# 8. Measurement of soft materials

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# Issues with soft materials

## Measurement problems

- holding the sample
- finding the surface
- maintaining hydration

## Low elastic modulus

- large displacements for low loads
- displacement limitation - low strain
- load limitation – instrument sensitivity

## Time dependent response

- viscoelastic creep on load
- viscoelastic recovery on unload
- viscoplastic deformation on load
- poroelastic responses in hydrated porous materials

# The problem with polymers

**Mechanical properties are non-equilibrium and time dependent:**

Ignore them (or load very rapidly)
Explore them (use the time-response)

**Several choices of methods for indentation:**

Indenter shape, load cycle, analysis method

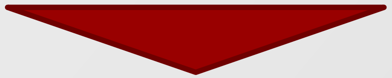
**How do the measured values relate to other test methods?**

Tensile, tensile creep, dynamic

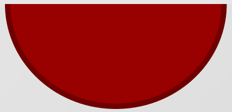
# Instrumented indentation methods

## Contact geometry:

Berkovich



Sphere



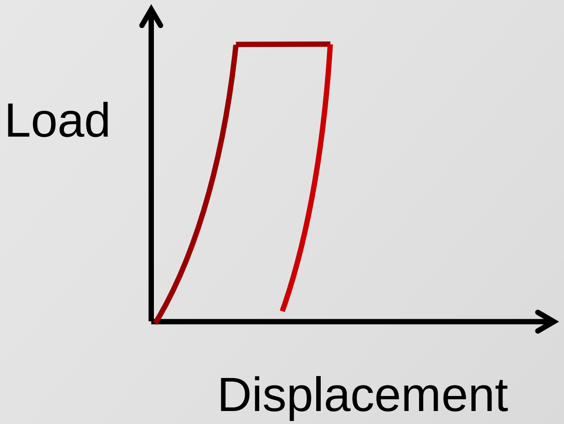
Flat punch

Punch: surface alignment < 1°
use tilt stage and AFM

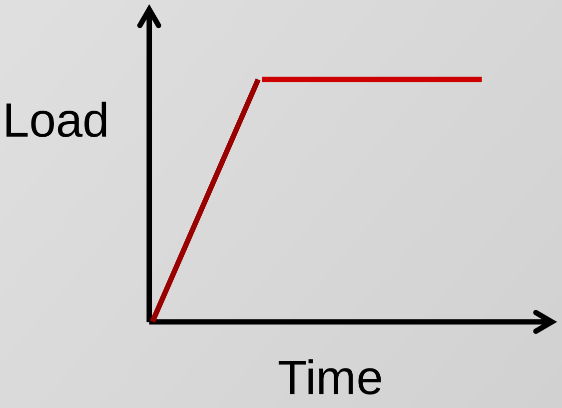
Known contact area and
unchanging during creep

## Load cycle and analysis method:

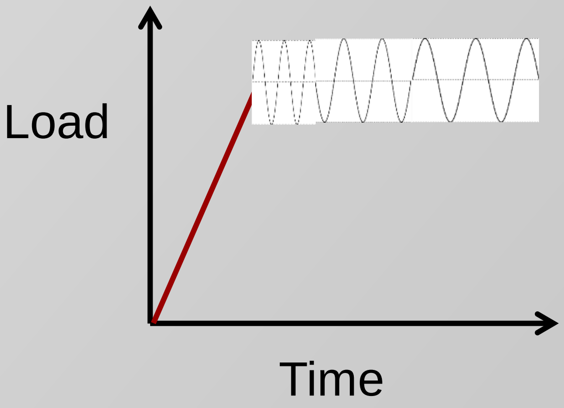
Load – unload




Ramp and hold

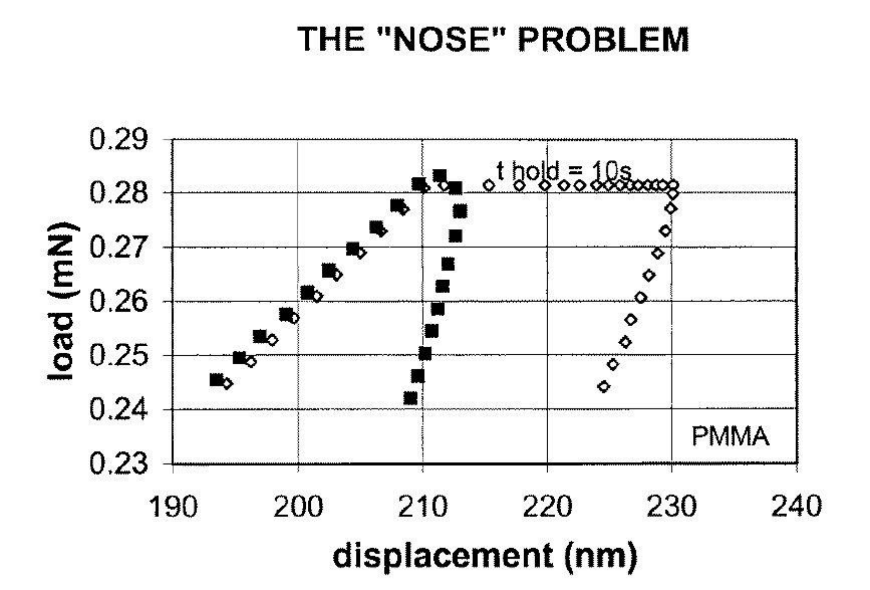



Dynamic

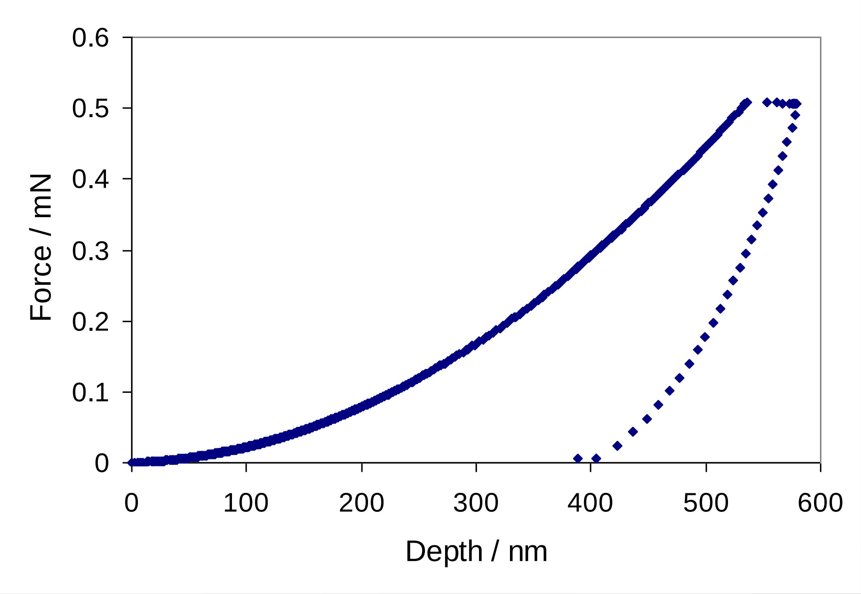


# Suitable approaches for polymers

Traditional approach:




Brisco et al, J. Appl. Phys D, 31, 2395 (1998)




