Compressional behaviour of Kevlar fibres

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The compressional deformation of poly(*p*-phenylene terephthalamide) (PPT) fibres of the Kevlar type has been followed by scanning and transmission electron microscope methods in order to explain changes in mechanical properties. A structural mechanism describing the mode of deformation is proposed which is based on the initial formation of kink-bands. The propagation of the latter appears to be unaffected by the presence of the axially pleated-sheet structure exhibited by Kevlar fibres. The proposed mechanism is consistent with an observed loss in tensile strength after compression. It is considered that the relatively poor compressional behaviour of aramid-type fibres arises from the weak lateral cohesion between their essentially rigid molecular chains, in agreement with the findings of Greenwood and Rose.

INTRODUCTION

Fibre reinforced composites with their high performance to weight ratios are potentially very desirable in certain industrial sectors and are finding general acceptance. In particular, components based on carbon fibre composites are well known in the aerospace and other specialized engineering fields, and show significant improvement[1] with regard to tensile modulus and weight over traditional metallurgical products, or indeed glass-reinforced composites.

A possible alternative to carbon fibres has been found with the development of aramid fibres, in particular the Kevlar[2] group, having a higher specific strength, greater extensibility and a high modulus (*Table 1*). Such aramid fibres are based on poly(*p*-phenylene terephthalamide) (PPT) which forms a liquid–crystalline system in solution due to the rigidity of the molecular chains. This leads to a highly ordered material whose unique structure of radially arranged pleated sheets has been described elsewhere[3]. Unfortunately the Kevlar variants have been reported as having relatively poor compressional properties[4] compared with other fibres, which may limit their use as reinforcement elements in engineering assemblies. The ratios of tensile to compressive strengths of 0° unidirectional epoxy composites containing carbon fibres, glass and Kevlar 49, are 1.1, 1.9 and 5.0 respectively. Greenwood and Rose[4] have shown that the relatively poor performance of Kevlar composites is due primarily to the very low compressive yield strength of the fibres themselves, not to the matrix component.

In this paper, therefore, we investigate the structural origin of these compressional deficiencies using electron microscope techniques and compare the compressional behaviour of Kevlar variants.

EXPERIMENTAL

The aramid variants studied during this work included Kevlar 29, Kevlar 49 (PPT) and PRD 49 (probably based on poly(*p*-benzamide)) fibres having diameters of ~12.5 μm. Because of the difficulties associated with the axial compression of single fibres of small diameter, the study has concentrated mainly on fibres deformed in such a way that compression is restricted to the inside of a loop. Additional information has been obtained from fibres extracted from axially compressed fibre–epoxy resin composites using 10% ethanolic potash solutions for 48 h.

Mechanical behaviour

Fibres were subjected to two types of bending: (1) the formation of a single loop of varying radius and (2) repeated flexing effected by reciprocating a length of fibre over a pulley of fixed radius.

Elastica test: Fibre samples were subjected to the elastica test[4,5] in which the size of a loop was progressively reduced and the corresponding dimensions of the major and minor axes measured optically. Providing the deformation is elastic, then the ratio of the major to the minor axes should, theoretically, be a constant value of 1.34. The onset of plastic deformation would then be indicated by an increase in this value.

Cyclic deformation: Single fibres were attached to a reciprocating arm and passed over a pulley of diameter

Table 1 Tensile properties

	Kevlar 49	Kevlar 29	E. Glass	Carbon Type 1	Carbon Type 2	PRD 49
Tensile strength (GPa)	2.6	2.6	2.4	2.0	2.6	2.3
Specific tensile strength (GPa)	1.79	1.80	0.93	1.02	1.4	1.58
Tensile modulus (GPa)	128	59	69	400	260	150
% Extension to break	2.4	4.0	4.0	0.5	1.0	1.8

