PRESSING AHEAD: UNVEILING MATERIAL INSIGHTS THROUGH DYNAMIC NANO-INDENTATION

Shivesh Sivakumar
Senior Engineer,
Covalent Metrology

July 25, 2024 at 11 AM Pacific Time

COVALENT METROLOGY

COVALENT ACADEMY
Industrial Applications of Advanced Metrology
Episode 38

Welcome, Viewers

COVALENT METROLOGY

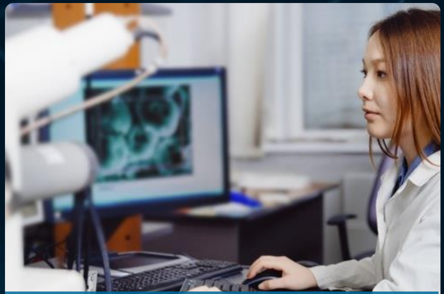
Modern, digitally-empowered analytical services platform delivering quality data and expert analysis to accelerate advanced materials and device innovation.

Comprehensive Solutions Stack

- *50+ Cutting-edge instruments in-house, 150+ Techniques*
- *Analytical Services*
- *Advanced Modeling*
- *Method Development*
- *Custom Consulting Solutions*

High-touch, High-Quality Services

- *Ionic Membership Program*
- *Enterprise Metrology Solutions*
- *Instant, Secure Access to Data and Reports*
- *Expanding Toolkit in Custom Digital Platform*

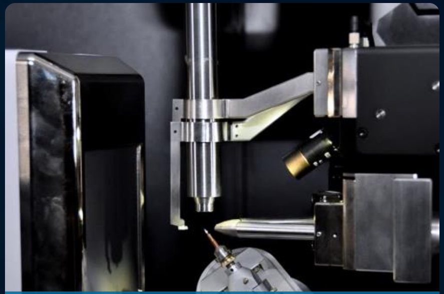


Flexible Business Models

- *LiveView^{TM} (real-time collaboration)*
- *Co-op and Tool-share Opportunities*
- *Training and Certification on Instrumentation*
- *Laboratory Audits*

Rich Network of Partnerships

- *Partner to World's Leading Instrument Manufacturers and Labs*
- *Expanding access to Advanced Instruments and Analysis Tools*
- *Lab Connections and Applications Learning*



Who We Are, Who We Serve

- *50+ People, 14 PhDs*
- *Comprehensive, Modern Analytical Capabilities*
- *$20M +State-of-art Lab in Sunnyvale, CA*
- *600+ Clients, 15-30 new clients / week*

Covalent's Analytical Services & Technical Groups

COVALENT METROLOGY

Enterprise Metrology Solutions: Failure Analysis & EM

Electron Microscopy

- S/TEM
  with EDS; EELS; Electron Diffraction; SAED
- FIB-SEM & HR-SEM
  with EDS; EBSD; 3D Tomography
- Lamella Preparation
  incl. specialized lift-outs

Failure Analysis

- Root-Cause Failure Analysis
- DPA / Mechanical X-section
- Dye & Pry Test
- Hot Spot Detection
- Emission Microscopy
- NIR / IR Imaging
- EBIC / OBIC failure analysis

Materials, Chemicals, and Surfaces

Microscopy & Profilometry

- Chromatic Aberration
- Digital Optical Microscopy
- Laser Scanning Confocal Microscopy
- White Light Interferometry
- Scanning Acoustic Microscopy (SAM)

Analytical Chemistry

- Mass Spectroscopy:
  ICP-MS and LA-ICP-MS; GCMS
- ICP-OES / GDOES
- Raman
- NMR (solid / liquid + 1,2,3 nuclei)
- XPS, UPS, ISS
- SIMS, TOF-SIMS

X-ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micro-computed X-ray Tomography (Micro-CT)
- 2D / 2.5D / 3D X-ray Inspection & X-ray Radiography
- ED-XRF / WD-XRF

Mechanical Testing

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM, PiFM)
- Nano-indent / Nano-scratch
- Rheometry / Viscosity
- DMA / TMA (bend/stretch/compression)
- Tensile testing

Misc. Material Properties

- Thermal Analysis: DSC, TGA
- Surface Zeta Potential
- Porometry / Pycnometry
- Gas Adsorption / Chemisorption
- Foam Density / Skeletal Density / Tap Density
- Particle Analysis: DLS / ELS / size distribution / zeta potential

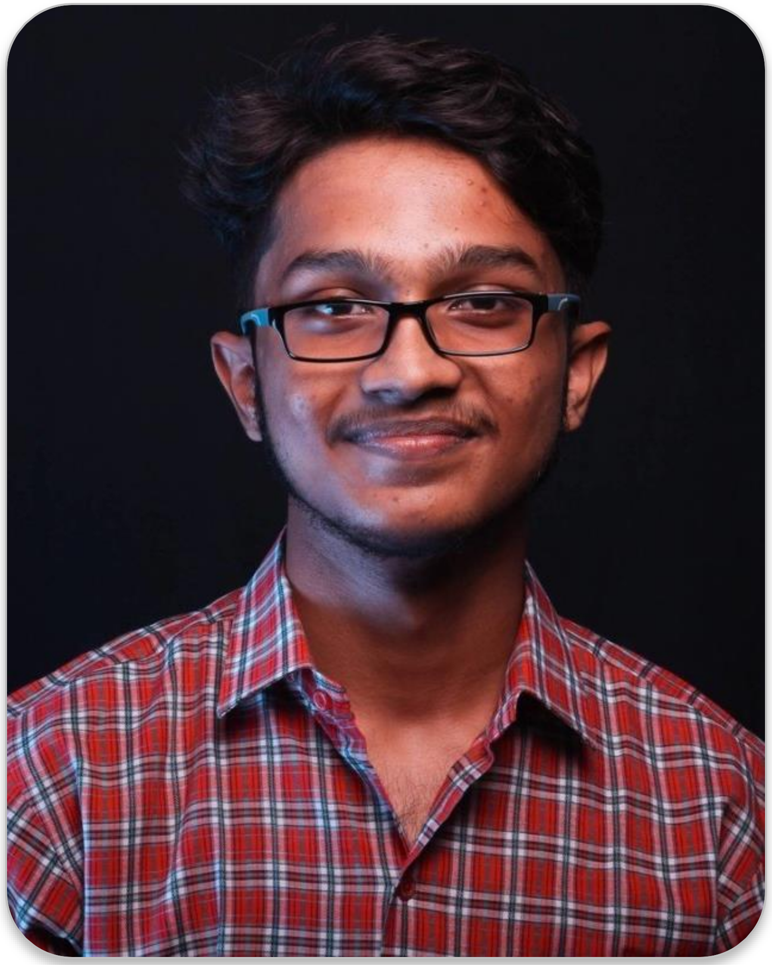
Optical Characterization

- Fourier Transformed Infrared Spectroscopy (FTIR and ATR-FTIR)
- Spectral Ellipsometry & Advanced Optical Modeling
- UV-Vis-NIR Spectroscopy

Introducing Today's Speaker

Shivesh Sivakumar

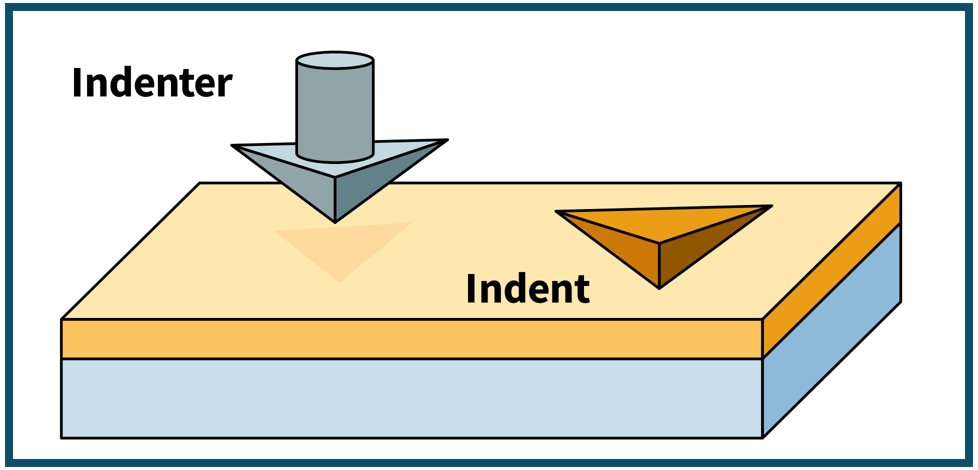
Member of Technical Staff, Materials, Chemistries and Surfaces
Covalent Metrology

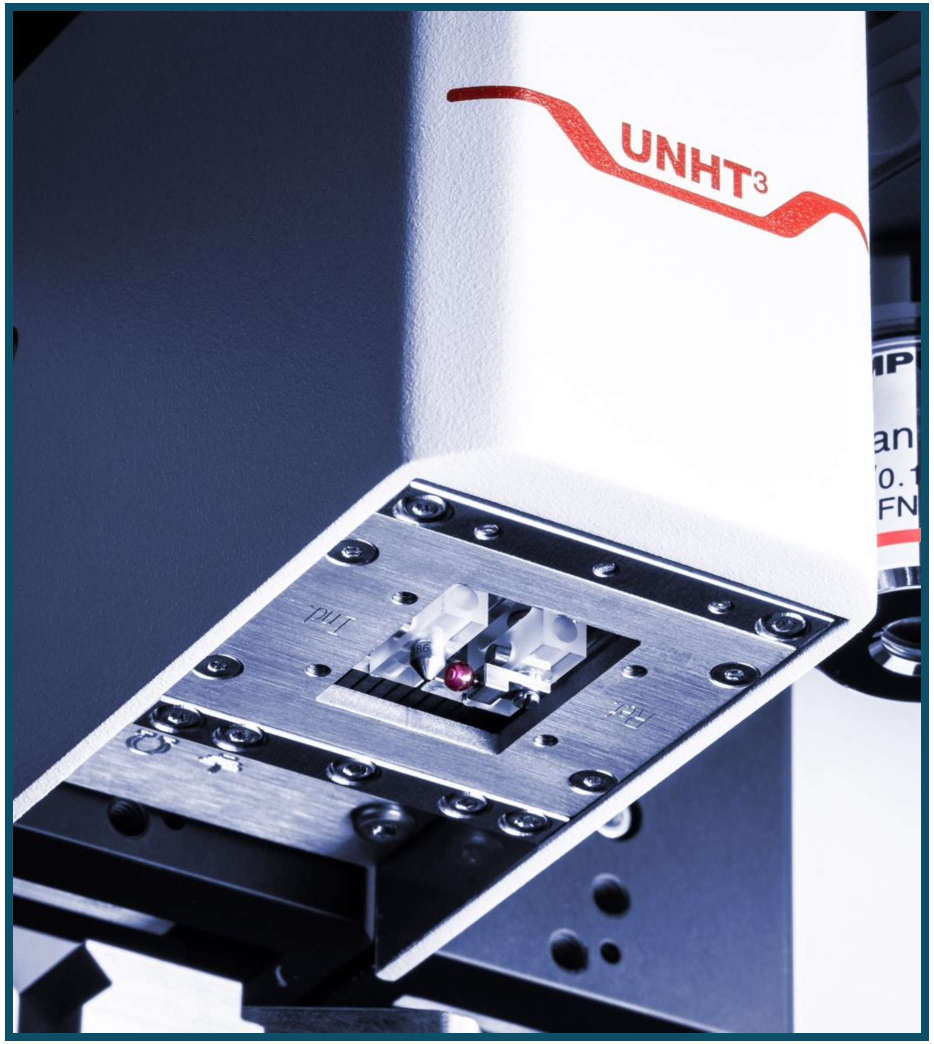


- Shivesh joined Covalent 3 years ago as a Senior Engineer and established a **proven record interfacing with customers and scoping effective testing strategies**.
- He has risen quickly to **lead the company's thermal and mechanical testing sectors** and was promoted in 2024 to his current MTS role.
- **Experienced in various experimental and theoretical techniques**, including **nanomechanical testing methods**, scanning probe microscopy, and *ab initio* modeling.
- Shivesh completed his **B.Tech in Materials Engineering at NIT Tiruchirappalli, India**, and an **M.S. at the University of Washington in Seattle**.

