Project 1 -- Characterization of Polymer Surfaces

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NIST/Industry Consortium on Polymer Interphases
Oversight Board Meeting
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Outline

- Objectives
- Overview of Progress
  - NanoIndenter capabilities
- Review of Scratch and Mar Literature
  - Review of AFM methods will include our results to date
- Surface Property Measurements
- Update Research Plan and Timeline

Objectives

- Develop advanced measurement techniques for evaluating surface mechanical properties of polymeric materials.
  - Can be used to help characterize interfaces and interphases as well as surfaces
- Relate material properties to deformation behavior under complex stress states.
- Correlate deformation to appearance.

Overview of Progress

- **Literature review paper completed.**
  - **Will be placed on the website by next week.**
- **Nanoindentation system purchase just awarded to MTS Nano Instruments.**
  - **Installation and calibration expected by July 1, 2001.**
  - **Additional equipment funds allocated to nanoindenter purchase ⇒ $240k**
- **Initial indentation and scratch testing with AFM completed for Phase 1 materials.**

Nanoindenter Capabilities

- XP head
  - Static indentation w/CSM
  - Dynamic indentation
  - Scratch testing
    - lateral force measurement
    - profilometry
  - 1 μN - 10 N load range
    - 75 nN resolution
  - Max depth > 1 mm
    - 0.02 nm resolution

- DSM head
  - Static indentation w/CSM
  - Dynamic indentation
  - 0.1 μN - 10 mN load range
    - 1 nN resolution
  - Max depth > 15 μm
    - 0.0002 nm resolution

Nanoindenter Capabilities (cont'd)

- **Automated data acquisition and control**
  - **Flexible, user-defined loading histories**
    - » **Constant loading rate, constant displacement rate, step loading, constant strain rate (self-similar tip geometry).**
    - » **Constant load scratching, constant loading rate scratching.**
  - **Standard and user-defined calculations**
  - **Feedback control using any measured or calculated parameter**
- **Precision x-y sample stage**
- **Vibration isolation**
- **Optical imaging system**

Review of Scratch and Mar Literature

Scratch and Mar Testing -- Terminology

- Field Simulation (Multi-Probe) Tests
  - Wet abrasion
    - Car wash simulation tests, crockmeter test
  - Dry abrasion
    - Rub tests
- Single-Probe Tests
  - Dedicated scratch/mar systems
  - Depth-sensing systems
  - Atomic force microscope
- Scratch vs. Mar
  - Scratch: $0.5\ \mu m < depth < 20\ \mu m$
  - Mar: $depth < 0.5\ \mu m$

Field Simulation Test Methods

- Incorporate complex, multiprobe mechanics
  - Scratch resistance determined through
    - » Mass loss
    - » Cycles to failure
      - Visual inspection
    - » Gloss measurements
    - » Gray scale changes
  - Large number of scratches often needed for measurable changes or to produce failure
    - » Severity of abrasive forces and length of testing can deviate from service conditions and produce misleading results
  - Distinguish between wet and dry abrasion
- Provide ratings, not quantitative measurements

Single-Probe Test Methods

- **Ford Laboratory Test Method BN 108-13**
  - **Five single-probe constant loads applied simultaneously**
  - **Probes are 1 mm diameter polished steel spheres**
  - **Loads for coatings range from 0.6 N to 7.0 N**
    - » **30 N load typically used for bulk polymers**
  - **Scratch speed is 100 mm/s**
  - **Scratch resistance defined by residual scratch depth**
    - » **Measured 24 h after scratching with optical interferometer at 5X**
    - » **Reported depths generally in the 0.5 μm to 10 μm range**
  - **For bulk polymers, additional "scratch visibility" measurement performed**
    - » **Polarized light microscope captures 1 mm length of scratch**
    - » **A gray scale value measured using image analysis**

Single-Probe Test Methods (cont'd)

