Atomic force microscopy on fibers

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Abstract

Natural and synthetic fibers exhibit a huge diversity regarding their dimension, structure and physical-chemical properties. The wanted properties of textiles are adjusted by directed selection, development and processing of fiber material. Atomic force microscopy offers as sole method the possibility to acquire quantitative information in the nano- and micro range under environmental conditions about the surface properties of fibers and textiles. Therefore is the application of atomic force microscopy for the characterisation of fibers regarding their topography, material distribution, wettability, elastic properties and for the evaluation of manufacturing- and modification processes invaluable. In order to underline this fact the state of the art of atomic force microscopy on fibers is shown, different operational modes are introduced, techniques of sample preparation are presented and the significance of atomic force microscopy is demonstrated with numerous examples of subsequently mentioned manufacturing and surface modification techniques: plasma-technology, chemical vapour deposition, melt-spinning of bicomponent fibers, wet-chemistry, microstructuring, compounding.
History

- 1986: Ruska; Nobel Prize for the design of the first electron microscope
- 1986: Binnig, Rohrer; Nobel Prize for their design of the tunneling microscope
- 1986: Binnig, Quate, Gerber; publication of the design and performance of the atomic force microscope (AFM)

![Figure: Interaction of the tip and the surface](image)


1986 is a very important year for surface science and nanotechnology. Ruska has won the Nobel Prize for his invention of the electron microscope, Gerd Binnig and Heinrich Rohrer have got the Nobel Prize in 1986 for their invention of the scanning tunnel microscopy (STM). Binnig, Quate and Gerber published in 1986 an article about an instrument which can be applied on conducting and insulating samples under environmental conditions.¹ The AFM with its “daughter” instruments such as the magnetic force microscope and the Kelvin probe microscope has become the most important scanning probe microscope.²
The atomic force microscope (AFM)

A laser beam is focused on the rear of the cantilever. The reflected laser beam is detected by means of a double segment photodiode. During scanning a varying deflection of the cantilever is achieved, due to the surface topography encountered. As a consequence the mirror plane for the laser beam changes, and thus its position on the photodiode. Therefore, the difference signal between the two segments of the photodiode is a sensitive measure for the deflection of the cantilever. One advantage of this system is the fact that it can be conveniently operated also under liquids.\textsuperscript{3,4}

Schematic diagram of the typical elements of an AFM
Forces

There are three modes of operation of an atomic force microscope, contact, intermittent and non-contact.\(^4\)

In the contact mode, the Lennard-Jones potential repels the tip, whereas in non-contact mode attractive forces like the van der Waals forces may act on the tip. Local electric charges on the surface may lead to attractive or repulsive electrostatic forces on the tip. In a similar way, magnetic forces may be of influence if the tip is coated with a magnetic material.

Stick-slip processes exert friction or lateral forces on the tip. Increasing the force on the tip can lead to plastic deformation or nanoindentation of the sample. Also, capillary forces may act on the tip. The interaction forces strongly depend on the separation between tip and sample and on the material properties of tip and sample.\(^2,3\)

Measurable forces range from 10 pN to mN.
AFM techniques

Contact Mode

In the contact mode the tip, which is mounted on a soft spring (cantilever), permanently stays in contact with the sample during scanning and since it is in contact the repulsive surface forces are active. The deflection of the cantilever is sensed and compared in a feedback system to some desired value of deflection. If the measured deflection, which is converted into a force using Hooke’s law, is different from the desired value the feedback amplifier applies a voltage to the scanner to raise or to lower the sample relative to the cantilever to restore the desired value of force. The voltage that the feedback amplifier applies to the piezo is a measure of the height of the features on the sample surface.

Contact mode – constant force: shear forces are acting on the sample

Force-versus-distance measurements

The atomic force microscope is not only a tool to image the topography of solid surfaces at high resolution. It can also be used to measure force-versus-distance curves. Such curves, briefly called force curves, provide valuable information on local material properties such as elasticity, adhesion and surface charge densities. For this reason the measurement of force curves has become essential in different fields of research such as surface science, materials engineering, and biology.

