Towards quantitative materials characterization with Digital Pulsed Force Mode imaging

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Abstract. The determination of the mechanical properties of polymer-surfaces is a widespread task in the AFM community. The most important step in measuring is the thorough calibration of the measurement setup. Here, we address that problem for the case of Digital Pulsed Force Mode measurements. We show that following our suggestions, one can get reliable and consistent quantitative data on the mechanical properties of polymers such as PMMA or SBR rubber. The influence of the individual cantilevers and their properties, as well as the variations due to the settings of the AFM are widely eliminated.

1. Introduction
The determination of the mechanic properties of thin polymeric films becomes more important, since the surface to volume ratio increases with proceeding miniaturization. Because of this, methods such as the Atomic Force Microscope (AFM) \textsuperscript{[1]} have been developed that are able to characterize surfaces with a high lateral resolution based on mechanical interaction \textsuperscript{[2–5]}. To analyze the lateral composition, resonant imaging modes \textsuperscript{[6, 7]} can be used. These modes are highly sensitive towards changes in the surface potential, but lack the possibility to control the normal force exerted on the sample at each measurement point. Currently two methods allow this kind of imaging, the Force-Volume-Mode or Jumping Mode \textsuperscript{[8,9]}, and the (Digital) Pulsed Force Mode (DPFM) \textsuperscript{[10,11]}. The DPFM has the advantage of being able to operate at much higher repeat rates than the others, thus allowing higher sampling of the scan-field.

However, calibration of the measurement setup is always crucial to AFM experiments. This is why in the following we describe our method for quantitative imaging and reliable data-analysis using the DPFM.

2. Materials and methods
2.1. Polymer samples
The sample system used here was a mixture of two parts by weight of polymethyl-methacrylate (PMMA) and one part by weight of styrene-butadiene-rubber (SBR) that has been dissolved in toluene to allow mixing of the two components. Then the solution has been brought onto

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the silicon substrate by spin-coating at 3000 revolutions per minute. During the spin-coating process, the polymers separate into two phases again and form a thin film with islands of PMMA surrounded by the SBR. From macroscopic experiments, one knows that the PMMA should be clearly discernable from the SBR due to its elasticity and much higher stiffness, while the SBR has to reveal a clearly rubber-elastic behavior. Furthermore, SBR should be by far stickier than the PMMA regions. The silicon underneath, of course, has to be the hardest of the materials with a literature value for its Young’s modulus of approximately 160 GPa.

2.2. Atomic Force Microscope
In the experiments presented here, we used a WITec AFM setup (www.witec.de) in ambient conditions. The setup was equipped with a 100 µm x 100 µm x 20 µm scanning table by PI GmbH (www.physikinstrumente.de). As cantilevers we used type OMCL-AC160TS Olympus silicon cantilevers with a stiffness of 42 N/m at a resonant frequency of 300 kHz. Throughout the experiments, most cantilevers had a stiffness of about 60 ± 5 N/m. The radius of each tip has been examined using an Scanning Electron Microscope (SEM) prior to and after the experiments. Thus we were able to observe that at 1.2 µN the tips broke off and lost their original sharpness of below 10 nm, but then remained constant at a radius of about 50 nm. As a sinusoidal modulation amplitude of the DPFM indentation curves, we used 1.5 µm, which was measured using a Vibrometer by SIOS GmbH (www.sios.de). The repeat rate of the curves has been 1 kHz.

2.3. Calibration and correction procedures
To be able to perform quantitative Force Distance Curve (FDC) [12–14] based measurements with the Digital Pulsed Force Mode, or any other comparable technique, one needs to control and calibrate every step of a measurement. First, the stiffness of the cantilever needs to be known. This can be obtained by measuring the deflection with respect to a calibrated cantilever. Second, the indentation measurements necessary to determine the Young’s modulus and other mechanical properties need to be compared to a calibration surface. We have used silicon as a calibration surface. The polymer sample was prepared on silicon, and silicon was exposed thereafter by scratching the polymer away. Third, the tip radius has to be measured in a SEM after the measurement. The radius is crucial for most mechanical data evaluation procedures. Fourth, phase shifts due to signal run-times in the AFM-setup have to be compensated for as demonstrated in figure 1 (a-d). The shift that is calculated in step number four then has to be applied to all the following position transformations. Fifth, the converted data now shows the cantilever deflection versus the position of the base of the cantilever. Finally, this has to be transformed into a display of the deflection versus the true tip position.

