JOURNAL OF MATERIALS SCIENCE 28 (1993) 785–788

The ultraviolet sensitivity of Kevlar 149 and Technora fibres

M. G. DOBB, R. M. ROBSON
Textile Physics Laboratory, The University of Leeds, Leeds, LS2 9JT, UK
A. H. ROBERTS
Directorate General of Defence Quality Assurance, Procurement Executive, Ministry of Defence, UK

The effect of ultraviolet radiation on the tensile properties of two engineering fibres, namely Kevlar 149 and Technora, is reported. Both fibre types show considerable loss in strength, but the former also exhibits a significant and unexpected fall in modulus. Electron microscope examination of the virgin and extended fibres revealed the structural reasons for the observed mechanical behaviour.

1. Introduction
The general degradation of polymers by ultraviolet irradiation is widely recognized [1], although depending on their chemical character some materials are more sensitive than others [2]. Such behaviour may limit the range of applications of the materials. It is the purpose of this paper to report on the effects of irradiation on two aramid fibres used for engineering purposes. One type, Kevlar 149 (an ultra-high-modulus variant), is based on poly (*p*-phenylene terephthalamide), (PPT), and the other, Technora, is a copolymer of PPT with poly(3,4′ oxydiphenylene terephthalamide) [3]. In particular, it is shown that although both Kevlar 149 and Technora lose considerable strength on ultraviolet irradiation, there is a significant loss in modulus only in the case of the former fibre. It should be noted that standard Kevlar 49 samples do not show this loss in modulus. An explanation for this behaviour is presented based on structural investigations.

2. Experimental procedure
2.1. Irradiation
Exposure was carried out continuously in a Xenotest 150 apparatus. A filtered xenon lamp was used producing radiation similar to natural sunlight in the visible and ultraviolet regions of the spectrum. The apparatus emitted a nominal total irradiance of 1250 $W\,m^{-2}$ in the 310–800 nm waveband, approximately 10% of which was distributed in the UV(A) spectral region (bandwidth 320–400 nm). Cut lengths from the fibre tows were mounted vertically in a carousel which orbited the xenon lamp at a rate of 5 r.p.m. During each orbit, the sample face was maintained normal to the radiation and after each revolution, the sample was rotated by 180° in order to achieve uniform exposure of the tow. Ideally, single filaments would have been exposed to avoid any screening effects, but this was considered impracticable and did not appear to affect the results. Exposure was carried out over a period of 14 days with continuous monitoring of temperature and humidity. Temperature was maintained in the range 43–47 °C and relative humidity varied between 35% and 38%. Samples were withdrawn after 1, 2, 4, 7 and 14 days, and from these, single filaments were immediately prepared and tested by the method described in Section 2.2.

2.2. Tensile Testing
Randomly selected single filaments were carefully extracted from the fibre tows and mounted on to guide cards to give a gauge length of 50 mm. Testing was carried out using an Instron 1195 tensile testing machine operating at a crosshead speed of 1 $mm\,min^{-1}$ and the tensile properties were calculated from the resultant chart output. Individual filament diameters were subsequently measured using a Vickers Instruments optical microscope coupled to a Vickers image splitting eyepiece with a combined magnification of $\times 1800$. The system, set up in the transmitted light mode, was calibrated against a standard tungsten wire of diameter 10.05 μm.

2.3. Microscopy
Both transverse and longitudinal sections of virgin and irradiated fibres were examined in a Jeol CX 100 transmission electron microscope (TEM) operating at 100 kV. Failed fibre ends were coated with a thin layer of gold in a Polaron sputtering unit and subsequently examined in a Cambridge Stereoscan (SEM) 150B at 20 kV.

TABLE I Tensile properties with exposure time for Kelvar and Technora aramid fibres

Sample	Days exposed	Tensile strength (GPa)	Strain to failure (%)	Initial modulus (GPa)	Average modulus (GPa)
Kevlar 149	0	2.48	1.40	144	177
	1	1.80	1.04	147	173
	2	1.35	0.82	147	165
	4	1.03	0.67	143	154
	7	0.81	0.61	137	133
	14	0.70	0.54	134	130
Technora (T200)	0	3.45	4.52	86	76
	1	3.12	4.10	87	76
	2	2.69	3.59	84	75
	4	–	–	–	–
	7	2.18	3.01	85	72
	14	1.80	2.60	86	69