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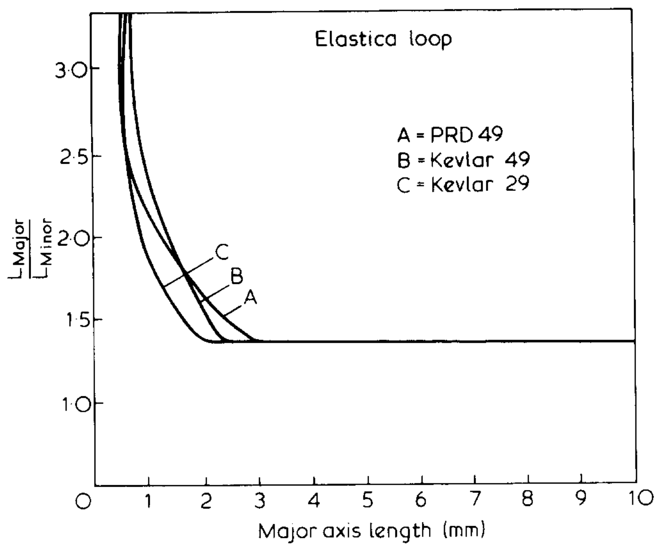

Figure 1 A plot of the ratio of major to minor axis against major axis for the Elastica test. A, B and C are for PRD 49, Kevlar 49 and Kevlar 29 respectively

0.48 mm set in jewelled bearings. A lap angle of 90° was used throughout the experiments and the fibre subjected to a constant tension by fixing a weight of 5×10^{-3} kg to the free end. The stroke of the reciprocating arm was $\sim 4 \times 10^{-2}$ m at a rate of 30 cycles per min. Kevlar 29 and Kevlar 49 fibres were both deformed for 10, 50, 100, 500 and 1000 cycles.

Mechanical testing. 20 mm lengths of fibre samples (ten for each deformation) were conditioned at 20°C and 65% relative humidity for 24 h and subsequently extended to failure in an Instron machine, employing pneumatic jaws to minimize slippage, at an extension rate of 2 mm min^{-1}. The average tensile strength was determined from the load–extension plots.

Structural investigation

Transmission electron microscopy (TEM): To delineate internal structural rearrangements within the fibres, some were stained with silver sulphide[6] and then deformed into loops. Stained and unstained fibres were embedded in Spurr resin and sectioned either longitudinally or, where appropriate, through the plane of the loops, using a diamond knife fitted to an ultramicrotome. The specimens were examined in a JEOL 100CX instrument operating at an accelerating potential of 100 kV using both bright and dark field techniques.

Scanning electron microscopy (SEM): All specimens were coated with a thin layer of gold and examined in a Cambridge Stereoscan operating at 20 kV. Progressive deformation of single fibres, as a function of loop size, was directly observed in the microscope by fixing one end of a looped fibre to the instrument stage and winding the other end around a capstan connected to the external stage controls of the microscope.

RESULTS

Compression during loop formation

A plot of the dimensions of the major axis against the ratio of the major to minor axes for loops of PRD 49, Kevlar 49 and Kevlar 29 is shown in *Figure 1*. Plastic deformation resulting from compression occurs firstly in PRD 49, then in Kevlar 49 and finally in Kevlar 29, corresponding to a compressive strain of ~0.5%. The curve for Kevlar 49 is consistent with that previously obtained by Greenwood and Rose[4]. This ranking is in the order of decreasing tensile modulus and increasing breaking strain of the fibres, an observation which is in agreement with results obtained for carbon fibres[7].

Examination in the *SEM* of the aramid variants, bent through varying degrees, shows a characteristic banding restricted to the inner surface of the loop. In the case of Kevlar 29 and 49 the bands appear to be singular and evenly distributed around the curve often at oblique angles to the fibre axis as shown in *Figure 2*. In contrast, the surface banding in PRD 49 (*Figure 3*) is highly branched but localized in regions where the fibre ultimately shows abrupt changes in direction. With decreasing radius the bands in PRD 49 pile up and tend to concentrate the deformation whereas in the Kevlar fibres numerous cross bands are formed all around the curve which help to distribute the increasing compression.

The origin and mechanism of formation of these surface bands has been investigated by examination of fibres of varying loop radii in both the scanning and transmission microscopes. *Figure 4* is a schematic diagram showing the various phases in the deformation which have been identified. The first indication of deformation in Kevlar fibres is the appearance of irregularly spaced single narrow bands lying at ~40–50 degrees to the fibre axis. In sections taken through the plane of the loop the banding is a surface step resulting from a narrow wedge-shaped region formed by an abrupt change in main-chain direction (i.e. a kink band). This feature is particularly apparent in silver sulphide stained fibres as shown in *Figure 5*.

