Bringing nanomechanical measurements into the real world

The use of nanoindentation for determining time-dependent behaviour in polymers

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Multiscale modelling IAG, NPL, 28th June 2007

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Presentation outline

1. Introduction to nanoindentation of viscoelastic materials
2. Methodologies for analysis of indentation creep data
3. Elevated temperature nanoindentation
4. Other nanomechanical test methods for viscoelastic properties
5. Summary and wish-list

Why use nanoindentation for viscoelastic characterisation?

1. Quick
2. Instrumented
3. Simple
4. Thin Film samples
5. Any geometry
6. Different temperatures
7. Different environments (humidities or testing in fluids)
8. Combinatorial approaches possible

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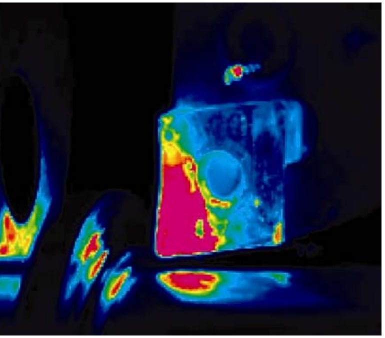
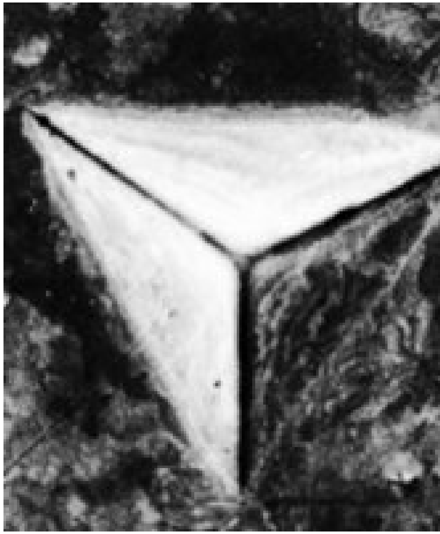
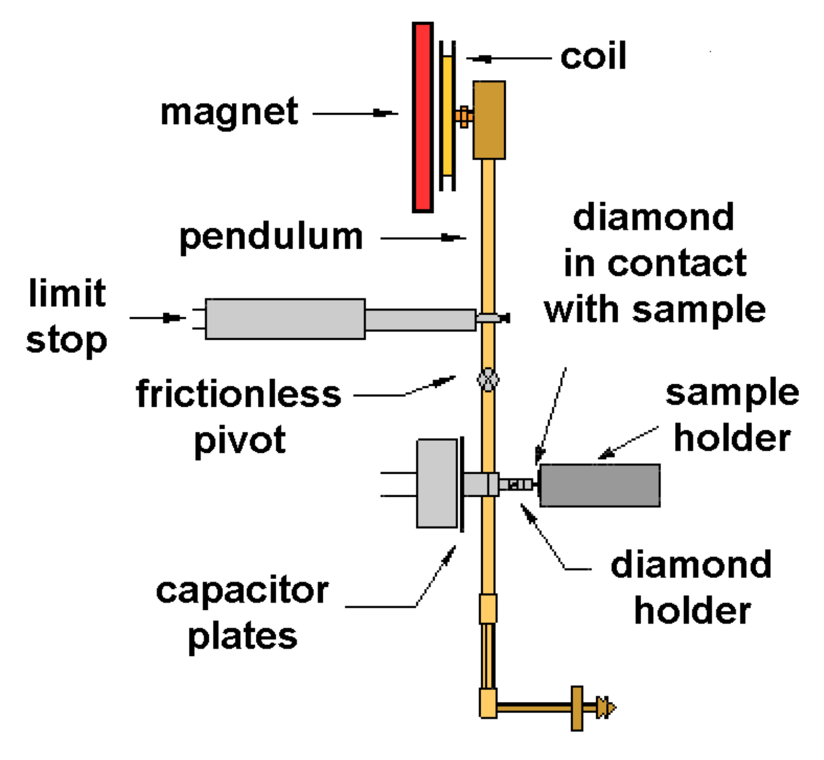
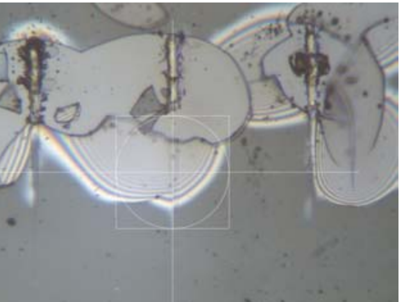
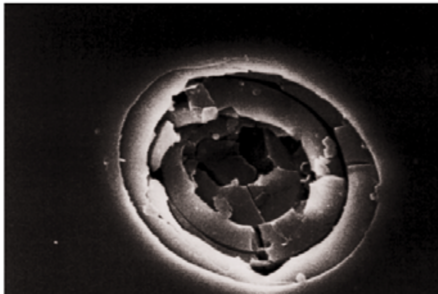




