Surface Nanomechanics of Coatings and Hydrogels

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Abstract
Due to the increasing use of nanostructured materials and thin coatings as barrier materials, it has become of high importance to measure and understand material properties on the nm to 100 nm length scales. In this article we demonstrate and discuss how atomic force microscopy techniques can be used to this end. It is demonstrated that the classical analysis based on the assumption of a purely elastic material response is a fair approximation for relatively stiff coatings (elastic modulus order of GPa), whereas viscous responses must be considered for soft materials (apparent modulus order of MPa) such as hydrogels.

1. Introduction
Very small probes are needed in order to determine local mechanical responses on the nm to 100 nm length scales. Such small probes are offered using the Atomic Force Microscopy (AFM) technique, where sharp tips with end radius of a few nms are commonly employed. This approach has successfully been used to determine variations in mechanical response over single core-shell nanoparticles [1], and to evaluate mechanical property variations across the interphase (interfacial region) between nanoparticles and polymer matrix in nanocomposites [2]. When performing such measurements one can choose between utilizing common single frequency methods and more sophisticated multi-frequency approaches.

Single frequency AFM modes include Peak Force Tapping (PeakForce QNM), Quantitative Imaging, QI, and Force Volume Mapping, where a complete force curve is acquired at each image pixel. Common to these modes is that the operator decides the maximum force applied, but they differ in terms of the tapping frequency used and how nanomechanical information is extracted from the force curves. As an example we illustrate how the captured force curve is analysed, see Figure 1 left panel, but we note that all these images cannot be extracted in all modes. Importantly, several images are obtained simultaneously over the same surface region. The surface topography is shown in one image and the other images are reconstructed from the force curves. The adhesion force image is extracted from the retraction force curve and displays the maximum attractive force experienced upon separation. The adhesion energy image is the integral of the difference between the zero force line and the attractive part of the separation curve, the energy dissipation image is the integral of the difference between the approach and separation curves and the surface stiffness is extracted from the slope of the separation curve. The surface deformation (indentation depth) at each pixel can also be extracted as illustrated in Figure 1.

It is also possible to evaluate the local elastic modulus of the sample surface by fitting a contact mechanics model to a part of the retrace force curve. Of these quantities the surface stiffness and elastic modulus are most easily compared to quantities determined by e.g. indentation methods. We note that when evaluating the elastic modulus using contact mechanics models it is implicitly assumed that the response is purely elastic. As will be shown in this article, using a hydrogel sample, this is far from always correct since the viscous response of such soft materials is significant.

One way to analyse viscoelastic systems is to use multi-frequency dynamic AFM methods. Such approaches provide more information on the surface nanomechanical response, but they are also less...
intuitive since they do not directly give a force vs. tip position curve. Recently, one such method, Intermodulation AFM (ImAFM) [3], has been utilized to gain detailed information on how both the surface of a soft sample and the cantilever tip moves in response to long-range and contact surface forces. In particular, it was shown that the common assumption of a static surface is incorrect for soft materials [4].

2. Results and Discussions
In this section we describe and discuss nanomechanical data obtained for two systems. The first is a relatively hard polymer coating designed for corrosion protection applications [5], whereas the other sample is a soft hydrogel of crosslinked polyHEMA. In both cases we illustrate typical surface-tip force curves and discuss how these are analyzed to provide nanomechanical information.

2.1. Nanomechanics of a corrosion protective coating
PTE Coatings (Gamleby, Sweden) provided the water-born hydroxyacrylic-melamine copolymer coating used in this example. The coating, with main components being a hydroxyacrylate resin mixed with the cross-linker hexakis(methoxymethyl)melamine (HMMM), was heat cured at 180 °C using different curing times in the range 2 – 30 minutes. More details on the corrosion protection performance after different curing times, and nanomechanical properties of this coating system can be found in our recent article [5].

