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The Fracture of Nylon 66 Yarns Which Have Been Exposed to Light

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Synopsis

It has been shown from earlier work in this laboratory that the fracture morphology of light-degraded, delustred nylon is different from that of unexposed, delustred nylon. This paper illustrates the effects on breaking strength, extension, and morphology of delustred and bright nylon yarns when exposed to daylight for different lengths of time and discusses what factors have influenced the breaking behavior of the samples. The scanning electron microscope (SEM) has been used to examine the broken filaments and has revealed a wealth of detail which would have been impossible to detect in a light microscope. Nylon 66, 17 dtex, semidull monofil was used throughout the initial experimental work and was exposed to daylight, from behind glass, for up to a maximum of 24 weeks during both the summer and winter months. Samples were removed after set exposure periods and tested to break on an Instron testing machine. The same monofil yarn was exposed before a xenon lamp to enable comparisons to be made between samples degraded by normal daylight and accelerated weathering conditions. Further samples of bright and dull nylon 66 yarns, exposed to daylight in Florida, have also been examined.

INTRODUCTION

Previous studies by Hearle and Cross[1] have shown that tensile failure of nylon gives a fracture morphology consisting of a V-notch leading to a catastrophic failure region, as illustrated schematically in Figure 1 and shown later in Figure 3. The notch is mirrored on the opposite end, while the catastrophic region is mated. The mode of formation of this type of fracture is ductile crack propagation: the deepening penetration of the crack causes higher stresses on the remaining part of the fiber, which extends by plastic drawing and so opens up the crack. Eventually, the stress in the unbroken part becomes large enough to cause complete failure.

In an early study, we examined a sample of nylon which had been in the laboratory for some long period of time, during which it had been exposed to light. The tensile fracture morphology of this fiber, shown in Figure 2, was strikingly different, being composed of many separate turrets over the whole fiber cross section. This led us to make a controlled investigation of the effects of exposure to light on the fracture morphology of nylon fibers. It has been known, almost since the first introduction of nylon fibers, that they suffered a loss of strength on exposure to light. For example, Coleman and Peacock[2] reported that nylon fabric strength fell to about 14% of its initial value after exposure for two months

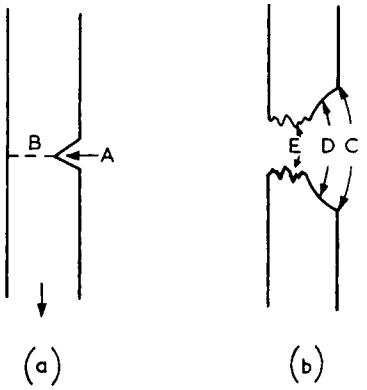


Fig. 1. Schematic illustration of crack propagation in nylon.

in Florida or Arizona. The loss in strength was not as great if ultraviolet radiation was excluded. It was also known[3] that fibers containing titanium dioxide as delustrant were affected more than bright fibers. This was related to the electronic spectra of titanium dioxide by Bevan et al.[4] Since the early days of nylon, light-degradation inhibitors have been developed, and these may now be added to commercial nylon fibers. The incidence of light degradation is thus less common than it once was, though it can still be a problem in particular applications.

EXPERIMENTAL

Choice of Method

The magnitude of the strength loss depends on various factors. It has been established that the important factors are (a) the amount of delustrant present

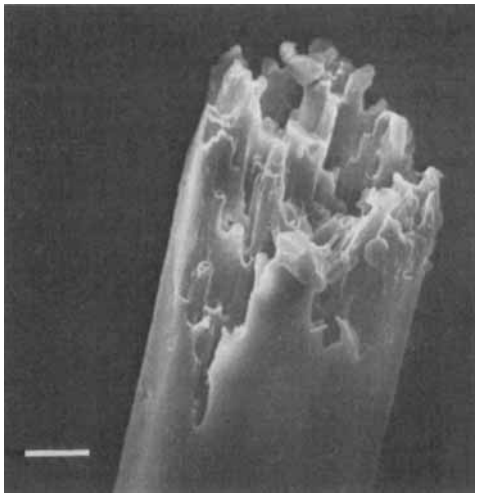


Fig. 2. Light-degraded nylon. Bar ≡ 10 μm.

in the nylon; (b) the light source; (c) whether exposed directly to the light source or from behind glass; (d) exposure time; and (e) filament linear density.

One of the most important factors is the wavelength of the light source. Sunlight contains a broad band of wavelengths, including ultraviolet, the small band of visible light, and the infrared region. It is, however, the effects of ultraviolet light, λ = 290 to 400 nm, that are the primary cause of radiation damage to fiber products. Wavelengths of light above 400 nm may help to accelerate ultraviolet degradation by increase in fiber temperature, or they may cause heat degradation, but these are only minor compared with the effects of ultraviolet exposure.[3] Light sources rich in ultraviolet are sunlight and accelerated test lamps (e.g., Xenotest and carbon arc lamps), while incandescent and fluorescent lamps are low in ultraviolet radiation. Degradation also occurs in other fibers such as polyester and rayon and, to a lesser extent, in acrylic fibers.

It was realized at the beginning of the research that experiments on the photodegradation of nylon would run for some considerable time; and, as this formed only a small segment of the general research program, limits had to be placed on the amount of work undertaken. For these reasons, certain factors had to be considered.

Light Source. Differences of opinions have been expressed on the validity of accelerated weathering tests in comparison with natural conditions[3] of direct exposure to sunlight. So it was decided to expose the sample to sunlight allowing for the longer exposure time and to do a few exposures on the Xenotest apparatus at a later date.

Method of Exposure. The results of years of exposure testing of fibers have shown that the rate of deterioration in strength is greatest when the sample is exposed directly to the sunlight. Samples exposed under glass have a higher strength retention for a given exposure time when compared with directly exposed samples. This is because ordinary window glass filters out the shorter, more harmful, ultraviolet rays in sunlight. However, direct exposure means direct exposure to all weather conditions: rain, wind, and dust. In order to have a more controlled environment, our specimens were exposed to sunlight from behind the laboratory windows. This reduced the degrading effects of sunlight but had the advantage of keeping the specimens clean and free from particles of dirt which are clearly seen in the SEM and can cover interesting detail in the fracture surface.

Type of Fiber Exposed. The diameter of the fiber has an effect on light degradation of nylon; a finer-diameter filament degrades more quickly than a coarser one. Also the amount of titanium dioxide present in the fiber has a significant effect on strength loss. To simplify test conditions, 17 dtex, semidull ICI nylon 66 monofil was used in the main series of tests.

Experimental Details

The 17 dtex monofil was chosen as being (at the time) a typical example of nylon produced for the hosiery trade and, being fairly coarse, it was easier to handle during specimen preparation and to examine in the SEM. For each exposure period, approximately 110 lengths of the monofil were mounted straight and without tension on cleaned black card and sealed in polythene bags. The cards were placed inside shallow photographic paper boxes and sealed to the window, with the filaments vertical. In this way, the samples were not in direct

contact with the window surface, thus preventing contact with any moisture condensation and also being kept free of dust. The first exposures were on a window facing approximately west; but during the summer of 1971, samples were exposed at three windows facing approximately south, west, and north (more exactly S.S.E., W.S.W., and N.N.W.). The samples were exposed for set periods of two days, three weeks, six weeks, 12 weeks, and 24 weeks during both the summer and winter months.

After the allotted exposure period, each set of monofils was removed from the window and kept in a dark place until strength testing. The specimens were broken on an Instron tensile tester, 100 filaments from each sample being tested, and their load/elongation curves plotted. Of the hundred breaks, a few of the high-, low-, and average-strength breaks were kept for examination in the SEM. The Instron settings were standardized throughout the experiment at a gauge length of 5 cm and a strain rate of 1.67×10^{-2} sec^{-1}. All tensile testing was carried out in a standard testing atmosphere of 65% R.H. and 20°C.

The broken fiber ends were mounted in a specially adapted specimen stub[5] capable of holding several ends in an upright position. The stubs were coated by thermal evaporation with either silver or gold (depending on the delay before examination in the SEM) in a vacuum coating unit using a rotating stub holder for maximum coverage. Both ends of the break were examined in the SEM at an accelerating voltage of 5 kV.

RESULTS

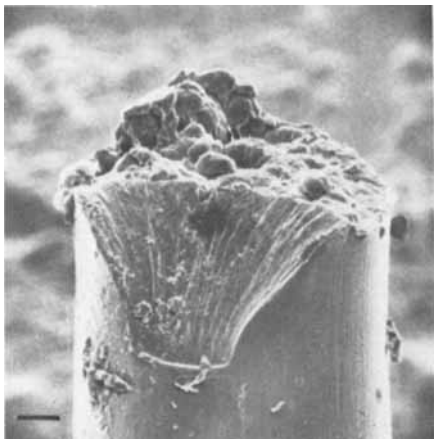
SEM Examination of Control Breaks

Although the usual form of tensile fracture of nylon fibers is that shown in Figure 1, variant forms have sometimes been found in the control tests in this investigation and in other concurrent studies. Examples are shown in Figure 3. Breakage starting from a line, either perpendicular as in Figure 3a or angled as in 3b, and breakage starting from multiple cracks, as in Figure 3c and d, are fairly common, but breakage starting internally, as in Figure 3e, is extremely rare. In all these examples, the basic mechanism of ductile crack growth followed by catastrophic failure is obvious. In the breaks starting internally, the crack develops as a hollow cone, mirrored by a similar cone on the opposite face.