The NanoTest pendulum







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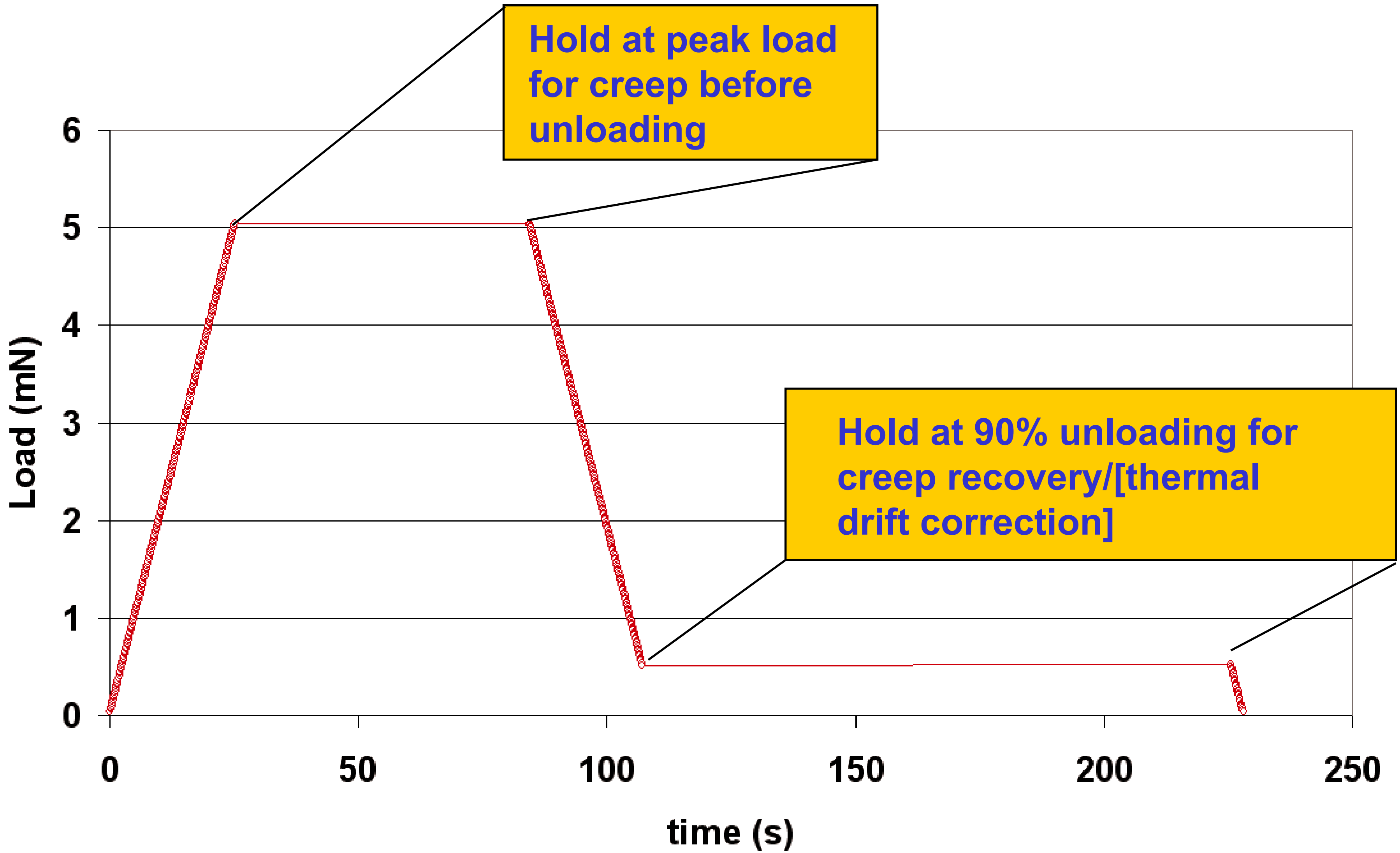
Typical load history for a polymer



Hold period in nanoindentation at constant force

Increase in depth = A*ln (Bt + 1)

(T Chudoba and F Richter, SCT 148 (2001) 191)

$d/d(0) = [m^{eff}]*\ln(t/\tau + 1)$

(P Berthoud et al J Phys D 32 (1999) 2923)

$d/d(0) = [A/d(0)]*\ln(t/\tau + 1)$

$d/d(0) = [A/d(0)]*\ln(Bt + 1)$

(BD Beake J Phys D 39 (2006) 447

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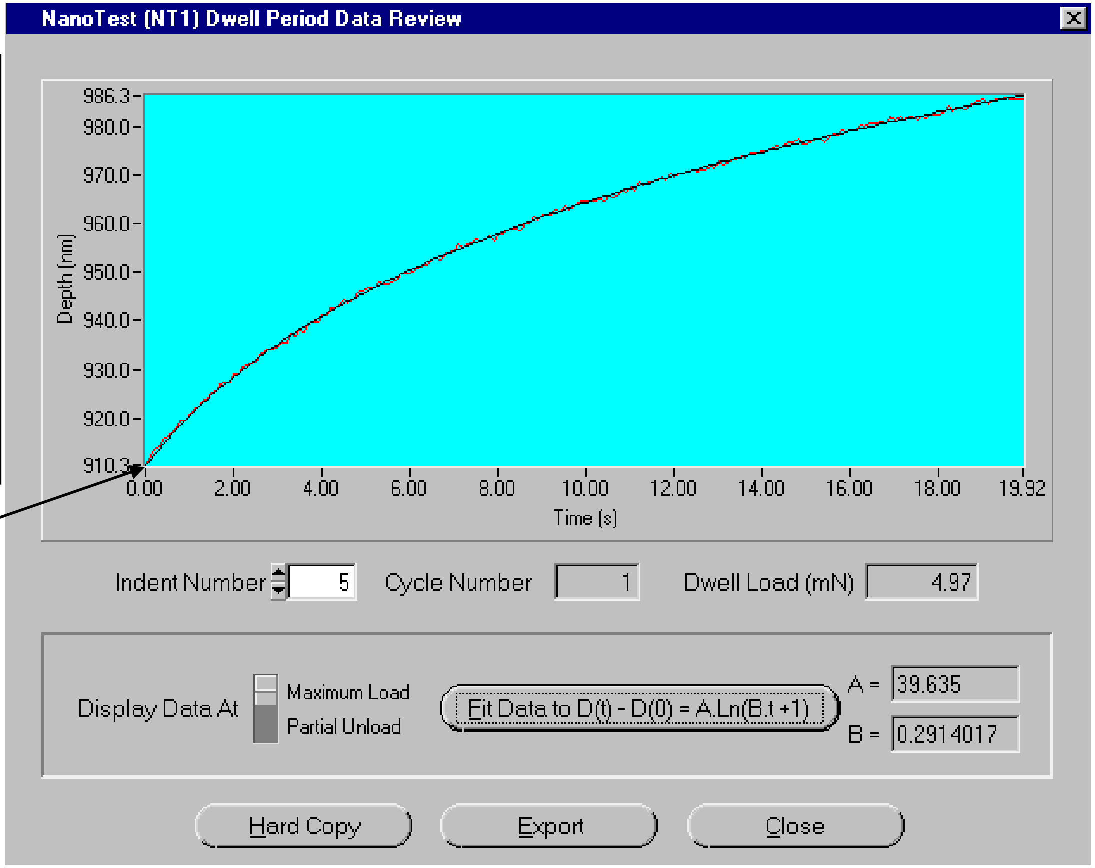
Nanoindentation creep analysis

Increase in depth during hold period at constant force = A*ln (Bt + 1)

Constant load tests
Constant stress if use flat punch



Initial strain d(0)

(A/initial strain) = strain rate sensitivity

B = 1/creep time

In this example PMMA 5 mN Berkovich indenter

$A/d(0) = (39.6/910) = 0.044$

$1/B = 3.44$

Trivial to determine A/d(0)