- **Progressive Load Testing (DuPont, CSEM)**
  - **Load ramped at a given loading rate using a single probe**
  - **Probes are typically diamond cones or spheres**
    - » **Tip radius varies widely in published literature from 1 μm up to 200 μm.**
  - **Maximum loads depend on tip radius**
    - » **(2-10) mN for (1-3) μm radius, 200 mN for 10 μm radius, and 10 N for 200 μm radius**
    - » **Where published, loading rates vary from 20 μN/s up to 1 N/s.**
  - **Scratch speed also varies with tip radius**
    - » **(5-25) μm/s for (1-3) μm radius, 50 μm/s for 10 μm radius, and 200 μm/s for 200 μm radius**
  - **Measure normal force, friction force, and penetration depth**
    - » **Combine with profilometry before and after scratching**
  - **Scratch resistance defined by a critical load**
    - » **Coatings often show distinct transition to fracture as load is increased.**
    - » **Many bulk polymers do not show such a transition**

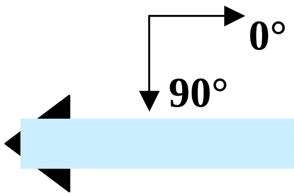
Single-Probe Test Methods (cont'd)

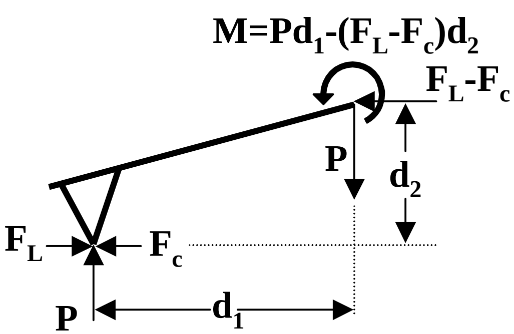
- General Single-Probe Testing
  - Utilize contant loading, progressive loading, or step function loading.
  - Pyramidal probes used for indentation studies used in addition to axisymmetric probes (spheres, cones)
    - » Berkovich
    - » Cube Corner (face and edge orientations)
  - Many gaps in published literature
    - » Test variables vary widely
    - » Very few systematic tests
    - » Most studies on a narrow range of materials
    - » Few studies of time and temperature dependent scratch behavior
    - » Modeling rarely utilized to understand property-performance relationships
    - » Relationship to appearance poorly understood.

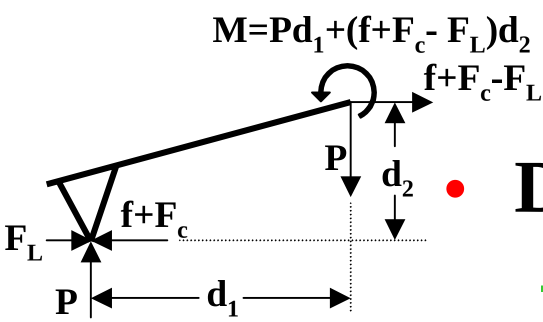
AFM Scratch/Mar Testing

- In general, scratch testing with commercially available AFM systems has many problems:
  - No force control in AFM force mode operation
  - Non-ideal tips
  - No force measurement during scratching
    - Even if lateral signal measured, no way to determine force
    - Often, both bending and twisting of probe can occur
  - Limited ranges of test variables (load, scratch length, etc.)
  - System nonlinearities
- Jones and co-workers control force through scanning system.
  - Instead of imaging, they use macros to perform single- and multi-pass scratch studies.
  - Now using a manufactured diamond conical probe.
    - Scan with normal probe tip and analyze residual damage.

