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Measuring nanoscale viscoelastic properties with AFM-based nano-DMA

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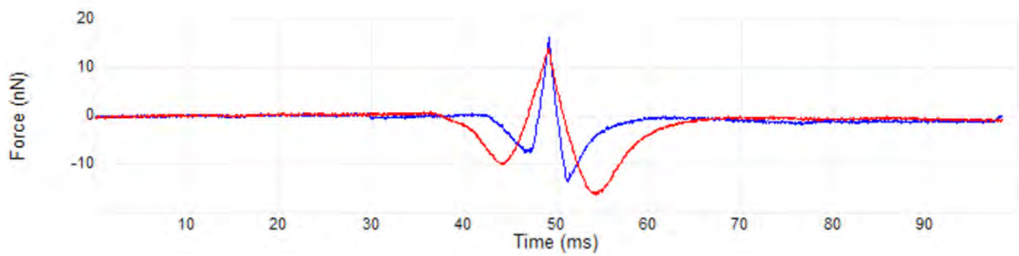
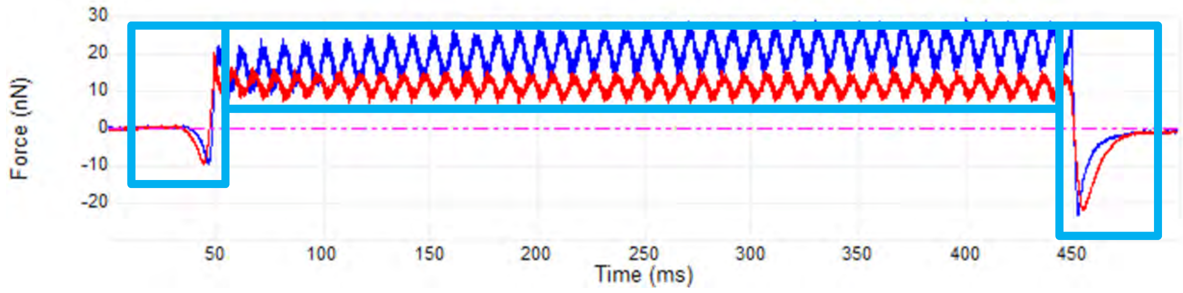
Q: What can we do to improve the capabilities of AFM in measuring viscoelastic properties of materials?

Imaging focused modes - not suited for quantifying viscoelasticity



- Probing sample impulsively
  - Plunge-in and rip-out in each cycle, make-and-break contact
  - Not a linear measurement
  - Since it's not linear, the nominal frequency is not the only frequency
  - Cannot really quantify frequency dependence
- Tapping based methods introduce added constraints
  - Frequencies fixed and 100,000x too high
  - Challenge in quantifying load and adhesion

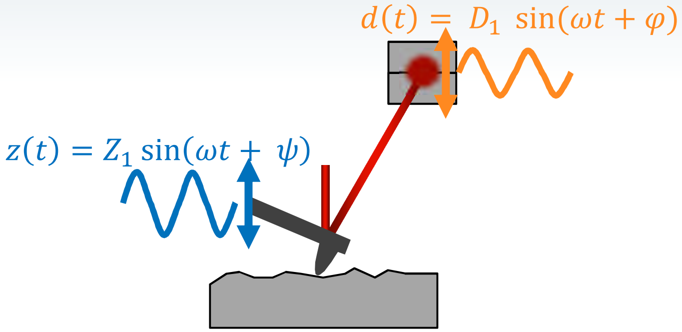
Start with time dependence
Basic idea of AFM mode for rheology

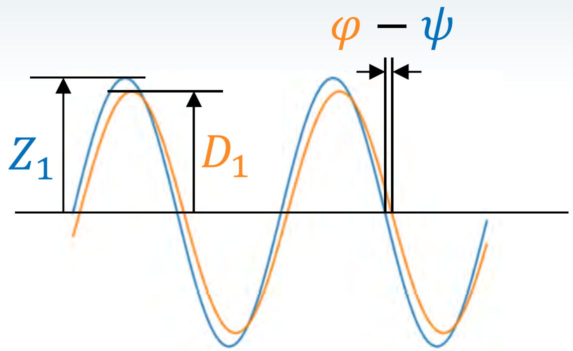


- Approach: Preload the sample at known force
- In contact: Modulate at well-defined, rheological freq, low amp
  - Low amplitude provides small perturbation in force: linear regime
  - Cover 0.1Hz to 300Hz: single frequency or spectrum
- Retract: fit with contact mechanics model that includes adhesion (e.g. JKR) to obtain contact radius (ac)
  - Need contact radius to extract moduli (E', E”) from raw data