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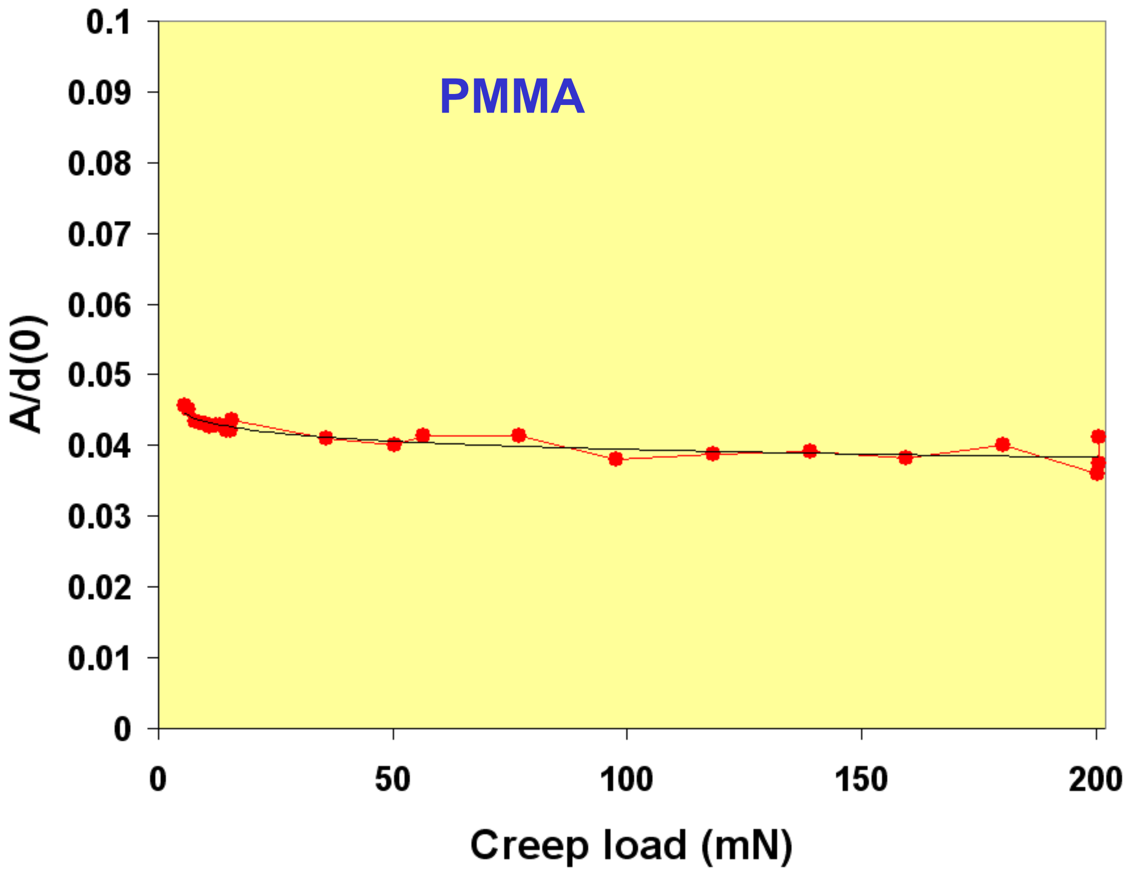
Nanoindentation creep analysis



1. A/d(0) as a material property?

ansition temperatures

olymer	$\varepsilon_e/\varepsilon(0)$	ε_r	T_g (°C)
ES	0.0155	0.939	206.4
C	0.0139	1.028	144.8
BS	0.0296	0.521	109.4
S	0.0320	0.477	107.5
urlyn	0.0220	0.395	57.4
TFE	0.0400	0.442	111.6
P	0.0440	0.325	−7.8
DPE	0.0130	0.696	−126.8
antoprene	0.0710	0.155	−46

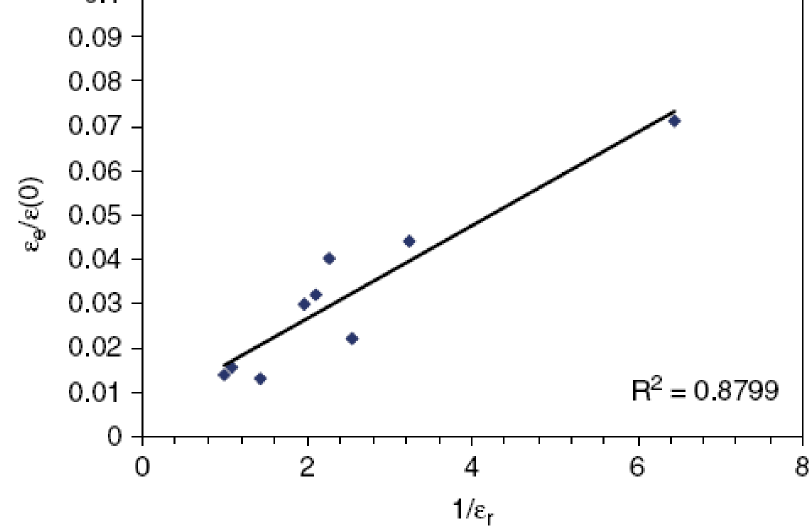
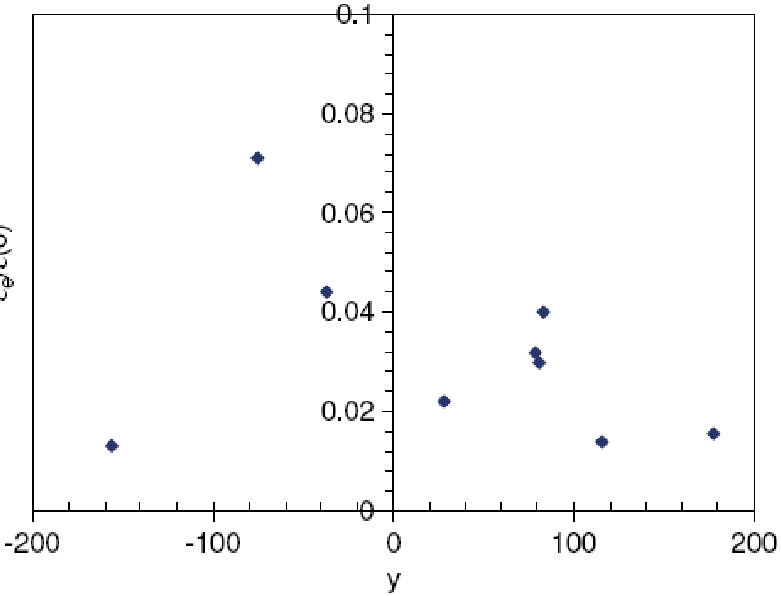


