Keysight Technologies
Probing Polymer Surface Properties with Multiple Imaging Modes

Application Note

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Introduction

During the past few years, several novel methods have been introduced in the field of atomic force microscopy (AFM) to image the mechanical properties of soft materials. Tribological and viscoelastic properties have been probed in friction force imaging under sliding contact (1, 2) as well as cantilever-modulation amplitude and/or phase imaging under continuous (1-3) or intermittent contact (4-6). On a viscoelastic material, regions of greater loss modulus dampen the cantilever modulation more substantially (1-4), that is, dissipate more strain energy. Enhanced viscoelastic dissipation also translates into greater friction under sliding contact (1, 2). Variations in storage modulus and adhesion on a viscoelastic material may further complicate frictional response. A systematic examination of competing mechanisms necessitates multiple, complementary imaging modes.

MAC Mode (7) atomic force microscopy (AFM), a Keysight Technologies, Inc. patented technique, enables the following special imaging modes with a single hardware package: lateral force (continuous sliding contact), amplitude and phase under force modulation (continuous contact), and height and phase under intermittent contact. Employing an AC magnetic field (solenoid) to modulate a cantilever with a paramagnetic coating **directly** yields a cleaner cantilever response function (frequency dependence) compared to indirect modulation via oscillation of the cantilever support. The amplitude response function at maximum driving amplitude for the cantilever used in the present work (nominal spring constant = 0.5 N/m) is shown in Figure 1. Imaging generally was performed at lower driving amplitudes and at frequencies of 90 kHz (resonance) for intermittent contact and 10 kHz (far below resonance) for force modulation mode. The single isolated peak indicates that a model of a damped, driven oscillator, conventionally used to describe the intrinsic cantilever response, is in fact a good starting point to understand more complex behavior under intermittent contact (4-6). This assumption is questionable if operating under indirect cantilever modulation, in which case multiple overlapping peaks are often observed.

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In this application note, we demonstrate the ability to image a polyvinyl alcohol (PVA) film in multiple modes with a Keysight scanning probe microscope (SPM). Films were cast from 10^{-3} wt% aqueous solution at room temperature onto cleaved mica. A total of four film constituents are contrasted in their response to the SPM probe in different imaging modes. A single 4 µm x 3.8 µm region is examined so that correspondences of material response in different modes can be made without ambiguity. The images reveal differences in the energy-dissipative character of various film components.

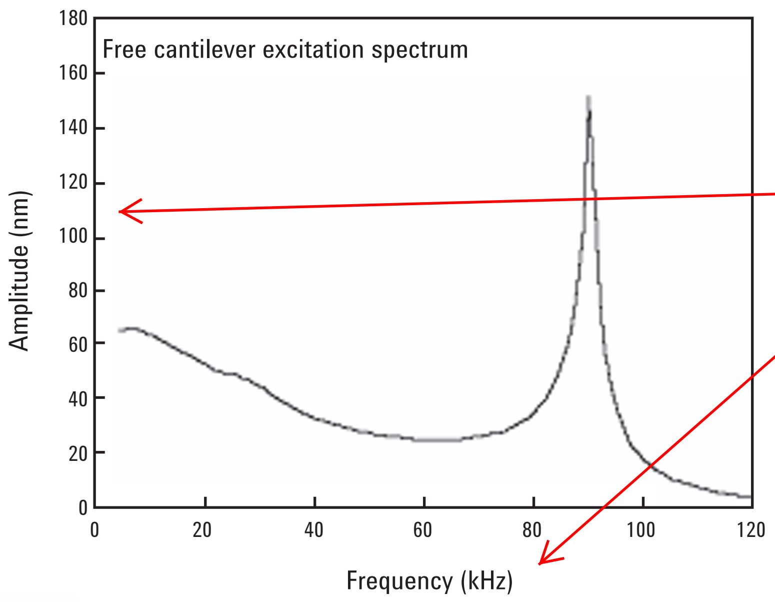

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Figure 1. Free excitation spectrum of a cantilever with a paramagnetic coating by a sinusoidal magnetic field.

