Characterisation Programme 2006-2009
Polymer Multi-scale Properties Industrial Advisory Group
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SE02: Improved Design and Manufacture of Polymeric Coatings Through the Provision of Dynamic Nano-indentation Measurement Methods

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Motivation for project

- Requirement for:
  - Local polymer properties

    (bearings, gears, cams, composites (matrix and interfaces))
  - Properties of small volumes in part design

    (e.g. mico-mouldings, packaging, coatings).

Nanoindentation has the resolution but polymers have time/rate dependent properties.
$\Rightarrow$ Dynamic measurement methods are required!

Presentation outline

- Dynamic Nanoindentation: Loss and storage modulus from indentation amplitude and phase as a function of oscillation frequency

- Nanoindentation creep experiments to obtain modulus and viscoelasticity time constants

Measuring time dependent properties.

Three methods:

1) Indentation cycles much faster than viscoelastic time constant of sample.
2) Oscillation of indenter/sample contact + measurement of relative amplitude and phase response (Dynamic Nanoindentation).
3) Indentation creep methods using step load followed by holding at constant force: **<u>the evolution of displacement creep is dependent upon the viscoelastic properties of the material</u>**.

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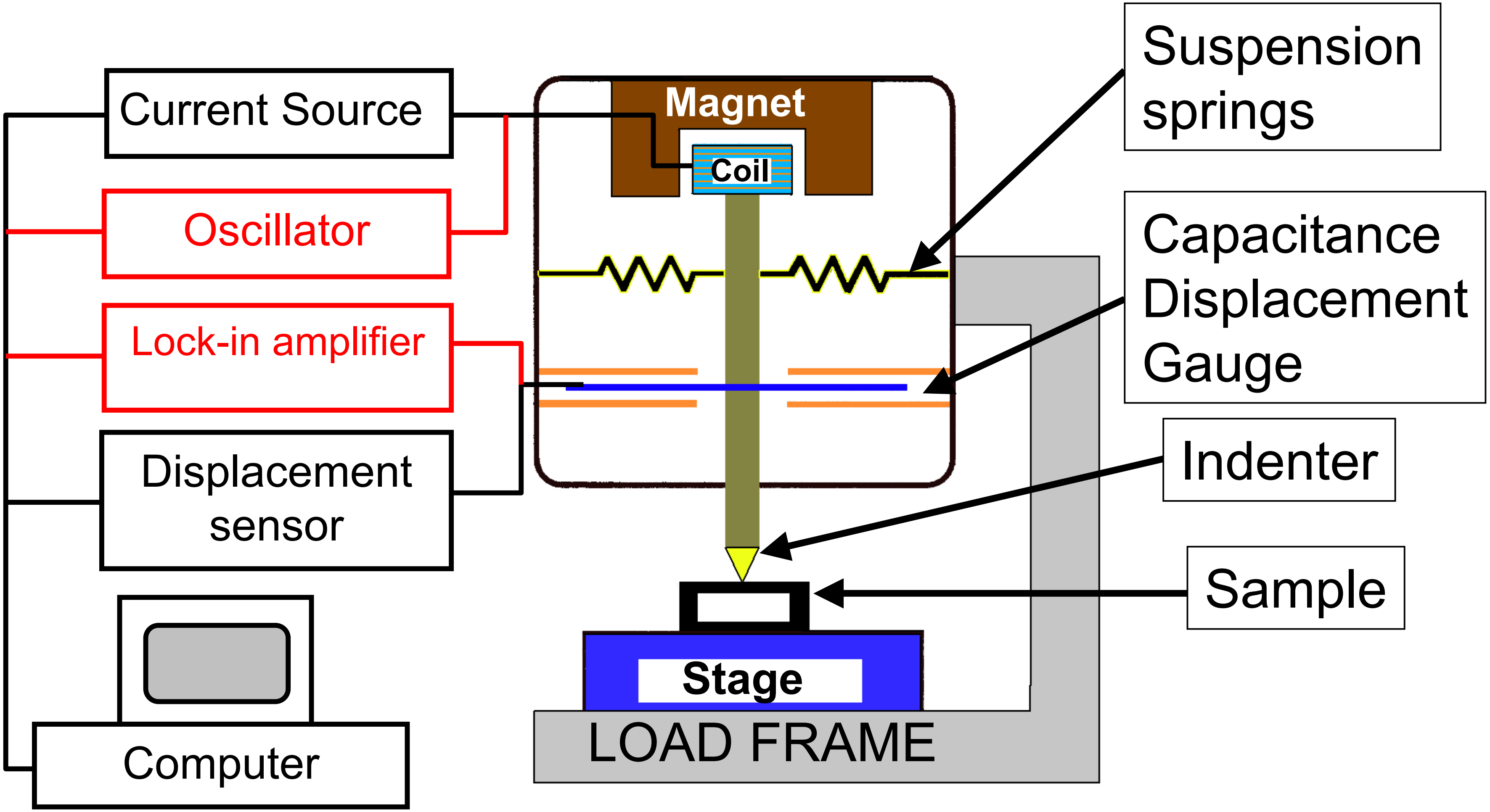
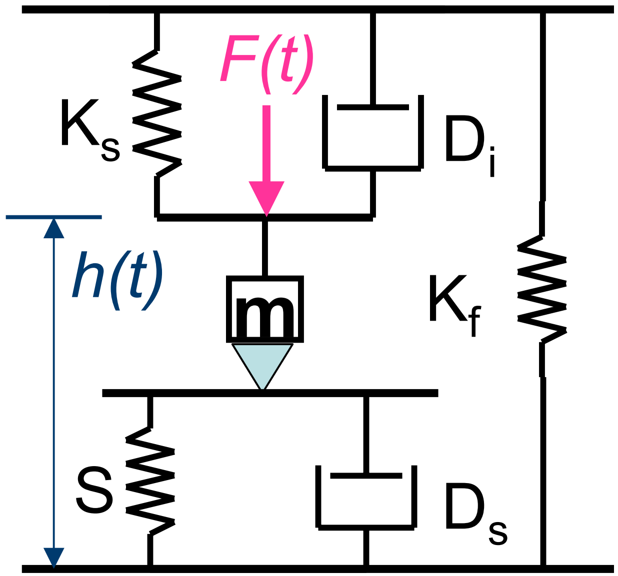
Instrumented (Nano)indenter Schematic



Quasi-static / Dynamic

Spring and dashpot model



E′= Storage modulus

E″= Loss modulus

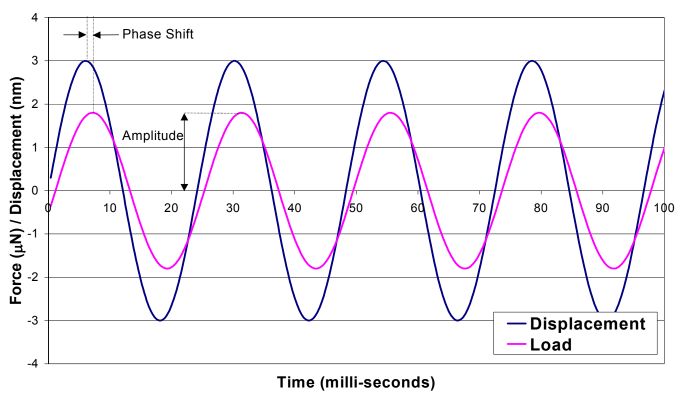
δ = Phase shift

Tan δ = Damping coefficient

$$\frac{F_0}{h_0} = \sqrt{\omega^2 D_{eq}{}^2 + \left(K_{eq} - m\omega^2\right)^2}$$

$$\tan\delta = \frac{\omega D_{eq}}{K_{eq} - m\omega^2}$$

$$\sigma = \left(E' + iE''\right)\varepsilon$$



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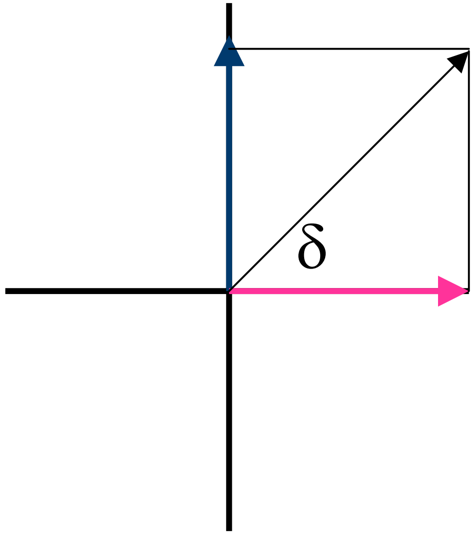
Dynamic contact mechanics



$$E' = \frac{S\sqrt{\pi}}{2\sqrt{A(h_c)}}$$ Storage Modulus

$$E'' = \frac{\omega D_s \sqrt{\pi}}{2\sqrt{A(h_c)}}$$ Loss Modulus

- Damping Coefficient and Stiffness are a function of specimen and indenter geometry.
- Loss and storage modulus are material properties.

