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Role of microvoids in aramid fibres

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The distribution of microvoids in high-strength aramid fibre has been established. The tensile and compressive behaviours of both untreated and silver sulphide-impregnated Kevlar 981 fibre are reported and the results are discussed in terms of the influence of microvoids on the mechanical performance.

1. Introduction

An indication of the presence of electron density discontinuities or microvoids in high-performance engineering fibres such as aramids of the Kevlar type based on poly (*p*-phenylene terephthalamide) is provided by the intense equatorial low-angle X-ray scattering, particularly in dried fibres [1]. Subsequent confirmation was obtained by labelling with scattering centres, such as silver sulphide, for direct observation in the transmission electron microscope.

It was clear that accessible needle-shaped microvoids, of dimensions approximately 12 nm long and 2.5 nm wide aligned parallel to the fibre axis, were mainly distributed in a band or skin around the periphery of the fibres. In recent work [2], it has been shown that the skin thickness is characteristic of the Kevlar variant so, for example, it is negligible in the high-modulus fibre Kevalr 149, whereas it forms approximately 60%–70% of the total cross-sectional area in the high-strength Kevlar 981.

In view of the relatively large proportion of microvoids in Kevlar 981 it appeared appropriate to us to provide a suitable test specimen for possible modification of the mechanical properties by suitable deposition of material within such features.

This paper, therefore, reports both the tensile and compressional behaviour of single Kevlar 981 fibres incorporating silver sulphide within the original microvoids, and sheds light on the role of these entities during fibre deformation.

2. Experimental procedure

2.1. Specimen treatment

Kevlar 981 fibres were treated with gaseous hydrogen sulphide at a pressure of 1380 kPa for 16 h and subsequently washed in alcohol for a few minutes followed by immersion in a 5% silver nitrate solution for 3–4 h according to a procedure described by Sotton and Vialard [3]. For comparison purposes other samples were treated with hydrogen sulphide gas alone or silver nitrate solution alone.

2.2. Mechanical testing

Virgin and treated fibres were conditioned for 24 h at 20 °C and 65% relative humidity. The average diameters of the samples were determined optically for use in stress calculations.

2.2.1. Tensile properties

For each sample, 20 individual fibres were extended at 10% min^{-1} to break in an Instron tester using a gauge length of 0.05 m. Data acquisition, such as average breaking load, stress and extension, together with initial modulus was provided by a computer linked directly to the Instron.

2.2.2. Compressional properties

The test method used was originally described by Allen [4]. Essentially individual fibres of length 0.05 m were extended in an Instron to desired stress levels, then cut at the centre of the gauge length with sharp scissors. Both halves of the fibre recoiled naturally and were carefully collected from the clamps. Optical observations under crossed polars were made on each half of the cut filaments (providing two tests per sample) to determine whether or not kink bands had formed due to compressive failure. The critical compressive strengths were determined using 250 fibres (the majority of fibres were stressed in the range 200–500 MPa). Typical results are given in Fig. 1 which shows the percentage of fibres exhibiting compressional damage as a function of compressional stress. The critical compressional stress was then taken as the level when 50% of the fibres contained kink bands.

2.2.3. Structural studies

Fibres incorporating silver sulphide were embedded in TAAB resin and both longitudinal and oblique sections cut on an ultramicrotome using a diamond knife. The specimens were then examined in a JEOL 100CX transmission electron microscope using bright-field and diffraction modes. Diagnostic CuK_α X-ray diffraction patterns of both virgin and treated fibres were recorded by a flat plate camera using pin-hole collimation at a specimen-film distance of 0.04 m. Step-scanning of the equatorial X-ray scattering was

TABLE I Tensile properties of Kevlar 981 (SD given in parentheses)

Treatment	Breaking load (N)	Breaking stress (GPa)	Breaking strain (%)	Initial modulus (GPa)
Virgin	0.26 (0.04)	3.65 (0.61)	3.00 (0.32)	120 (15)
$H_2S + AgNO_3$	0.19 (0.05)	2.71 (0.67)	2.36 (0.52)	114 (13)
H_2S	0.27 (0.04)	3.89 (0.57)	3.32 (0.35)	116 (12)
$AgNO_3$	0.28 (0.05)	3.93 (0.49)	3.39 (0.23)	118 (14)

performed using a computer-controlled diffractometer. Correction and analysis of the data in terms of lateral crystallite sizes were identical to methods described elsewhere [5].

3. Results

The tensile properties of the untreated and treated fibres are shown in Table I. In all cases the initial moduli are very similar. However, it is immediately clear that deposition of silver sulphide in the Kevlar fibres leads to a very significant fall in breaking stress and breaking extension, whereas treatments with hydrogen sulphide alone or silver nitrate alone have negligible effect.