Unload rate 10x greater than final creep rate

# Suitable approaches for polymers

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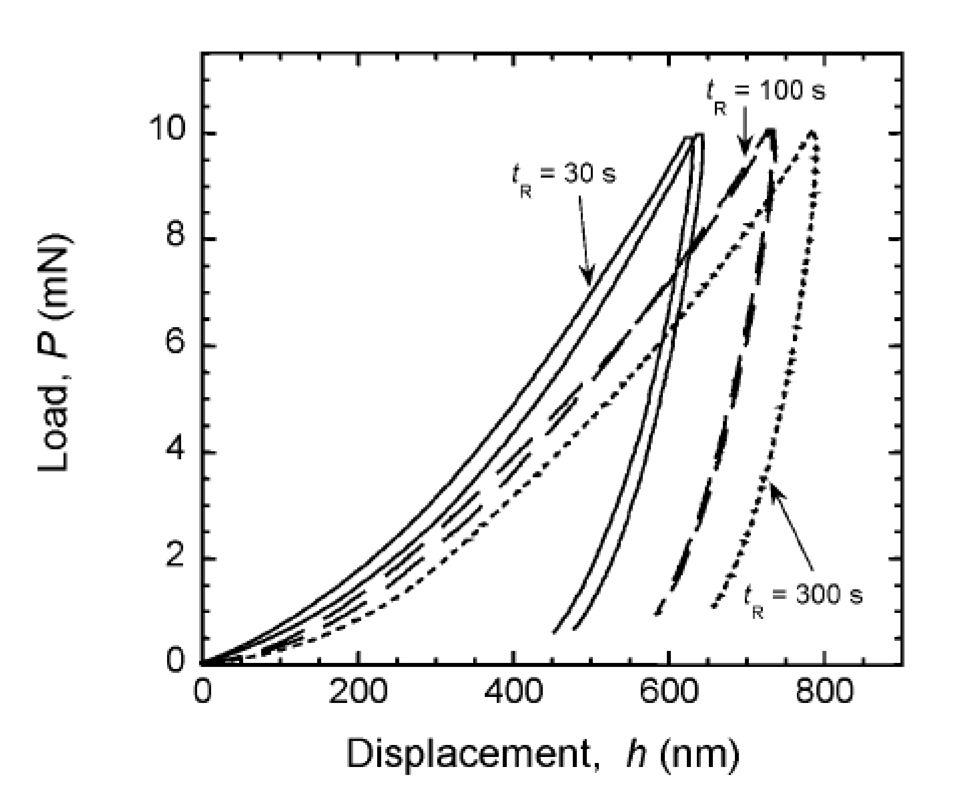
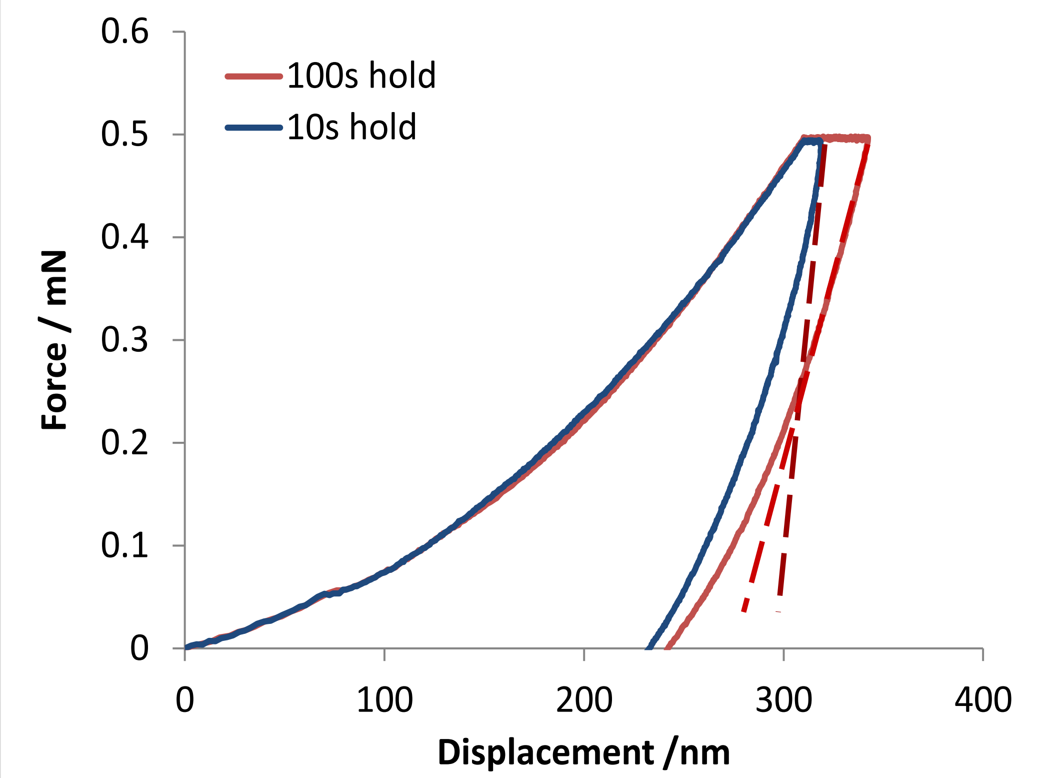
## Traditional approach

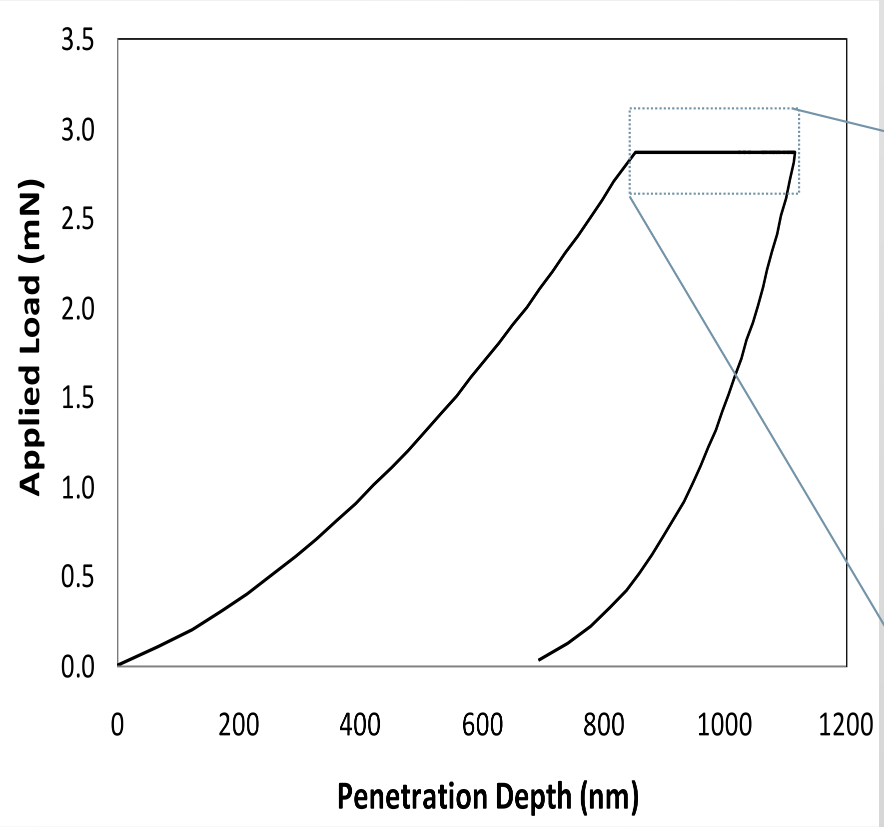
Effect of loading rate and hold time on dry dentine – material response is time dependent