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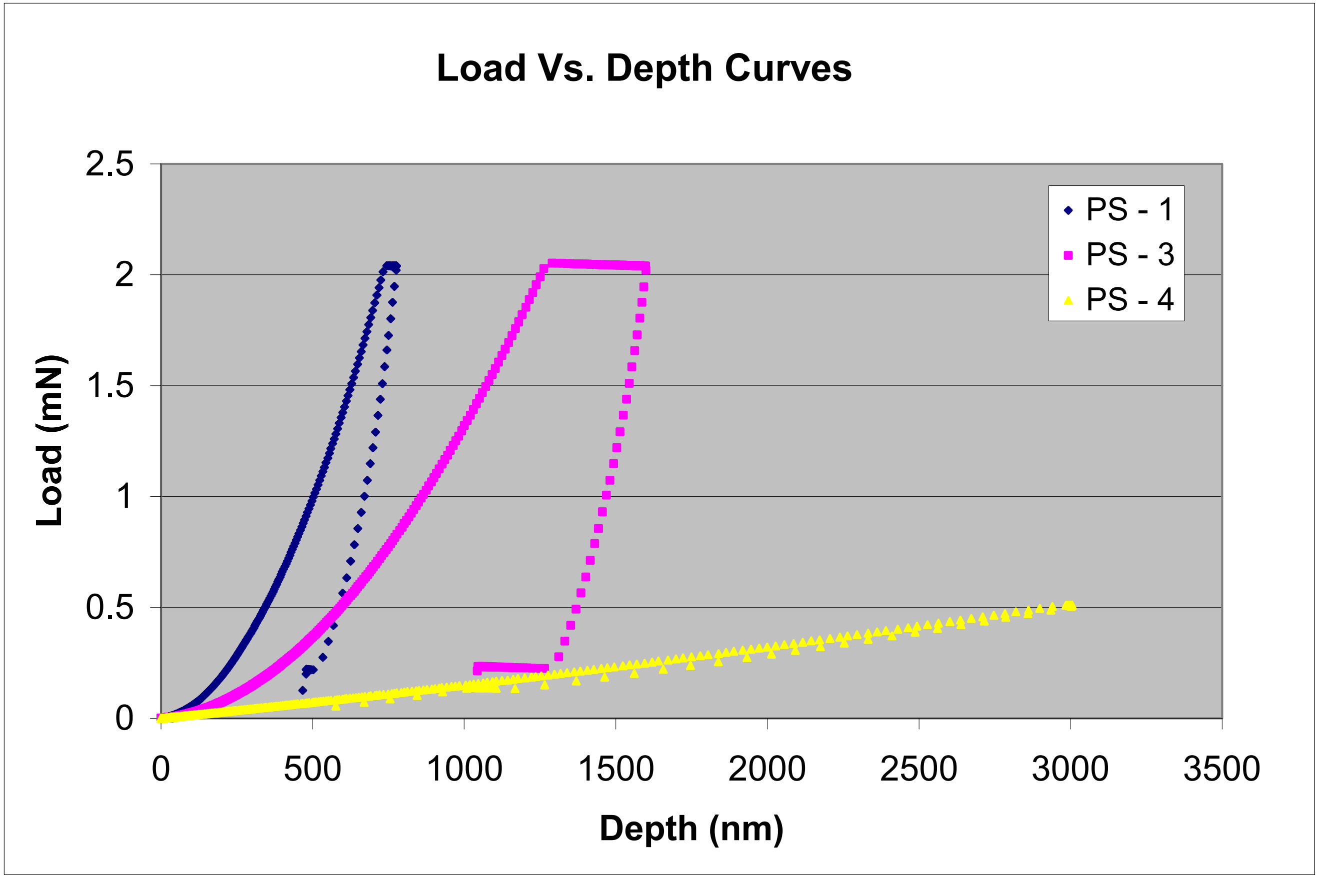
Sensitivity to primary calibration parameters

Summary of findings:

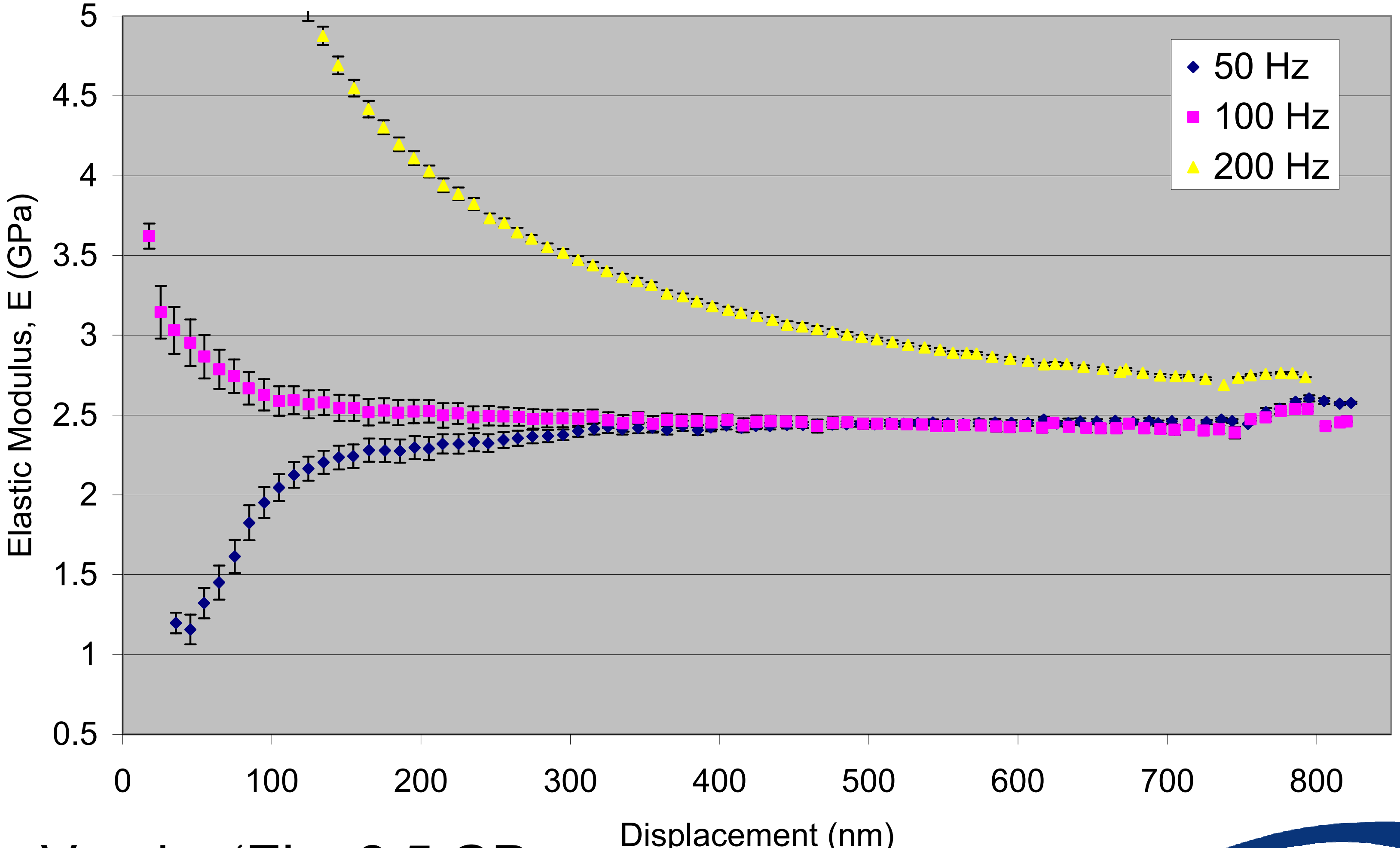
- Dynamic calibrations are sensitive to static calibrations
- Output results of E’ and E” are sensitive to dynamic calibration, particularly E”.
- Dynamic calibration “errors” within reasonable tolerances do not significantly affect E’ results, (within the experimental uncertainty for tests on highly repeatable samples).

Materials Tested: Commercially Available Standard Polymers

Quasi-static response:



Dynamic Indentation on PS-1 at different frequencies (Berkovich)



Vendor ‘E’ = 2.5 GPa

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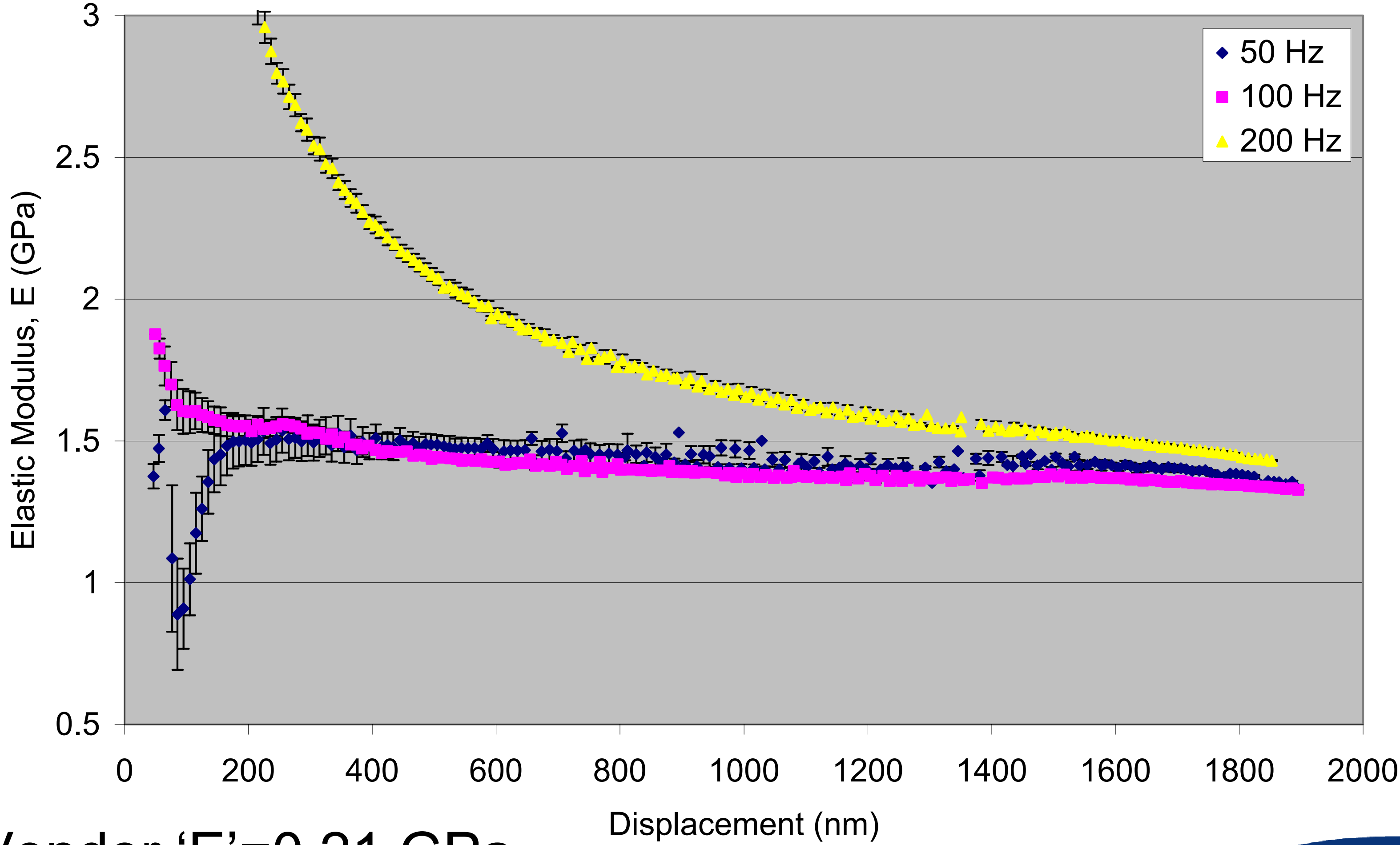
Dynamic Indentation on PS-3 at different frequencies (Berkovich)