T. Igarashi, S. Fujinami, T. Nishi, N. Asao, and K. Nakajima, Macromolecules (2013)

AFM-nDMA theory





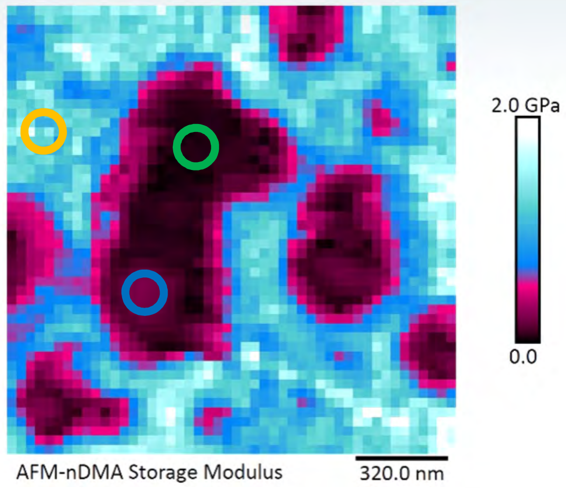
- Need to extract amplitude ratio (D_1/Z_1) and phase shift ($\varphi - \psi$) and do a little complex algebra to get stiffness = force/deformation
  - $S^* = S' + iS" = K_c D_1 e^{i\varphi} / [Z_1 e^{i\psi} - D_1 e^{i\varphi}]$
  - $S' = \frac{K_c D_1}{Z_1} \frac{\cos(\varphi-\psi) - D_1/Z_1}{(\cos(\varphi-\psi) - D_1/Z_1)^2 + (\sin(\varphi-\psi))^2}$
  - $S" = \frac{K_c D_1}{Z_1} \frac{\sin(\varphi-\psi)}{(\cos(\varphi-\psi) - D_1/Z_1)^2 + (\sin(\varphi-\psi))^2}$
  - Loss tangent is then: $\tan\delta = S"/S' = \frac{\sin(\varphi-\psi)}{\cos(\varphi-\psi) - (D_1/Z_1)}$

Two modes quantify viscoelasticity
E′, E″, tan δ at bulk DMA frequencies

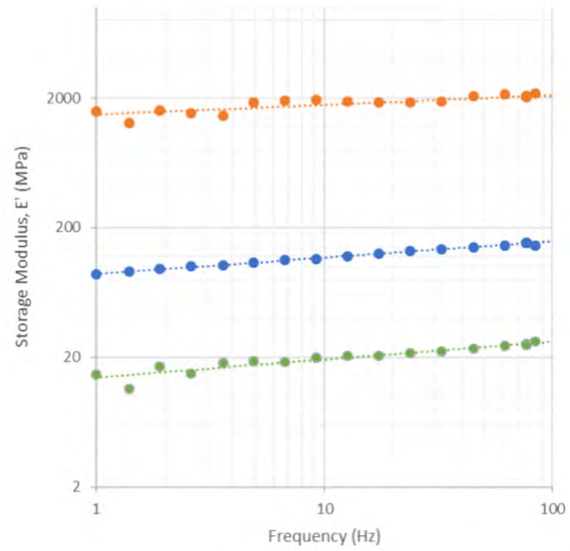
- Mapping with Fast Force Volume
  - Simple, single modulation segment embedded in force curve

AFM-nDMA storage modulus map of polymer blend (100Hz)

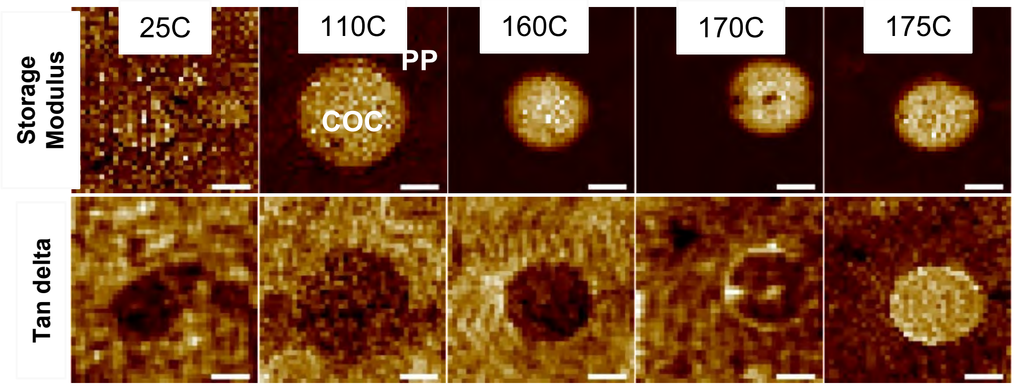
With correlated, frequency spectra at selected locations

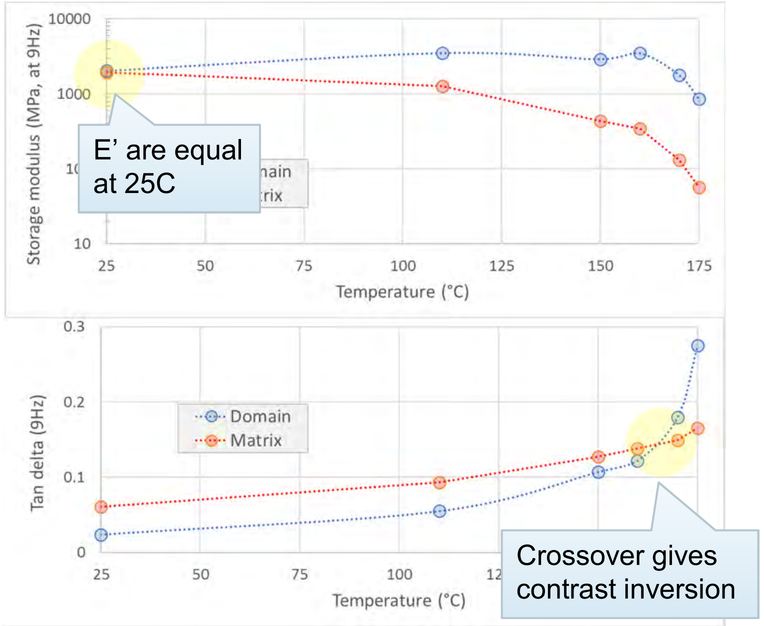


- Spectroscopy with RampScripting
  - measurements at multiple frequencies at a single point



