

Abrasive scanning with AFM on biocompatible polymers: measuring dry vs. swollen film thickness and probing properties

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ABSTRACT

In this study we exemplify raster-scan *abrasion* with an AFM probe at high force (in “contact mode”) to shear-displace relative soft (organic, polymeric) films on hard substrates, and nonperturbatively analyze the results at lower force. We delve into extra detail on polyacrylamide films chemisorbed on silanized glass surfaces via ultraviolet-initiated attachment and crosslinking. This ultrathin film system is a technological platform for DNA microassays; more generally, thicker polyacrylamide films are added as lubricious coatings on medical devices.[surmodics] One problem of interest to those engineering such films is measuring the degree of film *swelling* under aqueous immersion (and its relation to processing parameters). We present a methodology for this measurement using force-distance curve mapping over the scan-abraded and surrounding region. We demonstrate that conventional topographic imaging (i.e., under setpoint feedback) of this region is an erroneous means of quantifying swollen film thickness because of substantial mechanical compliance atop the swollen polymer; whereas force-distance mapping accounts for this compliance, and furthermore reveals interesting macromolecular behavior. We exemplify some algorithms for more advanced and quantitative analyses of these datasets.

Keywords: atomic force microscopy, nanotribology, biocompatible polymer, swelling, ultrathin films, lubricity

1 INTRODUCTION

Atomic force microscopy (AFM) is well known as a tool for imaging surface topography down to subnanometer scales on all types of materials, utilizing a scanning stylus (“tip”). Among other things the method is applicable to molecular monolayers and multilayers adsorbed to rigid substrates as well as surfaces of biocompatible synthetic materials such as polymers. Many such systems can be further probed under aqueous immersion. A challenge in common imaging is to keep the interaction between the scanning tip and the surface of interest minimal. If the interaction is too strong, material can be displaced or torn, detrimental to achieving good images and useful metrological data such as surface roughness. But the irreversible perturbation of a surface by the AFM tip also can be *utilized to an analyst’s advantage*.

On polyacrylamide (PAM) films for biomedical applications we demonstrate the results of high-force raster-scan abrasion that bares the substrate, which thus enabled film thickness measurements in subsequent low-force imaging. We present cases of both dry and aqueous (swollen) PAM films. For the dry case we find characteristically different topography, and contrasting friction force, on the bared substrate compared to the film surface. For the swollen case we perform force-distance curve mapping (“force volume”) under aqueous immersion to (i) probe steric forces at the surface of these film (as sensed during approach of tip to surface) as well as much softer mechanical character relative to bared substrate;[1-3] (ii) use these findings to adjust swollen thickness measurements (which are compared to dry-film controls); and (iii) explore both mechanical behavior and attractive/adhesive tip-sample forces derived from the soft and macromolecular (steric) nature of the films.

2 EXPERIMENTAL METHODS

Polyacrylamide films were adsorbed onto glass via a proprietary silane linkage protocol (Surmodics). Briefly, glass slides were treated with an aliphatic silane, and then coated with an aqueous solution of polyacrylamide containing a small amount of photoreactive co-monomer. Following drying, UV illumination created covalent bonding between the polymer film and the aliphatic silane.

Atomic force microscopy was performed with a Digital Instruments Nanoscope III/Multimode system equipped with an O-ring sealed, glass liquid cell provided by the manufacturer. Measurements in air were performed in ~30% relative humidity and those in liquid utilized distilled and deionized water. Topography/friction imaging in sliding contact mode, and the mapping of cantilever deflection vs. Z cycles (“force volume”), utilized V-shaped gold-coated silicon nitride cantilevers with nominal spring constant of 0.58 N/m and oxide-sharpened tip (radius ~20 nm). Abrasive raster scanning was achieved at deflections of approximately 240 nm while scanning 700 nm across regions at 4Hz scan cycles. Nonperturbative imaging was performed at a deflection of 1.7 nm and 2 Hz scan cycles. Common imaging processing (2D and line-by-line mathematical adjustments with masking) were performed with the freeware Gwyddion.[3] Basic processing of force volume data utilized Bruker’s Nanoscope Analysis v1.8. Special algorithms also were used to process and analyze these data as well as

construct custom mappings, employing a Visual Basic program written by the first author.[3]

