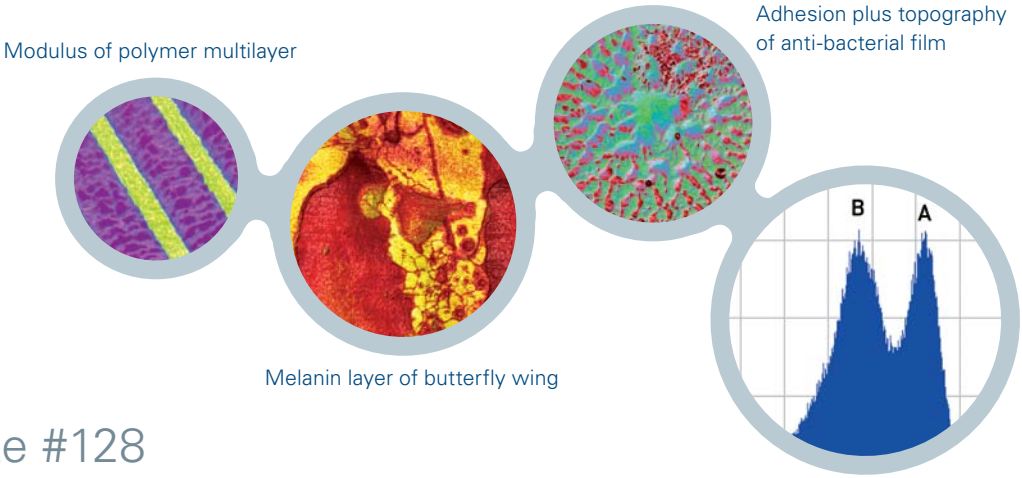

Application Note #128

Quantitative Mechanical Property Mapping at the Nanoscale with PeakForce QNM

The scanning probe microscope (SPM)[1] has long been recognized as a useful tool for measuring mechanical properties of materials. Until recently though, it has been impossible to achieve truly quantitative material property mapping with the resolution and convenience demanded by SPM researchers. A number of recent SPM mode innovations have taken aim at these limitations, and now, with Bruker's PeakForce QNM®, it is possible to identify material variations unambiguously and at high resolution across a topographic image. This application note discusses the principles and benefits of the PeakForce QNM imaging mode.

SPM and Mechanical Property Mapping

Researchers often use the SPM to acquire the force on the tip versus its vertical position. The resulting "force curves" can then be analyzed to determine a host of characteristics of the material beneath the tip. However, these force curves can only provide data at one point on the sample surface at a time. The technique of force volume imaging collects force curves at each pixel in an image and puts them together to map the properties across a larger sample.[2] Though more information is gathered, force volume imaging is typically very slow, which makes detailed mapping impractical. To solve this problem, Pulsed Force Mode was developed. This approach improves speed by using a relatively fast sinusoidal ramping.[3] Unfortunately, this also makes the material property measurements less quantitative.

The development of TappingMode™ imaging in 1993 was a key step forward in the functionality of SPM.[4] In TappingMode the probe is vibrated near the resonant frequency of the cantilever while it is scanned across the sample. The tip only contacts the surface for a small percentage of the time, keeping the tapping force low and the lateral forces negligible. Consequently, TappingMode has the ability to generate high-quality data for a wide range of samples, making it the dominant imaging mode for most SPM applications over the last ten years.

The data types obtained from TappingMode SPM are primarily topography and phase. PhaseImaging™ creates images of the phase of the tapping response, which is a function of the forces that the tip is experiencing. Since the probe is oscillating, it experiences attractive and repulsive forces depending on its position in the cycle in a way that is analogous to force curves. A drawback to the technique is that the resonant behavior of the probe also acts as a

filter, making it impractical to reconstruct the force curves with sufficient precision to extract quantitative mechanical information.[5–6] In 2008, HarmoniX® was released as a solution to this problem. HarmoniX adds a second sensor with a much higher bandwidth by offsetting the tip and measuring the torsional signal.[7–9] This technique has been successful in resolving material components in complex polymeric systems. The downsides of this approach are that (1) it requires special probes, (2) the operation of the technique can be complicated (especially in fluid), and (3) interpretation of the results is sometimes difficult.

PeakForce QNM provides the capabilities of HarmoniX without the complexity of operation and interpretation. Additionally, no special probes are required (although careful choice of probes is essential for best performance). PeakForce QNM uses Bruker's new Peak Force Tapping® technology for system feedback to deliver a number of important benefits.

- **High-resolution mapping of mechanical properties** – Scanning speeds and number of pixels in an image are similar to TappingMode. Analysis of force curve data is done on the fly, providing a map of multiple mechanical properties that has the same resolution as the height image. Sample deformation depths are limited to a few nanometers, minimizing the loss of resolution that can occur with larger tip-sample contact areas.

- **Non-destructive to tips and samples** – Peak Force Tapping provides direct control of the maximum normal force (and thus the deformation depth) of the sample, while eliminating lateral forces. This preserves both the tip and sample. Additionally, Peak Force Tapping enables Bruker's new ScanAsyst® feature, which automatically adjusts the scanning parameters in real- time to optimize the image and protect the probe and sample.

- **Unambiguous and quantitative data over a wide range of materials** – Analysis of the entire force curve for each tap allows different properties to be independently measured. Since a wide selection of probes is available, it is possible to cover a very broad range of modulus or adhesion parameters while maintaining excellent signal-to-noise ratios.

Peak Force Tapping

In scanning probe microscopy, there are two primary causes of tip and sample damage. Any lateral force that the tip exerts on the sample can cause the sample to tear (the tip plows through the sample). Likewise, lateral forces from a hard sample can cause the end of the tip to fracture and break off. Normal forces can also cause damage to both tip and sample. Even if there is not enough normal force to damage the sample, there can still be enough to deform the sample, increasing the contact area (and the effective probe size) and reducing the resolution of the scan. In Peak Force Tapping, the probe and sample are intermittently brought together (similar to TappingMode) to contact the

