Time-temperature superposition

Storage modulus mapping

Contrast inversion in maps of loss tangent

Application Note #154
Measuring Nanoscale Viscoelastic Properties with AFM-Based Nanoscale DMA

The development of heterogeneous materials like polymer composites, blends, and multilayers are of considerable importance in the chemicals industry. Bulk viscoelastic measurements are routine in establishing structure-property relationship for these materials. However, materials R&D often produces composites that contain nano-sized portions that do not exist in the bulk or that have properties influenced by the proximity of other components. A quantitative means of measuring the viscoelastic properties of such materials at the nanoscale has been a long-standing and elusive goal for atomic force microscopy (AFM). While AFM has the sensitivity and resolution needed to do the measurement, traditional AFM-based approaches are hampered by difficult calibration, poorly defined measurement frequency, and inadequate modeling of the tip-sample interaction. Now, with the development of the AFM-nDMA mode, these pitfalls can be avoided and the frequency and temperature dependence of viscoelastic properties in rheologically relevant ranges can be directly measured with 10nm spatial resolution. This application note explains the technology behind this technique and details the ways it enables investigation of previously inaccessible microscopic domains in heterogeneous polymeric materials.

Viscoelastic Measurements

Nanomechanical measurements have become among the most important measurements conducted with AFM, aside from topography. The inherent mechanical interaction between probe and sample allows an atomic force microscope to measure a sample's various mechanical properties, while the size of the contact allows the measurement to be localized at the nanometer scale. The most popular nanomechanical applications include measuring elastic modulus, adhesion, and friction. Viscoelastic materials, such as polymers and biological materials, have elastic properties that exhibit time-dependent behavior such as creep and stress relaxation. The viscoelastic properties are storage modulus, loss modulus, and loss tangent (tan δ). Nanoscale viscoelastic measurements are of interest primarily due to their influence on macroscopic material behavior and function.

An important segment of the chemicals industry is devoted to developing heterogeneous materials, such as polymer composites, blends, and multilayers. Bulk viscoelastic measurements are routine in establishing structure-property relationship for these materials, especially in the development of a material's mechanical properties. However, material research and development often produces composites or blends that contain nano-sized domains of components that do not exist in the bulk or have properties that are influenced by the proximity of other components (interphase). To fine-tune the characteristics of

such a heterogeneous material, the viscoelastic properties of the different components must be well-characterized. Thus, a tool to measure such properties on the nanoscale is essential for effective development of structure-property relationships in next-generation materials development.

The stress-deformation relationship of materials can be measured with either shear or uniaxial loads, resulting in shear modulus (G) or tensile modulus (E), respectively. For viscoelastic materials, the moduli are complex and have both real and imaginary parts. The real part (e.g., tensile storage modulus, E′) is the elastic or in-phase component of the response, and is given by (stress/strain)*cosδ where δ is the phase shift between the stress and strain. The imaginary part (e.g., tensile loss modulus, E″) represents the viscous or out-of-phase component of the response, and is given by (stress/strain)*sinδ. The loss tangent (tan δ) is the ratio between loss modulus and storage modulus.

Viscoelastic moduli often vary significantly with frequency and/or temperature. For example, in rubber-like polymers, the storage modulus typically has low values at low frequencies. As the frequency increases, the storage modulus increases dramatically, reaching a plateau at the modulus value of the glassy state at high frequencies. For the same materials, the loss modulus is low (primarily elastic) both at low and at high frequencies. The loss modulus peaks in the frequency mid-range, reflecting the presence of a glass transition between the rubbery and glassy states. Since the loss tangent is just the ratio of the loss modulus over the storage modulus (tan δ = E″/E′), it follows a similar trajectory to the loss modulus. The loss tangent is a practical and useful viscoelastic parameter, as it can pinpoint thermal and structural transitions in a material when measured as a function of temperature or frequency.