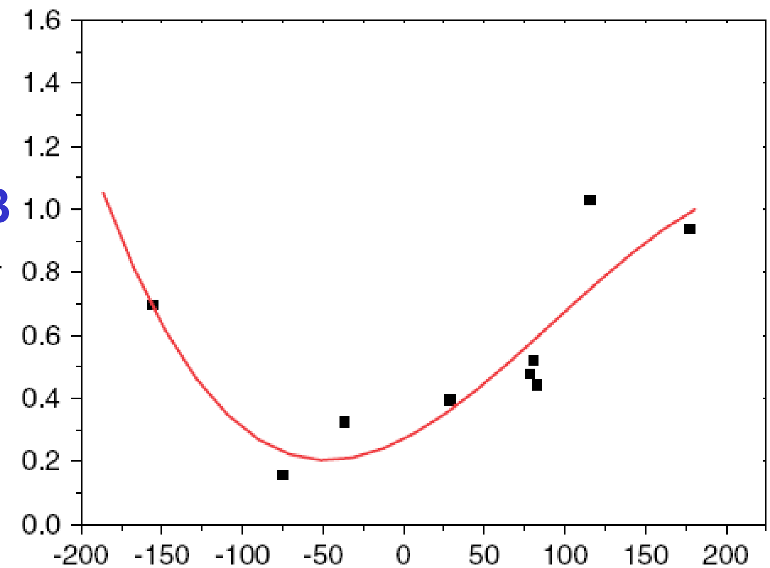
Figure 4. Strain rate sensitivity $\varepsilon_e/\varepsilon(0)$ as a function of creep time $1/\varepsilon_r$. The perfect fit would correspond to $R^2 = 1$.



gure 3. Strain rate sensitivity $\varepsilon_e/\varepsilon(0)$ as a function of y as defined Eqn (5).