With progressive deformation, individual kink band domains appear to propagate inwardly from the skin towards, and possibly beyond, the fibre axis (*Figure 6*). Simultaneously the wedge increases by further kinking of

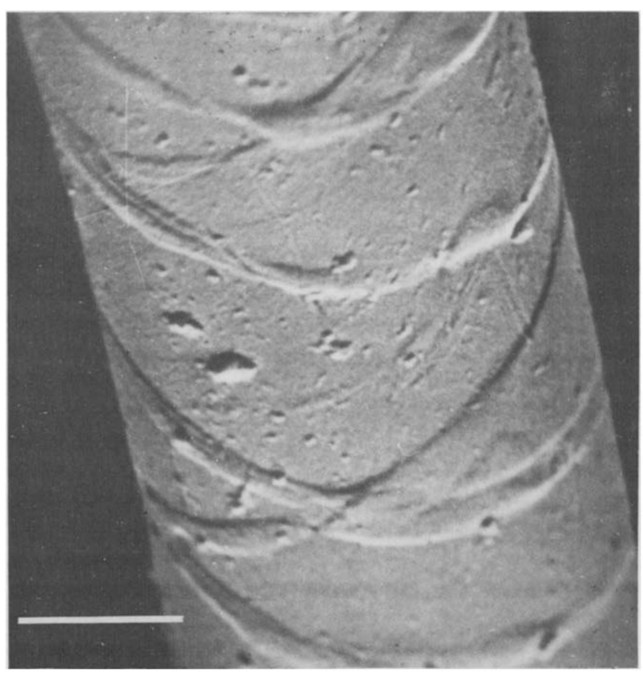

Figure 2 Typical surface banding of the inner surface of a Kevlar 49 fibre loop. Scale marker 4 μm

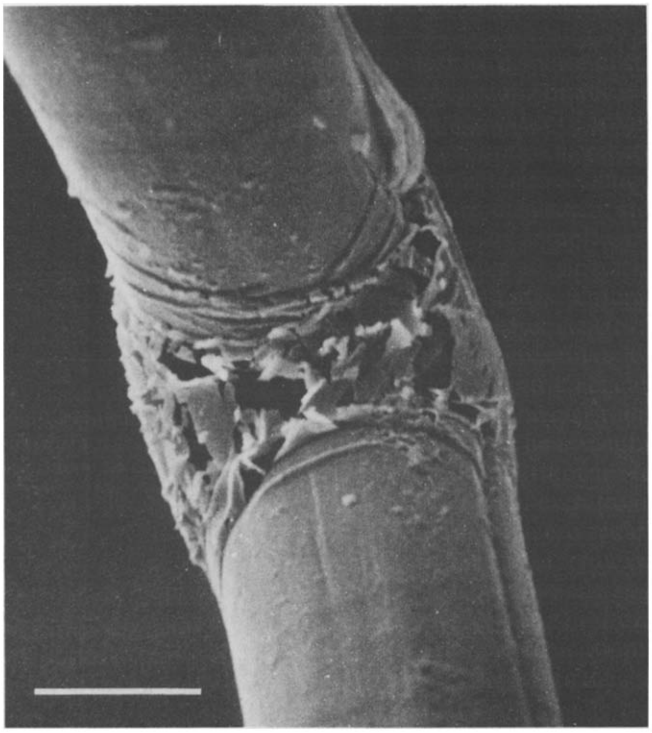

Figure 3 Surface deformation of the inner surface of a PRD 49 fibre loop showing gross buckling. Scale marker 7 μm

