Internal structure of Kevlar® fibres by atomic force microscopy

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The nanometre-scale resolution atomic force microscopy images of the internal structure of Kevlar® fibres made it possible to reconcile differences between existing proposed structural models. Detailed real-space structures of the 'pleats' in these fibres and evidence of chain-end segregation in fractured fibres revealed previously inaccessible structure–property relations.

Poly(p-phenylene terephthalamide) (PPTA) fibres exhibit tensile strength and modulus higher than those of glass and steel on a weight basis. Consequently, PPTA has found use in demanding applications such as bullet-proof vests, tyre cords, power lines, fibre optic cables, etc. These remarkable mechanical properties should be related to the fibre structure, a detailed study of which may lead to further improvement of the properties.

The structure of PPTA fibres has been investigated extensively. The following are among the models that have been proposed for common PPTA fibres, such as DuPont's Kevlar® aramid fibres, based on electron and optical micrographs as well as X-ray diffraction patterns of both intact and degraded fibres. Dobb et al.[1] described a supramolecular structure consisting of a system of sheets regularly pleated every 250 nm along the fibre axis and arranged radially. Morgan et al.[2] proposed a structure exhibiting a differentiation between core and skin regions. The core region consisted of stacked layers of crystallites made up of individual macromolecules of average length 220 nm, which were enclosed in a skin with random chain-end distribution. Li et al.[3] described a core structure consisting of mostly ~220 nm long crystallites which were stacked in layers along the axial direction and were hydrogen-bonded in the radial direction of the fibre, with some longer crystallites extending through two or more layers. A skin layer of unknown structure surrounded the core. A summary of the sketches for these three models can be found in reference 4. Instead of crystallites, a core region of imperfectly ordered fibrils and a skin made up of uniformly, axially oriented surface fibrils were suggested by Panar et al.[5]. A pleating of the core fibrils with a period of about 500 nm was proposed. Periodic defect layers spaced 35 nm apart along the core fibrils were also described[5].

Recently, atomic force microscopy (AFM)[6] and scanning tunnelling microscopy (STM)[7] have also been applied to study these fibre structures. Since the topographical information obtained is in real-space and three dimensions, these techniques are especially suited for studying structures without long-range order such as the PPTA fibres. Furthermore, no staining, ion-milling or, for AFM, conductive coating need be applied to the sample under investigation.

STM has been employed to study Pt-coated Kevlar® fibres ruptured by sonication[8]. A hierarchical fibrillar structure was proposed based on images obtained on a split fibre. In another investigation, AFM has been used to study the polymorphism in PPTA molecules[9]. However, the detailed real-space supramolecular structure of PPTA fibres has not been directly observed to date with these new techniques. Confirmation and clarification of some of the seemingly contradictory features in the various structural models described above still present a challenge.

In the present study, AFM was used to elucidate the supramolecular structure at nanometre scale and clarify its relation to the mechanical properties of PPTA fibres. The force microscope used was a Nanoscope II AFM (Digital Instruments). The tips used were microfabricated Ultralevers (Park Scientific), with a force constant of $0.03 \, \text{N m}^{-1}$. Typically the force detected in the direction perpendicular to the sample surface was between 1 and 100 nN. The PPTA samples were Kevlar® 49 fibres from DuPont. The fibres were embedded in epoxy, microtomed either along the fibre axis or at 45° to the axis, and deposited onto freshly cleaved, highly oriented pyrolytic graphite for imaging. No identifiable artifacts due to sectioning could be observed on any of the fibre images, although marks due to the microtoming knife were prominent in the epoxy block. All images shown are raw data without filtering during or after data collection.

Figure 1a illustrates a typical image of a longitudinal section of a Kevlar® fibre. Images obtained from more than 10 sections of several fibres deposited onto different pieces of graphite exhibit similar features. The fibre appears to show a skin–core differentiation, as has been observed previously[2,3,5]. The thickness of the skin layer shows variation among different fibres, and ranges

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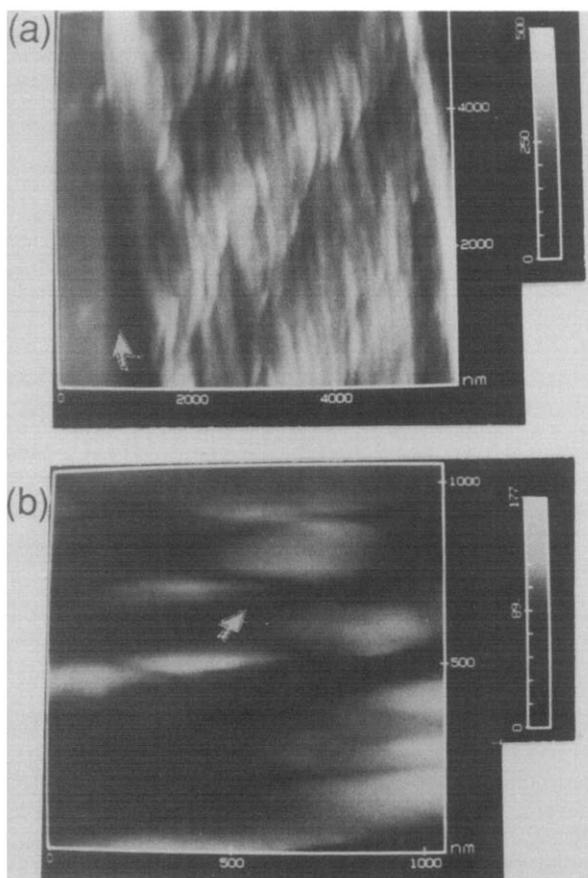† To whom correspondence should be addressed

