Polymer Bulletin 32, 235–240 (1994)

Polymer Bulletin

Surface morphology and nanostructure of high modulus polyethylene fiber

A. Wawkuschewski, H.-J. Cantow*, and S. N. Magonov

Freiburger Materialforschungszentrum FMF and Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität, Stefan-Meier-Strasse 31A, D-79104 Freiburg, Germany

Herrn Prof. Dr. Ing. E. H. Hansjörg Sinn zu seinem 65. Geburtstag herzlichst gewidmet

SUMMARY

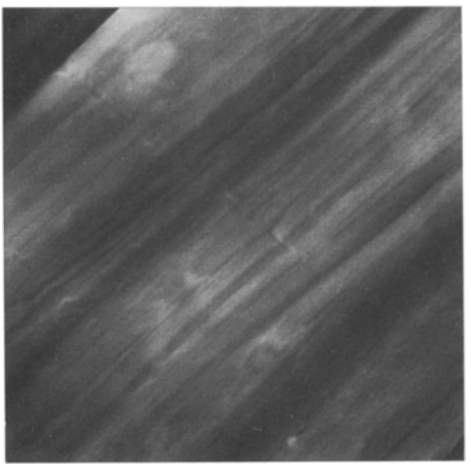
Surface morphology and nanostructure of the ultrahigh molecular weight polyethylene fiber Spectra 900 were examined by atomic force microscopy under water, with height and lateral force registration. Non-uniform surface morphology, where the bundles of microfibres are covered by interwoven randomly oriented fibrils ("hairs") and twisted ribbons, was registered in the large scale images. The nanofibril elements detected in the bundles and in the "hairs" are 5 - 8 nm in width. Periodical stripes found by lateral force measurement on individual fibrils *(long period)* were assigned to sequences of crystalline and less-ordered regions. The repeat distance of the *long period* varies from place to place being in the range of 10 - 20 nm. The complexity of the polyethylene fiber structure is supported by visualizing large crystallites, which were found in the ribbons splitfrom the fiber surfaces.

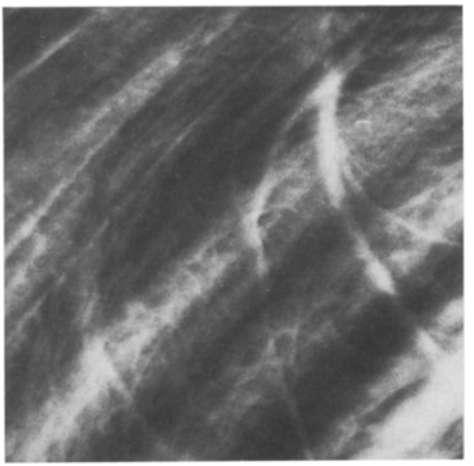
INTRODUCTION

Atomic force microscopy - AFM - is developing as an efficient tool not only in the analysis of surface topography, but also of surface mechanical properties (friction and elasticity)[1-2]. By probing repulsive force variations between a tiny sharp probe and a sample in contact AFM, one can reveal surface morphology and molecular or atomic order with spatial resolution higher than that of electron microscopy. This advantage is easily realized on flat and hard surfaces, however probing on soft and rough samples might lead to image artefacts. Thus, precautions are important in AFM studies of polymers [3], where the nanoscale image features can be screened by a convolution with a tip geometry. To improve reproducibility and resolution of AFM on polymer surfaces in the scale 1 - 100 nm, operation with minimal repulsive forces and with selected sharp tips is required. The finding that tip-sample forces in AFM under liquid are much lower than those at air was applied to the examination of soft biological samples [4]. Also in studies of drawn ultrahigh molecular weight polythylene - UHMW PE - tapes under water [5a] it is possible to enhance spatial resolution and to avoid surface damage due to smaller contact area. In these experiments the width of the smallest nanofibrils detected (10 - 15 nm) was 2-3 times smaller than that found in images obtained with ambient condition AFM [5b-5c]. In addition, while operating under water one can examine surfaces at different applied forces. This was effective for studies of *long period* features in the images of drawn UHMW PE tapes. Contrast variations correlated with a *long period* repeat distance of ~ 25 nm were found only at elevated forces. Their appearence is related to a partly irreversible indentation of less-ordered or amorphous regions, which are periodically arranged along the stretching direction being, in series with lamellar platelets [6].

*Corresponding author

In this paper we are presenting AFM results obtained on high modulus gel-spun PE fibers, Spectra 900. Despite numerous structural studies on PE fibers crucial questions concerning surface morphology, elementary fibril size, crystallite dimensions are still open [7]. Such information is indispensible for understanding and improving mechanical and adhesive properties.





