

Structural Aspects of High Modulus Aromatic Polyamide Fibres

M. G. Dobb, D. J. Johnson and B. P. Saville

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Structural aspects of high modulus aromatic polyamide fibres

BY M. G. DOBB, D. J. JOHNSON AND B. P. SAVILLE

Textile Physics Laboratory, University of Leeds, Leeds, U.K.

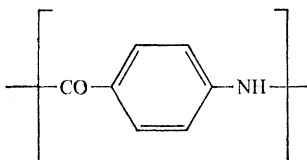
[Plate 1]

The molecular and supramolecular structures of an aromatic polyamide fibre (Kevlar 49) have been investigated by X-ray diffraction and electron microscopy. As a result, the main features of the fibre have now been defined. An attempt has been made to relate these findings to the exceptional mechanical properties.

INTRODUCTION

The recent development of aromatic polyamide fibres (Blades 1972) that exhibit exceptionally high tensile moduli represents a significant advance in fibre engineering. Potentially the mechanical properties can be varied over a wide range simply by varying the post-spinning heat treatment, consequently such materials are finding important industrial applications.

The aromatic polyamide fibres are characterized by –CONH– links in the *para* position between aromatic rings giving a fairly rigid chain.



This feature together with a relatively large number of hydrogen bonds per unit volume between CO and NH on adjacent chains contributes significantly to the high strength and axial modulus of elasticity.

Kevlar 49 aromatic polyamide fibres possess the attractive engineering features of relatively high tensile modulus 130 GN m^{-2} and strength 3.6 GN m^{-2} at a breaking extension of about 3%. They are not as brittle in bending as carbon fibres but survive intact by yielding in axial compression. Unfortunately these often desirable characteristics are offset by a correspondingly low value for shear modulus (1.62 GN m^{-2} in torsion).

SUPRAMOLECULAR STRUCTURE

The supramolecular structure of Kevlar 49 has been studied by electron diffraction and dark-field electron microscopy (Dobb *et al.* 1977). Diffraction experiments on sections clearly indicate that the fibres possess a radially oriented system of crystalline supramolecular units. Confirmation was obtained from sections cut at 45° to the fibre axis, from which dark-field images formed with the 200 reflexion show diffraction intensity confined to two opposite segments of the section.

Although not typical of all types of Kevlar, the most distinctive longitudinal feature of Kevlar

[75]

49 is the periodic organization revealed in dark-field images derived from meridional or off-meridional reflexions. A system of broad bands (figure 1) of spacing approximately 500 nm is associated with the off-meridional reflexions; another system of narrow bands, 30 nm in width, spaced at intervals of 250 nm, is associated with the meridional 006 reflexion. Tilting experiments, together with a dark-field procedure using only selected regions of the 200 reflexion, indicate that there is a uniform distribution of ordered crystalline material and that the dark-field banding is a manifestation of changes in crystalline orientation. The evidence is therefore compatible with a radial system of axially pleated lamellae (figure 2) possessing narrow transitional bands of periodicity 250 nm where the molecules lie parallel to the plane of the section. The angle between adjacent components of the pleat, estimated from the angular spread of the 200 reflexion in the electron diffraction pattern, is about 170° .

MOLECULAR STRUCTURE

Kevlar 49 type fibres consist essentially of rod-like molecules of poly *p*-phenylene terephthalamide (PPT). X-ray diffraction studies (Northolt 1974) indicate that there are two molecular chains in each monoclinic unit cell where $a = 0.79$ nm, $b = 0.51$ nm, $c = 1.29$ nm, $\gamma = 90^\circ$ (figure 3). Interchain hydrogen bonding occurs only along the (100) planes whereas weak van der Waal forces operate in other lateral directions.

Although direct microscopic observation of structure in a polymer is difficult to achieve because of an inherent sensitivity to the electron beam, recently lattice fringe images have been obtained (Dobb *et al.* 1978) which reveal the extent, perfection and orientation of the crystalline regions. Figure 4 shows part of a typical sheet of PPT obtained by ultrasonic irradiation, and lattice fringes derived from the 0.64 nm (002) meridional and the 0.43 nm (110) equatorial diffraction reflexions are indicated by M and E. The origin of the layer planes giving rise to these fringes is indicated in figure 3.

In large specimen areas, the meridional fringes M can be seen to form extensive systems 25–35 nm long, and lateral mismatch between blocks of these fringes indicates the corresponding extent of molecular order. Invariably, the individual arrays of equatorial lattice fringes E are significantly less extensive along the fibre axis direction than the meridional arrays, probably because changes in azimuthal orientation of the (110) lattice planes cause tilting out of the Bragg diffraction conditions. The distribution of lateral crystallite sizes, together with a mean value of 4.9 nm, have been obtained from measurements of individual arrays of the (110) lattice fringes. High resolution micrographs reveal very little evidence of lattice distortion in the fragmentation sheets except for the occasional appearance of curved layer planes. The mutual alignment of arrays of (110) fringes over extensive areas is compatible with an orientation angle of approximately 8° measured from wide angle X-ray data.