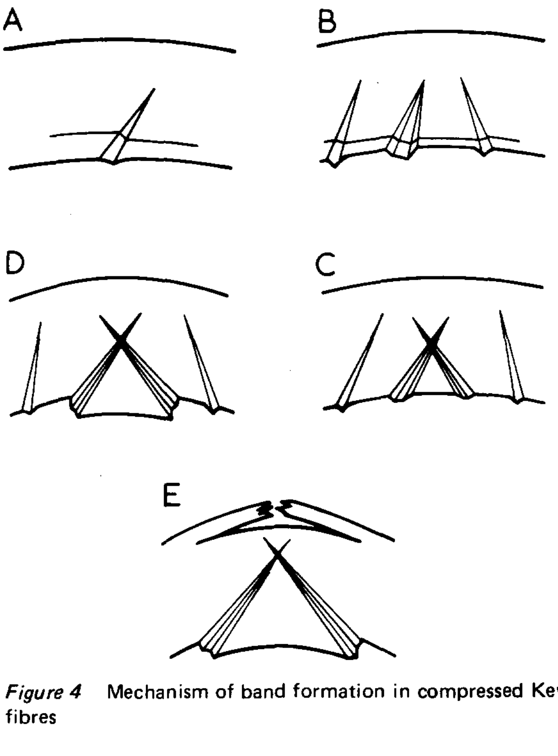

Figure 4 Mechanism of band formation in compressed Kevlar fibres

the molecular chains and new kink bands are formed at a distance on either side of the original feature (*Figure 4b*). When the single surface bands become regularly spaced at ~4 μm, cross bands start to form which intersect the original bands. The wedge-shaped region between such bands can accommodate further compression by lateral displacement towards the centre of curvature of the loop, and form large surface bands whose edges are characterized by abrupt changes in direction (*Figure 4d*). Any further compression, say in the formation of a knot, leads to progressive tensile failure of the outer regions of the fibre (those elements under extension) and associated delamination (*Figures 4e* and *6*). Ultimately the fibre will fail during the formation of a knot due to the fracture of delaminated layers of material commencing at the outer surface of the fibre and progressing inwards through the original compression zone (*Figures 6* and *7*).

The effect of structural deformation brought about by compression of fibres up to the level shown in *Figure 4d* is related to any subsequently applied tensile forces that may occur in either flexed reinforced materials, or in ropes, cables and woven fabrics. *Figure 8* shows the loss in tensile breaking strength of single fibres as a function of the number of bending cycles imposed over a free-running spindle. For the same number of cycles the decrease in strength of Kevlar 49 is considerably greater than that of Kevlar 29. Both curves are characterized by an initial rapid fall in strength after only a few cycles, followed by a more gradual decline.

Regularly spaced single narrow surface bands of limited length can be detected first in the *SEM* on these fibres after 100 cycles. As the number of bending cycles increases up to 1000, such bands become both wider and longer and are much easier to detect. Although surface bands are not easily detected, *TEM* examination of sectioned fibres indicates the presence of extremely narrow internal kink bands in fibres subjected to only a few bending cycles.

Axial compression

In many applications, aramid fibres are used to form rigid composite structures in which compressive behaviour may limit the stress carrying capacity. To simulate such deformation, unidirectional fibre–epoxy

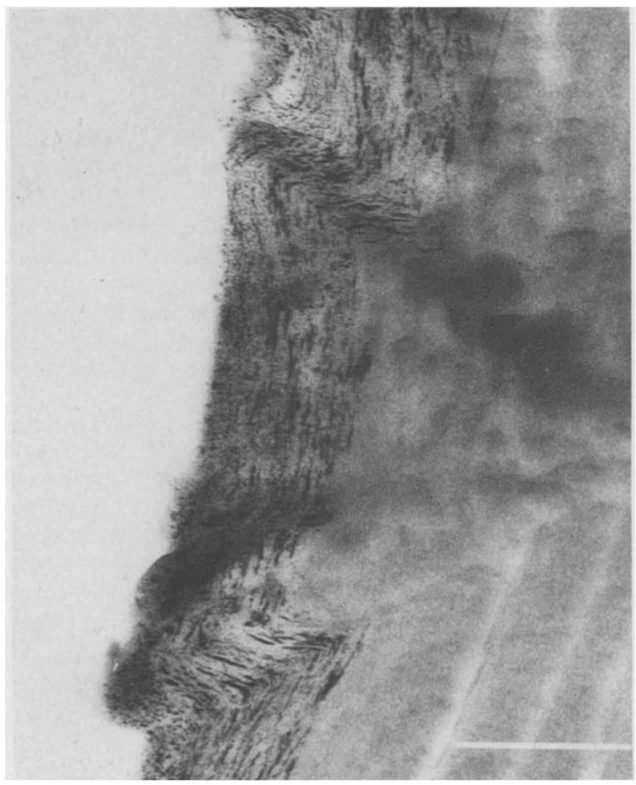

Figure 5 A longitudinal section through a Kevlar 49 fibre stained with silver sulphide and subsequently compressed, showing kink bands. Scale marker 0.5 μm

