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Atomic force microscopy on polymers and polymer related compounds

5. Carbon fibers

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SUMMARY

Results of Atomic Force Microscopy (AFM) on carbon fibers from polyacrylonitrile and pitch are presented in comparison with Scanning Electron Microscopy (SEM) and Scanning Tunneling Microscopy (STM) images. Single fiber surfaces and their cross-sections have been imaged on scales from microns to nanometers. Morphological details beyond the resolution of SEM were revealed by AFM and STM. Grain-type structure was verified on surface of numerous nanofibrils oriented along the main fiber direction. Grains are bigger on pitch-based fibers generally, and on fibers of both types after treatment at higher temperatures. In the atomic scale AFM images traces of graphitic structure were recorded. AFM artefacts on rough surfaces are demonstrated.

INTRODUCTION

Carbon fibers are closely related to polymers by their origin and applications in composite materials [1]. Characterization of fibers surfaces is an important task for understanding and optimization of adhesive properties. Scanning electron microscopy is traditionally used for this purpose. New microscopic methods, STM and AFM, can be applied to different carbon surfaces. Imaging surface features from macroscopic scale (hundred of microns scale) down to angstroms by these techniques looks very attractive. Conductivity of carbon fibres permits their direct visualization by SEM without metalic coating, and gives a possibility of STM examination. In first STM studies surface morphology and crystalline regions on nanometer scale were registered [2-3]. In many regions surface structures of graphitic-type were observed. However, STM images present surface maps of charge density and correlation between these electronic properties and surface profile is not well established.

AFM gives more direct approach to microtopography. In this technique an image presents a three-dimensional surface profile of interatomic force between a sharp probe and surface atoms. Unique perspectives of AFM were realized on low molecular compounds and polymers [4-6]. Flat surfaces of organic monocrystals, polymeric films cast from solution or spin-casting, as well as material surfaces prepared by ultramicrotomy, are suitable for AFM. Morphological features and molecular structure were resolved on such surfaces. However, due to pyramidal shape of tip (height is ~4 μm), there are definite limitations of AFM studies. Commercial Si_3N_4 tips have a curvature of ~40 nm. This circumstance should be taken into account during studies of rough surfaces of rod-like specimens such as carbon fibers.

In this paper AFM results on carbon fibers from various precursors will be presented. Same surfaces were imaged by SEM and STM. Such characterization of fibers seems to be profitable, due to various advantages and limitations of these techniques.

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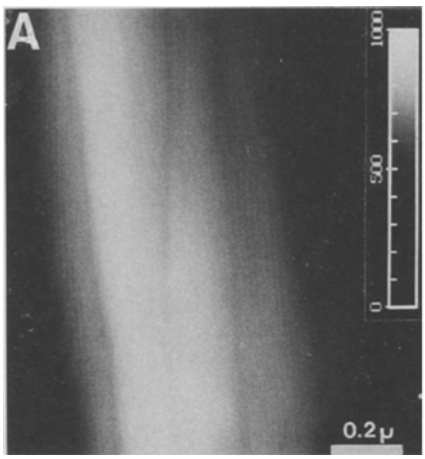
EXPERIMENTAL

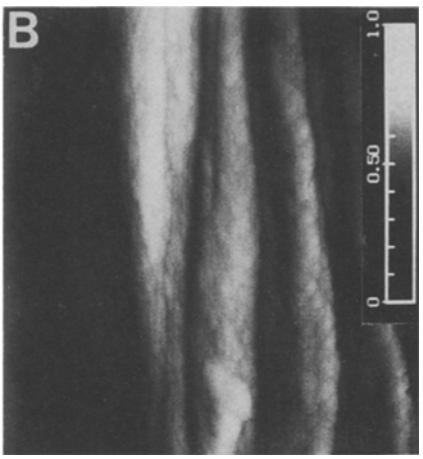
Polyacrylonitrile (PAN) based fibers, T300 and M40 (Toray), and pitch-based virgin fibers (A and E) were used in experiments. These fibers have different thermal prehistory, being treated at lower (T300 and A) and higher (M40 and E) temperatures. A and E fibers have a cylindrical shape, ~ 10 μm in diameter, whereas T300 and M40 have ellipse-like cross-section with main distances 5 and 8 μm. For microscopic experiments single fibers were fixed on surface of conductive silver glue. For examination of cross-sections they were cured in epoxy (Epon 80) matrix, and then surface perpendicular to main fiber direction was prepared by ultramicrotomy.