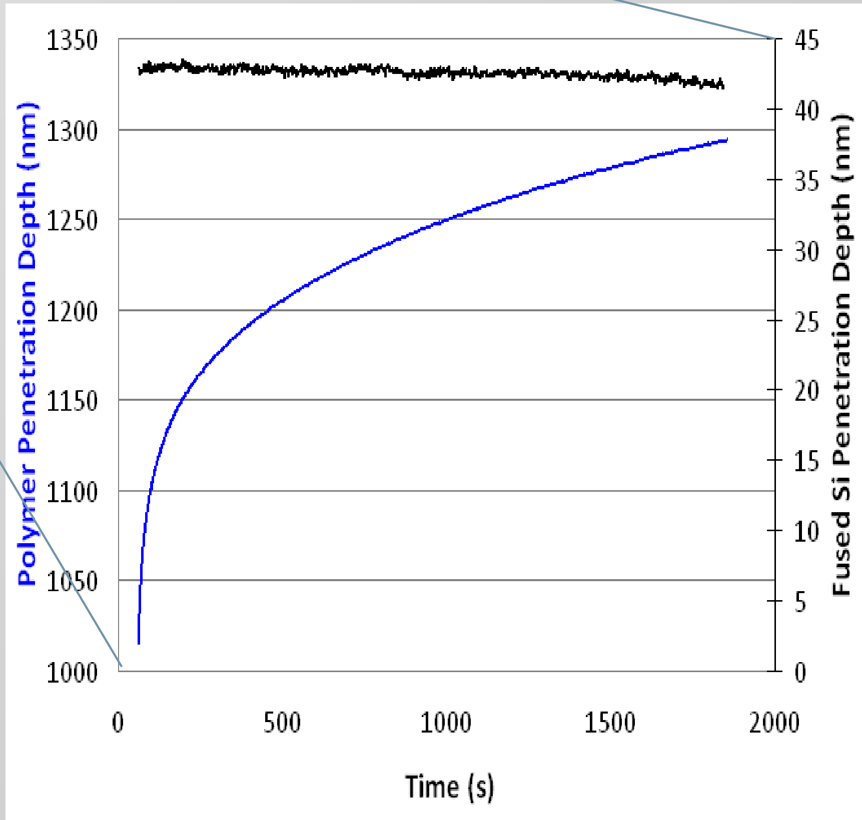



Oyen and Bushby, Int. J. Surf. Sci. Eng. 1 (2007) 180

# Long term creep response of polymer topcoat

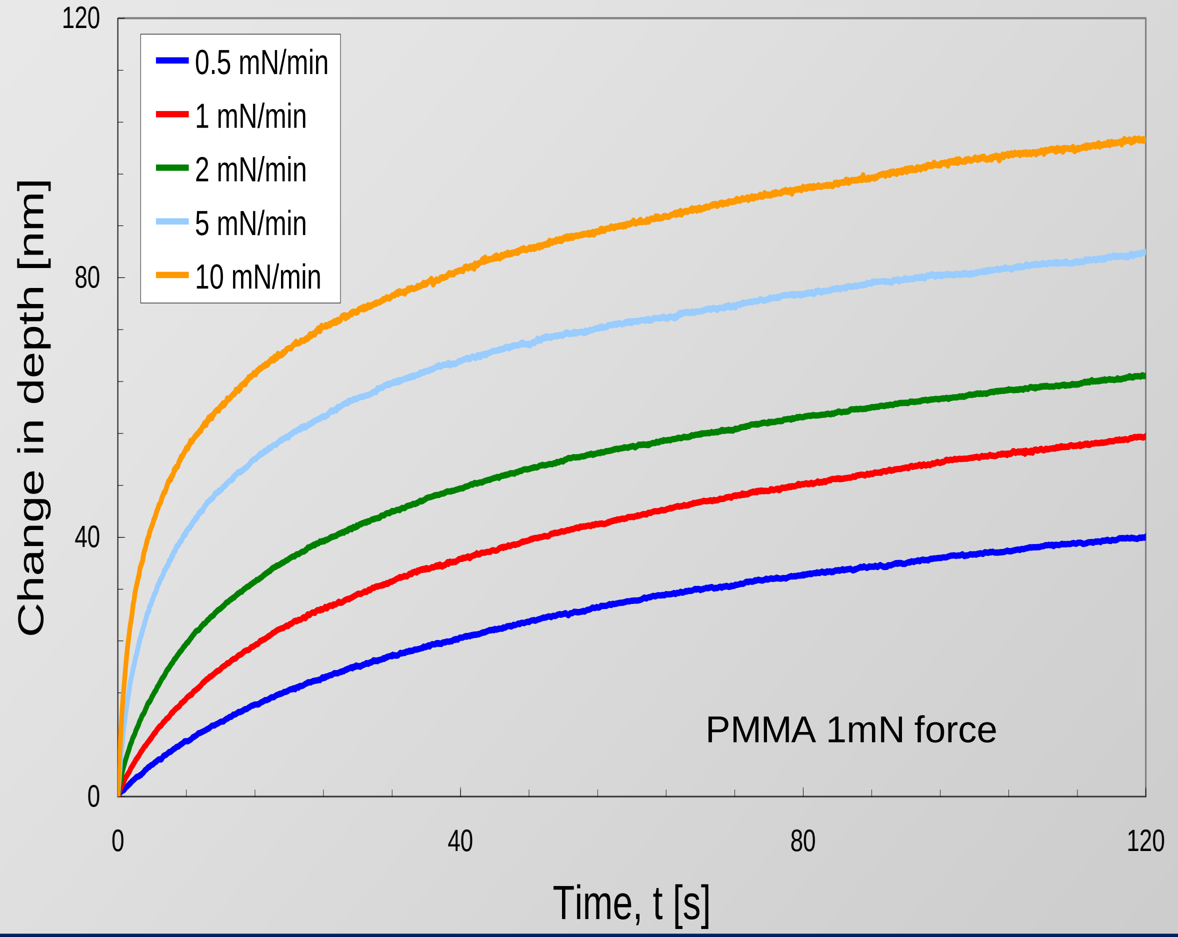



- •GEN III polymer topcoat
- •Spherical indenter (R = 10 µm)
- •3mN load, Loading rate 6 mN/min
- •30 minute pause at max. load

# Creep as a function of loading rate on PMMA

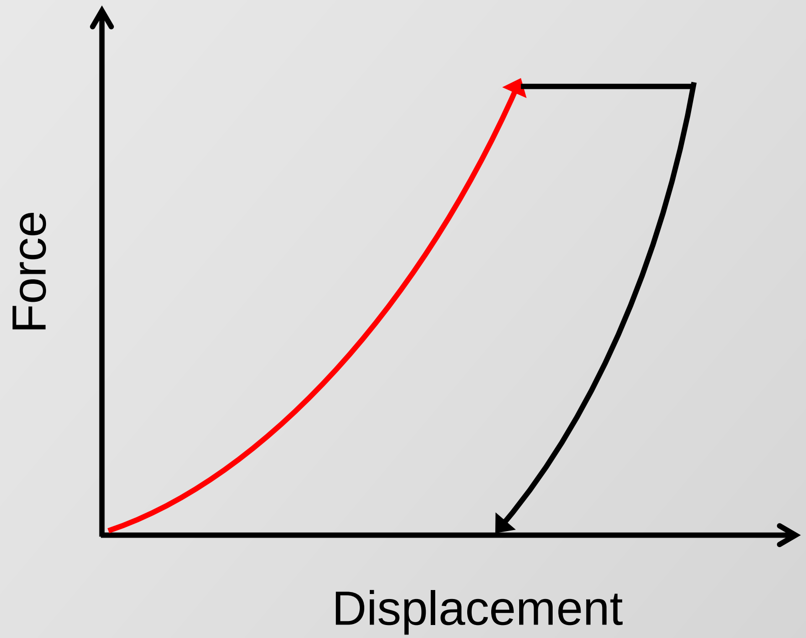
The creep behaviour is highly influenced by the loading rate used during the test. The faster the loading rate, the higher the creep.



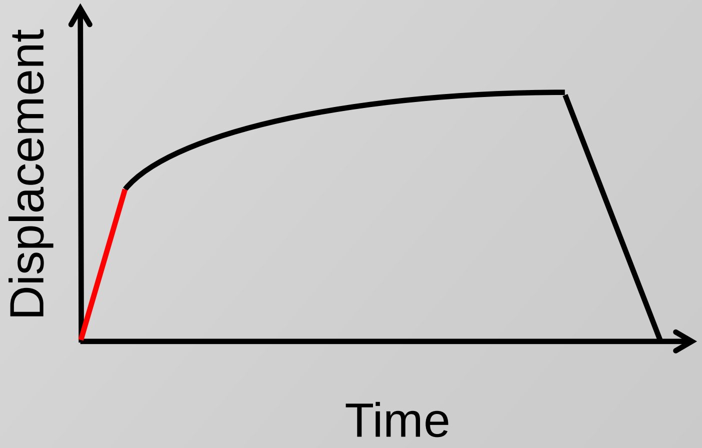
# Creep compliance method

For visco-elastic, creeping solids
Measure the time dependent response directly

**Ramp and hold cycle**



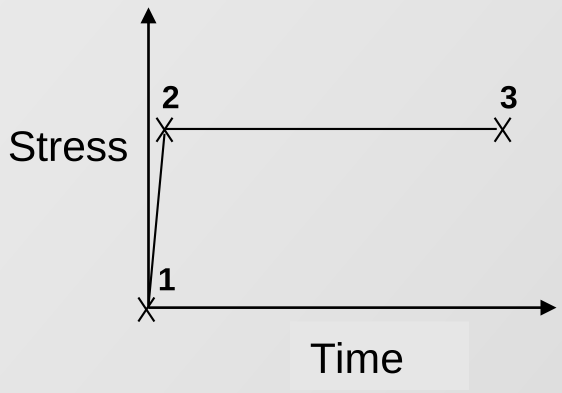

Loading
Hold
Unloading

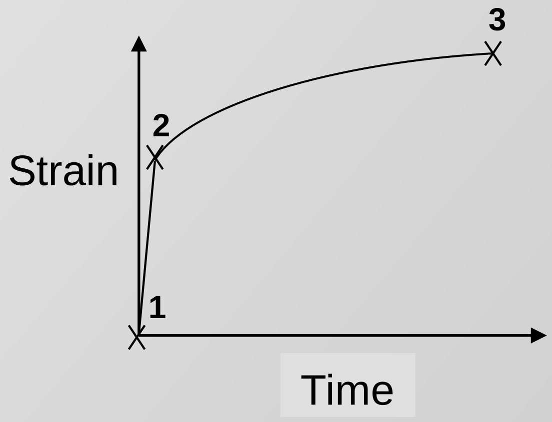



Load rapidly at controlled rate
Hold constant force to assess time dependent response (creep)

