Dynamic Nanoindentation Characterization: nanoDMA III

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Elastic-Plastic vs. Viscoelastic Materials Response

nanoDMA® Technology

Application Examples

- Elastic-Plastic
  - Thin-Hard-Coating
  - PM 2000 alloy
- Viscoelastic
  - 3D-Printed Polylactide
  - Silicone with crosslinking agent
  - Polycarbonate
Materials Covered in this Presentation

- Materials Properties
  - Elastic-Plastic Response
  - Viscoelastic Response
- Easy to identify by quasi-static indentation

Load-Displacement Curve

Materials Covered in this Presentation:

- Al\textangle 100\rangle
- PC
Materials Covered in this Presentation

- Materials Properties
  - Elastic-Plastic Response (Oliver&Pharr)
  - Viscoelastic Response
- Easy to identify by quasi-static indentation

**Load Function**

**Indentation Load (µN) vs Indentation Displacement (nm)**

- Unloading and Re-Loading Elastic
- Elastic and Plastic Deformation
- Al<100>
- PC
- Hysteresis
Materials Covered in this Presentation

**Elastic-Plastic Response**
- Thin Film Depth Profiling

**Viscoelastic Response**
- Investigation of Polylactide Filaments for 3D-printing.
- Comparision of nanoDMA III and Macro DMA tests on silicone with cross linking agent.
- Polycarbonate – Mastercurve.
Transducer & Controller Core Technology

- Capacitive displacement sensing
- Small inertia of moved parts <1 g
- Low intrinsic dampening

**Transducer Stability Specs**
- <0.2 nm displacement noise floor
- <100 nN force noise floor
- <0.05 nm/sec thermal drift

*Specs Guaranteed On-Site*

**Enabling Technology for Ultra-Small Materials Research**

- Load or Displacement Control
- 78 kHz Feedback Loop Rate
- 38 kHz Data Acquisition Rate
- Experimental Noise Floor <100 nN (Digital Controller)
- Enhanced Testing Routines
- Digital Signal Processor (DSP) + Field Programmable Gate Array (FPGA) + USB Architecture
- Modular Design
Quasi-Static Nanoindentation

Contact Depth ($h_c$)

$$h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S}$$

Contact Area ($A_c$)

$$A_c = f(h_c)$$

Initial Unloading Stiffness

$$S = \frac{dP}{dh}\bigg|_{h_{\text{max}}} = mA(h_{\text{max}} - h_f)^{m-1}$$

Power-law Fit to Unloading

$$P = A(h - h_f)^m$$

Elastic Modulus ($E$)

$$E_r = \frac{S \sqrt{\pi}}{2A_c}$$

Hardness ($H$)

$$H = \frac{P_{\text{max}}}{A_c}$$

Projected contact area (evaluated at maximum load)

Continuously measure properties as a function of contact depth, frequency, and time.

Dynamic force superimposed on quasi-static force
nanoDMA III Technology

- Lock-In Amplifier Frequency Range
- Frequency Range for Testing: 0.1 Hz – 300 Hz
- Typical Force Amplitude: 0.01 µN to 200 µN
- Typical Displacement Amplitude: 0.1 nm to 5 nm
CMX – Force & Displacement & Stiffness

- Dynamic Testing
  - Lock-In Amplifier
  - Force & Displacement vs. Time
  - Amplitude & Phase vs. Time
  - Stiffness vs. Time
  - CMX Profile: Hardness & Modulus

\[ E_r = \frac{S\sqrt{\pi}}{2\sqrt{A_c}} \]

\[ H = \frac{P_{\text{max}}}{A_c} \]

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Thin Film Nanoindentation

- DLC coating on high-strength steel
- Image of film edge on substrate
- In-situ SPM Metrology on coating:
  - Cross-Section Profile
  - Surface Roughness

**Steel Substrate:**
- Peak To Valley = 14.8 nm
- Average Roughness (Ra) = 2.5704 nm
- RMS Roughness (Rq) = 3.1151 nm

**DLC-Coating:**
- Peak To Valley = 4.5926 nm
- Average Roughness (Ra) = 0.3858 nm
- RMS Roughness (Rq) = 0.4599 nm

Film Thickness: 135 nm
Thin Film Nanoindentation

- 3 coatings on steel
- Berkovich Indenter
- CMX-depth profile

Steel Substrate

135 nm DLC
75 nm DLC
25 nm DLC
xSol High Temperature Stage
Nanomechanical Characterization at Temperatures up to 800°C