Scanning electron microscope "DSM 960" (Zeiss, Germany) was used in the experiments. The uncoated fibers surfaces were examined. Fiber cross-sections, however, were gold coated. Imaging in secondary electrons was conducted with acceleration voltages up to 30 kV. Higher contrast surface imaging was achieved at lower voltages.

AFM and STM measurements were carried out at ambient conditions with a commercial scanning probe microscopes "Nanoscope II and III" (Digital Instruments Inc., Santa Barbara, USA). AFM "A" and "D" heads and STM "D" head were used in the experiments. "D" heads with scan areas ca. 15 x 15 μm^2 were used for morphology studies. However, the maximum of piezodrive scan in the z-direction (ca. 4μm) as well as the shape of tip (especially in AFM) do not permit the profiling of whole fiber, and only the most elevated part (smaller than 5 μm in width) was imaged. "A" head (scan area ca. 0.6 x 0.6 μm^2) was used for imaging surface features in subnanometric scale. AFM "Nanoprobes" with force constants of 0.12 nN/m and mechanically sharpened Pt/Ir tips (0.8 / 0.2) were used in experiments. Presented STM and AFM images have been chosen as the characteristic ones after measurements as least in 5 various places with different tips. Other experimental details are found in [4-6].

Several comments about AFM measurements on rough surfaces should be done. Motions of cantilever, carrying a tip, or a sample, which is fixed to an electronically controlled piezodrive, can be registered in an experiment. Deflections of optical beam from cantilever, which are proportional to interatomic force between a tip and a sample, by means of a photodetector are converted to an electronic signal. The latest is used for driving the piezoelement carrying sample. There are two different AFM modes. In the height imaging mode, when sample vertical position is adjusted by piezodrive to keep cantilever deflection constant, the surface profile - measured from voltage changes applied to piezodrive - is correctly reproduced, especially, when feedback gain parameters are high. In this case variations of voltage applied to the piezodrive are presented by an AFM image. In the force imaging mode force variations determined directly from photodetector signal are shown in AFM image. Usually this mode is used for a detection of force map over flat surfaces as tip moves at an almost constant hight (low gain parameters of feedback). We have probed both regimes during imaging of fibers surface. Three images obtained at different conditions are shown in Fig.1A-1C. In the height imaging mode (integral and proportional gains were 2 and 4, respectively) a corrugation of a cylindric-shaped fiber is registered. However, poor contrast do not permit to resolve morphological details (Fig.1A). AFM force images of the same area, Fig.1B and 1C were obtained with the gains 0.13, 0 and 0.6, 0.8, respectively. Image (Fig.1B), recorded in the constant height regime, reveals only the most elevated parts of carbon fiber. Force profile correlates to morphological features observed in the height imaging mode, and more surface details are seen in this image in the comparison with the previous one. However, the highest contrast was achieved in the mixed mode of operation, when moderate gain parameters were chosen during force imaging (Fig. 1C). In addition to the morphological features observed in Fig.1B structure of protruded parts of fiber surface is revealed. It is clear that such AFM force images can be used for comparative studies of carbon