$Y = T_g - T_{exp}$

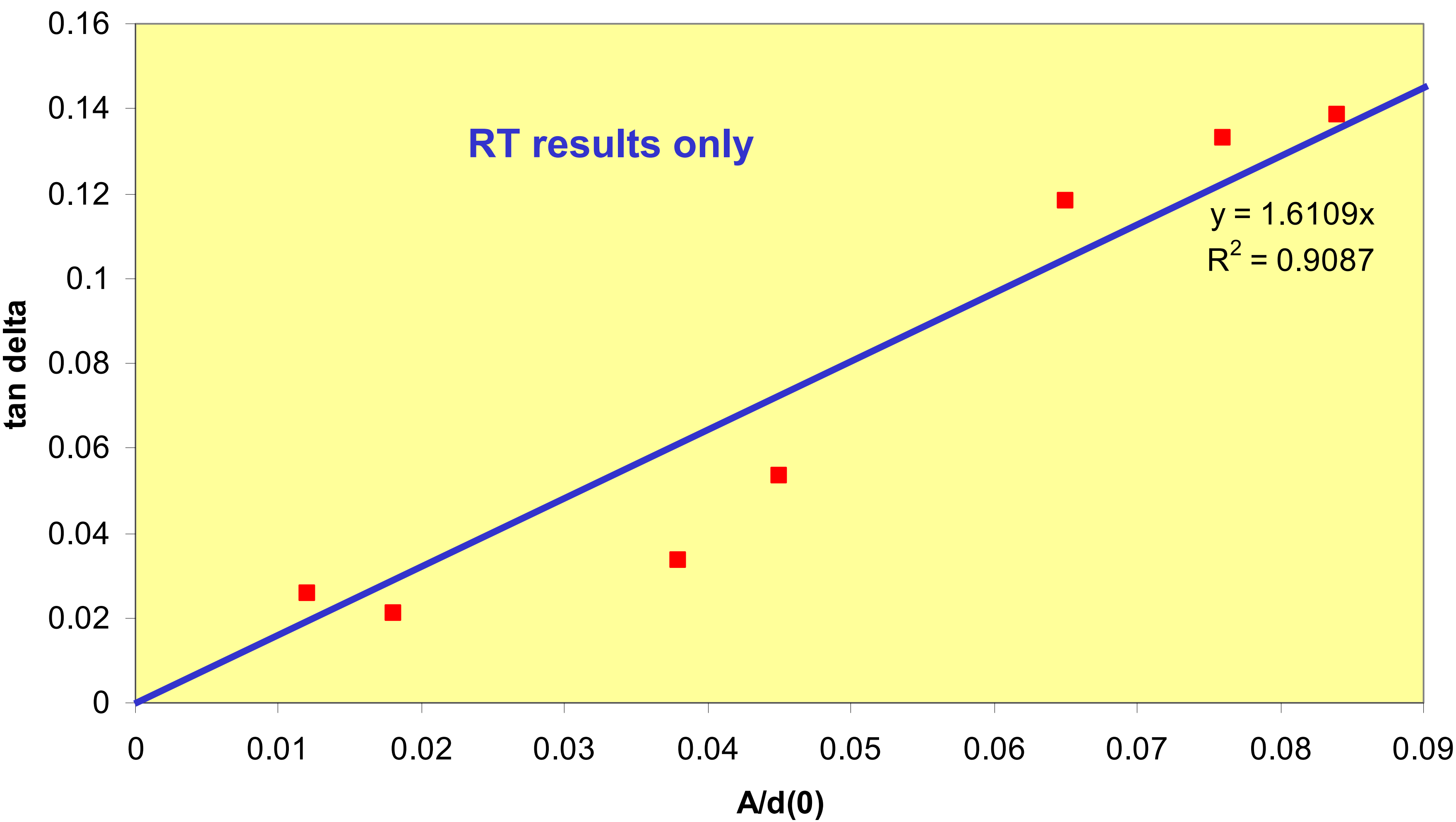
B

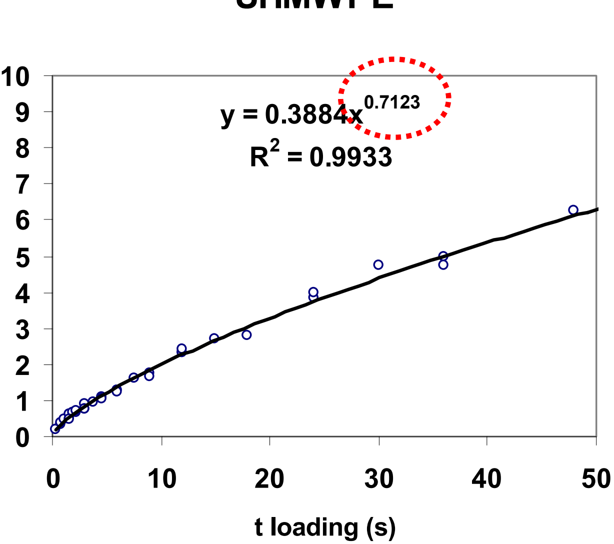


$Y = T_g - T_{exp}$

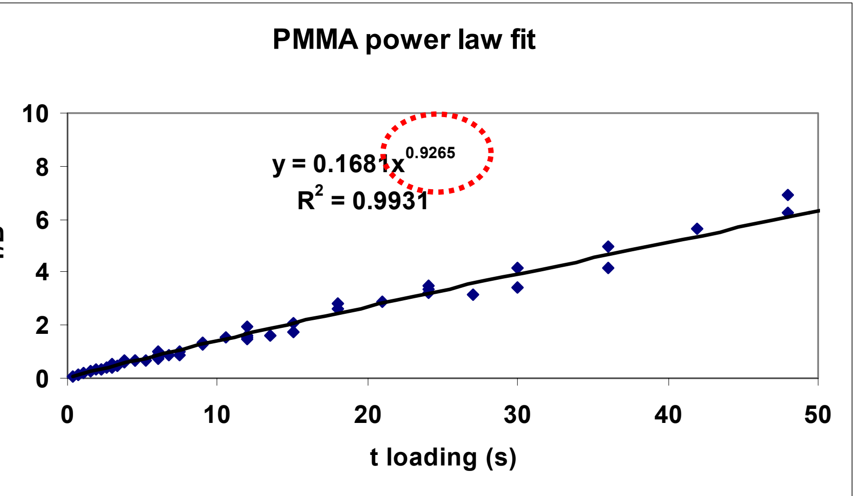
BD Beake, GA Bell, W Brostow and W Chonkaew, Polym Int 56 (2007) 773

tan delta vs A/d(0)





Power law exponents for fit of creep time (τ; 1/B) vs. time of linear loading



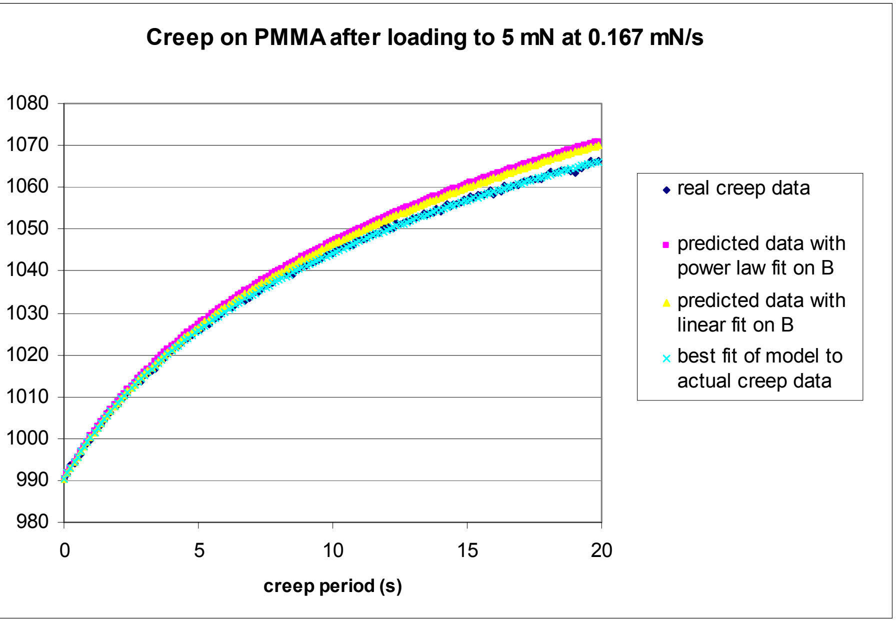
Polymer	Exponent
Biaxial PET	0.997
Uniaxial PET	0.980
PMMA	0.927
iPP "A"	0.820
iPP "B"	0.819
UHMWPE	0.712
H_2-UHMWPE	0.697
N_2-UHMWPE	0.678
He-UHMWPE	0.650

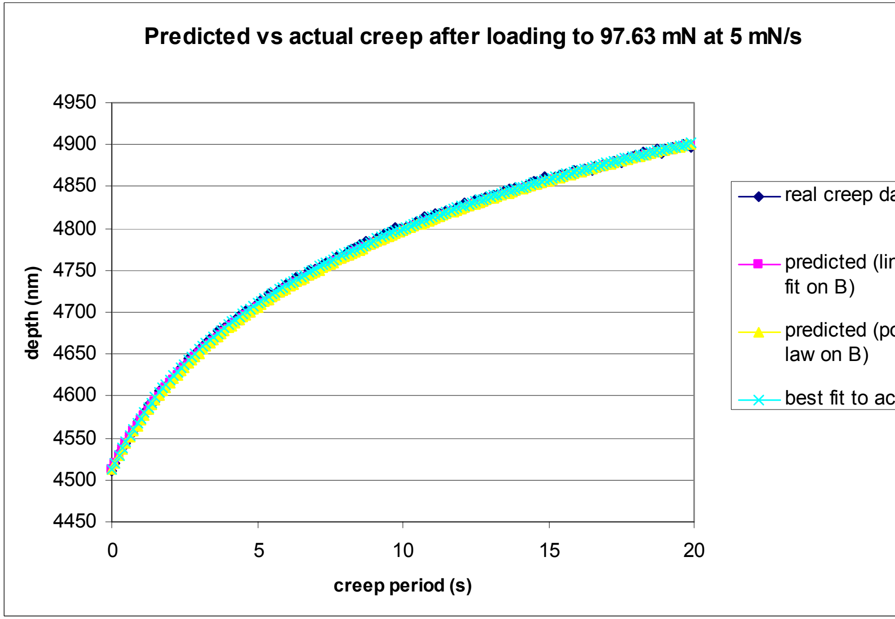
1. Variation of creep time vs. loading time is not linear
2. Fits go through zero – no obvious intrinsic creep time

Can we “predict” creep for any max load and any history?