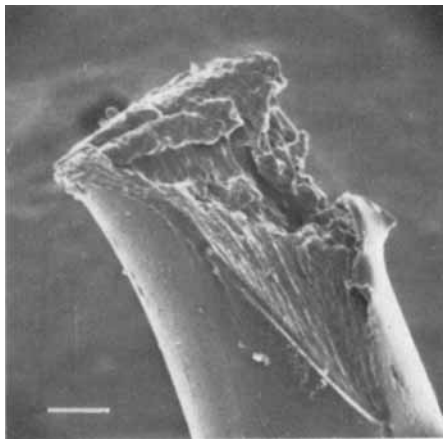
SEM Examination of Broken Light Exposed Fibers

After two days of exposure during the summer months, evidence of photodegradation of nylon can be detected in the fractured end, Figure 4a; small holes are present in the ductile crack region of the fracture. As the nylon is exposed for longer periods of three, six, 12, and 24 weeks during the summer, Figure 4b–e, respectively, the holes become more pronounced and the fracture region begins to break up into small turret-like formations, Figure 5. These turrets contain one or more holes and most have a funnel-shaped rim. This fanning out of the holes is very similar in appearance to the ductile region in the normal fracture and particularly to the internal break of Figure 3e.

In many of the holes seen in the breaks, a small particle, presumably of titanium dioxide, can be seen, Figure 6. These particles have been analyzed using



(a)



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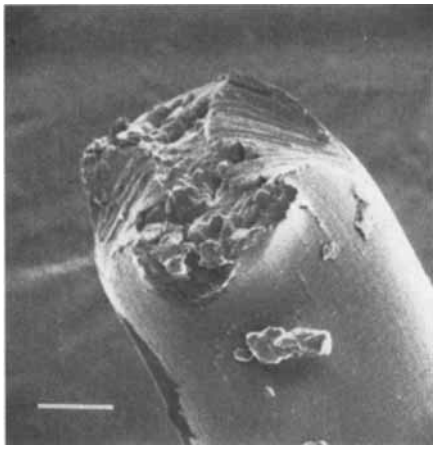

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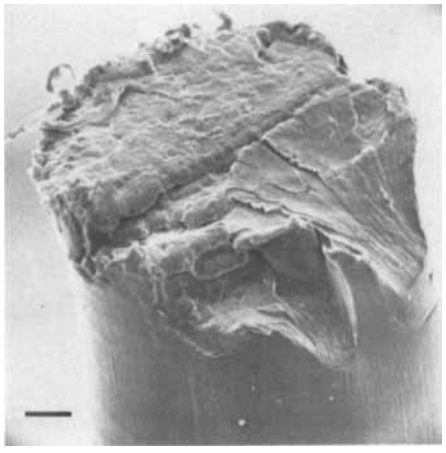
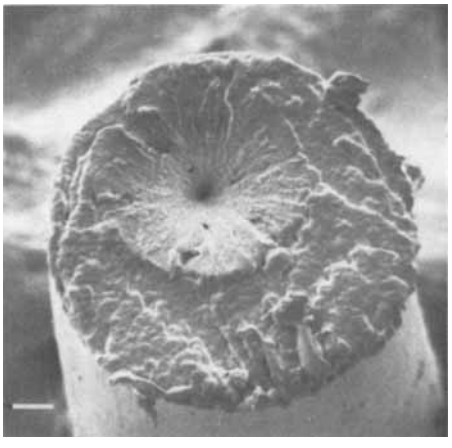


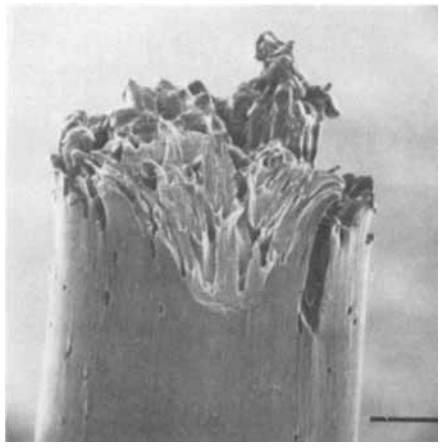
(d)



(e)

Fig. 3. Tensile fractures in nylon: bar ≡ (a) 5 μm; (b) 5 μm; (c) 10 μm; (d) 5 μm; (e) 3 μm.

(a)



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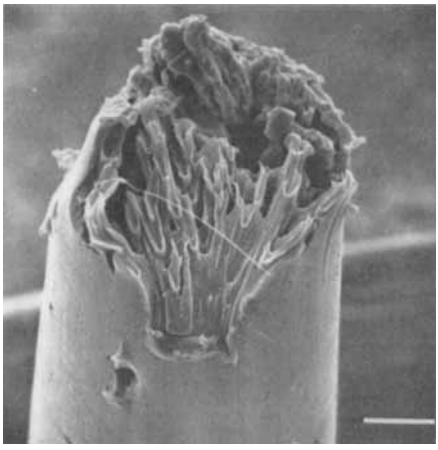

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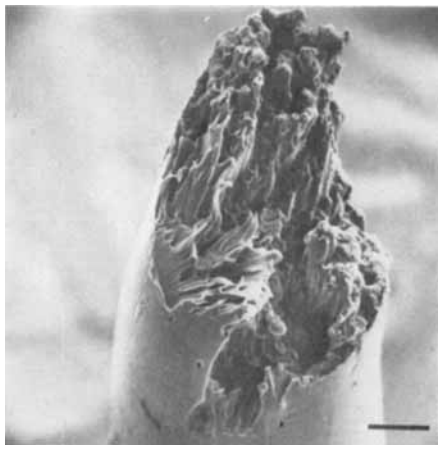

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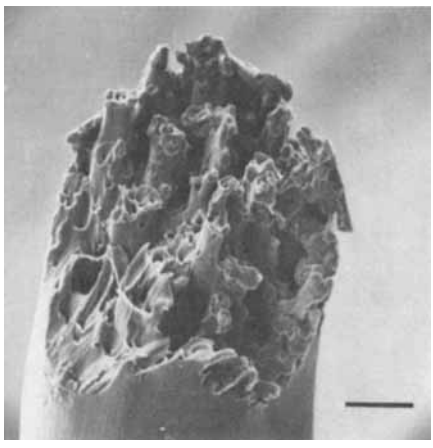


(e)

Fig. 4. Tensile fracture of delustred nylon 66 monofil after (a) 2 days, (b) 3 weeks, (c) 6 weeks, (d) 12 weeks, and (e) 24 weeks of exposure to daylight during the summer. Bars = 10 μm.

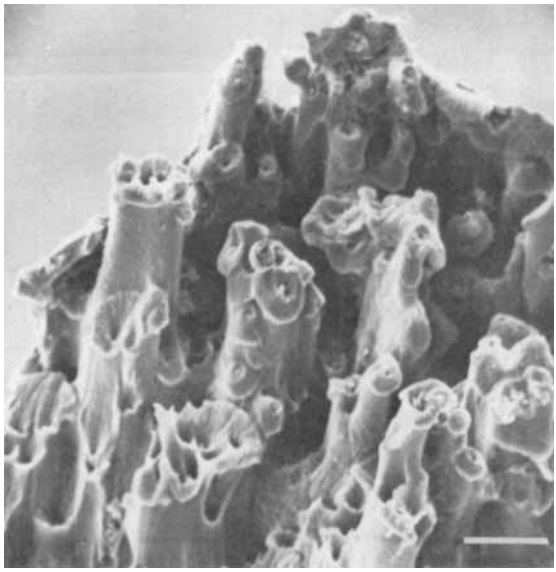


Fig. 5. Turret-like formations in tensile fracture of delustred nylon monofil exposed for 24 weeks during the summer. Bar ≡ 5 μm.

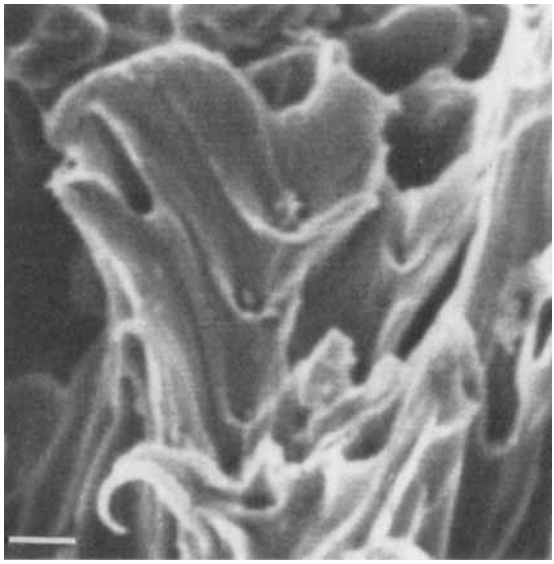


Fig. 6. Titanium dioxide aggregates in funnel-shaped holes. Bar ≡ 2 μm.

an Ortex energy-dispersive x-ray analyzer unit fitted to an S600 SEM provided by the courtesy of Cambridge Scientific Instruments Limited. When the analyzer is focused on a particle, the α and β peaks can be detected for titanium; but away from the particles, no titanium is found, as shown in Figure 7.

In addition to holes visible in the interior on the crack region of the fracture, holes can be seen on the surface of filaments exposed to light, Figure 8.

Another way of showing up holes in filaments is by observing the surface of the shear crack which runs along the filament in tensile fatigue failure. Figure

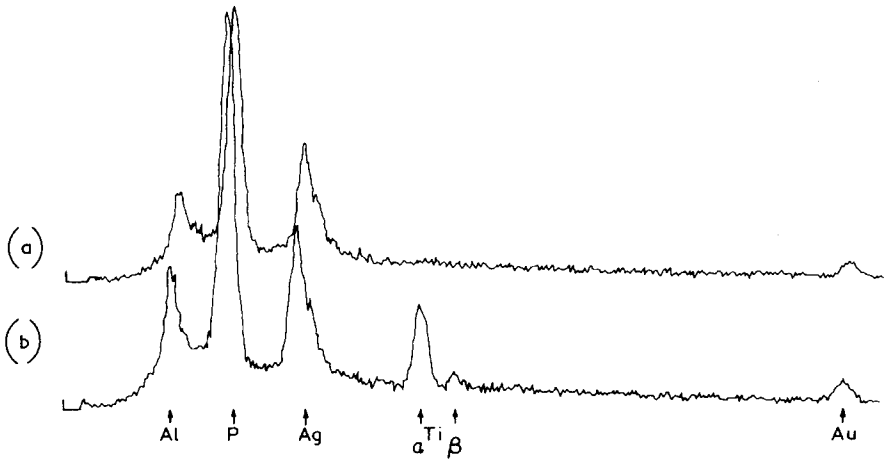


Fig. 7. X-Ray analysis of titanium dioxide aggregate in hole.

