much greater than the normal solubility of the diffusing material in the polymers [22]. Radiation doses of 10 Mrad or greater produce free-radical concentrations considerably higher than the normal oxygen solubility in nylon [11]. It would appear likely then that the annulus is highly crosslinked by oxygen bridges.

It was noted that the shape of the load-elongation curves acquired a distinguishing characteristic as a result of irradiation (Fig. 16). For a sample exposed to a 10 Mrad dose and with the tensile test conducted in air, type A was the curve universally observed, while type B was the only type found if the dose had been 50 or 60 Mrad. Intermediate doses showed a mixture, with the predominance of type A over type B decreasing as the dose increased. However, if the fibre was tested wet, type B was found exclusively for doses as low as 30 Mrad. Some type A curves were found at 20 Mrad and only type A curves were found at 10 Mrad. It is speculated that the step present in the type B load–elongation curve (Fig. 16) derives from the fracture of the skin and ductile propagation in the annulus. It appears that the presence of water decreases the mutual strengthening effect of the skin–annulus and annulus–core interactions, resulting in a further weakening of the irradiated material when wet, and concurrently causing the effect of annulus fracture to be seen in the load–elongation curves at the lower doses. The ultimate influence of the radiation-induced crosslinks is presumably to stiffen the annulus and thus reduce its extensibility relative to the core.

3.3.2. Breaking twist angle

The BTA in air (Table III) increases markedly from the control value of 39° to 52° at 10 Mrad

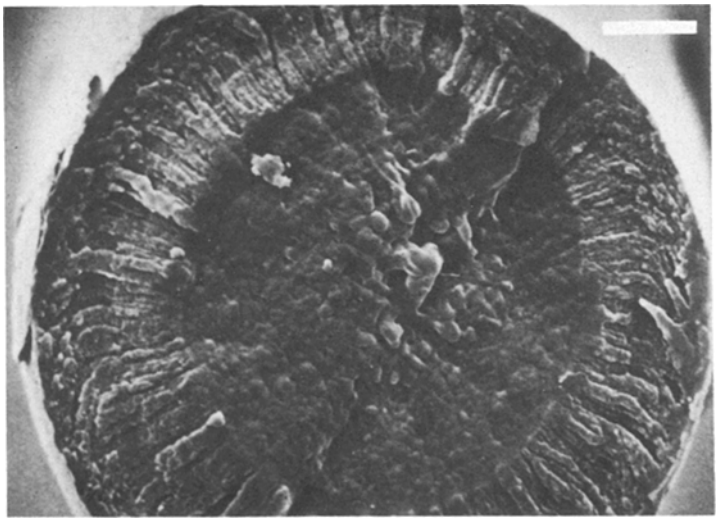

Figure 13 SEM of tensile fracture of 10 Mrad gamma-irradiated nylon 6 fibre, fractured in air (5 μm bar).

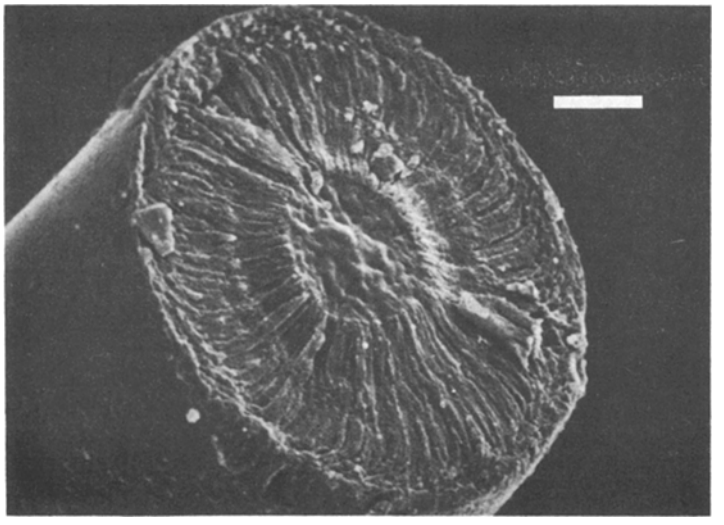

Figure 14 SEM of tensile fracture of 50 Mrad gamma-irradiated nylon 6 fibre, fractured in air (5 μm bar).