Results from the fibre recoil tests are presented in Fig. 1 where a well-defined shift in compressional resistance to a higher value is apparent after internal deposition of silver sulphide. Indeed the critical compressional stress increases by approximately 42% from about 300 MPa for virgin fibre to about 430 MPa for the treated fibre.

Bright-field micrographs, Fig. 2, show that the silver sulphide is distributed at discrete sites within a thick peripheral band of individual fibres. In particular the silver sulphide is in the form of needle-shaped deposits aligned approximately parallel to the fibre axis. The evidence suggests that such centres fill the original microvoids of the virgin Kevlar fibres [1, 2].

Analysis of the positions and integral breadth of the equatorial scattering from the 1 1 0 and 2 0 0 planes indicated little change in crystallographic parameters or in the apparent lateral crystallite size after silver sulphide deposition (see Table II). However, X-ray and electron diffraction studies of the treated fibres reveal an interesting aspect concerning the form of the

TABLE II The apparent lateral crystallite sizes

	(1 1 0) (nm)	(2 0 0) (nm)
Kevlar 981	4.52	4.04
Kevlar 981 + Ag_2S	5.19	4.47

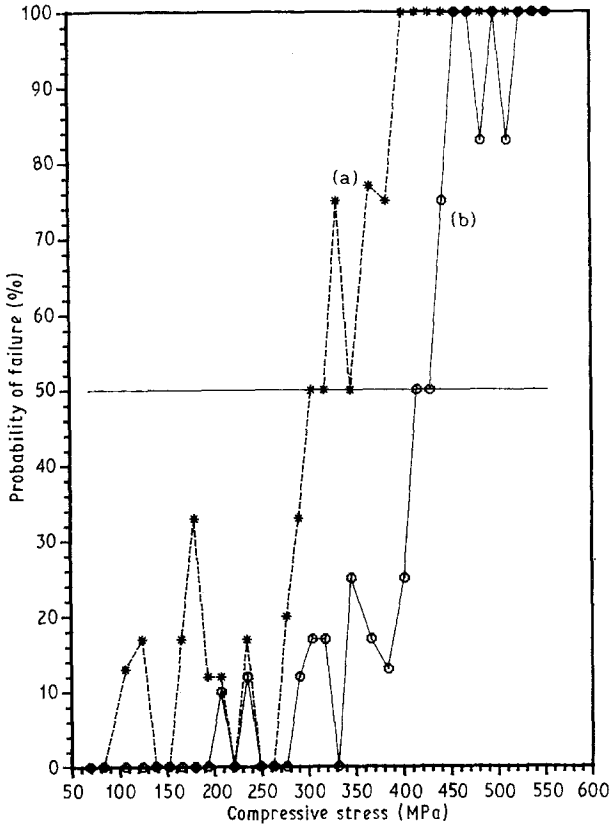

Figure 1 A typical plot of probability of compressive failure as a function of increasing stress in (a) untreated Kevlar 981, and (b) Kevlar 981 deposited with silver sulphide.

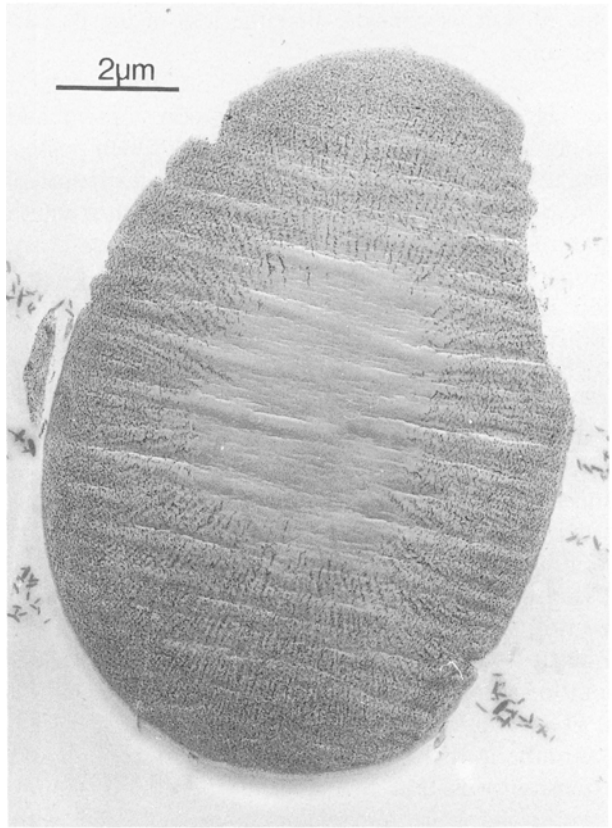

Figure 2 Bright-field transmission electron micrograph showing the distribution of microvoids in the Kevlar 981.