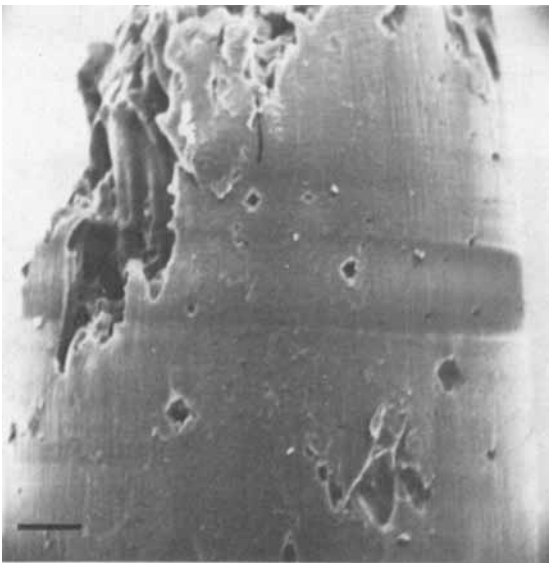


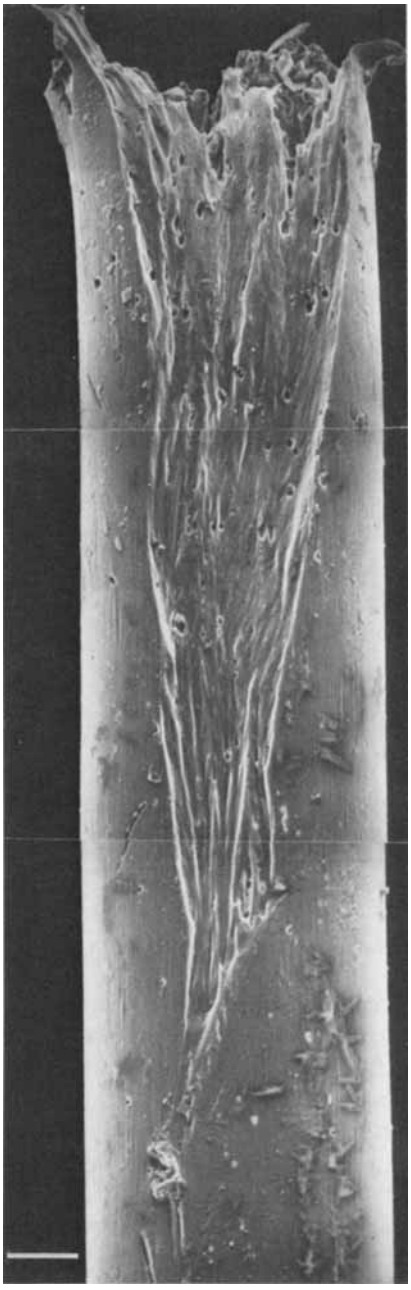
Fig. 8. Holes in the surface of light-degraded, delustred nylon 66 monofil. Bar ≡ 5 μm.

9a shows such a surface, and Figure 9b, a magnified view of some of the holes in the same surface. The opposite end of a fatigue break, Figure 9c, has a long tongue leading to a final failure region, shown in enlarged view in Figure 9d. The fatigue failure of light-degraded nylon is thus similar to that found in normal nylon, as reported by Bunsell and Hearle,[6] except that the tongues are usually shorter, and close examination of the final break regions shows the same type of turret-shaped structure as in tensile breaks. This is also reported in a further paper on fatigue failure of synthetic fibers by Bunsell and Hearle.[7]

Differences Between Summer and Winter Exposures

The effect of light degradation on fracture morphology is not so severe for samples exposed during the winter months, Figure 10a and b (six and 24 weeks

exposure, respectively), as it is on those exposed in the summer for the same lengths of time and shown in Figure 4c and e. The occurrence of holes and the breakup into separate fracture regions is much less marked. This would be expected since during the winter months the daylight hours are shorter and the intensity of the sunlight, and particularly the ultraviolet light, is lower.



(a)

Fig. 9 (*continued*)

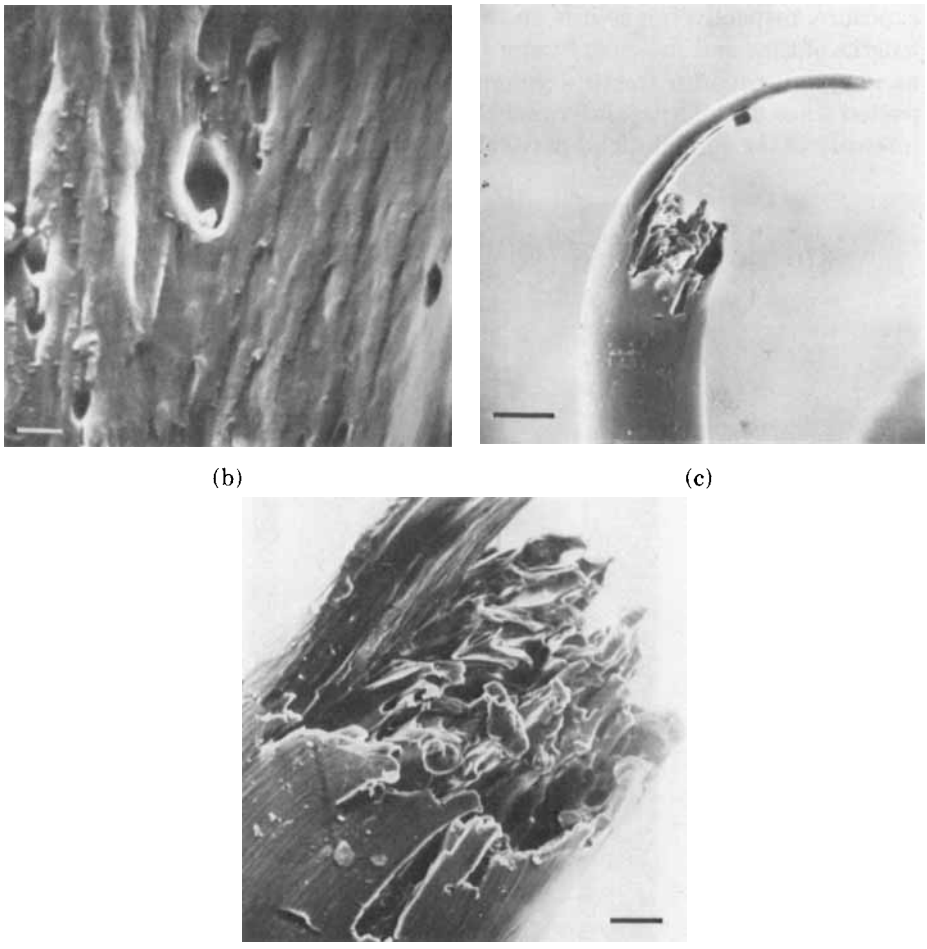
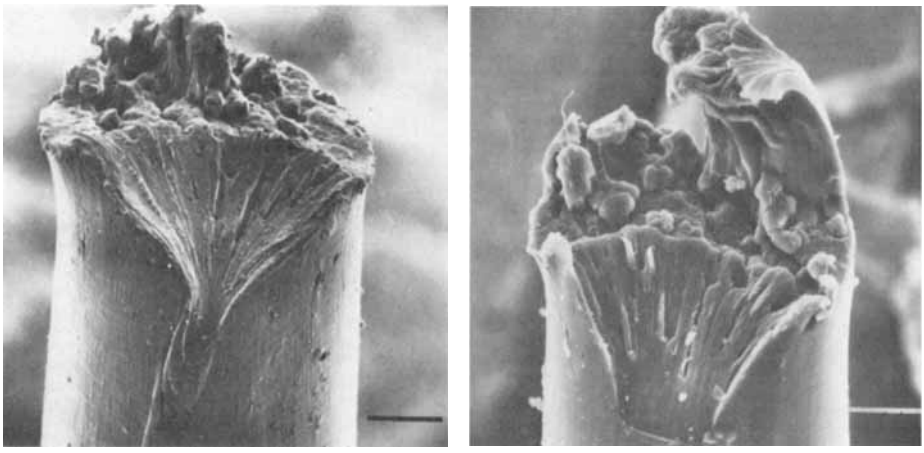


Fig. 9. (a) Holes in the surface of the shear crack of a tensile fatigue failure of delustred nylon 66 monofil; bar ≈ 10 μm. (b) Magnified view of holes; bar ≈ 1 μm. (c) Long tongue leading to final failure in tensile fatigue of nylon, opposite end of break of (a); bar ≈ 20 μm. (d) Magnified view of catastrophic region of (c); bar ≈ 5 μm.