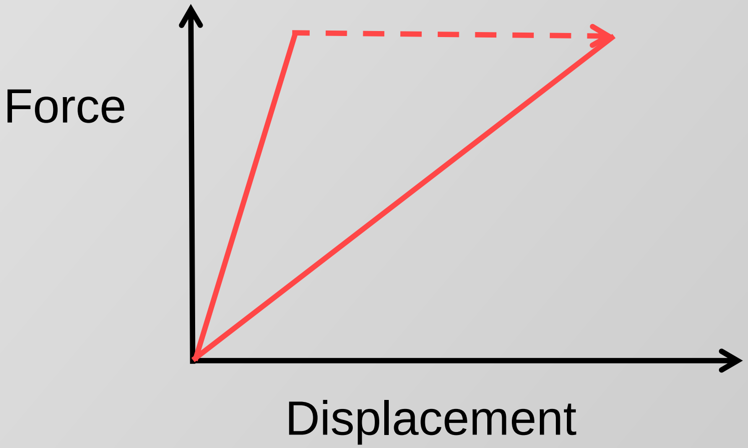
# Elastic-viscoelastic correspondence

Time dependent strain at constant stress

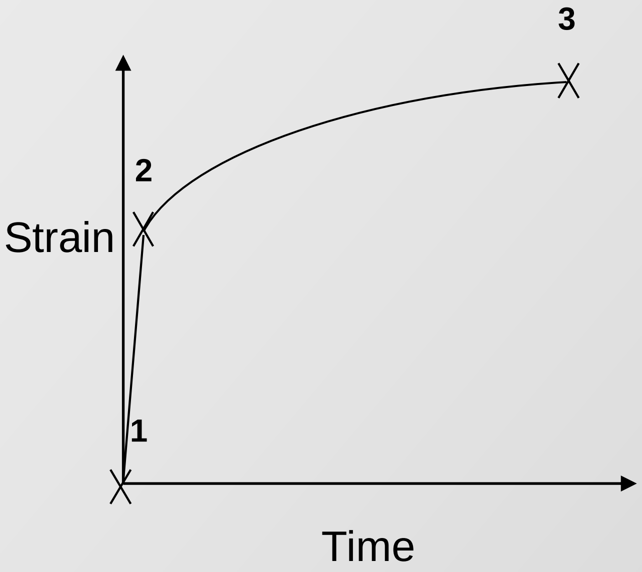



Creep displacement analogous to a changing elastic modulus



# Elastic-viscoelastic correspondence




In the experiment we sample the creep compliance function over a finite time scale.

We cannot load instantly (ramp 1 $\rightarrow$ 2)

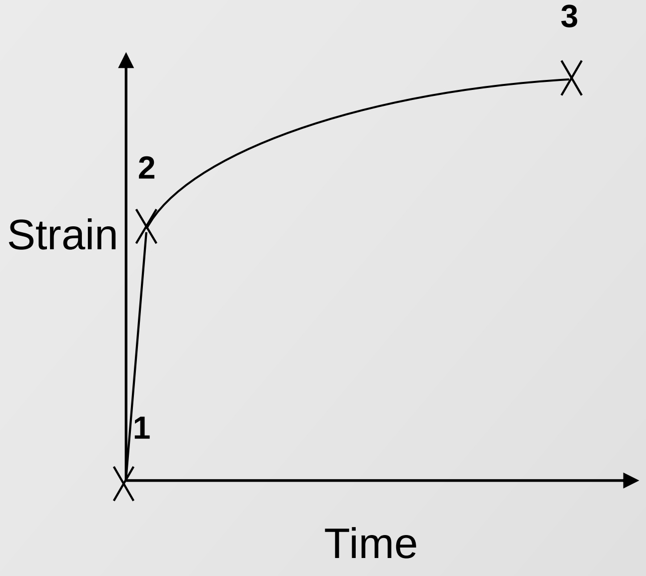
And we cannot hold indefinitely

In a practical experiment we can load in about 10 seconds at a constant load rate.

Then hold the load constant for 100s $\rightarrow$ 1000s

The unloading response is not useful

# Creep compliance method




We can sample the creep response over time in the ‘ramp and hold ‘ test cycle

The creep compliance function has to be solved for the loading (ramp) and creeping (hold) parts

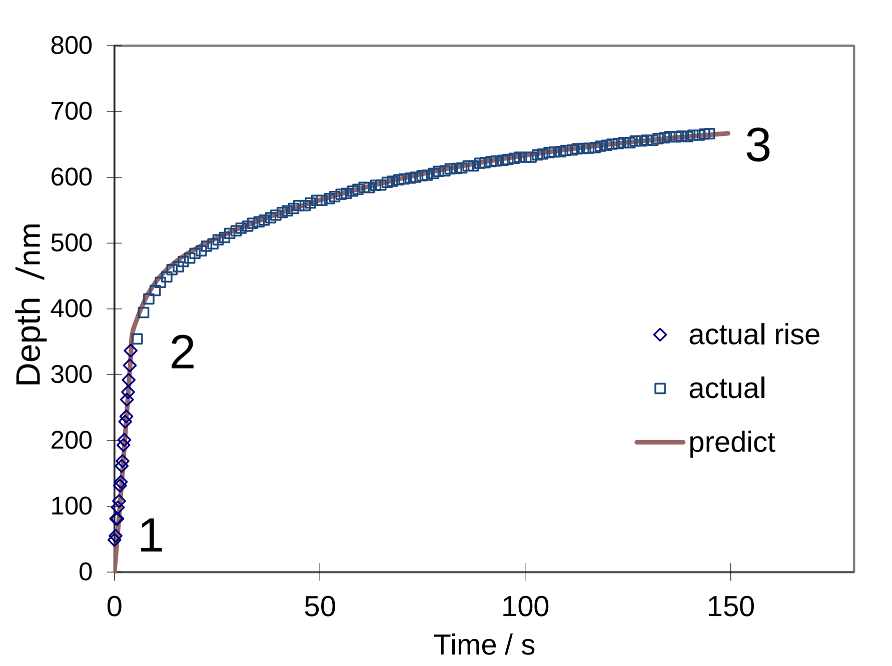
By fitting a function to the constant load segment (creep 2 $\rightarrow$3), the coefficients and time constants can be found

Load (1 $\rightarrow$ 2) in 10s
Hold (2 $\rightarrow$ 3) for 100s – 1000s

The creep compliance function represents the displacement vs time

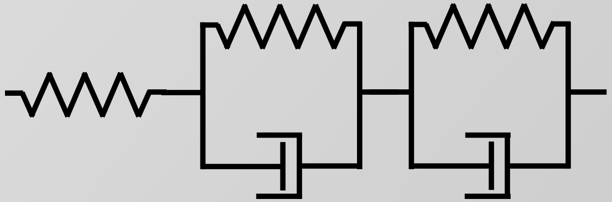
This is represented as a time-dependent elastic modulus in a Hertz contact model

# Creep compliance method




**Ramp and hold load cycle**

Fit displacement : time data
using 5 element exponential model



Prony series for 2 time constants
Described by 5 constants $C_0$, $C_1$, $C_2$, $\tau_1$, $\tau_2$

e.g. for spherical indenter, radius *R*, from Hertz equation $h^{\frac{3}{2}} = \frac{3}{4}\frac{1}{\sqrt{R}}\frac{(1-\nu^2)}{E}F$

Replace elastic modulus $E' = (1-\nu^2)/E$ with creep compliance function $J(t)$

# Creep compliance method

$$J(t) = C_0 - \sum C_i \exp(-t/\tau_i)$$

$C$ = compliance coefficients, $\tau$ = time constants

$$h^{3/2}(t) = \frac{3k}{4\sqrt{R}}\left[C_0 t - \sum C_i \tau_i \left(1 - \exp(-t/\tau_i)\right)\right]$$

For the ramp loading (1 $\rightarrow$ 2)

$$h^{3/2}(t) = \frac{3k}{4\sqrt{R}}\left[C_0 t_R - \sum C_i \tau_i \exp(-t/\tau_i)\left(\exp(t_R/\tau_i) - 1\right)\right]$$

For the constant load (creep 2 $\rightarrow$3)