Overview

- Background on nano-indentation
- Instrumentation (Anton Paar UNHT³)
- Introduction to dynamic nano-indentation (Sinus)
- Case studies with Sinus
  - Curing of epoxy adhesive
  - Stress-strain analysis of polymer film

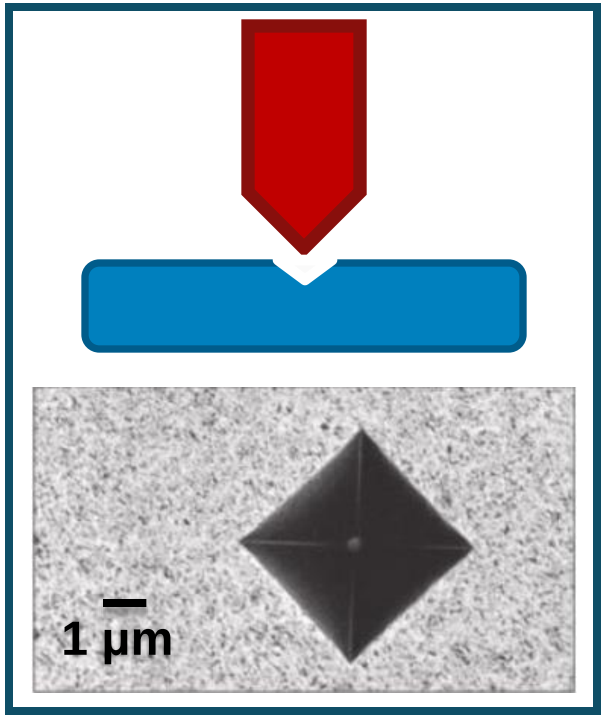


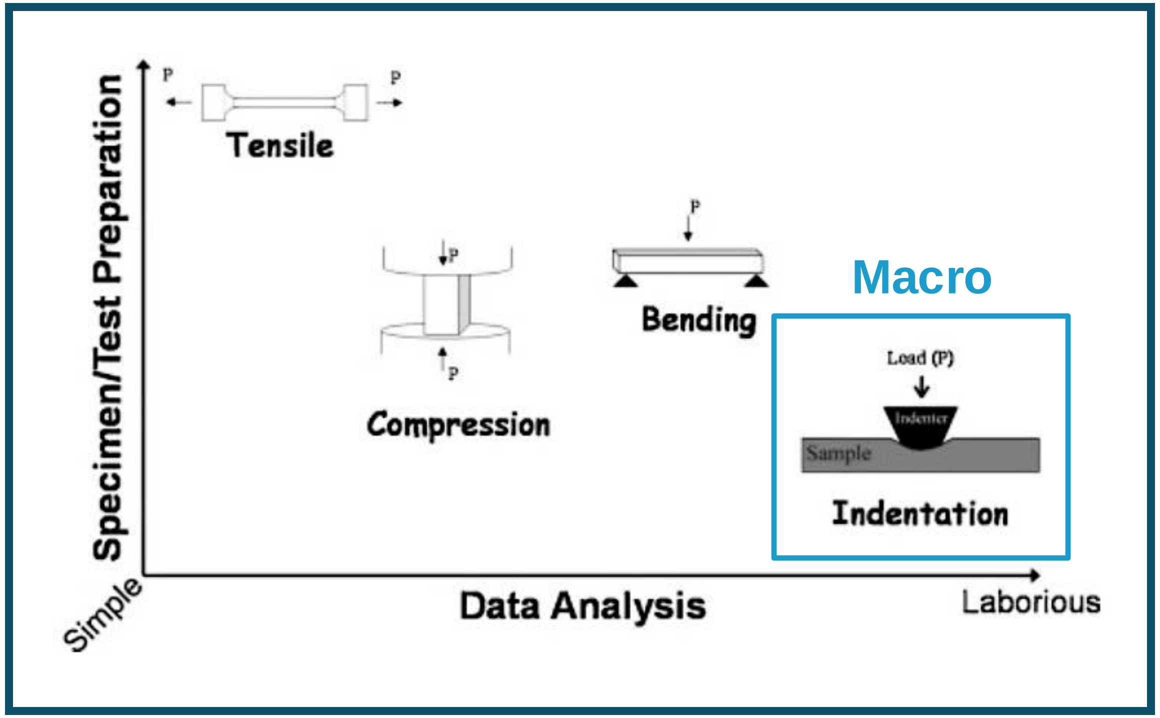


Pressing ahead

What is indentation testing?

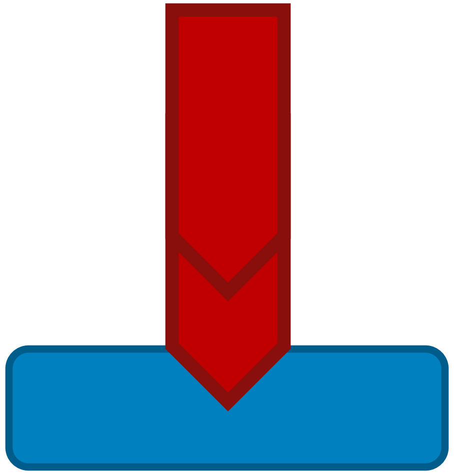
- Mechanical test derived from conventional hardness testing (Vickers, Brinell, etc).
- An indenter of known geometry is pressed into a sample surface.
- Measurement of imprint size yields hardness. Measurement is manual (optical).

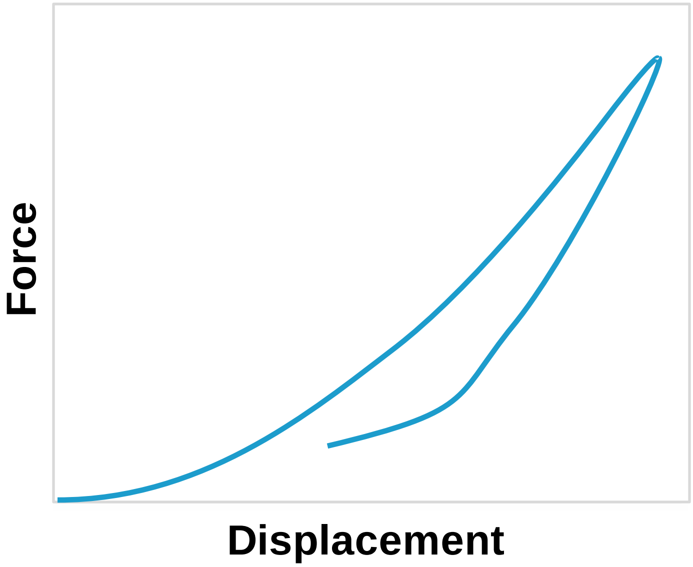




What is nano-indentation?

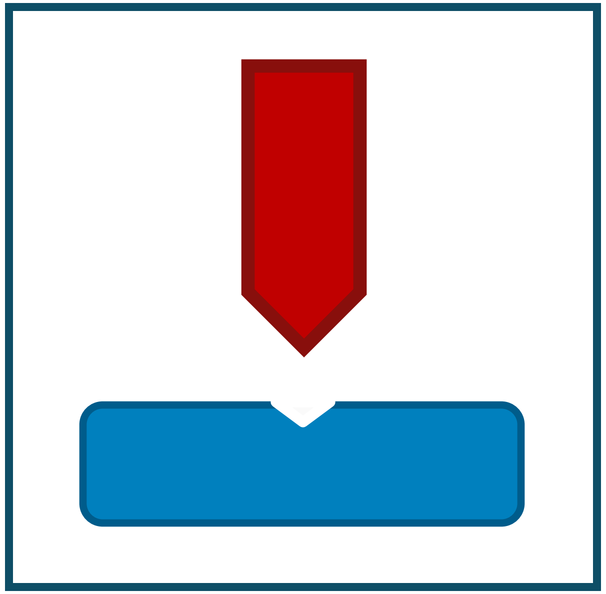
- Also known as instrumented indentation or depth-sensing indentation.
- Normal force and penetration depth are accurately measured to get an indentation curve.
- From the force-displacement curve, several mechanical material parameters can be calculated.

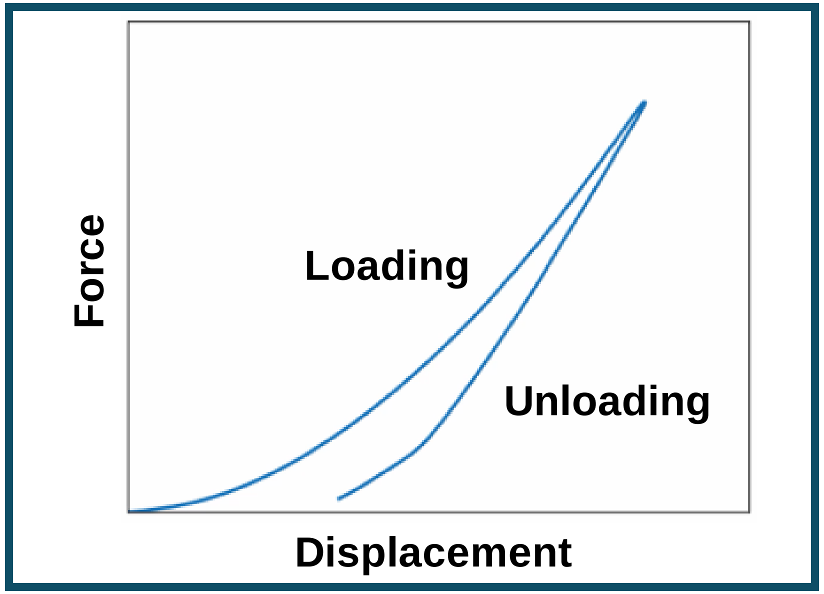


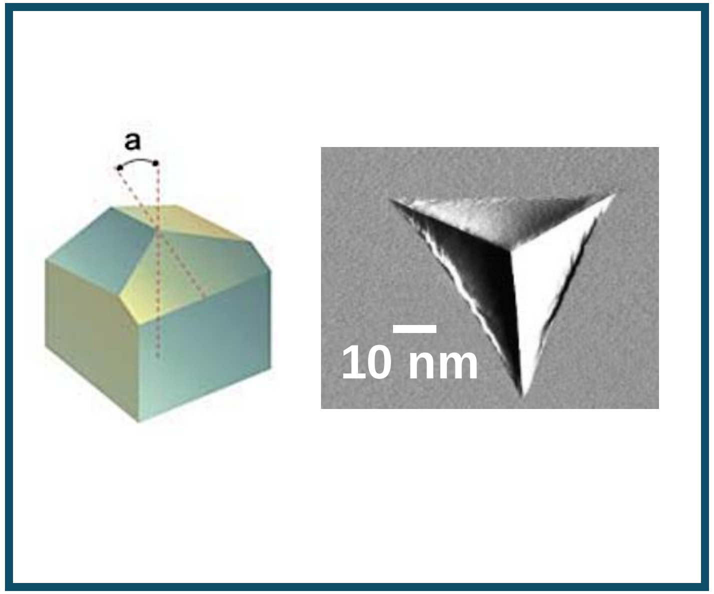


What is nano-indentation?

