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Structural characteristics of aramid fibre variants

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Recently new types of high-performance aramid fibre based on poly(p-phenylene terephthalamide) have been developed. This paper reports on their very different tensile behaviour and structural character as revealed by electron microscope and X-ray diffraction studies. The relationship between mechanical performance and structure of the variants is explored in detail, and performance-limiting factors are identified with a view to understanding how further improvements in properties may be achieved.

1. Introduction
The use of high-performance fibres, notably of the Kevlar type based on poly(p-phenylene terephthalamide), in many diverse engineering applications is well documented [1–3]. However, the general structure/performance relationships of such fibres are only slowly being elucidated. The purpose of this paper is to report on the structural and tensile characteristics of fibre variants such as Du Pont's newly developed high-modulus Kevlar type 149, the high-strength Kevlar type 981 and the recently introduced Akzo fibre, Twaron. Comparison of such information with that already available on the standard fibres will undoubtably lead to a better appreciation of structure/property relations and the identification of performance-limiting factors. The detailed structural studies have involved primarily transmission and scanning electron microscopy in combination with X-ray and electron diffraction.

2. Experimental procedure
2.1. Tensile properties
20 individual fibres were mounted on card holders having a gauge length of 200 mm. The average diameter of the fibres was determined from measurements of SEM images. Tensile properties were determined using an Instron 1122 tester operating at a rate of extension of 10% min^{-1}. The output from the Instron was fed to a microprocessor-controlled recorder/analyser programmed to directly determine the average stress, strain and modulus from individual fibre input parameters.

2.2. Electron microscopy
All the variants were examined in a Cambridge Stereoscan 150B operating at 20 kV. Internal detail was revealed by fracture of fibres in glycerol. The glycerol was then removed by hot water and the fibre was dried. A thin layer of gold was then sputtered on to the specimen surface. Both longitudinal and oblique sections of fibres were examined in a Jeol 100 CX transmission microscope operating at 100 kV. In some cases specimens were first impregnated with silver sulphide according to the method reported by Sotton and Vialard [4]. Selected-area electron diffraction patterns were obtained from approximately 1 μm diameter regions of single fibres.

2.3. X-ray Techniques
The charactersitic X-ray patterns of Kevlar fibres and the basic unit cell have been reported elsewhere [5]. Detailed wide-angle X-ray diffraction studies were carried out using Cu$K\alpha$ radiation supplied by a Hiltonbrook generator. Diffraction scatter was monitored by a microprocessor-controlled step-scan diffractometer. A scintillation counter was used to record the diffraction data at a scan rate of 20 readings per degree through the selected equatorial intensity peaks (1 1 0 and 2 0 0 reflections). Analysis of the data included (i) correction and normalization of the diffraction data, (ii) resolution of the total peak scattering from so-called background scatter, (iii) correction of the resolved profiles for instrumental broadening and (iv) resolution of the corrected profiles into individual peaks for calculation of integral breadth. The computational methods are described in detail elsewhere [6]. An assessment of the average degree of crystallite orientation was obtained from the azimuthal intensity profile of the meridional (0 0 4) reflections using the half-height width.

3. Results
It is clear from Table I that the tensile properties of Kevlar 29 and Twaron are comparable, although the former appears to be slightly weaker. Conventional Kevlar 49, although exhibiting similar strength, has a tensile modulus double that of Kevlar 29 but with a reduced breaking extension. A significant improvement in modulus over the other aramids is shown by Kevlar 149, but this appears to be achieved at the expense of reduced breaking extension. Furthermore the breaking stress is the lowest of all the variants although the average breaking load is comparable with that of Kevlar 981 fibres which have a much smaller cross-sectional area. It should be noted that

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TABLE I Average tensile properties