There is an equivalence between time (frequency) and temperature behavior in viscoelastic materials that arises from the relaxation behavior of the molecules within the sample.[1] This correspondence is formally expressed in terms of the time-temperature superposition principle or TTS. When modulus is measured over a range of frequencies, similar curves are obtained when the measurement is done at higher temperatures as are obtained at lower temperatures and a lower range of frequencies. Because these curves have the same shape, they can be superimposed onto one another to generate a "master curve" over a wide range of frequencies. Put another way, raising the temperature is equivalent to shifting to a lower frequency, while lowering the temperature is equivalent to shifting to a higher frequency. Finally, the shift factors used to generate the master curve can be analyzed via different models (WLF or Arrhenius) to parameterize this time-temperature relationship. In this way, data measured at one set of temperatures and frequencies can be used to determine behavior at a different set of temperatures and frequencies, making TTS and generation of the master curve very useful.

In the bulk, viscoelastic properties are measured with dynamic mechanical analysis, DMA (also known as dynamic mechanical spectroscopy, DMS). This measurement involves application of an oscillating stress to a macroscopic sample, with the response of the entire sample measured as a function of oscillation frequency. Depending on the sample properties and geometry, DMA can be performed in several different sample-mounting configurations, including three-point bending, shear, compression, and tension. Holding the sample in tension for dynamic mechanical tensile analysis (DMTA) offers the most direct comparison to the motion of an AFM tip and sample.

Previous AFM measurements of viscoelastic properties have suffered for several reasons. The first two challenges involve frequency space. Rheologists working with DMA typically work at frequencies of less than 200Hz, while AFM imaging modes are typically at much higher frequencies (kilohertz and higher) as they are optimized to provide images quickly. Additionally, in resonance-based techniques, the frequency of the AFM measurement is at very high frequencies as dictated by the cantilever dimensions. These frequencies are discrete (not tunable), and widely spaced (e.g., the second free eigenmode of a simple beam is 6.3 times the first).[2-4]

Perhaps even more important than the frequency mismatch, the imaging speed requirements of AFM have driven adoption of methods where the tip plunges into the sample and rips away from it at high speed, spending the minimum amount of time possible in contact. When the tip is making and breaking contact with the sample every cycle, the tip-sample interaction is very non-linear and the frequency of the measurement is not well defined but includes many harmonics of the nominal operation frequency.[5]

The final challenge to design an effective technique to measure viscoelastic properties revolves around the models used to extract the storage and loss modulus. The most challenging component of this involves measurement of and compensation for adhesion. In AFM of polymers, the adhesion between tip and sample is relatively large compared to the other tip-sample forces, and it often varies significantly across heterogeneous polymer samples. The adhesion is not measurable in many resonance-based AFM modes, making consideration of this important parameter, and ultimately its compensation, impossible. The primary contact mechanics models available for modeling adhesive tip-sample interactions for parabolic AFM tips are Derjaguin-Muller-Toporov (DMT) and Johnson-Kendall-Roberts (JKR). These models represent two limits in the range of possible adhesive behaviors, with the DMT model accounting for weak long-range adhesion (including outside the tip-sample contact area) while the JKR model accounts for stronger adhesion inside the tip-sample contact area.[6] Unfortunately, both models are purely elastic with no viscous component. Models that can extract both storage and loss modulus typically ignore adhesion and are therefore not appropriate

for application to AFM of polymers in air.[7, 8] These challenges make it clear that a different approach is required – one that provides well-defined rheological frequencies as a small perturbation to a carefully controlled preload.

A Different Approach for Viscoelastic Measurements with AFM

In designing a technique for the nanoscale measurement of viscoelastic properties (AFM-nDMA), there are some key considerations that need to be incorporated. First, the AFM tip-sample interaction must be operated at low, well-controlled loads. The modulation needs to occur in the linear tip-sample interaction regime, requiring even smaller perturbations in force exerted on the sample by the tip. Finally, the sample needs to be deformed at well-defined rheologically relevant frequencies. This refers to the low frequency regime of 0.1Hz to 100Hz, far from the traditional kilohertz and megahertz regime where atomic force microscopes usually operate.

Due to the low frequency of the measurements, AFM-nDMA measurements take time. It is therefore preferred to locate the region of interest with a faster method of imaging that also provides mechanical property contrast. PeakForce QNM® is particularly well suited to this function because it provides maps of modulus, dissipation, deformation, and adhesion relatively quickly and with high resolution.[9] Probes that are good for AFM-nDMA also typically work well with PeakForce QNM on the same materials, so there is no need to switch probes between measurements. Once the region or feature of interest has been identified (Figure 1a), single frequency images of viscoelastic moduli images can be collected through FASTForce Volume™ (FFV), as shown in Figure 1b. In this case, the storage modulus was mapped at 100Hz (frequencies of 50Hz or greater are recommended for reasonable acquisition times). Frequency sweep

measurements (Figure 1c) were then performed with a ramp scripting routine that used a series of segments to control preload, relaxation, modulation, and calculation of contact radius.

