Transition Temperature Microscopy
Nano-scale Thermal Analysis Technique

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Outline

• Introduction to Nano Thermal Analysis (NanoTA)
• Technology Overview
• Transition Temperature Microscopy (TTM)
• Applications in materials science and engineering
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
Sample Limitations for Normal Thermal Analysis

- **TMA** – 500um diameter/5um thickness (minimum quartz probe dia. of 200um)
- **DSC** – 0.100mg highly crystalline materials, 2-10 mg amorphous
- **TGA** – 5-10mg depending on maximum loss anticipated
- **DMA** – sample geometry is mode specific
Nano Thermal Analysis

ThermaLever™ Probe

Sample

\[ T_g = 152.4 \, ^\circ C \]
Atomic Force Microscope

[Diagram showing the components of an Atomic Force Microscope: laser beam, cantilever, tip, sample, xyz-stage, and 4 quadrant photo detector.]

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Enabling technology

ThermaLevers™ Probes*

- Controllable probe temperatures up to 450°C
- Heating rates up to 600,000°C/min

* Manufactured in partnership with

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Three crystalline samples and three amorphous samples were measured by bulk ThermoMechanical Analysis (TMA) and compared against LTA measurements.

\[
y = 1.0088x - 3.8173 \quad R^2 = 0.9811
\]

\[
y = 1.0027x + 0.2778 \quad R^2 = 0.9701
\]

\[
y = 1.0047x + 2.9657 \quad R^2 = 0.9581
\]

Slopes: 1.003 - 1.009
Offsets: -4 to +3°C

Data courtesy of G. Meyers and A. Pasztor, DOW
Technology Platforms

**nanoTA2**
Add-on accessory for AFM users

**VESTA**
Stand-alone Localized Thermal Analysis

AFM +

2007 WINNER 2007 WINNER 2008 WINNER

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Example: Multilayer Film

An optical image and nano-TA measurement on the four layers in a multilayer film composed of Nylon, PET and two forms of low density polyethylene.
VESTA head

Brightfield Optical Microscope

- Rapid, automated nano-TA measurements
- No AFM expertise required
- Transition Temperature Microscopy (TTM)

Motorized XY and Z Stages
Transition Temperature Microscopy

Tip engages to surface

Tip heating

Measure local thermal transitions

Automatically identify transition temp. T=132.4 °C

Color code phase transitions into map pixel by pixel

TTM image shows transition temperature variations

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Example TTM: LCD Multilayer Film

- High resolution thermal imaging and analysis
- Automated pixel by pixel analysis
Selected Medical Device Applications

- UHMWPE Orthopaedic Bearings
- Polyurethane Stress Corrosion Cracking
- Drug Coated Stents
- Extruded Catheters
- Contact Lenses
Example – Orthopaedic UHMWPE

PE (GUR 1050) 5 x 10^6 MW:
- Virgin
- Radiation cross-linked 100kGy

Vitamin E = alpha tocopherol
- Plasticization effect

Less alpha-tocopherol
More alpha-tocopherol
Example Explant UHMWPE Knee Bearing

Examine 2 specimen regions:
- Multiple thermal transitions in damaged region
- Undamaged region LTA like virgin material
Selected Medical Device Applications

- UHMWPE Orthopaedic Bearings
- Polyurethane Stress Corrosion Cracking
- Drug Coated Stents
- Extruded Catheters
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Example: Polyurethane Stress Corrosion

Environmental aging greatly lowers Tm

- 0.1 M CoCl₂, 20% H₂O₂
- 37°C
- Constant 250 g pull
- H₂O₂ changed 3X/week
- 1 month

Andy Hung(1), Khoren Sahagian(2), Mike Colvin(1), Roshan Shetty(2)
1) Boston Scientific, Valencia, CA, 2) Anasys Instruments, Santa Barbara, CA
Example: Polyurethane Stress Corrosion

- ESC domain: 122.5°C
- Polyurethane: 135.2°C
Selected Medical Device Applications

- UHMWPE Orthopaedic Bearings
- Polyurethane Stress Corrosion Cracking
- Drug Coated Stents
- Extruded Catheters
- Contact Lenses
Example: Drug Coated Stents