Example: Tan(δ) contrast inversion in a blend as function of temperature



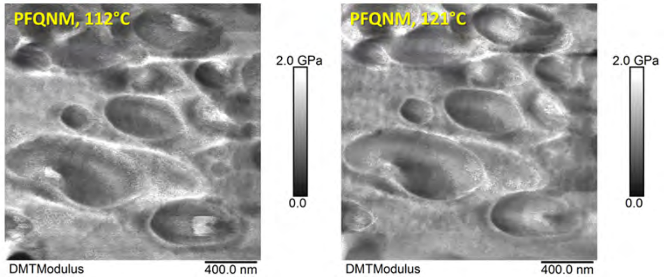


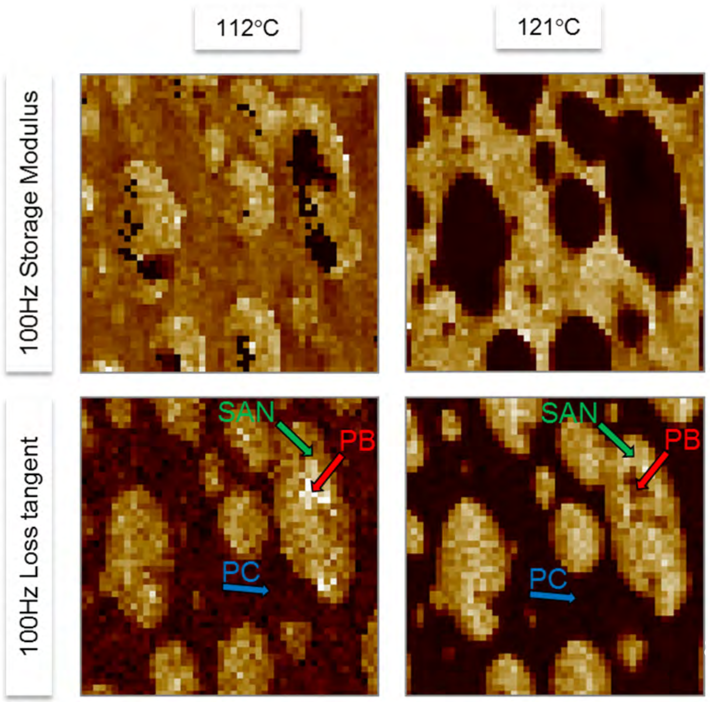
- PP and COC have equal E′ at 25C
- PP softens more rapidly than COC
- PP loss tangent is initially greater than COC with contrast inversion occurring as temp approaches COC glass transition

Example: Drastic modulus contrast change missed by other approaches

- The storage modulus map of PC-ABS at 100Hz changes drastically at 120C as SAN becomes soft and viscous

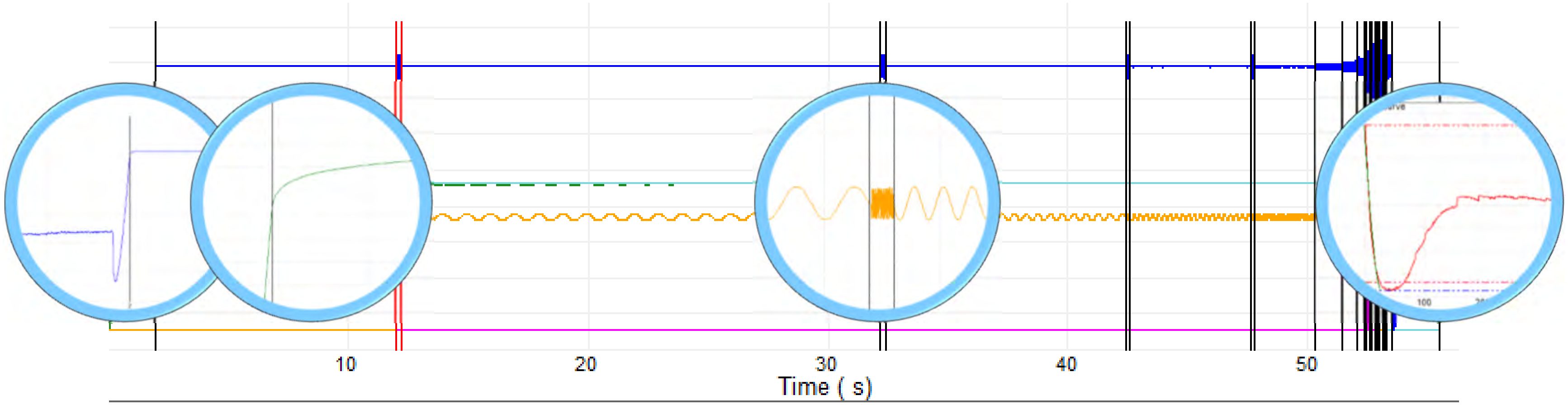
- A high frequency stiffness map (PFQNM) misses the effect