A typical force curve between the hydroxyacrylic-melamine coating and the probing tip is illustrated in Figure 1 (middle). It is from such data sets that local nanomechanical properties are determined. We note that in this case the hysteresis between force curves measured on approach and on separation is small (except for a tip-surface adhesion seen in the retrace curve). This suggests that the deformation of the surface due to compression by the tip is predominantly elastic, and thus it is a good approximation to analyze the repulsive part of the force curve using an elastic contact mechanics mode. In this case, due to the small probe radius and the low adhesion, we utilized the DMT model [6].

![Figure 1](image1.png)  
**Figure 1.** Typical force curves between an AFM tip and various samples. Left: Polystyrene sample in air. This panel illustrates how different nanomechanical properties are evaluated. Middle: The hydroxyacrylic-melamine coating measured in air on approach (trace) and retraction (retrace). Right: A cross-linked polyHEMA sample measured in water. Note the large hysteresis between forces measured on approach (trace) and separation (retrace) for this sample.

The topography, elastic modulus and deformation maps recorded simultaneously over the same surface area are illustrated for three curing conditions in Figure 2. We note that a relatively homogeneous surface layer is formed, with only small variations in height, elastic modulus and surface deformation. The curing time does, however, affect the mechanical properties significantly and the sample cured for 2 minutes is significantly softer than those cured for 10 or 30 minutes. This is due to a significantly lower conversion of the cross-linking reactions at the shorter curing time [5].
In our previous report we showed that even though the surface layer looks homogeneous and the corrosion protection performance is good, weak spots are present in the coating as can be observed after prolonged exposure times in corrosive environments [5].

![Figure 2](image-url)

**Figure 2.** Topography (left), elastic modulus (middle) and deformation (right) images measured with AFM for coatings cured for 2 min (a-c), 10 min (d-f) and 30 min (g-i) min. The cross-section topography, modulus and deformation data for the sample cured for 10 min are taken along the white lines shown in panels d-f, respectively. The data were recorded in air. From reference 5, with permission. DOI: https://doi.org/10.1016/j.apsusc.2018.06.284. Creative Commons user license: https://creativecommons.org/licenses/by-nc-nd/4.0/

It is worth pointing out that the deformation used in these AFM-based nanomechanical measurements is small, in our case 3-5 nm. Thus, in these types of measurements it is the surface nanomechanical properties that are determined, and these may differ from bulk mechanical properties even for perfectly elastic solids. There are several reasons for this. The degree of cross-linking at the surface may be lower than that in bulk due to e.g. depletion of cross-linking agents at...
the interface or reaction inhibition by oxygen, which would make the surface layer softer than the bulk material. On the other hand, surface tension effects will counteract deformation and render the surface layer stiffer than the bulk material. This feature is often referred to as a skin effect and it is suggested to be due to non-linear stress-strain relations caused by the small size of the probing tip [7,8]. Thus, it is not uncommon to observe an indentation depth dependence on the elastic modulus [9, 10].

2.2. Nanowear of a corrosion protective coating

A protective coating can only fulfill its function as long as it remains intact, and thus the wear resistance of the coating is essential for its function. Below we report data obtained after 35 days exposure to corrosive environment, 0.1 M NaCl, at which point the corrosion protection experiment was terminated. In order to investigate the initiation of wear we have developed a two-step AFM based procedure. In the first step the tip scans the surface in contact mode, and here different loads are used over different surface areas. During this step the lateral force on the tip is also recorded, as it allows determination of friction and observation of stick-slip phenomena. The second step involves gently recording the surface topography over a slightly larger area that includes the worn area. Examples of such data are shown in Figure 3. As reported in detail in our previous article it was observed that wear at low loads was due to smooth plastic deformation, followed at higher loads by plastic deformation giving rise to topographical ripple structures. At even higher loads abrasive wear was predominant. It was also shown that the topographical ripple structures observed after wear had the same periodicity as the stick-slip periodicity as observed during wear [5]. Thus, a direct correlation between stick-slip and plastic surface topography changes was observed for this polymer coating.