<table>
<thead>
<tr>
<th>Stent Type</th>
<th>Formulation</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand X</td>
<td>PDLLA + Drug A + excipients</td>
<td>Solvent 1</td>
</tr>
<tr>
<td>Brand Y</td>
<td>PDLLA + Drug B + excipients</td>
<td>Solvent 2</td>
</tr>
<tr>
<td>Brand Z</td>
<td>PDLLA + Drug C + excipients</td>
<td>Solvent 3</td>
</tr>
</tbody>
</table>

Local Thermal Analysis Maps of Drug Distribution
Selected Medical Device Applications

- UHMWPE Orthopaedic Bearings
- Polyurethane Stress Corrosion Cracking
- Drug Coated Stents
- Extruded Catheters
- Contact Lenses
Example: Extruded Catheters, Contacts

Catheter LTA - Tm

Contact Lens LTA – Tg (dry hydrogel)

Catheter Tm - very uniform

Contact lens Tg - not consistent
Additional Applications

- Thermal mapping of composites and polymer blends
- Characterizing defects
- Mapping film heterogeneity
- In situ analysis of coating/thin film
- Detecting weathering/degradation
Applications

- Thermal mapping of composites and polymer blends
- Characterizing defects
- Mapping film heterogeneity
- In situ analysis of coating/thin film
- Detecting weathering/degradation
Impact Modified Polymers

Sample: Polypropylene, Polyethylene and “rubbery” phase
TTM - Polymer Blend

Polystyrene and Poly(methyl methacrylate) polymer blend

Scan size 100 x 100 microns.

TTM clearly differentiates the different Tg values of the two materials

100 x 100 um TTM image
TTM: Fiber Reinforced Composites

Interfacial bonding is critical to performance

Contributed by Khoren Sahagian, Anasys Instruments

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Applications

• Thermal mapping of composites and polymer blends

• **Characterizing defects**

• Mapping film heterogeneity

• In situ analysis of coating/thin film

• Detecting weathering/degradation
Sidewall Haze

- Analyze amorphous/crystalline content across the sample

Data courtesy of L. Germinario, Eastman Chemical
Defects in Extruded Film - Blood Bag

85°C
65°C
100um
Applications

- Thermal mapping of composites and polymer blends
- Characterizing defects
- **Mapping film heterogeneity**
- In situ analysis coating/thin film
- Detecting weathering /degradation
Thin Film Heterogeneity

Measurement of the transition temperature gradient across a thin film
Mapping across PET bottle wall

PET Bottle Cross Sections

Measurements by K. Sahagian
Polyolefin Blown Film

Histogram of transition temperatures

TTMs show inhomogeneous crystallinity

Good!

LESS crystalline

Bad!

MORE crystalline

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Applications

- Thermal mapping of composites and polymer blends
- Characterizing defects
- Mapping film heterogeneity
- In situ analysis coating/thin film
- Detecting Weathering/degradation
TTM: Solid Lubricant Coating

Measurement of coating uniformity of lubricant

100um
Fiber Coupler-Mounting

Tg measurement of the thin epoxy layer holding the fiber to the substrate
Applications

- Thermal mapping of composites and polymer blends
- Characterizing defects
- Mapping film heterogeneity
- In situ analysis coating/thin film
- Detecting weathering/degradation
TTM: Weathering of PET Sheet

Transition Temperature Microscopy Images

Unexposed to UV light

Exposed to UV light

Transition Temperature peak shifted by ~ 90°C due to weathering
Summary

• Nanothermal analysis enables measurements of thermal properties on the micro and nanoscale
• Material characterization & identification
• Spatially and time-resolved measurements
• Transition Temperature Microscopy allows automated visualization of structure and heterogeneity
• Broad applicability in material science and engineering
Three crystalline samples and three amorphous samples were measured by bulk ThermoMechanical Analysis (TMA) and compared against LTA measurements.

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Polymer Standard Based Calibration

Three crystalline polymer samples are used to calibrate the tip-sample interface temperature.
Advantages of tip heating

• Heating rates up to 600,000 C/min
• Wide range of rate dependent studies
• Avoid re-crystallization
Pharmaceutical Tablets

100x100 micron Acetaminophen-HPMC mixture