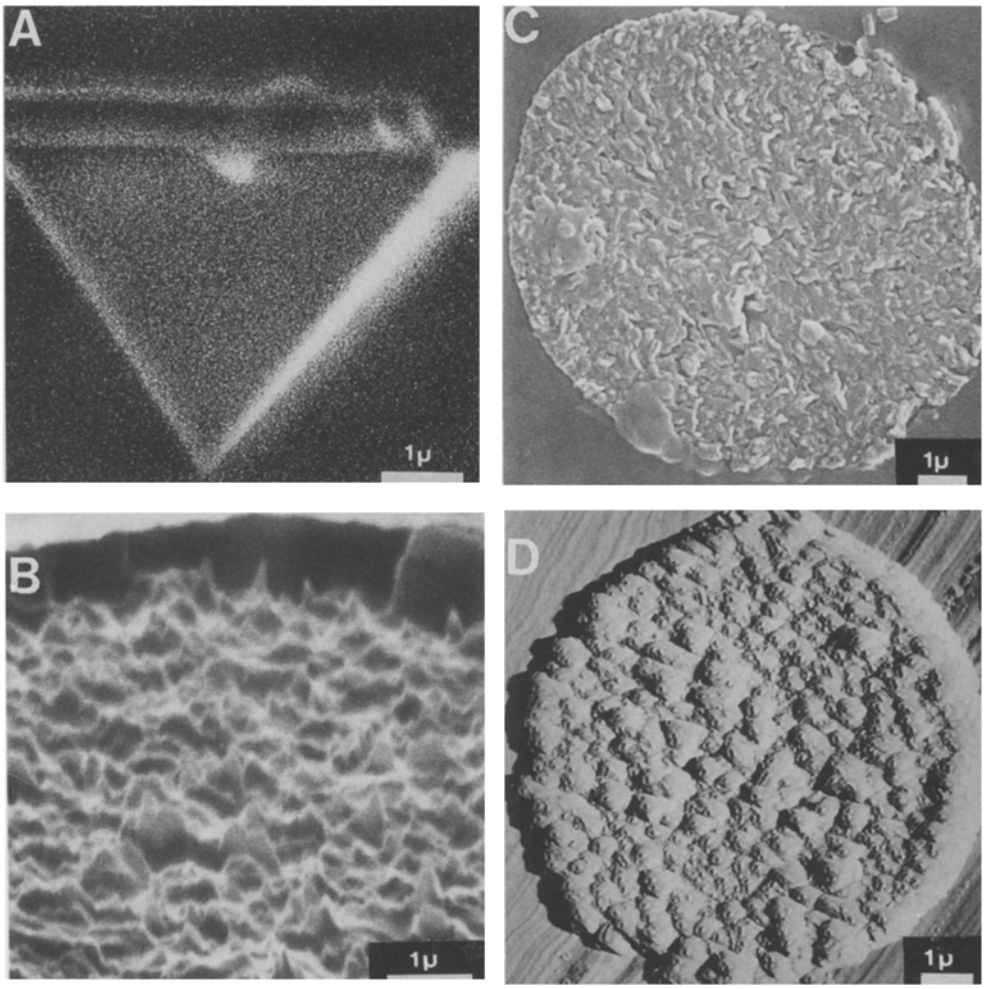
Figures 1A - 1C:
AFM images of T300 fiber recorded at different conditions

- A - height imaging mode
- B , C - force imaging mode

Gain parameters are indicated in the text
The vertical grey scale bars in these and in the following AFM and STM images indicate the height [nm] and force [nN] variations in the vertical (z) direction

fibers. However, frorn these images it is not possible to get a quantitative information about surface profile. These comments are also valid for STM, where the height and current modes (the latest mode is equivalent to the force imaging mode of AFM) can be used during experiments. In the experiments surfaces were imaged in both modes, however, the images with higher contrast were chosen for presentation.