Fibre	Breaking stress (GPa)	(SD)	Breaking strain (%)	(SD)	Initial modulus (GPa)	(SD)	Diameter (μm)	(SD)
Kevlar 29	2.6	(0.5)	2.9	(0.4)	77.1	(8.4)	12.6	(0.5)
Twaron	3.0	(0.4)	3.3	(0.4)	78.8	(6.5)	12.5	(0.5)
Kevlar 49	2.8	(0.5)	2.2	(0.4)	123.0	(8.4)	12.1	(0.5)
Kevlar 981	3.5	(0.6)	2.8	(0.4)	120.2	(14.6)	9.5	(0.6)
Kevlar 149	2.2	(0.3)	1.2	(0.2)	166.6	(11.0)	11.9	(0.5)

Kevlar 981 exhibits by far the highest breaking stress. Taking an overall view it is clear that aramid fibres have a potential for significant improvement in tensile performance, although at present there appears to be a trade-off between individual parameters.

A valuable technique for revealing the presence of voids within a material consists of treatment with hydrogen sulphide gas and subsequent immersion of the fibre in a silver nitrate solution [4]. In this way silver sulphide is deposited in the voids, which can be easily detected when sections are examined in the transmission electron microscope. It has been shown [5], using this method, that Kevlar fibres possess a porous skin region consisting of arrays of needle-shaped voids aligned approximately parallel to the fibre axis. In this study, the skin (Fig. 1) of high-strength Kevlar 981 was much thicker (up to 2 μm) than in any other variants; indeed, in the case of Twaron it rarely exceeded 0.15 μm in thickness. Also of interest within the skin of Kevlar 981 were thin bands ($\sim$30 nm), spaced axially at about 500 to 600 nm, which were devoid of silver sulphide as shown in Fig. 2. Comparison with dark-field images of the same region showed that the bands (voidless regions) coincided with the turning points of adjacent components of the pleat structure. Since voids are thought to be located mainly between radially arranged pleated sheets, then the banding observation may well represent a more efficient localized packing in the vicinity of the transition zone (where the molecules lie parallel to the fibre axis) between adjacent components of the pleated sheets. The dimension of the banding is identical with that reported elsewhere [7] for the length of the transition zone.

It is generally recognized in fibre science that orientation plays a profound role in determining mechanical properties, for example high orientation promotes efficient load-sharing between molecular chains. Azimuthal scans through the meridional 004 reflections can be used to estimate the average overall degree of orientation. As shown in Table II, Kevlar 149 has by far the highest orientation, followed by Kevlar 981, Twaron and Kevlar 49. Such a ranking is compatible with the observed tensile moduli, but not with the observed strengths. Comparison of selected-area diffraction patterns (Figs. 3 and 4) taken from longitudinal sections of skin (or peripheral regions) and core regions clearly show that the former is more highly oriented. The appearance of additional reflections in the skin diffraction pattern of Kevlar 981,