Force curves show how the force changes, when the sample surface approaches the tip. At large separations there is no interaction and the observed force is zero and if we assume that there are no long-range forces like, e.g. electrostatic charging forces. At position 2 the tip jumps into contact due to attractive van der Waals interaction. As the sample is further moved towards the tip the total force acting on the cantilever becomes repulsive.
When the sample is retracted again, the force is reduced along the line from position 3-4. Below the zero force line in the diagram the net force acting on the cantilever becomes attractive, because the tip is held at the surface due to adhesion. In 5 the adhesion force and the cantilever load are just balanced and the tip flips off the surface when further retracting the sample. The value of the pull-off force can be reduced significantly by imaging under liquids due to elimination of capillary forces.

**Processes during the acquisition of a force-versus-distance curve (see text)**

Important information can be extracted from a force curve such as elastic modulus, work of adhesion, plasticity, thickness of a thin layer deposited on a substrate.

*Chemical force microscopy*

Chemical force microscopy is a variation of AFM in which the probe is modified with specific functional groups (e.g. polar or non-polar) and the recorded interactions between the probe and surface are used to explore the chemical composition of the surface.\(^5\)
**Dynamic Mode**

In contrast to the contact mode, both the intermittent and the and non-contact modes are dynamic since the cantilever is oscillated close to its resonant frequency above the surface. In the intermittent mode, the tip’s average position is in the region of the attractive forces. When fully extended the tip touches the surface atoms of the sample and reacts on the repulsive forces. The resulting interaction between the tip and the sample forces causes a slight shift in the resonance frequency and changes the vibration amplitude and phase with respect to the driving frequency. To maintain a constant force, the amplitude or the phase signal is used as the input in the feedback circuit. This mode is generally used for looking at soft specimens since it is less likely to cause specimen damage than the contact mode. The non-contact mode relies on the long-range attractive forces and is therefore more suitable for examining magnetic structures or those that exhibit high surface attractive forces. The achievable resolution is less than that of the contact and intermittent mode.3, 4

![Dynamic mode, a piezo oscillates the cantilever at a constant amplitude: shear forces are reduced.](image)

**Phase contrast**

The oscillating cantilever, driven by a piezoelectric crystal, enables a new form of contrast to be recorded. The phase-contrast image is produced by monitoring the phase difference between the cantilever’s oscillations and the standard signal, which drives the piezoelectric crystal during the intermittent mode. Certain surface properties including friction, adhesion and viscoelasticity affect the magnitudes of the phase. Applications include contaminants, mapping of different components in composite materials and differentiating regions of high and low surface adhesion or hardness.6
**EFM**

The electric force microscope utilizes electrostatic forces or force gradients between a conductive tip and a sample for signal generation.

**MFM**

In magnetic force microscopy magnetostatic forces are measured by interaction of magnetic domains on a surface with a magnetized tip.

**Sample preparation**

The bicomponent fibers were either bonded on a double-sided adhesive tape or were fixed on a thin layer of a spin-coated resin which can be molten below the glass temperature of the thermoplastic fibers (A). For the determination of the elastic modulus the fibers were fixed above a slit of defined width and cut exactly at one end (B). Then, the fibers were bent at the end by means of the cantilever. For imaging the cross-section, the fibers were embedded in an epoxy resin, then either cut by a saw or by a microtome and polished on emery papers with different grades of roughness (C).

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Sample preparation techniques: standard fixation (A), bending test (B), preparation of cross-sectional sample (C)
What is special on fibers?

The fiber dimension and geometry has an important impact on fiber properties like reflectance, wettability, adhesion etc. The surface-to-volume ratio increases by three orders of magnitude changing the radius from 10 microns to 10 nanometers. One of the most characterizing features of a surface is its adhesion. Fibers with a diameter larger than 3 μm show a curvature-independent adhesion force using a tip with $r_{\text{tip}} = 50 \text{ nm}$.\(^7\)