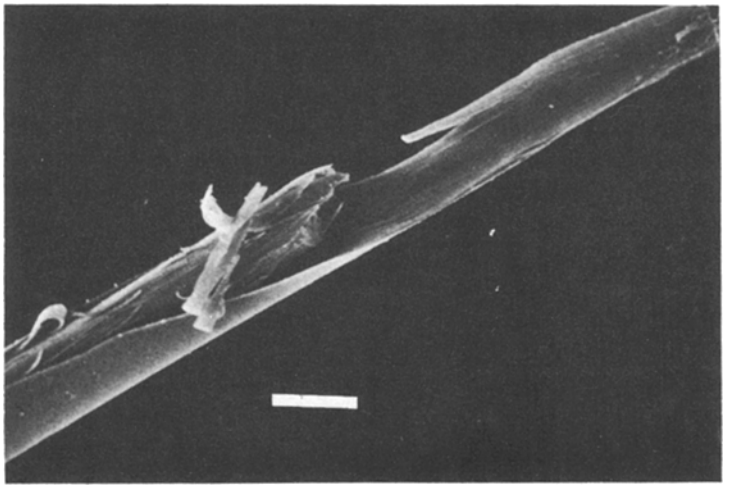

Figure 15 SEM of tensile fracture of 40 Mrad gamma-irradiated nylon 6 fibre, fractured in water (50 μm bar).

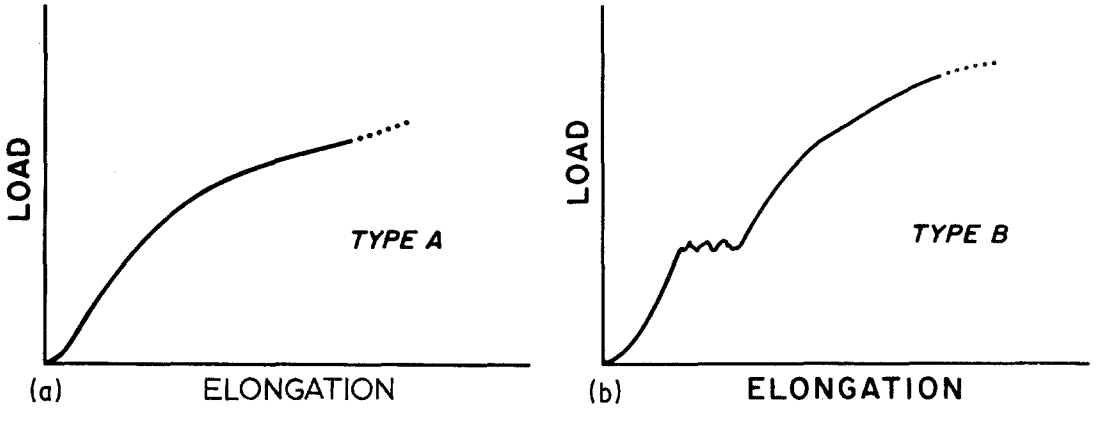

Figure 16 Different types of tensile curves observed during testing of gamma-irradiated nylon 6 fibres.