PMMA

$$A/d(0) = 0.0477x^{-0.0414}$$
$$1/B = 0.1297x + 0.0173$$





Reasonable agreement of predicted creep with actual

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UHMWPE

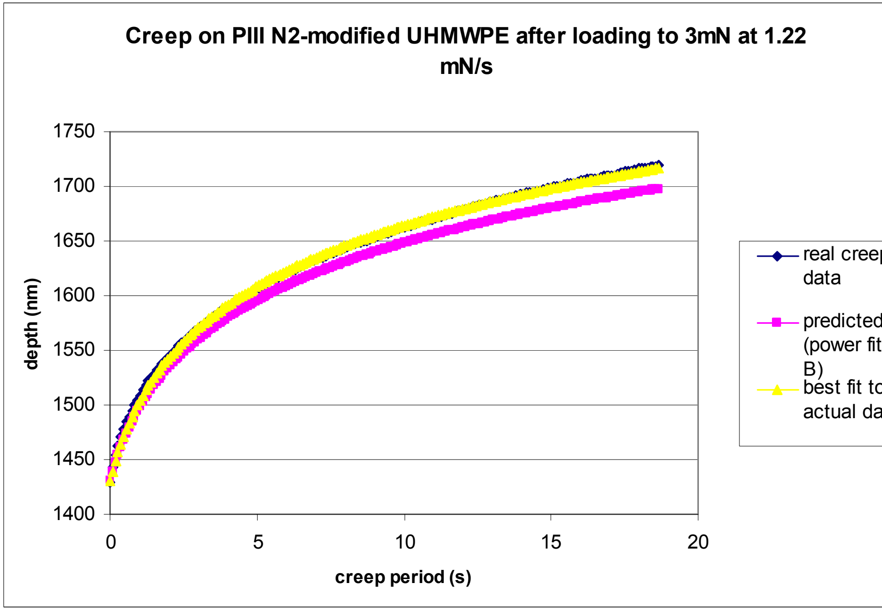
$A/d(0) = 0.0709x^{-0.0952}$

$1/B = 0.3884x^{0.7123}$

N_2-PIII UHMWPE

$A/d(0) = 0.0651x^{-0.0816}$

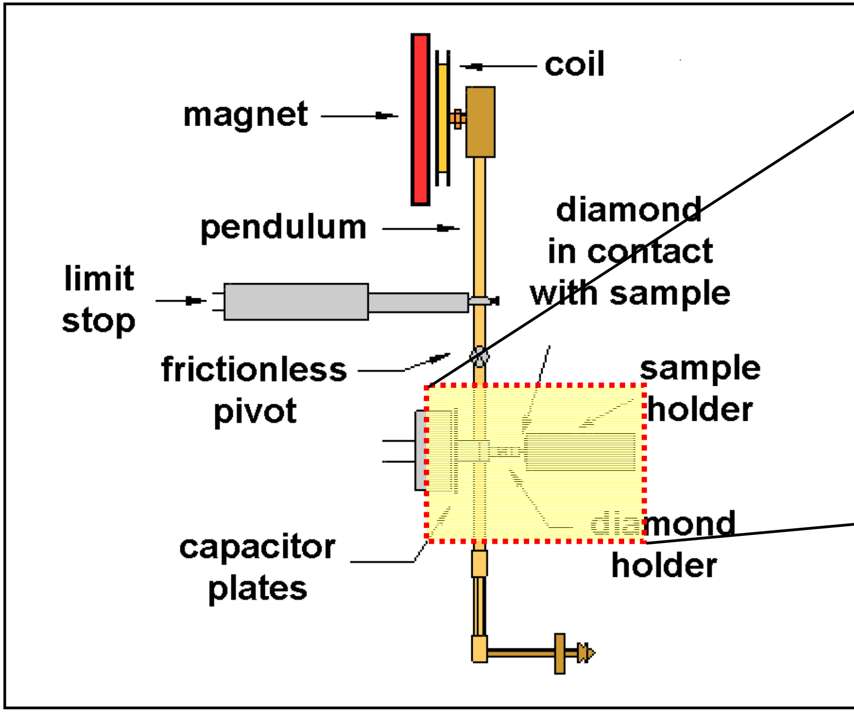
$1/B = 0.4462x^{0.6778}$



- **Agreement between predicted and experimental creep**

- **Gradient in mechanical properties after ion-implantation responsible for poor fits**

The NanoTest solution: "isothermal contact"



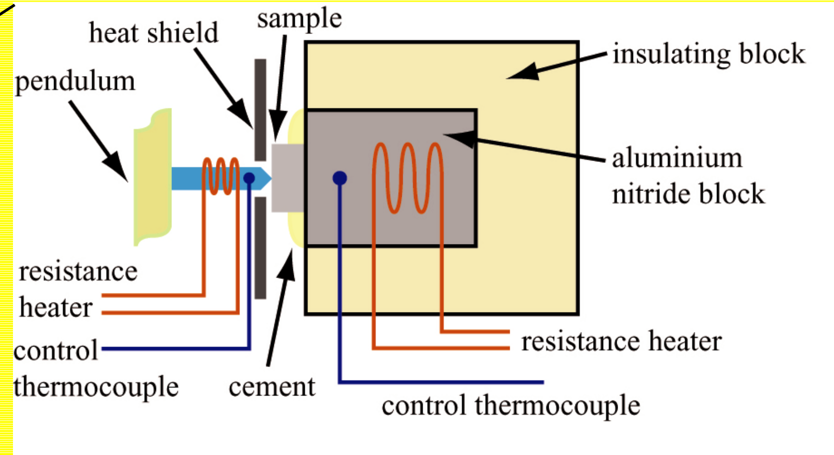


Diagram of hot stage courtesy University of Cambridge

- Horizontal loading configuration has key advantages for drift-free high temperature testing – heat flows up away from electronics
- Separate heating of probe and sample ensure no heat flow occurs on contact
- Nanoindentation and nano-scratch testing up to 750 °C
- Thermal drift minimal (under 0.01 nm/s at 500 °C)
- Applications in fuel cells, hard coatings, TBCs, SMAs, polymers etc

High temperature nanoindentation testing of PET film samples of differing crystallinity

1. **Undrawn PET film** (amorphous; experimental non-heat set material from U. Palermo)
2. **Uniaxially drawn PET film** (~33% crystalline; experimental heat set material from ICI; nominally additive-free)
3. **Biaxially drawn PET film** (~45-50% crystalline; commercial heat set Melinex from ICI; additive-free)

Film	Test temp/C				
Amorphous PET	60	70	80	90	110
Uniaxial PET	60	70	80		
Biaxial PET		70	80	90	110