Vendor 'E'=0.21 GPa
(More consistent with the loss modulus)

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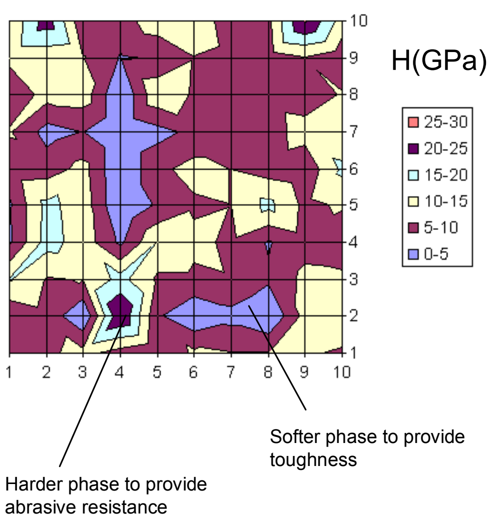
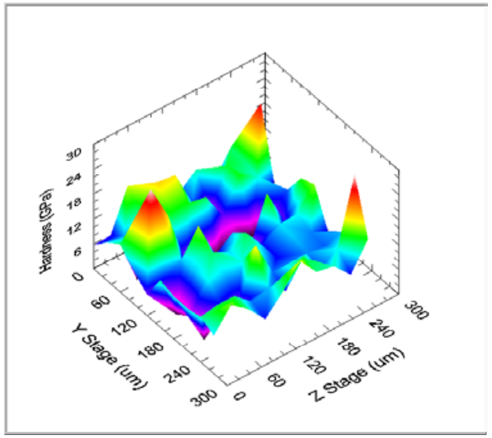
Testing at temperature :

MicroMaterials NanoTest

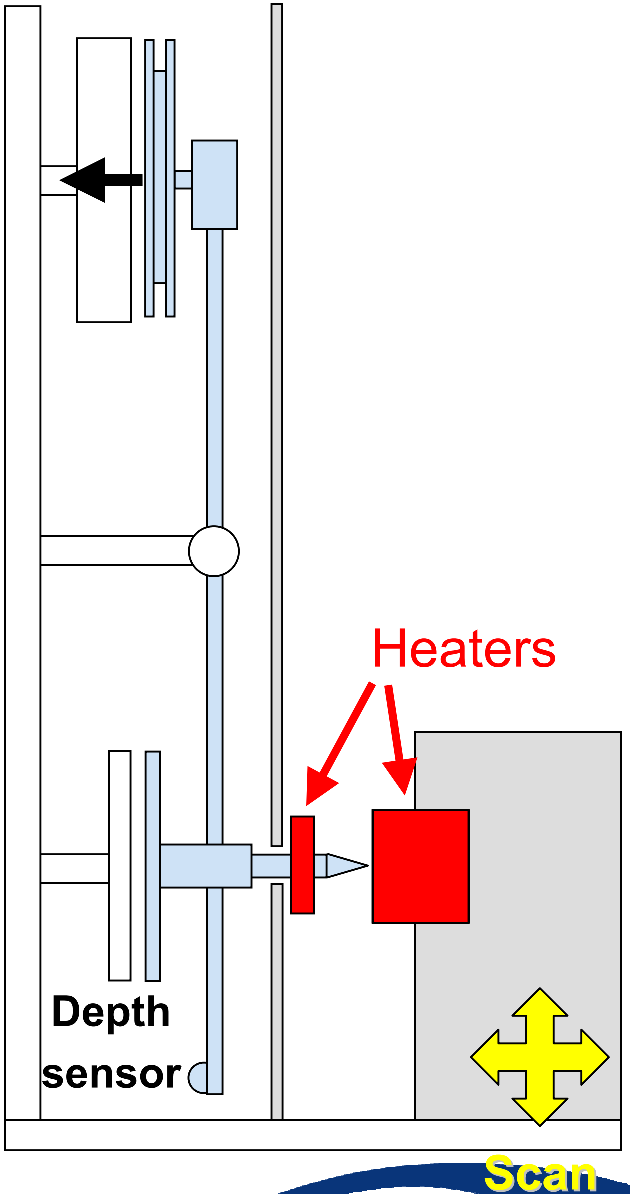
Hot stage – sample temp ≤500°C

Mapping the hardness of tribological coatings





5.2 micron Ion-beam Assisted Deposition (IBAD) Alumina; Stephen Abela, Unversity of Malta



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Preliminary measurements at different frequencies (NPL modified Nanotest)

- Need a solution that is compatible with future hot stage use
- Pendulum damping is adjustable
- Dynamic response should be similar to impact calibrations
- NPL system able to measure ~200 frequencies per hour. (c.f. NanoII 1 per day)

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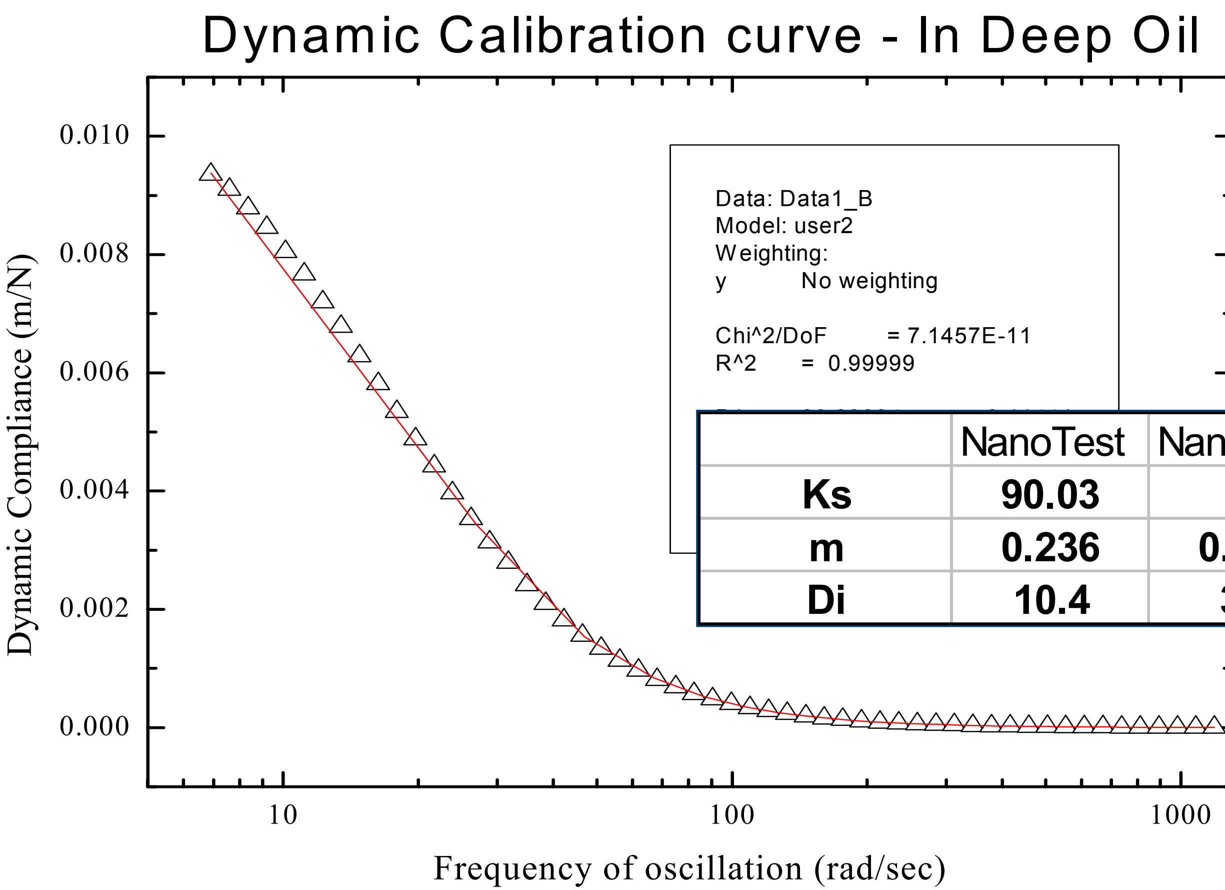
Nanotest Dynamic Compliance vs. Damping