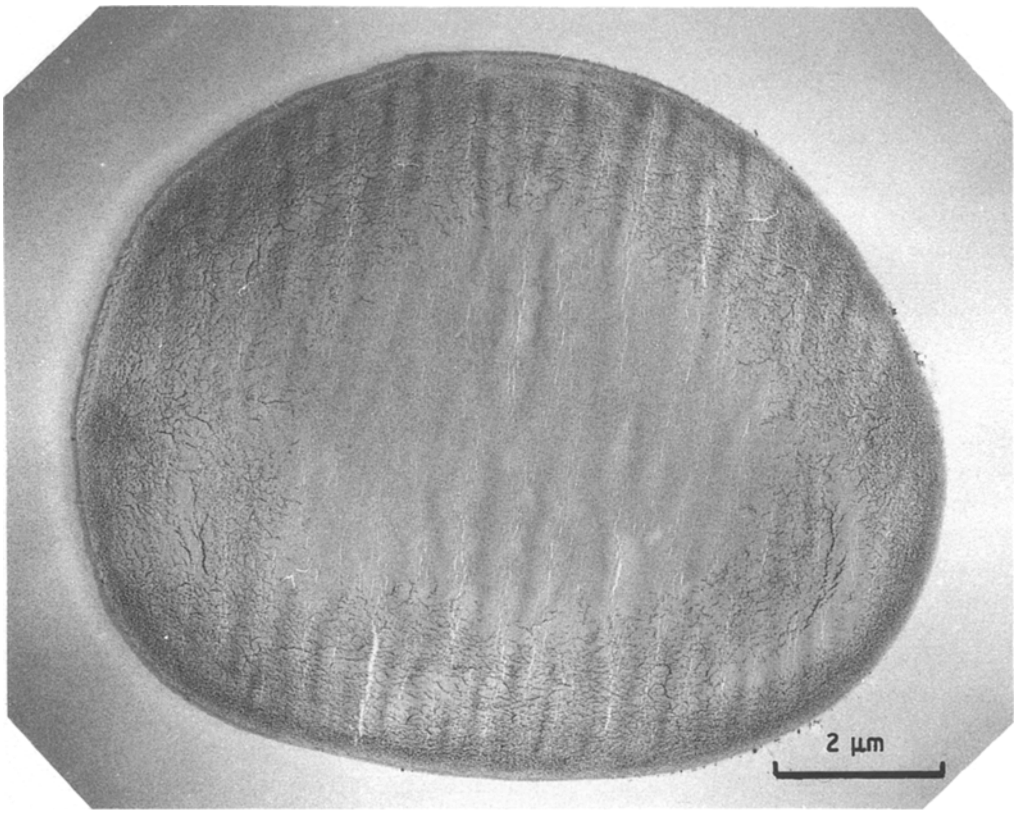

Figure 1 TEM. Oblique section through Kevlar 981 showing skin/core texture.