The possibility of artefacts in AFM should be considered. In some case AFM image will present the convolution of a surface features and a tip. Due to this effect the apparent size of nanofibrils with diameter comparable or smaller than a curvature of AFM tip can be larger than a real one. It was shown that when the surface detail (or details) are sharper than a Si_3N_4 tip "reverse imaging" - imaging tip - can be observed [8]. An analogous situation occurs, when AFM is applied for studies of fiber cross-section. SEM images of an AFM tip and a cross-section area of carbon fiber, which are shown in Fig. 2A-2B, indicate that tip details can be found in the AFM pictures of this surface. Numerous indentical features, found in the AFM image, Fig. 2C-2D show these artefacts. In several cases platelet features of different size were found in cross-section images. This is probably an indication of a defective truncated pyramidal shape of a probe. Tip images are more pronounced on sharp edges. During cutting a part of carbon fiber may be removed leaving holes with sharp edges, Fig. 3A-3B. Imaging of

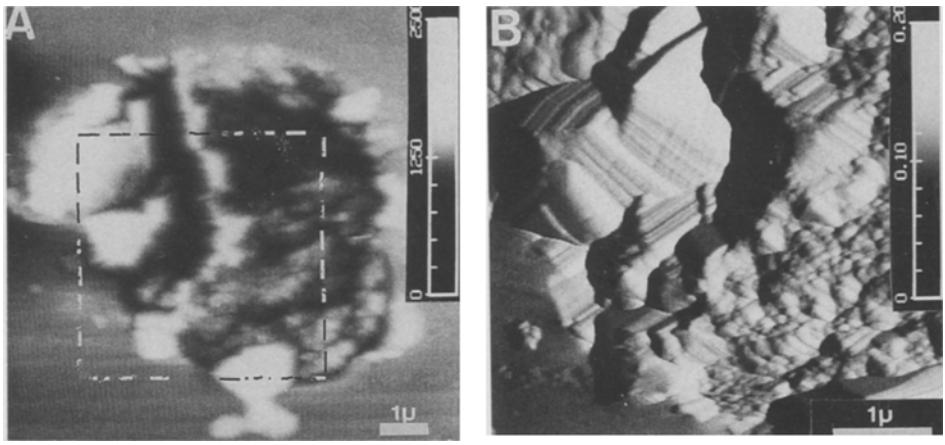


Figures 2A-2D: A - C: SEM images of AFM tip (A) and cross section of pitch E - fiber (B • side and C • top view) • D: AFM image of pitch E - fiber cross section

such holes yields arrays of tip-like features, especially in the force imaging mode, when tip was climbing on a elevated part. (Signal was recorded during scan from right to left.) These and other results [8] show that careful approach in AFM applications is necessary. The discussed artefacts detected in AFM on rough surfaces might also occur in STM imaging. SEM is more reliable technique for such cases.

RESULTS

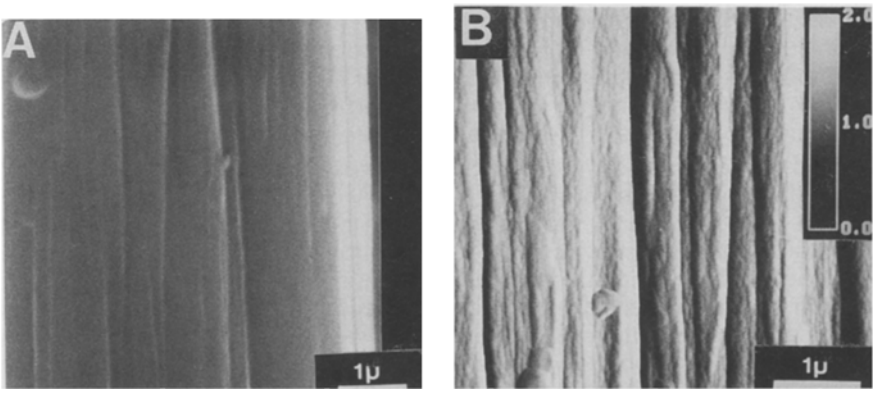
At present, when AFM applications are widespreading, the comparison of images with results of other surface techniques is extremely important. AFM observations on different carbon fibres are compared with SEM and STM. SEM and AFM images of the M40 fiber are shown in Fig.4A-4B. Both images demonstrate linear morphology, however, the better resolution of surface grain-like features by AFM is undoubtful. It is known that poor vertical sensitivity of SEM is related to the fact that intensity variations (in flux of secondary electrons) only higher than 5% can give differences in contrast. In AFM