	NanoTest	NanoII	
Ks	**90.03**	**40**	**N/m**
m	**0.236**	**0.007**	**Kg**
Di	**10.4**	**3.8**	**Ns/m**

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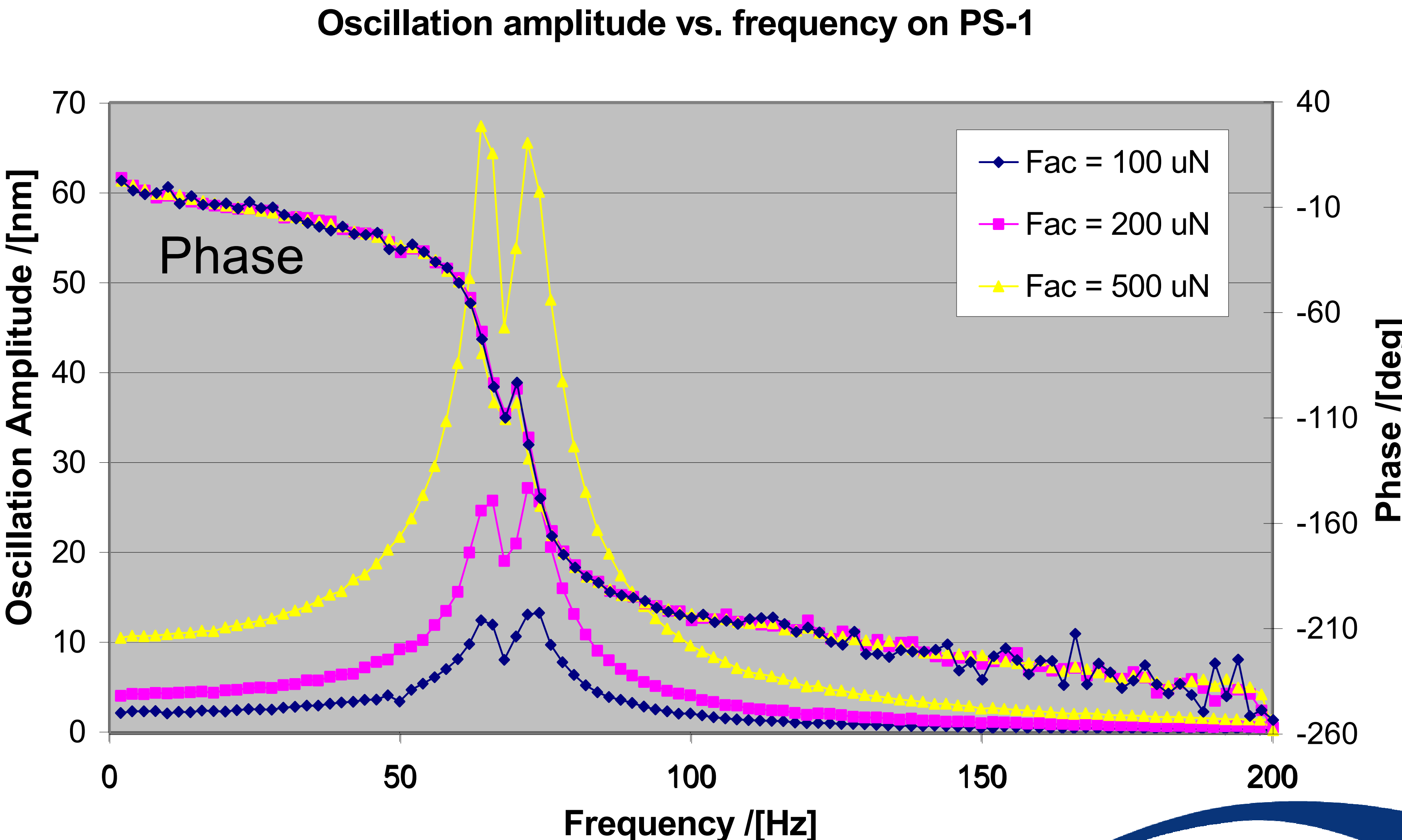
Oscillation response when damped and in contact with PS-1



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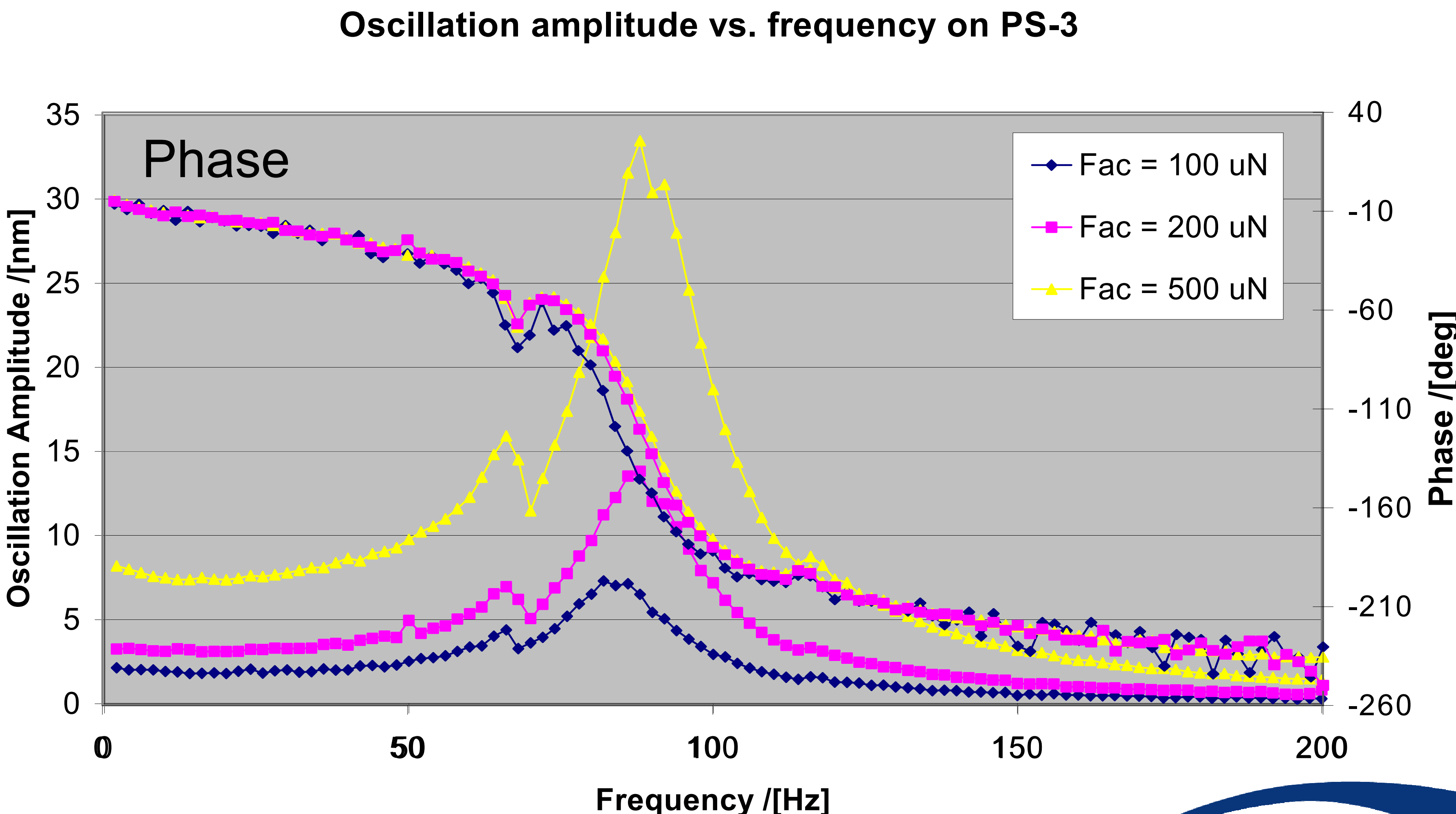
Oscillation response when damped and in contact with PS-3



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Next steps with Dynamic Nanoindentation

- Reduce amplitudes of oscillation (NanoTest)
- Validate calibration procedure
- Calculate modulus results from data
- Compare results with NanoII and DMA

Indentation Creep experiments

Determination of modulus and viscosity
from “load and hold” data.

Viscoelastic Indentation Analysis

- The current investigation builds on previous studies utilising spherical and conical indentation testing and integral analysis of polymer indentation data.*
- Analysis is based within the context of the Hertzian contact problem by Lee and Radock.**

*M.L. Oyen, Phil. Mag. 1-17 (2006)

**J. Appl. Mech. 27 438 (1960).

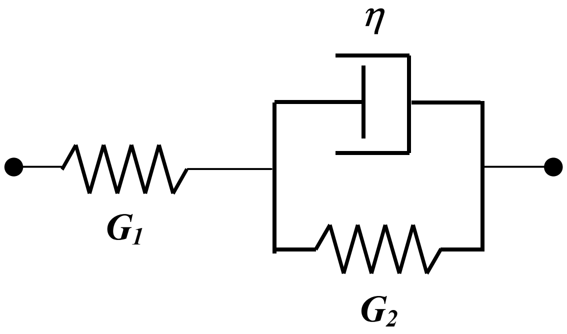
Viscoelastic Indentation Analysis

Governing equations in force-displacement (P-h) variables:

- For indentation with conical/pyramidal indenter:

$$h^2 = \frac{\gamma^2}{\pi \tan\psi} \frac{P}{2G} \longrightarrow h^2 = \frac{\gamma^2}{\pi \tan\psi} \int_0^t J(t-u) \frac{dP(u)}{du} du$$