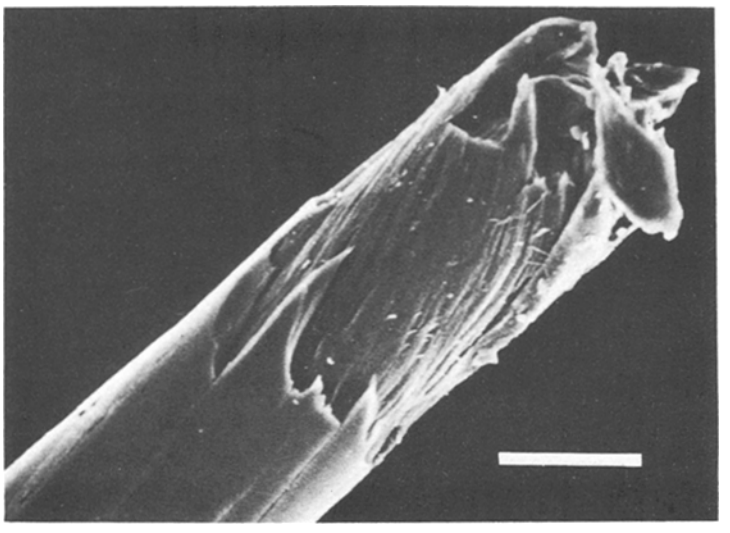

Figure 17 SEM of BTA fracture of 30 Mrad gamma-irradiated nylon 6 fibre, fractured in air (20 μm bar).

and remains essentially constant with further dose increase. A gradual monotonic increase with increasing dose is manifested in the wet BTA values.

The SEM of the BTA fractures both in air and in water also show the skin-core effect (Figs. 17 and 18).

3.3.3. Flex tests

The mean flex lives (Table IV) showed a dramatic dependence on load at the lowest dose: at both humidity levels, the 4.8 g load reduced the mean life to a few hundred flexes. On the other hand, at a 2.9 g load the mean flex life was about 50 000 at 65% RH and 85 000 at 30% RH. For the higher load, irrespective of humidity, the flex life continued a slow decline with increasing dose.

In contrast to the effect of humidity found for the proton irradiations (Table II), it was found that the gamma irradiated material had a lower flex life at the higher humidity (Table IV). The mean flex life at the 20 Mrad dose using a 2.9 g load (Table IV) indicates an opposite effect, that is, an increased flex life at the higher moisture content. However, the failure diagrams (Fig. 19b) show an overlap, not a clear distinction. Using the failure diagram as a test of significance, then, belies the differences in mean flex life at 30 and 65% RH at this load, and we assert the trend of lower mean flex life at higher relative humidity for gamma irradiated materials to be general. We believe that an increase in moisture content of the fibre, occasioned by exposure to a higher RH, will serve to weaken the skin/core interface hydrogen bonds. It

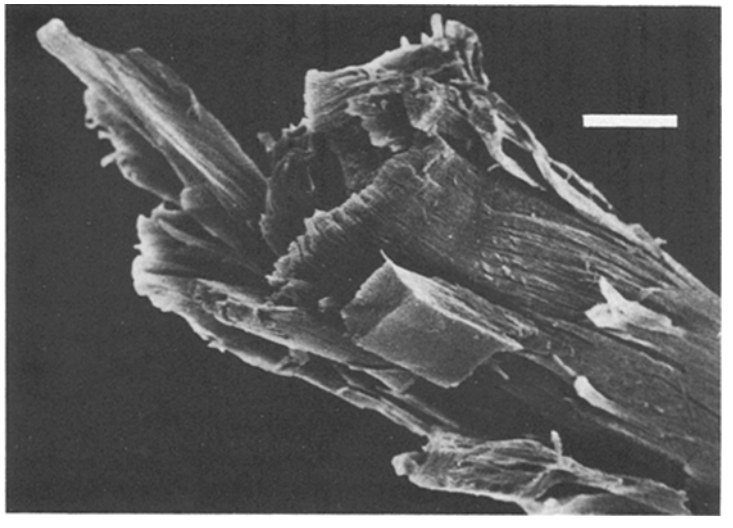

Figure 18 SEM of BTA fracture of 50 Mrad gamma-irradiated nylon 6 fibre, fractured in water (10 μm bar).