Results of Altering the Geographic Direction of Exposure

The experiments to compare the effects of direction of exposure with changes in fracture morphology and strength loss show that there is very little difference in fracture morphology between the samples exposed in approximately southerly and westerly directions, but the effect of less strong sunlight on the samples exposed in a northerly direction is fairly easily discernible from the fracture appearance. Figure 11a, b, and c show the effect of sunlight on nylon 17 dtex monofil exposed for 12 summer weeks in southerly, westerly, and northerly directions, respectively. All these illustrations are of fibers which have medium strength according to the strength test results. The filaments exposed to the stronger sunlight for 12 weeks have a less well-defined ductile draw region and very rough catastrophic area, whereas those exposed in a northerly direction have better defined ductile and catastrophic regions. This difference in fracture



(a) (b)

Fig. 10. Tensile break of nylon exposed to daylight during the winter months, (a) 6 weeks, (b) 24 weeks. Bars ≡ 10 μm.

appearance due to exposure direction shows more clearly in filaments exposed for shorter times than in those exposed longer, e.g., 12 and 24 weeks, probably because the fracture morphology is changing so drastically with the longer exposure times. The tensile strength results, Figure 12b, indicate that those filaments exposed in a southerly direction have the lowest average strength, and those exposed in a northerly direction have the highest strength value.

Stress–Strain Curves and Strength

A selection of fiber stress–strain curves is shown in Figure 12a and b. The first set, Figure 12a, shows the mean curves for the control and the mean curves after various levels of exposure; and the second set, Figure 12b, gives curves for samples exposed to different directions. Values of strength and breaking extension, with 95% confidence limits for strength values, are given in Table I. It is remarkable how small a change in breaking conditions has occurred as a result of the exposure to light, even though there has been a large change in apparent fracture morphology.

The most notable change is a lowering of the initial modulus, with less stress developed during the first 10% of extension.

SUBSIDIARY EXPERIMENTS

Samples Exposed to Xenon Lamp

Accelerated testing or weathering is used to assess, in a relatively short period of time, the resistance to light degradation of fibrous materials. However, as there are differences of opinion on the validity of this type of testing, samples of the 17 dtex nylon monofil have been exposed to a Xenotest lamp for periods of 50, 100, and 200 hr and the results compared with sunlight-exposed samples. There is very little strength loss even after 200 hr of exposure, Figure 12c and Table II, and only a slight drop in the initial modulus. Figure 13a, b, and c shows

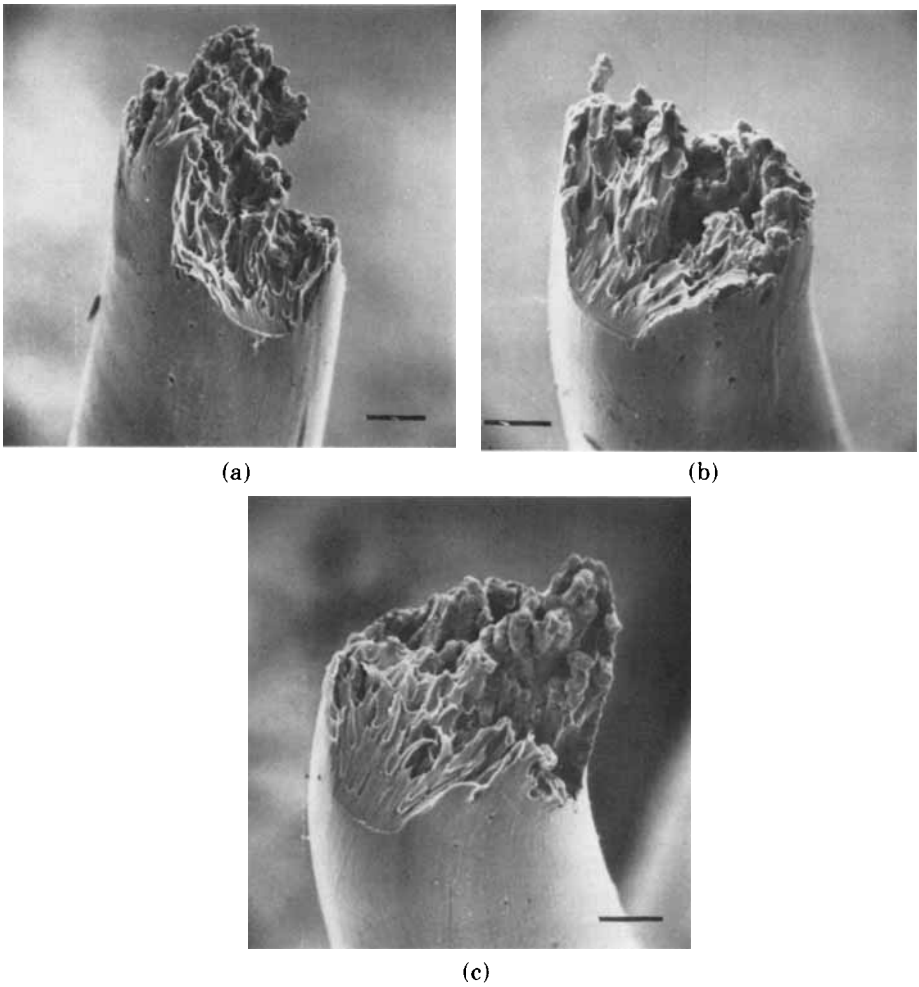


Fig. 11. Effect of direction of exposure on fracture morphology: (a) 12 weeks S.S.E.; (b) 12 weeks W.S.W.; (c) 12 weeks N.N.W. Bars ≡ 10 μm.

the fracture appearance of nylon exposed for 50, 100, and 200 hr, respectively. The fracture appearance of the 50-hr sample compares more closely with nylon samples exposed to sunlight for three weeks (facing north) in the summer and for 24 weeks in the winter, the 100 hr to three weeks (S) in the summer and six weeks (N) in the summer and the 200 hr to 12 weeks (W) in the summer. An extended initiation region has been observed in some of the fracture surfaces of the Xenotested nylon, as in Figure 14a. However, this has also been observed in a few of the sunlight-degraded nylon fractures, Figure 14b, and also in nylon chemically degraded by hydrogen peroxide bleaching.

The appearance of the filament surface of these Xenotested samples showed that they were coated with a crystalline substance, Figure 15a and b, (200-hr sample), which has either been deposited on the surface or is a modification of the fiber surface. The layer is quite thick on the 200-hr sample and is present on both 50- and 100-hr samples but to a lesser extent. The monofil has been tested as received from the manufacturer, and this crystalline deposit may result

from some modification of a spin finish. In an endeavour to establish the cause of this coating, samples will be exposed to the Xenotest before and after scouring at some future date. If, however, this coating is what is normally to be expected from these accelerated weathering tests, then the results obtained are not comparable to normal weathering conditions, because the sunlight-degraded nylon has not been scoured before testing and shows no evidence of a crystalline surface layer. The difference might be due to the nature of the radiation, but it is probably more likely to be a result of the combination of conditions in the Xenotest apparatus consequent upon the greater intensity of exposure needed in an accelerated test. The type of fracture pattern established for Xenotested samples is similar to the sunlight-degraded nylon, but exposures in excess of 200 hr are required to obtain fracture morphology similar to that of the 24 weeks of exposure to light during the summer.

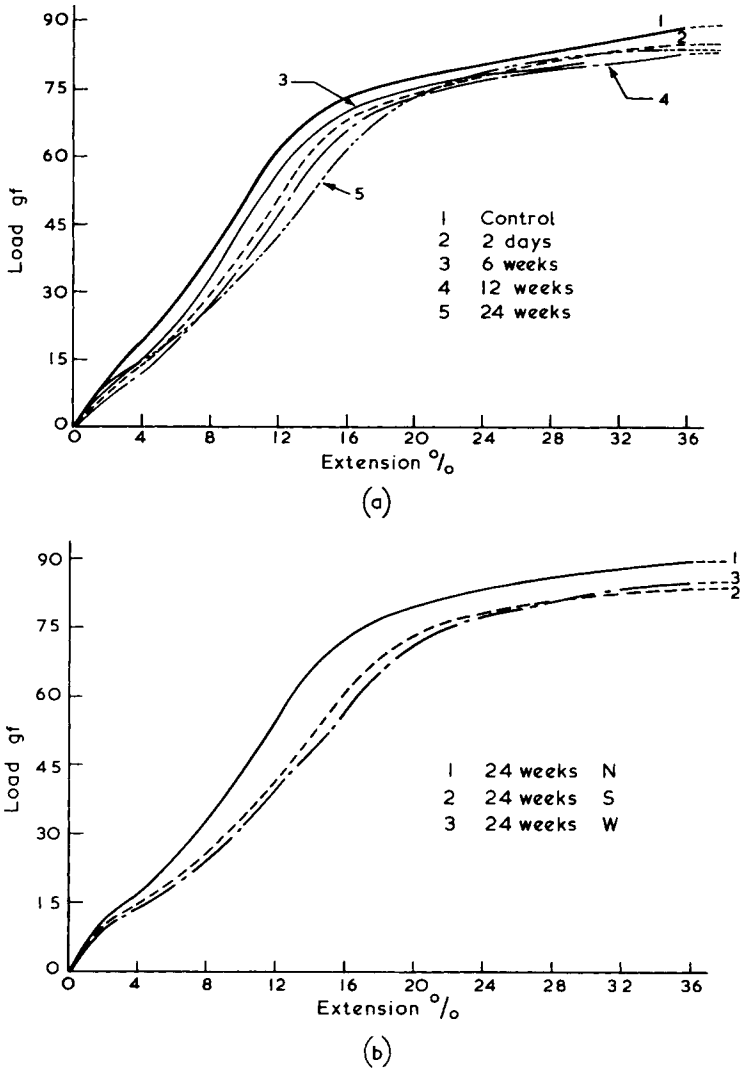
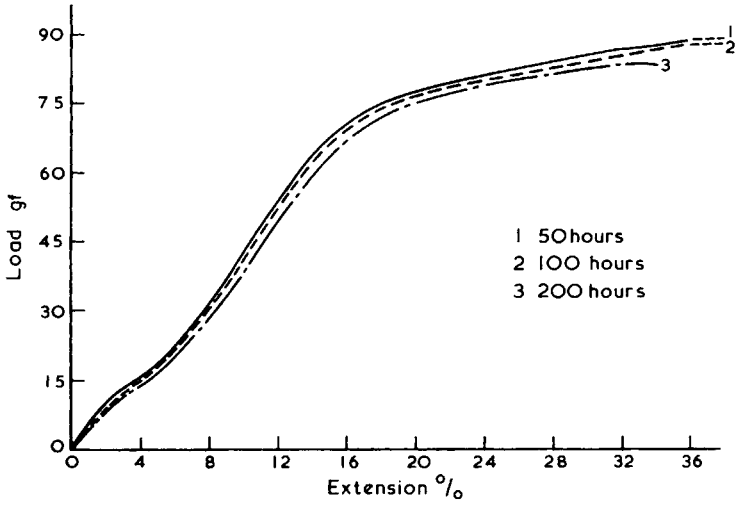


Fig. 12 (*continued*)



(c)

Fig. 12. (a) Selection of stress–strain curves of light-degraded delustred nylon monofil. (b) Effect of direction of exposure on stress–strain curves. (c) Stress–strain curves of nylon exposed to xenon lamp for 50, 100, and 200 hr.