0° Vs. 90° Scratching

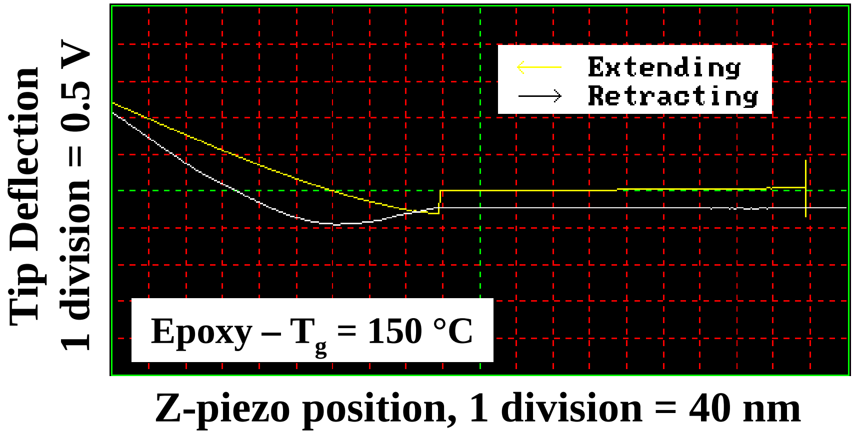


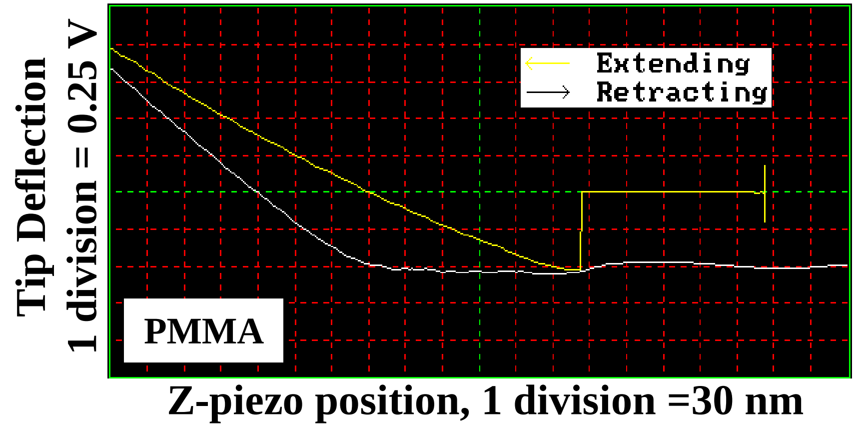


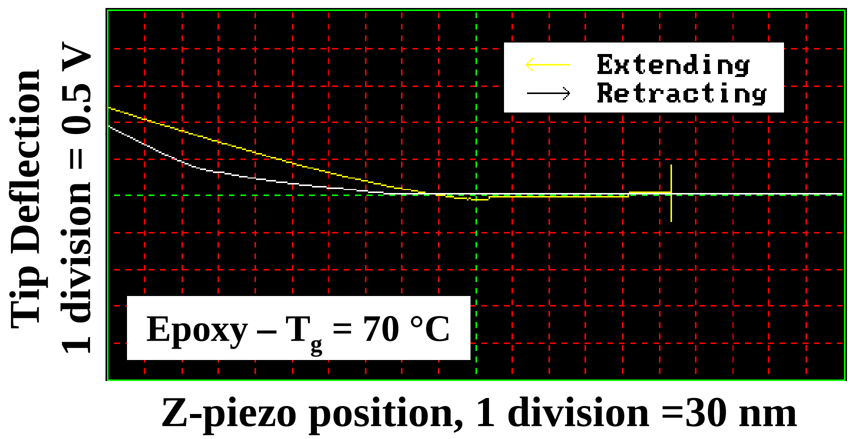


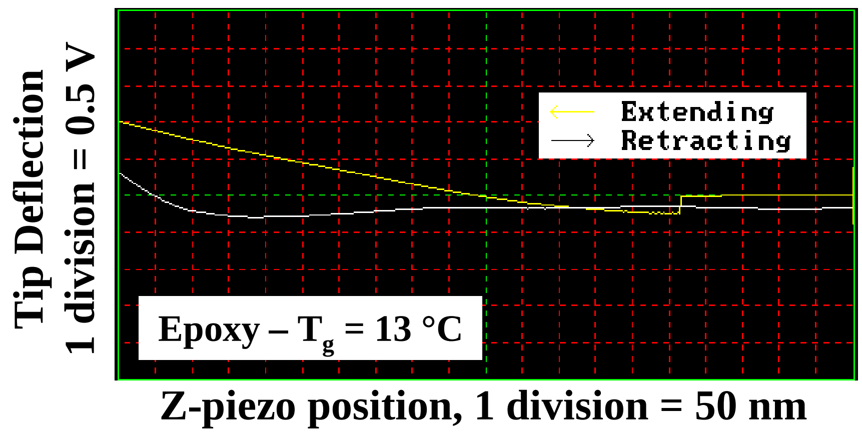
- AFM scratch tests are normally performed in the 90° orientation:
  - Normal force determined by probe bending
  - Lateral force related to probe twisting
    - » Probe spring constant in bending can be measured
    - » No methods exist to measure probe spring constant in twisting
    - » Both bending and twisting of probe often occur
- Du et al. performed 0° scratching.
  - Utilized data from both indentation and scratching along with FBDs of probe to determine friction forces.