The frequency range available with the AFM-nDMA spans many orders of magnitude from 0.1Hz to 20,000Hz. The lowest frequency measurements are recommended only for those studies that really require properties to be measured in this frequency space, as these measurements are relatively slow. Measurements above 300Hz require an additional actuator (HFA) to expand the range of accessible frequencies. The HFA provides Z modulation that is independent of frequency and quite reproducible, enabling the wide spectrum DMA measurements.

The first step in an AFM-nDMA spectroscopy measurement is to bring the tip into contact with the sample and apply a preload of a known force set by the user (see A portion of Figure 2). Once in contact, modulation occurs at a low amplitude and well-defined frequencies (see C and E) to maintain a linear tip-sample interaction regime. Both amplitudes and frequencies are set by the user. Finally, the tip is pulled away from the sample and the adhesion and full retract curve are measured (see D).

On viscoelastic samples, the sample deformation will continue to increase for the full duration of the measurement, causing the contact area to slowly increase. Learning lessons from the dynamic nanoindentation community, this is addressed in three ways. First, after applying the preload a segment is included to allow for sample relaxation (see B portion of Figure 2). Second, reference segments at a given frequency are collected periodically throughout the measurement as well as just before the tip is pulled away from the sample, to allow for later estimation of the contact radius throughout the measurement (see two E segments). Finally, the

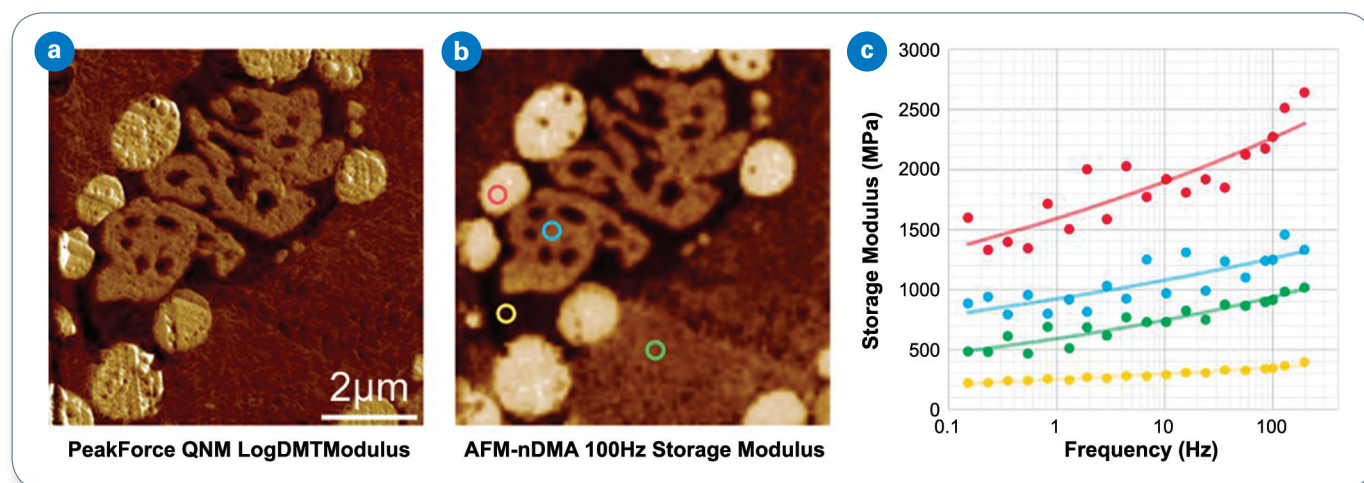**PeakForce QNM LogDMTModulus** **AFM-nDMA 100Hz Storage Modulus**