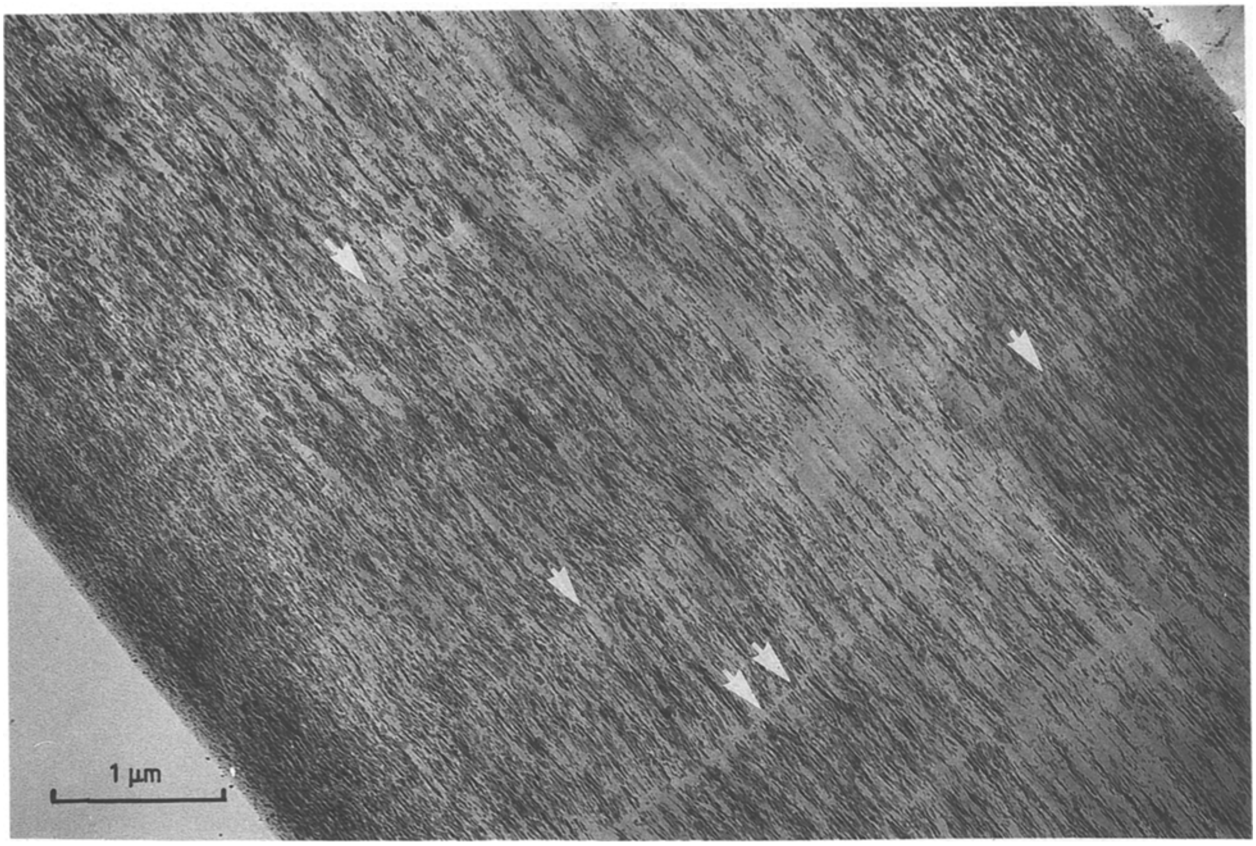

Figure 2 TEM. Longitudinal section through Kevlar 981 showing regular banding (devoid of silver sulphide) in skin region.

TABLE II Diffraction data

Fibre	Lateral crystallite size (nm)		Overall orientation (deg)	Skin thickness (μm)
	110	200		
Kevlar 29	4.51	3.96	25.0	0.3 (average) to 1.0
Twaron	5.41	4.48	22.2	0.15 (average)
Kevlar 49	5.08	4.06	14.4	0.3 (average) to 1.0
Kevlar 981	4.52	4.04	19.7	2.0 (average) to 1.0
Kevlar 149	9.14	5.85	13.5	Negligible

which are discrete rather than extended arcs or rings, is particularly interesting since it indicates that the silver sulphide in the voids of the fibre is in the form of highly oriented crystals (epitaxial growth). Such a system might be expected to have a marked effect on the mechanical properties of the fibre.

Although Kevlar 29 and Twaron have roughly similar tensile properties, significant differences in structure have been detected. For example Twaron appears to have a thinner skin region, but more significantly reveals numerous discontinuous core defects when viewed in the optical microscope. Detailed SEM examination of this inner region was made by fracturing fibres in glycerol and a representative micrograph is shown in Fig. 5. The micrographs show the usual axial banding in the outermost regions of the fibres

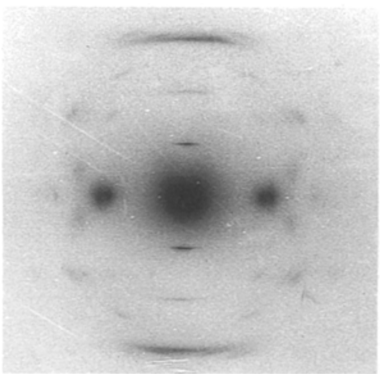

Figure 3 Electron diffraction pattern of the skin region of Kevlar 981.

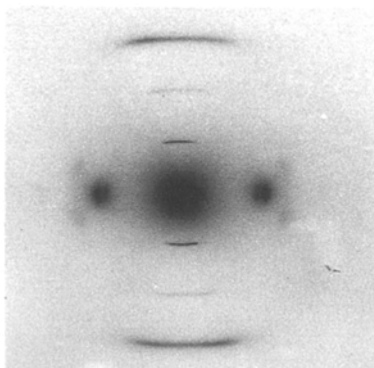

Figure 4 Electron diffraction pattern of the core region of Kevlar 981.