Figure 1 (a) A 5.8 × 5.8 μm^2 image of a longitudinal section of a Kevlar 49 fibre. The fibrillar structure of the fibre can be clearly observed. The more densely packed skin and the rippling, interlocking core fibrils are clearly distinguished. The arrow points along the fibre axis. The unit of the greyscale bar is nanometres in all the images. (b) A 1.05 × 1.05 μm^2 image illustrating a region of the core adjacent to the skin. The arrow points to the interlocking braid/pleat structure typical of the core

Figure 2 (a) A 1.05 × 1.05 μm^2 image of several fibrils near the centre of the core of the fibre. The fibrils appear to exhibit a pseudoperiodicity of 30–50 nm along the axis of the fibre. The arrow points to one of the 'defect bands'. (b) A 775 × 775 nm^2 image of a fibril broken loose from the fibre. The fibril appears to be flexible

approximately between 100 nm and 1 μm in the images obtained. The skin fibrils appear to be merged and indistinct. In the core region, the individual fibrils are clearly discernible, and appear to have a diameter range of approximately 100–200 nm. From *Figure 1a*, the fibrils show a pleating arrangement along the fibre axis. A close-up view of the core fibrils, shown in *Figure 1b*, shows clearly that the pleating appearance is due to adjacent fibrils braided together to form a tightly interlocked structure. A braid/pleat periodicity of about 500 nm along the axis of the fibrils observed is consistent with observations made on fractured HCl-degraded Kevlar® fibres by Panar *et al.*[5].

Some of the core fibrils exhibit a fine intrafibrillar structure. *Figure 2a* shows a close-up view of several interlocking fibrils in the core. Within each fibril, there exists a pseudoperiodicity of 30–50 nm along the fibril. This pseudoperiodicity can also be seen in an image of a loose fibril in *Figure 2b*, indicating that this feature might be inherent in the fibrils, and not due to the packing of the fibrils in the fibre. This pseudoperiodicity appears to be similar to what Panar *et al.*[5] interpreted as defect bands in their study of a surface replica of an HCl-etched fibre with transmission electron microscopy. The existence of defect bands in these high-strength fibres is reconciled by the suggestion that the molecular chains are expected to extend largely across defect zones, resulting in relatively high tensile strength[5]. Note the
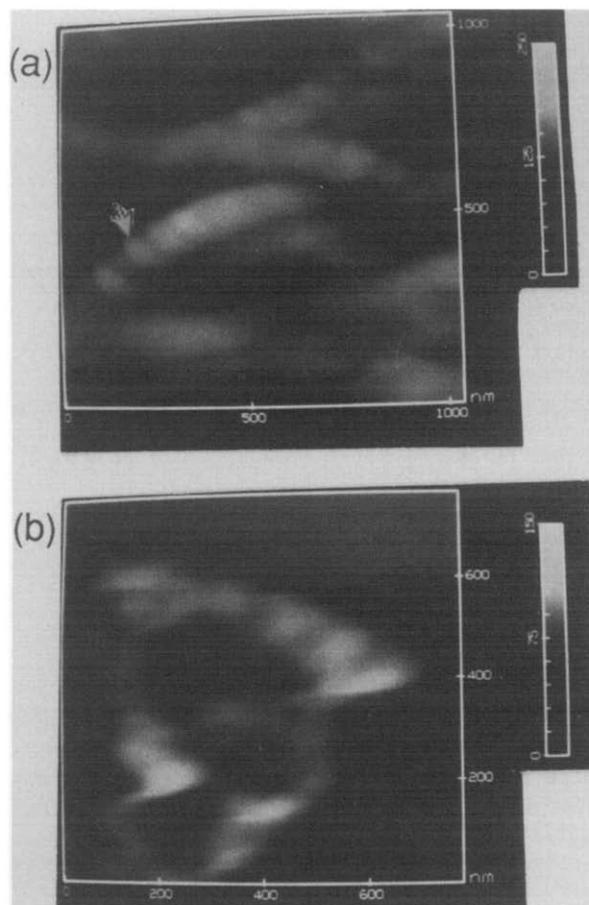
capability of AFM to image structural defects without the need to perform chemical etching of the fibres prior to imaging.

