Nondestructive characterization of advanced polymeric materials using spectroscopy and atomic force microscopy

Atomic Force Microscopy
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Atomic Force Microscopy
3D Optical Microscopy
Fluorescence Microscopy
Tribology
Stylus Profilometry
Nanoindentation

Innovation with Integrity
Sample Courtesy: Dr. Jamie Hobbs University of Sheffield
During Growth

PHB/V poly(hydroxybutyrate-co-valerate) crystal growth from amorphous phase after quenching. 20x20um scan (26MPixels) in TappingMode

After Growth

Sample Courtesy: Dr. Jamie Hobbs University of Sheffield
Spherulite growth rates are consistent with earlier measurements.

Front growth rate ~ const for each temperature.

Secondary Nucleation model ignores variations in growth rate of individual lamellae.

Rate of nucleation (T) affects spherulite structure.

![Graph showing spherulite growth rate vs. temperature](image)
Tapping Mode phase contrast inversion prevents consistent interpretation

Phase contrast depends on AFM configuration:
- Low tapping force, phase contrast due to adhesion
- At higher tapping forces, the elasticity may dominate
PeakForce QNM calculates sample properties directly from force curves

- Complete force-distance relation between tip and sample is analyzed in real-time, allowing:
  - Feedback based on the peak force, protecting the tip and sample
  - Mechanical properties mapped simultaneously with topography
  - Individual curves can be examined and re-analyzed offline
  - Off-resonance: allows combination with other techniques

\[ F - F_{adh} = \frac{4}{3} E^* \sqrt{R(d - d_0)^3} \]
Rapid growth of PeakForce Tapping publications

- Wide range of research areas
- ~75% are using PeakForce QNM for unique information it provides
- February 2015 update: Current count is >650 publications (Google Scholar returns >900!)
- Papers are overrepresented in ‘high impact’ journals
PeakForce QNM for high resolution imaging: Topography & Adhesion

“Green Chemistry Approach to Surface Decoration: Trimesic Acid Self-Assembly on HOPG”

- Molecular resolution with PF-QNM to complement STM results
  - Periodicity ~1.6nm
  - Adhesion map provides resolution similar to PFT topography
- PFT is able to characterize multilayers, STM not
- PFT more gentle than STM
  - Network disruption in images taken at 5 min intervals with STM
  - No disruption from PFT over 48 hours

PeakForce QNM for high resolution stiffness mapping

“Commensurate–incommensurate transition in graphene on hexagonal boron nitride”

- No signal in Contact or Tapping Mode
- Signal in Modulus and Friction as predicted, but not in Adhesion
- Periodicity depends on rotation of lattices, as does the width of the domain walls in the modulus signal
- Within the domains, graphene deforms to match the BN lattice

• Modulus was found to be linearly related to PVC mass fraction (\&T_g) in homogeneous blends, allowing interface composition to be inferred with resolution \sim 10\text{nm}

• Investigation of PnBMA/PVC interface interdiffusion after annealing (110\text{C}) for different durations
  • Diffusion length \sim \sqrt{t} with mutual diffusion coeff of 0.31\text{nm}^2/s
  • Step in composition appears in interface after 16hours

Applying Time-Temperature Superposition to Analyze Force Maps Across Frequency

“Nano-Palpation AFM and Its Quantitative Mechanical Property Mapping.”

- Long term goal: standardization of AFM modulus measurements for ISO standard (SBR/IR blend)
- Apparent modulus expected to be influenced by time dependent deformation and adhesion
- Comparison of JKR and DMT model analysis shows JKR better for these samples (DMT off by ~25%)
- TTS analysis based on WLF equation has good agreement with bulk measurements of storage modulus for PF-QNM at 250-1000Hz

The Challenge with Conductive Measurements on Soft samples

**Severe limitation**

- Electrical & mechanical property mapping based on contact mode
- Severe damage/contamination on polymer samples
- Compromised and low resolution measurements

“Perhaps one of the most significant practical challenges to using CAFM is obtaining a good electrical image without causing significant damage to the sample. Patience and a willingness to sacrifice many AFM cantilevers in the name of science, are often necessary.”

Combine Conductivity Measurement With PeakForce Tapping Force Control!

- Tip oscillates at 1kHz. Contact time is typically 20 – 200 µs
- Measure both current during contact time & peak current
- Requires very fast Conductive AFM electronics:
  - 20kHz bandwidth, <100fA noise
  - Range <100fA to >100nA
PeakForce TUNA for quantitative property measurement of V:Ti/SEO nanocomposite

“Quantitative Nanoelectric and Nanomechanical Properties of Nanostructured Hybrid Composites by PeakForce TUNA.”

• “[PF-TUNA] allows one to simultaneously map the topography, modulus, adhesion, and conductivity of advanced materials on delicate samples that cannot be imaged with conventional conductive AFM.”

• Current correlated to positions of individual particles in topography

• High adhesion and low current are observed at the nano particle boundaries rich in PS phase

PF-TUNA for high-resolution mapping of current on polymer-nanotube composites

“Nanoscale investigation of the electrical properties in semiconductor polymer-carbon nanotube hybrid materials.”

- Topographic imaging can confirm that the CNTs are dispersed and the P3HT fibers grow perpendicular to the CNT
- High-res PF-TUNA current map impossible in Contact Mode
  - Indicates current is controlled by the spreading resistance
- Negligible lateral forces and normal force ~50pN make it possible to map current distribution over individual nanofibers

KPFM-Kelvin Probe Force Microscopy

KPFM measures the work function difference of tip/sample.

<table>
<thead>
<tr>
<th>AM</th>
<th>Amplitude-Modulation</th>
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</thead>
<tbody>
<tr>
<td><strong>FM</strong></td>
<td>Frequency-Modulation</td>
</tr>
<tr>
<td>✓ Better spatial resolution</td>
<td></td>
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<tr>
<td>✓ Better accuracy</td>
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Combine with PF-QNM:
- Improved sensitivity
- Mechanical property mapping

Physical Review B 2005, 71(12) 125424
PF-KPFM for quantitative characterization of work function

“Remove the Residual Additives toward Enhanced Efficiency with Higher Reproducibility in Polymer Solar Cells.”

**PF-KPFM surface potential images**

- **Pure polymer**
- **Device A**
- **Device B**
- **Device C**

- PF-KPFM shows that the methanol wash (Device C) increased the work function difference.
- This reduced the electron injection barrier, leading to better device performance.

PeakForce KPFM for correlated property mapping

“Giant switchable photovoltaic effect in organometal trihalide perovskite devices”

- Switchable photocurrent 10000x larger than on other ferroelectric photovoltaics!
- PeakForce KPFM was used to correlate topography, Potential and Adhesion
  - Ruled out topographic influence on work function
  - Confirmed presence of a different material
- Variation in work function and adhesion is thought to be due to ion motion during poling

Summary: AFM with PeakForce Tapping

**Empowering Polymer Researchers with Nanoscale Information**

- Atomic Force Microscopy excels at investigating surfaces and interfaces.
- PeakForce Tapping improves on previous AFM modes, providing precise force control for routine high-resolution imaging.
- PeakForce QNM, TUNA, and KPFM enable quantitative property maps to be captured along with topography, providing new insight into nanoscale sample behavior.
- Adoption of PeakForce Tapping technology has seen rapid growth in many research areas as demonstrated by the ever increasing number of high impact publications since its release.