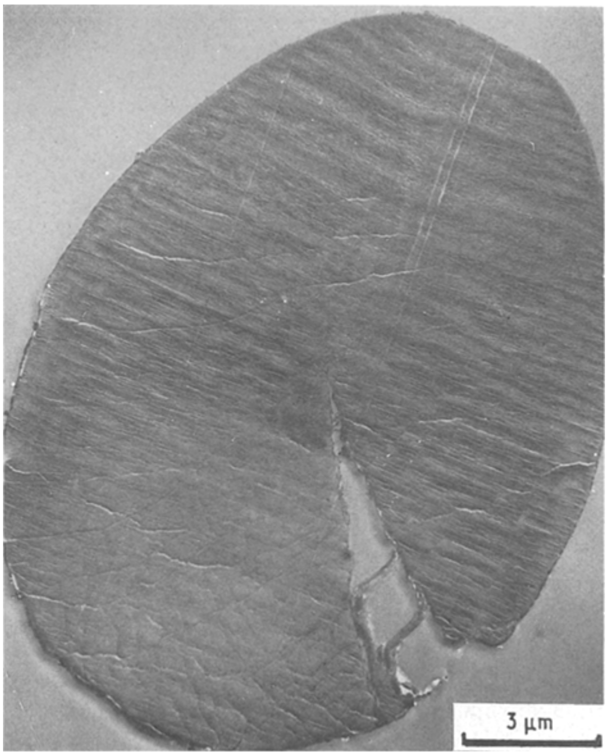

Figure 1 Transmission electron micrograph of an oblique section through the defect region of a Kevlar 149 fibre.

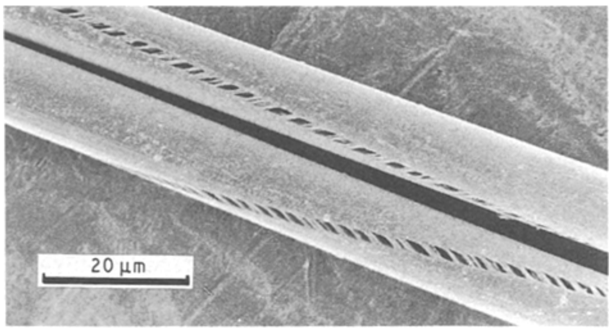

Figure 2 Scanning electron micrograph of Kevlar 149 fibres showing helical track of defects.

3. Results

The tensile data are shown in Table I. It is clear that both fibre types lose considerable strength due to the irradiation; however, particularly interesting is the loss in overall modulus of the Kevlar 149 samples compared with the modulus retention by the Technora fibres. It was decided, therefore, to seek an explanation for this behaviour.

Sections of untreated and exposed fibres were examined in the TEM. Technora has an approximately circular cross-section with no macro-defects on the surface, whereas Kevlar 149 shows a series of large wedge-shaped defects as shown in Fig. 1. The defects appear to penetrate to the centre of each fibre and, as shown by SEM studies, take the form of sinusoidal or helicoidal tracks of varying pitch along the fibre length. Typically the defects (holes) are regularly distributed along the tracks (Fig. 2) with sheared and disoriented material (as deduced from X-polar optical studies) bridging between adjacent holes [4].

After ultraviolet irradiation for 7 days, both Kevlar 149 and Technora exhibit changes in the surface layer about 200 nm deep. Indeed, examination of sections in the TEM reveals a peripheral band containing numerous electron-transparent regions (holes) which are approximately circular and of diameter 15 nm as shown in Figs 3 and 4. These regions are different in shape and dimensions from the larger, lozenge-shaped voids normally found in untreated Kevlar 149 fibres as seen in Fig. 3. It is interesting to note that the clay-like material used as a surface coating on Technora [5] does not appear to be an effective protection against ultraviolet irradiation because numerous electron-transparent regions can be observed directly under individual clay-like particles. The presence of electron-transparent regions clearly suggests loss of material from the surface layer but the mechanism remains obscure at present. Conceivably, bond scission by the ultraviolet light could lead to evolution of gaseous products or indeed the depolymerization induced may give rise to volatile products which "boil-off" in the high vacuum of the electron microscope.

In order to understand the behaviour of the irradiated fibres in more detail, fracture mechanisms were studied. In particular, both irradiated and untreated

Figure 3 Transmission electron micrograph of a longitudinal section through ultraviolet irradiated Kevlar 149 showing a surface layer of voids.

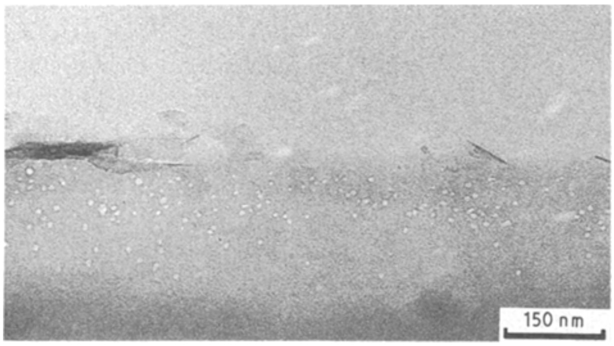

Figure 4 Transmission electron micrograph of a longitudinal section through ultraviolet irradiated Technora showing a surface layer of voids. Note the presence of clay-like particles on the fibre surface.