3 RESULTS AND DISCUSSION

3.1 Dry polyacrylamide films in air

Figure 1 contains representative raster-abrasion results, and thereby comparative film and substrate surface morphologies. The deflection error signal while imaging in contact mode reveals the different lateral scales of topography. Power spectral density computations from the different surface regions show dominant fourier wavelenths of topography centered around 80 nm in both cases, but differences are apparent in the length scales regimes of of 20-60 nm, being more dominant on the bared substrate, and 100-250 nm, being more dominant on the unperturbed film. Clearly the surface morphology of dry PAM films does not merely reflect that of the underlying substrate. Standard deviations of height (so-called R_q or RMS roughness) on each region (not shown here) were not remarkably different.

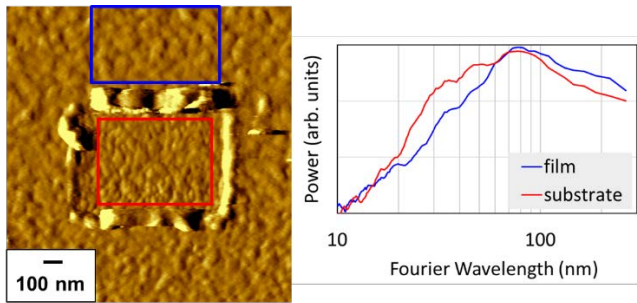


Figure 1: (left) Deflection (error signal) image of a dry-state PAM film following raster-abrasion of a 700-nm wide subregion to bare the hydrophobized glass substrate. (right) Power spectral density functions (log-log) computed from Fourier-analyzed subregions demarcated by correspondingly colored rectangles shown in the image.

Figure 2 contains height and friction force images on scan-abraded PAM as well as histogram distribution functions to quantify characteristic differences. A 2.5 nm dry film thickness is identified, exhibiting elevated dissipative character (in sliding friction).

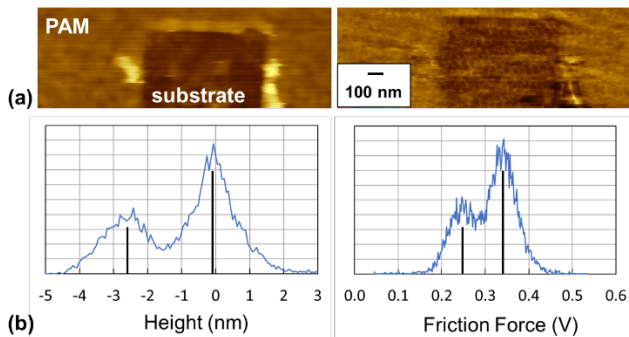


Figure 2: (a) Images of height (left) and friction force (right) of a dry-state PAM film following raster-scan abrasion of a 700-nm wide subregion to bare the hydrophobized glass substrate. (b) corresponding quantification of the measured quantities in each image as distribution functions (ordinate being pixel counts), showing height centroids 2.5 nm apart; friction force on the bared substrate is ~70% of that on PAM.

3.2 Immersed polyacrylamide films

Figure 3 presents qualitative and quantitative aspects of swollen PAM films in aqueous medium. Although the range of heights is marginally greater than on dry films (e.g., as seen in RMS roughness), an increased lateral coarseness of “granularity” is much more significant. This is quantified by comparing the power spectral density plot in Figure 3b to that in Figure 1.