Bright Yarn Exposed to Florida Sunlight

Samples of nylon 66 high-tenacity bright multifil yarn of approximately 7.5 dtex per filament, wrapped on white rectangular cards and exposed for periods of two and three months in sunlight in Florida, were supplied by the courtesy of the E. I. du Pont de Nemours and Company. The two-month exposure

TABLE I
Sunlight-Exposed Test Sample; 17 dtex Semidull Nylon 66 Monofil
(ICI Fibres Limited)

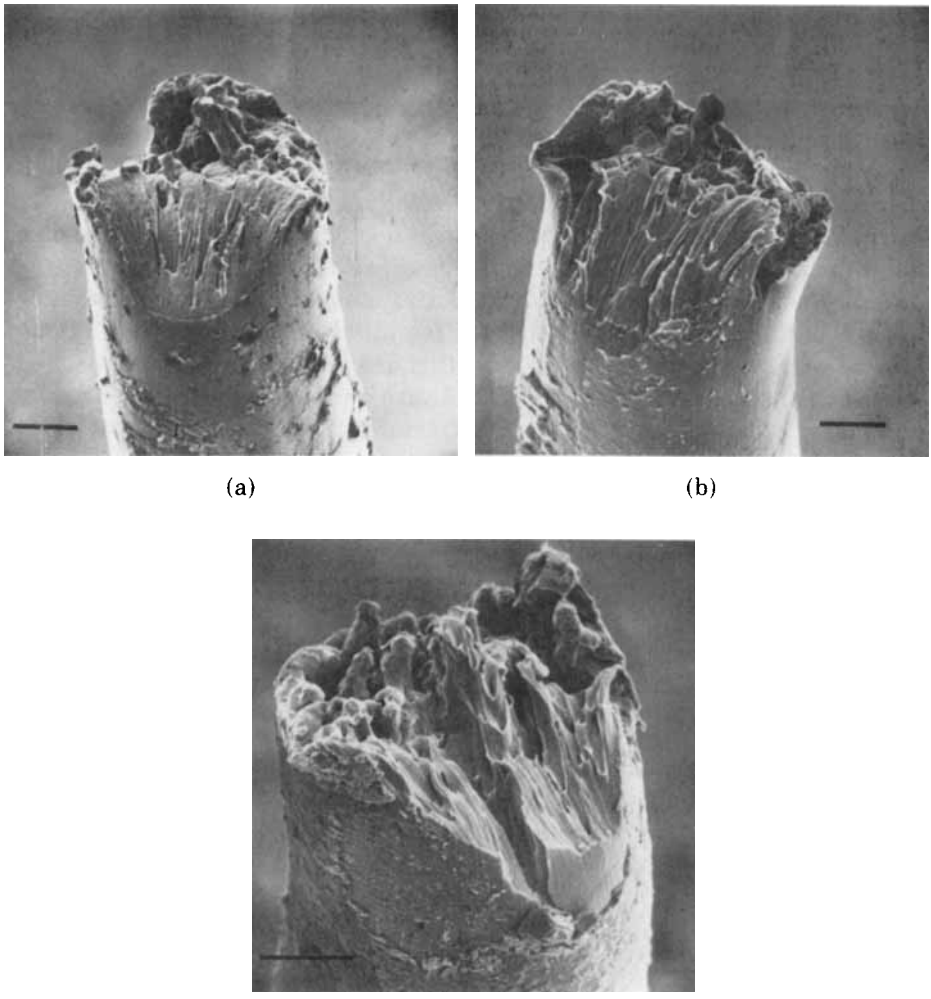
Exposure	Breaking load, gf	95% Confidence limits	Breaking extension, %
Control	88.2	±0.5	35.0
3 Weeks			
SSE	84.7	±0.6	36.5
WSW	85.4	±0.6	36.1
NNW	85.3	±0.7	34.7
6 Weeks			
SSE	83.1	±0.5	31.3
WSW	84.3	±0.5	35.7
NNW	85.7	±0.7	31.8
12 Weeks			
SSE	81.7	±0.4	31.7
WSW	81.9	±0.4	35.3
NNW	85.8	±0.5	30.5
24 Weeks			
SSE	82.7	±0.3	30.2
WSW	85.0	±0.3	34.1
NNW	87.8	±0.4	31.1

TABLE II
Xenon Lamp Results; 17 dtex Semidull Nylon 66 Monofil
(ICI Fibres Limited)

Exposure	Breaking load, gf	95% Confidence limits	Breaking extension, %
50 Hours	89.1	±0.7	36.1
100 Hours	87.0	±0.7	33.0
200 Hours	80.1	±0.8	26.2

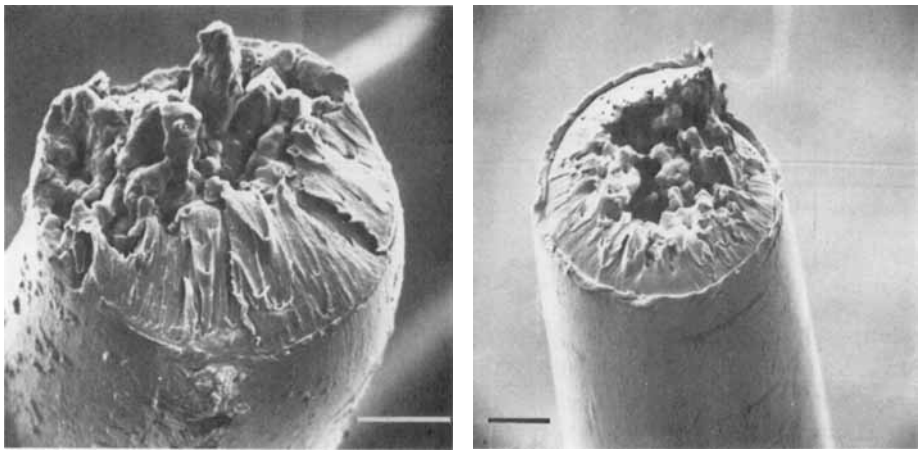
samples have received a total of 16,370 langleys: 5983 ultraviolet langleys and 111 sun hours. The figures for the three-month samples are not known but are assumed to be approximately 50% greater than the above figures.

Fifty individual filaments from the exposed yarns were broken separately on



(a) (b) (c)

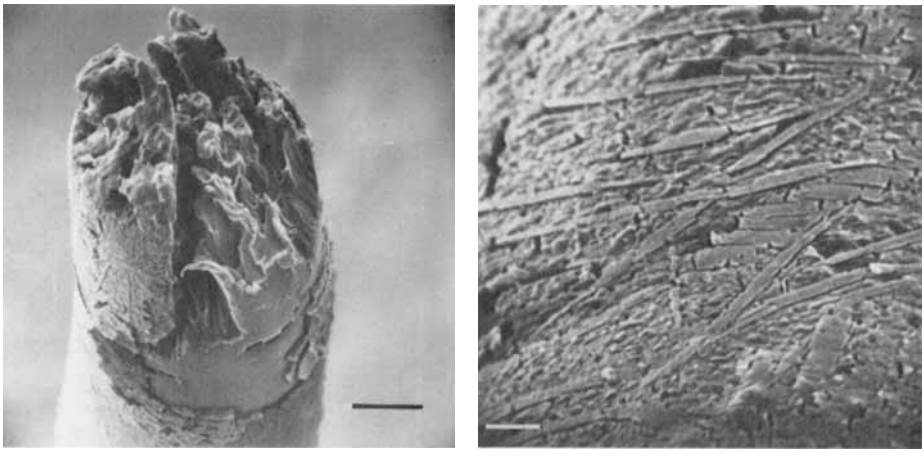
Fig. 13. Fracture appearance of nylon exposed to xenon lamp for (a) 50 hr, (b) 100 hr, and (c) 200 hr. Bars ≡ 10 μm.



(a) (b)

Fig. 14. Extended initiation region in nylon exposed (a) to xenon lamp and (b) to sunlight. Bars = 10 μm.

an Instron tensile tester (under the same testing conditions as for 17 dtex nylon 66), and there has been little strength loss between the two- and three-month exposure samples compared with the control, Figure 16; the three-month sample has lost only approximately 6% of that of the control sample, Table III. The filaments in these samples contain little or no delustrant and are classed as a bright yarn; and it is interesting to note that, although the strength loss characteristics are similar to those of the 17 dtex monofil light-degraded samples, their fracture morphology is entirely different. Figure 17a, showing a typical ductile break, and Figure 17b, showing that of a tensile break having two initiation regions, are both from the control yarn and are typical of the fractures obtained for this sample. But similar fracture patterns also occur in the two-month exposure sample, Figure 17c and d, and the three-month exposure sample,



(a) (b)

Fig. 15. (a) and (b) Crystalline coating on nylon surface after 200 hours exposure to xenon lamp. Bar = (a) 10 μm; (b) 2 μm.