Determine 3 parameters to describe elastic behaviour

Instantaneous modulus $E_0$' (elastic)

$$E'_0 = E'(0) = \frac{1}{J(0)} = \frac{1}{(C_0 - \sum C_i)}$$

Infinite time modulus $E_\infty$' (relaxed)

$$E'_\infty = E'(\infty) = \frac{1}{C_0}$$

Measure of extent of viscoelasticity

Creep ratio, CR $= 1 - \frac{E'_\infty}{E'_0}$

# Ramp and frequency sweep test method

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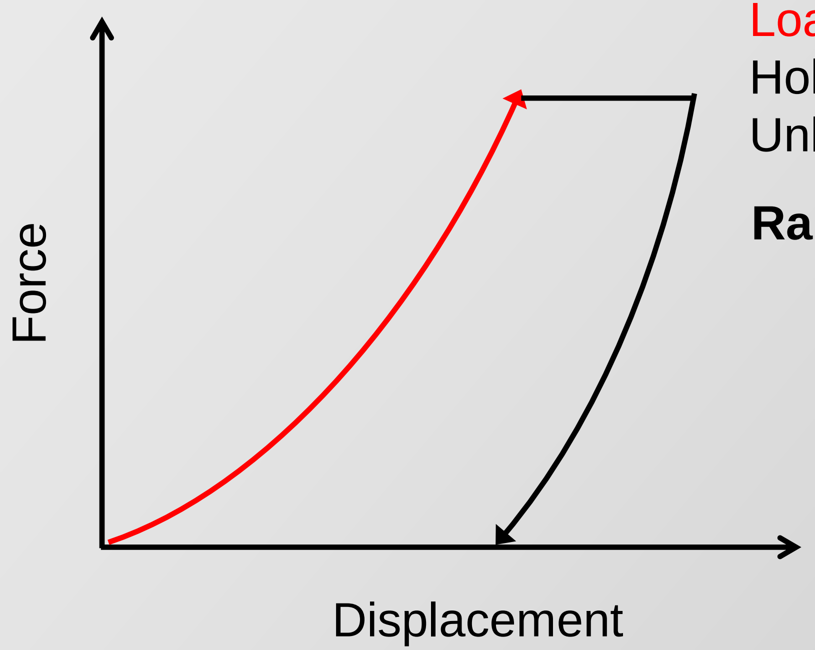
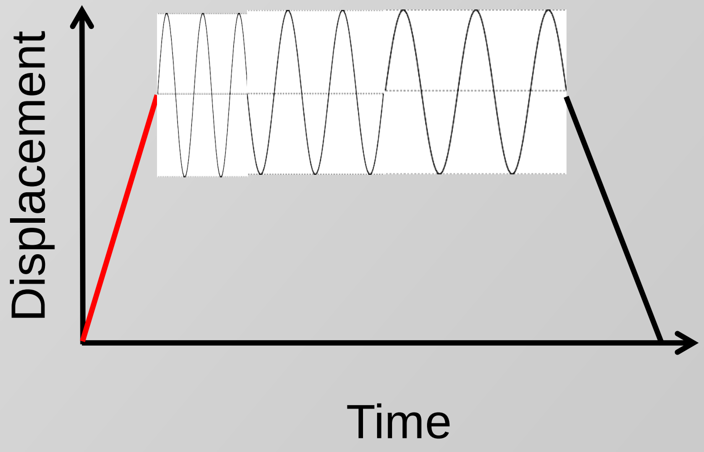


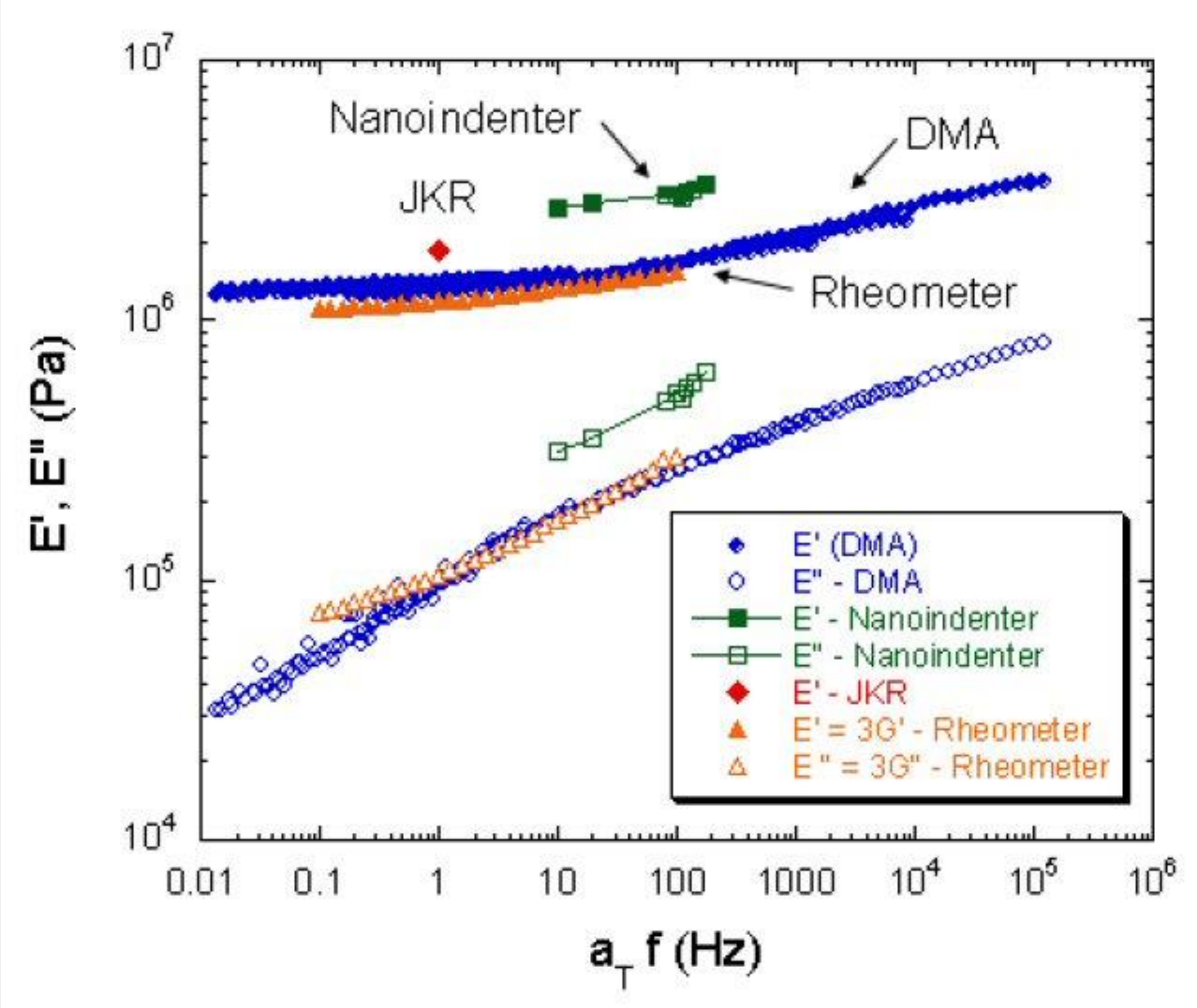

Loading
Hold
Unloading

**Ramp and frequency sweep**




Load rapidly at controlled rate
Oscillate force to assess frequency dependent response
Storage modulus E’,  loss modulus E” and  tan$\delta$