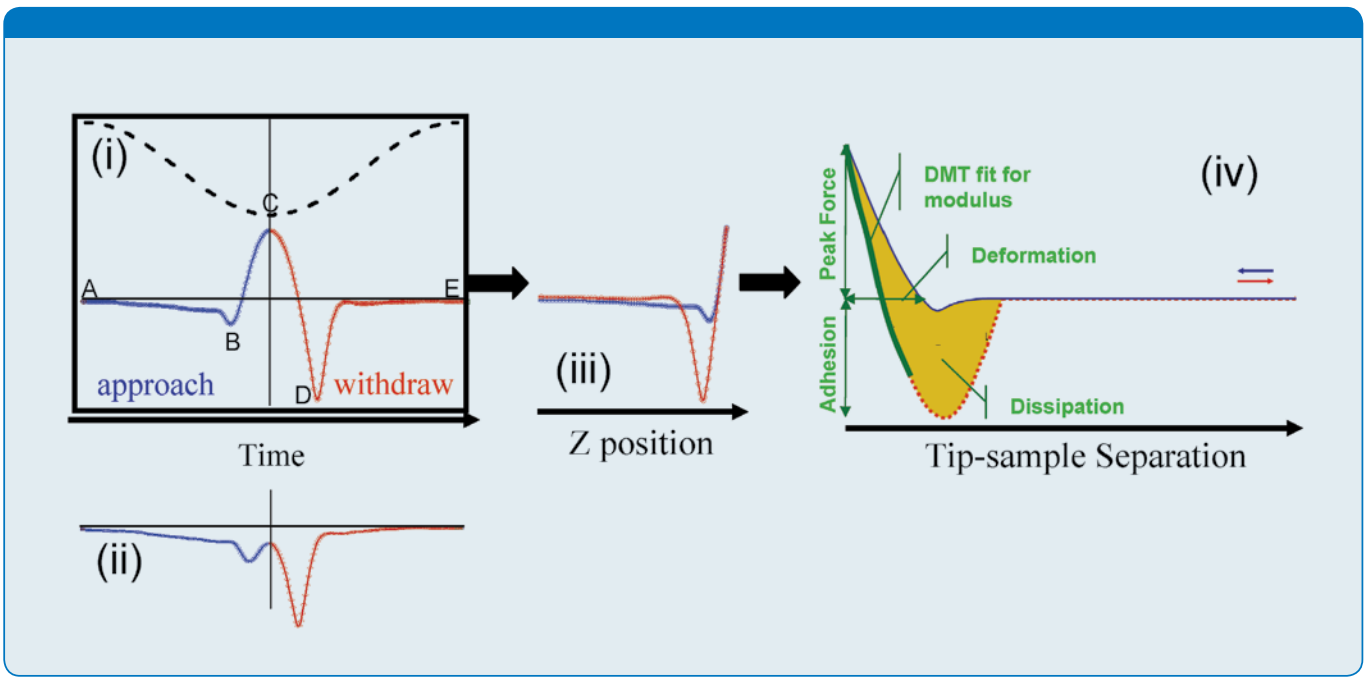

Figure 1. Force curves and information that can be obtained from them:
(i) Plot of force and piezo Z position as a function of time, including (B) jump-to-contact, (C) peak force, (D) adhesion:
(ii) Plot of force vs. time with small peak force:
(iii) A traditional force curve eliminates the time variable, plotting Force vs. Z piezo position:
(iv) For fitting purposes it is more useful to plot force vs. separation where the separation is calculated from the Z piezo position and the cantilever deflection.

surface for a short period, which eliminates lateral forces. Unlike TappingMode where the feedback loop keeps the cantilever vibration amplitude constant, Peak Force Tapping controls the maximum force (Peak Force) on the tip. This protects the tip and sample from damage while allowing the tip-sample contact area to be minimized.

Figure 1(i) demonstrates what happens when the periodically modulated probe interacts with the surface. The top (dashed) line represents the Z-position of the modulation as it goes through one period plotted as a function of time. The lower line (solid) represents the measured force on the (TESP type) probe during the approach (blue) of the tip to the sample, while the red part represents the force while the tip moves away from the sample. Since the modulation frequency is about 2kHz in the current implementation, the time from point A to point E is about 0.5ms. When the tip is far from the surface (point A) there is little or no force on the tip. As the tip approaches the surface, the cantilever is pulled down toward the surface by attractive forces (usually van der Waals, electrostatics, or capillary forces) as represented by the negative force (below the horizontal axis). At point B, the attractive forces overcome the cantilever stiffness and the tip is pulled to the surface. The tip then stays on the surface and the force increases until the Z position of the modulation reaches its bottom-most position at point C. This is where the peak force occurs. The peak force (force at point C) during the interaction period is kept constant by the system feedback. The probe then starts to withdraw and the force decreases until it reaches a minimum at point D. The adhesion is given by the force at this point. The point where the tip comes off the surface is called the pull-off point. This often coincides with the minimum force. Once the tip has come off the surface, only long range forces affect the tip, so the force is very small or zero when the tip-sample separation is at its maximum (point E).

As the system scans the tip across the sample, the feedback loop of the system maintains the instantaneous force at point C at a constant value by adjusting the extension of the Z piezo. Figure 1(ii) illustrates an interesting and unique challenge for peak force control. Here the controlled peak force at point C is actually attractive. This can occur when the peak force is small and the attractive forces are relatively large. Looking at the measured force in this plot, one might infer that the force at C is not the maximum force. In fact, the addition of the long range attractive forces cause the stress beneath the center of the probe tip to be compressive (and greater) at point C even though the measured force on the probe is less than that at point A. The small peak in the attractive background is caused by the repulsive force at the very apex point of the tip. The total interaction force is integrated over all of the tip atoms. While the tip apex atoms feel a repulsive force, the neighbor atoms, which consist of far more volume, can still be feeling an attractive force. This leads to a net negative force overall. Even when the peak force is negative, Peak Force Tapping can recognize the local maximum and maintain control of the imaging process.

Figure 1(iii) shows the same data as figure1(i) but with the force plotted as a function of the distance. Since we control the Z position of the modulation as a function of time and we measure the deflection of the cantilever as a function of time, it is possible to eliminate the time variable and plot the force against the Z-position. These plots can then be compared directly with the force- distance curves that have been used for decades by researchers interested in measuring mechanical properties of their samples with SPM, but at a several orders of magnitude faster measurement speed. One complication of the fast data acquisition is the excitation of cantilever resonance at the pull-off point. This ringing is negligible for a stiff lever, such as the TESP used in figure 1. The oscillation is more pronounced for softer levers. Peak Force Tapping control has the ability to identify the repulsive force and respond to this interaction only, regardless of the magnitude of the snap-off ringing.

Once a force curve is obtained, it is must be converted to a force versus separation plot for fitting and further analysis. The tip-sample separation is different from the Z position of the modulation since the cantilever bends. Figure 1(iv) is a sample of a force-separation plot illustrating the types of information that can be obtained. The most commonly used quantities are elastic modulus, tip-sample adhesion, energy dissipation, and maximum deformation.

