

## Measuring Viscoelastic Master Curves at the Nanoscale in Polymer Composites

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Viscoelastic properties of bulk materials are usually measured with dynamic mechanical analysis, DMA (also known as dynamic mechanical spectroscopy, DMS). This measurement involves application of an oscillating stress or strain to a macroscopic sample, with the response of the sample measured as a function of oscillation frequency. When DMA frequency spectra are collected over a range of temperatures, the principle of Time-temperature superposition can be used to assemble them into a “Master curve” which spans a much wider range of frequency at one temperature [1]. When heterogeneous samples are measured using this macroscopic technique, no information about the properties of the microstructure is available – only the spatially averaged properties of the whole sample.

Atomic Force Microscopy (AFM) has the resolution and mechanical sensitivity to provide the needed local mechanical property information. However, previous AFM measurements of viscoelastic properties have suffered from several drawbacks. The first two issues 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. Additionally, in resonance-based techniques, the frequency of the AFM measurement is dictated by the cantilever dimensions. These frequencies are discrete (not tunable), and widely spaced [2, 3]. Perhaps even more important than the frequency mismatch, the desire for increased imaging speed has driven adoption of AFM 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 [4].

In designing a technique for the nanoscale measurement of viscoelastic properties (AFM-nDMA), there are some key considerations that need to be incorporated [5-8]. First, the AFM tip-sample interaction must be operated at low, well-controlled loads. Next, the modulation needs to occur in the linear tip-sample 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 0.1 Hz to 100Hz, far from the traditional kHz and MHz regime where AFMs usually operate.

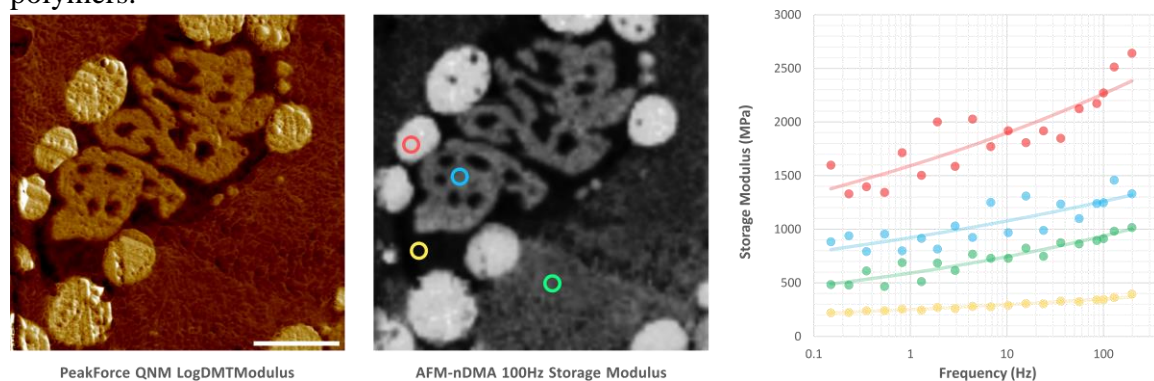
On viscoelastic samples, the sample deformation will continue to increase for the full duration of the measurement, causing the contact area to increase (especially for long duration, low frequency spectra). Bruker AFM-nDMA addresses this by adding a relaxation segment just after applying the preload. Additionally, reference segments at a given frequency are collected periodically throughout the measurement to allow for later estimation of contact radius evolution [8].

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 [9, 10]. Figure 1 (left) shows a PeakForce QNM image of a four-component polymer blend where all components are easily differentiated. This DMTModulus map was acquired in ten minutes and provides a good overview to allow selection of areas

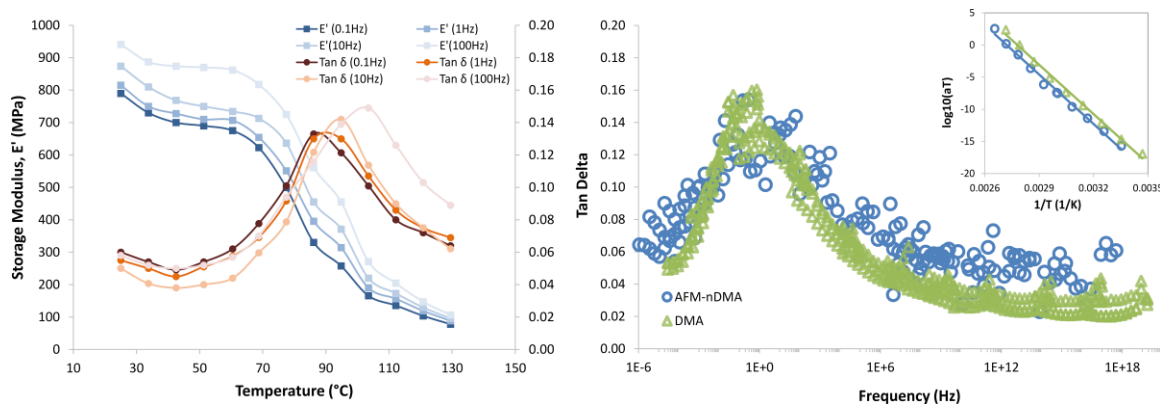
of interest for further investigation. Next, a *FASTForce* Volume AFM-nDMA map was collected and the resulting 100Hz storage modulus map calculated (Fig. 1, center). Finally, single points were selected for individual ramp scripting measurements over a wide range of frequencies (Fig. 1, right) for the storage modulus plotted as a function of frequency in the range of 0.1-200Hz. Comparison of the spectra shows that the COC component 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 on a homogeneous polymer: fluorinated ethylene propylene (FEP). Figure 2(left) shows the AFM-nDMA spectra plotted against temperature. As expected, both the storage modulus and loss tangent curves shift to higher temperatures when collected at higher frequencies. By shifting this series of curves in frequency, master curves for FEP viscoelastic properties can be created. The loss tangent master curve from the AFM-nDMA data (Fig. 2, right - blue 'o') 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 (Fig. 2, right - inset). The activation energy from the AFM-nDMA master curve (490kJ/mol) matches very well that from the bulk DMA master curve 489kJ/mol).

These results demonstrate that quantitative viscoelastic property measurements of nanoscale domains in heterogeneous 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. A full TTS analysis of FEP results over a range of temperatures and frequencies agrees with bulk DMA and yields the expected Arrhenius activation energy. Measurements on a four-component blend demonstrate viscoelastic property mapping and the importance of the frequency of the measurements to understand 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.



**Figure 1.** A four-component polymer blend composed of COC (Cyclic olefin copolymer – red circle), PP (polypropylene - blue), LLDPE (linear low-density polyethylene - green), and elastomer (yellow). Comparison of mechanical property maps generated with PeakForce QNM (left), AFM-nDMA at 100Hz (center), and spectra at selected points on the sample (right). 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 30minutes. Each spectrum took about 10min to collect.



**Figure 2.** Left pane: AFM-nDMA storage modulus (left axis) and loss tangent (right axis) of fluorinated ethylene propylene. The blue squares are storage modulus vs. temperature plots at 0.1, 1, 10, 100Hz (darkest to lightest blue respectively), while the brown circles are the loss tangent plots at 0.1, 1, 10, 100Hz (darkest to lightest brown). Right pane: Time-temperature superposition analysis of FEP. Loss tangent master curves from AFM-nDMA (blue ‘o’) compared to that from bulk DMA (green ‘Δ’). Inset: TTS shift factor vs.  $1/T$  plot for Arrhenius activation energy analysis. Linear fits give activation energies from bulk DMA and AFM-nDMA of 489 and 490kJ/mol respectively.

## References

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