Figures 1a - 1c: AFM height images at different places. Fiber orientation is indicated by an arrow. Scanning areas: (a) 3.65 x 3.65 μ^2 • (b) 2.05 x 2.05 μ^2 • (c) 4.08 x 4.53 μ^2 • A gray scale contrast spans over 100 nm height variations.

EXPERIMENTAL

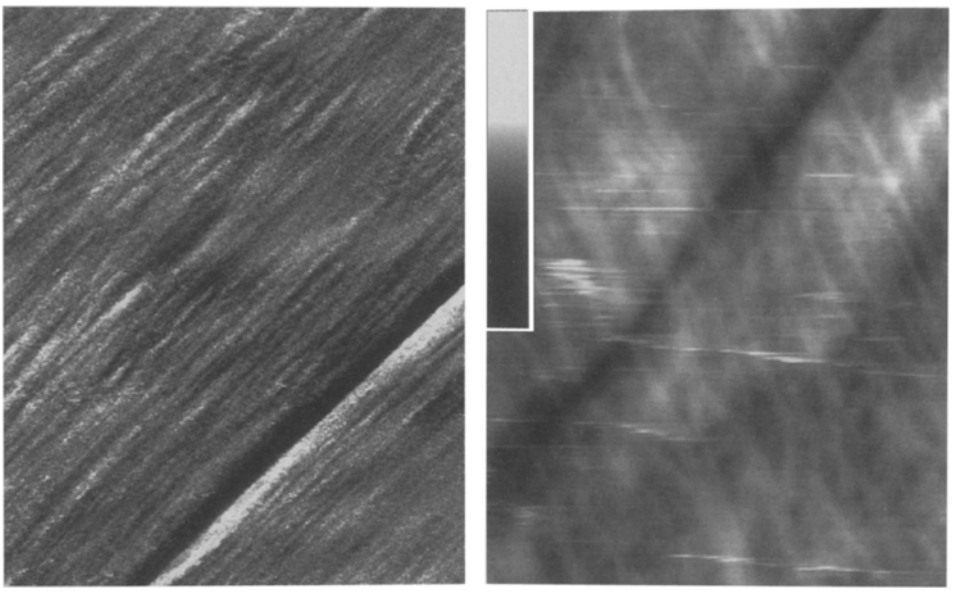
Virgin gel-spun PE fibers Spectra 900 (Allied Signal, Inc.) were examined with AFM. Studies were conducted in a liquid cell, which was filled with bidistilled water. A scanning probe microscope "Nanoscope III" (Digital Instruments Inc., Santa Barbara, USA) was used in the experiments. Uniaxially oriented samples were positioned along the x direction of the microscope stage, and images were recorded at a rotation angle of 45°. In order to diminish the possibility of surface damage scanning was conducted in constant force mode (high gain parameters). In such a case the height, HT, and lateral force, LT, images were registered simultaneously. Although on the corrugated fiber surface LF images can not be assigned to friction

maps, these images provide enhanced contrast in visualization of morphological features. Commercially available Si probes ("Nanoprobes") with the apex radius smaller than 10 nm were chosen for the studies.

RESULTS AND DISCUSSION

In the light microscopy and scanning electron microscopy, SEM, micrographs the surface of UHWM PE fibers appears smooth and uniform with a fibrillar texture formed during the drawing process [8]. Large scale AFM images obtained on areas of several square microns in various places showed that the surface morphology of the Spectra 900 fiber effectively is not uniform, Fig. 1a - 1c. Though one can find smooth places, where main morphological features are presented by compactly packed linear fibrils oriented along the stretching direction (Fig. 1a), in other places the fiber surface looks quite different. Some fiber areas are coated by tiny interwoven fibrils ("hairs"), Fig. 1b-1c, which are randomly oriented with respect to the main fiber direction. Occasionally, we have also observed arrays of ribbons of 9 - 12 nm in width, which were oriented perpendicular to the stretching direction. We have never found areas with "hairs" and ribbons on drawn PE tapes [5], which look similar to smooth areas shown in Fig. 1a. Thus, the features observed on Spectra 900 fibers may be a consequence of the mechanical treatment of the fiber skin in the spinning process. Though imperfections found on fiber surface might have no significant influence on their mechanical properties, they are important when considering adhesion between fiber and matrix in polymer composites [9]. It is worth noting that the peculiarities of fiber surface morphology observed by AFM are undetectable by SEM because its vertical resolution is much inferior.