Figure 1. Comparison of mechanical property maps of a four-component polymer blend composed of COC (red), PP (blue), LLDPE (green), and elastomer (yellow) generated with PeakForce QNM (a) and AFM-nDMA (b) at 100Hz, and spectra at selected points on the sample (c). The spectra show that COC grows in stiffness most rapidly with frequency, followed by PP, LLDPE, and elastomer. This PeakForce QNM 512x512 image (2µm scale bar) was collected in about 10 minutes, while the 100Hz AFM-nDMA 70x70 map took 30 minutes. Each spectrum took about 10 minutes to collect.
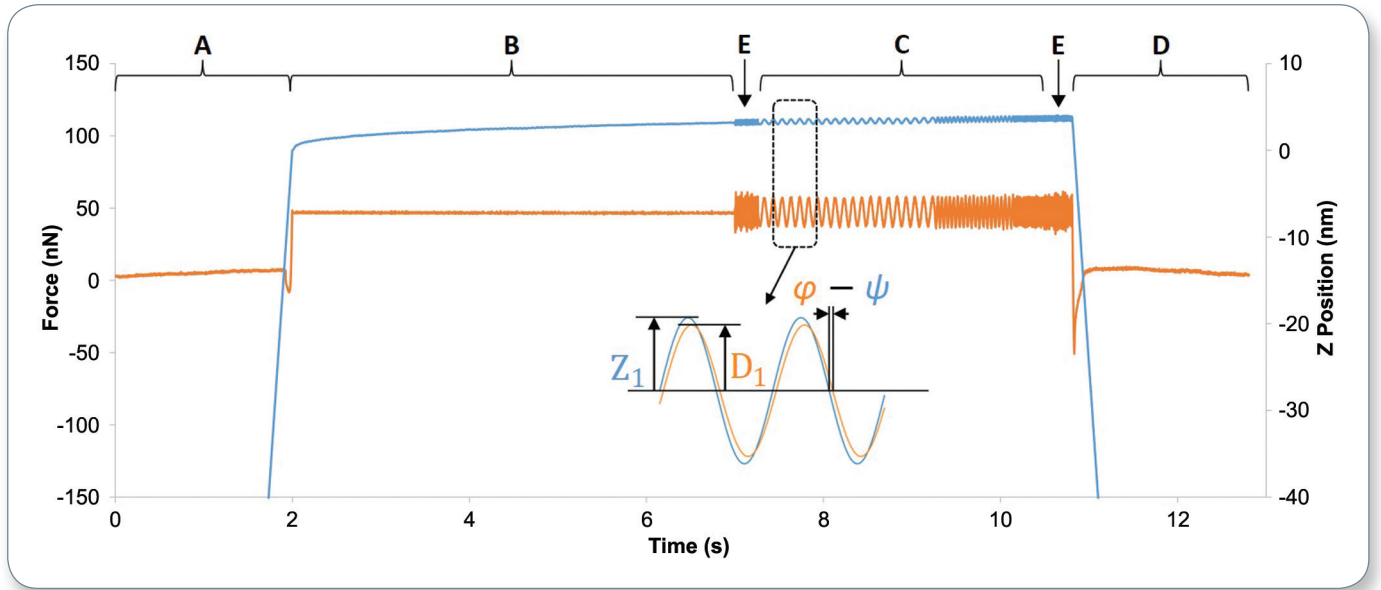
Figure 2. Typical AFM-nDMA spectroscopy force (orange) and Z position (blue) data. The tip is brought into contact and a preload is applied (marked A); the system waits for creep relaxation (B); low-amplitude modulation occurs at various frequencies, including reference frequencies (C and E); and the tip is retracted from the sample (D). Inset shows the key parameters to be extracted from the modulation segments: the deflection amplitude, D_1, the Z amplitude, Z_1, and the phase shift between Z and deflection ($\varphi - \psi$).

frequency order of the measurements is shuffled to avoid misinterpretation of property variation with contact time as a frequency dependence. Spectroscopy measurements can require several minutes to acquire a single point measurement, depending on the frequencies involved. For single-frequency mapping measurements, the measurement at each point is kept as simple as possible to reduce the total time of acquisition, and includes only three segments: approach, modulate, and retract.