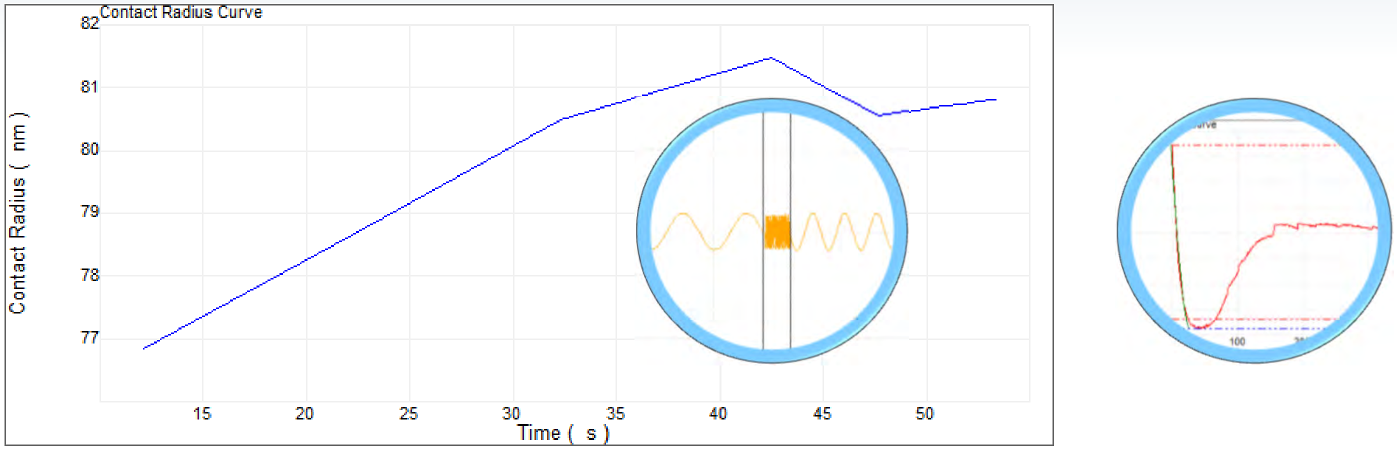
PC-ABS: this drastic change with temperature is not apparent in PFQNM elastic modulus maps

How are these spectra collected?



- An AFM-nDMA "RampScript" has segments that allow for control of preload, relaxation, modulation, and calculation of contact radius
- Low frequency segments use raw deflection for better filtering, while higher frequencies use lock-in based demodulation

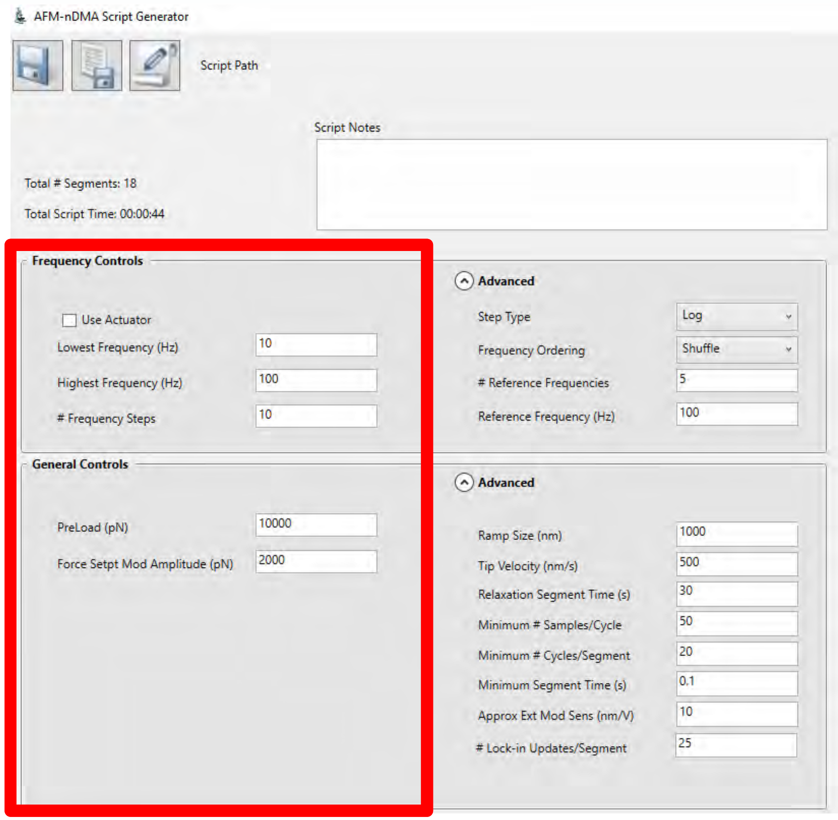
Managing changes in contact radius



- To get moduli E’, E’’, we also need a contact mechanics model like JKR to estimate contact radius (ac)
  - $E' = \frac{S'}{2a_c}$; $E" = \frac{S"}{2a_c}$
- Reference segments correct evolution of contact radius over time
  - Measure *S’(f$_{ref}$)* and assume *E’(f$_{ref}$)* is constant during script

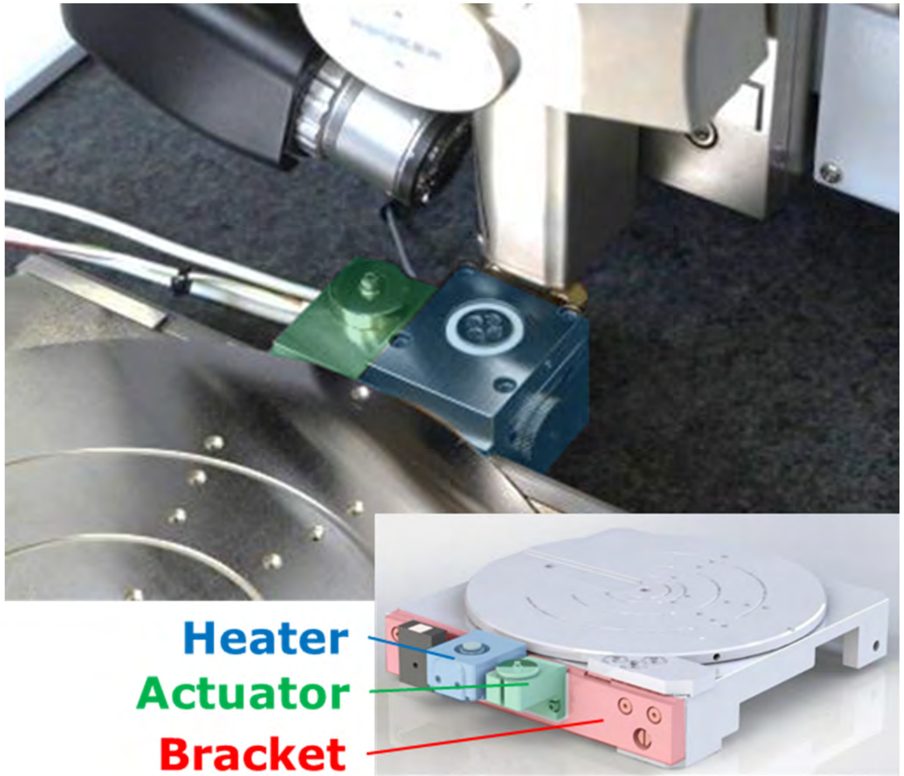
Setting up AFM-nDMA spectroscopy
Efficient generation of scripts