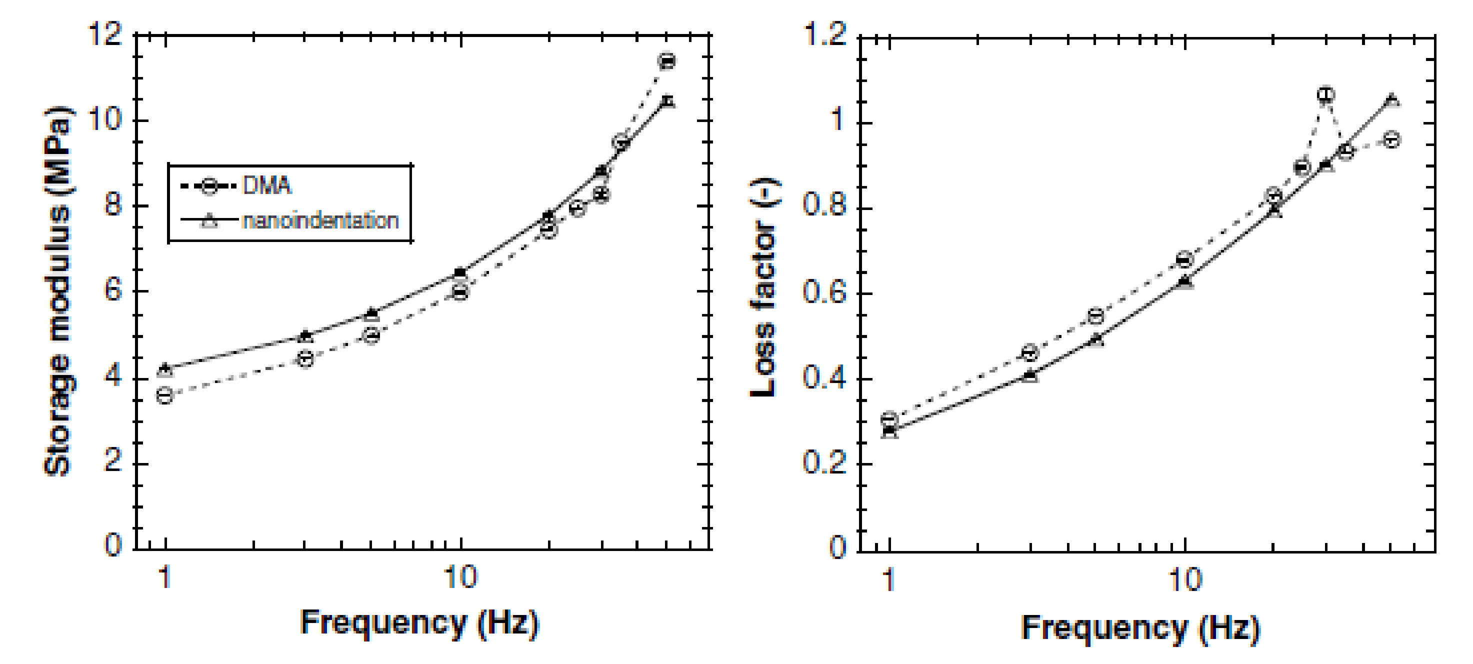
# Comparison of methods – DMA vs dynamic indentation




White *et al*, MRS Sypm Proc Fall 2004

# Comparison of methods – DMA vs dynamic flat punch indentation

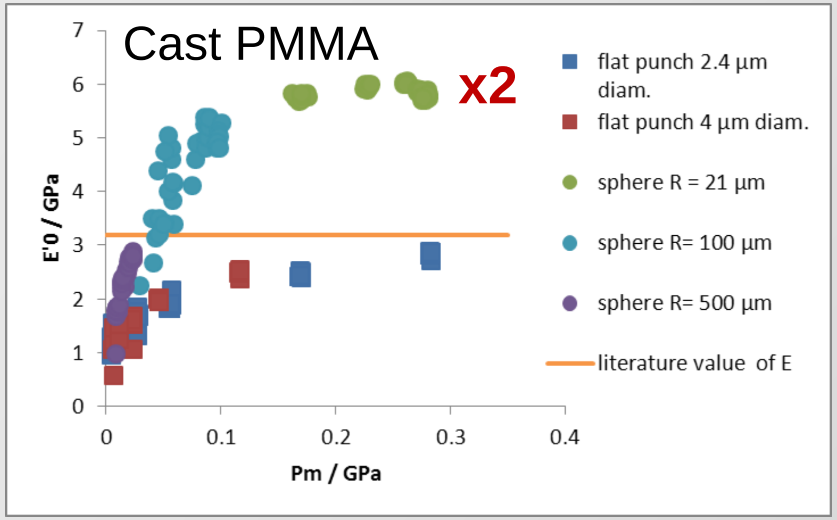
Indentation bulk highly plasticized PVC : Flat punch indenter

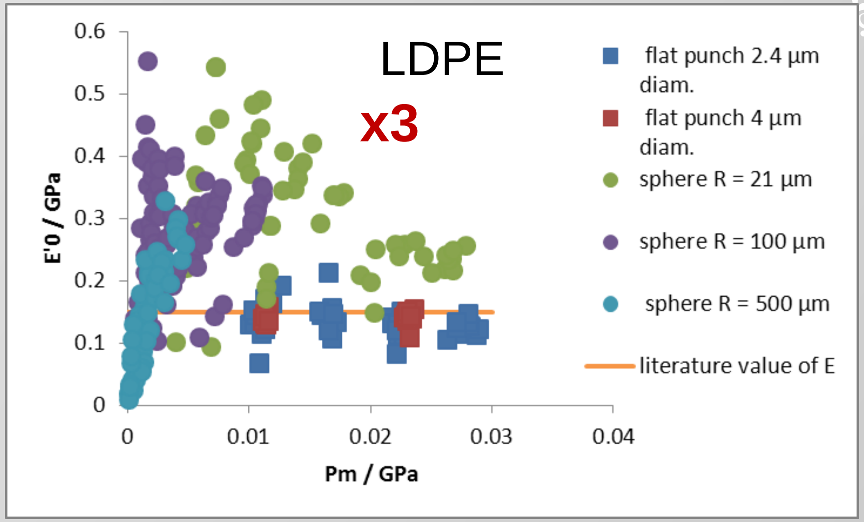



Herbert, Oliver & Pharr: J. Phys. D: Appl Phys **41** (2008) 0749021

# Comparison of methods – spherical vs flat punch indentation

$E_0$ from creep compliance




Below Tg

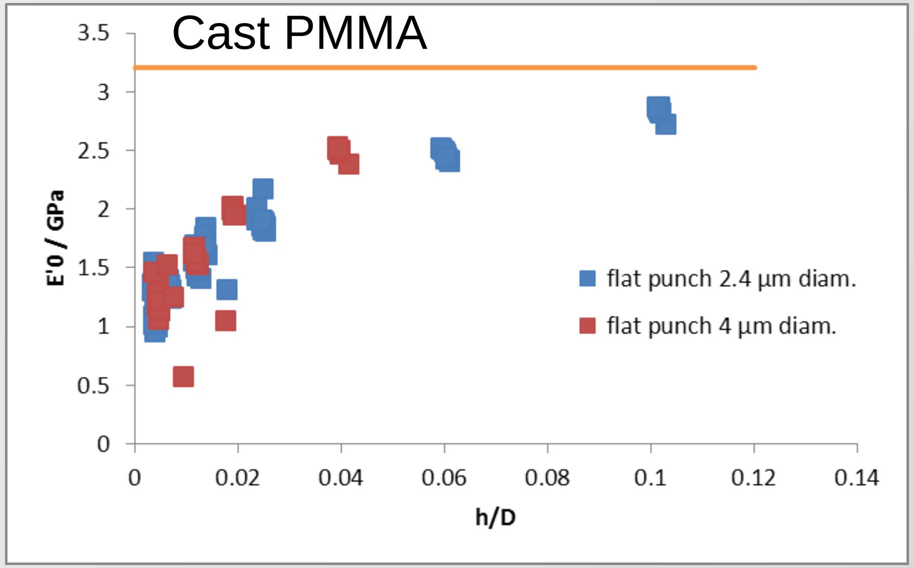
Above Tg

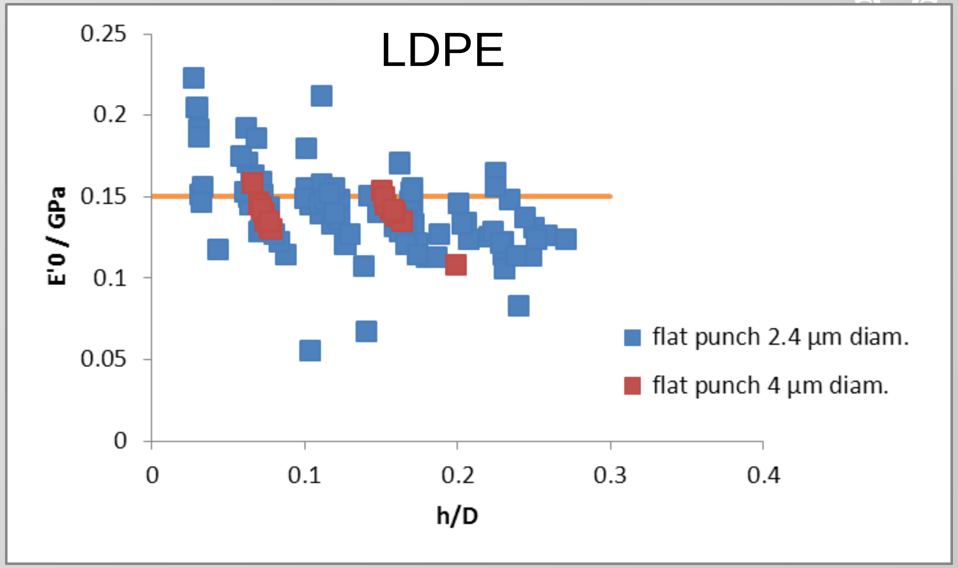
Spherical indenters

- contact area assumed from Hertzian mechanics – sink-in
- pressure dependence? / surface roughness?