One of the main challenges in analysing textile fibers with AFM techniques is the fact that the sample presented to the tip is curved and often fairly corrugated. This limits the range of techniques or modes applicable and the variations in possible scanning parameters. However, as magnification is increased and the typical x-y-scan size is reduced, the relative corrugation and curving become less of a factor and the possibility of using other techniques without producing a range of artefacts becomes feasible. Data treatment such as flattening and anti-glitch filtering improves the visualization of small features on the surface. Elastic deformations define the regimes of operation of the AFM. The calculation of the contact radius as a function of elastic constants, tip radius, and applied force reveals that true atomic resolution is strictly limited to forces below $10 \text{ pN}$.\(^8\) This is still correct for the sharpest tips available. The measurement of local sample elasticity has a limited lateral resolution of 10-100 nm.\(^9\)
State of the art

AFM has become a technique which can probe topography, interfacial properties and manipulate structures on the nanoscale. Concerning imaging, the major progress has occurred in the ability of AFM to analyse surface structures non-destructively and in a physically relevant environment. Meanwhile, AFM has been able to visualise single macromolecules with sizes of around 5 nm and thus has become a new analytical method for the characterisation of polymers regarding their size, flexibility and macroconformation. Concerning properties, AFM has become a unique technique in probing local adhesion, friction and elastic response of various materials. This is based on the ability to measure forces as small as picoNewtons and probe areas well below 100 nm. The peculiar sensitivity of the force probe to different types of static and dynamic interactions provides a great number of contrast mechanisms which can map the surface structure regarding the chemical composition and physical properties.

AFM provides information about the electromagnetic (blue), mechanical (violet), topographical (green) and chemical properties of fibers (yellow).
In fiber science only a few papers making use of AFM have been published to date. These have concentrated on keratin fibers (wool, hair), polypropylene, polyethylene, carbon, aramid, PA, PET, melamine and various composite fibers such as polyamide or polypropylene reinforced with carbon or aramid fibers.\textsuperscript{10-16} One of the first papers utilising AFM on textile fibers was published in 1993.\textsuperscript{10} This work proved to be significant in the study of aramid fibers as the AFM results made it possible to clarify aspects of existing proposed structural models due to the visualization of structural features previously inaccessible.

AFM studies on the surface of PE fibers show that nanofibrils with similar width (5-7 nm) are the main structural elements.\textsuperscript{11} In the case of PP fibers it is pointed out that a spherulitic structure dominates the fiber surface in gravity spun and as-spun fibers of low draw-ratio.\textsuperscript{12} AFM imaging revealed, as winding speed increases, that there is a gradual deformation of the spherulites into a shish-kebab structure. For drawn filaments the surface structure is predominantly fibrillar in character. A well oriented-fibril-structure along the fiber axis could be observed on the surface of PA fibers.\textsuperscript{13} Following annealing in a vacuum or treatment in phenol solution increased crystallinity. The surface fibrils joined together and built up wider fibril bounds with hollow places between them. The nanoindentation capability of the AFM was used to study the effect of lubricant on the microhardness of PA and PET filaments.\textsuperscript{14} The outcome of the study indicates that the spin finish components ethylene oxide and propylene oxide (EO/PO) have a greater softening effect on the surface of PA fibers than on those of PET.

Cotton fiber cell walls were analysed to determine the effect of chemical treatments on cell wall organisation and topography. The influence of pH on the pull-off forces on cellulose surfaces was measured for chemically functionalised probe tips with hydroxyl, acidic and methyl terminated functional groups.\textsuperscript{15} AFM has been used to observe the surface structure of cotton fibers treated with three different cellulases, which differ in their hydrolytic and binding activity.\textsuperscript{16}

A new micromechanical technique was developed to study the mechanical properties of single collagen fibrils.\textsuperscript{17} The Young modulus of single collagen fibrils at ambient conditions was determined after depositing the fibrils on a substrate containing microchannels.

The nanostructural and elastic properties of single polymeric poly(L-lactat acid) (PLLA) nanofibers were investigated using AFM.\textsuperscript{18-22} Imaging reveals a shish-kebab structure. A
nanoscale three-point test is performed to obtain the elastic modulus. Nanoindentation experiments performed on similar fibers showed that the result for the elastic modulus is in good agreement with the nanoscale three-point bend test.