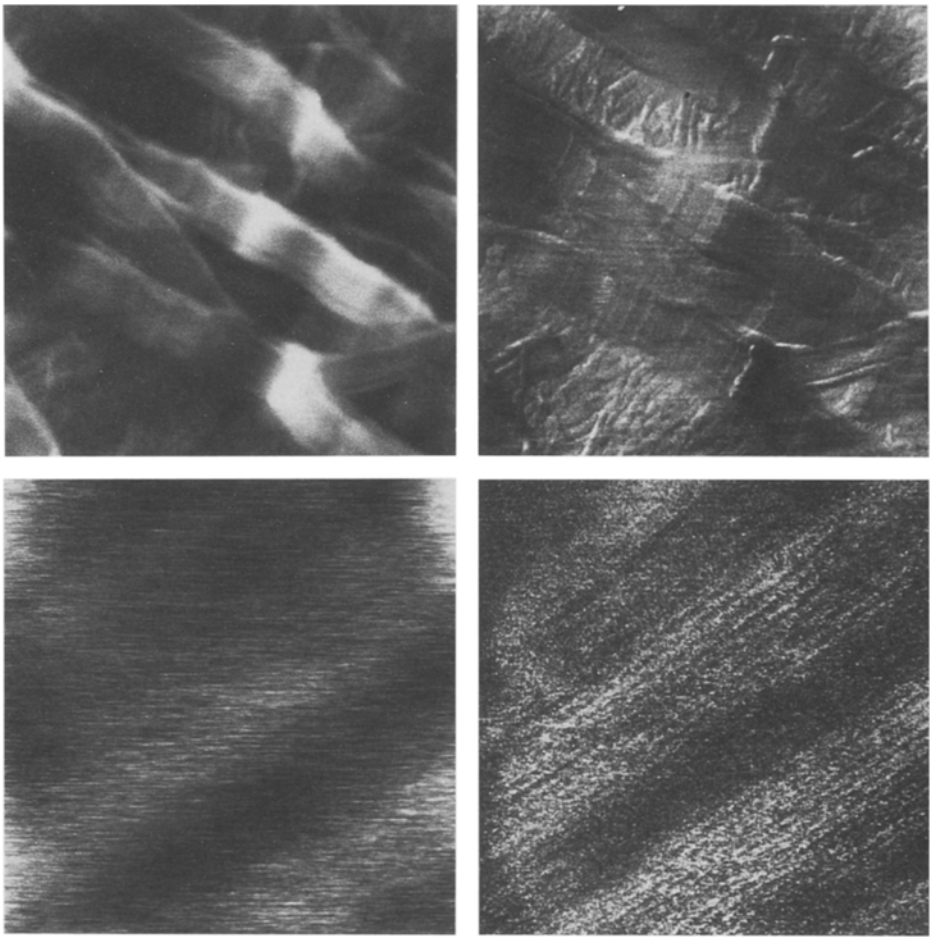
At higher magnification the structural elements of surface areas with different



Figures 2a - 2b: AFM images of smooth and "hairy" parts of Spectra 900 fiber. Scanning area is (a) 480x600 nm^2 and (b) 456x570 nm^2.
A gray-scale contrast shows the normal cantilever deflections within 10 nm.

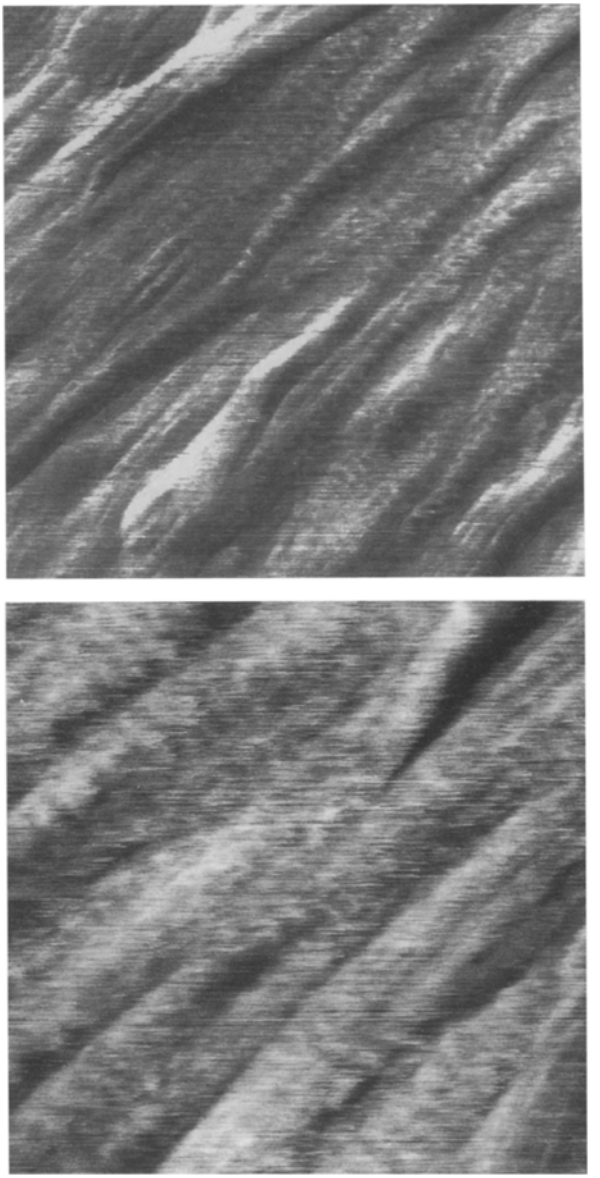
morphology are well resolved. The most thin nanofibrils, which were found in the oriented bundles on smooth areas and in 'hairs', are ca. 5 - 8 nm in width (Fig. 2a -2b). These nanofibrils are twice as thin as those found in UHMW PE tapes with a draw ratio 70 [5a], but they are in agreement with the width of nanofibrils (5.7 nm) obtained from the synchrotron X ray diffraction experiments on Spectra 900 [10]. From the AFM images it is difficult to determine correctly the length of nanofibrils because it is virtually impossible to follow the individual fibrils in the bundle from one end to the other. Nevertheless even the distinguished parts of individual nanofibrils are longer than estimated from diffraction data (ca. 175 nm) [10]. Randomly arranged white stripes observed in images of the "hairy" part (Fig. 2b) may be related to ends of fibrils broken in the spinning process.