Figures 3A-3B: AFM images of cross section of T-300 fiber
A: image in the height mode • B: zoom-part of area in A, recorded in the force mode

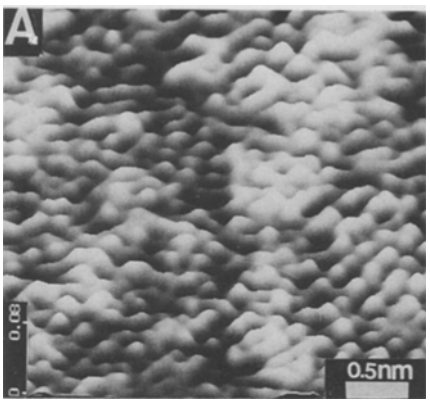
and STM due to strong dependence of surface probing interaction on separation between tip and surface vertical resolution is higher. The atomic scale AFM image, Fig. 5A, can be regarded as the confirmation. The arrangement of AFM patterns in this image reproduces the positions of C- atoms in the crystalline region of fiber surface. However, it was more difficult to receive this image than to reach atomic resolution on fiber surface by STM [3].

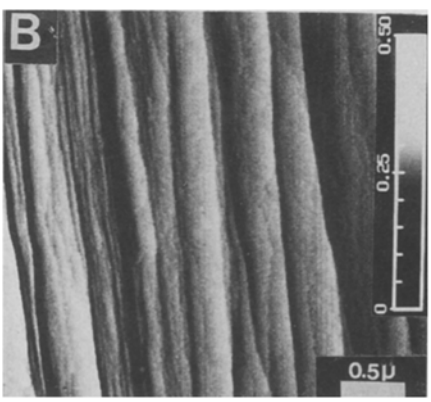
Surface topography of carbon fibers reveals a fibrillar-type morphology, which is a consequence of stretching of precursor material. Straight and partly interwoven nanofibrils with width varying from 300 nm to 50 nm are distinguished in large scale images of PAN fibers, i.e. Fig. 4B and 5B. On surfaces of A and E fibers straight nanofibrils are more uniform with diameters varying from 80 to 100 nm, Fig. 5C. This morphology is typical for highly oriented polymers that was demonstrated on polyethylene [4]. Surface corrugations due to fibrillar structure were determined from the heght images. They are in the range of ca. 200 nm on $1\mu m^2$ in PAN-based fibers an slightly smaller in pitch-based fibers. It should be noted that deep valleys probably were not profiled correctly due to finite size of probe.

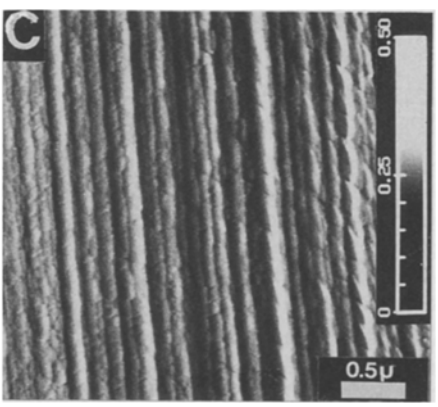


Figures 4A-4B: Images of M40 fiber surface by SEM (A) and AFM (B)