Typical Scratch Force Curves for Phase 1 Materials





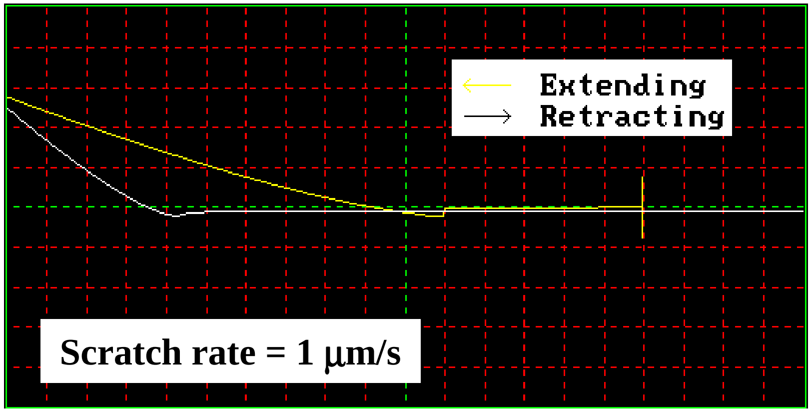




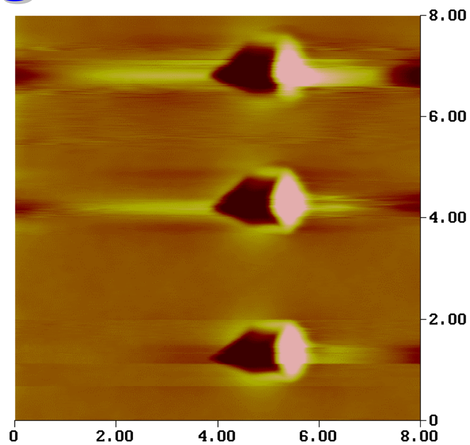
- **Viscoelastic effects lead to a decrease in force during scratching**

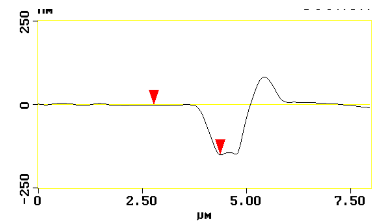
Time-Dependent Scratch Behavior for Low T_g Epoxy

