Nanoscale Thermal Analysis

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Research Challenges for Nanomanufacturing Systems
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Motivations

• Nanomanufacturing needs characterization for research, product development & process control.
  – “You can’t manage what you can’t measure”

  Rear Admiral Grace Hopper:
  – “One accurate measurement is worth one thousand expert opinions”

• Successful nanomanufacturing needs robust, easy-to-use instruments
  – Instruments operated by technicians and manufacturing floor personnel
Some driving questions…

• What the &%*# is that?
• Where did component X go?
• What phase is my material?
• Throughput…

Syndiotactic polystyrene
High Impact Engineering Plastic

AFM images courtesy of Veeco Instruments
AFM Introduction

**Diagram:**
- **Setpoint** → **Error** → **Gain**
- **Cantilever motion**
- **Z drive**
- **Laser**
- **XY scan**
- **Photodetector**
- **Atomic Force Microscope (AFM) Image**

**Instruments:**
- Z drive
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**Keywords:**
- Atomic Force Microscope (AFM)
- Image
- XY scan
ThermoMechanical Analysis (TMA)

Thermomechanical analysis measures sample displacement as a function of temperature, time and applied force.

- Identify thermal transitions (e.g. glass transitions)
- Transitions signatures of material composition
Microfabricated Thermal Probes*

- \( R = \frac{V}{I} \sim \) Tip Temperature \( (T) \)
- \( \Delta T \) direct measure of absorbed heat
- Also heat locally to measure thermal expansion

* Developed in collaboration with Prof. W. King, UIUC
Nano Thermal Analysis (NanoTA)

• AFM probe with an integrated heater to measure thermal properties of samples

• Ramp tip temperature and monitor the lever to see observe thermal transitions (Tg, Tm)
Correlation to Bulk Thermal Analysis

Three crystalline samples and three amorphous samples were measured by TMA (left) and DSC (right) and compared against nano-TA measurements.

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

Slopes: 0.995 - 1.002
Offsets: +2 to +7°C

Data courtesy of G. Meyers and A. Pasztor, DOW
Example Applications

- Thermal analysis can enable localized identification of components in blends, composites, multilayers
- Detection of material changes caused by wear, defects, UV exposure, etc.

A scan of a PS-PMMA blend (left) showing the indents in the surface caused by the temperature ramps. The temperature ramps taken on the blend are shown on the right.
Advantages over bulk thermal analysis

- Conventional AFM images with sub-30nm spatial resolution
- Thermal analysis on heterogeneous samples with sub-100 nm resolution
- Local heating to over 500 °C at heating rates up to 600,000 °C/min
  - Eliminates thermal drift issues that plague bulk sample heating approaches
  - Provides much faster sample throughput
- Map the temperatures across the sample with a resolution of <0.1 °C
Sample: Toner particles embedded in epoxy and microtomed
Shown below is a 15 x 7.5 µm topographic scan of toner particles embedded in epoxy and microtomed. To the left are the corresponding nano-TA scans.
The AFM images reveal different microstructures and the nano-TMA results show very different behavior through the glass transition.

Data averaged from 3 lenses.
The existence of different solid-state forms such as polymorphs, solvates, hydrates, and amorphous form in pharmaceutical drug substances and excipients have downstream consequences in drug products and biological systems.
Scanning Thermal Microscopy

• AFM image with simultaneous nanoscale temperature metrology

Magnetic recording head

Epoxy composite
Point & Click Nanothermal Analysis

Brightfield Optical Microscope

Laser Detection System

XY Stage

Thermal Probe

Sample
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.
Summary

• Nano-TA extends the capabilities of the AFM by adding localized thermal analysis for localized identification of components and material forms in nanoscale polymers, pharmaceuticals and devices

• Scanning Thermal Microscopy can map thermal conductivity and temperature distributions

• New instruments allow rapid, automated, easy to use localized thermal analysis in environments ranging from R&D to process quality control
Backup
NanoTA AFM accessory

New DSP based control electronics and software have been designed to more accurately control the nano-TA probes with faster ramping and improved signal to noise. This controller is an accessory that operates on most commercial SPMs.