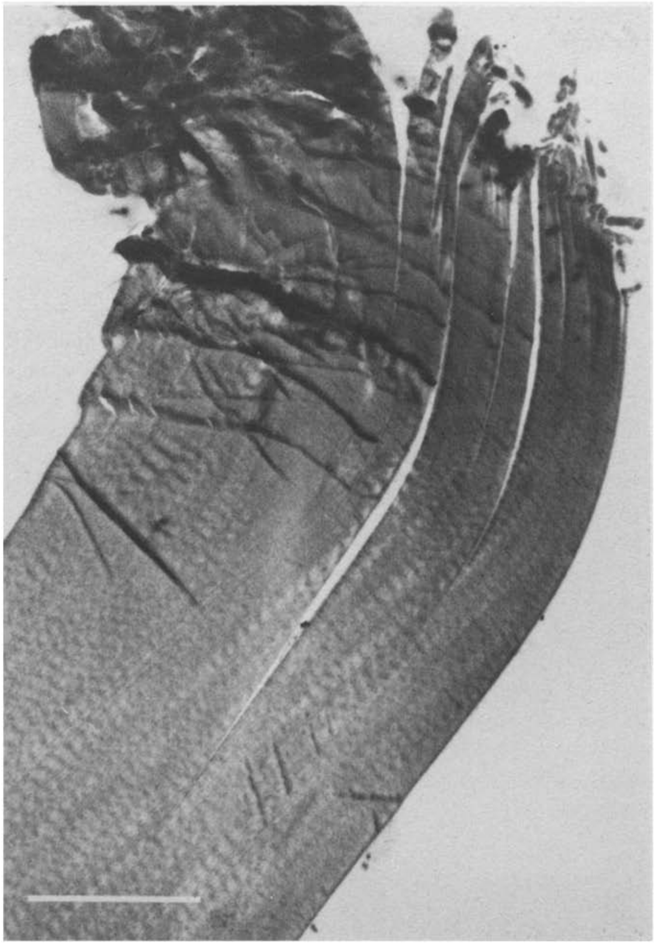

Figure 6 Longitudinal section through a fibre loop showing internal kink bands and delamination of the outer layers. Scale marker 6 μm

composites (fibre volume fraction ~55%) were subjected to a uniaxial compression in contrast to the previously considered case of bending. Fibres extracted from the composite which were compressed well beyond the yield stress, reveal in the *SEM* massive lateral displacement of whole segments as shown in *Figure 9*. This behaviour allows the fibres to accommodate any additional compression by assuming a curved or sometimes almost sinusoidal configuration (*Figure 10*). In the transmission microscope, sectioned fibres show discrete shear bands extending equally across the whole fibre (*Figure 11*) in which the chain direction changes abruptly with respect to adjacent fibre segments (in some cases 90° or more). Within each band the chains appear to be deformed through a constant angle. After subsequent tensile stress to failure, examination of these compressed fibres reveals two main features. Firstly it appears that the displaced segments are capable of realignment along the direction of the applied force and secondly, that the fracture face, unlike the very long oblique failure surfaces associated with a normal tensile failure[8], is of limited axial extent and occurs within the kink band region. Such a fracture face is shown in *Figure 12* and consists of parallel rows of lamellae, the length of which is defined by the boundaries of the kink bands. The spacing of the lamellae is probably associated with the presence of microcracks in the kink bands as discussed below.

DISCUSSION

The fundamental characteristic of compressed aramid fibres is the formation of a well defined region corresponding to an abrupt change in orientation of the molecular chains with respect to the fibre axis. This change in orientation arises from approximately equal and opposite changes in chain direction at the boundaries of the region (kink band). Aramid polymers can be regarded as essentially rigid molecular chain systems, therefore any decrease in axial length of a fibre, brought about by compression, cannot be accommodated by a gradual change in chain direction but might be expected to give rise to excessive localized strain in the system either leading to complete chain rupture or permanent deformation. Consequently, all the chains within the kink band will be sheared with respect to each other (i.e. molecular delamination or a loss of lateral cohesion) unless gross deformation, including chain rupture, occurs at the kink band boundaries.