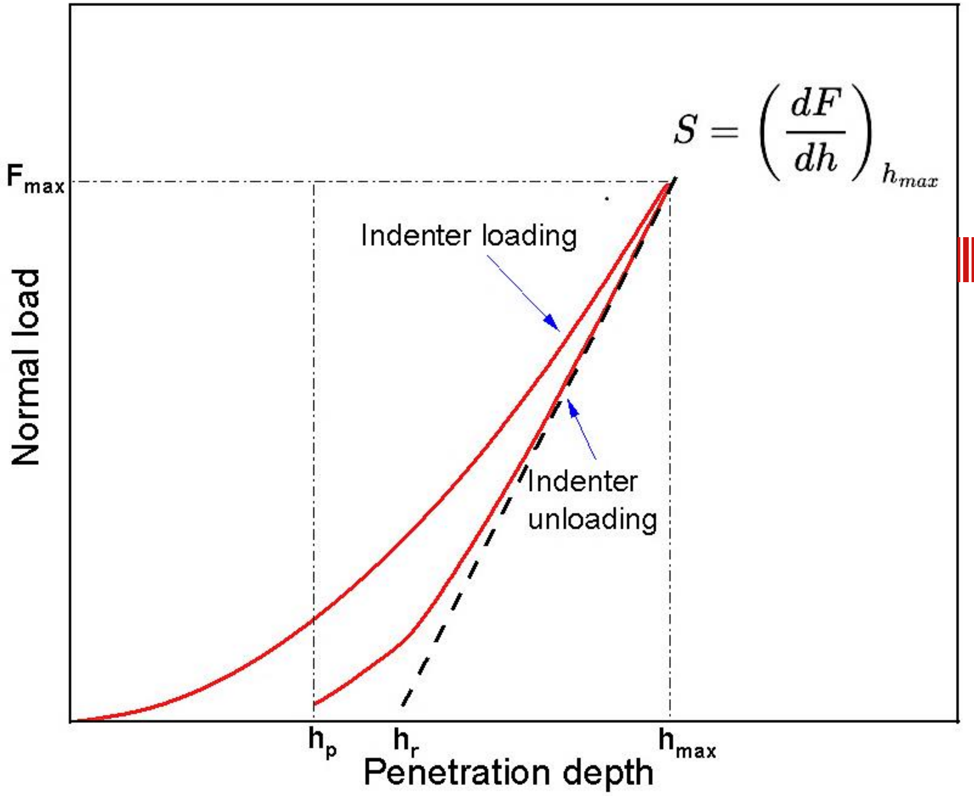
- Also known as instrumented indentation or depth-sensing indentation.
- Normal force and penetration depth are accurately measured to get an indentation curve.
- From the force-displacement curve, several mechanical material parameters can be calculated.
- Berkovich indenter is most popular; used for ceramics, metals, thin films, polymers.







Nano-indentation calculations – Oliver and Pharr model

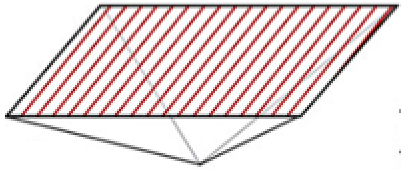


- Slope of unloading curve is the stiffness of the material.
- Oliver and Pharr method involves fitting a polynomial to the unloading curve.

Calculate Contact Depth

$$h_c = h_m - \varepsilon \frac{F_m}{S}$$

Calculate Projected Area of Contact



$$A_p = C_0 {h_c}^2 + C_1 h_c + C_2 {h_c}^{1/2} + C_3 {h_c}^{1/4} + \cdots$$

Calculate Hardness

$$H_{IT} = \frac{F_m}{A_p}$$

Calculate Reduced Modulus

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

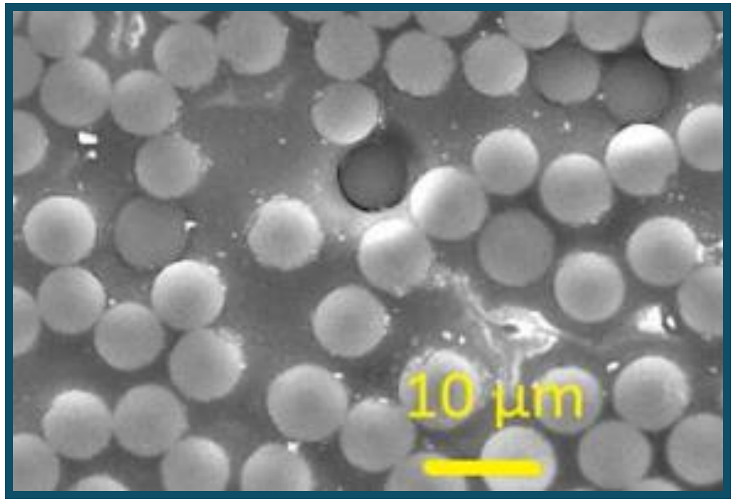
Calculate Modulus

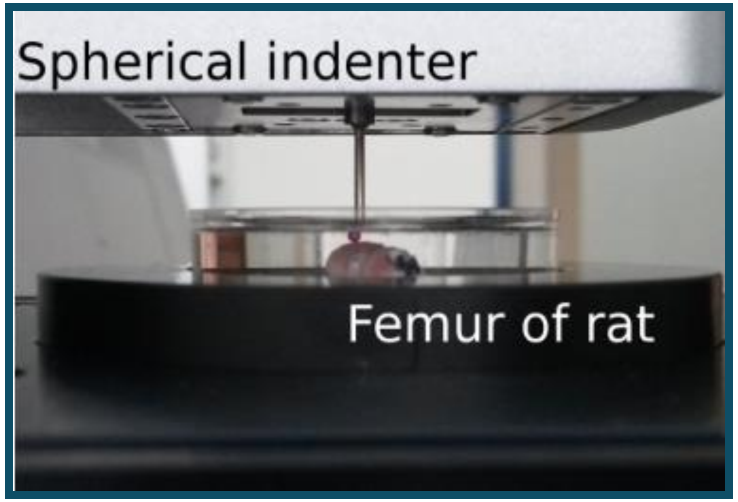
$$\frac{1}{E_r} = \frac{(1 - v^2)}{E_{IT}} + \frac{(1 - {v_i}^2)}{E_i}$$

from properties of indenter tip and sample's Poisson's ratio, v

What kind of problems can you solve with nano-indentation?

- **Semiconductors/micro-electronics:** mechanical properties (modulus, hardness etc).
- **Thin films and coatings:** hardness, residual stresses.
- **Protective coatings:** fracture toughness.
- **Metals and alloys:** hardness at weld interface.
- **Composites and multiphase materials:** mechanical properties of different phases.
- **Biomaterials:** stiffness of cartilage, bone and dental implant materials; creep of biomaterials.

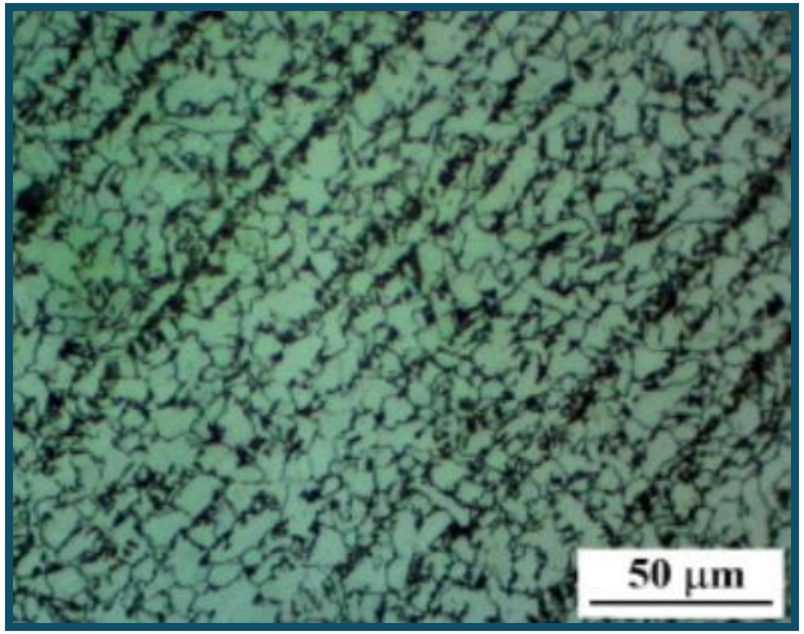




What kind of problems can you solve with nano-indentation?

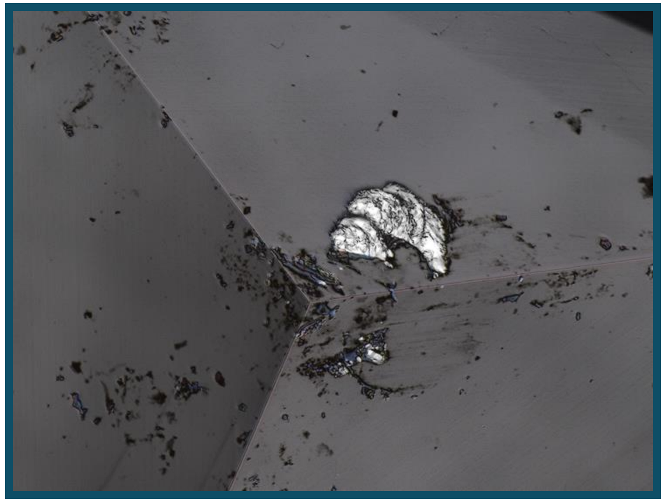
COVALENT METROLOGY

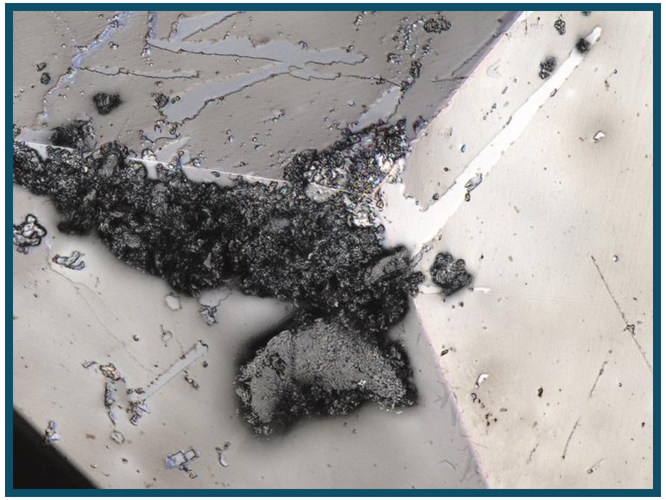
- **Deposited materials:** depth profiling of mechanical properties.
- **Polymer coatings:** adhesion, vibration damping.
- **Soft metals and polymers:** stress-strain analysis, yield strength.



Challenges / best practices with nano-indentation

- Tip area calibration is important to making accurate and repeatable measurements.
- Dirty indenters and surfaces can cause inaccurate measurements.
- Minimize **substrate effects** by keeping indent depth within 10% of film thickness.
- Ensure **surface roughness** is significantly lower than indent depth (depth > 10x average roughness).
- Proper sample mounting avoids compliance issues.

