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Scanning force microscopy of nanofibrillar structure of drawn polyethylene tapes

1. Different modes and tips

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SUMMARY

Different scanning force techniques and specially selected probes were employed to examine the nanofibrillar structure of gel-drawn ultra high molecular weight polyethylene. In order to avoid image artifacts and observe details of the surface structure with an improved resolution, the quality of probes was controlled with a new calibration gauge. Images recorded in the lateral force and tapping modes showed more structural features than those obtained in the normal force mode. Particularly a regular striped pattern was detected on the surface of nanofibrils. According to its repeating distance, ca. 25 nm, this pattern is consistent with the *long period* of UHMW PE observed earlier by SAXS and TEM.

INTRODUCTION

Ultradrawn of gel-crystallized ultra high molecular weight polyethylene - UHMW PE - is used for preparation of strong fibers (1). The superior mechanical properties are related to the uniaxial orientation of the extended chains in the resulting fibrillar structure. Although, the deformation process and the structure of the fibres have been studied intensively, it was yet not possible to visualize the structural details directly and to correlate structural variations with the variations in mechanical properties (2).

While diffraction studies give usually an averaged information on a heterogeneous structure, microscopy techniques provide a direct structural information. The possibilities of microscopy were expanded with development of Atomic Force Microscopy (AFM) - the first representative of Scanning Force Microscopy (SFM) (3). These techniques are based on probing the interaction forces between a sharp tip and a surface. In AFM the repulsive interatomic force was employed for the surface analysis, and later different force interactions and various detection methods were applied. Applying SFM to polymers enables to registrate surface features in the range from hundreds of microns to subnanometer range (4).

In recent AFM studies on UHMW PE tapes with different draw ratio, rather peculiar details of the structural rearrangement could be observed during

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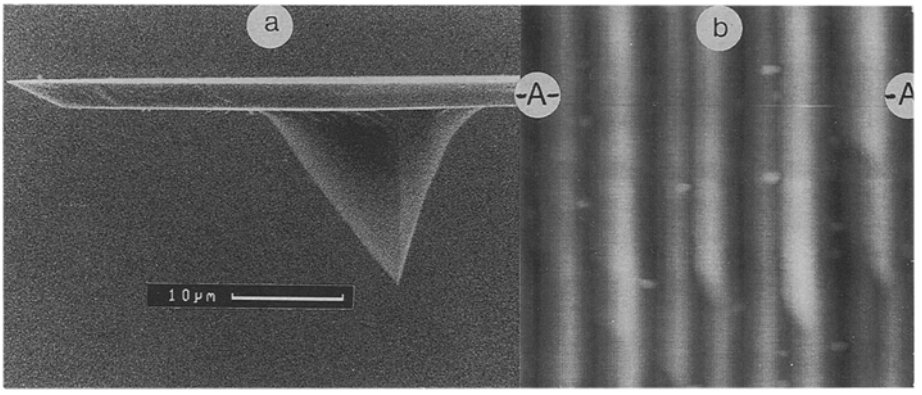
stretching (5). In particular, it was depicted how stretching proceeds in the first step by lamellae sliding and in the second step by gradual transformation of lamellae crystallites into nanofibrils. Nanofibrils with an averaged diameter of 50 nm were formed in the necking region and did not change their dimension significantly upon further drawing. High resolution images allowed to visualize the extended polyethylene chains directly.

However, the method has still distinctive limitations. Artifacts occur due to the convolution of the tip shape with the surface structure and because of the deformation of the relatively soft polymers by the hard and sharp AFM tips (6). The present paper is focused on the application of new SFM techniques and selected tips. This is the possible way to overcome above mentioned limitations and to visualize fine structural details routinely and unambiguously.

EXPERIMENTAL

Drawn UHMW PE tapes were prepared as reported elsewhere (5). SFM experiments were performed under ambient conditions with a "Nanoscope III" equipped with a multimode microscope head. This apparatus allows to scan the surface in the contact regime with simultaneous registration of the normal and lateral force components and enables imaging by the new tapping mode, TM (7). In the contact SFM, normal (repulsive) and lateral components of the interaction between a probe and a sample are measured by the vertical and torsional deflections of the cantilever, respectively. Consequently, these modes can be named as normal force (NF) mode and lateral force (LF) mode. One of the problems of contact microscopy, which is based on probing the interatomic repulsive force, is the deformation and



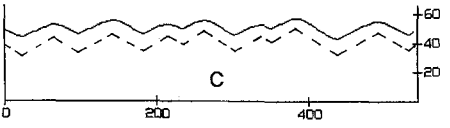


Fig 1a - 1c: (a) Scanning electron micrograph of Si tip ("Nanoprobe") (b) AFM height nanograph of the (305) face of $SrTiO_3$. Gray scale contrast indicates height variations within 30 nm. (c) dotted line-an actual saw-tooth contour of the gauge and solid line - a profile along the A-A line in (b)

damage of soft surfaces. Recently introduced TM is based on the detection of the amplitude variations of a forced oscillation of the cantilever generated by means of a piezoelement. The oscillation frequency is chosen close to the eigen frequency of the probe (ca 300 kHz). During engagement a sample is moved towards the oscillating probe till its amplitude will decrease to the set-point level. Then scanning proceeds with the feedback, which keeps the almplitude at the set level. Due to the absence of friction force and a short time of contact the probability of surface modification in TM is diminished. The gentle interaction can be of significant advantage if SFM is used for the investigation of soft materials such as polymers.