Tip Deflection
1 division = 0.5 V



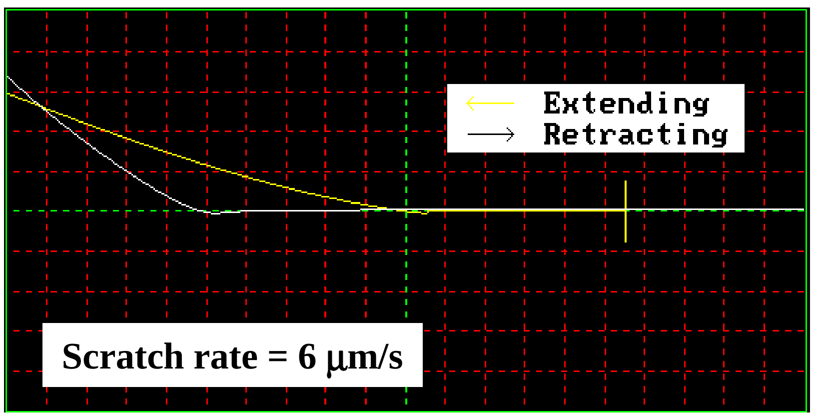
Z-piezo position, 1 division = 50 nm



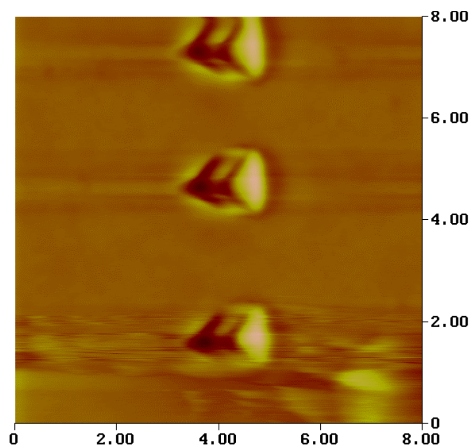


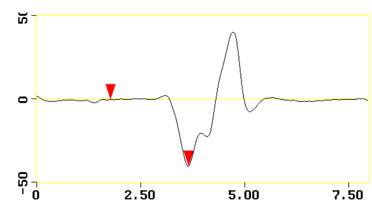
6 minutes after scratching

Tip Deflection
1 division = 0.5 V



Z-piezo position, 1 division = 50 nm





21 hours after scratching

- Scratches made in 0° configuration.

Typical Ranges of Test Parameters

Test/System	Tip material	Tip geometry	Load Range	Depth Range	Speed/length
AFM	Diamond	Non-ideal < 0.1 μm radius	(1 - 400) μN	(10 –250) nm	(1-70) μm/s (1 –70) μm
AFM	Diamond	90° cone 1 μm radius	50 μN - 4 mN	50 nm - 1 μm	(35-70) μm/s 70 μm
Ford	Steel	sphere 500 μm radius	(0.6 - 7) N 30 N	(0.5 –10) μm	100 mm/s ?
LTDS	Diamond	Berkovich pyramid < 0.1 μm radius	(1 – 7) N	50 μm	500 μm/s (1 – 10) mm
CSEM	Diamond	Sphere 2 μm radius	(0 - 5) mN	(0.5 – 1) μm	5 μm/s ?
CSEM	Diamond	Sphere 200 μm radius	(0.5 – 10) N	?	200 μm/s ?
CSEM	Diamond	? 10 μm radius	(0 – 190) mN	(0 – 20) μm	50 μm/s 3 μm
DuPont	Diamond	60° cone, 3 μm radius ?, (1-2) μm radius	(0 – 8) mN	(1 – 4) μm	25 μm/s (1 – 10) mm
NanoIndenter	Diamond	Berkovich pyramid < 0.1 μm radius	(0.02 – 16) mN	(0 – 1.5) μm	(10-25) μm/s 500 μm
NanoIndenter	Diamond	Cube corner pyramid (0.5-2) μm radius	(0.02 – 16) mN	(0 – 2.5) μm	25 μm/s 500 μm