Quantitative Material Property Mapping

The foundation of material property mapping with PeakForce QNM is the ability of the system to acquire and analyze the individual force curves from each tap that occurs during the imaging process. To separate the contributions from different material properties such as adhesion, modulus, dissipation, and deformation, it is necessary to measure the instantaneous force on the tip rather than a time-average of the force or dissipation over time, as is done in TappingMode PhaseImaging. This requires a force sensor that has a significantly higher bandwidth than the frequency of the periodic interactions. In Peak Force Tapping, the modulation frequency is intentionally chosen to be significantly lower than the cantilever resonant frequency. The force measurement bandwidth of a cantilever is approximately equal to the resonant frequency of the fundamental bending mode used for force detection. As a result, a properly chosen cantilever is able to respond to changes in instantaneous interaction force with an immediate deflection change during Peak Force Tapping.

As mentioned above, the force curve is converted to a force versus separation plot (see figure 1(iv)) for fitting and further analysis. The separation, which is the negative of the deformation (sometimes called indentation depth), is obtained by adding the Z position of the piezo modulation to the cantilever deflection. A constant can be added to the separation to make it zero at the point of contact if it can be determined, but this is not required for many analyses. This process is equivalent to removing frame compliance in indentation measurements. These force-separation curves are analogous to the load- indentation curves commonly used in nanoindentation.

The curves are then analyzed to obtain the properties of the sample (adhesion, modulus, deformation, and dissipation) and the information is sent to one of the image data channels while imaging continues at usual imaging speeds. The result is images that contain maps of material properties (false colored with a user selectable color table). Since the system can acquire up to eight channels at once, it is possible to map all of the currently calculated properties in a single pass. Offline analysis functions can calculate statistics of the mechanical properties of different regions and sections through the data to show the spatial distribution of the properties.

Figure 1(iv) illustrates how common mechanical properties are extracted from calibrated force-separation curves. Analysis of the force curves with other models is possible by capturing raw data with the "High-Speed Data Capture" function. High-speed data capture provides about 64,000 raw force curves (typically several scan lines) that can be captured at any time during scanning and can later be correlated with the analyzed data in the image. This allows users to apply their own models to the raw data to study more unusual materials and properties.

Elastic Modulus

To obtain the Young's Modulus, the retract curve is fit (see the bold green line in figure 1(iv)) using the Derjaguin–Muller–Toporov (DMT) model[10]

$$F - F_{adh} = \frac{4}{3} E^* \sqrt{R(d - d_0)^3}.$$

$F - F_{adh}$ is the force on the cantilever relative to the adhesion force, R is the tip end radius, and $d - d_0$ is the deformation of the sample. The result of the fit is the reduced modulus E^*. If the Poisson's ratio is known, the software can use that information to calculate the Young's Modulus of the sample (E_s). This is related to the sample modulus by the equation

$$E^* = \left[\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_{tip}^2}{E_{tip}} \right]^{-1}.$$

We assume that the tip modulus E_{tip} is infinite, and calculate the sample modulus using the sample Poisson's

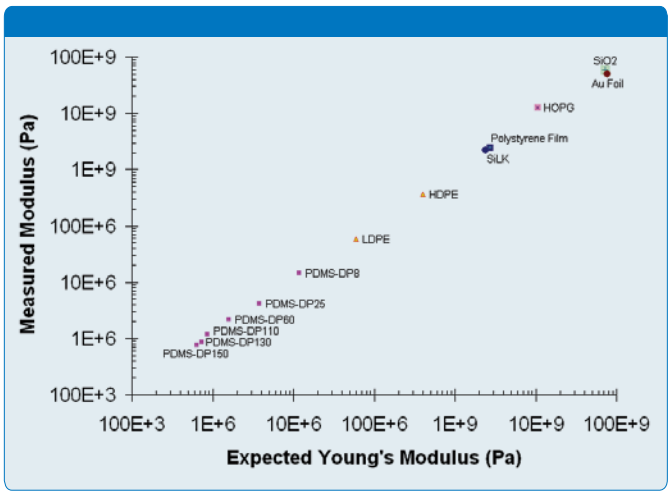

Figure 2. Plot of Measured Modulus vs. expected Young's Modulus (from the literature or from SPM Nanoindentation). Multiple probes were used with different spring constants to cover the entire range. Each probe was individually calibrated using the absolute method.

Ratio (which must be entered by the user into the NanoScope® "Cantilever Parameters"). The Poisson's ratio generally ranges between about 0.2 and 0.5 (perfectly incompressible) giving a difference between the reduced modulus and the sample modulus between 4% and 25%. Since the Poisson's ratio is not generally accurately known, many publications report only the reduced modulus. Entering zero for the parameter will cause the system to return the reduced modulus.

PeakForce QNM provides quantitative modulus results over the range of 700kPa to 70GPa provided the appropriate probe is selected and calibrated, and provided that the DMT model is applicable. Calibration is done either by comparing to a reference sample (relative method), or by measurement of tip end radius and spring constant (absolute method). In either method, the deflection sensitivity must also be measured. While calibration is still a several step process, it has been made significantly easier than HarmoniX calibration by eliminating several steps and by automating the calculation of several parameters. An experienced user can complete a calibration in less than ten minutes.

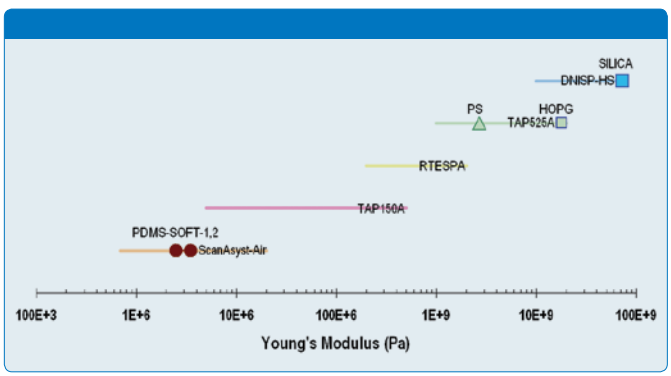

Figure 3. Modulus ranges covered by various probes. The modulus and Bruker part number of the reference sample for each range is also indicated.

Figure 2 demonstrates that this works for a wide range of materials from polydimethylsiloxanes to silica. The data in figure 2 was collected with a set of probes that were selected to have the most accuracy over a range of modulus. Figure 3 lists the probe types used and gives the approximate modulus range for each probe type. The data was acquired on homogeneous samples and the system was calibrated using the absolute method.