TABLE IV Effect of gamma radiation on the flex life of nylon 6 fibres conditioned at 30% RH or 65% RH at 21° C with selected applied loads. Mean flex lives (× 1000)

Dose (Mrad)	30% RH*		65% RH	
	2.9 g	4.8 g	2.9 g	4.8 g
0	–	28.9	–	306
10	85	0.62	50.6	0.27
20	14	0.32	34.3	0.07
30	8.8	0.13	1.3	0.008
40	0.30	0.082	0.21	0.002
50	0.038	0.002	0.028	–

*RH = relative humidity.

can be observed in SEM (Fig. 20) that the skin is stiff and under these conditions it readily separates from the core. At the lower humidity levels, both the integrity of the skin and its attachment to the core are better. Also, we have concluded from tensile and BTA measurements that the core becomes more brittle with gamma irradiation [6]. We suggest then that the skin participation in the flex fatiguing process is greater at the lower than at the higher humidity. Raising the humidity causes some weakening and dissociation of the hydrogen bonds knitting the skin together and the skin to the core. This favours the formation of cracks on the fibre which may serve as nucleation centres, and places additional demands on the core to maintain the fibre integrity while flexing. The core, however, is embrittled and thus the ultimate effect of the increased fibre moisture content is to lower the flex life.

Some differences in flex fatigue processes occurring in the irradiated materials can be inferred from an examination of SEMs. There is a progression from ductile to brittle fracture with increasing dose or with energetics of the test parameters, i.e. load and/or mositure content. Fig. 21 is comprised of four parts, corresponding to the four combinations of load plus relative humidity. Fig. 21a, that of the lowest energetics (2.9 g and 30% RH), and to a lesser extent Fig. 21b, show a fibrillar fracture, with longitudinal splitting. The fracture becomes progressively more of the brittle type in Fig. 21b, c, and d. At high doses the fracture was found to have a brittle appearance under all test conditions [6].

The SEM of the gamma irradiated material also showed the formation of transverse cracks at periodic intervals along the fibre after being mechanically tested. Fig. 22 shows a dramatic instance of segmentation of the skin into regular "platelets". Other, less dramatic, instances of regular segmentation were also observed [6]. The periodicity may be an effect of drawing. While exploring stress-ageing of nylon 6,10, Richards and Kramer [23] noted "a curious 'ringing' of the stress following the yield point", while drawing filaments at a critical strain rate, together with an opaque patch occurring periodically along the length of the filament. The ringing was seen when the load, with a fairly uniform period, cyclically rose to a maximum and precipitously dropped by approximately 10 to 15%. The ringing and the opaque patches were attributed to excessive adiabatic heating at the neck during drawing. The periodic opaque patches were assumed indicative of the presence of microvoids in the structure of the drawn filament. In another paper [24], no cracking of nylon 6 irradiated with ultraviolet light was evident on undrawn filaments while periodic cracking, similar to that seen here, was found with drawn filaments. The existence of cracks was shown, in that instance, to be associated with residual stress in the material. The periodicity of the cracks may be a result of the ringing phenomenon associated with drawing as noted above.

The radiation-chemical process which may contribute to the cracking and platelet formation in Fig. 22, is the formation of the oxygen bridges in the outer layers of the material [19]. In this way, the regions between the thermal runaway sections (the necks), which are weakened by the microvoids, are stiffened. Applied stress, particularly in a shear mode as by twisting, would conceivably cleave this "skin" along these microvoid-replete areas.

4. Summary and conculusions

The result of irradiation of nylon 6 fibres with the electromagnetic and charged particle radiations as employed in this study is a progressive deterioration of ultimate tensile properties, an increase in brittleness (as evidenced by an increasing BTA), and a decreasing flex life, with increasing dose. The effects are most pronounced in the first interval of dose; i.e. 10 Mrads gamma irradiation in air and 12 μC (approximately 60 Mrads) of high energy protons in vacuum. The deterioration of these mechanical properties generally levels off with subsequent dose increases. An exception was noted in the data of the proton-irradiations. The flex life of the material irradiated at the 43 μC level when tested at 65% RH and 2.9 g load was