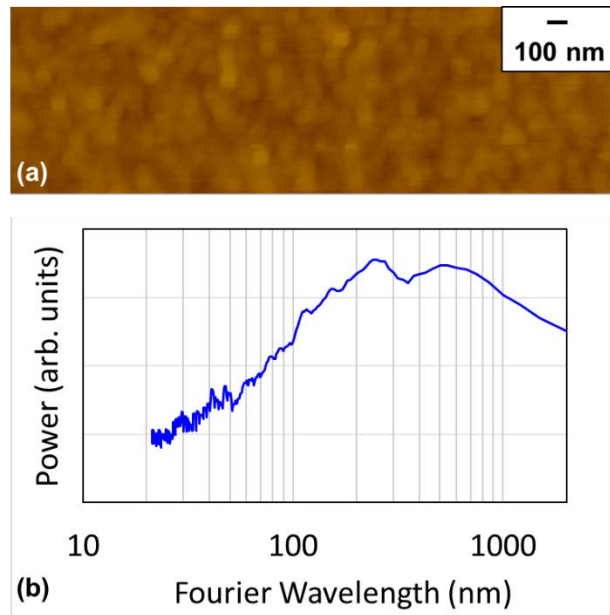


Figure 3: (a) Characteristic topography of aqueous-immersed PAM films, with standard deviation of height approximately 0.7 nm. (b) Power spectral density function (log-log) illustrating the coarser lateral length scale of topography compared to dry films (e.g., Figure 1).

3.3 Scan abrasion on immersed PAM films

Figure 4 presents representative scan-abrasion results on swollen PAM films immersed in water. Figure 4a contains a height image and two cross sectional, averaged profiles. The profiles aid in identifying a subregion of the abrasion area that truly extends to the substrate. The apparent swollen film thickness is 10.0 nm as quantified in film versus substrate surface histogram height distribution functions, as demonstrated in Figure 4b.

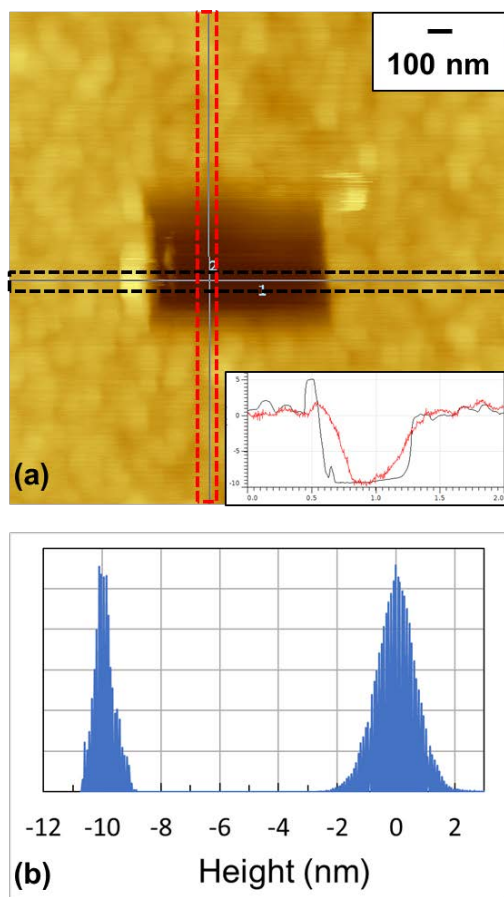


Figure 4: (a) Nominal height image of an aqueous immersed, swollen PAM film following raster scan abrasion of a 700-nm wide region. Inset contains 20-row/column averages within the demarcated rectangular regions of corresponding color. (b) Statistical evaluation of apparent film thickness via height distribution functions (ordinate being pixel counts), showing centroids 10.0 nm apart. The left distribution derives from the lowest subregion within the abraded region, whereas the right distribution derives from the entire film surface away from the abraded region, collected in a larger 3x3- μm image.

Because a water-swollen film is expected to be much more mechanically compliant than a hard, inorganic substrate, force-distance mapping was utilized both within and beyond the abrasion region to account for differences in this compliance. (The ultimate loading force at the end of each approach was selected to match the applied load utilized during sliding contact mode imaging.) Indeed, representative processed force-distance curves in Figure 5a illustrate remarkable differences in both mechanical rigidity (slope at leftmost portion of curve) and the sign of tip-sample force interaction upon first onset of tip-sample interaction. A gradual increase of repulsive force as tip approaches surface is observed atop the polymer film, whereas a van der Waals attractive force is first sensed above the bare (silanized glass)

substrate followed by a very steep repulsive force as expected for an inorganic material. The total inward deformation of film at the ultimate load is approximately 5 nm. This number could be used to upward-adjust the determination of 10 nm stated above.