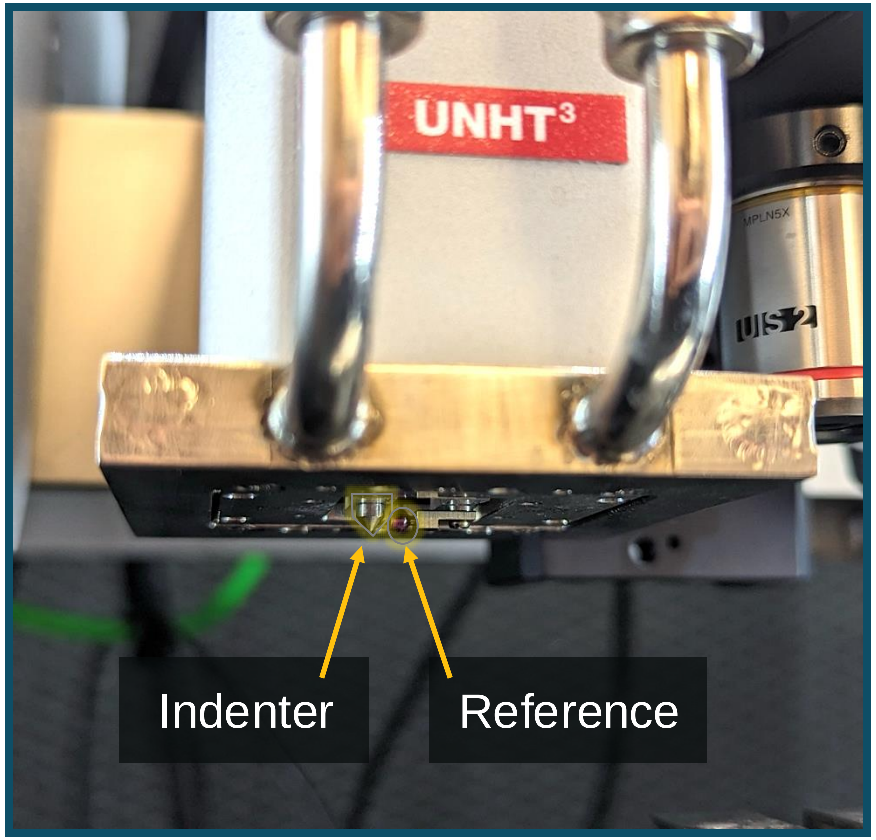




Instrumentation

Anton Paar UNHT^3

- The most accurate nano-indentation tester
  - Two independent depth and load sensors provide true control of forces and indentation depth
  - Unique patented active top surface referencing
- The nano-indenter with the highest stability on the market
  - Negligible thermal drift down to 10 fm/sec without any depth correction
  - Excellent accuracy for long-time measurements such as creep tests.



Anton Paar UNHT³

COVALENT METROLOGY

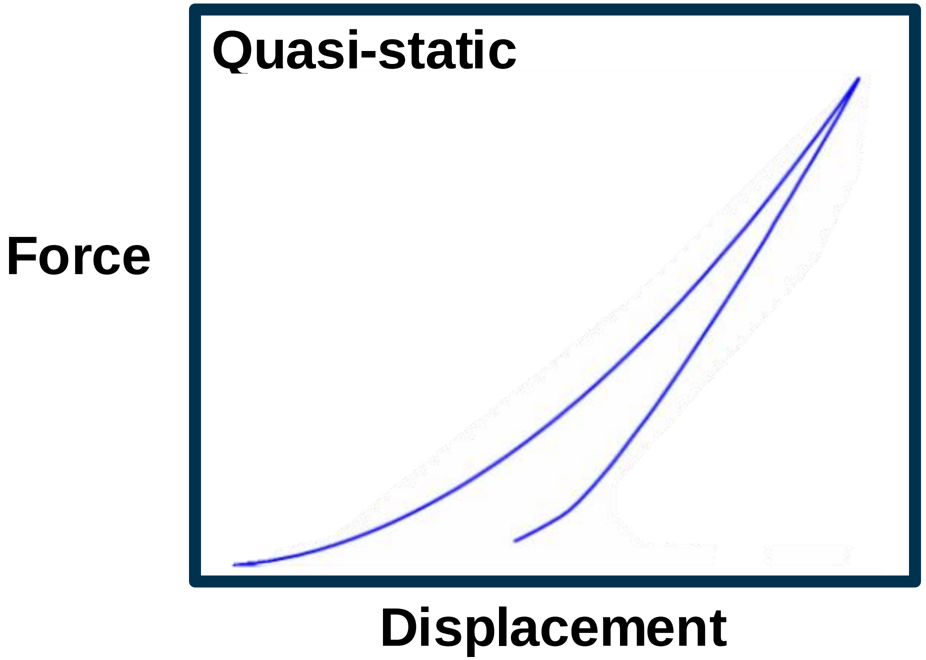
- High throughput and measurement speed (>600 measurements per hour)
  - **A sample can be measured immediately after installation without waiting hours for thermal stabilization**
  - Quick Matrix mode: more than 600 measurements per hour
- **Additional dynamic analysis with Sinus**

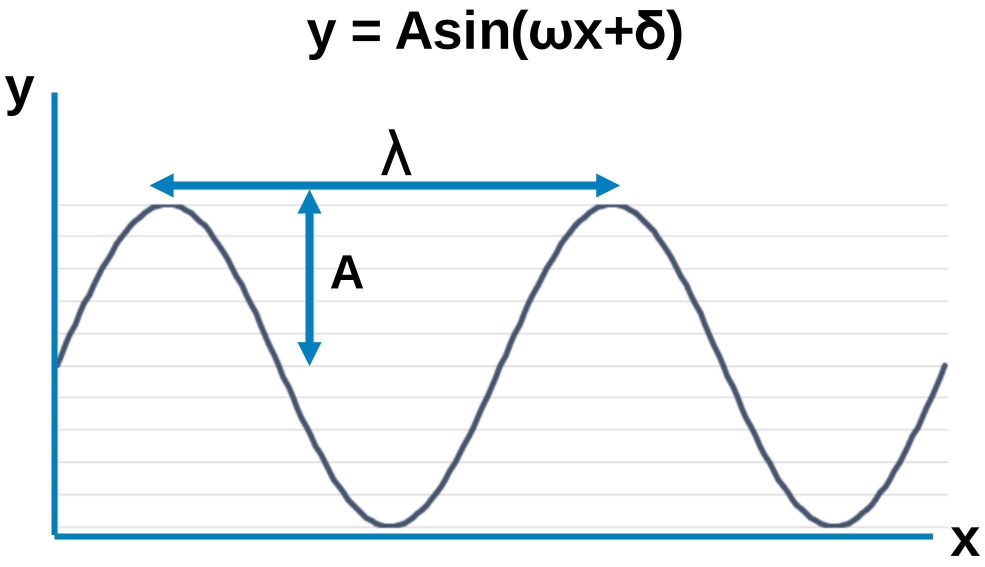
Parameter	Value
Load range	0.01 mN – 100 mN
Load resolution	0.1 µN
Maximum penetration depth	100 µm
Depth resolution	0.1 nm
Temperature range	Up to 200 °C
Frequency range	0.1- 40 Hz

Dynamic nano-indentation (Sinus)

What is Sinus?

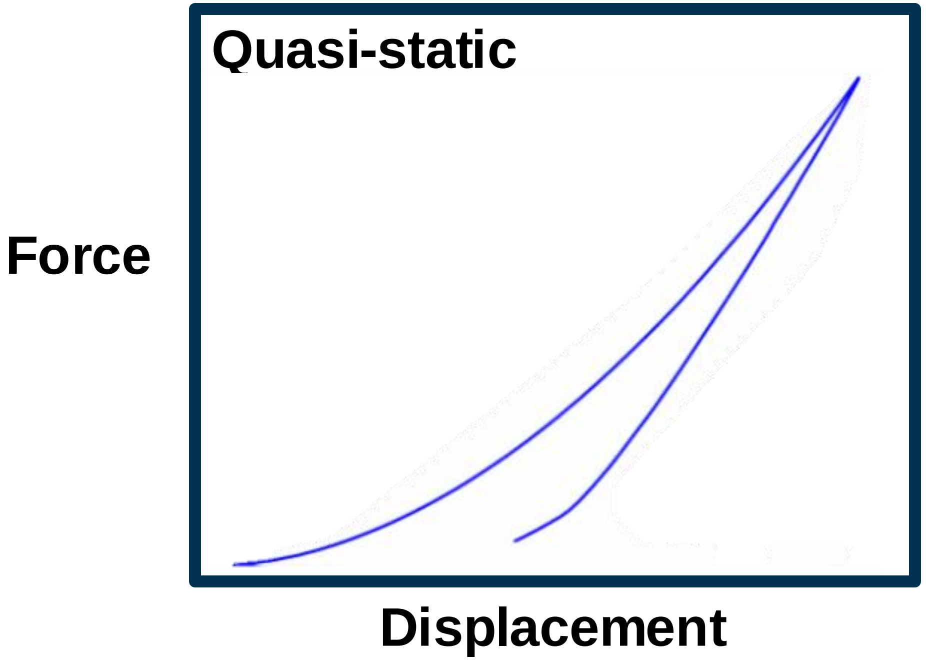
- Also called continuous stiffness measurement (CSM).
- Harmonic oscillations are superimposed to the quasi-static load profile.

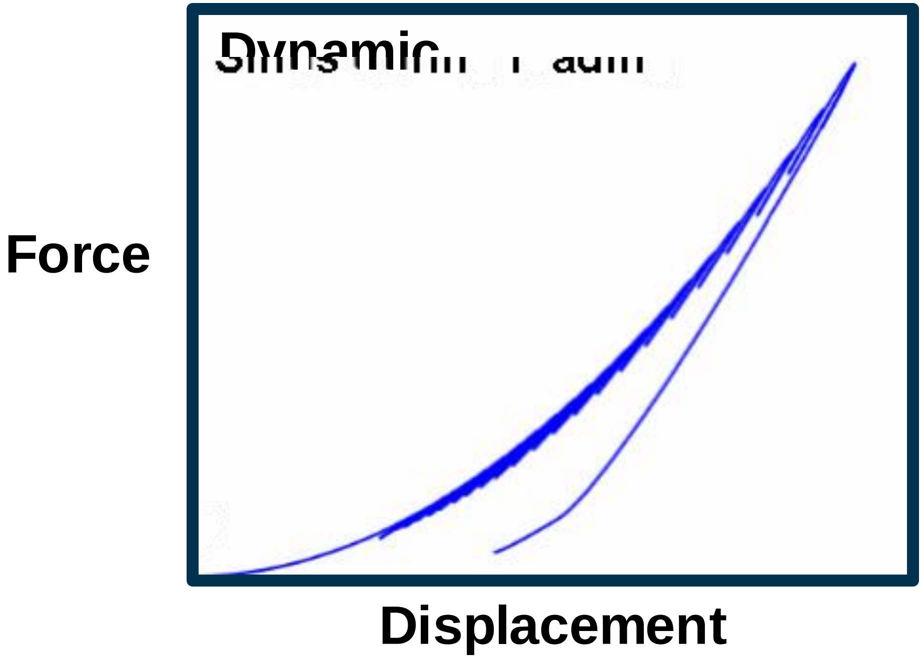




What is Sinus?