Figures 5A-5C:
AFM images of
- A: M40 fiber
- B: T300 fiber
- C: E fiber

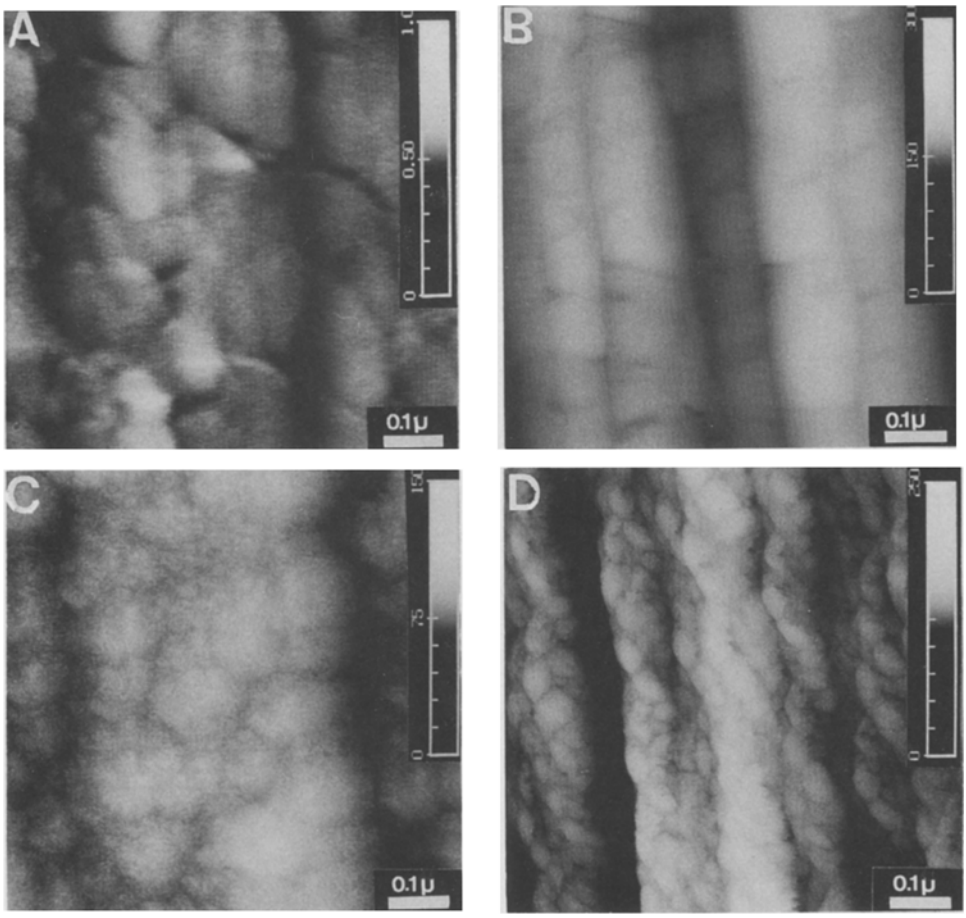






Although it is shown that AFM presents more detailed surface information than SEM the comparison of AFM and STM images is also important. Generally, the spatial resolution of periodical structures in the AFM images is comparable with the STM resolution. The STM and AFM images of different fibers in the submicron scale are presented in Fig. 6A-6D and Fig. 7A-7D. In addition to numerous striations along the main fiber direction numerous details in shape of grains of different size are resolved in all images. Slightly elongated grains of 20-40 nm in width are surface features of T300 fiber as revealed in AFM images. Bigger grains of 100-200 nm in width are charactestic for surface of M40 fiber, which is a high modulus fiber due to thermal treatment at higher temperature. The enlarging of surface grains after treatment at higher temperature is seen from AFM and STM images of fibers received from both precursors. It is also evident that grains on surface of PAN-based fibers are smaller than in pitch-based fibers.

STM yields more resolved images of carbon fibres than AFM, Fig. 6C-6D and 7C-7D. Grains in STM images is smaller than in AFM. A better STM resolution is probably connected with an imaging mechanism. STM is based on probing a local surface electron density on energy levels involved in electron tunneling by more advanced tip atom. Charge density maps presented by STM image can be more related with distrubution of graphitized regions on carbon fiber surface than with real topography. AFM is based on registration of intermolecular repulsive force that gives the more direct surface visualization. However, due to less sharp AFM tips, a multiple contact between probe and and surface is possible. That might limits a resolution of surface details in range of 40 nm, the estimated curvature of probe end.