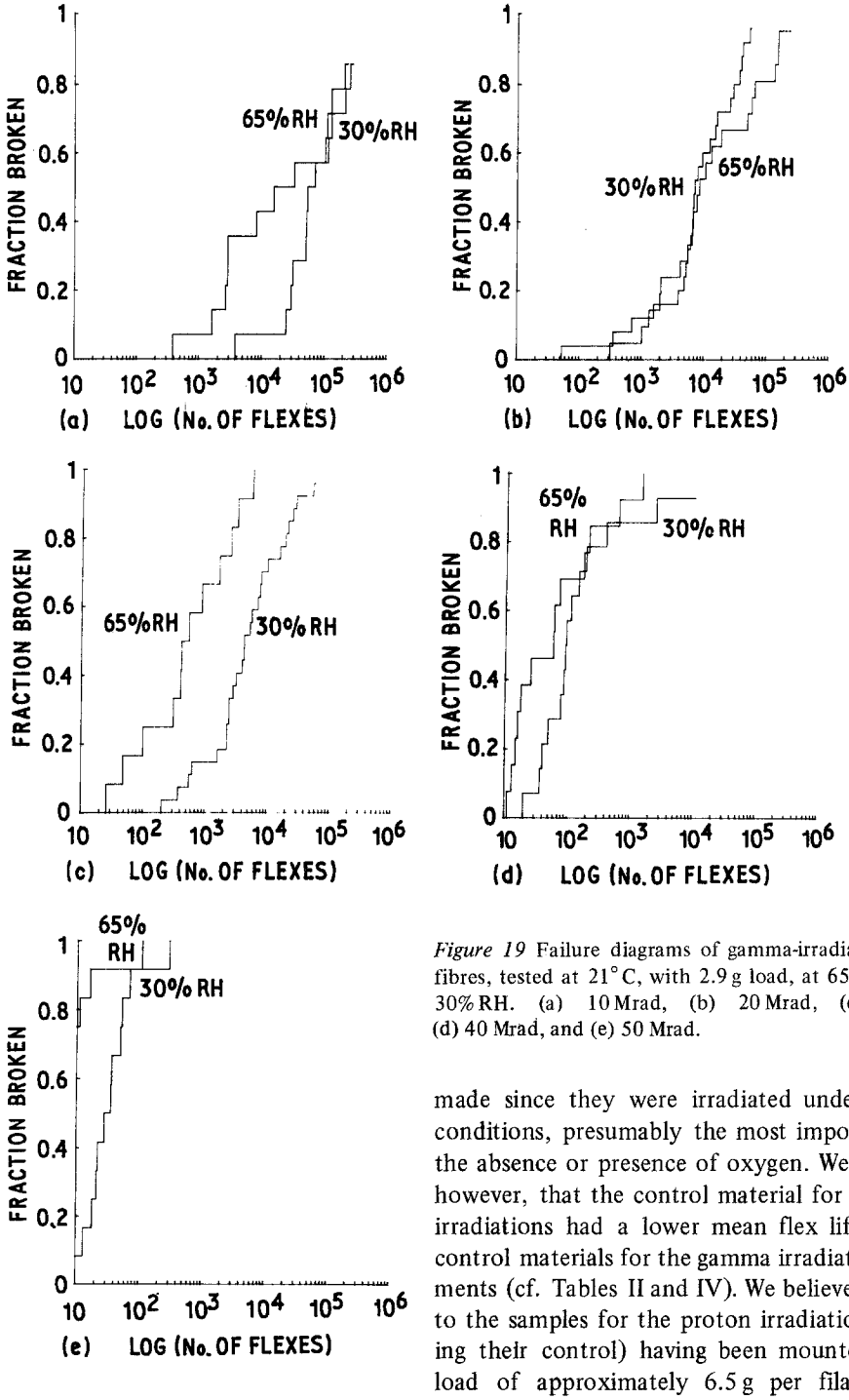

Figure 19 Failure diagrams of gamma-irradiated nylon 6 fibres, tested at 21° C, with 2.9 g load, at 65% RH and at 30% RH. (a) 10 Mrad, (b) 20 Mrad, (c) 30 Mrad, (d) 40 Mrad, and (e) 50 Mrad.

markedly higher than the 24 μC material, under the same conditions. A possible explanation is that the increased moisture present acts essentially as a plasticizing agent. The longer life afforded by a lower applied load, allowed sufficient time for the moisture to penetrate the material.