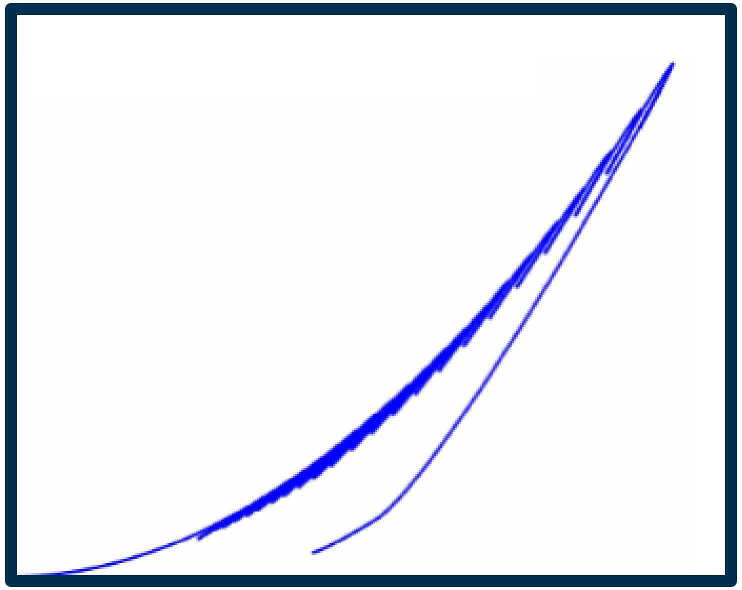
- Also called continuous stiffness measurement (CSM).
- Harmonic oscillations are superimposed to the quasi-static load profile.



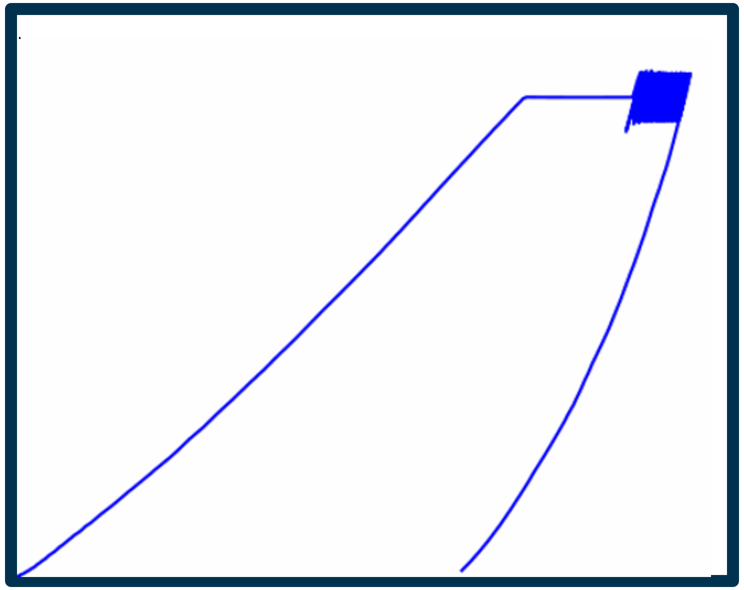


Sinus methods

Sinus during loading



Pause Sinus

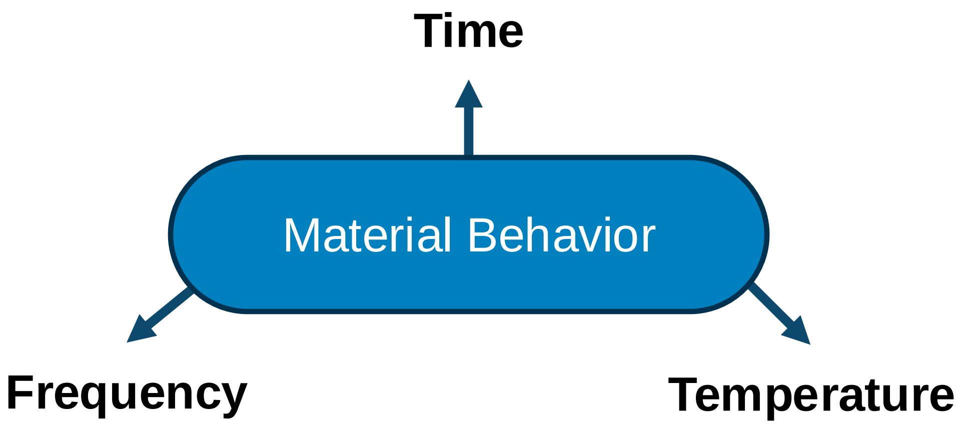


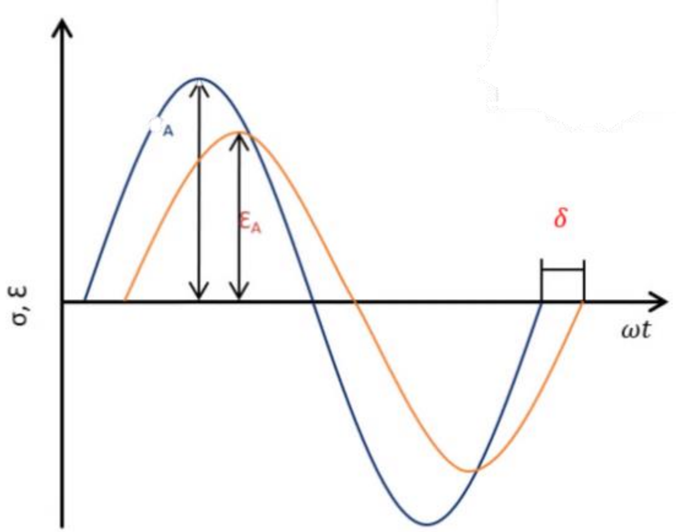
- Depth profiling of mechanical properties
- Stress-strain analysis

- Viscoelastic properties of polymers

Refresher on DMA (Dynamic Mechanical Analysis)

- DMA is used to gather information about a material‘s mechanical properties in dependence of:
  - Temperature
  - Time and/or
  - Frequency

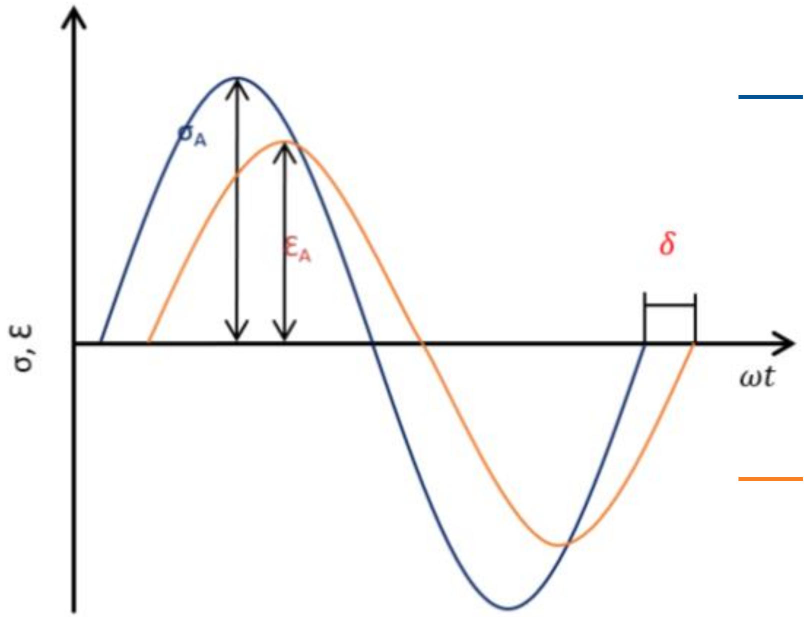




- Excitation of a specimen with a sinusoidal stress/strain
  → Measurement of the response (phase shifted) strain/stress
- Calculation of the resulting Complex Modulus is important for polymers as they show viscoelasticity

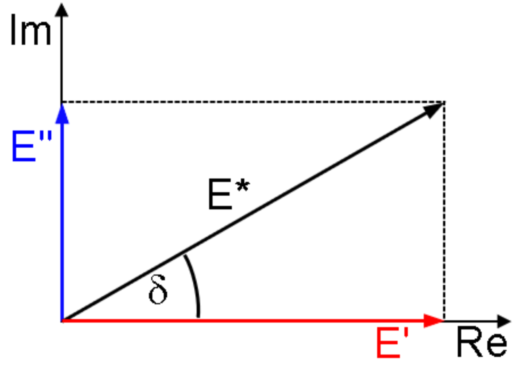
Refresher on DMA (Dynamic Mechanical Analysis)

COVALENT METROLOGY



Stress
$\sigma(t) = \hat{\sigma} * \sin(\omega t)$

Strain
$\varepsilon(t) = \hat{\varepsilon} * \sin(\omega t - \delta)$



$$E^* = E' + iE''$$

$$|E^*| = \frac{\hat{\sigma}}{\hat{\varepsilon}} = \sqrt{E'^2 + E''^2}$$

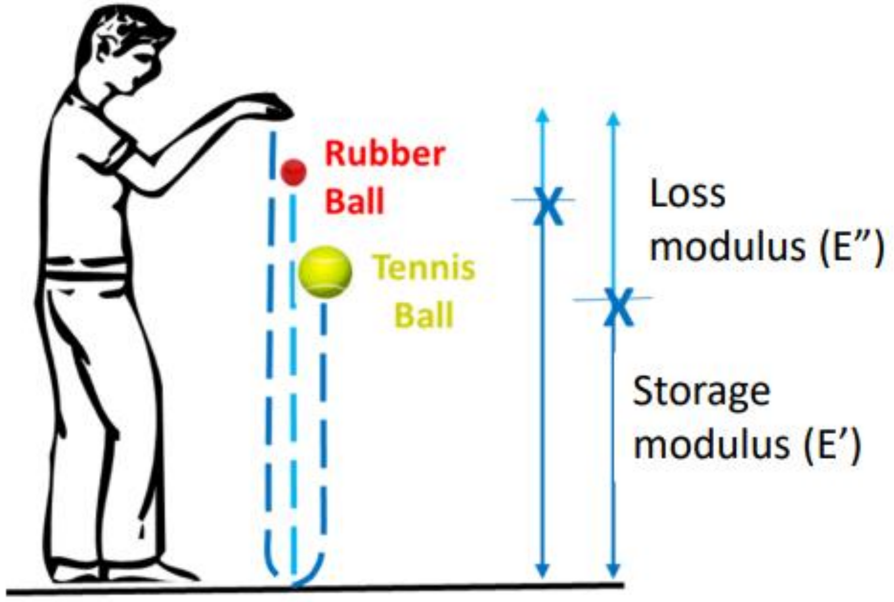
$$\tan\delta = \frac{E''}{E'}$$

Complex Modulus E* [Pa]
- "Dynamic" modulus

Storage Modulus E' [Pa]
- **Elastic** contribution
- Stored deformation energy

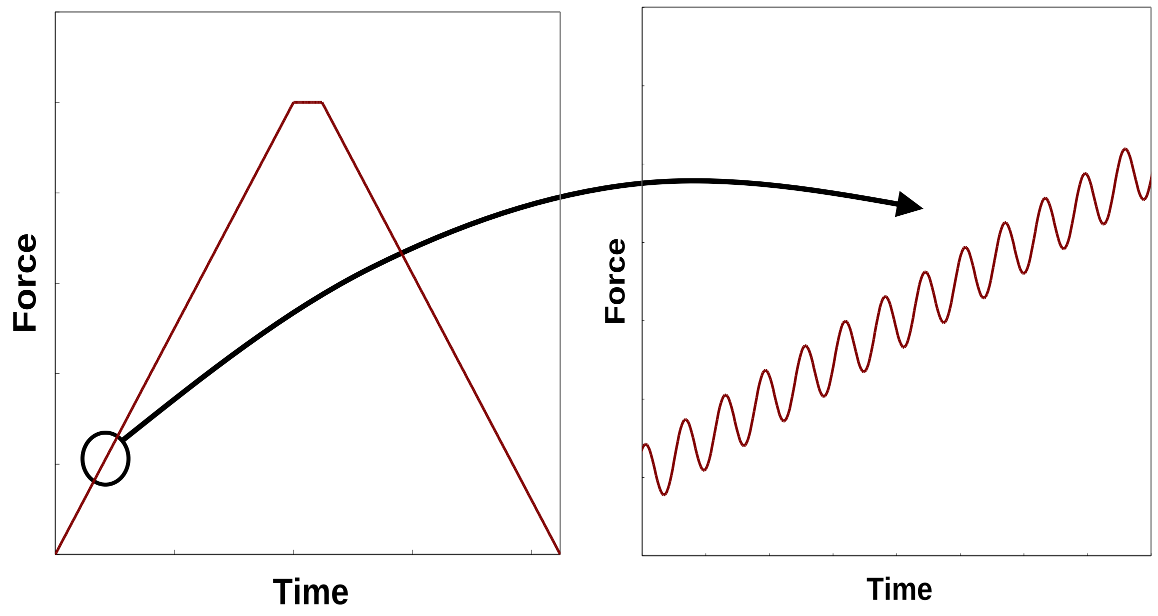
Loss Modulus E" [Pa]
- **Viscous** contribution
- Dissipated deformation energy