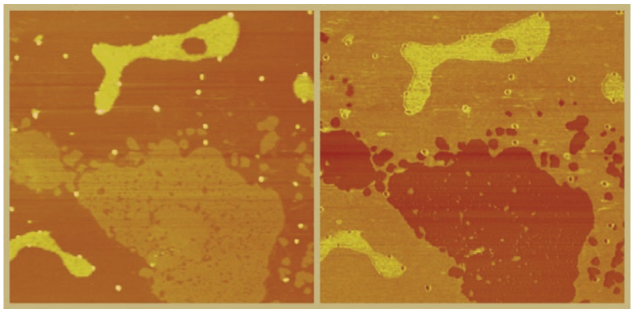

Figure 2. Height/friction force images (left/right) of a 4 µm x 3.8 µm region of a PVA film. Brighter regions correspond to higher surface elevation or frictional force.

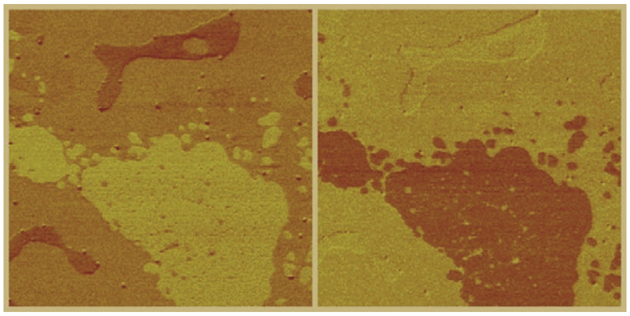

Figure 3. Amplitude/phase images (left/right) obtained in force modulation mode. Brighter regions correspond to higher amplitude or phase.

Figure 2 displays height/friction force images (left/right) of the 4 µm x 3.8 µm region of interest. Brighter regions correspond to higher surface elevation or frictional force. All regions are PVA, that is, the 10 nm thin film (8) completely wets the mica substrate. Via surface elevation, we differentiate four types of locations. The thinnest film region is termed Region A. The large island dominating the bottom half of the image is 1.4 nm higher than Region A and exhibits the lowest frictional signal. Smaller islands of the same height also display the same low friction. We refer to all of these low-friction moieties, large and small, as Region B. Additional large islands, for example, at the top center, extend 3.7 nm above Region A; we refer to these moieties as Region C. The relative frictional forces imaged on Regions A:B:C are 3.2:1.0:4.9. Finally, we note small, roughly circular objects typically 80 nm in diameter and 8 nm tall, relative to Region A, scattered across the imaged region (but frequently located at the edges of the islands of Region C). The frictional signature of these objects is dominated by edge effects and thus cannot reliably identify material type. We call these moieties Region D.

Figure 3 contains amplitude/phase images (left/right) obtained in force modulation mode at cantilever modulation amplitudes of several nm. Brighter regions correspond to higher amplitude or phase. The amplitude signal varies among Regions A, B, and C (1.00:1.03:0.98, respectively), whereas the phase image measurably differentiates only Region B (darker) from the others (by about 1 degree). Region D is again dominated by edge effects. The total phase lag between driving modulation (solenoid voltage) and response modulation (photodetector output voltage) includes a time lag in the response of the material (strain) to the imparted force (stress). Th[illegible]es to the dissipative characteristics of the material (3).

Add (a)

Add (b)

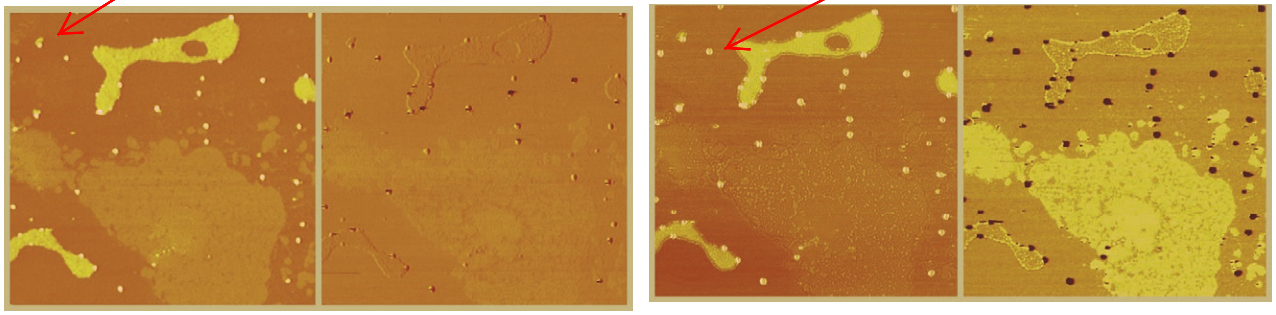

Figure 4. Height/phase images (left/right) acquired in intermittent contact mode at two values of setpoint amplitude (fraction of free-oscillation amplitude): (a) 0.94 and (b) 0.47