Figures 6A-6D: AFM and STM images of pitch-based carbon fibers
- A, B: AFM images of A and E fibers
- C, D: STM images of A and E fibers

CONCLUSIONS

- Possibilities of AFM imaging of carbon fibers surfaces at large scale and with atomic resolution are demonstrated in comparison with SEM and STM. AFM appears to be more sensitive in visualization of carbon fibers surfaces than SEM. STM, however, gives the images with highest resolution.
- Fibrillar morphology was observed on all fibers, while the distribution of straight fibrils on surface of pitch-based fibers is more uniform than that in PAN-based ones.
- Presence of grain-type surface features on fibers surfaces - unresolved by SEM - was shown with AFM and STM. Grains are bigger on surfaces of pitch-based fibers and of PAN fibers after thermal treatment at higher temperature.
- Artefacts of AFM were shown during imaging of carbon fiber cross-section. They are caused by tip geometry.

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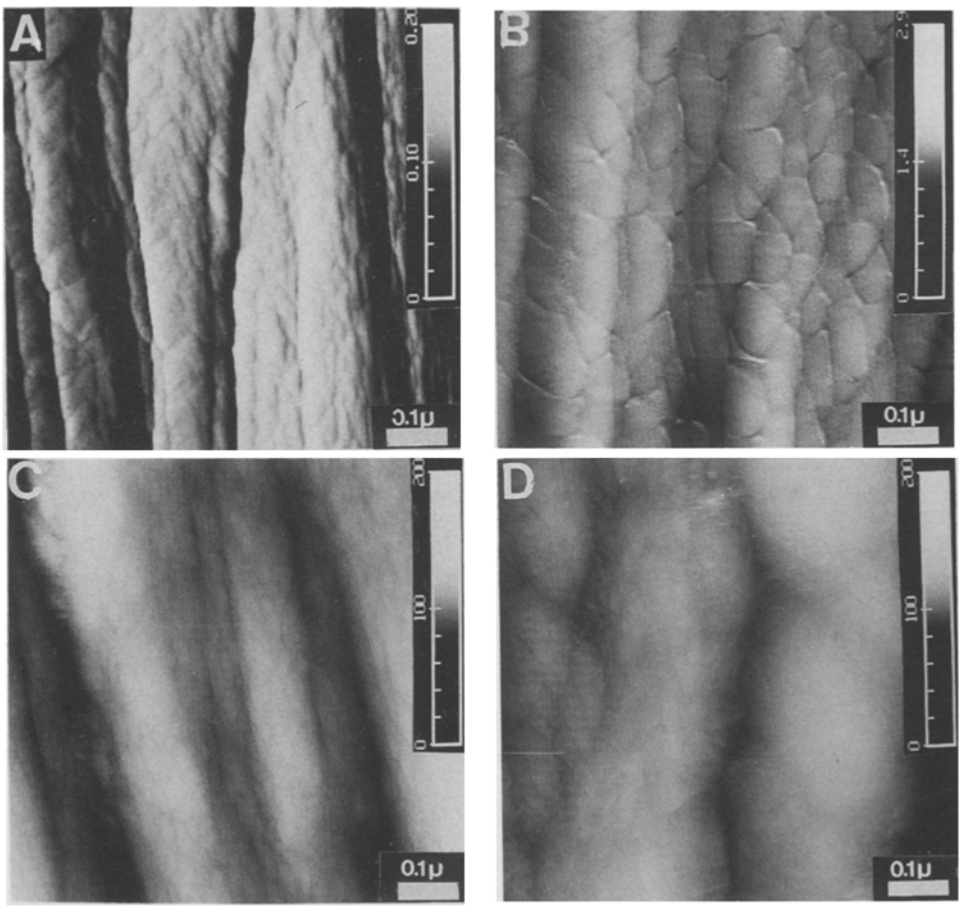

Figures 7A-7D: AFM and STM images of PAN-based carbon fibers
- A, B: AFM images of T300 and M40 fibers
- C, D: STM images of T300 and M40 fibers

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