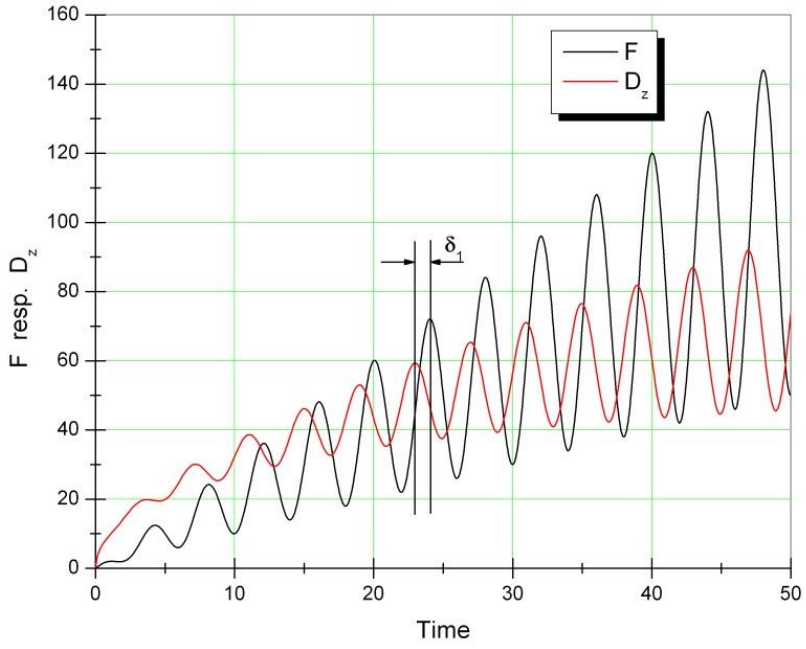
Loss Factor tan δ [-]
- Dimensionless damping factor
- 'Index of viscoelasticity'



DMA by nano-indentation

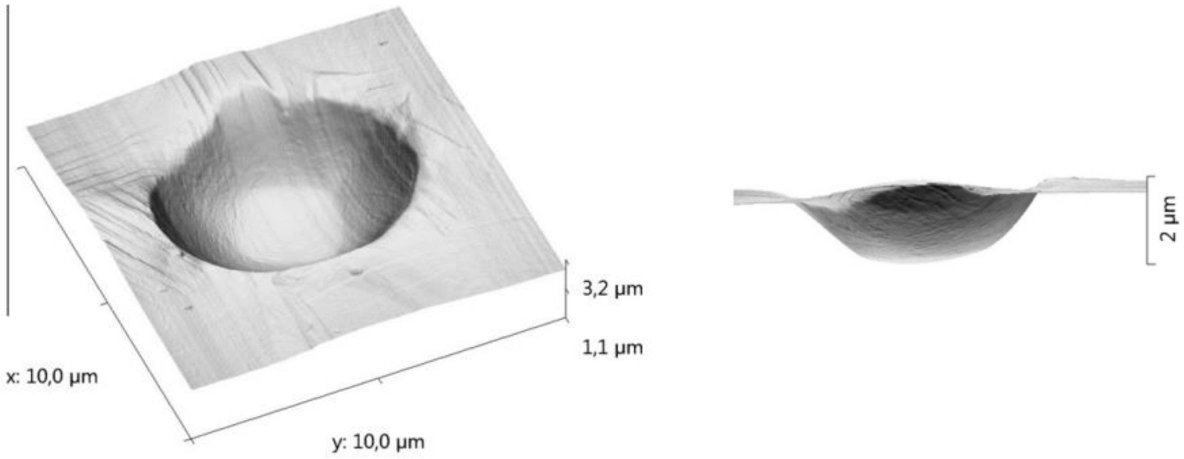
- Sinus measures δ and calculates the complex modulus!
- Powerful tool for viscoelastic characterization of polymers.



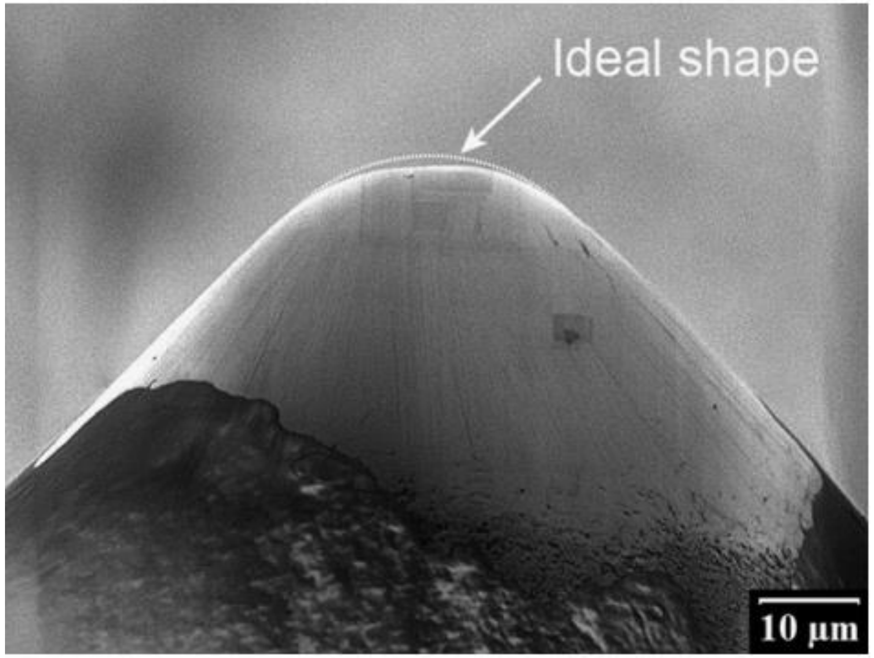


Challenges/best practices with Sinus

- Sinus amplitude typically not to exceed 10% of indentation load.
- Constant strain rate loading for polymers; sufficient dwell time to mitigate creep.
- Verify calibration of indenter; ideal indenter shape (R_{eff})?
- Frequency range is limited compared to bulk DMA.



AFM image of indent



SEM image of indenter

Applications and Case Studies

Case Study 1: Curing of Epoxy Adhesive

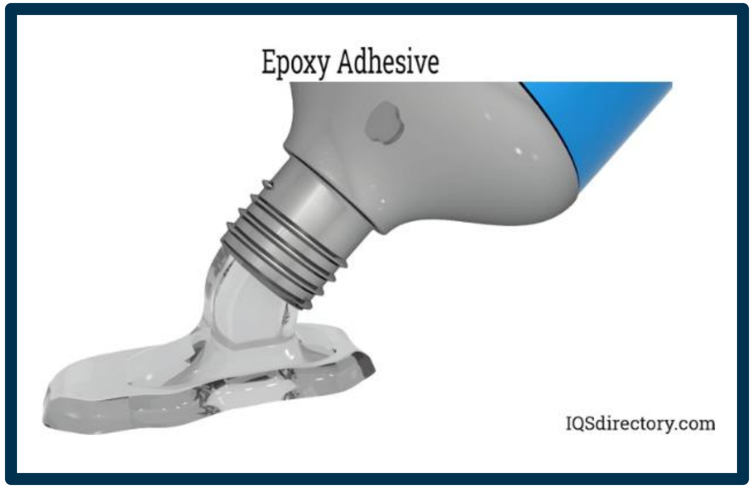
Introduction

Motivation:

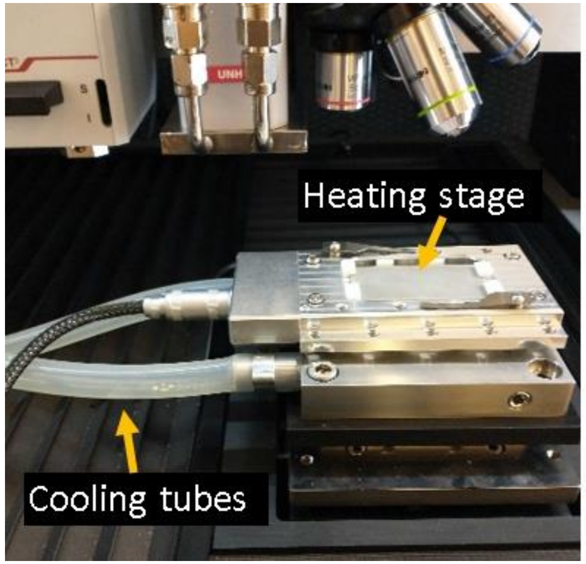
Epoxies are widely used adhesive materials whose mechanical properties depend on the degree of cure. Incomplete curing of epoxy can lead to downstream problems such as delamination.

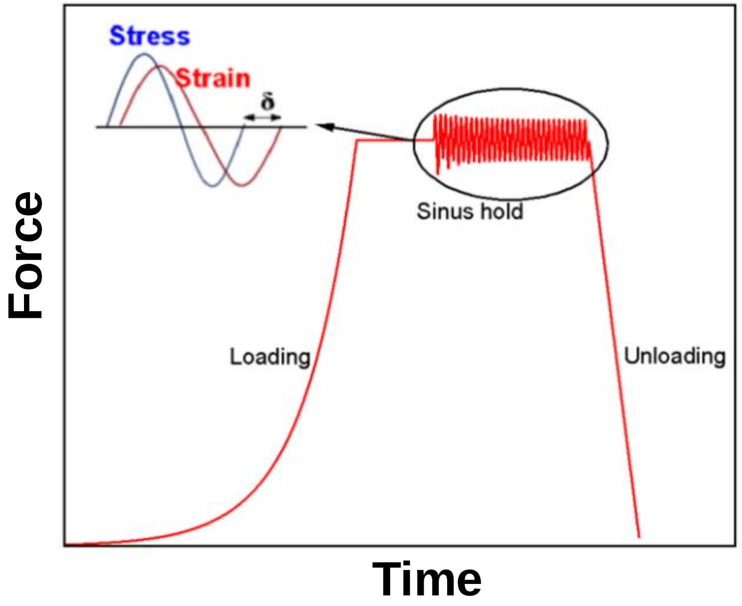
Problem Statement:

Investigate viscoelastic properties (E’, E’’ and tan δ) near cure state of epoxy. The epoxy is 60 μm thick and lies on a substrate. Previous DSC work showed a cure onset around 150 °C, which guided nano-indentation.