*Keratin fibers* (wool, hair) and their nano-mechanical properties were studied.²³⁻²⁵ Thin films are essential elements for many emerging industries. *Advanced lubricants* and *spin finishes* are the outcomes of basic and applied research on thin films.²⁵ A formalism has been developed, based on a series combination of linearly compliant elements, from which film thickness and elastic moduli can be inferred from the detailed structure of force-versus-distance curves. Adhesion measurements on the surface of keratin fibers, nylon and polyethylene, showed that in water and at high relative humidity the surface of keratin fibers is more akin to a polyamide. Literature has focused on using the AFM to study surface roughness, coefficient of friction, adhesive force, and wear (tribological properties) to increase understanding of how shampoos and conditioners interact with the hair cuticle.²⁶⁻²⁸ The coefficient of friction and adhesive force data on various scales for virgin and chemically damaged human hair, both with and without conditioner treatment, were presented. Microscale and nanoscale tribological characterisation was performed with AFM tips of various radii on human hair. AFM was used to study early stages of physical degradation and aging of melamine fibers, one of the latest high performance fibers.²⁹
Empa Research

*Plasma-technological deposition of nanoporous coatings*

The deposition of nano-scaled coatings on textiles starting at several nanometers in thickness to obtain a complete coverage of the textile surface can provide a high surface functionality, e.g. for adhesion or wettability improvement, while using a low amount of material. Nano particles embedded in a surface layer or a coating are used for drug release, photo catalytically active or antimicrobial interfaces. Their area per volume ratio also depends on the density of the nano particles within a matrix and their size distribution. Nanoporous coatings containing functional groups are of high interest for their improved dyeability and as anti-fogging or non-fouling surfaces.

For the sample with pore depths < 2 nm shown above the surface area increased by 0.9%, which leads to durable superhydrophilicity on PET textiles and improved dyeability.\textsuperscript{30, 31}
Chemical vapour deposition of nanofilaments

The combination of the hydrophobicity of the silicone and the surface topography formed by silicone nanofilaments renders the coated material (glass or PET) superhydrophobic.\textsuperscript{32} The Cassie-Baxter wetting mechanism on superhydrophobic surfaces implies that only the asperities of the surface are wetted, while water does not penetrate into grooves. This is supported by the force-distance curve measurements. The irregular withdrawal behaviour of the approach-retract cycle is thought to be related to the step-by-step release and disentanglement of filaments from the tip that became adhered when the tip was in contact with the surface. The force-displacement experiment confirms the filament length of several hundred nanometers and, furthermore, shows that the filaments are flexible.

From the force retraction curve and the single pull-off events due to physisorption we can conclude that the filament lengths range from 100-500 nm and that there is no attractive capillary force acting on the tip. No wetting took place at environmental conditions.
Melt-spinning of bicomponent fibers

Bicomponent fibers were spun by coextrusion of the polymers polypropylene (PP), polyethylene terephthalate (PET) and the high performance polymer polyphenylene sulfide (PPS) with the pilot melt-spinning plant SPIDER resulting in three different bicomponent fibers with core/sheath geometry: PET/PP, PET/PPS and PPS/PET.\textsuperscript{33}

The topographical cross-sectional view on the PET/PP-bicomponent fiber embedded in epoxy resin shows a remarkable height difference between core and sheath of ca. 1 µm after sawing and polishing. Probably the difference is a result of a smaller expansion of the PET core whose linear thermal expansion coefficient is 3 times smaller than that of PP (2x10^{-4} K^{-1}). The fiber cross section also reveals cavities between core and sheath, additionally. The phase contrast image shows only small differences in phase shift between the different polymers and the epoxy resin, with the phase for PP > PET > Epoxy, revealing that the PP is the softest material of the three polymers due to its amorphous state, and Epoxy being the stiffest polymer due to its three-dimensional network.
Wet-chemical treatment of PET and PPS

The chemical resistance of both the PET and the PPS sheath of the new bicomponent fibers consisting of PPS and PET against concentrated NaOH solution was tested and AFM imaging was performed on a treated PPS/PET and a PET/PPS fiber. Roughness analysis revealed that the roughness of the bicomponent fiber with PET as sheath material is about 10 times higher after hydrolysis as compared to the bicomponent fiber with PPS sheath. Hydrolysis leads to a porous structure with an average roughness of 7-10nm. The phase contrast image detects small areas of isolated particles, probably free standing crystalline regimes or additives like titanium dioxide.