- Low Thermal Expansion Design
- Tight Temperature Control
- Uniform Sample Temperature
- Probe Tip Heating in Uniform Environment
- Easy Sample Mounting
- Atmosphere Control
- Fast Warm-up and Stabilization
- Constructed to Handle Temperatures up to ~1000°C; Limitation by Tip Material
Reference Creep Testing

- Quasi-static load is held constant (in this case 5 mN).
- A relatively small (∼1 nm) amplitude sinusoidal force is superimposed at user-specified frequency (in this case 220 Hz).
- Force amplitude, displacement amplitude, and phase shift are measured, allowing contact stiffness to be measured continuously.

\[
E' = \frac{k\sqrt{\pi}}{2\sqrt{A_c(h)}} \\
A_c = \left(\frac{k\sqrt{\pi}}{2E'}\right)^2
\]
nanoDMA III incorporates a reference frequency technique for thermal drift correction during the course of an experiment.

- Enables the measurement of contact area without relying on the raw displacement data. The continuously measured stiffness is used to accurately determine contact area and contact depth in-situ.
- In-situ drift compensation during long duration frequency sweeps and creep tests.

Calibrated tip area function relates contact depth to contact area:

\[ A(h_c) = C_1 h_c^2 + C_2 h_c + C_3 h_c^{1/2} + C_4 h_c^{1/4} + C_5 h_c^{1/8} + C_6 h_c^{1/16} \]
Converting Depth to Strain Rate

Tensile Testing

\[ \varepsilon = \frac{\dot{h}}{h} \]

- Uniform Stress
- Uniform Strain

Indentation Testing

The strain rate is the indenter velocity divided by the indentation depth.
(Pyramidal Indenter)

\[ \dot{\varepsilon} = \frac{\dot{h}}{h} \]

The mean contact pressure, is the applied force divided by the projected contact area. This is also the definition of hardness.

\[ \sigma = \frac{P}{A} = H \]
Steady State Creep

- Strain rate varies with stress and temperature:

\[ \dot{\varepsilon} = A\sigma^m e^{-Q/RT} \]

- Depth \( h \) and velocity \( \dot{h} \) are determined from a fit to the creep curve. Pressure equals the hardness value.
PM 2000 ODS Alloy: FeCrAl alloy with dispersed oxide nano-particles

High creep resistance of dispersion hardened materials
• Typical stress exponent $m = 20 \ldots 200$ (creep rate drops fast with stress)
• Interaction of dislocation with dispersed oxides:
  • Small particles can be passed by climbing
  • Line energy between particle and dislocation is reduce
  • Thermal activation and external stress needed
• Mechanism is highly dependent on external stress

Indenter Used: Berkovich – Sapphire
Shield Gas: 95%N5%H

Plot $\ln(\dot{\varepsilon})$ versus $\ln(H)$ and slope is stress exponent ‘m’.

<table>
<thead>
<tr>
<th>Temp. (C)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>78.5</td>
</tr>
<tr>
<td>500</td>
<td>15.7</td>
</tr>
<tr>
<td>600</td>
<td>8.6</td>
</tr>
<tr>
<td>700</td>
<td>8.2</td>
</tr>
</tbody>
</table>

$m \sim 80$: typical for ODS alloys

$m \sim 8$: thermal activated dislocation motion

## Viscoelastic Matter

<table>
<thead>
<tr>
<th>Domain of Testing</th>
<th>Strain Rate</th>
<th>Frequency</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant Strain Rate Testing</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indentation Creep Testing</td>
<td>x</td>
<td></td>
<td></td>
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<tr>
<td>Creep and Recovery Testing</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>nanoDMA III Testing</td>
<td>x</td>
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<tr>
<td>nanoDMA III Testing + xSol</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
Polylactide Characterization

- Viscoelastic Response
- Time Dependent Deformation
- Hardness depends on strain rate

Experimental:
- A constant strain rate is achieved by exponential loading.
- $T = 23^\circ$C
- Force Amplitude/Quasi-static Force $<<1$
- Dynamic Frequency 110 Hz
- Small displacement amplitude of 1-2 nm
Depth Profile

- Viscoelastic Response
- Time Dependent Deformation
- Reduced modulus is strain rate independent
- Hardness (stress under indenter) relates to a strain rate
• A load function with combined strain rate segments results in the respective hardness readings.