# Flat punch indentation

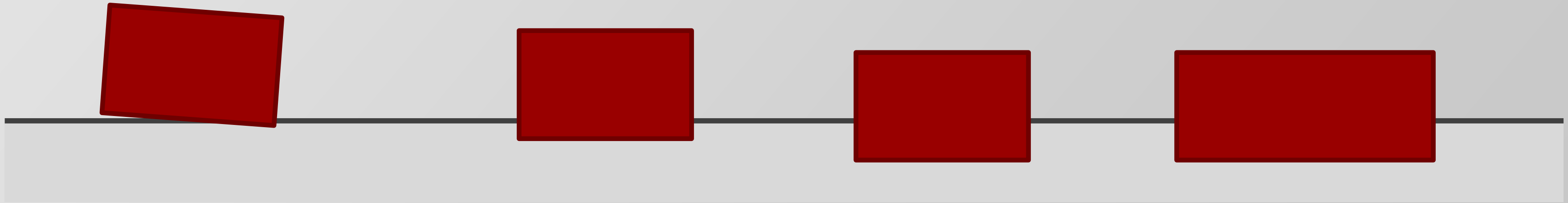
$E_0$ from creep compliance



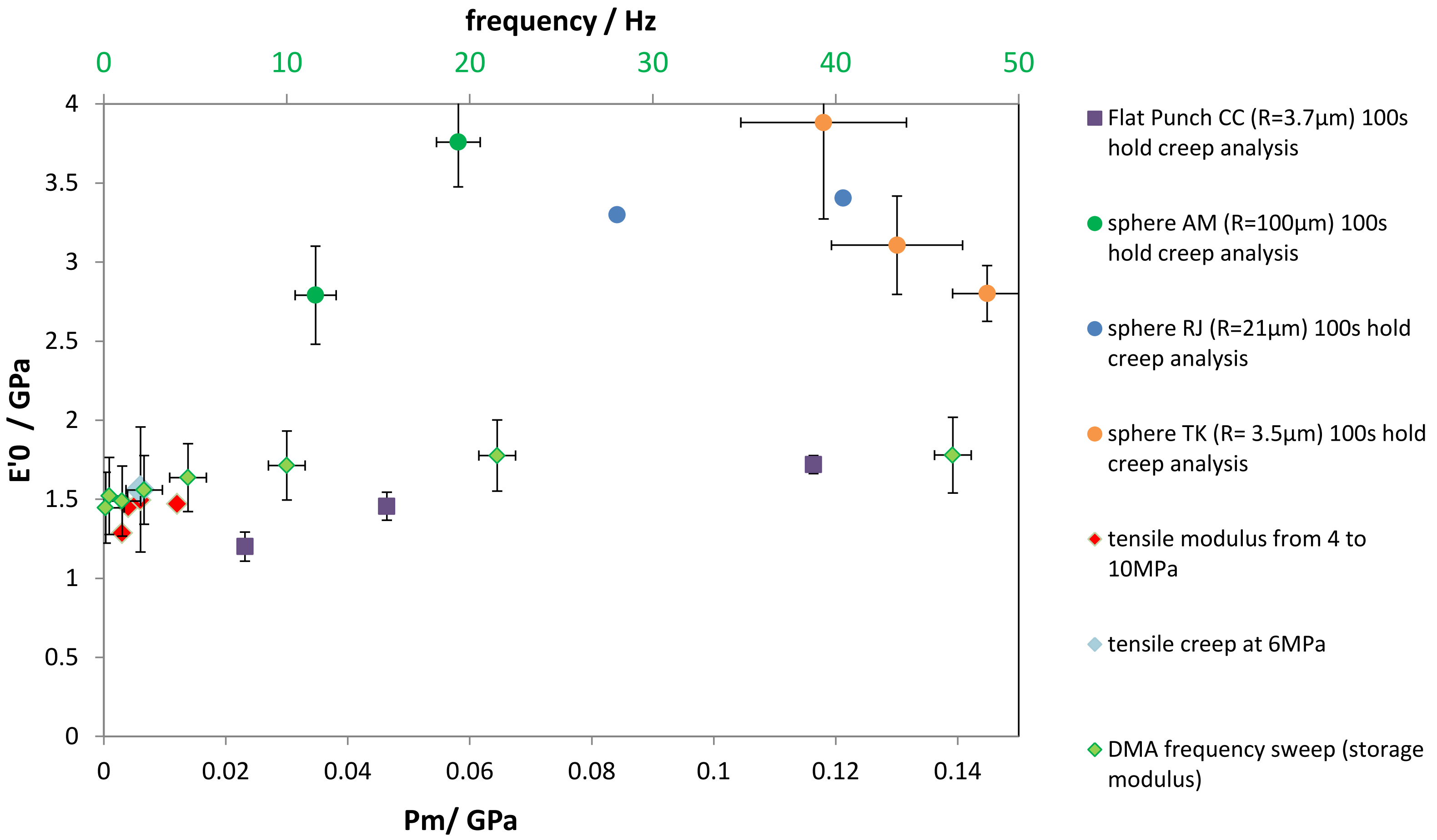




Flat punch indenters give moduli close to literature

- Independent of aspect ratio, diameter to depth (not true for thin films)
- Incomplete contact at low pressure?