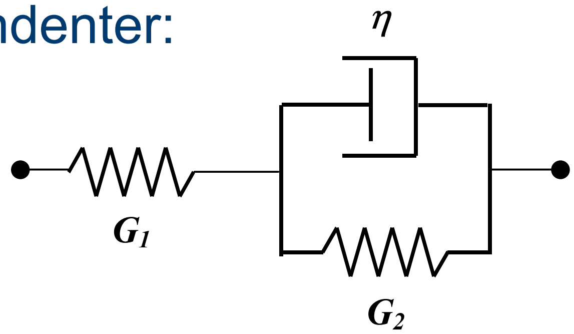
Integration takes place over applied loading conditions to obtain closed-form expressions for the load-displacement-time response for the creep function corresponding to a simplified model:



Conical / Pyramidal Analysis

- For indentation with conical/pyramidal indenter:

$$J(t)=\frac{1}{G_1}+\frac{1}{G_2}\left[1-\exp\left(\frac{-t}{\tau_c}\right)\right] \qquad \tau_c=\frac{\eta}{G_2}$$



- Resulting closed form expression for hold creep:

$$h^2(t)=\frac{\gamma^2}{\pi\tan\psi}\left[rt_0\left(\frac{1}{G_1}+\frac{1}{G_2}\right)-\frac{r\tau_C}{G_2}\exp{-t/\tau_C}\left(\exp{t_0/\tau_C}-1\right)\right]$$

- Expression used for fitting mechanical data:

$$h^2(t)=C_1-C_2\exp\left(-t/\tau_C\right)$$

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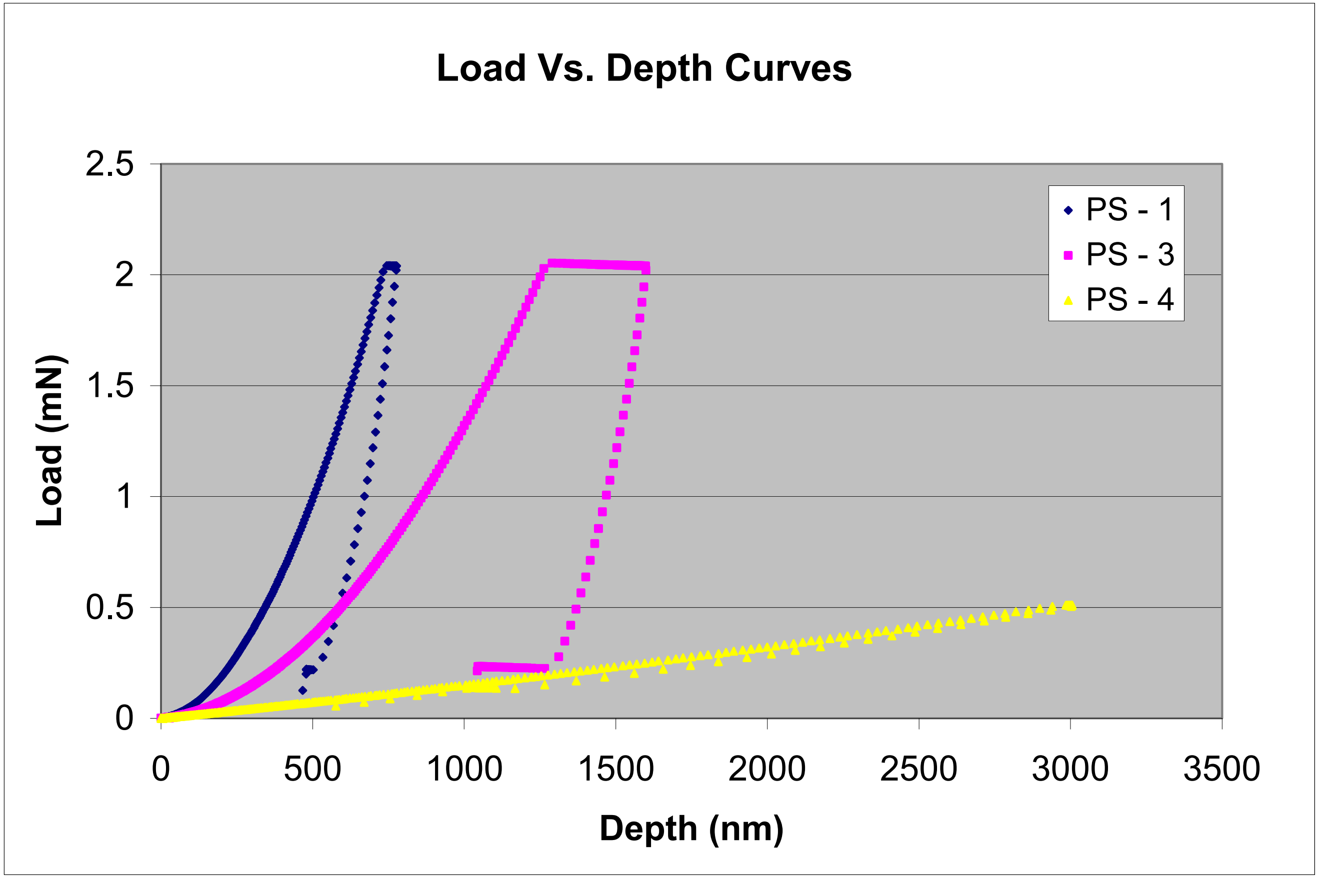
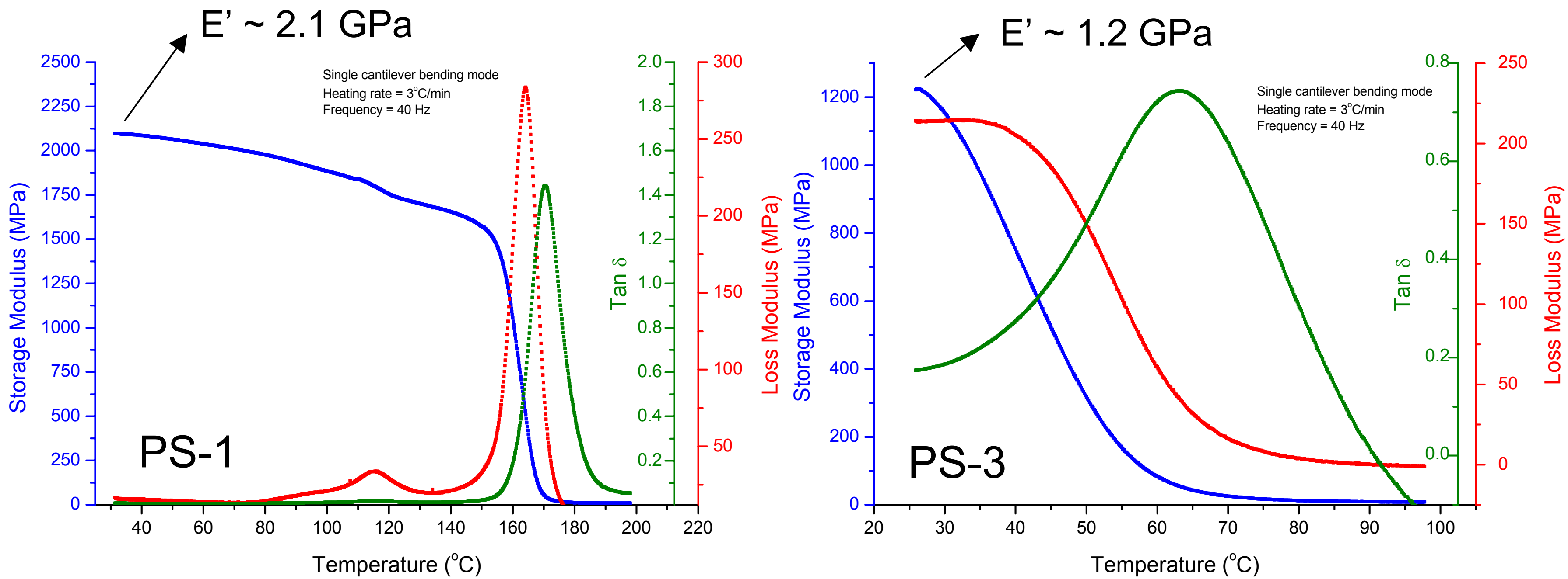
Materials Tested: Commercially Available Standard Polymers

Quasi-static response:



Dynamic Mechanical Analysis (DMA)



Vendor Nominal Values:

Material	Elastic Modulus, E (GPa)	Poisson's ratio, ν
PS-1	2.5	0.38
PS-3	0.21	0.42
PS-4	0.004	0.5

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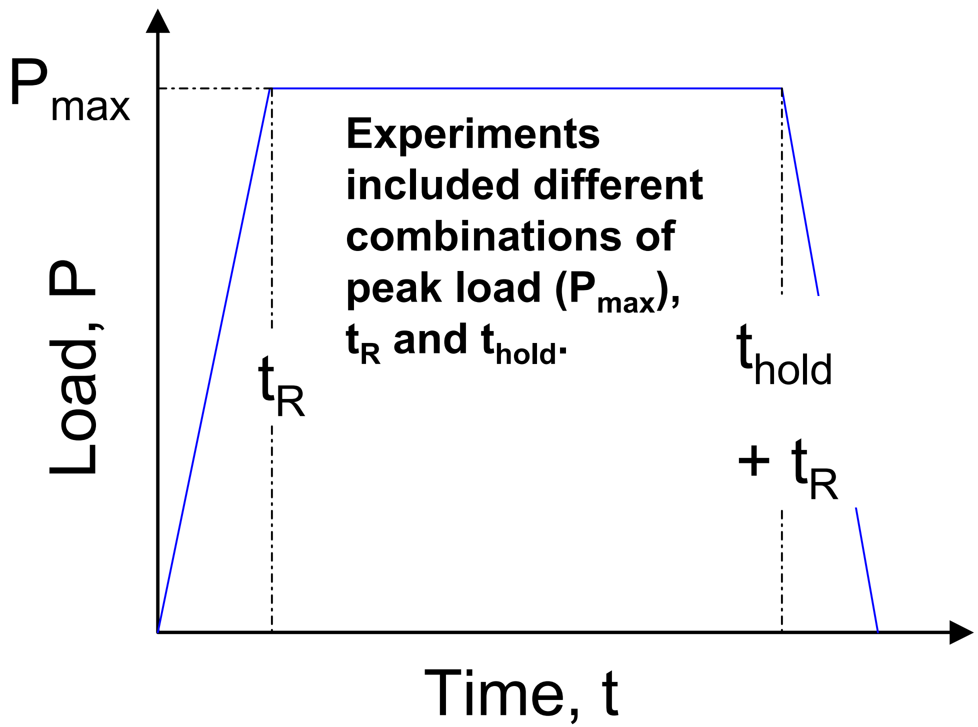
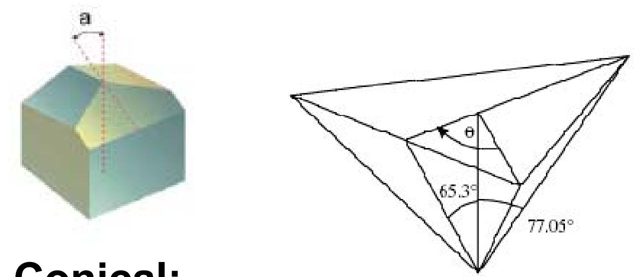
Indentation Creep Experiments