3. Results and discussion
By the appropriate handling of the DPFM data, the force curves can be transferred from the time domain (Fig. 2 (a)), to the position of the cantilever base (Fig. 2 (b)), and finally to the actual indentation depth (Fig. 2 (c)) of the tip of the cantilever into the sample material. This indentation depth includes two phenomena. First, the deformation of the compliant sample material. Second, the deformation of the silicon tip. The latter effect especially becomes visible when operating the DPFM on hard surfaces such as the reference material. In this case, a silicon wafer was used as a substrate for the polymers and made visible by scratching away them using a scalpel. Having the sample material in the same scan-field as the reference allows to calibrate the apparatus in-situ. Thus, for each scan-line the calibration parameters can be derived and the phase shift described above can be continuously adjusted.

Plotting the force data over the indentation depth now allows us to apply an analysis based on continuum mechanics models [15,16] such as the JKR-model [17] by Johnson-Kendall-Roberts.
Figure 1. Correcting the phase shifts. (a) Without correction. (b) -15° shift still shows an intersection and a large hysteretic loss. (c) -16.8° results in a well corrected force trace, while in (d) the run-times are overcompensated and the loop widens again at -19°.

or the DMT-model [18] by Derjaguin-Muller-Toporov. In the present case we used a JKR-based model to fit our data. Furthermore, energies such as the hysteresis during a single loop or the detachment energy needed to pull-off the tip of the cantilever from the sample surface become accessible. Material contrasts can then be obtained for various different quantities.

Figure 3 (a) shows the corrected topography. This can only be computed if one has calibrated the system very carefully. It corresponds to the original height of the material as if the tip would follow the surface features without applying any normal force. Compared to the topography as measured at the set-point force (Fig. 3 (b)) which is usually believed to be the real topography, one observes that the polymers dewet in an almost perfectly flat surface towards the air interface. This is necessary to minimize the surface energy of the polymer-air boundary. The resulting initial thickness of the polymers has been determined as: 58 ± 1 nm for the PMMA and 50 ± 2 nm for the SBR regions. Calculating the Young’s modulus for each curve also allows to create a map of the surface elasticity at the given repeat rate of 1 kHz. This is shown in figure 3 (c). We obtain a modulus of 42.6 ± 10.5 GPa for the PMMA islands and an average modulus of 0.84 ± 0.64 GPa for the SBR regions. Since the areas underneath the force traces equal an energy, we are also able to calculate for example a map of the energy dissipated by the sample surface during each cycle. We call this the hysteretic loss. The average values for the investigated materials are: (0.30 ± 0.023) \(10^{-15}\) J or (1.88 ± 0.14) keV for PMMA and (5.2 ± 0.04) \(10^{-15}\) J or (32.50 ± 0.03) keV for SBR. However, the more intuitive quantity is the percentage of energy that is lost during such a cycle. It is the energy of hysteresis divided by the energy imported into the sample during the approach. The map is shown in figure 3 (d).
Figure 2. Force responses on the different surface regions. The green curve has been recorded on silicon, the black curve shows the response of the PMMA islands and the red one on SBR. (a) Deflection signal versus time. (b) Transferred to the position ordinate of the cantilever base (as modulated). (c) Repulsive force versus the indentation depth of the tip into the sample material.

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Figure 3. Material contrasts that can be derived from the analysis. (a) Reconstructed topography image as if no force was exerted on the surface. (b) Original topography as measured at the set-point force. (c) Young's modulus of the surface. (d) Relative dissipation during one approach and retract cycle.

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