AFM-nDMA Data Analysis

The amplitude and phase of the cantilever deflection and Z-piezo motion collected during modulation segments like those shown at C in Figure 2 can be analyzed to obtain the sample viscoelastic properties at the modulation frequency.[10, 11] The Z-piezo motion is described by

$$z(t) = Z_1 \ sin(\omega t + \psi) \qquad (1)$$

while the cantilever deflection can be described by

$$d(t) = D_1 \ sin(\omega t + \phi) \qquad (2)$$

If the amplitude ratio (D_1/Z_1) and phase shift (φ-ψ) are extracted (Figure 2, inset), one can calculate the complex "dynamic stiffness" or force divided by deformation:

$$S^* = S' + iS'' = \frac{force}{deformation} = \frac{K_c D_1 e^{i\phi}}{(Z_1 e^{i\psi} - D_1 e^{i\phi})} \qquad (3)$$

Separating the real and imaginary parts of equation 3 results in the storage stiffness (real) and loss stiffness (imaginary) components. The loss tangent (tan δ) is simply the ratio of the two:

$$S' = \frac{K_c D_1}{Z_1} \frac{cos(\varphi-\psi)-D_1/Z_1}{(cos(\varphi-\psi)-D_1/Z_1)^2+(sin(\varphi-\psi))^2} \qquad (4)$$

$$S'' = \frac{K_c D_1}{Z_1} \frac{sin(\varphi-\psi)}{(cos(\varphi-\psi)-D_1/Z_1)^2+(sin(\varphi-\psi))^2} \qquad (5)$$

$$tan\ \delta = S''/S' = \frac{sin(\varphi-\psi)}{cos(\varphi-\psi)-(D_1/Z_1)} \qquad (6)$$

The relationship between dynamic stiffness and the storage and loss modulus are simply:

$$E' = \frac{S'}{2a_c} ; \ and \ E'' = \frac{S''}{2a_c} \qquad (7)$$

where the contact radius (a_c) is determined from the final step in either the FFV ramp or the ramp script where the tip is pulled away from the sample (see D in Figure 2). This segment is fit with an adhesive contact mechanics model such as DMT or JKR to obtain the contact radius at the beginning of the retract.

Calibration and Probes

Quantitative nanomechanical measurements with AFM have long struggled with the need for accurate calibrations involving the probe and system, specifically the tip shape, cantilever spring constant, and detector sensitivity. Bruker now offers pre-calibrated probes with rounded, well-defined tips, providing confidence in their shape and

dimensions.[12] These tips have spherical apices with radii of either 33nm or 125nm (individually measured via SEM), providing a controlled contact area for indentation depths up to 100nm or 500nm, respectively. Tip shape is especially important for measurements on heterogeneous samples where a constant load will result in different indentations on the different components based on the component's material properties. With these probes, it is possible to calculate the contact area for a wide range of indentation depths. The rounded geometry of the probe shape further promotes linear deformation mechanisms, which are the only ones accounted for in elastic models.[13]

The spring constant of each probe is also pre-calibrated with a laser Doppler vibrometer (LDV), providing an accurate measurement of this important cantilever parameter and obviating the user from this step. These probes are offered in a range of spring constants from 0.25N/m to 200N/m, appropriate for a wide range of sample stiffness. Table 1 lists the available pre-calibrated probe types along with nominal spring constant, tip radius, and recommended range of storage modulus to be measured. Note, however, that AFM-nDMA is not limited to only the probe choices listed in this table. The 125nm tips provide improved signal-to-noise level over the 33nm tips, reducing the chance of plastic deformation, while the sharper tips provide better resolution for samples with small features. The pre-calibrated parameters are easily read into the system by scanning the QR code on each cantilever box, which contains the spring constant, resonance frequency, quality factor, tip radius, and tip half-angle for each individual cantilever. Once the QR code is scanned, there is no need for adjustment or "fudging" of the parameters, and no sample of known stiffness is required.

Probe Type	Spring Const. (N/m)	Tip Radius (nm)	min E' (MPa)	max E' (MPa)
SAA-HPI-DC-125	0.25	125	0.1	10
RTESPA150-125	5	125	2	200
RTESPA300-125	40	125	20	2,000
RFESPA-40-30	0.9	33	0.8	80
RTESPA150-30	5	33	4	400
RTESPA300-30	40	33	40	4,000
RTESPA525-30	200	33	200	20,000

Table 1. AFM-nDMA optimized probes and the corresponding storage modulus ranges for which these probes are best suited. These probes are supplied with pre-calibrated spring constants (via LDV) and tip radii (via SEM). Note that AFM-nDMA is not limited to the probe choices listed here.