- Load time input function:

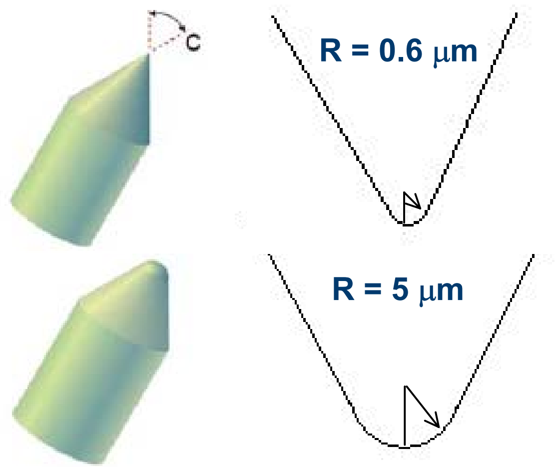


Indenter tips used:

Pyramidal (Berkovich):



Conical:



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Indentation Creep Experiments

Load (mN)	Rise time (s)	Berks	Con 0.6 μm	Con 5 μm
8	5 (LL)	√	√	√
4	5 (LL)	√	√	√
2	5 / 20 / 80 (LL)	√	√	√
	6 / 10 / 19 / 70 (LS)		√	
	19 / 70 (LS)			√
1	5 (LL)	√	√	√
0.5	5 (LL)	√	√	√
0.25	5 (LL)	√	√	√
0.125	5 (LL)		√	√
0.075	5 (LL)		√	√

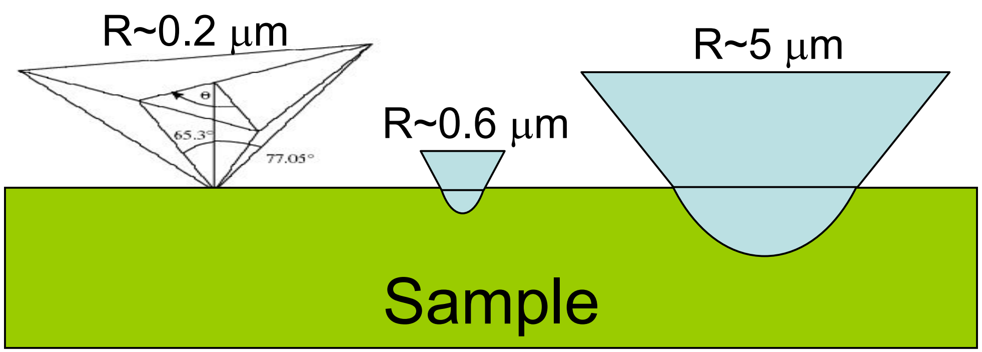
LL: Constant loading rate

LS: Constant strain rate

Indentation Creep Experiments

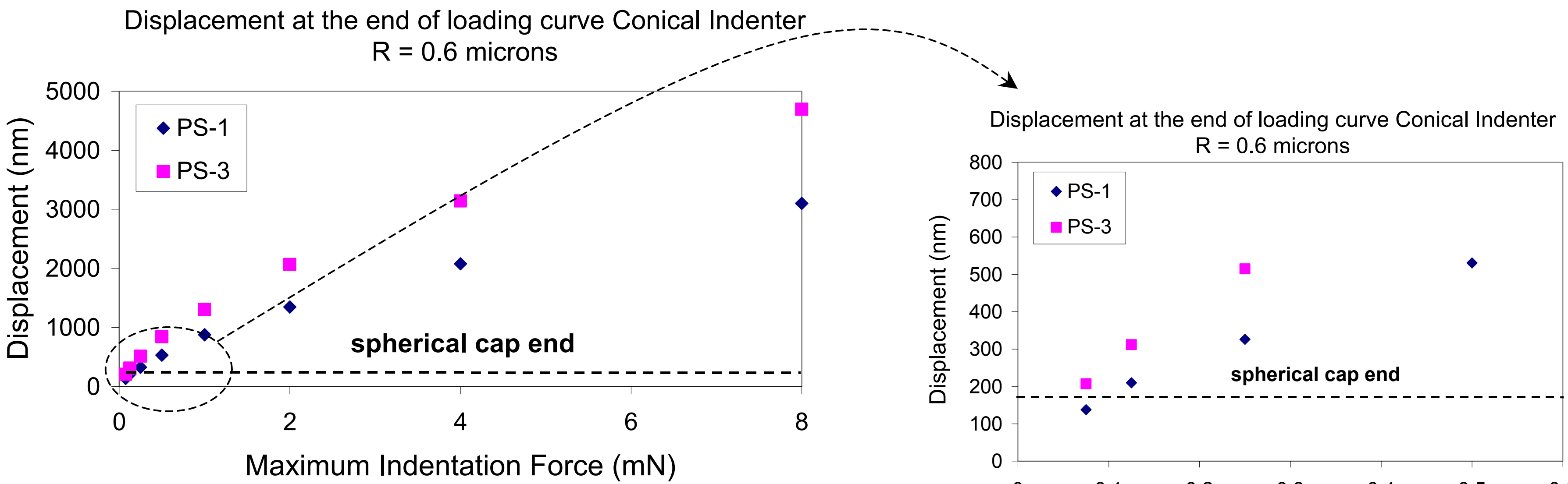
Conical / Pyramidal Analysis $h^2(t) = C_1 - C_2 \exp(-t/\tau_C)$

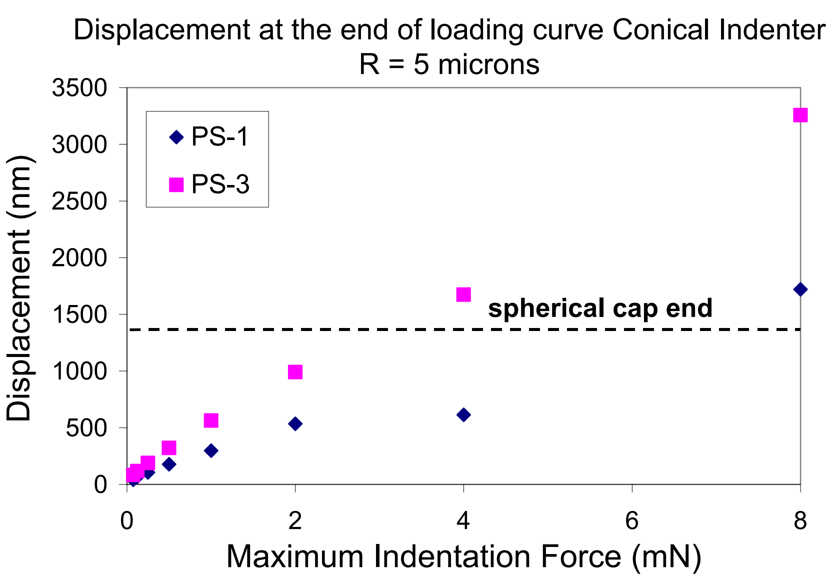
applied to the three indenters.



*Investigate effect of varying max. loads and rise times.