- Quick set up with DMA focus
  - Frequencies, preload, modulation amplitude
- Advanced parameters if wanted
  - Log vs linear frequency distribution
  - Frequency shuffle avoids artifacts
  - Modify reference segments
  - Change length of relaxation segment
  - Adjust any ramp parameter
- Or edit segment-by-segment in general ramp scripting interface
  - Maximum flexibility



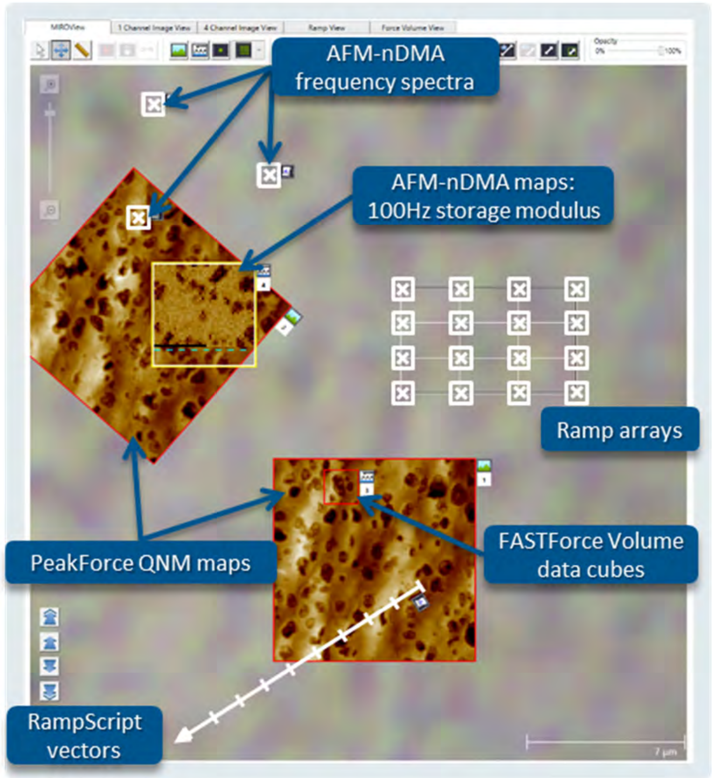
New hardware for AFM-nDMA
Installs at rear of Dimension Icon chuck

- Fast, low drift heater, RT to +250C
  - Up to 2cm samples, prefer <1mm thin for fast equilibration
  - High power, water cooled, 5x faster stabilization than Bruker's std heater – in practice, stabilization time paced by sample
  - 0.1Hz-300Hz frequencies available while heating
- High frequency sample actuator, expands frequency range to 20kHz at RT



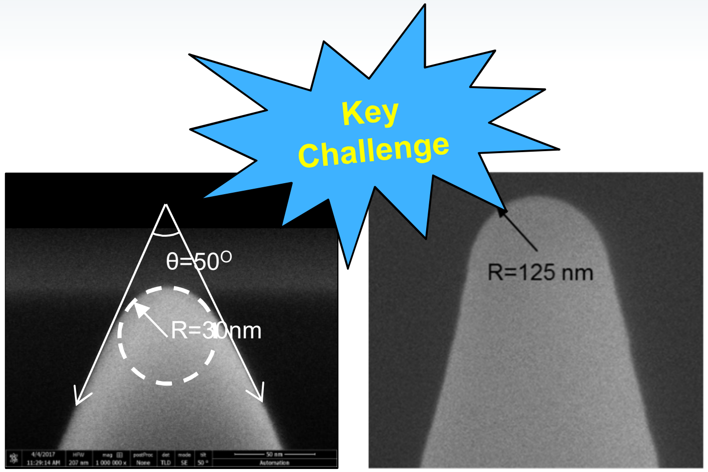
Workflow for locating and navigating
Optical → fast AFM maps → AFM-nDMA

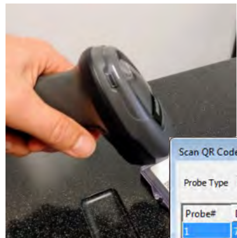
- MIROView: Optical image is the canvas
- Start AFM with PeakForce QNM mapping
  - Uses same tips as AFM-nDMA
  - Fast, hi-res, elastic modulus, calibrated
  - Resolve small domains, structure detail
- Then targeted rheological measurements
  - Use PFQNM to ID ROI
  - AFM-nDMA maps, arrays, vectors, points

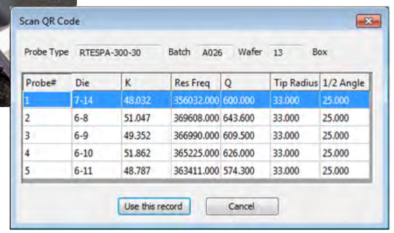


Addressing good calibration Probe solution with software integration

- Characteristics of a probe solution
  - Controlled tip radii, SEM measured
  - LDV measured spring constant, matched to sample modulus
- No reference sample required