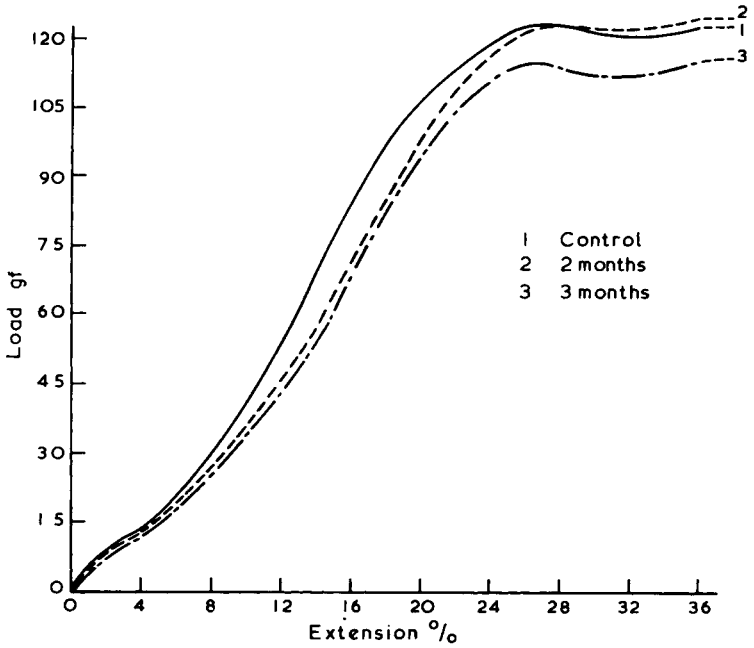


Fig. 16. Stress–strain curves of bright, high-tenacity yarn exposed to daylight for 2 and 3 months in Florida.

Figure 17e and f. In these samples, which have no delustrant, there are no holes or turret-shaped structures occurring in the fracture as with the light-degraded delustred nylon, and no holes have been detected in the surface of the filaments. It has been noted, however, that there are more jagged-type breaks, as shown by the opposite ends of a break in Figure 18a and b occurring in the bright yarns, than in similarly exposed delustred monofil. However, jagged breaks can occur in this monofil when exposed for a short time to light, such as two days of exposure during the winter, Figure 18c.

Dull Trilobal Yarn Exposed to Florida Sunlight

Another set of yarns was exposed to Florida sunlight, under glass, facing south at a 45° angle. These consisted of types of trilobal multifil nylon 66 yarns of 22 dtex per filament, containing titanium dioxide and made in the laboratory by du Pont. The two yarns were cooled in different ways, so that sample A (high quench) contained no spherulites and sample B (no quench) had a high spherulite

TABLE III
Samples Exposed to Florida Sunlight; 7.5 dtex Bright Nylon 66 High Tenacity (du Pont)

Exposure	Breaking load, gf	Breaking extension, %
Control	54.6	27.2
2 months	54.2	27.4
3 months	51.2	25.3

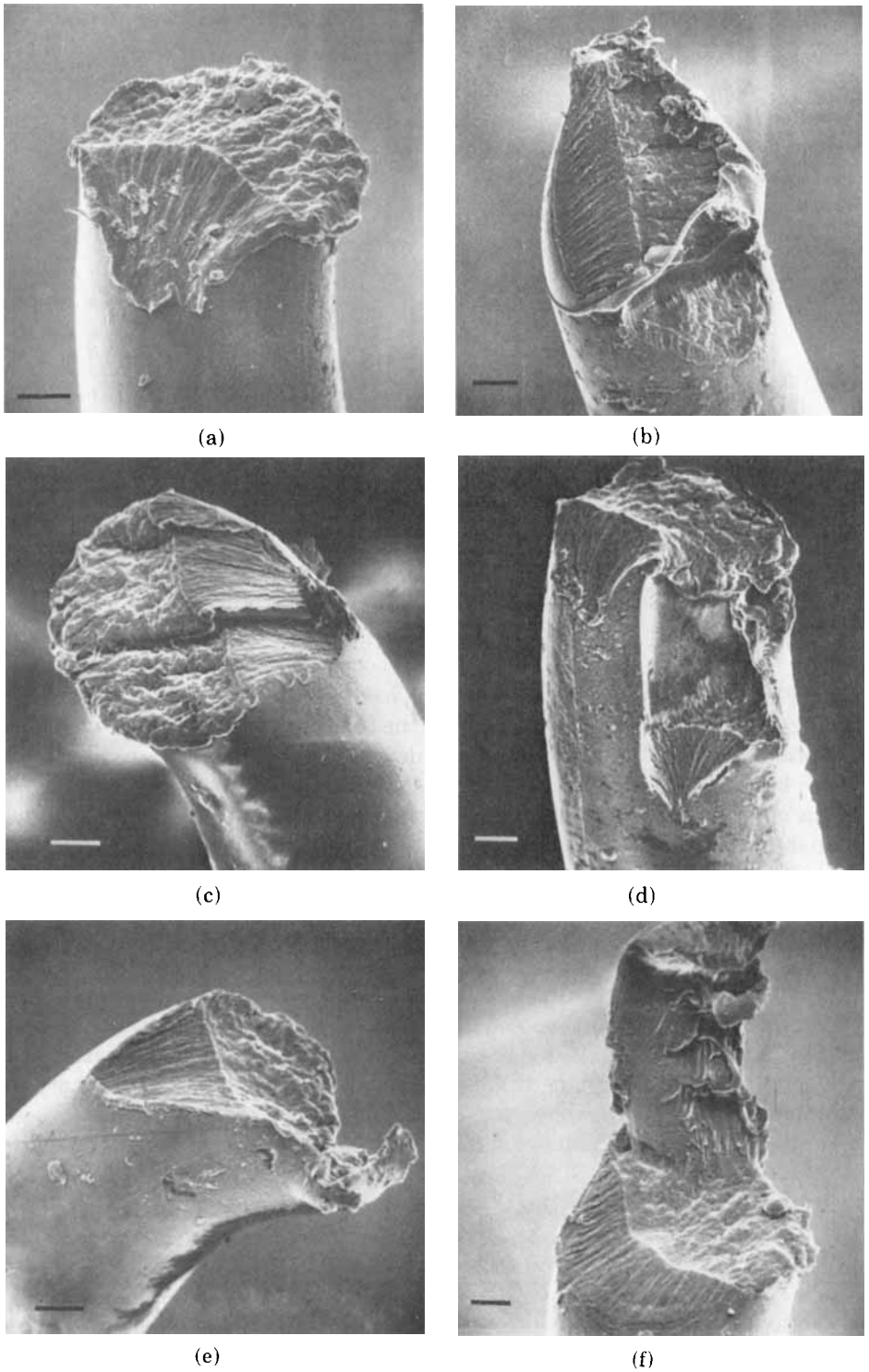
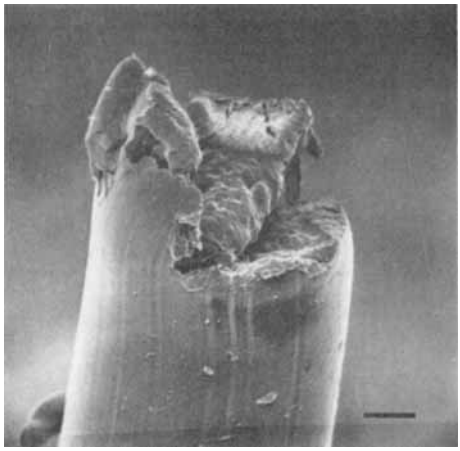
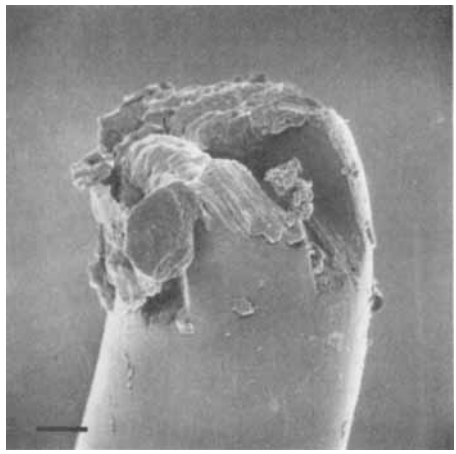


Fig. 17. (a) and (b) Fracture appearance of bright, high-tenacity nylon 66 yarn, control; bars ≡ 5 μm. (c) to (f) Fracture appearance of bright, high-tenacity nylon 66 yarn exposed to daylight in Florida for 2 months (c and d) and 3 months (e and f); bars ≡ 5 μm.



(a)



(b)

(c)

Fig. 18. (a) and (b) Jagged breaks in light-degraded, bright, high-tenacity nylon 66 yarn; bars ≅ 5 μm. (c) Jagged break in delustred nylon 66 monofil exposed for 2 days; bars ≅ 10 μm.

content. The stress–strain curves are shown in Figure 19, and breaking strength and extension values are given in Table IV. After 600 hr of exposure, the breaking extension has reduced to below the yield region; and after 1000 hr, there has been severe strength reduction. There are only small differences between the two samples in breaking strength and extension.

Examination in the scanning electron microscope shows that the control specimens break in the normal way, Figure 20a, with the break starting at the outermost part of a lobe. The 600 hr-exposed specimens show the usual breakup into separate fracture regions, Figure 20b, together with some transverse surface cracking. Higher magnification views show clearly the titanium dioxide particles at the base of the separate turrets, Figure 20c, and how breaks which start from separate cavities link up, Figure 20d.