Direct comparisons of flex life of the proton irradiated and gamma irradiated samples cannot be made since they were irradiated under different conditions, presumably the most important being the absence or presence of oxygen. We may note, however, that the control material for the proton irradiations had a lower mean flex life than the control materials for the gamma irradiation experiments (cf. Tables II and IV). We believe this is due to the samples for the proton irradiations (including their control) having been mounted under a load of approximately 6.5 g per filament, and maintained at the resulting constant strain for at least three weeks prior to testing. A stress-induced orientation, or strain-ageing, phenomenon [23] may have occurred which we speculate results in the lower flex life. The materials used in the gamma radiations were not subjected to a similar history: they were always in a relaxed state, including during their radiation treatment.

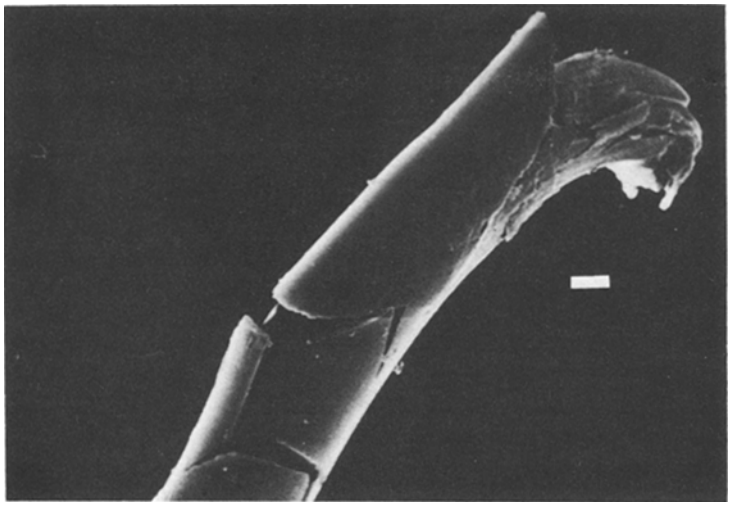

Figure 20 SEM of flex fatigue failure of 40 Mrad gamma-irradiated nylon 6 fibre tested at 4.8 g, 65% RH (10 μm bar).

The presence or absence of oxygen during the radiation treatment is most likely the singular distinguishing aspect between the two high energy radiations employed in this study. The annulus/core morphology found in the gamma irradiated materials was not in evidence for material irradiated with protons in vacuum. The morphology of the proton-irradiated tensile breaks showed a fractography by SEM with the characteristics of a brittle material. Flex fatigue fracture surfaces often displayed step-like formations characteristic of kink bands.

The more intense, high energy radiations may be used to develop an accelerated ageing pro-