Scan QR Code

Probe Type RTESPA-300-30 Batch A026 Wafer 13 Box

Probe#	Die	K	Res Freq	Q	Tip Radius	1/2 Angle
1	7-14	48.032	356032.000	600.000	33.000	25.000
2	6-8	51.047	369608.000	643.600	33.000	25.000
3	6-9	49.352	366990.000	609.500	33.000	25.000
4	6-10	51.862	365225.000	626.000	33.000	25.000
5	6-11	48.787	363411.000	574.300	33.000	25.000

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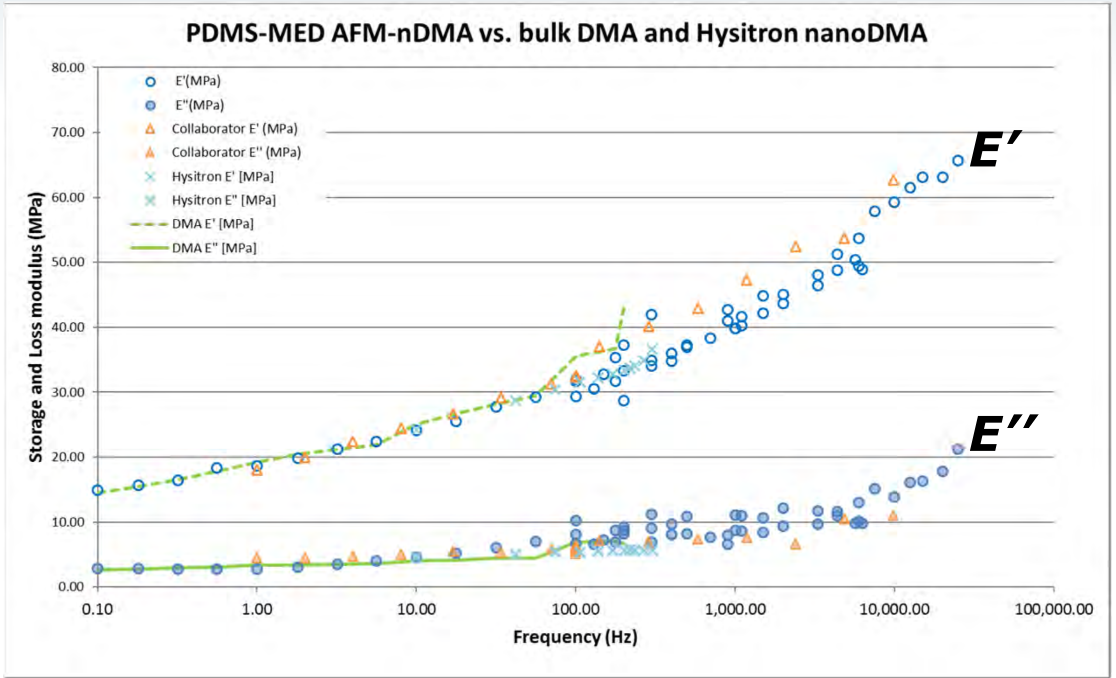
Can a nanoscale measurement tie directly to bulk DMA?

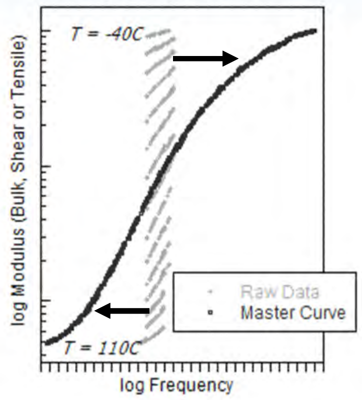


- Nanoscale AFM-nDMA results show excellent agreement with
  - micrometer scale Hysitron Nanoindenter
  - millimeter scale Bulk DMA
- Consistent results across labs and operators (no reference samples)
- Directly cover bulk frequencies and extend to 20kHz with external actuator

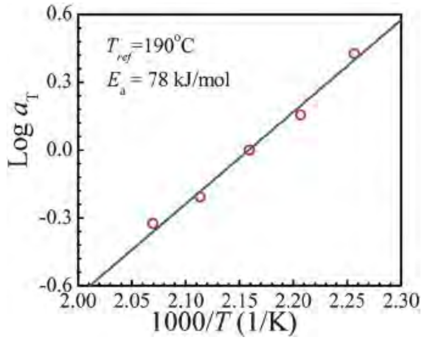
Time Temperature Superposition

- Collecting frequency spectra at several temperatures enables a more complete analysis
- TTS principle: near glass transition, raised temperature is equivalent to lowered frequency and vice versa
- Master curve: single curve resulting from shifting data measured at different temperatures
- Shift factors: can be parameterized via either WLF or Arrhenius model.
    - Arrhenius equation gives activation energy from temperature dependence of a rate – energy needed to kick off a mechanical relaxation process