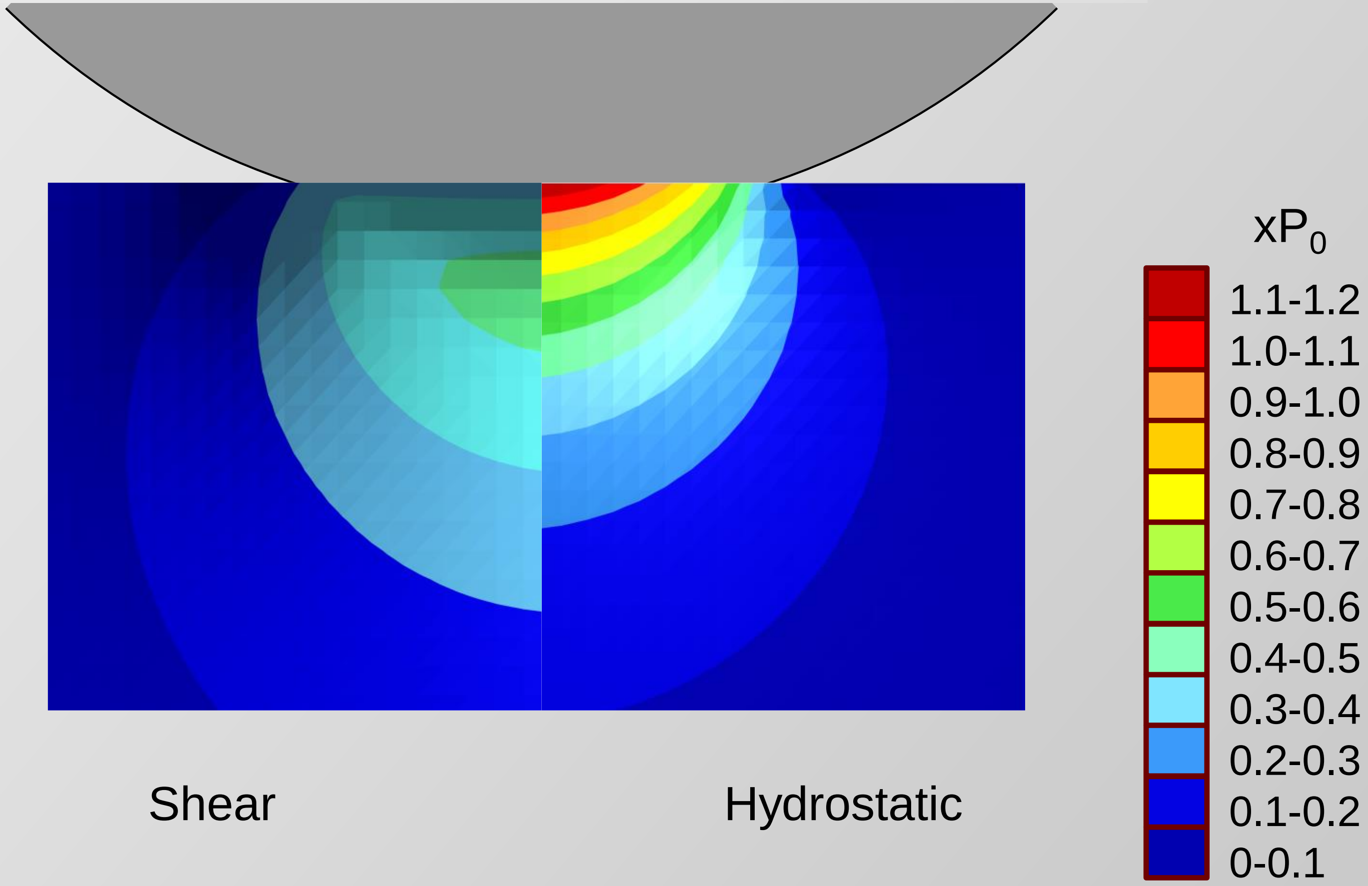


# Comparison of methods

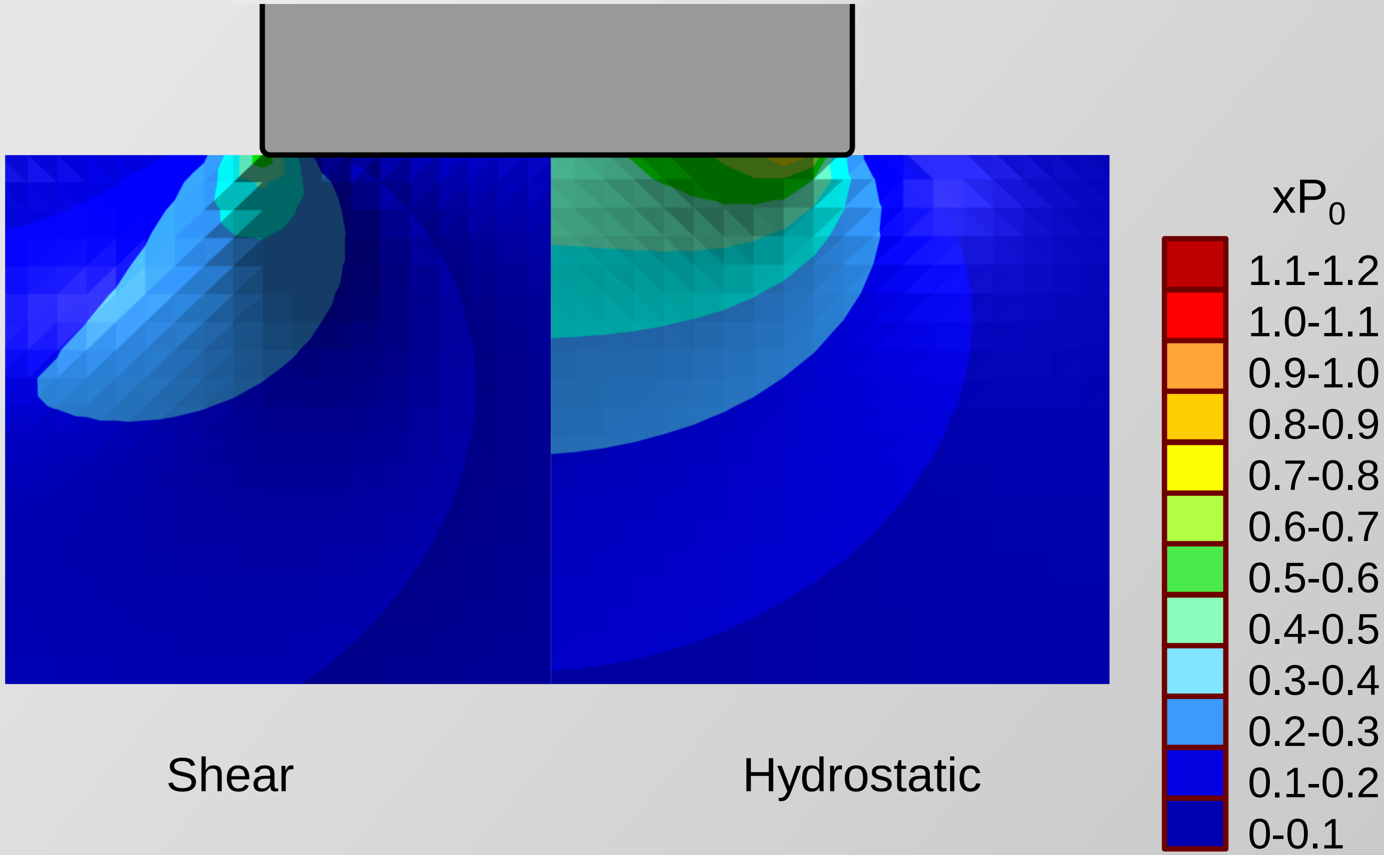



PMMA 50µm film – tensile vs indentation geometries

# Stresses beneath a spherical contact



# Stresses beneath a flat punch contact




Shear

Hydrostatic

# Sphere vs flat punch: why so different?

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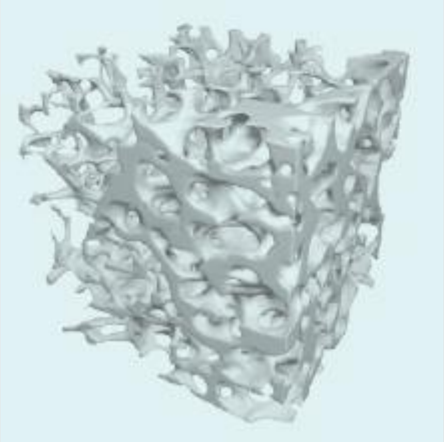
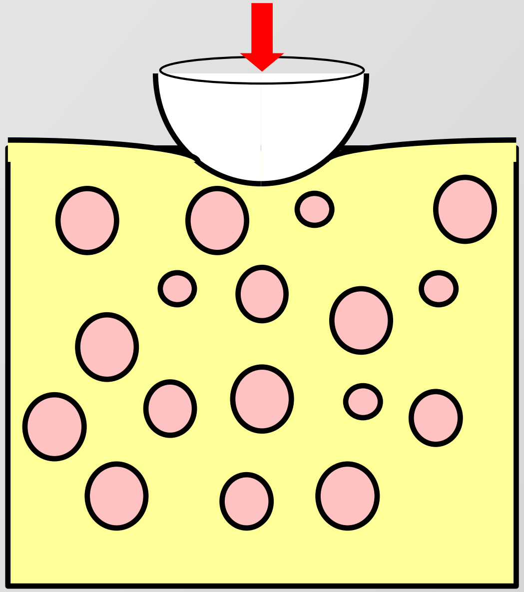
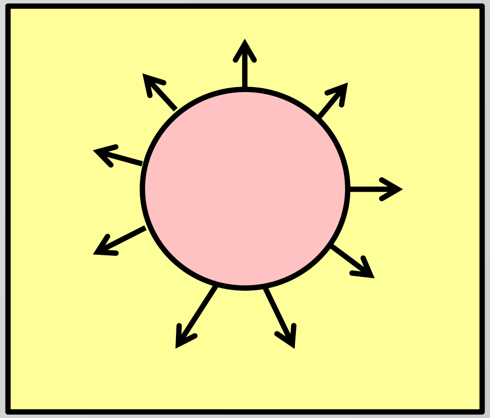
| Sphere | Flat punch |
| --- | --- |
| Shear and hydrostatic components below centre of indenter | Max Shear at perimeter of indent hydrostatic below indenter |

- Reduction in free volume due to hydrostatic component of stress
- Reduction in configurational entropy – increases elastic stiffness?
- Elastic modulus dominated by shear
- Unconstrained shear in punch indentation gives representative moduli
- Creep compliance and dynamic measurements possible with flat punch

# Poroelastic solids







Under indentation pressure, the viscous fluid in the pores elastically deforms the surrounding matrix. The time-dependence comes from the viscous flow.

These results can be used to find the permeability and effective pore size by Infiltrating with fluids of different viscosity

The poroelastic response is size dependent (depends on stressed volume and flow path length). Visco-elastic response is not size dependent.

# Summary

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- **Soft solids – problems of creep and adhesion**
- **Can make non-sense of the unloading behaviour (no-longer elastic recovery)**
- **Measure the time dependence directly (viscous flow of material)**

  **Creep compliance**
  **Frequency dependence**

- **Influence of indenter shape**

  Berkovich and Spherical indenters
  **do not** give representative modulus values
  **do not use** conventional indentation approaches

  Flat punch indenter
  – contact area known and unchanging with creep (alignment issues)

- **Poroelastic solids – time dependent because of viscous fluid flow (size dependence)**