Finally, there are a few calibration parameters that cannot be pre-calibrated because they are system dependent. The photodiode deflection sensitivity can be calibrated either through a thermal tune, or by conducting a force curve on a stiff sample, such as sapphire. The amplitude and phase of the Z position also need to be calibrated, where the phase can depend on the probe and probe (or sample) mounting. These parameters are calibrated on sapphire by running the identical AFM-nDMA or force volume script with the same probe as is used to measure the sample.

Results

AFM-nDMA is designed to measure localized viscoelastic properties as a function of frequency or temperature on heterogeneous samples. The first step in the measurement is to image the sample with a conventional AFM imaging method, such as PeakForce QNM. Figure 1a shows a PeakForce QNM image of a four-component polymer blend where all components are easily differentiated. This 512x512 image was acquired in ten minutes and provides a good overview to allow selection of areas of interest for further investigation. A FASTForce volume AFM-nDMA map was then collected at 100Hz (the resulting storage modulus map is shown in Figure 1b). Although these maps can be collected at the same frequencies as those available in ramp scripting measurements, frequencies less than about 50Hz are less practical for image acquisition due to the amount of time needed, and the risk of drift during the measurement. This 100Hz 70x70 map was collected in about 30 minutes. Finally, single points were selected for individual ramp-scripting measurements over a wide range of frequencies, as shown in Figure 1c for the storage modulus plotted as a function of frequency in the range of 0.1 to 200Hz. The blend was composed of cyclic olefin copolymer (indicated with a red circle), polypropylene (blue), linear low-density polyethylene (green), and elastomer (yellow). Comparison of the spectra shows that COC has the largest storage modulus followed by PP, LLDPE, and elastomer. The storage modulus of the COC and LLDPE nearly doubles over the frequency range measured, while the other components vary less dramatically.

To check for consistency between methods, viscoelastic measurements by AFM-nDMA were compared with bulk DMA, the industry standard for such measurements. Figure 3 compares the storage modulus (E') and loss modulus (E'') of polydimethylsiloxane (PDMS) as measured by three methods: 1) bulk tensile strain modulation DMA (green lines); 2) an instrumented nanoindenter (light blue 'x'); and 3) AFM-nDMA in a Santa Barbara lab (dark blue 'o') and 4) AFM-nDMA in a collaborator's lab (orange 'Δ') (performed on a different AFM system than the one at the Santa Barbara lab, with a different probe and different AFM operator). There is excellent agreement among all these methods for both E' and E'': about 5% RMS deviation between bulk and AFM-nDMA for E', and about 25% for E''. It is important to note the difference in frequency ranges accessible by the two

methods. While DMA and indenter methods can typically only measure moduli at frequencies up to around 200Hz, the AFM-nDMA method enables measurements at up to 20,000Hz with the addition of an external actuator.
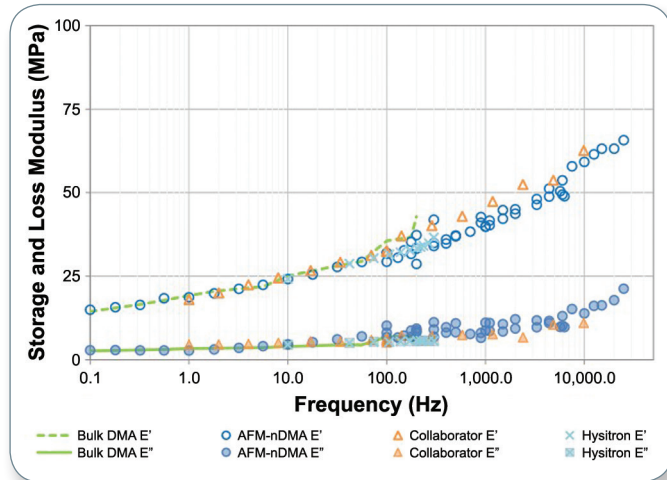

Figure 3. Storage modulus (E') and loss modulus (E'') spectra of polydimethylsiloxane at 25°C. The green dashed and solid lines are storage and loss modulus as measured with bulk DMA. The light blue 'x' were from an instrumented nanoindenter, while the dark blue '○' and orange 'Δ' used AFM-nDMA in either the Santa Barbara lab or in a collaborator's lab.