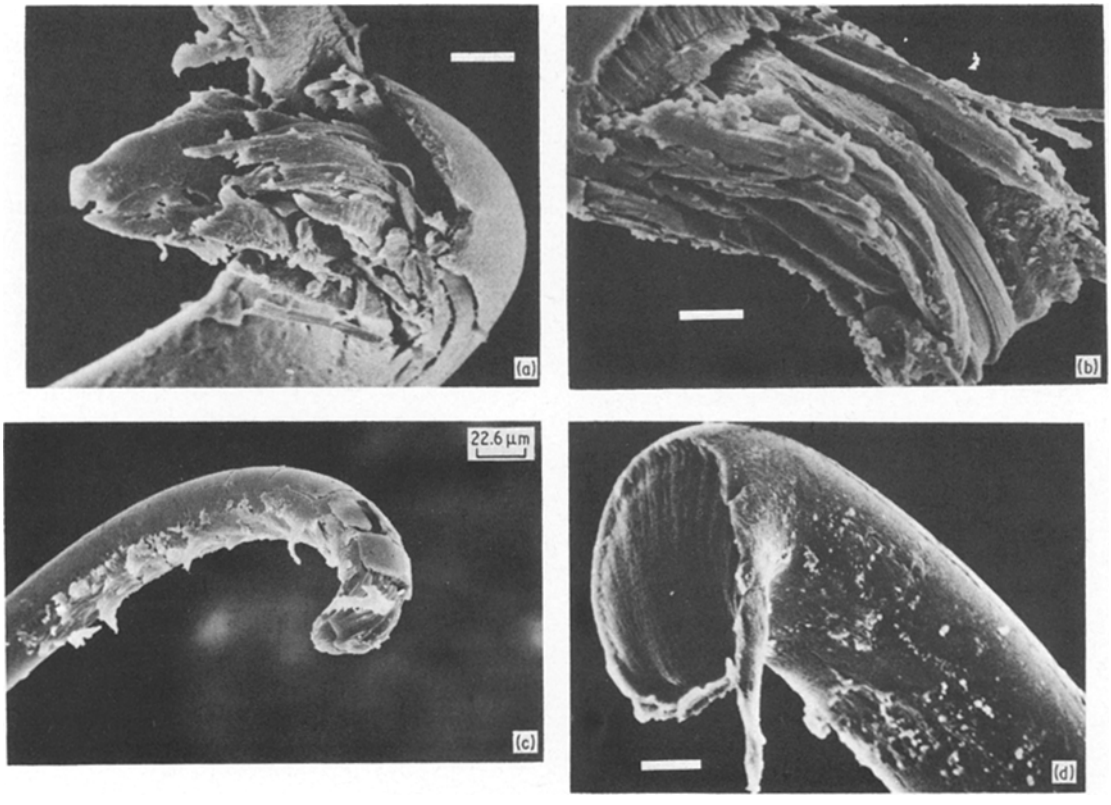

Figure 21 SEM of flex fatigue failure of 10 Mrad gamma-irradiated nylon 6 fibres tested at: (a) 2.9 g, 30% RH (10 μm bar), (b) 2.9 g, 65% RH (10 μm bar), (c) 4.8 g, 30% RH (23 μm) bar), and (d) 4.8 g, 65% RH (10 μm bar).

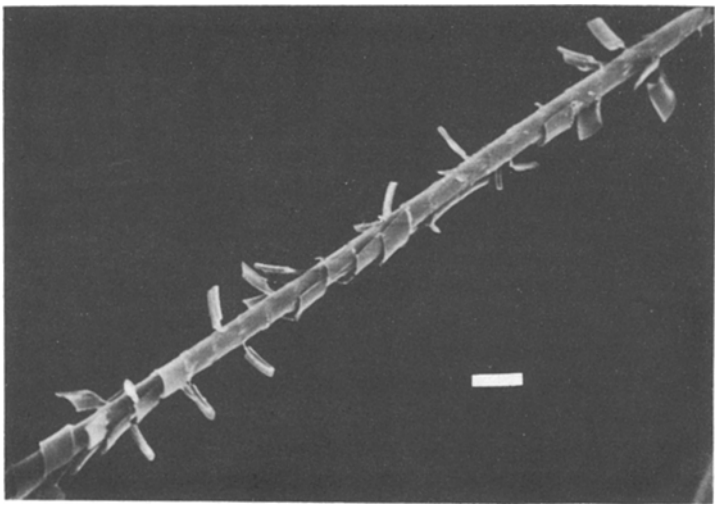

Figure 22 SEM showing the regular segmentation of the skin on fractured 60 Mrad gamma-irradiated nylon 6 fibre, BTA tested wet (50 μm bar).

gramme. Using tensile strength as a rough indication of the ageing effects of radiation treatments, our data here, combined with that of an earlier sunlight study [4], have the following implications. A two-month exposure (air) to summer sunlight (Davis, CA) results in a strength which is approximately the same as that resulting from a 1.0 min (12 μC) irradiation with 4.5 MeV protons (vacuum), or ten hours (10 Mrads) irradiation with Cobalt-60 gamma radiation (air). In general, the other mechanical tests show similar rapid deterioration. There were distinctive differences in flex fatigue behaviour between the three treatments, which mandate further study.