If the DMT model is not appropriate, the modulus map will still return the fit result, but it will be only qualitative. Some cases where the DMT model are not appropriate include cases where the tip-sample geometry is not approximated by a hard sphere (the tip) contacting an elastic plane, cases where mechanisms of deformation other than elastic deformation are active during the retracting part of the curve (at these time scales), and cases where the sample is confined vertically or laterally by surrounding material (close enough to effect the strain in the deformed region). If this is suspected, High Speed Data Capture can acquire the individual force curves across a section of interest to examine the force curves directly and potentially apply more advanced fitting models.

PeakForce QNM can be quite repeatable if care is taken in the calibration process. Recent experiments on homogeneous samples where the absolute method was used to measure samples in a range between 1MPa and 400MPa ten times each (with different probes) resulted in a relative standard deviation of less than 25% for all samples. If the goal is to discriminate between components in a multi-component system where the modulus of one component is known, the modulus noise level is more interesting. For the measurements in the study, the relative standard deviation was never more than 6%.

Adhesion

The second mechanical property acquired in the mapping is the adhesion force, illustrated by the minimum force in figure 1(iv). The source of the adhesion force can be any attractive force between the tip and sample. In air, van der Waals, electrostatics, and forces due to the formation of a capillary meniscus can all contribute with the relative strengths of the contributions depending on such parameters as Hamaker constants, surface charges, and hydrophilicity. For example, if either sample or the probe surface is hydrophilic, a capillary meniscus will typically form, leading to higher adhesion that extends nanometers beyond the surface. For polymers in which the long molecules serve as a meniscus, the adhesion can extend tens of nanometers beyond the surface. The adhesion typically increases with increasing probe end radius. Simple models based on surface energy arguments predict the adhesion to be proportional to the tip end radius.[11] The area below the zero force reference (the horizontal line in the force curve) and above the withdrawing curve is referred to as "the work of adhesion." The energy dissipation is dominated by work of adhesion if the peak force set point is chosen such that the non-elastic deformation area (the hysteresis above the zero force reference) in the loading/unloading curve is negligible compared to the work of adhesion.

Adhesion force becomes a much more meaningful and important quantity if the tip is functionalized. In this case, the adhesion reflects the chemical interaction between specific molecules on the tip and sample. The adhesion map in this case carries the chemical information.

Dissipation

Energy dissipation is given by the force times the velocity integrated over one period of the vibration (represented by the gold area in the figure 1(iv)):

$$W = \int \vec{F} \cdot d\vec{Z} = \int_0^T \vec{F} \cdot \vec{v} dt \ ,$$

where W represents energy dissipated in a cycle of interaction. F is the interaction force vector and dZ is the displacement vector. Because the velocity reverses its direction in each half cycle, the integration is zero if the loading and unloading curves coincide. For pure elastic deformation there is no hysteresis between the repulsive parts of the loading-unloading curve, corresponding to very low dissipation. In this case the work of adhesion becomes the dominant contributor to energy dissipation. Energy dissipated is presented in electron volts as the mechanical energy lost per tapping cycle.

Deformation

The fourth property is the maximum deformation, defined as the penetration of the tip into the surface at the peak force, after subtracting cantilever compliance. As the load on the sample under the tip increases, the deformation also increases, reaching a maximum at the peak force. The measured deformation may include both elastic and plastic contributions. With known tip shape and contact area, this parameter can also be converted to the hardness (although this is usually only applied in cases where the dominant deformation mechanism is plastic deformation). Maximum sample deformation is calculated from the difference in separation from the point where the force is zero to the peak force point along the approach curve (see figure 1(iv)). There may be some error in this measurement due to the fact that the tip first contacts the surface at the jump-to-contact point (figure 1(i), point B) rather than at the zero crossing.

Comparison with Force Volume and Pulsed Force Mode

The earliest mechanical property mapping was performed by force volume, which is still often used to acquire quantitative nanomechanical data. Force volume collects force curves triggered by the same maximum repulsive

force while scanning back and forth over the surface. Collecting a force volume image usually takes several hours because individual force curves generally take about a second to collect, and a map needs thousands of force curves to be useful. This speed limitation was greatly improved by Pulsed Force Mode, which modulates the Z piezo at about 1kHz, allowing property mapping in much shorter time. Pulsed Force Mode is primarily used as a property mapping method with the trigger force of a few nanonewtons or more. Below one nanonewton, parasitic motion of the cantilever can dominate and cause feedback instability.

Peak Force Tapping modulates the Z piezo in a similar fashion to force volume and Pulsed Force Mode. However, it can operate with interaction forces orders of magnitude lower, i.e., piconewtons. Such high-precision force control is enabled by data pattern analysis within each interaction period. When the relative Z position between the probe and sample is modulated, various parasitic cantilever motions can occur (defined as variation in the cantilever deflection that occurs when the tip is not interacting with the sample). These motions include cantilever oscillation excited by the pull-off, as well as deflections triggered by harmonics of the piezo motion or viscous forces in air or fluid. The parasitic deflection limits the ability of Pulsed Force Mode to operate with very low forces. Low force control happens to be the most important factor in achieving high-resolution imaging and property measurements. For example, if the tip end has $1nm^2$ area, 1nN force will lead to 1GPa stress at the tip end. Such stress is sufficient to break a silicon tip. To lower the stress below the fracture stress of silicon, the control force needs to be no more than a few hundred piconewtons. For samples softer than silicon, the required controlling force to avoid significant deformation or damage is even lower.

During Peak Force Tapping operation, the parasitic deflection signal and its data pattern are analyzed by comparing the known sources of force artifacts, such as cantilever resonance at pull-off, harmonics of the modulations, and other system actuation sources. The signature of the interaction is extracted from the parasitic deflections. The feedback loop can choose any point in the force curve to control tip-sample interactions instantaneously. For Peak Force Tapping, the peak point in the repulsive interaction is chosen as the control parameter, similar to the triggered level in force volume mapping.

A major advantage of Peak Force Tapping is its broad operating force range, from piconewtons to micronewtons. At the high-force end, it coincides with traditional mechanical mapping techniques, namely force volume and Pulsed Force Mode, yet can generate quantitative data with the new advanced quantitative nanomechanical procedure. In the low-force regime, it matches the interaction force achievable by light tapping in TappingMode but with much improved stability and ease of use in all environments.