Aim: By comparing the properties of the amorphous sample with other PET samples of differing crystallinity we hoped to be able to deconvolute effects of Tg and crystallisation

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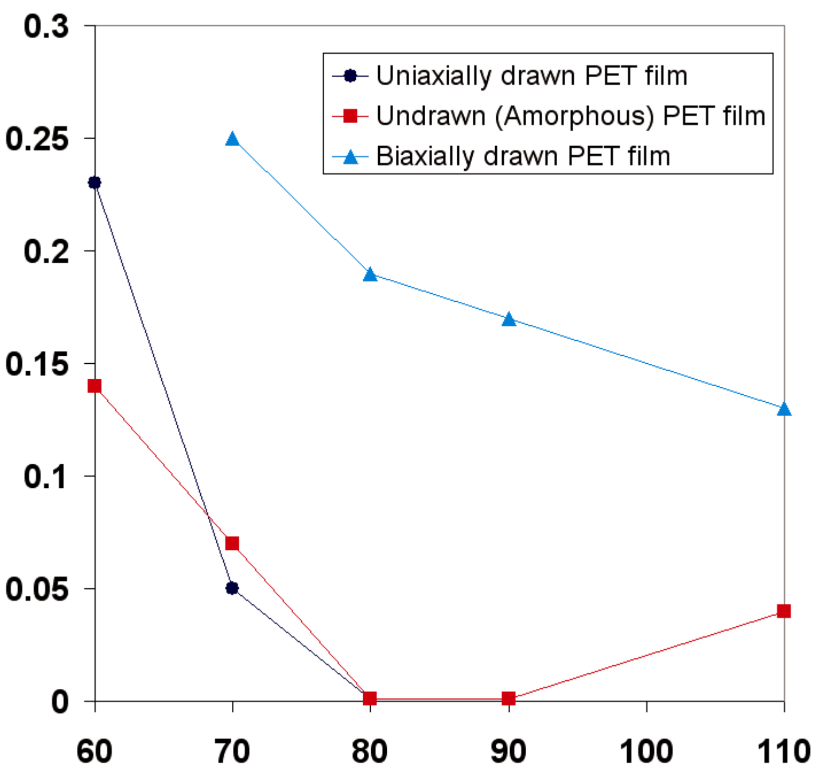
Investigating nanoscale polymeric behaviour at glass transitions…

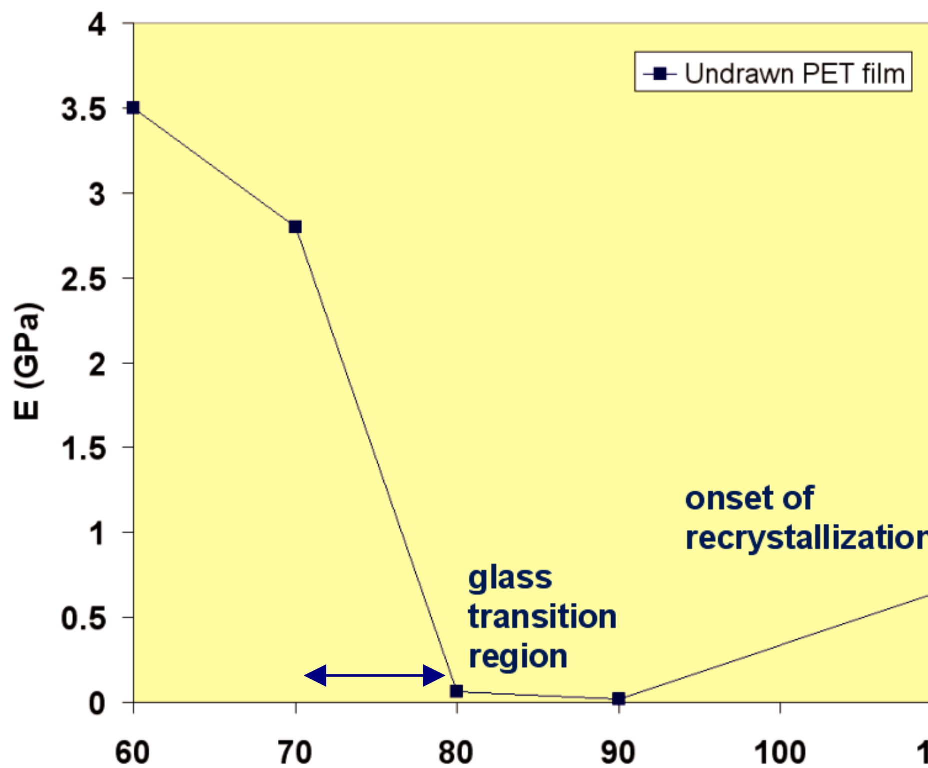
Vol. 7, 1–4,

Elevated Temperature Nanoindentation and Viscoelastic Behaviour of Thin Poly(ethylene terephthalate) Films

Ashley Gray and Ben D. Beake*

Micro Materials Ltd., Byre Units 1-3, Wrexham Technology Park, Wrexham, LL13 7YP, UK