The very weak fibers, subject to 1000 hr of exposure, frequently show a character generally similar to those which have been less exposed, as in Figure 21a,

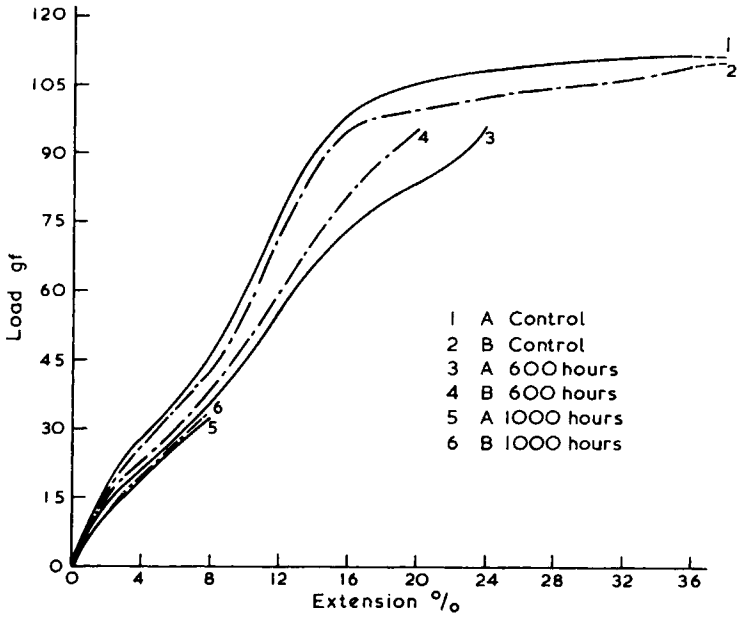


Fig. 19. Stress–strain curves of delustred, trilobal nylon 66 yarn exposed to Florida sunlight for 600 and 100 hr.

but with a greater density of turrets, a greater tendency for the break to spread along the fiber length, and more noticeable surface cracking, Figure 21b. In many instances, the surface cracking is extremely severe, as shown in Figure 21c and d, which are opposite ends of a fiber broken in the middle of a cracked zone. The cracks are seen at higher magnification in Figure 21e, in which other lines of incipient final breakage are visible. In other instances, the breaks occur in separate regions, linked by axial splits, as shown in Figure 21f and g.

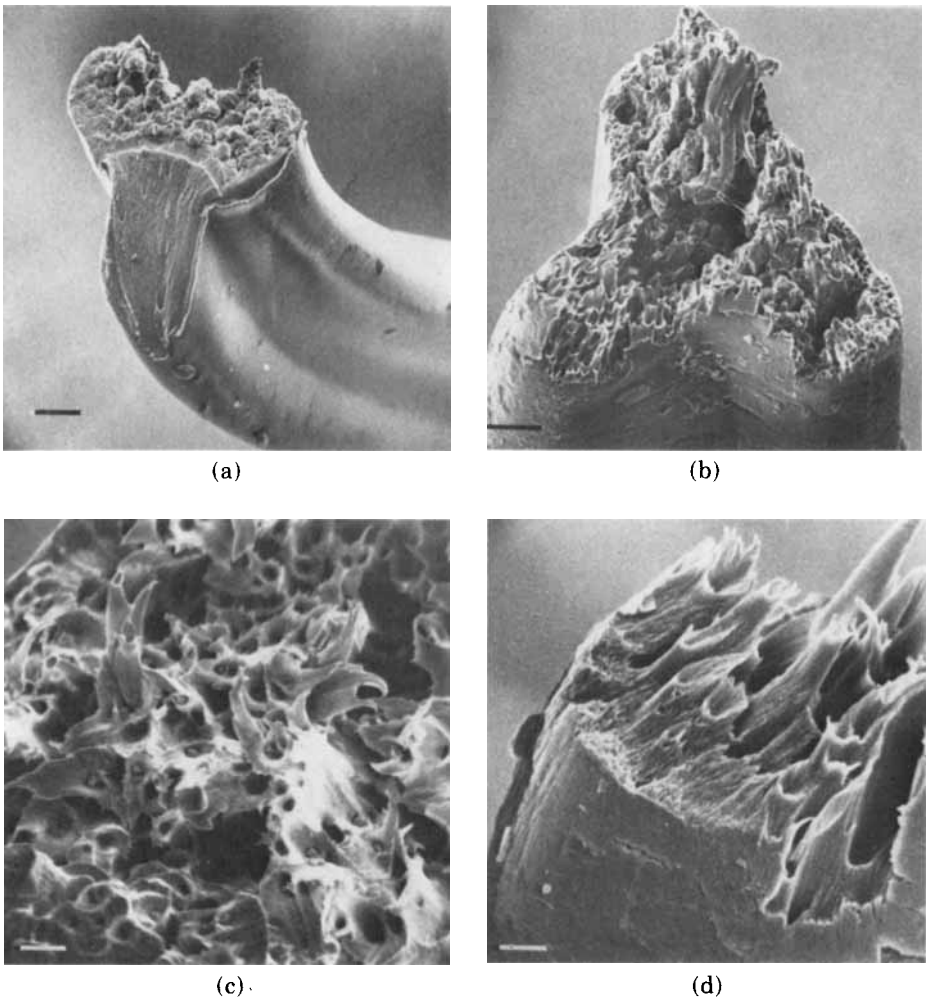
DISCUSSION

Although the fracture morphology is so different in delustred nylon fibers which have suffered prolonged exposure to light, it seems likely that the basic fracture mechanisms are not very different.

TABLE IV
Samples Exposed to Florida Sunlight; 22 dtex Dull Trilobal Nylon 66 (du Pont)

Exposure	Breaking load, gf	*S.D.*	Breaking extension, %
A Control	120.5	±20.1	41.9
A 600 Hours[a]	84.6	±18.8	18.4
A 1000 Hours[b]	28.9	± 9.3	6.8
B Control	113.2	±19.2	40.0
B 600 Hours[a]	94.2	±19.1	20.7
B 1000 Hours[b]	28.5	± 9.3	6.3

[a] 65,330 Total langleys; 37,123 ultraviolet langleys.
[b] 120,370 Total langleys; 59,922 ultraviolet langleys.

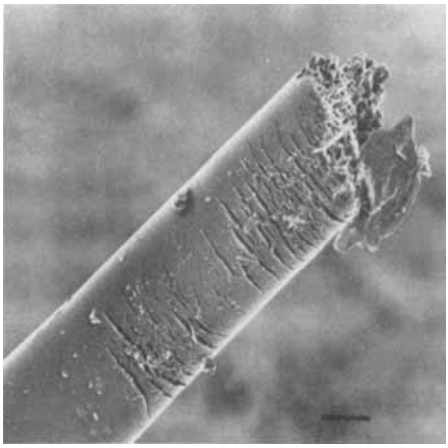


(a) (b)

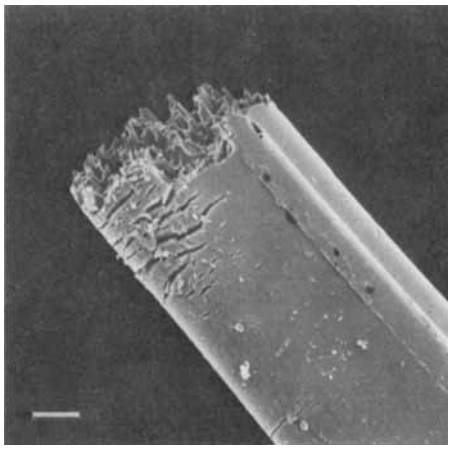
(c) (d)

Fig. 20. (a) Tensile break of delustred, trilobal nylon 66 control yarn; bar ≡ 10 μm. (b) Fracture appearance of delustred trilobal nylon after 600 hr of exposure to sunlight; bar ≡ 10 μm. (c) Titanium dioxide aggregates at the base of separate turrets; bar ≡ 2 μm. (d) Linking of separate cavities during fracture; bar ≡ 2 μm.

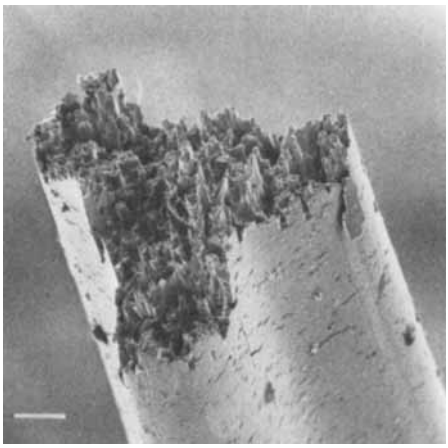
It is known[4] that titanium dioxide serves to catalyze the oxidative degradation of nylon in the presence of ultraviolet radiation. This results in the formation of cavities round the pigment particles. These can be seen in the optical microscope, and also cause an increasing opacity of the filaments. Figure 22 is a TEM micrograph of titanium dioxide particles[8] obtained in this instance from polyester fibrous material by extraction in several changes of hot *o*-chlorophenol, each extraction followed by centrifuging. The particles were sprayed from solution onto carbon-coated specimen grids. The individual particle size is extremely small (~100 nm), and the particles could not be detected in an optical microscope. The small specks of delustrant seen in delustred fibers are in general aggregates of titanium dioxide. With the larger aggregates, the nylon matrix flows around the pigment during the drawing process of filament production, forming cigar-shaped voids. This "flow" around the pigment aggregates can