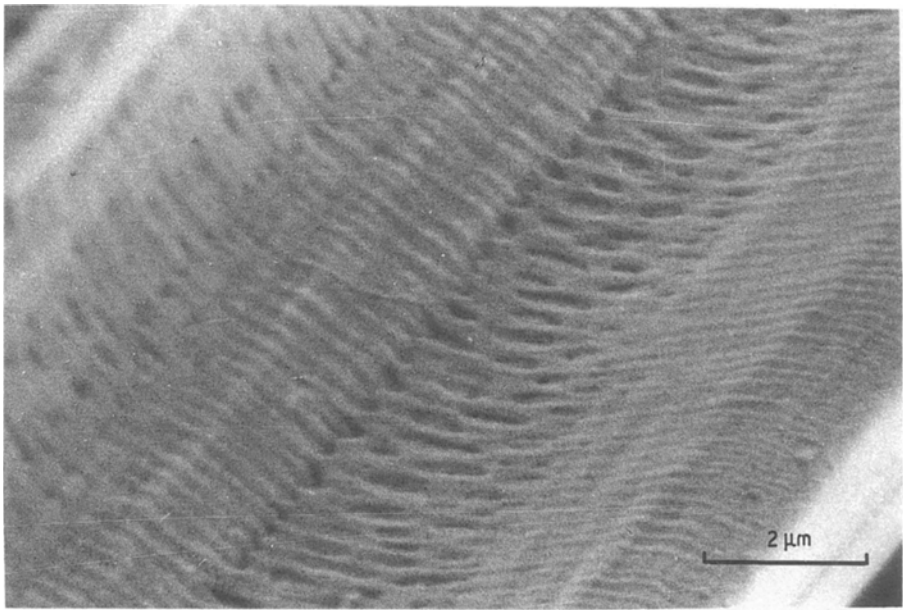

Figure 5 SEM. Core defects in Twaron.

(associated with the pleated sheet) but also a central defective core where segments of the pleat are interrupted by holes. It would seem that the coagulation conditions are such that a thin rigid skin is initially formed which constraints the fibre diameter. Subsequent loss of solvent from the interior and eventual removal of coagulant during drying results in shrinkage and voiding of the core region. The conditions of coagulation of Twaron appear to be different from those of Kevlar, as the skin is thinner and core defects of the type described have not been observed.

In addition to the slightly better orientation of Twaron compared with Kevlar 29, analysis of the X-ray equatorial reflections indicates a slightly higher apparent lateral crystallite size, particularly of the 1 1 0 planes. It is interesting to recall, however, that the crystallite size of the high-strength variant Kevlar 981 is almost identical with that of Kevlar 29, although the former has a significantly higher orientation. It should be noted that in previous work [5] on different spools of Kevlar 49 there appeared to be a direct correlation between orientation and lateral crystallite size.

As might be expected, the structure of Kevlar 149 is very different from that of the other aramids examined, but some of the detail was completely unexpected. Surface examination of individual fibres in the SEM revealed typically a helical track of ellipitically shaped holes of various sizes, whose axes lie at an angle of about 45° to the track as shown in Fig. 6. In some cases the track takes a sinusoidal form. Such a phenomenon probably arises from the rotation of fibres as they are drawn past a rigid surface, such that different parts of the fibres are subjected to different stresses. Clearly the stress levels are excessive, leading to localized breakdown of shear manifested in the form of holes. Examination of longitudinal sections in the TEM suggests that the depths of some holes are of the order of a third of the fibre diameter. Moreover, longitudinal sections taken through regions adjacent to the holes indicate that a combination of translational and shearing forces have operated, leading to localized changes in molecular orientation. This evidence is supported by optical microscope studies using crossed polars. Thus, when the fibre axis is