Comparison with TappingMode and HarmoniX

The phase of the TappingMode cantilever vibration relative to the drive is a useful indication of different mechanical properties. Unfortunately, the phase signal reflects a mixture of material properties, depending both on dissipative and conservative forces.[12–13] Since elasticity, hardness, adhesion and energy dissipation all contribute to phase shift, phase alone does not provide enough information to quantify or discriminate between all of these properties. Additionally, the phase signal depends on imaging parameters such as drive amplitude, drive frequency, and setpoint. This makes it difficult and sometimes impossible to interpret the source of the contrast, leaving the user to conclude that there are differences in the sample without further knowledge of contributing physical factors. Figure 4 demonstrates this difficulty with phase imaging and compares it to PeakForce QNM for a multilayer polymer sample. It is often assumed that the phase contrast is primarily caused by variations in sample modulus. Comparing figure 4(f) and (b), it is clear that this is not true in this case. By tapping harder (reducing the amplitude setpoint), one would expect to deform the sample more, increasing the contribution of the modulus to the phase. Surprisingly, in (c) the contrast does not change significantly. The PeakForce QNM data (e) shows that the phase signal is dominated by the adhesion independent of tapping setpoint for this tip-sample interaction. It is easy to see that one must be very careful in interpreting phase results, even for qualitative use. The PeakForce QNM modulus channel, on the other hand, has unambiguous contrast that can be quantified, as shown in the trace of (f). The narrow strips have a modulus of about 300MPa, while the wide ones have a modulus of about 100MPa.

HarmoniX microscopy is a TappingMode technique that uses many harmonics of the tapping drive signal to reconstruct the force curves that occur during tapping. From these force curves the material properties can be measured independently. The harmonic signals are excited at each tap in the TappingMode oscillation period. They are detected by measuring the torsional motion of the special HarmoniX cantilever during TappingMode imaging. The torsional bending of the cantilever acts as the high-bandwidth force sensor and allows force separation plots to be extracted during tapping and analyzed in real-time. HarmoniX is a very powerful mode, and it has the benefit of working with TappingMode feedback and phase imaging for easy comparison with previous results. On the other hand, HarmoniX mode shares all the difficulties of TappingMode in imaging control. It can be challenging to use, especially in fluids where the cantilever Q is much lower. Additionally,

interpretation can be complex if the torsional sensor doesn't have enough bandwidth, if perturbations to the flexural motion become significant, or if cantilever overtones coincide with integer multiples of the drive frequency.

There are two other TappingMode derived modes that have recently gained popularity: TappingMode while observing a separate harmonic of the tapping drive,[5] and Dual AC mode.[14–15] Single harmonic imaging depends on either special cantilevers or a lucky coincidence of an overtone with a harmonic, while Dual AC adds a second frequency (usually at an overtone) to the vibration driving the cantilever. Both of these techniques provide contrast that is analogous to phase contrast in that they do not fully separate the mechanical properties and therefore cannot be quantified.

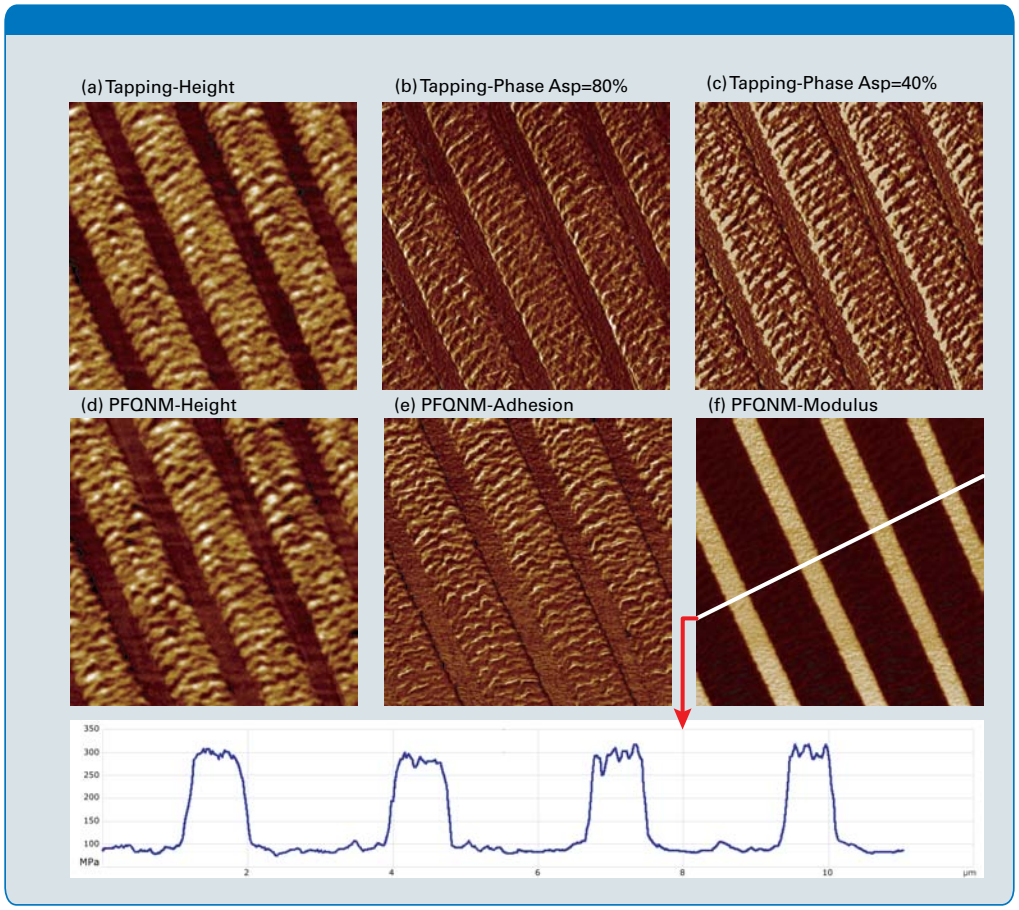

Figure 4. Multilayer polymer optical film comparing results obtained with TappingMode PhaseImaging (a-c) and PeakForce QNM (d-f) (10µm scan size). The phase image in (b) was collected with an amplitude setpoint of 80% of the free amplitude, while the amplitude setpoint in (c) was 40%. The trace profile from (f) is the modulus along the line in (f) from left to right. Note that the tapping phase result (b) is nearly identical to the PeakForce QNM adhesion image (e) and the contrast is inverted relative to the modulus image.

A common characteristic of all these tapping-based nanomechanical mapping technologies is that they are all dependent on higher frequency components. Theoretically, in order to accurately reconstruct the real-time tip-surface interaction, an infinite number of frequency components are needed. HarmoniX can detect 15 to 20 harmonic components, rendering a good approximation, and thus is effective for many materials in reconstructing tip surface interaction and deriving quantitative data. Fewer frequency components will further limit the ability of a technique to derive quantitative data.