Kevlar fibres were broken in air and the ends examined in the SEM. This approach proved to be most fruitful because it was evident that different mechanisms were operating. In the case of untreated fibres, the broken ends consisted of split sheets of material whose fracture faces appeared to be independent of the spiralling defects. In contrast the fracture faces of the irradiated fibres followed precisely the track of these defects as shown in Fig. 5a and b. Moreover fibres extended to just before breaking point showed "unzipping" of the bridging regions between adjacent holes along the spiral defect (Fig. 6).

The data shown in Table I for irradiated Kevlar 149 may be misleading in that they imply an overall decrease in modulus along the entire stress–strain plot. However, close examination of the curves revealed another interesting phenomenon not observed in either untreated Kevlar 149 or irradiated Technora. Typically the curves for irradiated material showed a marked yield point (e.g. after 7 days exposure at a strain around 0.35%) where the modulus dropped from a value normally associated with that of the unexposed fibre, as shown in Fig. 7. Indeed there appears to be a general trend of decreasing yield strain with increasing exposure times. In some fibres this region of reduced modulus was followed by an increase in modulus up to the point of break.

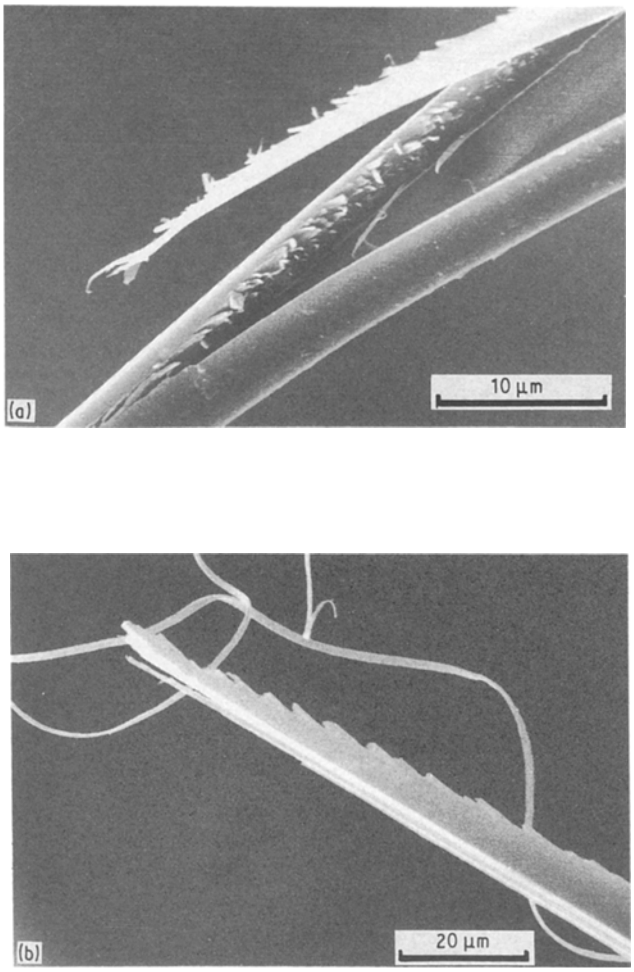

Figure 5 :Scanning electron micrographs of the fractured ends of ultraviolet irradiated Kevlar 149 showing (a) failure along the spiral defect track, and (b) the ratchet-like nature of the unzipped fracture surface.

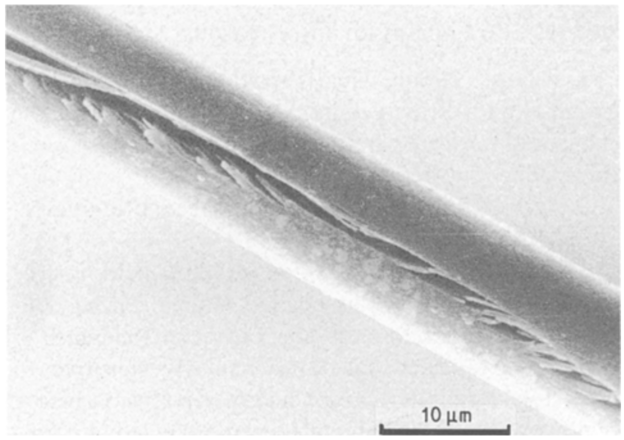

Figure 6 Scanning electron micrograph showing initiation of the unzipping process.

4. Conclusions

From these observations it is now possible to account as follows for the anomalous tensile properties in structural terms.