![Topography (left) and phase image (right) of a PPS/PET core/sheath bicomponent fiber after treatment with concentrated NaOH solution](image)

The images above clearly demonstrate the complementary information provided by the phase contrast image. The less pronounced contrast correspond in the phase shift image corresponds to the amorphous state of the PPS/PET fiber, as supported by thermal analysis.
Mechanical bending

A new micromechanical technique\textsuperscript{17,20} was used to study the mechanical properties of single bicomponent fibers. Young’s modulus was determined at ambient conditions from a bending test after depositing the fiber on a slit formed by two microscope slides (see section “sample preparation”).

![Principle of the microscale bend test (left); force approach curves for the micromechanical bend test on two (red) and four (blue) times drawn PPS/PET-fibers](image)

The microscale bend test shows clear differences in the force-distance-curves obtained for two differently drawn PPS/PET and PET/PPS bicomponent fibers. The elastic modulus is extracted from the slopes of the curves using cantilever mechanics.\textsuperscript{2} The elastic modulus of a four times drawn PET/PPS fiber with a volume ratio of 1/2 is higher by a factor of 3 than that of a two times drawn PPS/PET fiber with a volume ratio of 2/1, which is in good agreement for monocomponent fibers consisting of pure material.\textsuperscript{7}
Microstructuring of fibers

A roll embossing device has been developed to laterally microstructure textile fibers, using a roundabout thermoplastic molding. The surface relief of a stamp (nickel shim) is transferred onto the surface of a fiber, by molding a thermoplastic material at a temperature well above its glass transition temperature. A sophisticated system with unaligned pressure rolls ensures that the embossing effectively covers the entire fiber surface. This process has similarities to the hot embossing of surface structures into thin polymer sheets for the fabrication of diffractive optical elements or into thin thermoplastic resists as used in the nanoimprint process. Roll embossing is a process highly suitable for mass-fabrication at industrial scale, process speeds can be up to some meters per second. Possible applications are textile copyright marks, dye-less fiber colouring via diffraction, or substrates for biomedical applications with controlled cell growth.

To achieve optical effects, two kinds of microstructures were imprinted on PMMA fibers. A plasma silver coating was applied to achieve reflective surfaces required for more distinct optical effects. Periodic microstructures render rainbow optical effects, while alternating microstructures lead to sparkling optical effects. In order to simulate the optical behaviour the exact structure of the imprinted structure has to be known. AFM imaging provides the quantitative information about the shape, depth and groove density and allows to formulate suggestions how to improve the manufacturing process.
New materials

Compounds

Carbon black (CB) is a material, today usually produced by the incomplete combustion of petroleum products. CB is a form of amorphous carbon that has an extremely high surface-to-volume ratio and as such it is one of the first nanomaterials to find common use. CB is often used as a pigment and reinforcement in rubber and plastic products. In addition to providing electrical conductivity to the plastic compound, CB also provide lasting protection against ultraviolet light degradation.

Adding CB to a blend of SEBS/PP prior to kneading and extrusion

From phase contrast images of a compound consisting of styrene-ethylene-butylene-styrene based thermoplastic elastomer (SEBS) and polypropylene (PP) we can see that - keeping the ratio between SEBS and PP constant - there is a homogenous distribution of the two polymers after addition of CB. This fact corresponds with an increased electrical conductivity, showing that the percolation of CB took place.
Smart Temperature and Humidity Responsive Materials

Academic and industrial research is focusing on the development of smart materials and their implementation in products, including textiles,\textsuperscript{36} that could be used in the daily life. The temperature responsive materials are promising for clothing applications, especially if the trigger temperature is in the physiological range to increase the comfort of the wearer.

AFM investigations were performed on a temperature responsive film of poly(N-vinylcaprolactam) placed in an environmental chamber, with controlled temperature and relative humidity.

![Dependency of the PVCL film thickness $d$ on temperature $T$ and humidity $RH$](image)

The thickness of the film can be adjusted by the environmental humidity and temperature, which may induce changes in the physical properties of the film. Thus, films with temperature responsive permeability and coefficient of friction could be obtained.
References