Sections obtained at 45° enable the observation of features around the centre of the fibre, which is usually not possible in sections along the fibre axis. As expected, the skin–core structure is again observed in *Figure 3a*. In addition, in the centre of the fibre there appears to be a core fibre of about 1.4 μm in diameter. A close-up view of the core fibre is shown in *Figure 3b*. In this image, bands of segmented fibrils along the fibre axis are revealed. The lengths of the bands range between 200 and 300 nm. Comparing the images obtained for typical longitudinal sections (*Figure 1*) and this image (*Figure 3b*), we note that these band-like structures with abrupt boundaries tend to occur on some parts of the fibrils only when the fibre is microtomed at 45° to the fibre axis, which necessarily fractures the fibre. In other words, if the fibrils had not been fractured, these band-like fibrils, as shown in *Figure 3b*, would not be so distinct. Both Morgan *et al.*[2] and Li *et al.*[3] also observed rod-shaped entities of approximately 200 nm in etched or fractured fibres using electron microscopy. They explained that the abrupt band boundaries could be due to molecular crystallites which happened to be ending at the same planes. For Kevlar®, which consists of PPTA with a typical weight-average molecular weight of about 40 000, the average chain length is expected to be about
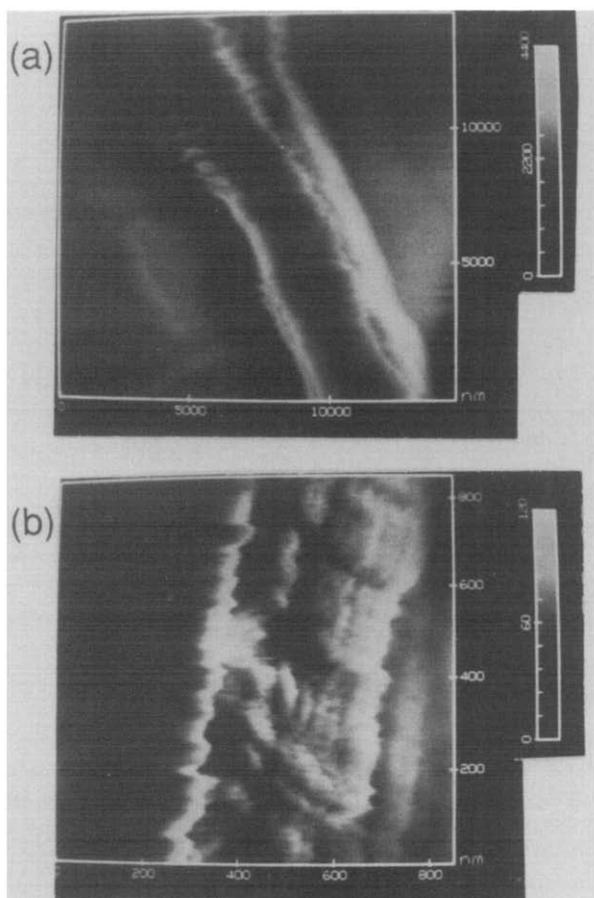
Figure 3 (a) A $14.5 \times 14.5 \, \mu m^2$ image of a $45°$ section of a Kevlar 49 fibre. The skin–core structure can be observed. In the centre of the core region, there appears to be a core fibre of about $1.4 \, \mu m$ diameter. (b) A $850 \times 850 \, nm^2$ image of the core fibre. Image rotated $45°$ relative to (a). Bands of segmented fibrils of approximately 200–300 nm in length and 20–30 nm in diameter are observed. The fibrils appear to be fractured at specific planes along the axis, resulting in the observed bands. The length of the bands may be related to the size of the molecular crystallites

210 nm. Smith and Termonia[10] suggested that molecular crystallites in Kevlar® exhibiting this type of chain-end segregation may in fact be energetically favourable and therefore should exist in the fibre; they showed with their kinetic model calculations that the tensile strength of the fibre could be weakened by the presence of this segregation. Consequently, our observation supports the

notion that these boundaries in the core may be mechanically the weakest part of the fibre structure.

The structural information presented above clearly differentiates the existing models for the structure of Kevlar®. Except for the pleated sheets[1], the main features of the other three models were observed in this relatively simple experiment. In addition, the details of the pleats showing the interlocking relationship between adjacent fibrils in the core region, the merged and indistinct fibrils in the skin layer, the existence of the central core fibre and the transformation of the fibrillar structure in the central core fibre to crystallite-like fibrils upon fracturing the fibre were observed for the first time. Based on our results, we conclude that the high strength of PPTA fibres may be accounted for by their fibrillar structure, the interlocking arrangement of the fibrils and the presence of a strong skin layer. On the other hand, there appear to be defect points at the ends of molecular crystallites in the core of the fibre, which may be vulnerable to mechanical damage. Further studies will investigate whether it is possible to adjust the strength of the PPTA fibres by varying the degree of interlocking and merging of the fibrils, by eliminating, or minimizing chain end segregation, and by increasing the thickness of the skin layer.

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