As described above, master curves are important tools for polymer scientists to explore viscoelastic properties over a wide range of frequencies and temperatures. The first step in generating a master curve is to collect a series of viscoelastic spectra at different temperatures. Figure 4 shows the storage modulus (blue) and loss tangent or tan δ (orange) acquired via AFM-nDMA over a temperature range from 25°C to 130°C and a frequency range of 0.1 to 100Hz on fluorinated ethylene propylene (FEP). As the temperature increases, the material becomes softer as demonstrated by a lowering of the storage modulus. The 90°C peak in the loss tangent is due to the material's glass transition temperature (Tg). As expected, the softening and peak in loss tangent occur at higher temperatures when the measurement is conducted at higher frequencies.
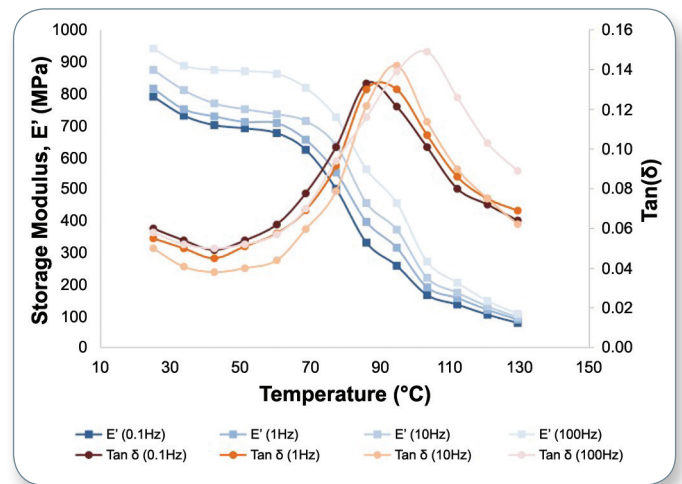

Figure 4. AFM-nDMA storage modulus (left axis) and loss tangent (right axis) of fluorinated ethylene propylene. The blue squares are storage modulus versus temperature plots at 0.1, 1, 10, and 100Hz (darkest to lightest blue respectively), while the brown circles are the loss tangent plots at 0.1, 1, 10, and 100Hz (darkest to lightest brown.

By shifting the series of curves from Figure 4, a master curve for FEP loss tangent is then created. Figure 5a shows that the loss tangent master curve from the AFM-nDMA data (blue '○') compares favorably with bulk DMA (green 'Δ'). These master curves span a very wide range of frequencies of about 24 decades. Finally, the activation energy can be calculated from the shift factors used to generate the master curves (Figure 5b). The activation energy from the AFM-nDMA master curve (490kJ/mol) matches very well that from the bulk DMA master curve (489kJ/mol).
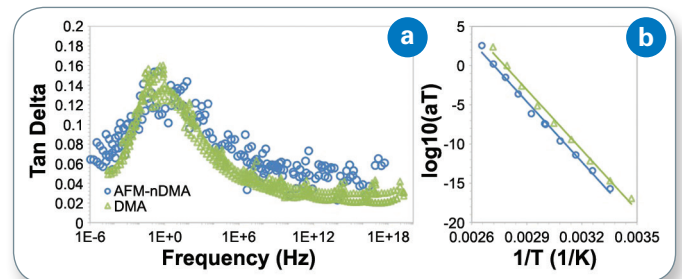