The structure of twisted ribbons, which were split from the fiber surface, is rather complicated, Fig. 3a - 3b. One can distinguish fibrils bordering the central part of the ribbon on both sides. A central part is ca. 90 nm in width and consists of brighter



Figures 3a - 3d: Simultaneously recorded AFM HT (left) and LF images (right) of ribbons at Spectra 900 surface • 1.05 x1.05 μ^2 (upper) • 48x48 nm^2 (lower).

linear elements aligned along the main fiber direction. These images resemble the morphological features of polyethylene extended chain crystals.This analogy is confirmed by the molecular scale images, Fig. 3c - 3d. Striations distinguished in the lateral force image can be assigned to extended crystallites, which provide the brighter contrast of corresponding places in the HT image. Thus, contrast variations along the ribbon can be assigned to sequences of crystallites, which are connected by less ordered regions (darker spots). We found that interstriation separations exist not only in the range of PE interchain distances (0.5 nm), but in essentially larger ones too. The larger separations may be assigned to distances between steps of neighboring crystallographic sheets forming PE crystal. Similar features were found in the molecular scale images of crystallites in drawn UHMW PE tapes [6]. Thus, the analysis of ribbons demonstrates that they consist of crystallites, which are 70 nm in length and 25 nm in width. Their width exceeds that found in diffraction measurements (13 nm) on Spectra 900 fiber [9]. In such a case the width of the crystallite exceeds the width of the nanofibrils. According to the diffraction data the crystallite length in Spectra 900 fiber varies from 5 to 13 nm, which is essentially smaller that the length of crystallites in the ribbons. Despite some correlations between structural parameters determined from AFM images and X-ray diffraction, one should take into account that ribbons are only one type of structural elements found in the PE fiber.



Figures 4a-4b: AFM LF images of smooth part of fiber, indicating the presence of periodical contrast variations (a) 765x765 nm^2 • (b) 319x319 nm^2. LF image contrast indicates differential signal variations of horizontal detectors.

The more characteristic structural features can be found by studying nanofibrils, which are the dominating elements of fiber construction. As in the case of drawn UHMW PE tapes the images of Spectra 900 fiber recorded at higher forces demonstrate the periodical variations of the image contrast along the stretching direction, Fig. 4a- 4b. This finding shows that nanofibrils consist of sequences of crystalline (brighter spots) and less-ordered regions (darker spots) arranged in series along the fiber direction. At present it is difficult to describe "less-ordered regions" more precisely. In the highly crystalline materials such as the investigated fiber, these regions may be built up more by conformationally highly restricted rigid amorphous domains than by mobile amorphous domains. Thus, bright spots in the AFM images (Fig. 4a- 4b) are related to more perfect crystallites, which are much smaller than those detected in the ribbons. In contrast to PE tapes where a *long period* of 25 nm has been observed in any surface region, the repeat distance of contrast variations in the fiber images is smaller and varies from one place to another in the range of 10-20 nm. These variations of long period might explain the fact that this period was not systematically determined in diffraction studies of PE fibers [6]. However, the presence of disordered regions in PE fiber was detected by Raman spectroscopy [12]. The observation of *long period* features in PE fiber indicates that the fiber structure is quite different from the continuous crystal. Thus, it is still not possible to explain unequivocally the superior mechanical properties of these fibers, which - at least at surface - have not the characteristics of a PE single crystal.

ACKNOWLEDGEMENT • We cordially thank Dr. G. Smith and Dr. G. C. Weedon (Allied Signal Inc.) for the presented samples of virgin Spectra 900 fiber.

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Accepted November 8, 1993 C