Maximum Indentation Force vs. Displacement





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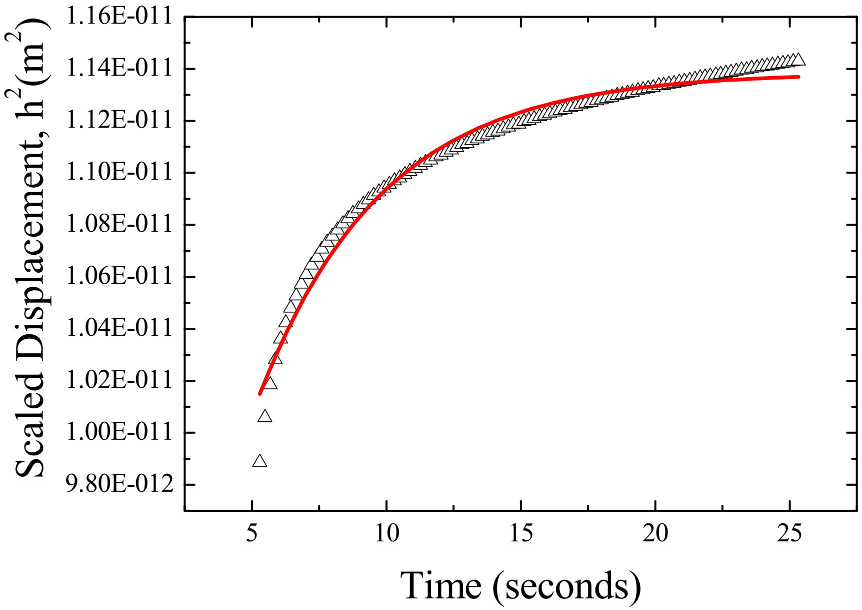
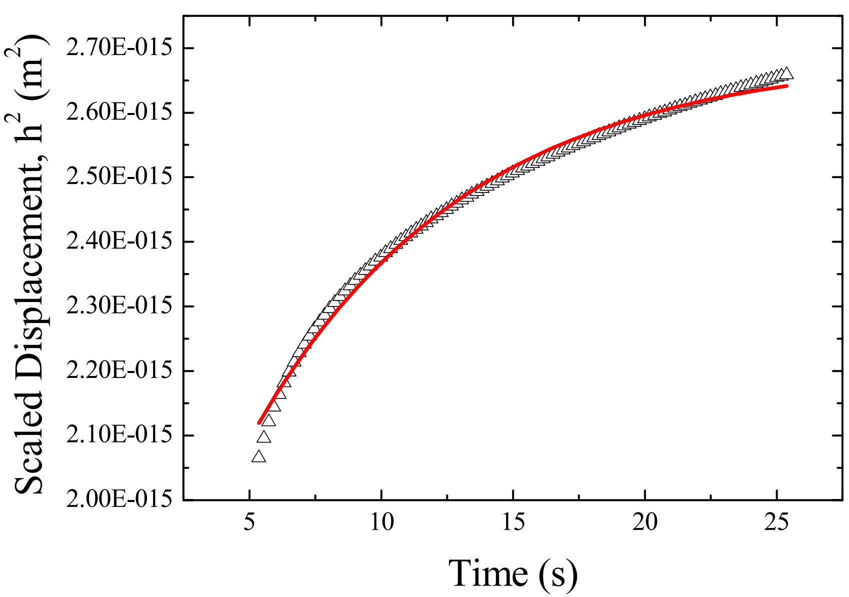
Conical Analysis: PS1 and PS3 Creep Response

PS-1



PS-3



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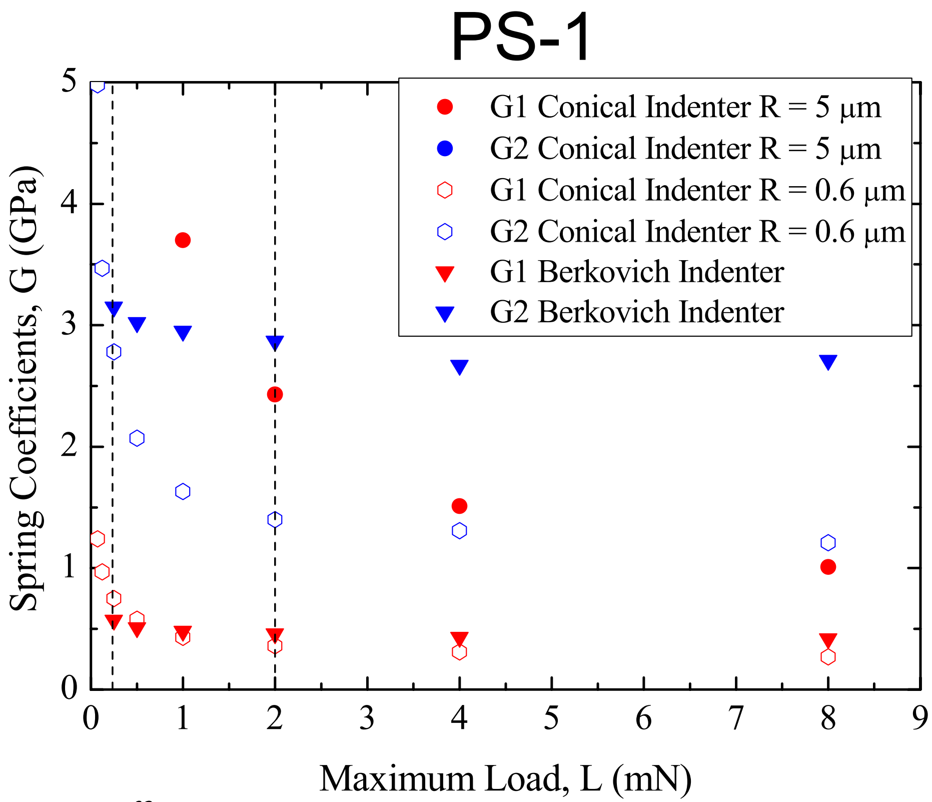
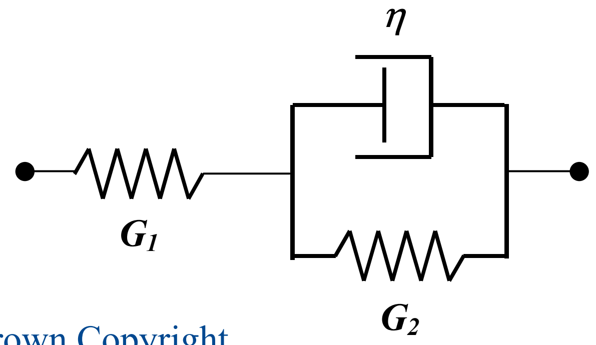
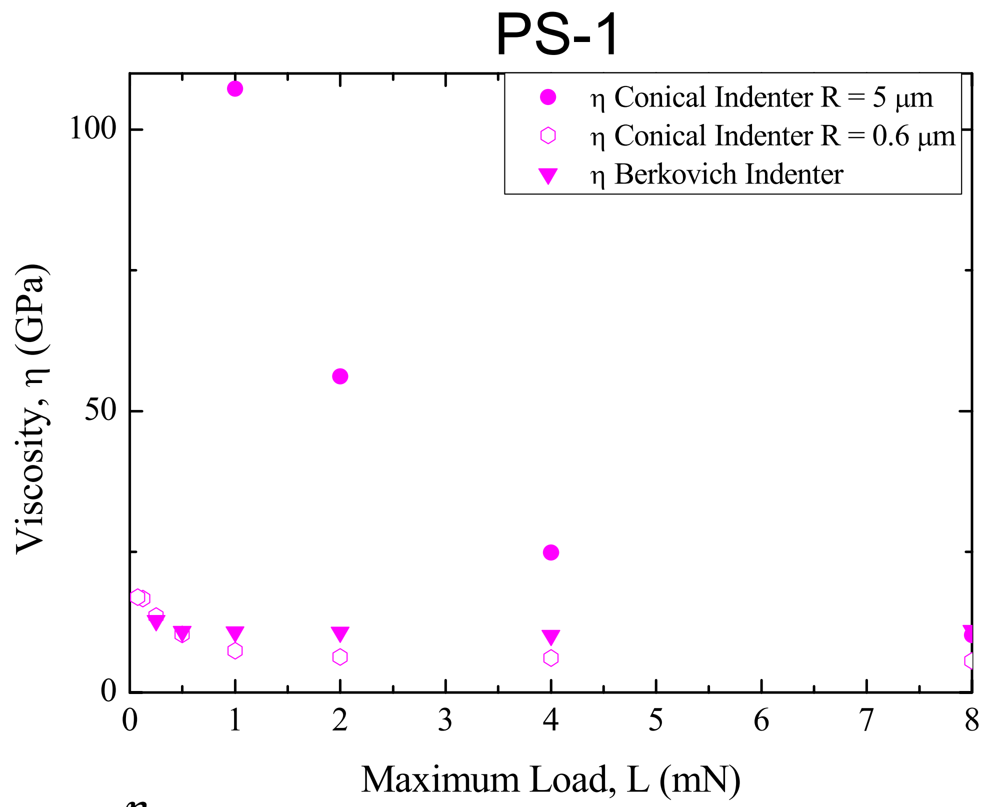
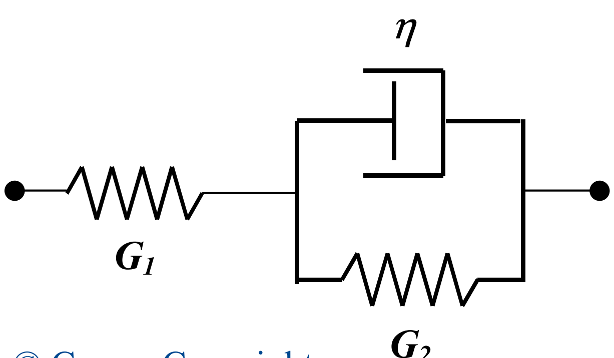
Conical Analysis: Calculated Spring Constants (G_1 and G_2)