Measuring Surface Mechanical Properties

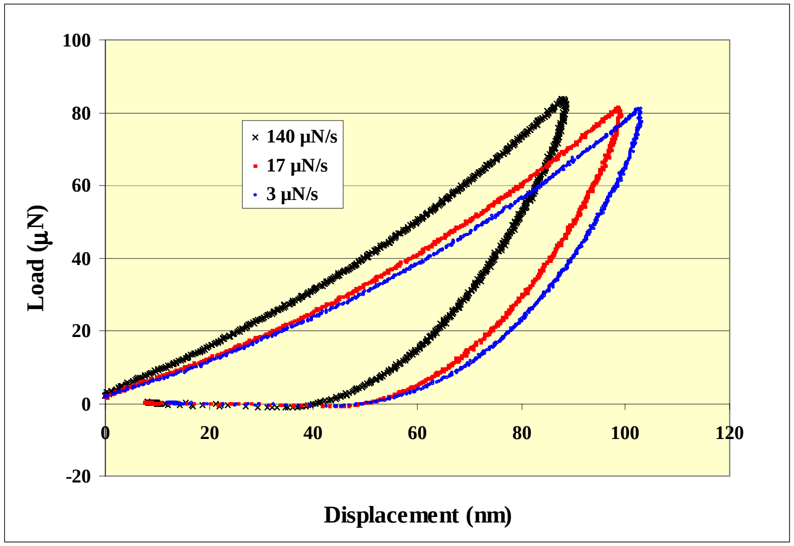
Summary of Modulus Measurements

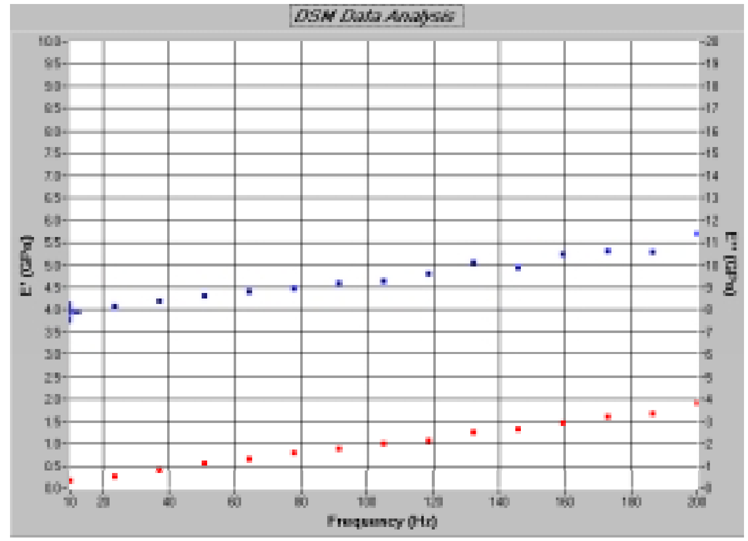
Material	Nominal	Quasi-static DSI/O-P	Quasi-static DSI/BR-SS	AFM/ BR-SS	IFM/ Hertzian	Dynamic DSI/CSM
BCB (T_g > 350°C)	2.9	3.6 ± 0.2	3.5 ± 0.3	5.1 ± 0.8	2.8 ± 0.7	3.5 ± 0.1
Epoxy -- T_g = 150°C	1.8	--	--	5.9 ± 0.4	4.4 ± 0.7	6.7 ± 0.1
Epoxy -- T_g = 68°C	2.0	--	--	4.4 ± 0.2	--	5.0 ± 0.1
Epoxy -- T_g = 13°C	0.4	--	--	1.9 ± 0.1	1.5 ± 0.3	--
PMMA (T_g = 114°C)	3.3	5.1 ± 0.1	--	6.8 ± 0.5	--	5.8 ± 0.1
PS (T_g = 99°C)	3.1	--	--	--	4.8 ± 0.5	--

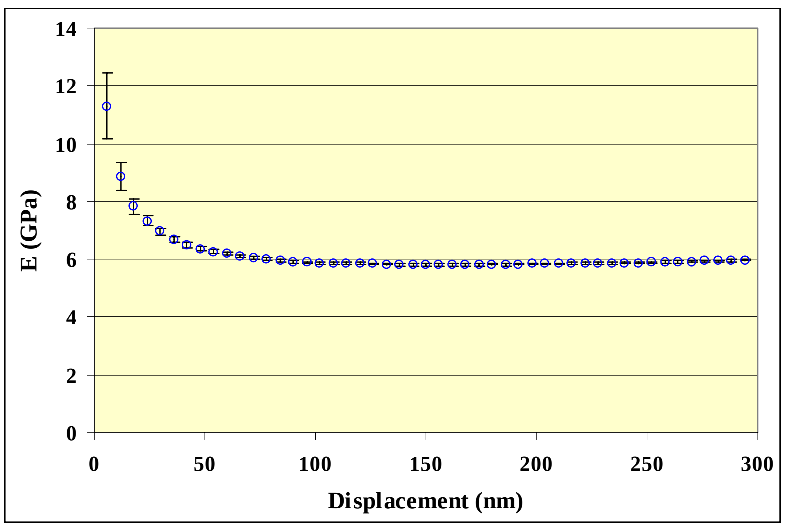
	Load rates (µN/s)	Displacement rates (nm/s)	Tip Radius (nm)
AFM	10-100	100-1000	10-20
DSI	1-100*	1-200	50-100
IFM	~1	1-2*	>1000