The presence of needle-shaped voids or electron density discontinuities in the Kevlar 49 fibres is strongly suggested by the intense small angle equatorial X-ray scattering produced by dry fibres. Analysis of the data indicates that these voids have a mean radius of gyration, about the fibre axis of 2.0 nm. Images of the sheet-like products of fragmentation show no evidence for such features and the voids are probably located in planes parallel to these sheets.

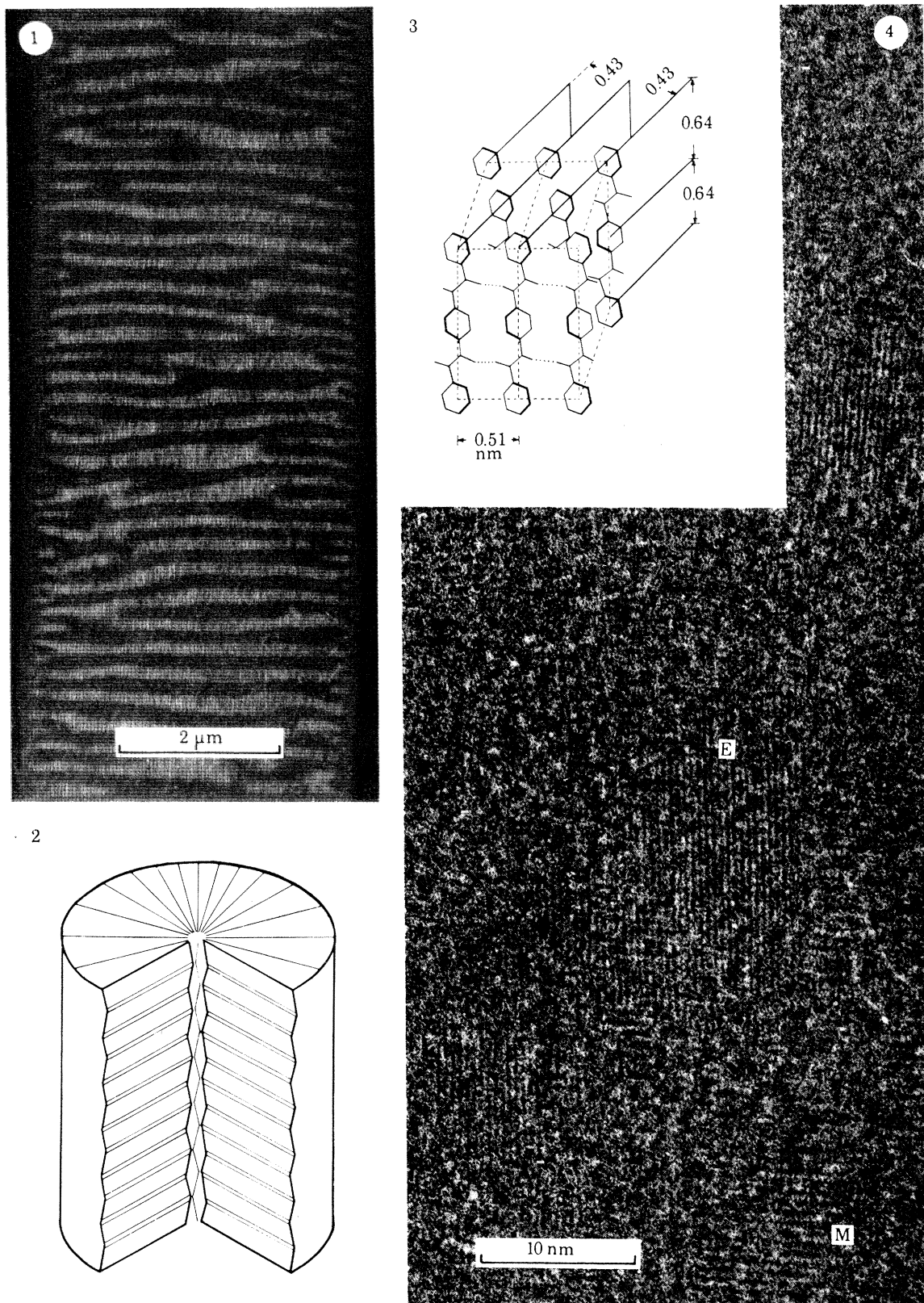


FIGURE 1. Dark-field micrograph of a longitudinal section through Kevlar 49 showing axial banding (magn. $\times 13250$).