Mathematical fitting attempts of the force-indentation trend on the film (not included here) indicate that a purely solid-solid contact mechanics cannot account for the full trend. Hertzian mechanics (of sphere-flat geometry) can adequately fit the data from 0-2 nm distances in Figure 5a but not that from 2-5 nm distances. Presumably the latter trend is that of steric force interactions, generally requiring a very different force-distance “law”. [1]

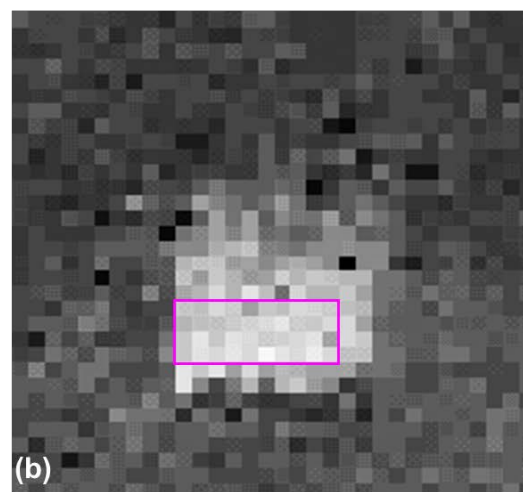
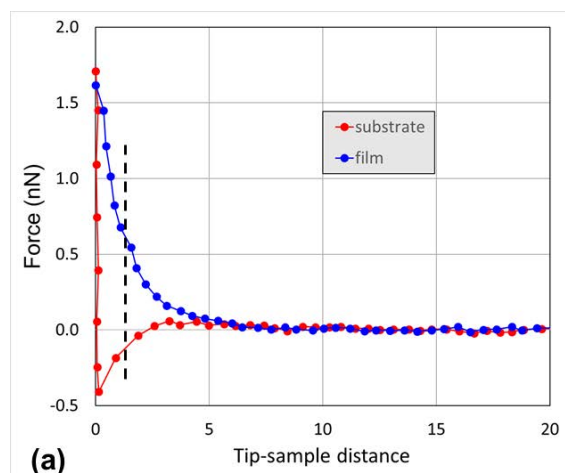


Figure 5: (a) Comparison of (fully processed) force-distance curves on bared substrate compared to unperturbed, swollen film, each deriving from an average of 10 raw force curves acquired in force volume. Strongly different force *gradients* (positive and negative) at approximately 1.5-nm distance are marked with a vertical dashed line. (b) Approximate force gradient map derived from 32x32-site force volume data. The magenta rectangle denotes the bared or nearly bared portion of the abraded region. Brighter depicts a more strongly positive gradient, meaning attractive force.

Figure 5b contains a special rendering of vertical force gradient sensed by tip during approach, contrasting regions of dominant attraction (bright) from those of dominant steric repulsion, at the same distance (vertical dashed line in Figure 5a) relative to the ultimate approach point.

4 CONCLUSIONS

Raster-scan abrasion is a straightforward and useful method for measuring nanoscale polymer film thickness. Ultrathin polyacrylamide (PAM) films UV-crosslinked and bound to silanized glass surfaces can be analyzed in this fashion in both the dry and water-swollen (immersed) states. PAM films swell by ~600%, from 2.5-nm thickness when dry to approximately 15-nm thickness when swollen, if accounting for the farthest outward reach of polymer chains, defined as producing a measurable steric repulsion force on the AFM tip. Straightforward attempt to image scan-abraded (substrate-bared) regions as well as the surrounding film at 1.7 nN applied load in contact mode produces a measurement of 10 nm apparent thickness, whereas further accounting for 5 nm total compliance (mechanical, steric) under these imaging parameters, as quantified by force-distance curve mapping and appropriate data post processing, adjusts this number upward to ~15 nm. Additionally, the lateral “granularity” of swollen PAM films was found to increase substantially compared to dry films, whereas vertical metrics of roughness (i.e., range of highs and lows) was not remarkably increased in the swollen state.

REFERENCES

- [1] J. N. Israelachvili, “Intermolecular and Surface Forces”, Academic Press, 1991.
- [2] H. -J. Butt, B. Cappella, and M. Kappl, Surf. Sci. Rep. 59, 1, 2005
- [3] G. Haugstad, “Atomic Force Microscopy: Understanding Basic Modes and Advanced Applications” (Wiley 2012).

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