Figure 4 displays height/phase images (left/right) acquired in intermittent contact mode at two values of setpoint amplitude (fraction of free-oscillation amplitude): (a) 0.94 and (b) 0.47. The height image in (a) is similar to the sliding contact image of Figure 2, but is higher quality (from removal of shear forces) and slightly reduced in contrast because of mechanical effects. In (b), the height image is strongly affected by mechanical response. As a result, the imaged surfaces of Regions B, C, and D "sink" relative to Region A at reduced setpoint (b). This means that Region A need not be raised as much to reduce the cantilever amplitude by a given amount. Thus, Region A dampens the cantilever modulation substantially more than Region B (by 1.1 nm “height” difference) and slightly more than Region C (0.3 nm). The phase image in Figure 4a faintly differentiates Region B from the others, by 0.1 degrees. The difference is more dramatic in (b), reaching 0.9 degrees. This phase differentiation of Region B is analogous to the result in force modulation mode, but opposite in sign. Region D shows a dramatically lower phase in (b), by about 45 degrees. Substantial phase differentiation of Region C from Region A only occurs at edges and is most likely topographic in origin.

Operation at resonance in intermittent contact mode can produce very large phase shifts because of the modified shape and position of the resonance (in frequency domain) compared to free oscillation (4). There are additional contributions to the phase shift in intermittent contact mode due to the repeated break of adhesive contact (6), as well as air damping and variations in long-range forces (van der Waals, electrostatic) with changing tip-sample distance (9). Moreover, the kinetic energy of the tip can be substantial in intermittent contact mode; the amount of energy absorbed by the sample also may affect the phase shift (4, 5). Therefore, the phase shifts measured in intermittent contact may differ substantially (even in sign) from force modulation mode.

The phase differentiation of Region B from A and C in both continuous and intermittent contact modes indicates important dissipative differences. Together with reduced damping in intermittent contact and markedly lower friction, it is clear that Region B is less dissipative in every measurement. The amplitude images in force modulation mode also track relative variations in friction: amplitude is smallest on the highest-friction region (C) and largest on the lowest-friction region (B). Smaller (larger) amplitude is consistent with more (less) energy dissipation. Compared to Region A, Region C displays no significant difference in phase and slightly reduced damping in intermittent contact, but substantially greater friction and amplitude damping under force modulation mode. It is important to realize, however, that in friction and (continuous-contact) force modulation the magnitude of energy dissipation strongly depends on the quasistatic deformed volume. Force modulation also involves dynamic dissipation, but the phase results on Regions A and C indicate no substantial differences. In intermittent contact, the dissipation is determined entirely by dynamic phenomena. Consequently, there is little contrast between Regions A and C.

In summary, parallel characterization with multiple imaging modes allows one to contrast regions of dissimilar dissipative character within a polymeric material. One implication is the ability to differentiate structures varying in crystallinity. PVA crystallizes to a variable degree depending on preparation history (10); in particular, annealing produces greater crystallinity. Upon heating samples like that characterized above, larger regions of the lowest-friction component (Region B) formed. Thus, it seems clear that these regions of reduced dissipation are highly crystalline. Films prepared from higher-concentration aqueous solutions were thicker and increasingly dominated by the presence of Region C; Region A was entirely absent at the highest concentrations examined (1%). Apparently, Region A derives from close proximity to the mica substrate. This may not change the essentially amorphous character of Region A compared to Region C, but adhesion to substrate or confinement effects may reduce relaxational freedom. Furthermore, the underlying rigid substrate may reduce the deformation volume on Region A and thereby “extensive” energy dissipation, whereas “intensive” dissipation reflecting molecular conformation (2) may remain essentially the same as in Region C.

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