Strain Rate Spectrum

- High Strain Rates: Constant strain rate testing; 0.01 / 0.05 / 0.1 / 0.5 1/s (left)
- Low Strain Rates: 1 hour reference creep experiment

• High Strain Rates: Constant strain rate testing; 0.01 / 0.05 / 0.1 / 0.5 1/s (left)
• Low Strain Rates: 1 hour reference creep experiment
Temperature Dependent Testing

- Temperature range for 3D printed parts
- Polylactide is thermoplastic
- What is the glass transition temperature $T_g$ about?
  - Structural changes
  - Mechanical changes

As 3D-printed

Deformed at $T>T_g$
**xSol Sample Heating Solution**

- Low Thermal Expansion Design
- Tight Temperature Control
- Uniform Sample Temperature
- Probe Tip Heating in Uniform Environment
- Interfaces with all testing modes:
  - Quasi-static Testing
  - nanoDMA III Testing
  - Scratch Testing
  - In-situ SPM imaging
Viscoelastic behavior tested between 23°C and 100°C:

- Creep response to a fast loading step
- Sample recovery after fast unloading
Creep and Recovery Analysis

Creep Rate = Creep displacement / Holding time (10s)
Recovery Rate = Recovery displacement / Holding time (10s)
Dynamic Model

- Experimental
  - Model fit   \( R=0.9999 \)

\[
F = F_o \sin \omega t
\]

\[
X_s = \frac{F_o}{\sqrt{(k-m\omega^2) + (C_s+C_i)\omega^2}}
\]

\[
\phi = \tan^{-1} \left( \frac{C_s+C_i}{k-m\omega^2} \right)
\]

\[
k = K_s + K_i
\]

\[
K_s = 2E_s \sqrt{\frac{A}{\pi}} = 2E_s h \sqrt{\frac{24.5}{\pi}}
\]

\[
K_s'' = C_s \omega
\]

- Mass of the indenter 350 mg
- System damping coeff. 0.01 Ns/m
- Specimen damping coeff. question mark
- Spring constant 300 N/m
- Contact stiffness question mark

S.A. Syed Asif, K.J. Wahl and R.J. Colton
Dynamic Measurement of Hardness, Reduced Modulus, Storage Modulus, Loss Modulus, Tan Delta

Typical displacement amplitude: 0.1 – 5 nm

The contact area is assumed to stay constant during the load cycle. No opening and closing at the edge of the contact area.

xSol Stage for Temperature Control:

- nanoDMA III testing between 23°C and 100°C
- 5 indentations per temperature
- Displacement amplitude 1 nm
- Dynamic test at 10 Hz at max load
xSol Stage for Temperature Control:

- $E'$, $E''$ and tan($\delta$) are averaged
- $E'$ drop from 23°C to 100°C
- Tan($\delta$) peak at approx. 80°C
Comparison of nanoDMA III and macro DMA storage modulus and tan delta for 4 silicone samples with varying amounts of crosslinking agent.
Polycarbonate Storage and Loss Modulus as a Function of Frequency and Temperature

Frequency: 10-300 Hz; Temperature: 75-175°C
nanoDMA III - Temperature

...Time-Temperature Superposition

Polycarbonate Tan Delta vs. Temp/Frequency

Polycarbonate Superposition Tan Delta

Predict viscoelastic properties over a broad frequency range, well outside the experimental range actual measurements can be conducted...
Polycarbonate 150°C Master Curves

Combine Frequency Sweeps and Use WLF Equation for a Full Time-Temperature Analysis

\[
\log \alpha_T = -14.34(T - 150) \frac{49.69 + (T - 150)}{}
\]
Bruker’s improved nanoscale dynamic mechanical testing enables:

- A truly continuous measurement of $x$ ($x =$ hardness, storage modulus, loss modulus, complex modulus, tan-delta, etc.) as a function of contact depth, frequency, and time.
- Application and testing accuracy across a wide range of materials—from hydrogels to ultra-hard coating.
- Drift correction allows for long-duration frequency sweeps and creep tests to be reliably performed.
- Overcomes the inaccuracies of stiffness measurements on viscoelastic materials when employing quasi-static indentation. Measurements of $E'$, $E''$ and tan delta comparable to measurements at larger length scales.
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