![Figure 3](https://doi.org/10.1016/j.apsusc.2018.06.284)

**Figure 3.** Wear experiments conducted with an AFM tip on a sample cured for 10 min before (a,b) and after (e,f) exposure to 0.1 M NaCl for 35 days, as well as on a sample cured for 30 min before (c,d) and after (g,h) exposure to 0.1 M NaCl for 35 days. The load was increased step wise as marked in the images. Contact mode topography images under the indicated loads, recorded during the wear experiment, are shown in panels a, c, e and g. Peak Force topographical images recorded after the wear experiment are shown in panels b, d, f and h. From reference 5, with permission. DOI: https://doi.org/10.1016/j.apsusc.2018.06.284.
2.3. Nanomechanics of a hydrogel surface

The nanomechanical response for a thermoplastic nanocomposite, where the coating stiffness varies with temperature, was recently reported [11] and illustrates that coatings with varying stiffness can be studied by means of AFM. In the next example we consider a very soft material, a cross-linked polyHEMA hydrogel studied in aqueous solution where it is fully hydrated. In air, the hydrogel is significantly harder and shows a surface nanomechanical response that is humidity dependent as will be reported in a forthcoming publication. A typical tip-sample force curve for this case is illustrated in Figure 1 (right). Here we observe a large hysteresis between forces measured on approach and separation, signifying that viscous effects are of importance during the time scale of the measurements. We also note an adhesion on separation that arises from stretching of polymer chains that bind to the tip.

In order to investigate the nanomechanical response of this sample we adopted an experimental approach similar to that used for studying nanowear in the previous example. We probe different surface areas with different loads and evaluate the load-dependent nanomechanical response. In the example below we illustrate the surface topography (Figure 4, left) and how the apparent elastic modulus varies with indentation depth (applied load) (Figure 4, right). We use the term apparent modulus to acknowledge that the mechanical response is not elastic but rather viscoelastic.

We note that the apparent modulus increases with increasing indentation depth (Figure 4, right). Note that the indentation depth for this soft material is significantly larger than for the polymer coating discussed above. The load dependence of the apparent modulus suggests that the hydrogel sample is less cross-linked at the surface, and there are also some dangling polymer tails as observed in the force curve (Figure 1, right). At higher compression the indentation is deeper and the response of the cross-linked hydrogel material further below the surface becomes more important, but viscous effects still preclude determination of the elastic modulus. Thus, for such soft samples as hydrogels viscous responses cannot be ignored. For this reason no single value of apparent modulus (or, alternatively, surface stiffness) can characterize the mechanical response. Instead it is more appropriate to report the load dependence of these properties at a defined measuring speed. Viscous effects also have to be taken into account when performing indentation measurements with other techniques and evaluating the data according to the Oliver-Parr methodology [12]. It is our opinion that multi-frequency techniques, such as ImAFM, that separate viscous and elastic responses have an advantage over single frequency AFM techniques for studying such samples. One example of such a study can be found in a recent article [4].

![Figure 4. Topography (5x5 µm²) of a cross-linked polyHEMA sample (left) and the apparent modulus as a function of indentation depth (right) determined using a constant driving speed of 5 µm/s.](image-url)
3. Conclusions
AFM-based techniques can be used for measuring force vs. distance data, and from these it is possible to extract local nanomechanical surface properties. The data evaluation is relatively straightforward for samples showing a predominantly elastic response, and here elastic modulus and surface stiffness can be evaluated using classical contact mechanics theories. For soft samples, special protocols need to be adopted to allow determination of the indentation (or load) dependence of the extracted nanomechanical data. This is due to the importance of viscous effects for such samples. AFM-based techniques are also of great importance for investigating the initiation of wear and wear mechanisms under different load and shear conditions, and we have suggested an experimental protocol for such measurements.

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