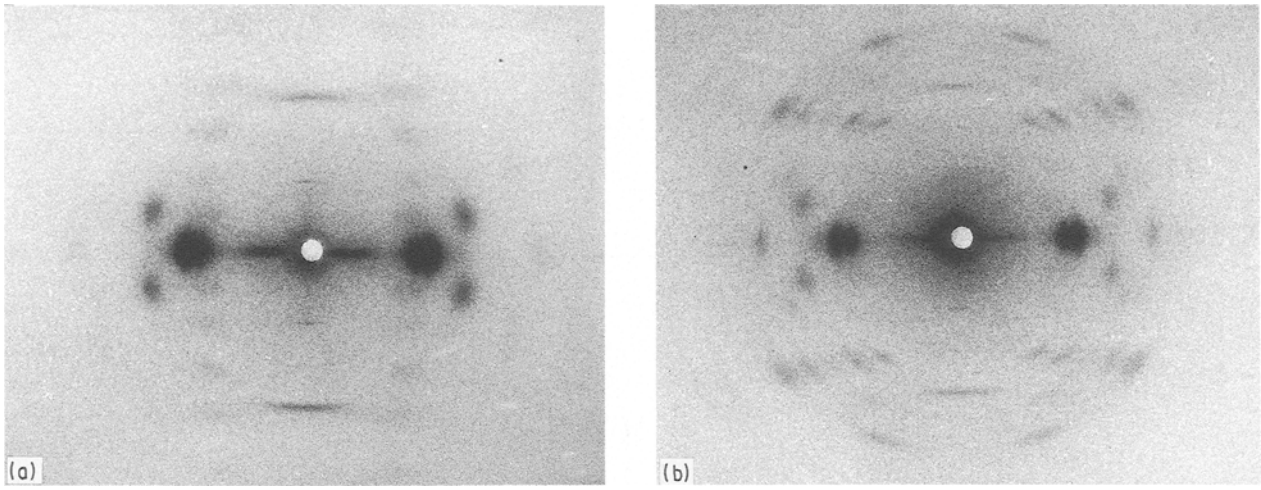

Figure 3 X-ray diffraction patterns of (a) Virgin Kevlar 981 fibre, and (b) Kevlar 981 impregnated with silver sulphide.

silver sulphide. For example, Fig. 3a and b show the X-ray patterns of virgin and treated Kevlar 981 fibres, respectively, where the additional reflections (seen in the latter) arise from crystalline silver sulphide deposited not in a random manner but with a preferred orientation. It would therefore appear that this crystal orientation is controlled by the form of the original microvoids leading to epitaxial growth within the fibre.

4. Discussion

Mechanical testing shows a situation whereby the tensile strength of the fibre is somewhat reduced whereas the resistance to compressional stress is enhanced. Let us consider first the loss in tensile performance.

As reported elsewhere [2], there appears to be a correlation between microvoid or skin content and strength; thus, for example, Kevlar 981 which possesses the greatest skin content has the highest strength of all the Kevlar variants. One feature of a high-strength material is the ability to minimize transverse crack propagation and, consequently, it is tempting to suggest that the microvoids act as deflectors of small transverse cracks along axial or off-axial directions. On the other hand, crystalline silver sulphide filling the original voids would tend to provide a path for transverse crack propagation leading to premature failure of stressed fibres. Indeed such a physical mechanism is supported by the fact that chemical degradation by either hydrogen sulphide alone or silver nitrate solution alone does not appear to be involved in the loss of tensile performance. Moreover examination of fracture faces in the scanning electron microscope indicates a change from the extensive longitudinal splitting of virgin fibres to more transverse-like failure of fibres containing silver sulphide.

Another possible reason for the loss in strength and extensibility is that the molecular chains originally forming the walls and regions adjacent to the voids are pinned by the silver sulphide deposits and, consequently, cannot rearrange or align sufficiently well in order to accommodate the increasing stress during extension. In this way, premature breakage may occur without necessarily lowering the modulus.

Conceivably both the above mechanisms may contribute to the observed tensile performance.

In the case of enhanced compressional resistance the detailed mechanism remains somewhat obscure. For example, it may be argued that the higher compressive failure strength results from, on the one hand, an effective increase in fibre cross-sectional area due to infilling of the microvoids or on the other hand, true reinforcement of the fibres by an aligned array of rigid crystallites of silver sulphide. It is clear, however, that the mechanism is very different from that reported for various types of carbon fibres where increasing structural disorder appears to favour significant improvement in compressional strength [6]. This work clearly indicates the role of microvoids in Kevlar fibres and shows that approriate infilling is capable of modifying significantly the mechanical performance. Exploration of impregnating materials other than silver sulphide is perhaps indicated for any commercial exploitation.

Acknowledgements

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