TTS master curve construction

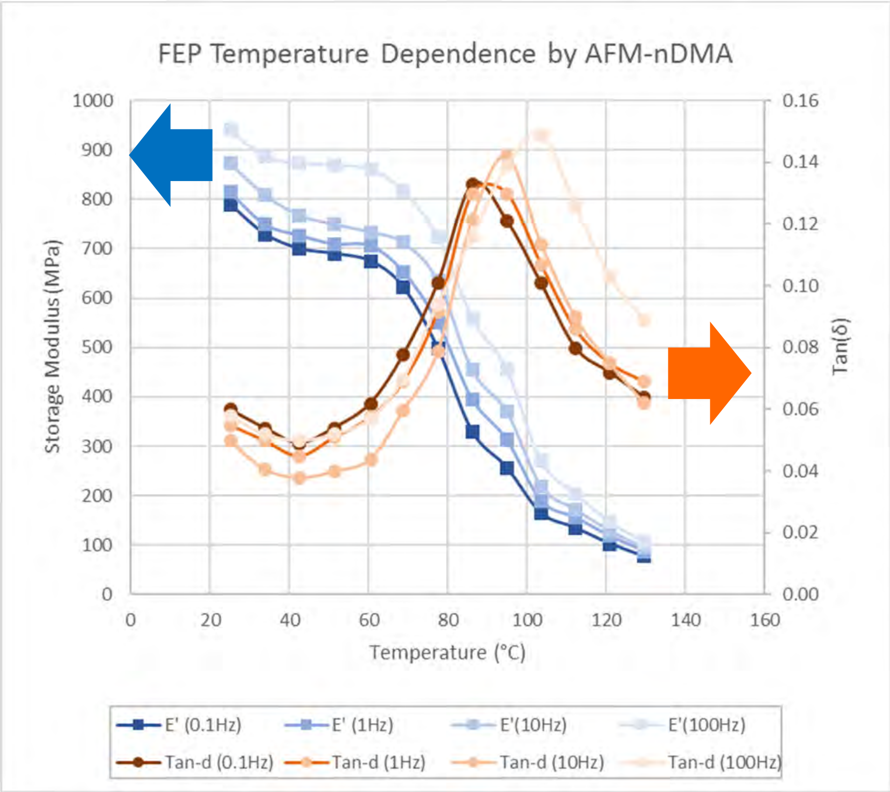


Activation energy analysis for a polymer
Arrhenius: ln(aT) = - Ea/R (1/T – 1/To)

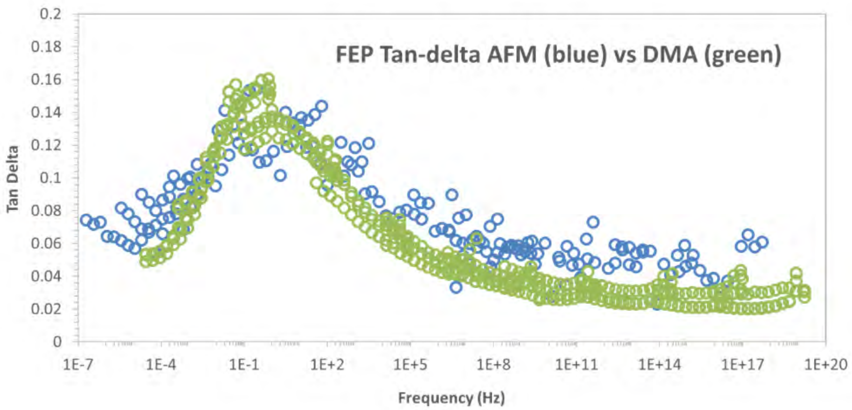


Temperature dependence for fluorinated ethylene propylene

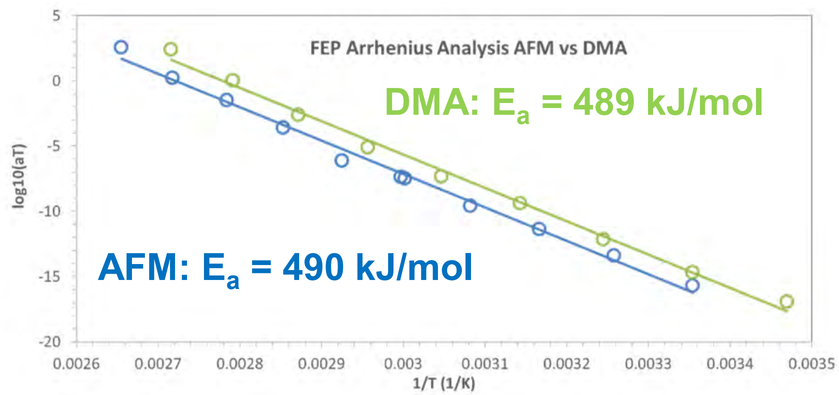
- Qualitatively shows expected behavior
- Glass transition apparent in storage modulus and loss tangent
- Expected frequency dependence
- How well does it match bulk?



Full TTS from AFM data
Compared to bulk DMA on same sample



WLF Loss Tangent Mastercurve



Arrhenius Activation Energy Analysis

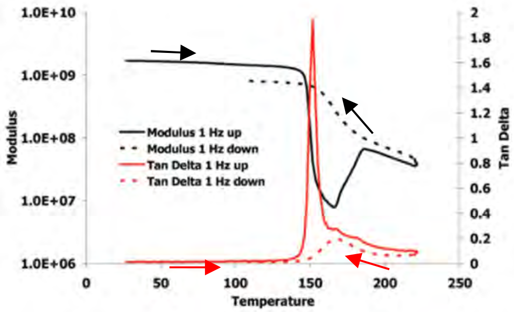
- Master curves from AFM-nDMA data match bulk DMA reasonably well including glass transition temperature and the strong change in properties there
- Arrhenius analysis of TTS shift factors from AFM data also agrees with bulk

Correlating changes in nanomechanical properties with microstructural changes

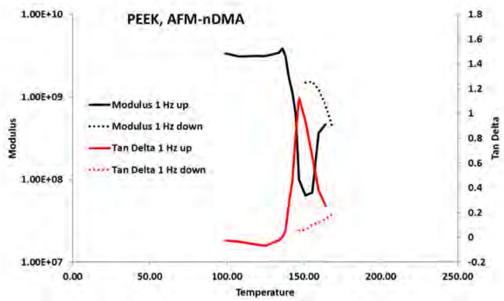
- Temperature controlled measurements of PEEK with AFM-nDMA spectra