In all TappingMode techniques, the feedback uses the near-resonance amplitude as a control parameter. In a normal tapping control, the peak interaction force varies from a fraction of a nanonewton to tens of nanonewtons, depending on the operating amplitude, cantilever spring constant, and set point. Such interaction force is well controlled when cantilever oscillation is in a steady-state. However, when the tip is scanning on a sample surface, especially a rough surface, the amplitude error occurring at the sharp edges can correspond to interaction force one order of magnitude higher than that of a steady-state. Amplitude error incurred force is a leading cause of tip damage. Such damage occurs because the feedback is not directly controlling interaction force. In contrast, Peak Force Tapping directly controls the peak force on the sample. This protects the tip and sample while maintaining excellent surface tracking.

Summarizing Mechanical Property Mapping Modes

Figure 5 summarizes the nanoscale mechanical mapping techniques available with SPM. Of the mechanical property mapping techniques, PeakForce QNM has by far the most precise control of peak force, while retaining the speed and resolution of TappingMode. The TappingMode-based techniques are relatively fast and high resolution, but only HarmoniX has the ability to independently measure different mechanical properties, and none of them directly control the peak force.

	PeakForce QNM	HarmoniX	TappingMode PhaseImaging	Single Harmonic	Dual AC	Pulsed Force Mode	Force Volume
Young's modulus and adhesion mapping	Yes	Yes	Mixed & Parameter dependent	Mixed & Parameter dependent	Mixed & Parameter dependent	Qualitative	Possible offline
Deformation depth mapped	Yes	Yes	No	No	No	No	Possible offline
Quantitative modulus range	0.7Mpa – 70GPa	10 Mpa – 79GPa	—	—	—	—	<1MPa – 100GPa
Adhesion noise level	<10pN	200pN	—	—	—	<1nN	<10pN
Feedback on peak force	Yes	No	No	No	No	Yes	Yes
Peak force	<100pN	<5pN	<3nN	<10nN	<5nN	<20nN	<50nN
Lateral resolution	<5nm	<10nm	<5nm	<10nm	<10nm	<50nm	<100nm
Simultaneous high-resolution imaging	Yes	Yes	Yes	Yes	Yes	Moderate	No
Mapping time	4 minutes	4 minutes	4 minutes	4 minutes	4 minutes	4 minutes	18 hours
Easy to use	Yes	No	Yes	No	No	No	No

Figure 5. Comparison of different SPM modes for mapping mechanical properties at the nanoscale.

The key factor that allows PeakForce QNM to cover such a broad range of quantitative nanomechanical measurements is its ability to use a wide range of cantilever probes in all environments. Using cantilevers with a spring constant between 0.3N/m and 300N/m, allows PeakForce QNM to achieve force control from piconewtons to micronewtons. Piconewton force control, normally only possible in fluid, can also be applied in ambient conditions, yielding improved image quality and tip protection over even best practice TappingMode. This force range can facilitate quantitative characterization of materials, with modulus ranges from hydrogels to metals and semiconductors.

Practical Applications

Polymer Blend

It is often interesting or necessary to image samples under fluid or at temperatures above or below room temperature. PeakForce QNM works well in these environments and has several benefits over TappingMode. For one, it is not necessary to re-tune the cantilever when the temperature is changed or when changing from air to fluid operation. In TappingMode, a temperature change causes changes in resonant frequency and Q of the cantilever, making it imperative that the drive amplitude and frequency are adjusted whenever the temperature is changed significantly. With Peak Force Tapping, the system is not being driven at the cantilever resonance, so it is not sensitive to changes in probe resonant frequency and Q.

A temperature-controlled experiment done with PeakForce QNM is shown in figure 6. In this example, a mechanical blend of syndiotactic polypropylene (sPP) and polyethylene oxide (PEO) was exposed to a sequential heatingcooling procedure with different rates of temperature change. The sample temperature was increased enough that the PEO-matrix melted, but the sPP domains stayed in the solid state to serve as reference marks in the area of interest. In the first cycle the sample was rapidly heated up until the PEO completely melted (b). The temperature was then allowed to rapidly drop, causing quick crystallization of the PEO (c). One can see that when compared to the initial morphology (a), the PEO topography underwent minor changes. This demonstrates the so-called "memory" effect of fast cooling, where the original crystallization nuclei are still active even though polymer appears to be totally melted.

During the second heating-cooling cycle, the temperature was lowered more gradually. Figure 6(e) shows abrupt transition from melt to solid state 1/3 of the way from the frame bottom (the system was scanning up the frame at the time). It's worth noting that, in this case, the PEO morphology becomes completely different from the original morphology in (a), indicating reorientation of the lamellae from an edge-on (a) state to a flat-on state (f). The images in (g–i) are modulus maps corresponding to the second crystallization cycle. Based on the topography in the upper portion of (e) you might conclude that the PEO is completely crystallized, but looking at the corresponding modulus map in (h), you can see that there is a soft (dark) circular area just