The reliability in the surface maping and the SFM resolution depends strongly on the shape of the probe apex, especially if structural details in the mesoscopic range (<100 nm) are to detected. Commercial pyramidal Si_3N_4 probes and more sharp Si tips ("Nanoprobes"), Fig. 1a, were employed for the measurements. By means of a recently introduced calibration gauge "Mesoscale" (8), shape and sharpness of the probe can be evaluated in the nanometer range. The gauge is a specially treated (305) surface of a single crystal of $SrTiO_3$, which has an atomically defined saw-tooth profile. The AFM image of this surface recorded with one of the best Si tips and the vertical profile in the horizontal direction A - A are shown in Fig. 1b - 1c. Deviations in the SFM micrographs from the actual profile indicate that the tip apex has a radius of about 10 nm. All Si_3N_4 and Si tips, which were used for the SFM measurements reported here, were selected by means of this calibration gauge. Approximately 1 of 3 commercial Si tips and only 1 of 15 pyramidal Si_3N_4 tips are most suitable for mesoscopic measurements. For TM studies Si tips, which are longer than those used for the contact AFM studies were applied. Their quality has been also preliminary checked with the calibration gauge.

RESULTS AND DISCUSSION

Large scale AFM images of PE tapes at draw ratio $\lambda = 10$ and 70, recorded in air with the selected Si_3N_4 tip, show the linear patterns of 30 - 50 nm in width, Fig. 2a - 2b. They were assigned to polymer nanofibrils formed during stretching process. Such nanofibrils are seen only in selected places in the necked material ($\lambda = 10$), but are the dominating surface features of highly stretched tape. The width of these linear patterns correlate with that of nanofibrils, which was determined by transmission electron microscopy (TEM) studies of this material (9). These images were registered with the selected Si_3N_4 tip that allows to improve the resolution in comparison with that achieved in the reported experiments with arbitrary chosen Si_3N_4 tips (5). The width of the linear features recorded in earlier experiments was varying from 20 - 90 nm with maximum of distribution near 50 nm.

SFM nanographs, which were recorded by employing three different imaging modes are presented in Fig. 3a - 3c. All pictures show nanofibrils with

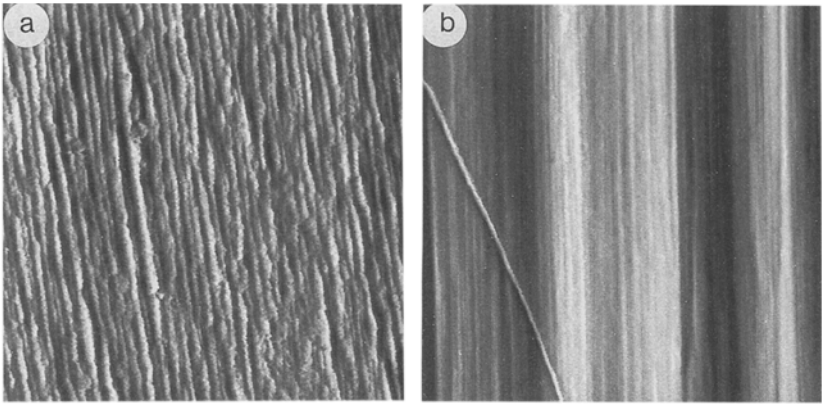


Fig. 2a - 2b: NF micrographs of UHMW PE tapes with (a) - $\lambda = 10$ and (b) $\lambda = 70$ which were recorded with the selected Si_3N_4 tip. Scanning area is 1.5 x 1.5 μ^2 in both cases. Gray-scale contrast indicates force variations.