- AFM-nDMA in agreement with bulk measurements
  - Irreversible change as sample crystallizes
  - Strong tan-δ peak at 150C, disappears on ramp down

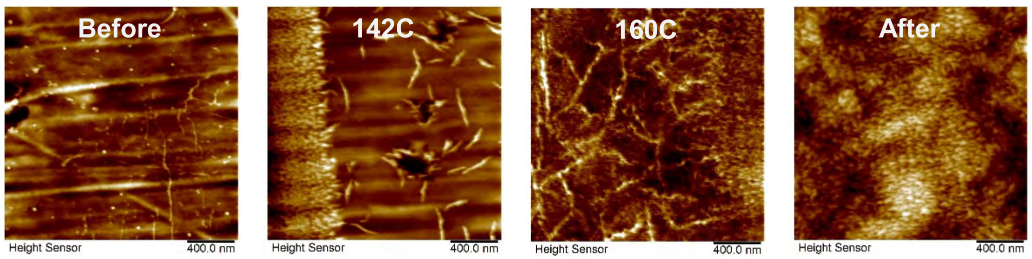
- AFM-nDMA provides both quantitative modulus data and correlated high-resolution structural information



Bulk DMA (Perkin Elmer)

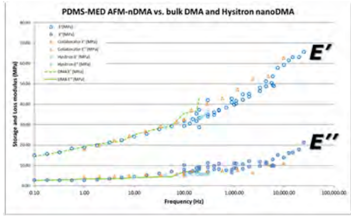


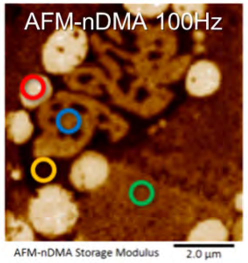
AFM-nDMA

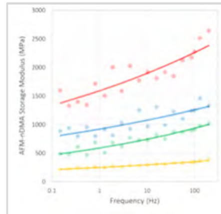


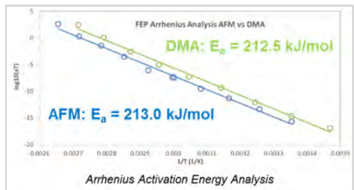
Summary
Viscoelastic analysis of polymers with the spatial resolution of AFM

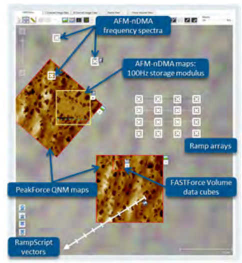
- AFM-nDMA measures E′, E″, tan(d) directly at rheological frequencies
- Linear measurement, corrected for intrinsic creep effects
- Results match well with Hysitron & bulk DMA
- AFM data allows for full TTS analysis
- Spatial resolution of better than 50nm







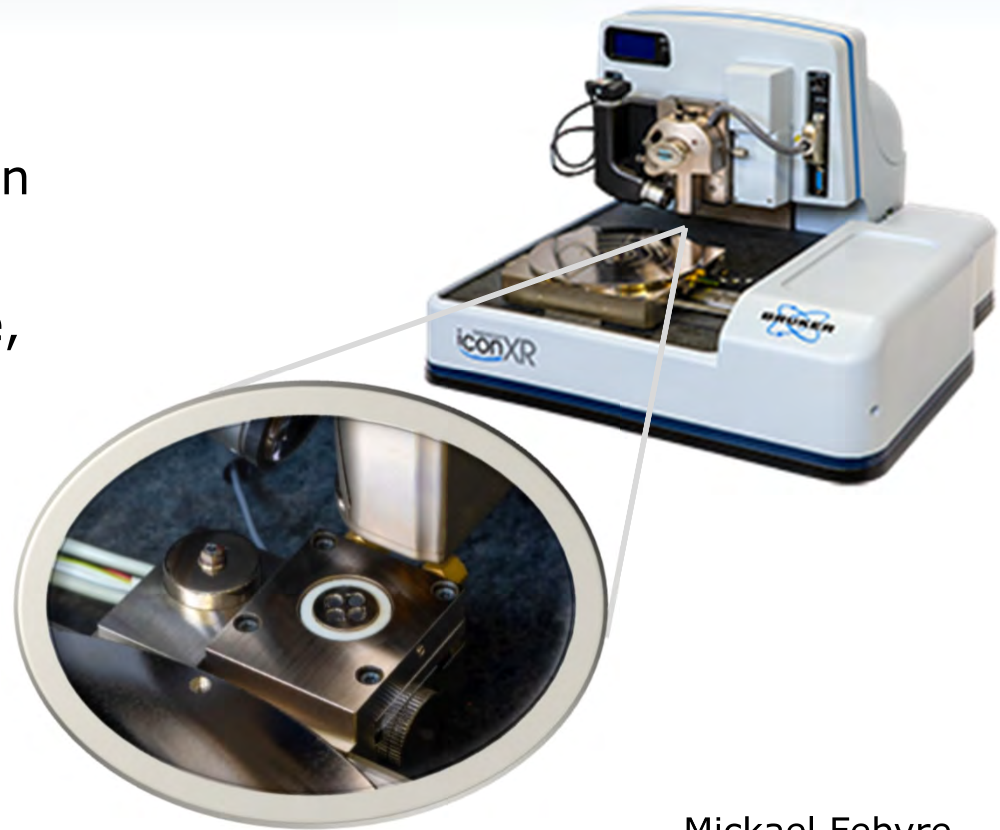




The AFM-nDMA product

BRUKER

- Accessory for Dimension Icon
- Includes hardware, software, test samples, calibrated probes
- HW is modular add-on to Dimension stage



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QUESTIONS?