Methods



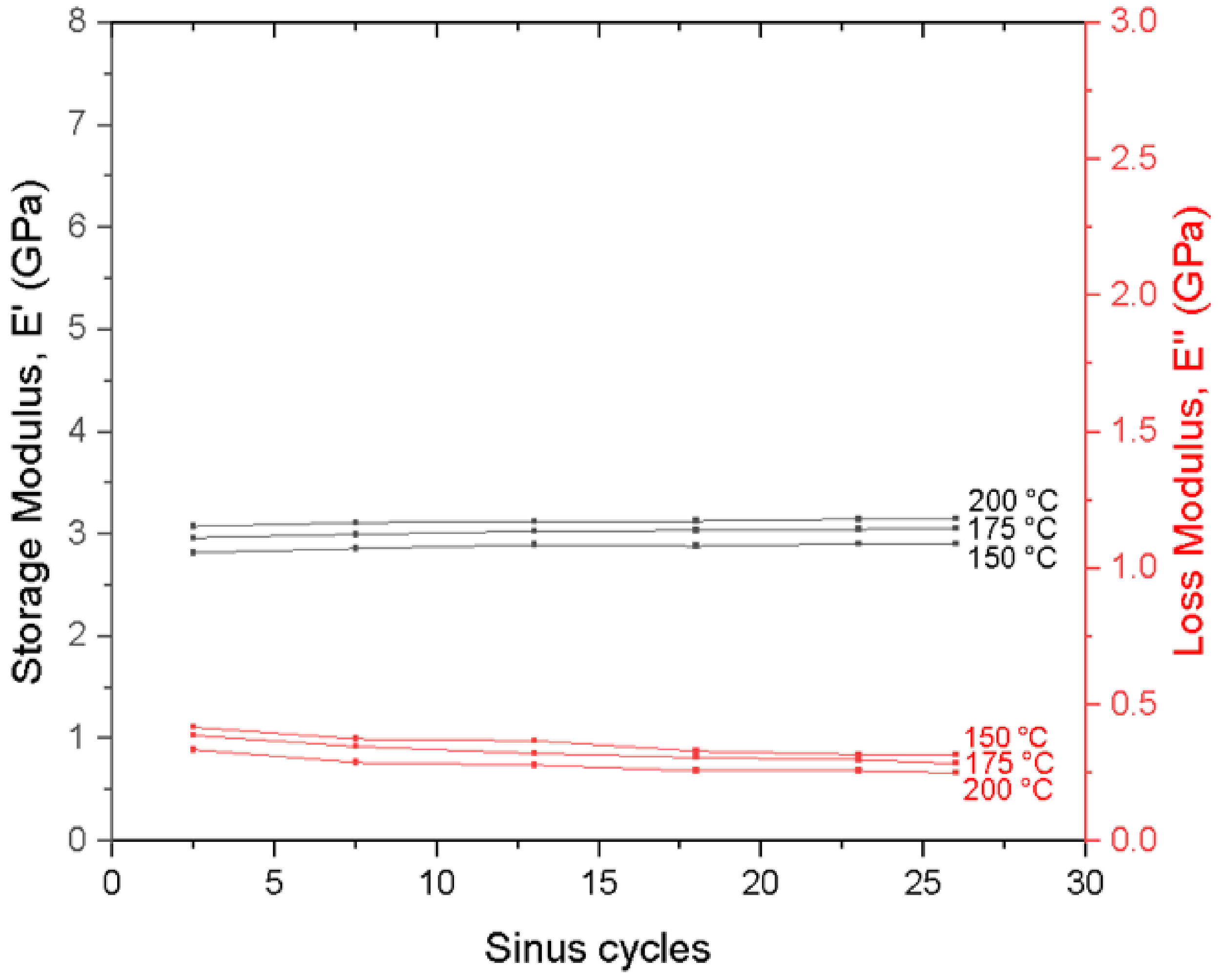


Parameter	Value
Indenter	Spherical, 20 micron radius
Sinus profile	Pause Sinus
Dwell time	Load pause = 15 s Sinus pause = 30 s
Load profile	Constant strain rate 0.1 s^{-1}
Temperature	150, 175, 200 °C; Quick mode
Max load	75 mN
Sinus amplitude	7.5 mN
Sinus frequency	10 Hz

Results: E' and E"

COVALENT METROLOGY

- Storage modulus (E') increased with temperature, indicating that the adhesive becomes stiffer as the temperature rises.
- Loss modulus (E") decreased with rising temperature suggests that the adhesive exhibits reduced viscous deformation energy at elevated temperatures.
- Progress in curing with temperature correlated with a transition to a more rigid state.

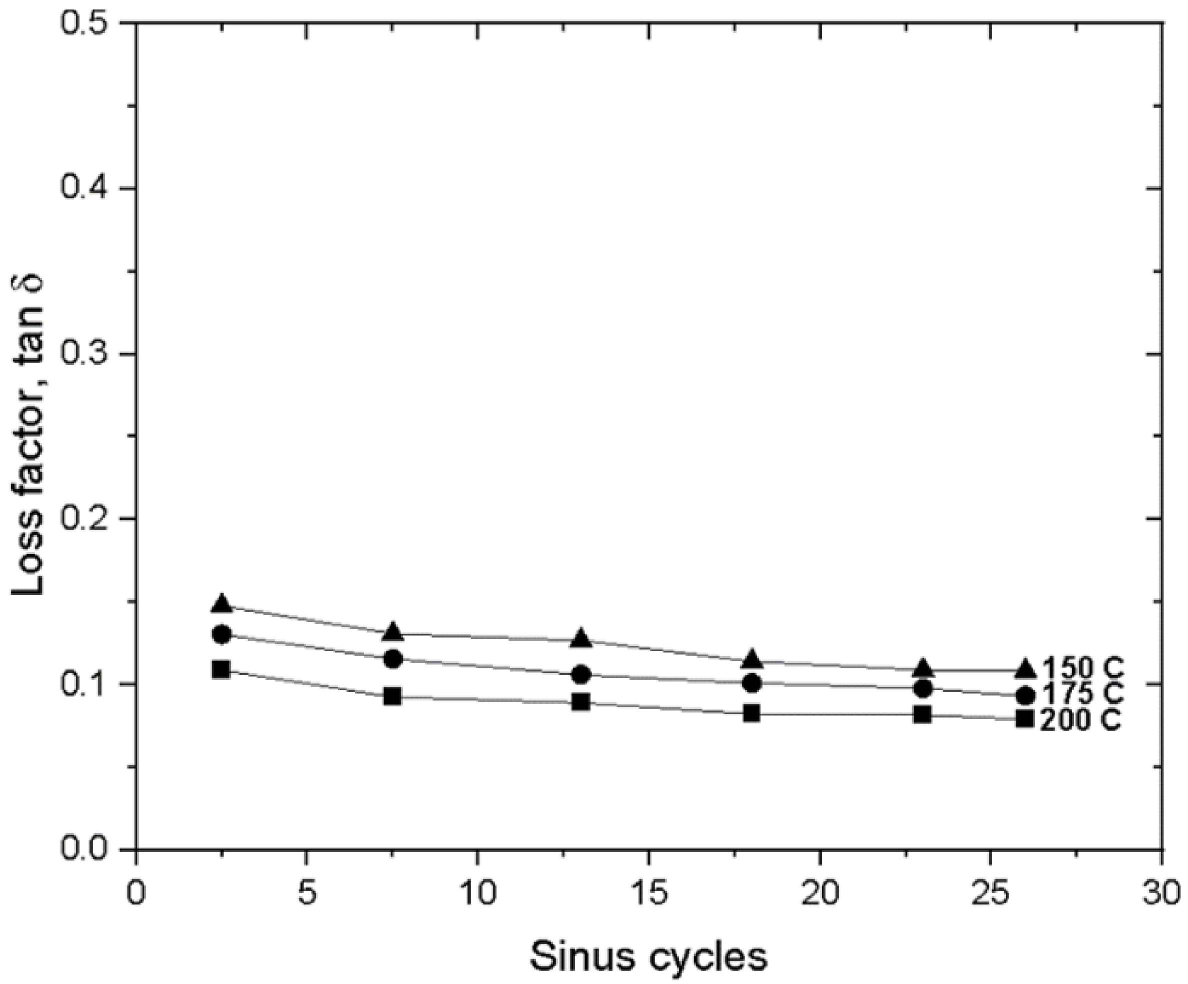


Results: tan δ (loss factor)

- Tan δ, which represents the material's damping capacity, decreased with temperature.

- A more rigid adhesive is associated with higher strength and load-bearing capacity.

- Monitoring changes in E', E'' and tan δ can help with quality control and process optimization to ensure consistency.



Case Study 2: Stress-Strain Analysis

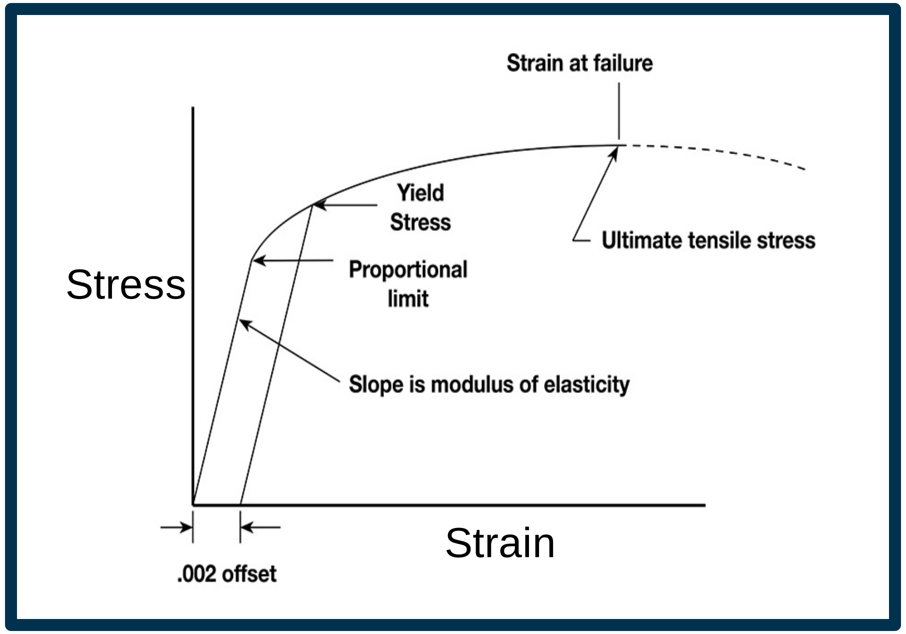
Introduction

Motivation:

Polycarbonate films are widely used in microelectronics, such as printed circuit boards. The films experience mechanical and thermal stresses, which can lead to failure.

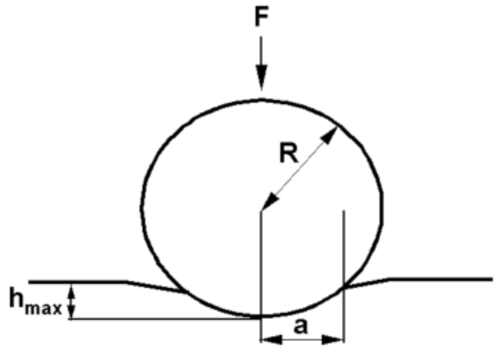
Problem Statement:

Determine the yield stress of a polycarbonate film.



Background

- Spherical or flat-punch indenters apply gradual strain.
- Select indenter based on material properties (modulus, thickness) to ensure shear stress exceeds Tresca/Von Mises stress of material.
- Verify indenter with techniques like AFM (R_{eff}).
- Applicable to polymers and soft metals.
- Determine representative stress (σ) and strain (ε) using load (F) and contact radius (a), with constants K and C.