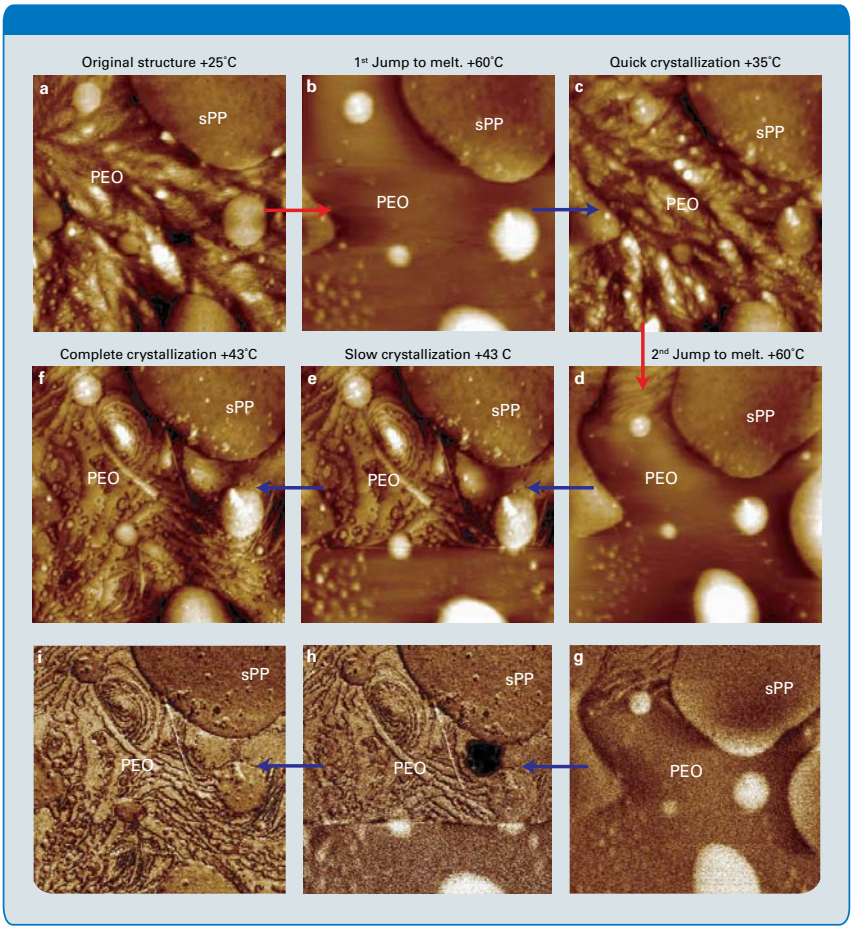

Figure 6. Cycle of heating and cooling of polymer blend of syndiotactic polypropylene and polyethylene oxide. Images a–f show height of the surface during the process, while g–i show the modulus of frames d–f respectively. Scan size 5um.

to the right of the center of the image that disappears when the sample has fully crystallized (i).

If this experiment were done in TappingMode, it would be necessary to adjust drive amplitude and frequency several times during each heatingcooling cycle (generally this is done just before collecting an image if the temperature has changed by more than about 10°C). Since Peak Force Tapping operates far from the cantilever resonance frequency, heating induced resonance frequency drift has no effect on the feedback, so it was not necessary to adjust the drive amplitude or frequency during the entire experiment. In fact, as long as the laser reflection stays on the photodetector, the imaging can proceed continuously and without adjustment during any experiment involving sample heating and cooling.

Operation of Peak Force Tapping is intrinsically identical in fluid, ambient and vacuum. This is in contrast to TappingMode where dramatic changes in the resonant dynamics of the probe in the three environments result in much more complexity in operation and variation in performance. By operating at a frequency far below the resonance, Peak Force Tapping removes the complex resonant dynamics and replaces it with simple and stable feedback on the peak force. Cantilever tuning is not required and it is not necessary to adjust drive amplitude and setpoint when imaging conditions change. Furthermore, Peak Force Tapping can achieve equal or better force control than TappingMode imaging in all the environments by using a broad range of cantilevers, making high-quality imaging much easier to achieve with this control mode. Finally, the lack of a need for special probes means that PeakForce QNM can be used with other techniques that do require special probes, such as Nanoscale Thermal Analysis with VITA.[16]

Brush Molecules

Polymer macromolecules have been an interesting, but challenging sample for SPM since the 1990s.[17] One example of this class of molecule is the poly(butyl acrylate) (PBA) brush molecule.[18] This molecule has a long backbone with many short, flexible side chains. The conformation and physical properties of these molecules are controlled by a competition between steric repulsion of densely grafted side chains (brushes) and attractive forces between the brushes and the substrate. They can be either flexible or stiff, depending on the grafting density and the length of side chains. Molecules can switch their conformation in response to alterations in the surrounding environment, such as surface pressure, temperature, humidity, pH, ionic strength, and other external stimuli. Molecular brushes are a very informative model system for experimental studies of polymer properties.[18]

Figure 7 shows a set of images collected of PBA using PeakForce QNM. In the height image (a) the backbone is clearly visible both as a long isolated molecule and as a folded set of molecules (a molecular ensemble). In the modulus map (b) it is clear that the soft (dark) backbones are surrounded by areas that are slightly stiffer, presumably where the short side chains are present. Figure 7(d) is a histogram showing the relative frequency of various modulus values in the image. The peak at 62MPa is from the background (mica covered by low molecular weight amorphous polymer), while the broad peak at 31.9MPa is from the brush molecules and molecular ensembles. By examining the region given by the red square in (b) it is possible to see that there are two peaks in the modulus of the molecular ensemble, as shown in figure 7(e). The one at about 25MPa corresponds to the backbone of the chains, and the one at about 32MPa corresponds to the surrounding

