Characterization of synthetic fibers using the atomic force microscope

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Abstract. Plasma-modified PET-monofilaments, newly developed functional bicomponent fibers and electrospun PEO-nanoscaled fibers were investigated using the atomic force microscope. Contact mode measurements revealed small changes in topography by changing the oxygen-content during hexamethyldisiloxane plasma-deposition. Adhesion measurements proved the increasing surface energy with increasing oxygen-content as calculated by JKR theory. Simultaneous measurements of the topography and phase shifts on bicomponent fibers demonstrated the change of the surface roughness and elastic homogenity of the PET-surface after hydrolysis with NaOH solution. Cross-sectional imaging showed differences in thermal expansion and hardness of bicomponent fibers. Nanoscaled unsupported electrospun fibers were visualized in the dynamic mode. Bending of differently drawn bicomponent fibers by the AFM-cantilever allowed direct access to the elastic modulus.

1. Introduction

Synthetic fibers are widely used in many applications, including technical textiles and clothing. The development of synthetic fibers with new material properties via melt- or electrospinning is a challenging task that involves control of parameters like temperature and pressure control, fiber formation, cooling, drawing, or winding. All of these individual steps have an influence to the final structure of the fiber on the macroscopic and molecular scale. Drawing for example affects the orientation of the macromolecules as well as the degree of crystallization. Both the orientation and the degree of crystallization have an enormous impact to mechanical fiber properties like stiffness and elongation. The post-treatment of the fiber surface on a nanometer scale can be used to make it hydrophilic, hydrophobic, conductive, porous etc. [1].

The use of atomic force microscopy (AFM) is reported in the present study to measure local properties on curved fiber surfaces. The sample preparation and the fixation are important steps to
assure reliable measurement conditions of the fiber geometry. We present results obtained on a selection of different advanced fibers and thus demonstrate the power of AFM as a valuable tool to elucidate local topographical and material properties of bicomponent fibers [2], nano-scaled fibers and plasma-modified fibers [3]. In particular, the selection of examples include novel bicomponent fibers with core/sheath configuration from our pilot melt-spinning plant.

2. Methods

2.1. Fiber synthesis and modification
Commercially available PET monofilaments were modified by means of plasma treatment in a continuous low pressure process. Hexamethyldisiloxane (HMDSO) was deposited under different conditions (ratio HMDSO:O$_2$ = 1:0, 1:1, 1:4) resulting in weaker silicon-like hydrophobic HMDSO-layers and hard quartz-like hydrophilic HMDSO/O$_2$-layers [3].

Bicomponent fibers were spun by coextrusion of the polymers polypropylene (PP), polyethylene terephthalate (PET) and the high performance polymer polyphenylene sulfide (PPS) by means of the pilot melt-spinning plant SPIDER [6] resulting in three different bicomponent fibers with core/sheath geometry: PET/PP, PET/PPS and PPS/PET [2].

Aligned polyethylene oxide (PEO) nanofibers were electrospun from 8 wt % in an aqueous solution with a regulated flow rate of 0.02 ml/min and potential difference of 20 kV across the two electrodes with a separation of 150 mm.

2.2. Sample preparation
The bicomponent fibers were either bonded on a double-sided adhesive tape (Scotch) or were fixed on a thin layer of a spin-coated resin (Epikote) which can be molten below the glass temperature of the thermoplastic fibers. For imaging the cross-section, the fibers were embedded in an epoxy resin (Araldit), then cut by a saw and polished on emery papers with different grades of roughness. For the determination of the elastic modulus the fibers were fixed above a slit of defined width and cut exactly at one end. Then, the fibers were bent at the end by means of the tip. The slopes of the force-displacement-curves provide the information for calculating the elastic modulus E of the fibers.

2.3. AFM-measurements
AFM-measurements were performed with a commercial AFM (easyScan 1 and 2, Nanosurf AG, Switzerland). In contact and force spectroscopy mode a cantilever (NanoProbe Pointprobe CRC) having a spring constant $k_{tip} = 0.2$ N/m and radius of tip $r_{tip} < 10$ nm was used. In dynamic and phase contrast mode a cantilever (NanoProbe NCRC) having a spring constant $k_{tip} = 48$ N/m, resonance frequency $f_{res} = 190$ kHz, and a tip radius $r_{tip} < 10$ nm was applied. All measurements were carried out under controlled atmosphere (T= 295 K, relative humidity RH= 40%).