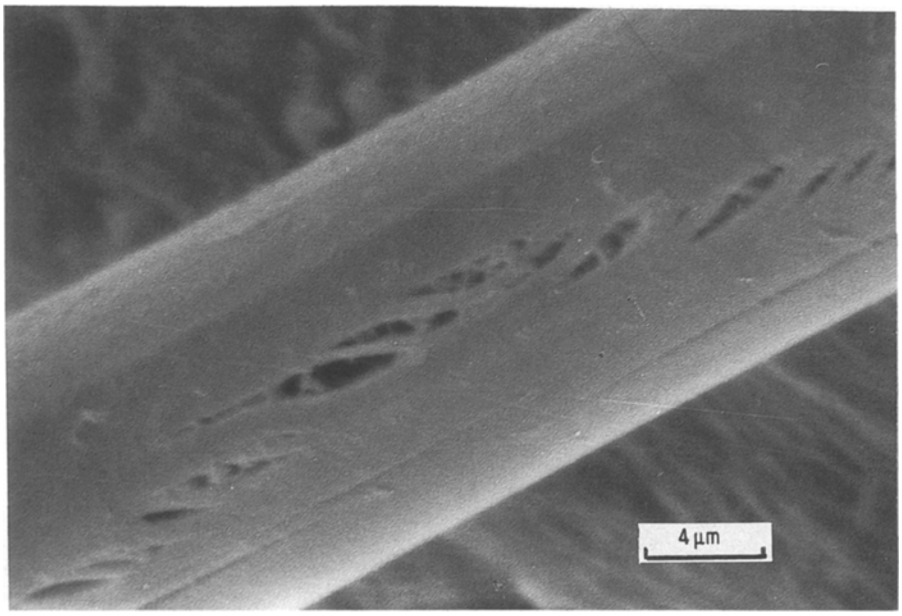

Figure 6 SEM. Defects following a helical path in Kevlar 149.