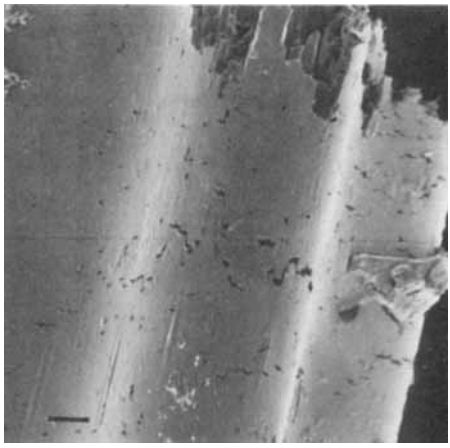
(a)



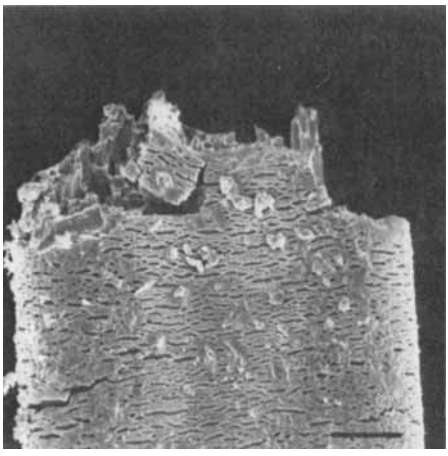
(b)



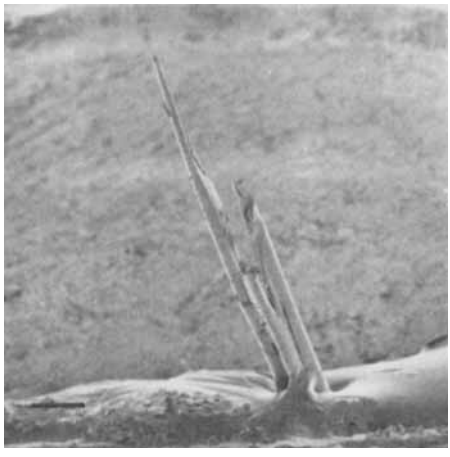
(c)



(d)

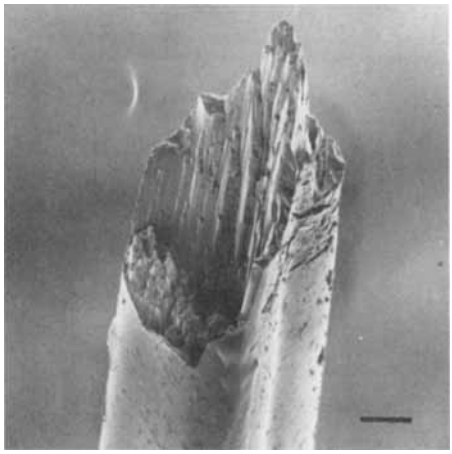


(e)



(f)

Fig. 21 (*continued*)



(g)

Fig. 21. (a) Fracture appearance of delustred, trilobal nylon exposed for 1000 hr; bar ≡ 10 μm. (b) Cracking of filament surface near the break; bar ≡ 5 μm. (c) and (d) Severe surface cracking, (c) and (d) are opposite ends of the same break; (c) bar ≡ 20 μm, and (d) bar ≡ 10 μm. (e) Severe and extensive surface cracking near breaking also showing other lines of incipient final breakage; bar ≡ 10 μm. (f) and (g) Breaks occurring at separate regions linked by axial splits; (f) bar ≡ 100 μm, and (g) bar ≡ 10 μm.

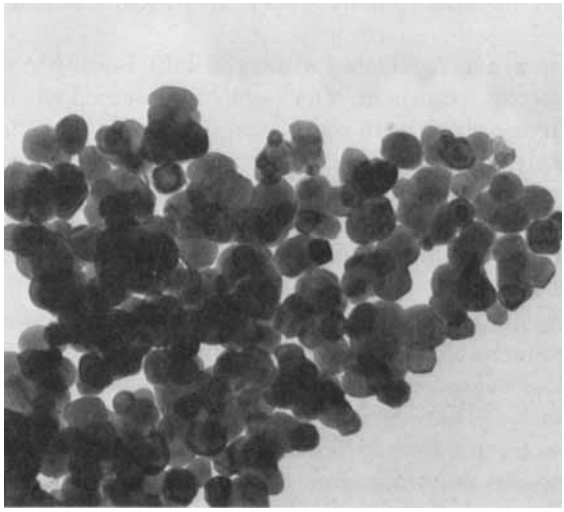


Fig. 22. TEM micrograph of titanium dioxide particles extracted from polyester fibers by hot *o*-chlorophenol. (Courtesy of Mr. S. C. Simmens.)

be detected in the polarizing microscope. Improved filament production techniques have, over the years, reduced the aggregate size and improved the dispersion; larger aggregates are now less common.

Optical microscope examination of light-degraded nylon shows that the pigment cavities become enlarged, often into complex shapes, possibly as a result of pigment movement within the cavity, causing more photodegradation. With filaments having a small aggregate size, it is more difficult to discern optically

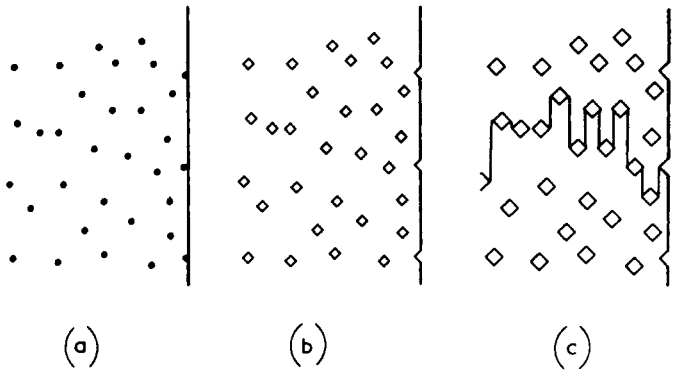


Fig. 23. Schematic diagram of the breakdown of light-degraded nylon.

the actual shape of the cavity, though it is probably a little less cigar shaped than before.

The cavities produced by light degradation around TiO_2 particles act as starting points for ductile crack growth, giving, in effect, a multiplication of internal breaks of the type shown in Figure 3e. As these internal cracks develop, the remaining material will draw, opening the cracks into cones. Eventually, the stress in the regions linking neighboring cones becomes large enough to cause total failure, and the cones join up to give the many turrets observed in the fractured fibers. This form of breakdown is illustrated schematically in Figure 23.

The final failure will be associated with axial splitting as the separate breaks link up: this is a prolification of an effect which is observed when tensile breaks start in more than one place, as in Figures 3d, 17d and f, and 18a, b, and c.

In the moderately exposed fibers, the strength is not substantially altered despite the change in the details of the fracture mechanism, because the breaking load is still given by the force required to cause continued ductile crack propagation. This force is the same whether it is occurring at a single large crack or many small ones, since it is really the force required to continue the plastic drawing of the remainder of the material to higher local strain values.

Most of the specimens which we tested have not been exposed for long enough to cause a large loss in strength in modern nylon fibers containing inhibitors. However, Zeronian et al.[9] have recently published scanning electron micrographs of the appearance of nylon fibers after exposure to light from a xenon arc lamp. At a moderate exposure, 267 hr for semidull and 168 hr for dull, when the strength has reduced by 67%, there were just a few voids apparent on the surface. But after 672 hr, the voids had grown and linked up into a sponge-like network which would obviously have little strength. The semidull yarn then had a strength retention of only 11%, and the dull yarn was too weak to handle. The final set of yarns which we tested, after 1000 hr of exposure in Florida, showed a similar strength reduction and a development of a sponge-like material. In these circumstances, the degradation has occurred to such an extent that the whole material is weakened.

Fujiwara et al.[10] also show the gradual development of large pits into a spongy network as the strength of nylon 6 filaments decreased with increasing exposure to light.

The change in the initial part of the stress–strain curve is probably due to the rupture of those tie molecules which are nearly fully extended in their path between crystalline regions. These would generate a larger initial resistance to deformation that the tie molecules with a more irregular path, which can easily extend by straightening. The initially tauter tie molecules are also likely to be those most prone to scission on exposure to light; but, since they would be broken before final fracture, they would have little effect on the strength. The increase of strength of the samples exposed for 24 weeks, if it is not a statistical artefact due to choice of test specimens, must be due to a more uniform sharing of the load within the structure.

The severe loss in strength of highly light-degraded nylon will be due to an increase in internal void size and greater chemical degradation of the nylon matrix. In nylon 66 yarn degraded to 50% of its original strength; and with a near-opaque appearance in the optical microscope, treatment with hot benzyl alcohol causes worm-like cavities branching off the main pigment cavity to show up when the fiber is examined by phase-contract microscopy using plane-polarized light.[8] In these worm-like cavities, small aggregates of titanium can be detected which probably stem from the breakup of the main pigment aggregate. It would seem, therefore, that the breakup of the filament matrix is very extensive due to the deleterious action of ultraviolet light.

In studying the liability of nylon fibers to light degradation, it may be useful to examine the change in fracture morphology, which occurs rapidly and would give a guide to the susceptibility to damage without the necessity for the very prolonged exposures needed to find large enough strength loss.

In bright nylon, where the degradation does not result in a localized growth of cavities, the effects of a long-enough exposure to sunlight is to lead to weakening of the whole structure as a result of chain scission.

An example of current interest in problems of light degradation is the extensive experimental and statistical study reported by Swallow.[11] He correlates the breaking strength test results of several combinations of treatment and weathering exposure on extrahigh tenacity and high-tenacity nylon 66 and medium-tenacity nylon 6 materials, and his conclusions are very similar to those given in this paper. Strength losses were greater for full weathering conditions than behind Perspex, and the results of xenon tests gave no worthwhile information on certain samples and limited information on others, particularly those exposed behind Perspex. There was no mention in the report on whether the nylon materials contained any delustring agent.

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