Biomaterial Characterization Using Nanoscale Thermal Analysis and IR Spectroscopy

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About Anasys Instruments

- Founded in 2005 to expand the capabilities of probe microscopy and nanoscale characterization
- Over 100 years of combined experience in SPM, spectroscopic and thermal sciences
- Pioneers in
  - nanoscale thermal analysis
  - nanoscale IR spectroscopy

Santa Barbara, CA
Enabling Technology

*Developed in collaboration with inventor Prof. W. King, UIUC
*Manufactured in partnership with

<table>
<thead>
<tr>
<th>Key Features</th>
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</thead>
<tbody>
<tr>
<td>Controllable probe temperatures up to 450°C</td>
</tr>
<tr>
<td>Heating rates up to 600,000°C/minute</td>
</tr>
</tbody>
</table>

ThermaLevers™ Probes*

- Less than 30 nm end radius

AFM Phase Image

700 nm Scan on Rubber Blend
Characterizing Morphology

Sample: Environmental Stress Cracking of Polyurethane

Sample: Polypropylene, Polyethylene and “rubbery” phase
Sample: Polypropylene, Polyethylene and “rubbery” phase
The Study of Interfaces

Interfaces ≠ Bulk

Polymer + Polymer
Polymer + Air
Polymer + Substrate
Sample: PA6-PET Blend

AFM Phase Image showing interface

Annealing Temp vs Bulk % Crystallinity

<table>
<thead>
<tr>
<th>Annealing Temp</th>
<th>% crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>3.8%</td>
</tr>
<tr>
<td>110°C</td>
<td>3.4%</td>
</tr>
<tr>
<td>115°C</td>
<td>6.2%</td>
</tr>
<tr>
<td>120°C</td>
<td>5.4%</td>
</tr>
<tr>
<td>135°C</td>
<td>22.5%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Annealing Temp</th>
<th>Amorphous Tg</th>
<th>Crystalline Melt (onset)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>87.1°C</td>
<td></td>
</tr>
<tr>
<td>110°C</td>
<td>88.1°C</td>
<td></td>
</tr>
<tr>
<td>115°C</td>
<td></td>
<td>207.4°C</td>
</tr>
<tr>
<td>120°C</td>
<td></td>
<td>212.3°C</td>
</tr>
<tr>
<td>135°C</td>
<td></td>
<td>204.3°C</td>
</tr>
</tbody>
</table>

NATAS 2010 - Characterizing the Surface Crystallinity of Polymers using Nano-scale Thermal Analysis
Sample: ultra thin coatings of PS and PMMA

$t > 100$ nm
Slight increase of $T_g$ with decreasing the film thickness regardless of the molecular weight

$t < 100$ nm
Slight decrease of $T_g$ with decreasing the film thickness regardless of the molecular weight
When Interface Properties Dominate

1) Small/complex morphology

2) Surface sensitive interactions

3) Thin coatings
NanoTA allows for localized thermal property measurements/mapping

Reliable & Reproducible

Sample: Boundary Layer in a Polyurethane insulation
TTM image 100x50um
Drug Dispersion & Coating Thickness

100um x100um micron Acetaminophen-HPMC mixture
Where AFM meets IR spectroscopy

nanoIR
Diffraction Limits of IR

\[ d = \frac{1.22\lambda}{NA} \]

<table>
<thead>
<tr>
<th>Sampling Method</th>
<th>Diffraction limited resolution*</th>
<th>Practical resolution limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission</td>
<td>(2\lambda)</td>
<td>(~10-30 \mu m)</td>
</tr>
<tr>
<td>ATR</td>
<td>(0.5\lambda)</td>
<td>(~3-10 \mu m)</td>
</tr>
</tbody>
</table>

Normalized Band Area

Distance (\( \mu m \))

\(~8 \mu m\)
nanoIR—how it works

- Deflection Laser
- Photodiode
- Cantilever
- Sample
- Prism
- Pulsed, tunable IR Source

- Cantilever ringdown
- Time
- Frequency
- Spectrum
- Wavenumber

- FFT
- Amplitude
- Deflection
### Spectrum creation

#### Absorption Spectrum

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Spectral Range</td>
<td>1200*-3600 cm(^{-1})</td>
</tr>
<tr>
<td>Spectral Resolution</td>
<td>&lt;16 cm(^{-1})</td>
</tr>
<tr>
<td>Max Image Size</td>
<td>100 um x 100 um</td>
</tr>
<tr>
<td>Spectral acquisition time</td>
<td>~1 minute per spectrum (or less)</td>
</tr>
</tbody>
</table>
Mechanical property imaging

Topography

Contact resonance

nanoIR: Nanoscale IR Spectroscopy
Biodegradable Polymer blends

Topography

IR Absorption at 1725 cm$^{-1}$

Point spectrum
Mapping viral infection of *E. coli* bacteria

T5 bacteriophage

No infection

Partially invaded

Largely invaded

This work was supported in part by NIST-ATP Award #70NANB7H7025 and the National Science Foundation Award NSF-SBIR 0750512. Collaborator acknowledgements do not imply endorsements from respective institutions.
Multifunctional measurements

A Topographic

EAA  Nylon  EAA

2 µm

B Spectroscopic

C Mechanical

D Thermal
Conclusions

- nanoTA allows us to probe the thermal properties of sub-micron morphologies
  - Heterogeneous structure
    - MW
    - Crystallinity
    - Cross link density
  - Depth profiling
  - Surface properties
- nanoIR allows for unique chemical identification on sub-micron morphologies
  - Powerful combination of
    - Chemical
    - Mechanical