Hertzian contact model

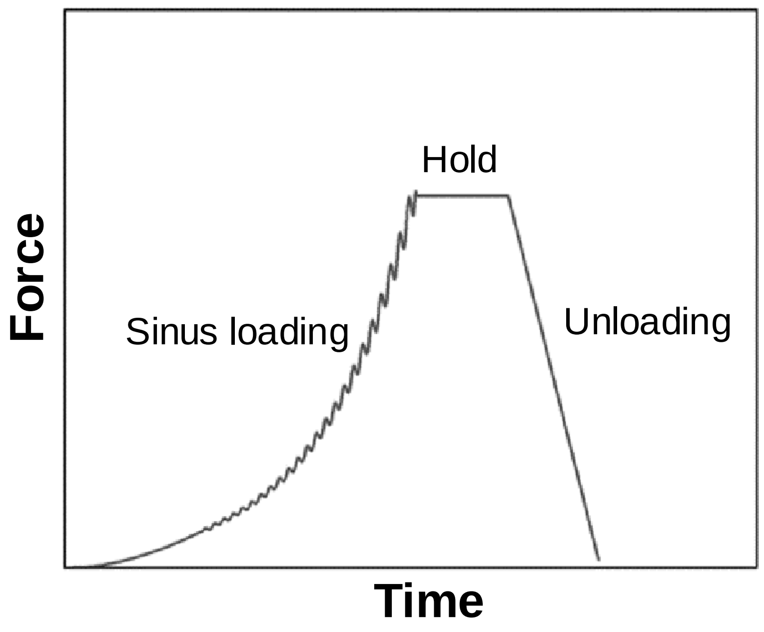
$$\sigma = \frac{F}{KA}$$

Stress

$$\varepsilon = C\frac{a}{R}$$

Strain

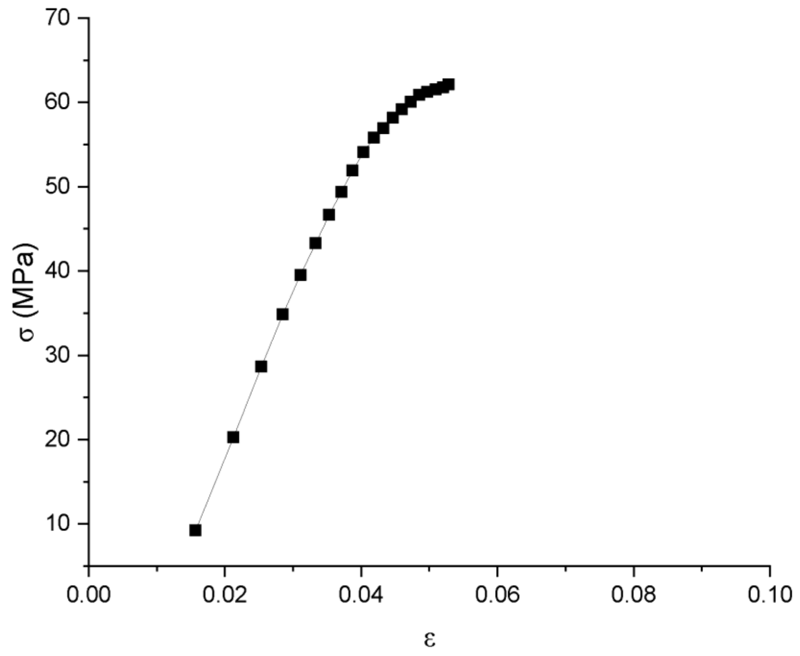
Methods

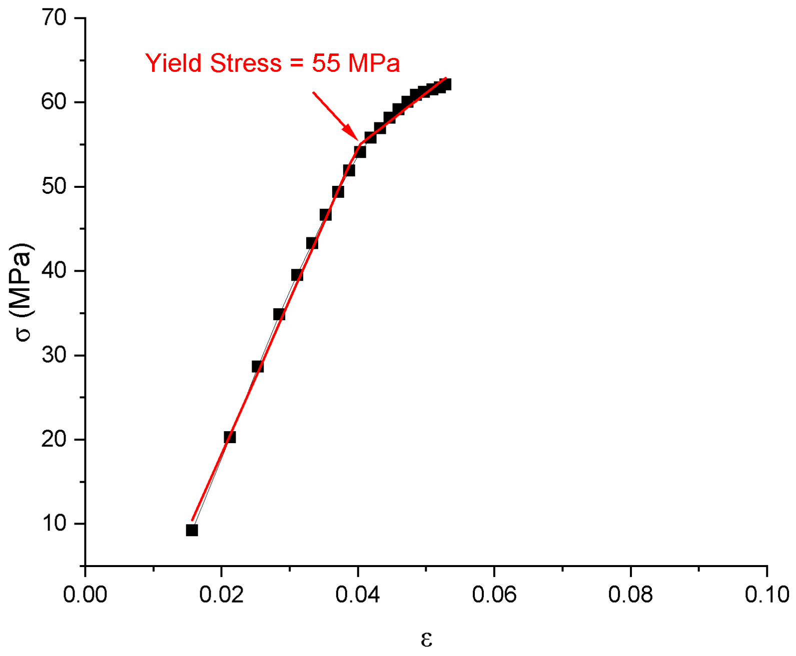


Parameter	Value
Indenter	Spherical, 20 micron radius
Load profile	Constant strain rate 0.1 s^{-1}
Max load	10 mN
Sinus amplitude	1 mN

Results

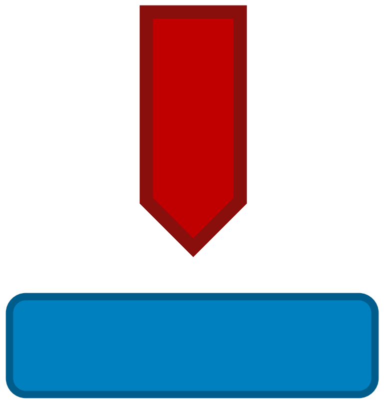
- Stress-strain analysis revealed elastic region, onset of plastic deformation and plastic region.
- Software allows automatic stress-strain analysis to calculate yield stress.
- Yield stress helped benchmark mechanical performance.

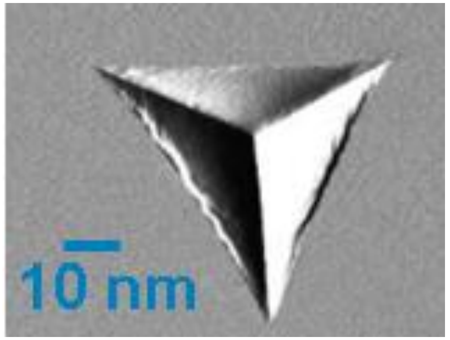


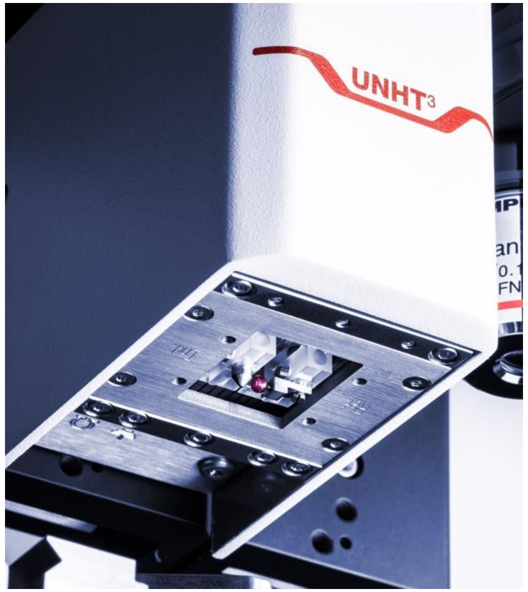


Conclusions and key take-aways

- Nano-indentation is a powerful tool for nano-scale mechanical characterization.
- Sinus unlocks advanced capabilities such as depth profiling, stress-strain analysis and viscoelastic characterization.
- Sinus is the only technique suitable for advanced mechanical characterization of polymer thin films.
- Accurate measurements require careful calibration and proper sample mounting.
- Frequency range of Sinus is limited compared to conventional DMA.

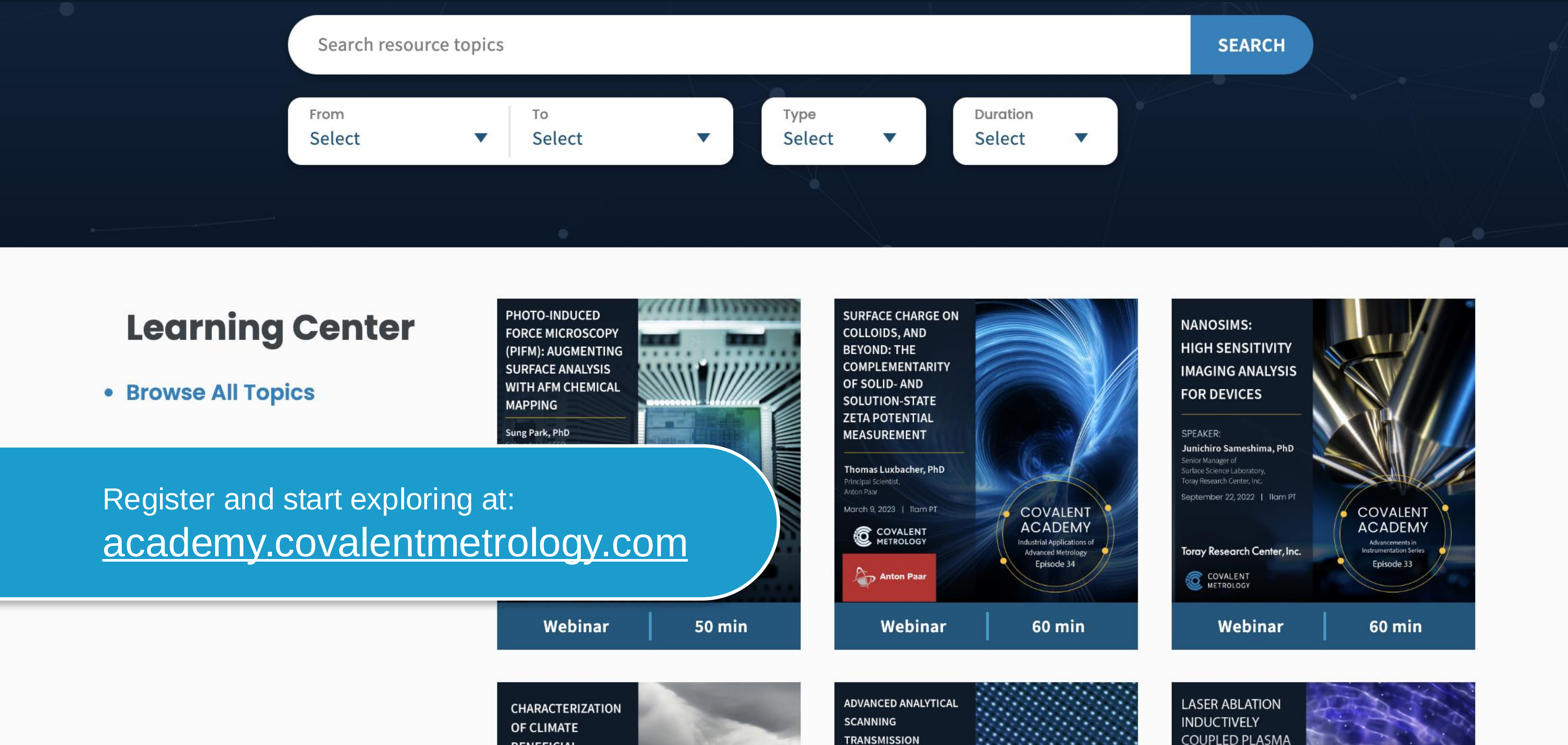






View On-Demand Recordings in the Covalent Academy

COVALENT METROLOGY



Register and start exploring at:
academy.covalentmetrology.com

COVALENT METROLOGY

Q & A Session

COVALENT METROLOGY

Thank you.