References

1. M. S. ELLISON and H. P. LUNDGREN, *Text. Res. J.* **48** (1978) 692.
2. S. H. ZERONIAN and M. S. ELLISON, *J. Appl. Polym. Sci.* **24** (1979) 1497.
3. M. S. ELLISON, L. D. FISHER, K. W. ALGER and S. H. ZERONIAN, *ibid* **27** (1982) 247.
4. M. S. ELLISON, Y. FUJIWARA and S. H. ZERONIAN, in "Physicochemical Aspects of Polymer Surfaces", edited by K. L. Mittal (Plenum Press, New York, 1983) p. 843.
5. F. A. MAKHLIS, "Radiation Physics and Chemistry of Polymers" (Wiley, New York, 1975).
6. M. S. ELLISON, PhD thesis, University of California, Davis (1982).
7. D. C. PREVORSEK, W. J. LYONS and J. C. WHITWELL, *Text. Res. J.* **33** (1973) 963.
8. D. C. PREVORSEK, P. J. HARGET, R. K. SHARMA, and A. C. REIMSCHUESSEL, *J. Macromol. Sci. Phys.* **B8** (1973) 127.
9. P. D. FRAYER, J. L. KOENIG and J. B. LANDO, *J. Macromol. Sci.-Phys* **B6** (1972) 129.
10. J. ZIMMERMAN, *J. Polymer Sci.* **XLVI** (1960) 151.
11. *Idem*, in "The Radiation Chemistry of Macromolecules", Vol. 2, edited by M. Dole (Academic Press, New York, 1973) p. 127.
12. D. T. GRUBB, *J. Mater. Sci.* **9** (1974) 1715.
13. D. C. PREVORSEK and Y. D. KWON, *J. Macromol. Sci.-Phys.* **B12** (1976) 447.
14. A. PETERLIN, *ibid.* **B19** (1973) 401.
15. R. D. VAN VELD, G. MORRIS and H. R. BILLICA, *J. Appl. Polym. Sci.* **12** (1968) 2709.
16. J. W. S. HEARLE, *Text. Mfr.* **99**: Jan/Feb, 14; Mar, 12; May, 20; July, 44; Aug, 40; Sept, 16; Oct, 40; Nov, 12; Dec, 36 (1972); **100**: Jan, 24; Mar, 24; April, 34; May, 54; June, 44 (1973).
17. H. H. KAUSCH, "Polymer Fracture" (Springer-Verlag, New York, 1978).
18. D. C. BASSETT, "Principles of Polymer Morphology" (Cambridge University Press, Cambridge, 1981).
19. B. RANBY and J. F. RABEK, "Photodegradation, Photooxidation, and Photostabilization of Polymers" (John Wiley and Sons, New York, 1975).
20. W. SBROLLI, in "Man-Made Fibre, Science and Technology", Vol. II, edited by H. F. Mark *et al.* (Interscience, New York, 1968) p. 227.
21. I. NARISAWA, M. ISHIKAWA and HIROYUKI OGAWA, *J. Polym. Sci.: Polym. Phys. Ed.* **15** (1977) 1055.
22. J. CRANK, "The Mathematics of Diffusion" (Oxford University Press, London, 1956).
23. R. C. RICHARDS and E. J. KRAMER, *J. Macromol. Sci.-Phys.* **B6** (1972) 229.
24. Y. FUJIWARA and S. H. ZERONIAN, *J. Appl. Polym. Sci.* **27** (1982) 2773.

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