TEM studies have revealed microcracks aligned parallel to the chain direction within the kink bands. Such

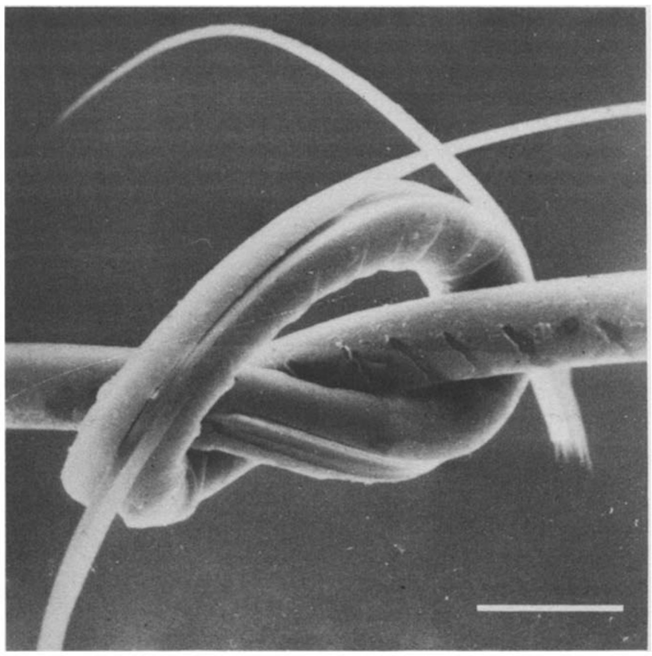

Figure 7 A knotted fibre showing surface banding and delamination of outer layers. Scale marker 20 μm

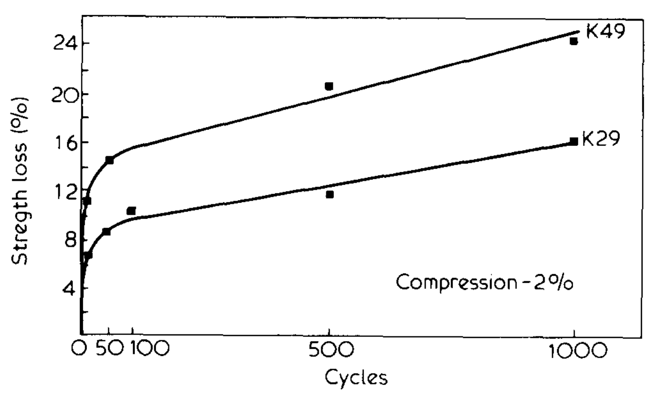

Figure 8 A plot of percentage strength loss against number of flexural cycles for Kevlar 29 and 49 fibres

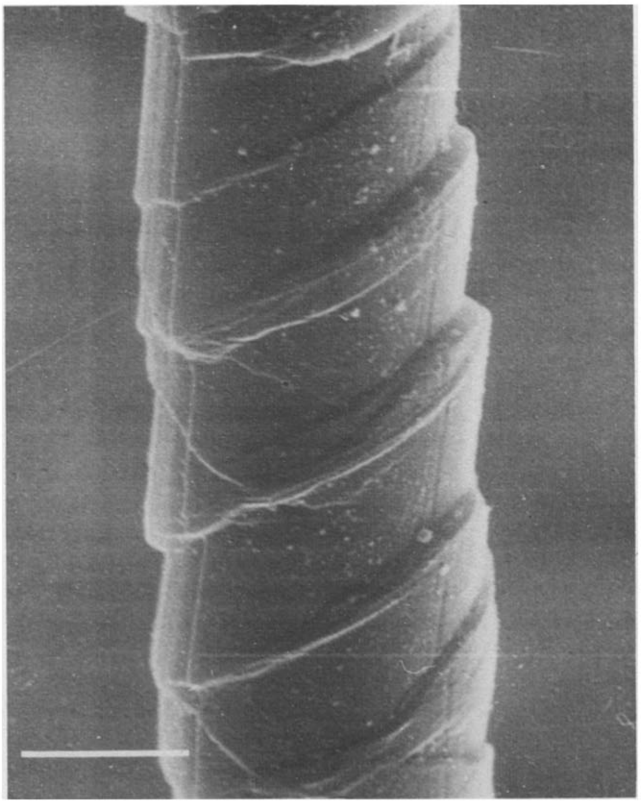

Figure 9 Fibre extracted from an axially compressed composite exhibiting lateral displacement of segments. Scale marker 6 μm

observations may indicate that the degree of shearing between adjacent molecular chains is non-uniform, leading to the complete separation of blocks of chains within the kink bands.