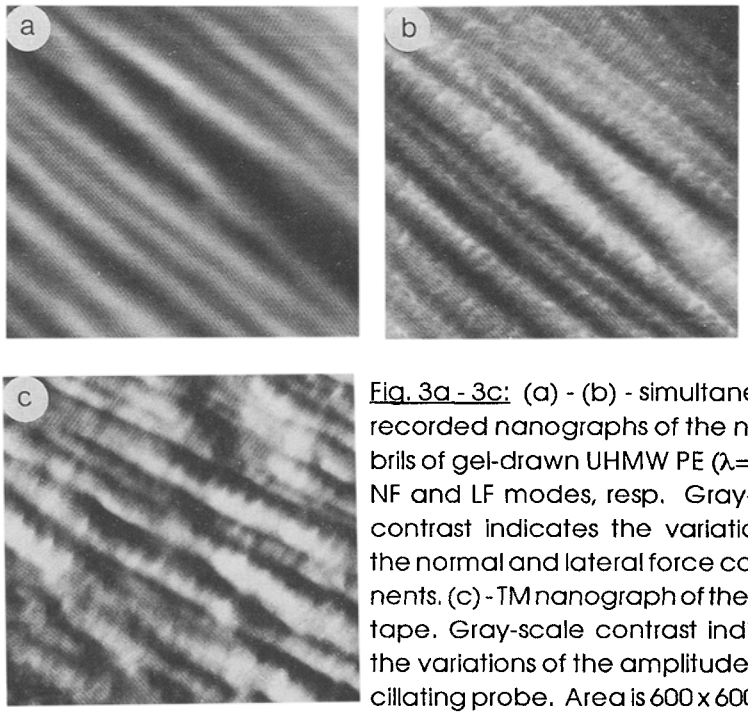


Fig. 3a - 3c: (a) - (b) - simultaneously recorded nanographs of the nanofibrils of gel-drawn UHMW PE (λ=10) in NF and LF modes, resp. Gray-scale contrast indicates the variations of the normal and lateral force components. (c) - TM nanograph of the same tape. Gray-scale contrast indicates the variations of the amplitude of oscillating probe. Area is 600 x 600 nm^2.

a diameter of about 40 nm. As the radius of the probe apex of the Si tip apex was estimated to be around 10 nm and as the surface profile of the densily packed nanofibrils is rather flat, tip shape - related image distortions are insignificant. The most detailed images of the surface structure of nanofibrils were recorded by means of the LF and tapping modes. In contrast to the featureless surface of fibrils seen in the NF mode image, Figs. 3a, the images registered in these modes allowed to visualize a regular striped pattern along

the nanofibrils with a periodicity of ca. 25 nm, Fig. 3b - 3c. This value is consistent with the *long period* of gel-drawn UHMW PE determined in SAXS experiments and in TEM micrographs of ultrathin sections of solution crystallized UHMW PE fibres (2d, 9). The periodic structure at the surface of the nanofibrils was observed first with a so called "super tip" when the corresponding image was recorded in the NF mode (10). However, these images exhibit a poor *long period* contrast, which is not well reproducible.

The image recorded in the LF mode (Fig. 3b) exhibited a more resolved and corrugated features than those found with other modes. This effect was already mentioned earlier in the discussion of the nanographs recorded on the surface of the gel-drawn tape ($\lambda = 70$), (11). During present study we also found the LF nanographs, which resemble a shish-kebab type structure, Fig. 4. Despite of the improved resolution and the detection of structural elements in mesoscale, several important questions of SFM are still opened. Nature of contrast in SFM nanographs is of a special importance. The SFM contrast may be caused either by true variations in height or by a difference in modulus and/or friction between crystalline and disordered parts of the nanofibrils. However, on flat surfaces changes of the lateral force component are caused by variations of friction between the probe and different surface regions. On corrugated surfaces, the response of the lateral component is rather complicated because the repulsive force directed along the normal to an inclined surface element does also contribute to the torsional deflection of the cantilever. To deconvolute different constituents of the contrast it will be helpful to conduct the SFM measurements with different forces and varying temperature as well as in combination with other methods.

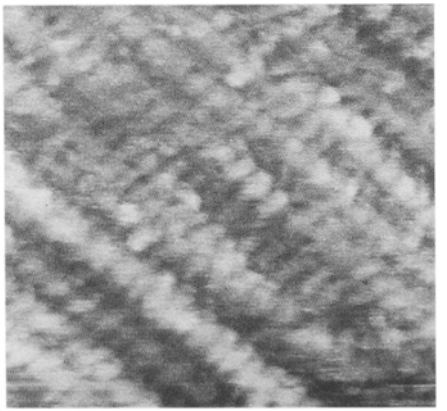


Fig. 4: LF nanograph of UHMW PE tape ($\lambda = 10$), which shows nanofibrils with shish-kebab type structure. Area is 450 x 450 nm^2. The meaning of gray-scale contrast is the same as in Fig. 3c.

CONCLUSION

In conclusion, SFM technique allows to visualize structural details on polymeric surfaces which have been beyond the scope of conventional electron microscopy methods. Mesoscopic calibration of the probe apex is essential

to approach the image of the actual surface structure and avoid tip-related artifacts. Well calibrated Si tips enable to depict the nanofibrils with a diameter about 40 nm. Contrast variations with a periodicity of ca. 25 nm in the lateral force and tapping mode nanographs are related to *long period* of drawn PE tapes and fibres, which have been recorded by SAXS and TEM.

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