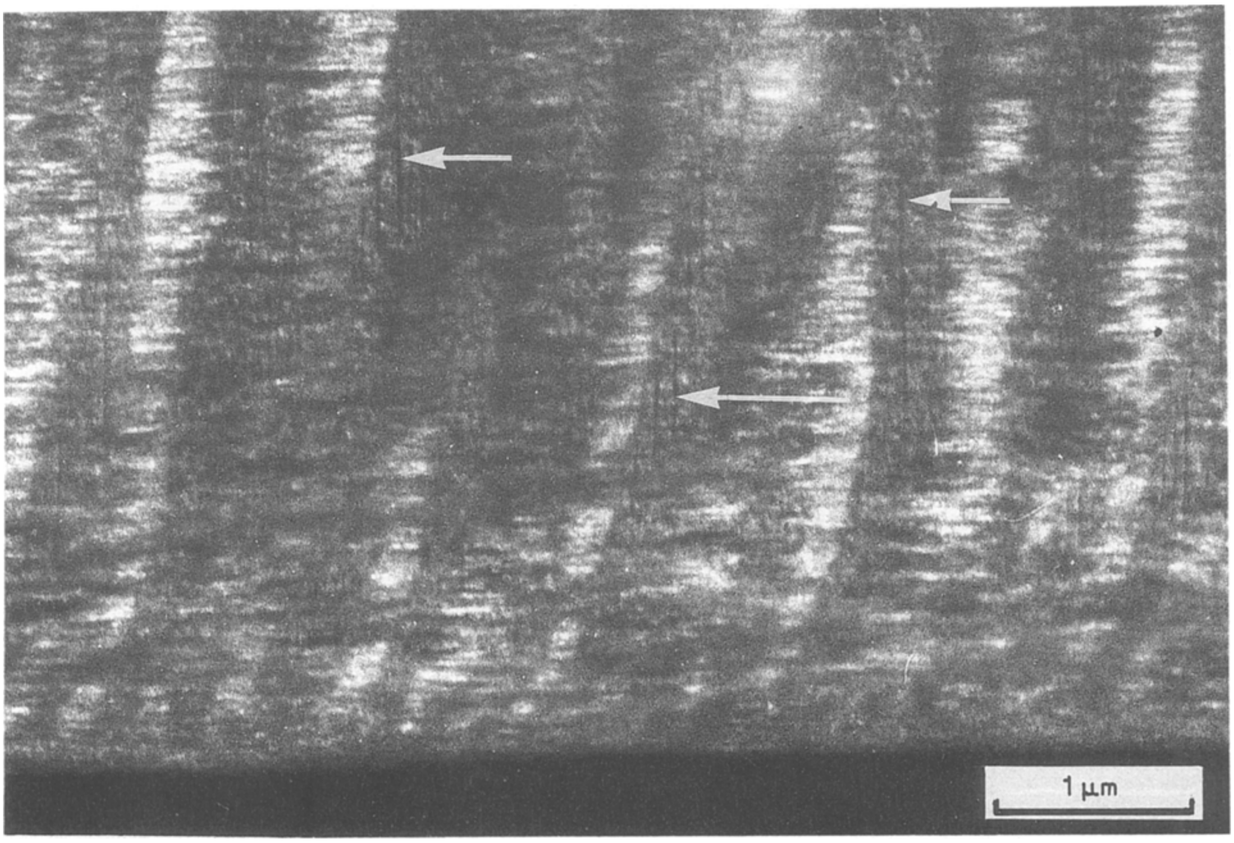

Figure 7 TEM. Dark-field image of a longitudinal section through Kevlar 149 showing line defects.

arranged parallel to the polarization direction a system of thin oblique bright bands on a dark background can be observed which are associated with the spiral track of the defect. On rotation of the fibre so that the axis lies at 45° to the polarizer, the fibre appears bright but with dark oblique bands.

Another characteristic feature of Kevlar 149 is the high intensity of the large number of discrete reflections in the X-ray diffraction pattern. Step-scan analysis of the equatorial 1 1 0 and 2 0 0 reflections reveals a dramatic increase in the apparent lateral crystallite size as compared with other variants. Indeed the size in the 1 1 0 direction is almost double that found for Kevlar 981. Such data indicate a much higher degree of chain packing perfection, most probably along the hydrogen-bonded sheets.

As might be expected, the dark-field images derived from the off-meridional reflections in the electron diffraction pattern are particularly intense, and clearly show alternate bright and dark bands indicative of the pleated structure. Similar observations were made on all the other aramid variants. However, in the case of Kevlar 149, the normally non-diffracting band was considerably mottled, indicative of the presence of diffracting material. Such diffraction probably occurs as the result of a reduced pleat-angle bringing structural elements closer to the diffracting condition. It is interesting to note that the TEM micrographs of longitudinal sections of Kevlar 149 occasionally exhibit clusters of thin dark bands arranged axially of spacing 30 to 40 nm, as shown in Fig. 7. It is probable that such features are associated with those seen in etched Kevlar 49 fibres reported by Panar *et al.* [8], who suggested that they represent a potentially weak link in the structure which must be successfully bridged to result in satisfactory strength. The observations are consistent with defect layers which include large proportions of chain ends. Such an explanation may well account for the marked difference in appearance of fractured ends of Kevlar 149 compared with other aramids. Indeed, in the latter cases fracture faces are axially stepped over extensive lengths of the fibre (oblique fracture), whereas with Kevlar 149 the tensile fracture tends to be more brittle and follow a more transverse path.

4. Conclusions

The tensile properties of aramid fibres arise from the combined effect of a number of structural features. It is difficult to identify the individual contributions, mainly because fibre specimens exhibiting differences in only a single structural feature were not available. Nevertheless there are indications that high molecular orientation, low skin content (more chains per unit cross-sectional area) and large crystallite size favour the development of high modulus. On the other hand fibre strength is adversely affected by gross morphological defects, for example the presence of substantial cracks in the high-modulus variant Kevlar 149. These features seem to result from excessive fibre stressing during processing to achieve high orientation. It would also appear that a large skin content favours the attainment of high strength. Indeed in Kevlar 981 (possessing a relatively small diameter) the skin content is very much larger than in any other variant, being of the order of 65%. The reason for this is not immediately apparent, since the high void content and hence the number of chains passing through a given area is relatively low. However, the electron diffraction studies do indicate that the overall chain orientation in the skin region is very much better than in the core, which would tend to enchance the load-bearing capability.

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