3. Results and Discussion

3.1. Adhesion measurements on plasma-modified PET monofilaments using contact mode
The topography images of plasma-modified PET filaments reveal small differences in surface roughness for different grades of HMDSO:O$_2$-content. The PET surfaces modified with HMDSO:O$_2$ (1:4) show a rougher structure (not shown) in comparison to the pure HMDSO-surface (Fig. 1 left). The adhesion force increases with increasing oxygenation by a factor of three (Fig. 1 right).
The adhesion force was measured in the spectroscopy modus and is transformed to surface energy per unit area by means of the JKR theory [4] which takes the deformation of the surfaces into account. The measured work of adhesion ranges from 600 mJ/m² (HMDSO:O₂ = 1:4) to 200 mJ/m² (HMDSO).

3.2. Dynamic mode and phase contrast imaging of bicomponent and nano-scaled electrospun fibers

The chemical resistance of bicomponent fiber surfaces against concentrated NaOH solution was measured gravimetrically [3]. The effect of hydrolysis is visualized on a PPS/PET core/sheath bicomponent fiber (Fig. 2). The roughness of the bicomponent fiber with PET sheath is about 6 times higher after hydrolysis as compared to the chemically untreated PPS/PET bicomponent fiber. Hydrolysis leads to a porous structure (Fig. 2 left) with an average roughness of 7.2 nm. The phase contrast image reveals small areas of isolated particles (Fig. 2 right, black spots), probably free standing crystalline regimes or additives like titanium dioxide. The PPS-sheath of a PET/PPS bicomponent fiber remains unaffected and is comparatively smooth (average roughness = 0.74 nm, not shown).

Figure 3 shows the cross-sectional AFM-image of a PET/PP core/sheath fiber. The topographical view on the PET/PP-bicomponent fiber (Fig. 3 left) shows a 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 \( (2 \times 10^{-4} \text{ K}^{-1}) \). The fiber cross section also reveals cavities between core and sheath, additionally.

![Topography and Phase Shift](image)

**Fig. 3:** left: topography, right: phase shift

The phase shift depends on the time-averaged surface stiffness \( \langle s \rangle \) and contact radius \( r_c \), the cantilever properties \( Q \) (quality factor) and \( k \) (spring constant) and the effective modulus \( E^* \) as follows [5]:

\[
\Delta \phi \approx \langle s \rangle \left( \frac{Q}{k} \right) = \varepsilon \langle r_c \rangle E^* \left( \frac{Q}{k} \right)
\]

This equation shows that phase imaging provides a map of stiffness variation on the sample surface such that a stiffer region has a higher positive phase shift and hence appears brighter in a phase image. The phase contrast image (Fig. 3 right) shows only small differences in phase shift between the different polymers and the epoxy resin, with \( \Delta \phi \text{ PP} > \Delta \phi \text{ PET} > \Delta \phi \text{ Epoxy} \), reflecting the larger contact radius \( r_c \) of the tip in the weaker polymer according to the above-mentioned equation. Enhancement of the contrast by optimizing the cantilever properties and measurement conditions is possible.

It turned out that imaging of oriented unsupported electrospun PEO nano-scaled fibers was possible only in dynamic mode due to the reduction of shear forces present in contact modus, allowing the determination of the dimensions both in vertical and lateral direction (Fig. 4). The electrospun PEO nanofibers have diameters varying from 350 to 690 nm.

![Topographical and Cross-Section Images](image)

**Fig. 4:** left: topographical image, right: diagonal cross-section

### 3.3. Bend test on bicomponent fibers

The microscale bend test shows clear differences in the force-distance-curves (Fig. 5) obtained for two different bicomponent fibers differing in core/sheath-volume ratio, composition and draw ratio. The elastic modulus is extracted from the slopes of the curves using cantilever mechanics [8]. The
four times drawn PET/PPS fiber with a volume ratio of 1/2 is stiffer by a factor of 2-5 (elastic modulus $E_2 = 6 +/- 2$ GPa) than the two times drawn PPS/PET fiber with a volume ratio of 2/1 ($E_1 = 2 +/- 0.7$ GPa).

Fig. 5: Force-displacement curve for two differently drawn bicomponent fibers (red: 2x, black: 4x)

4. Conclusions
Contact mode reveals even small changes in roughness after plasma-treatment of the fiber surface. Oxygenation of a thin HMDSO layer leads to structural changes. Adhesion measurements allow differentiation of surface energies, which are in agreement with contact angle measurements [4]. Dynamic mode together with phase contrast provides complementary information about topography and elastic properties on chemically modified surfaces, as shown on a hydrolyzed PET-sheath of a PPS/PET core/sheath-bicomponent fiber. Phase contrast imaging reveals differences in local sample hardness. Dynamic mode is applicable to unsupported fibers such as electrospun nanofibers in a nonwoven-structure. Elastic modulus of nano- and micro-scaled single fibers is directly accessible with a bending experiment. Further experiments will be performed for a deeper understanding of the correlation between fiber processing and adhesion, mechanical properties and fine structure of the surface.

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