FIGURE 2. Diagram of supramolecular structure of Kevlar 49 depicting a radially arranged pleated system.

FIGURE 3. Unit cell of poly-*p*-phenylene terephthalamide.

FIGURE 4. Lattice fringe image showing both equatorial (E) 0.43 nm and meridional (M) 0.64 nm spacings (magn. $\times 2.65 \times 10^6$).

IMPLICATIONS

The mechanical performance of this polymer can be directly associated with specific structural features. In particular, the relatively high modulus can be ascribed to a number of factors including (a) an extended-chain configuration as indicated by the absence of any low angle meridional or near meridional diffraction scattering, (b) the presence of *para*-linked rigid phenylene rings along the main chain, (c) planarity of the amide group, associated with resonance stabilization, leading to the formation of a hydrogen-bonded rigid sheet system, and (d) high crystalline order and orientation. A small loss in potential modulus may be expected on account of the pleated system. Similarly, the comparatively high ratio of the tensile strength to the modulus (cf. carbon fibres) and low shear modulus can be related to the poor lateral cohesion arising as a direct consequence of weak lateral planar bonding of linear molecules. In this way, an originally transverse crack would tend to be deflected along the fibre axis. A similar process of delamination would also account for the low compressive strength.

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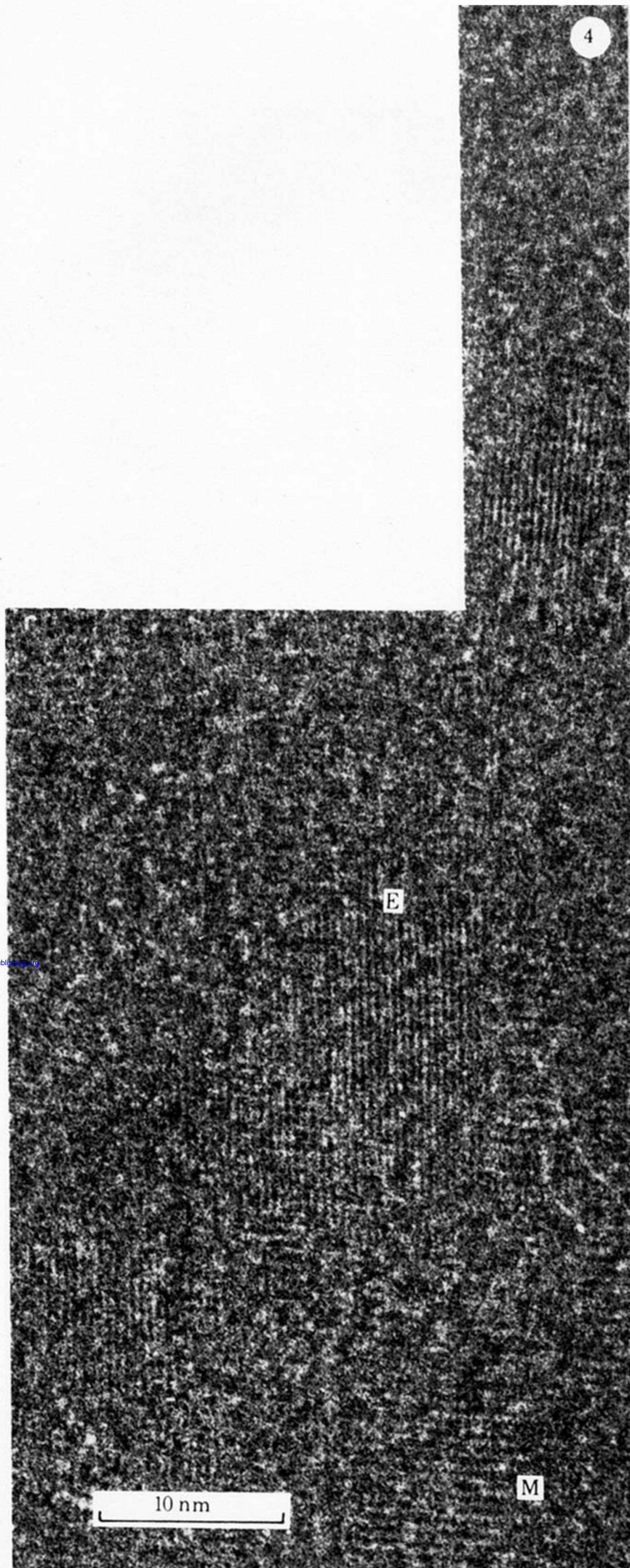


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