A photon of ultraviolet light ($n = 310$ nm) has an energy of about 386 kJ which, if absorbed by a polymer, is capable of significant bond breakage (for example, bond dissociation energies of C–C and C–N

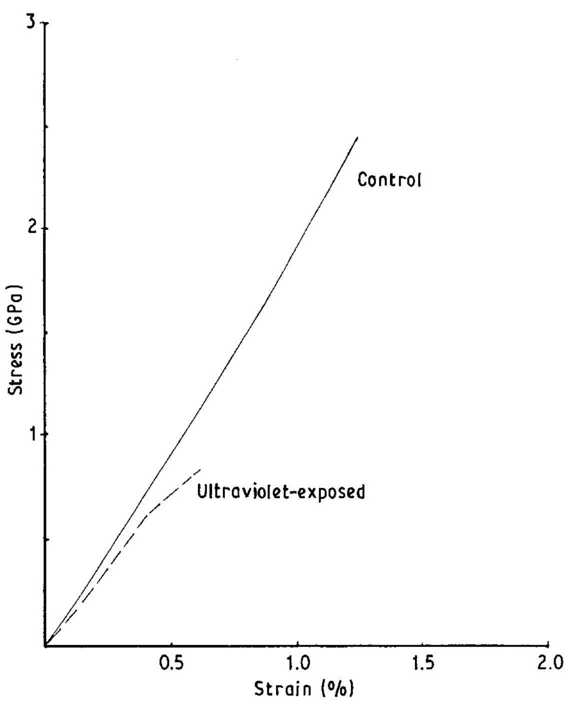

Figure 7 Schematic stress–strain curves for virgin and ultraviolet irradiated Kevlar 149 fibres.

bonds are about 336 and 277 kJ mol^{-1}, respectively [6]. Peripheral layers of material in both Kevlar 149 and Technora are progressively damaged (probably depolymerized) by the ultraviolet light effectively reducing the overall breaking strength of the fibres. From the data given in Table I it is clear that the percentage loss in strength of Kevlar after irradiation for a given time is considerably greater than that observed in the case of Technora. It is suggested that this result originates for three reasons:

1. a larger surface area is irradiated in Kevlar 149 because the ultraviolet light can penetrate into the interior of the fibre via the defect holes and consequently produce more extensive damage;
2. early failure of radiation-damaged bridging regions along the spiral defect;
3. the line defects detected in dark-field micrographs of Kevlar 149 associated with localized concentrations of chain ends (see Fig. 7, in Reference 4) would be expected to be particularly sensitive to ultraviolet irradiation and hence fail in tension before regions where the chain ends are more evenly distributed [7].

In contrast to the change in strength, the modulus of the fibres which is a reflection of the bulk properties should remain almost constant as observed in the case of Technora. However, when considering the observed modulus reduction in Kevlar the following points should be noted. For reasons already discussed, the strength of Kevlar 149 decreases with exposure; consequently, the strain to failure also decreases. Owing to the unusual shape (for an aramid) of the virgin Kevlar 149 stress–strain curve, i.e. increasing stiffness with strain, the "average modulus" will be seen to decrease as failure strain decreases. The distinction between this phenomenon and the "yield point" effect observed in irradiated Kevlar 149 should therefore be noted. In the case of Kevlar 149 the surface bridging regions between adjacent holes constituting the spiralling defect are seriously degraded by the ultraviolet irradiation and, as individual fibres are stressed, are the first regions to fail. This then allows shearing or slippage to take place along the spiral track so that the fibre then acts as a helix whose behaviour is manifested by the sharp decrease in modulus observed in the stress–strain curve.

It is interesting to note that Kevlar fibres extended near to break (well into the region of lower modulus) then relaxed and re-extended, do not show a yield point in the stress–strain curve. During the second cycle the bridging regions have already failed.

Acknowledgement
This work was carried out with the support of the Procurement Executive, Ministry of Defence.

References

1. J. F. MCKELLAR and N. S. ALLEN, "Photochemistry of Man-made Polymers" (Applied Science, London, 1979) p. 37.
2. A. DAVIS, in "Developments in Polymer Degradation", edited by N. Grassie (Applied Science, London, 1977) pp. 249–78.
3. J. BLACKWELL, R. A. CAGEAO and A. BISWAS, *Macromolecules* **20** (1987) 667.
4. M. G. DOBB and R. M. ROBSON, *J. Mater. Sci.* **25** (1990) 459.
5. *Idem*, in "Techtextil Symposium", Frankfurt, Vol. 1.1. (1989) p. 7.
6. E. A. MOELWYN-HUGHES, "Physical Chemistry" (Pergamon Press, Oxford, 1961) p. 1042.
7. M. PANAR, P. AVAKIAN, A. C. BLUME, K. H. GARDNER, T. D. GIERKE and H. H. YANG, *J. Polym. Sci. Polym. Phys. Ed.* **21** (1983) 1955.

Received 12 November 1991
and accepted 25 June 1992