Figure 5. Time-temperature superposition analysis of FEP: (a) loss-tangent master curves from AFM-nDMA (blue '○') compared to that from bulk DMA (green 'Δ'); (b) TTS shift factor versus 1/T plot for Arrhenius activation energy analysis. Linear fits give activation energies from bulk DMA and AFM-nDMA of 489 and 490kJ/mol, respectively.
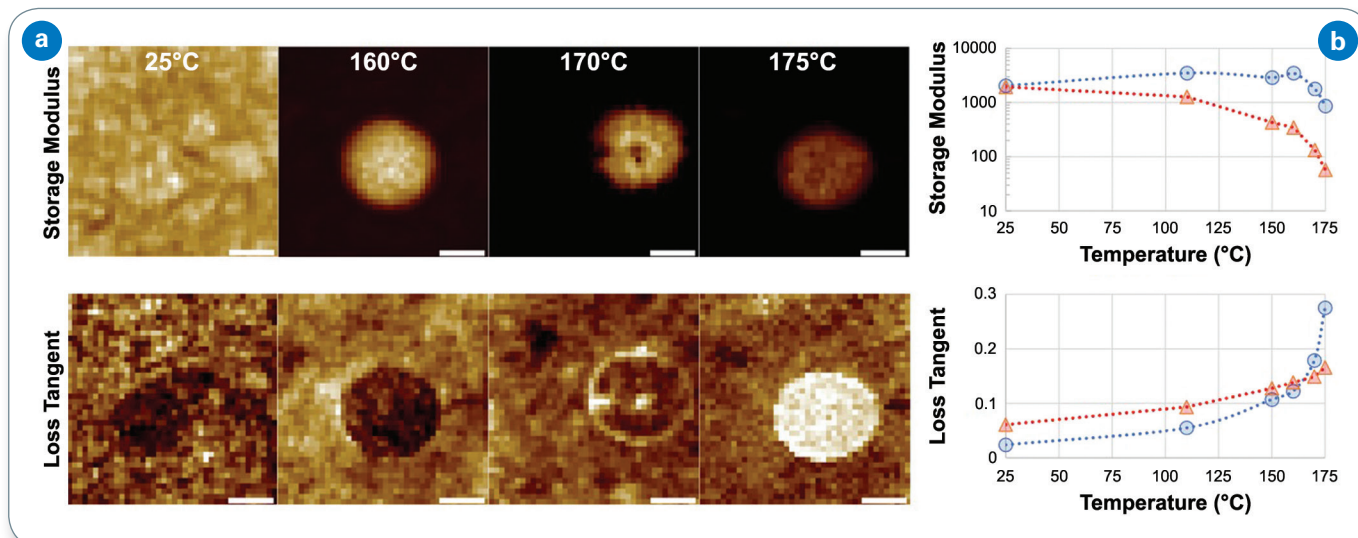
Figure 6. Storage modulus (top row) and loss tangent (bottom row) of a PP-COC blend: (a) 100Hz AFM-nDMA maps with increasing temperature (500nm scale bar); (b) plots of storage modulus and loss tangent at 10Hz versus temperature. Blue circles were measured within the COC domain and red triangles were from the PP matrix.

One of the most exciting applications of AFM-nDMA is to probe viscoelastic properties of highly localized spatial domains, a capability that is critical to many kinds of materials, including blends and nanocomposites. A blend of a polypropylene (PP) matrix with a 1µm diameter domain of cyclic olefin copolymer (COC) is shown in Figure 6. The progression of the viscoelastic properties of these two materials as a function of temperatures from 25°C-175°C is shown in the series of 100Hz AFM-nDMA storage modulus and loss tangent plots. The two materials start out at equivalent E' values at ambient conditions, but quickly diverge as the temperature increases and two materials approach their respective thermal transition points. The loss tangent images reveal an inversion of relative loss tangents between the two materials at 175°C. E' and tan δ values were calculated from their respective domains in the image and plotted as a function of temperature in the corresponding graphs adjacent to the maps.

Conclusions

Quantitative viscoelastic property measurements of nanoscale domains in heterogeneous polymeric materials are now possible. AFM-nDMA directly addresses the frequency and temperature dependence of viscoelastic properties in the rheologically relevant range, avoiding the pitfalls of traditional AFM imaging modes. As seen in the PDMS test case, E' and E'' values compare well with bulk DMA measurements from 0.1 to 200Hz (and can be extended to 20,000Hz using external actuator). A full TTS analysis of FEP results over a range of temperatures and frequencies also agrees with bulk DMA, and yields the expected Arrhenius activation energy. Additional measurements on a blend of PP and COC demonstrate viscoelastic property mapping and the importance of consideration of the temperature and frequency to understand even qualitative material behavior. AFM-nDMA adds a powerful, quantitative capability for measurement of viscoelastic properties, which compares well with established techniques while enabling investigations of the microstructure as well as bulk properties of heterogeneous polymers.

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