Any fibre exhibiting even a single kink band would be expected, therefore, to show a loss in tensile strength because, in comparison with undeformed regions, the straightened kink band domains will be more inhomogeneous. They contain voids resulting from molecular delamination and show loss of orientation which may subsequently cause chain rupture. Compressed specimens, unlike undeformed fibres, exhibit fracture faces of limited axial length, after subsequent tensile stress, which correspond with the position and extent of kink bands. An immediate drop in strength is observed in the subsequent tensile testing of fibres subjected to a low number of flexural cycles (*Figure 8*). After this initial fall, the strength loss continues to increase, albeit at a slower rate with increasing number of cycles. Such behaviour can be explained in terms of the gradual growth in extent of the original kink bands as observed in the electron microscope. As the kink bands are known to straighten under subsequent tension, this implies that during the flexing process, the boundaries of the band act rather like a hinge which may concentrate further damage in the immediate vicinity. If the kink boundary extends across the whole width of the fibre, as in the case of a compressed fibre

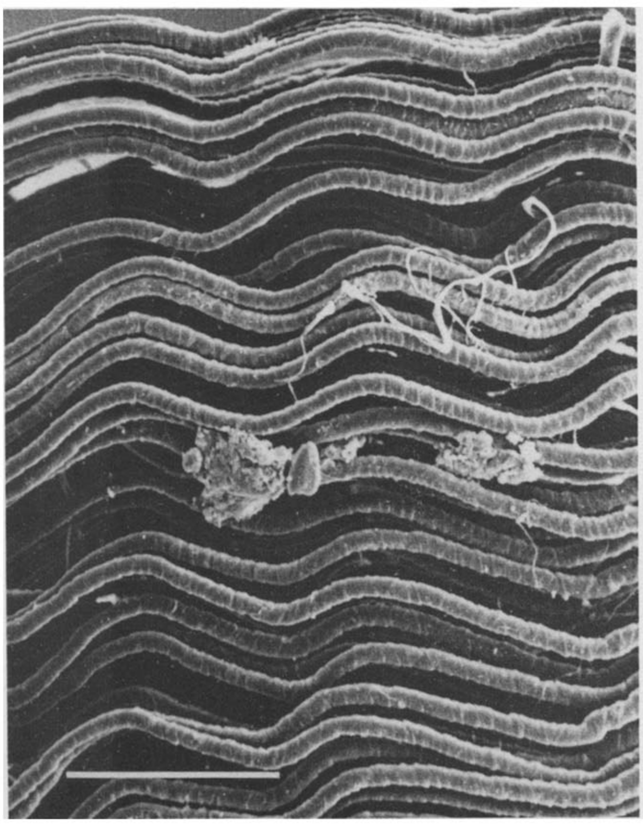

Figure 10 An array of fibres extracted from an axially compressed composite showing permanent sinusoidal deformation. Scale marker 150 μm