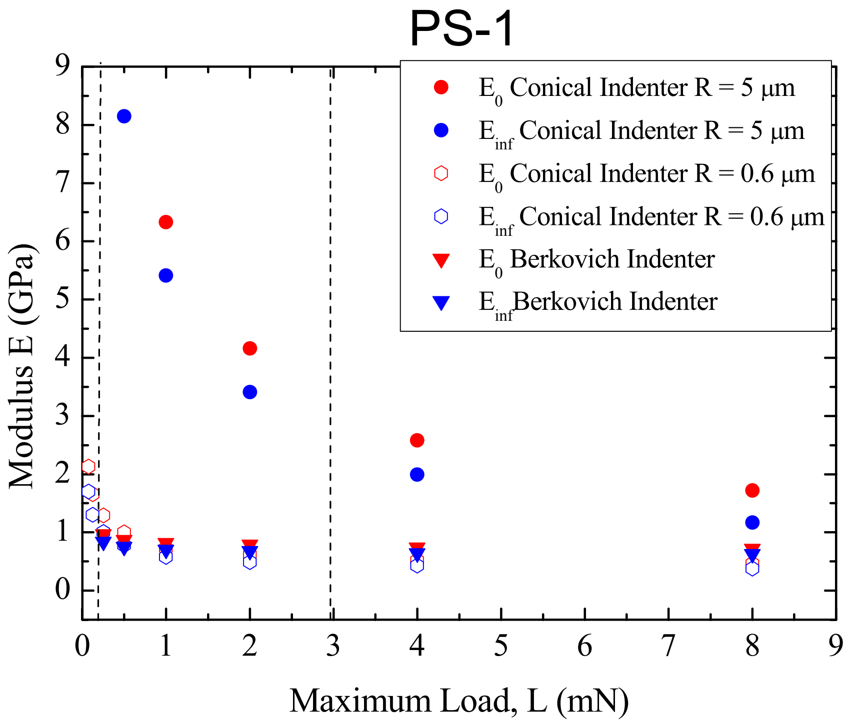


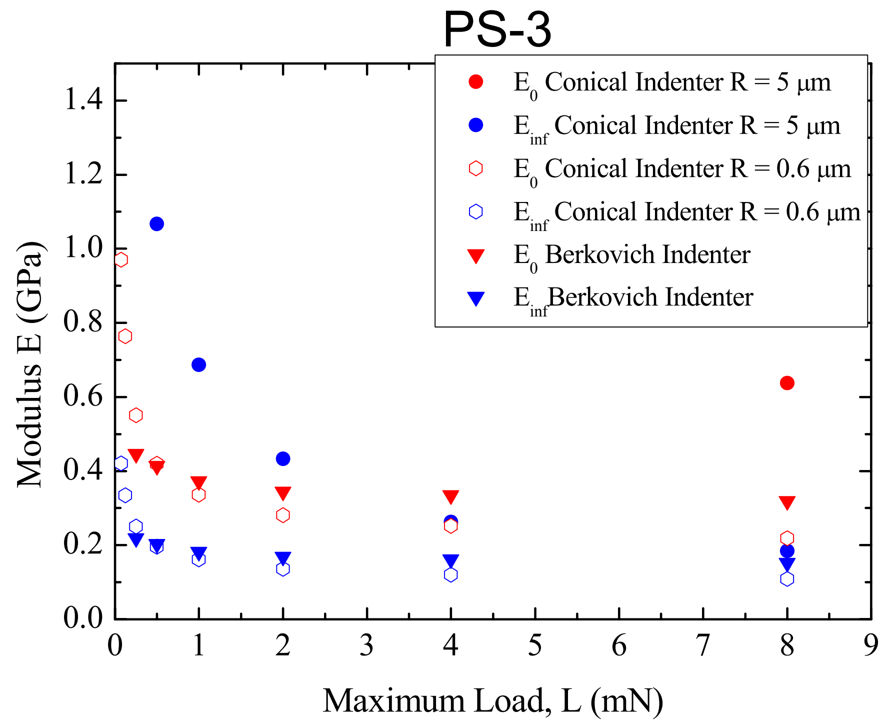
Conical Analysis: Calculated Viscosity



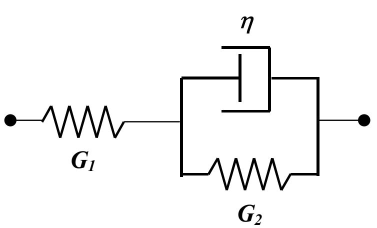


Conical Analysis: Calculated Elastic Modulus (E_0 and E_{inf})





$$J(t) = \frac{1}{G_1} + \frac{1}{G_2}\left[1 - \exp\left(\frac{-t}{\tau_c}\right)\right]$$



$$G_0 = (1/2)\left[\lim_{t\to 0} J(t)\right]^{-1} = G_1$$

$$G_\infty = (1/2)\left[\lim_{t\to \infty} J(t)\right]^{-1} = (1/G_1 + 1/G_2)^{-1}$$

→

$$E_0 = 2G_0(1+\upsilon)$$

$$E_\infty = 2G_\infty(1+\upsilon)$$

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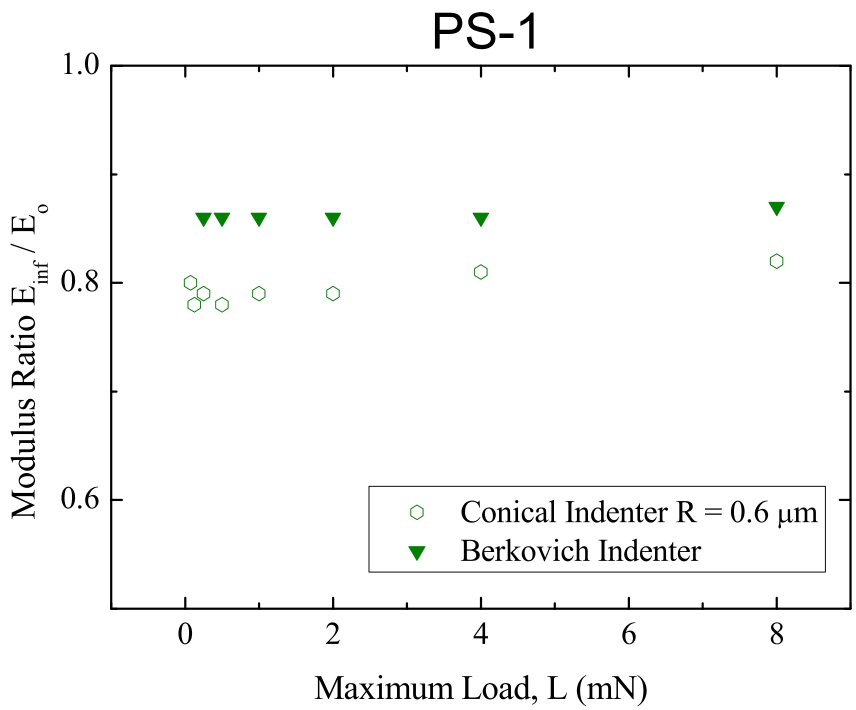
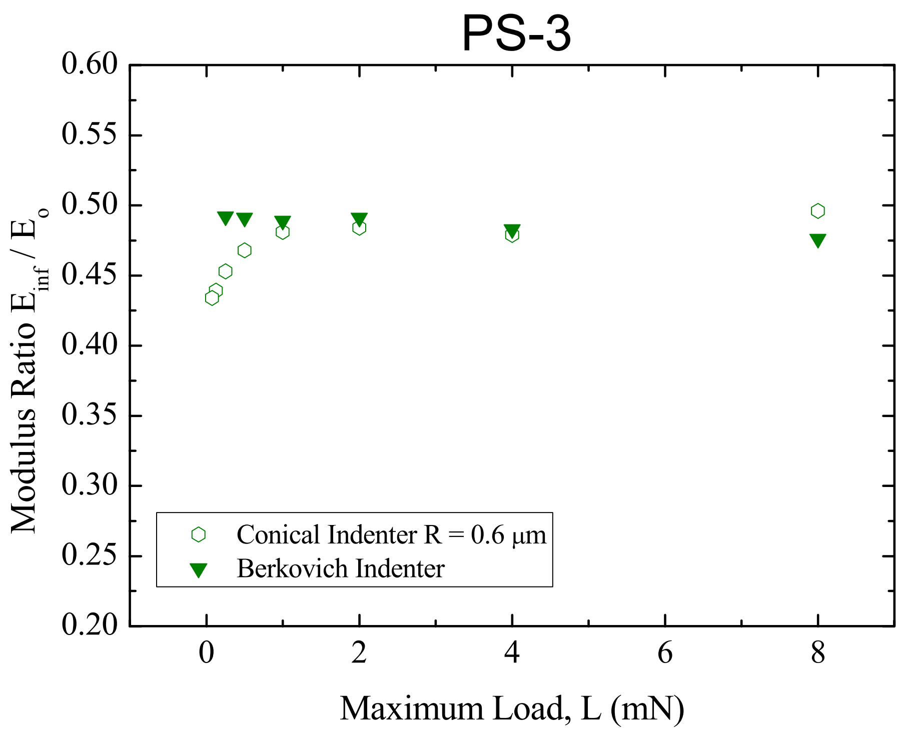
Conical Analysis: Calculated E_∞/E_0 Ratio





E_∞/E_0 is a measure of polymer "elasticity"

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Discussion / Conclusions

- Need better standards for testing mechanical behaviour of viscoelastic materials

	Vendor nominal	*DMA*		*Dynamic Nano-Indentation*	
	E (GPa)	**E’ (GPa)**	**E” (GPa)**	**E’(GPa)**	**E’’(GPa)**
PS1	**2.5**	**2.1**	**0.09**	**2.5-2.6**	**0.017**
PS3	**0.21**	**1.2**	**0.19**	**1.3-1.7**	**0.21**

- Creep measurement techniques allow for measurements of “short” E_0 and “long” E_∞ values in the same test.
- When stating E values, time frames of methodology employed must be specified.

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Discussion / Conclusions

- Sharp indenters (i.e. Berkovich) are challenging due to “additional” time-independent plastic deformation under sharp contact.
- Obtained modulus values are smaller than true elastic modulus of the material : conical / pyramidal analysis still under investigation.
- Results from conical analysis are largely independent of max. applied force for Berkovich and Conical (R = 0.6 μm) indenter tests.
- Deviation of modulus values was observed at low loads where indenter geometry is spherical.

Next Steps:

- Apply spherical analysis to Creep indentation test + use spherical indenter with R > 100 μm.
- Creep indentation tests vs. Greg/Louise predictions on modelled polymeric materials.
- Analyse creep data when applying a constant strain rate step load. (In collaboration with Cambridge University)
- ***Aim: Identify the agreement between methods as a route to validation of indentation derived viscoelastic property measurements.***
  Draft ISO New Work Item

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