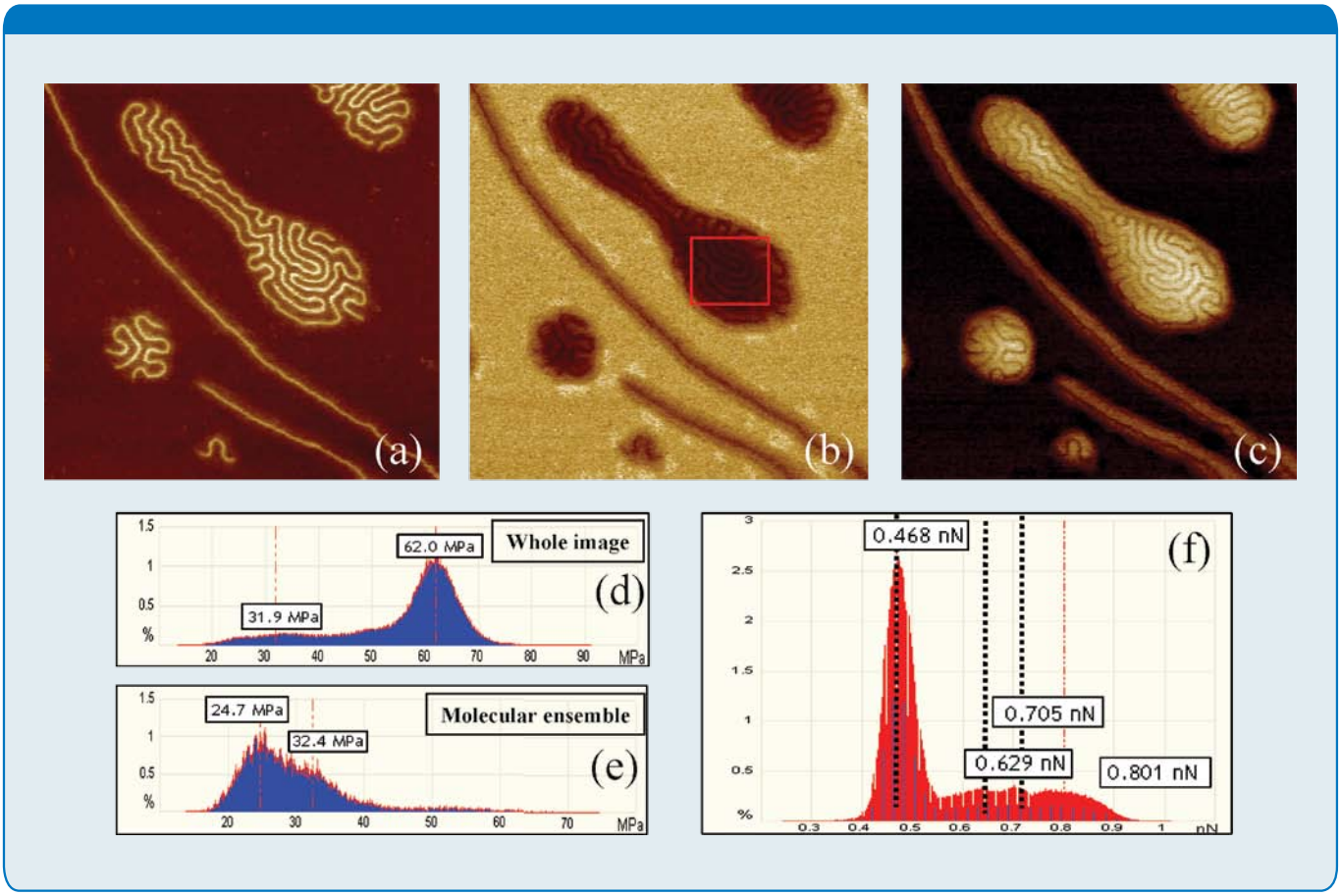

Figure 7. Poly(butyl acrylate) brush-like macromolecules and molecular ensembles on a mica substrate. (a) Height, (b) modulus, (c) adhesion, (d) histogram of modulus map, (e) histogram of area within red box in modulus map, (f) histogram of adhesion map. Sample was imaged with a MultiMode® 8 using PeakForce QNM with a scan size of 500nm. Sample courtesy of Sergei Sheiko (University of North Carolina, Chapel Hill, NC) and Krzysztof Matyjaszewski (Carnegie Mellon University, Pittsburgh, PA).

region filled with short brushes. These numbers are not expected to be quantitative since the molecules are small in comparison to the tip and the deformation of the sample. Even though the DMT model is not appropriate in this case, the qualitative interpretation that darker regions are softer than the brighter regions leads us to speculate that the polymer backbones are being partially supported by the short side chains.

In the adhesion image (c), the background appears dark with very little adhesion as indicated in the adhesion histogram (f) by the peak at 0.47nN. The histogram also has three other peaks: the backbones at about 0.63nN, the brushes of single molecules at about 0.71nN, and the brushes of molecular ensembles at about 0.8nN. The greater adhesion for the molecular ensembles is likely due to the greater number of brushes available to bind with the tip in those regions.

SPM has provided unique opportunities to observe single polymer molecules as they move, order, and react on surfaces. PeakForce QNM now makes it possible to map their mechanical properties as well, providing new insight into the behavior of these macromolecules.

Nanoparticles

The adhesion data type is sensitive to attractive interactions between the tip and sample in a way that is similar to chemical force microscopy (which uses lateral force microscopy in contact mode). Unlike with lateral force microscopy, PeakForce QNM can measure the attractive forces with negligible lateral force and very low normal force, allowing it to be used with very delicate or weakly bound samples.

For example, figure 8 shows an antibacterial film consisting of poly(methyl methacrylate) (PMMA) and silver nanoparticles. From topography alone (a), it is difficult to tell the locations of the silver nanoparticles. The adhesion map (b), however, reveals distinct nanoparticles (indicated by smaller circles) as well as an area enriched in many particles (large circle). Contact mode imaging would likely push the particles out of the way, making it impossible to see them. TappingMode PhaseImaging might be able to

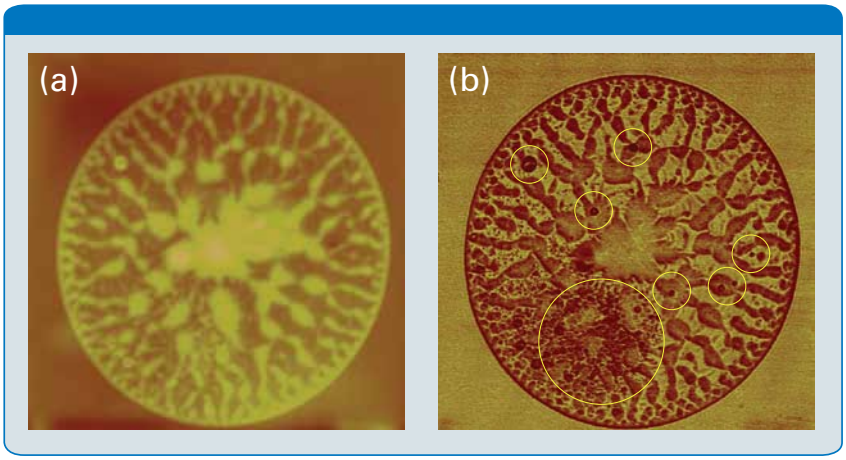

Figure 8. Anti-bacterial film consisting of poly(methyl methacrylate) (PMMA) and silver nanoparticles. Sample was imaged on a Dimension Icon® using PeakForce QNM at a scan size of 13.5µm. Sample courtesy of Mishae Khan and Daniel Bubb (Rutgers University, New Brunswick, NJ).

see the difference in the particles if the probe and imaging parameters were chosen correctly, but PeakForce QNM can see differences in adhesion, modulus and dissipation independently, making it more likely that there will be a difference in one of the data channels.

Conclusion

The unambiguous and quantitative modulus and adhesion data provided by PeakForce QNM can help researchers answer the critical question of what materials they are seeing in their topographic images. Additionally, it is now possible to study the variation and position of mechanical properties across a surface with ease, and at previously unattainable resolution. This imaging mode is non-destructive to both tip and sample since it directly controls the peak normal force and minimizes the lateral force on the probe. Maps of mechanical properties such as Young's modulus, adhesion and dissipation are automatically calculated at the rates and resolutions expected by advanced SPM users. Since force distance data is analyzed directly, there is no ambiguity regarding the source of image contrast, as often occurs in other techniques. Mechanical property maps are quantitative, low noise, and can span a very wide range of property values. These capabilities of PeakForce QNM will provide researchers with critical material property information to enable better understanding of their samples at the nanoscale.

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