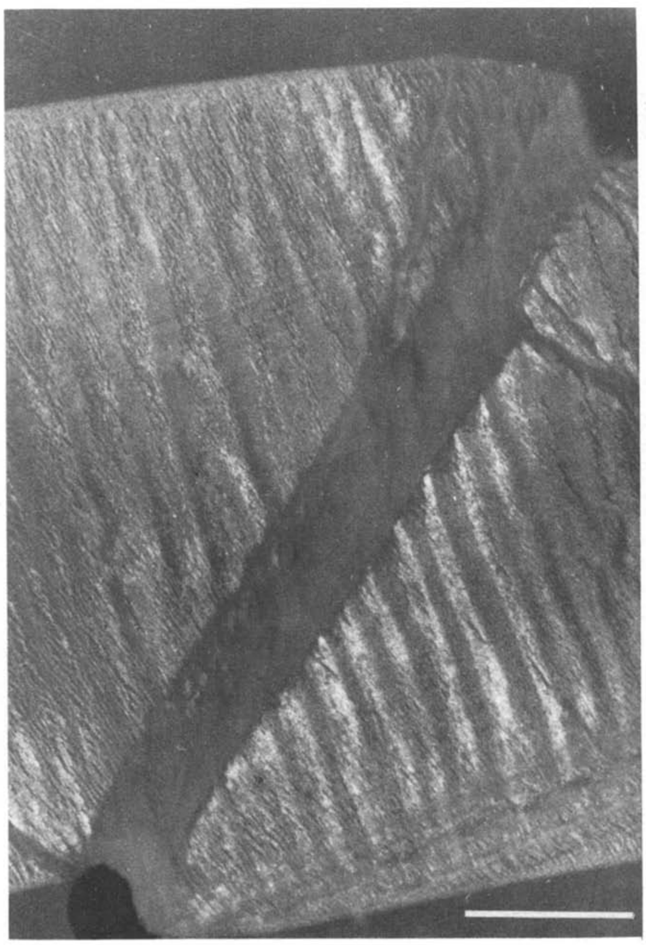

Figure 11 Dark field micrograph of a longitudinal section through a compressed Kevlar 29 fibre showing intersection of a kink band with the periodic banding associated with the pleated sheet. Scale marker 3 μm

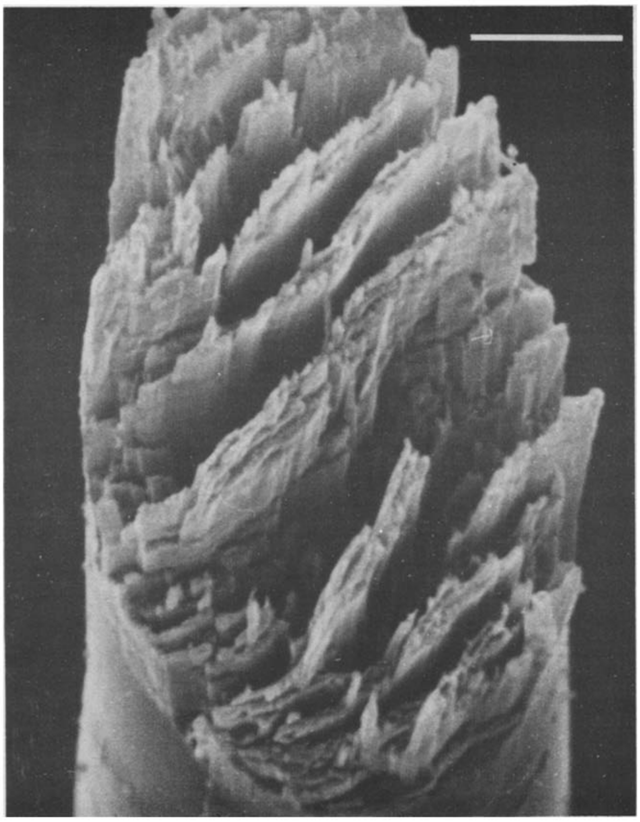

Figure 12 Fracture face of Kevlar 29 broken in tension after initial compression. Scale marker 4 μm

composite, such a mechanism will allow considerable lateral displacement of fibre segments (*Figure 9*).

As reported previously[3], Kevlar fibres possess an axially pleated structure with a repeat of ~ 500 nm. One might expect such a feature to accommodate some compressional deformation. However, since kink bands appear at < 1% compression, the amount accommodated by increasing the pleat angle must be very small. Examination of fibres subjected to compressional forces show kink bands intersecting an array of axial dark-field bands associated with the pleated structure, (e.g. *Figure 11*). The presence of the pleated structure would appear to have little or no influence on the initiation and subsequent propagation of the kink bands.

CONCLUSION

The structural factors expected to impart resistance to compressional forces (i.e. high compressional modulus) will be:

(1) A high rigidity of the molecular chains which implies that strain cannot be accommodated by bond rotation as in a flexible chain system.

(2) A high degree of molecular order which will tend to restrict appreciable molecular movement because of bonding forces.

However, a high modulus does not necessarily lead to high strength. This will depend on the magnitudes of the above effects since they effectively control the stress at which the assembly ceases to act as a rigid system.

The lack of strong lateral bonds in the aramids which could form interlinks between molecular domains is to be contrasted with the situation in carbon fibres which exhibit a much higher compressional strength due not only to the presence of lateral covalent bonds, but also their random transverse orientation. Thus in the Kevlar fibres one would expect a compressive stress to initiate shear between, or delamination of, adjacent chains, as a result of the low lateral strength arising from relatively weak Van der Waal forces and the oriented hydrogen bonding between chains[9]. As indicated by Greenwood and Rose[4] such weak bonding will control the compressive behaviour of the fibres.

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