***controlled**

Effect of Loading Rate for PMMA

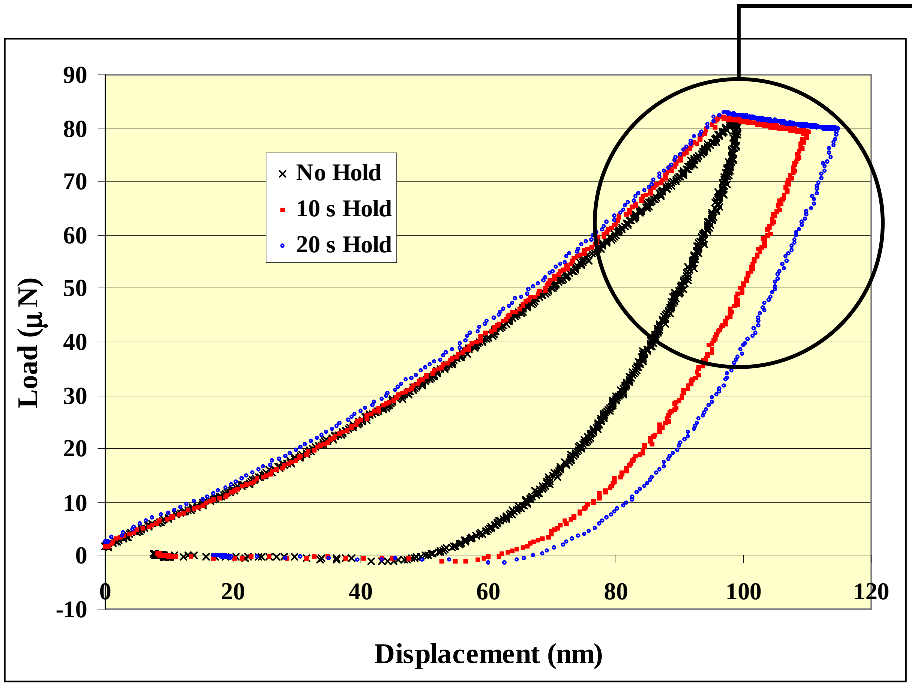


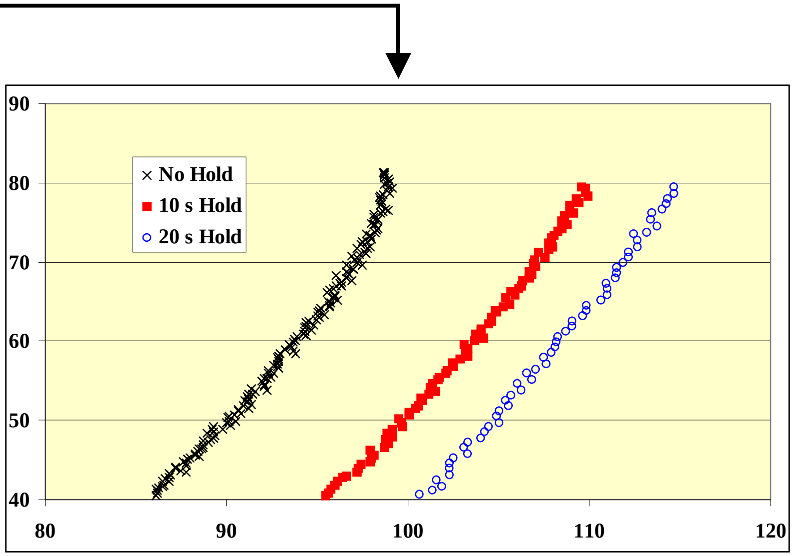




- **Measured values of E ranged from 6.1 GPa at high loading rates to 5.0 GPa at low loading rates.**
- **Dynamic testing yielded an increase in E' with frequency from 4.0 GPa to 5.7 GPa.**
- **Continuous stiffness measurements at 75 Hz yielded E = 5.8 GPa.**

Effect of Dwell Time for PMMA





- **Hold periods can be useful for measuring creep response of a material.**
- **A sufficient dwell time also can reduce some of the effects of viscoelasticity on the curvature of the unloading curve.**
  - **For no hold period, E = 5.3 GPa (17 μN/s loading rate).**
  - **For the 10 s and 20 s hold periods, E = 4.6 GPa.**

Next Steps

- **Determine best methods for characterizing surface roughness as related to scratch/mar.**
- **Tip characterization project (summer student).**
- **With NanoIndenter:**
  - **Characterize time-dependent and dynamic mechanical response of surfaces for Phase 1 materials**
    - » **Link to time/rate-dependent response to scratch/mar**
  - **Explore the usefulness of friction coefficient measurements in single-probe scratch/mar testing.**
    - » **Effects of probe geometry**
  - **Begin appearance studies**
- **Begin model development**

Updated Research Plan and Timeline