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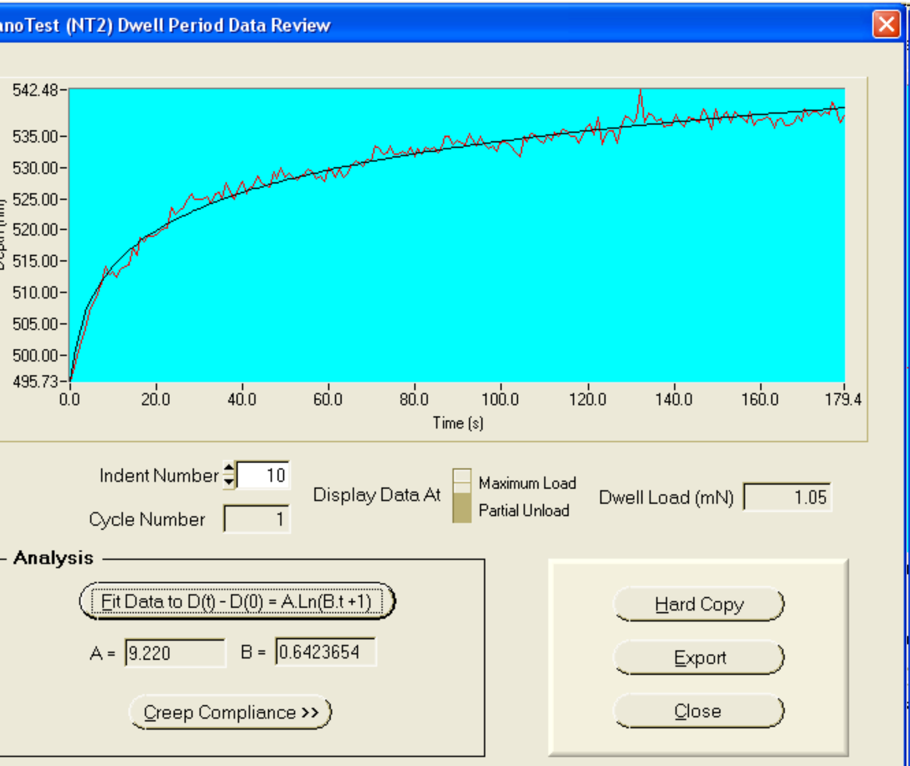
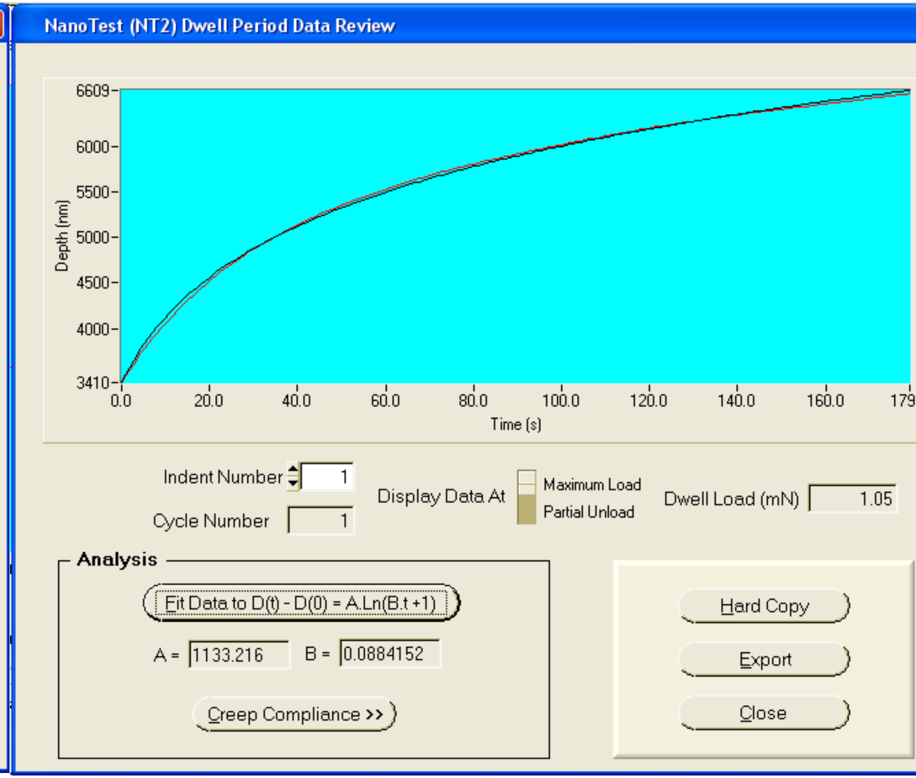
High temperature creep

Amorphous PET
50 nm creep at 60 C

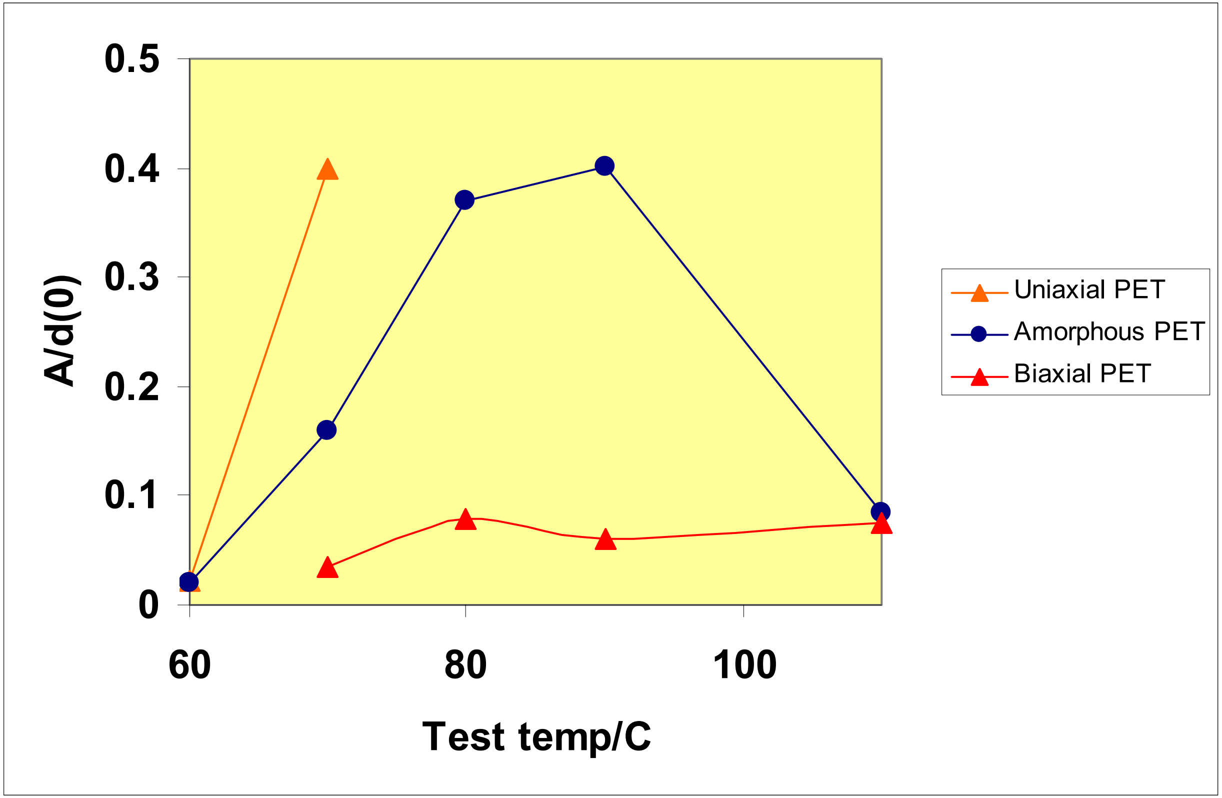


Amorphous PET
3200 nm creep at 90C



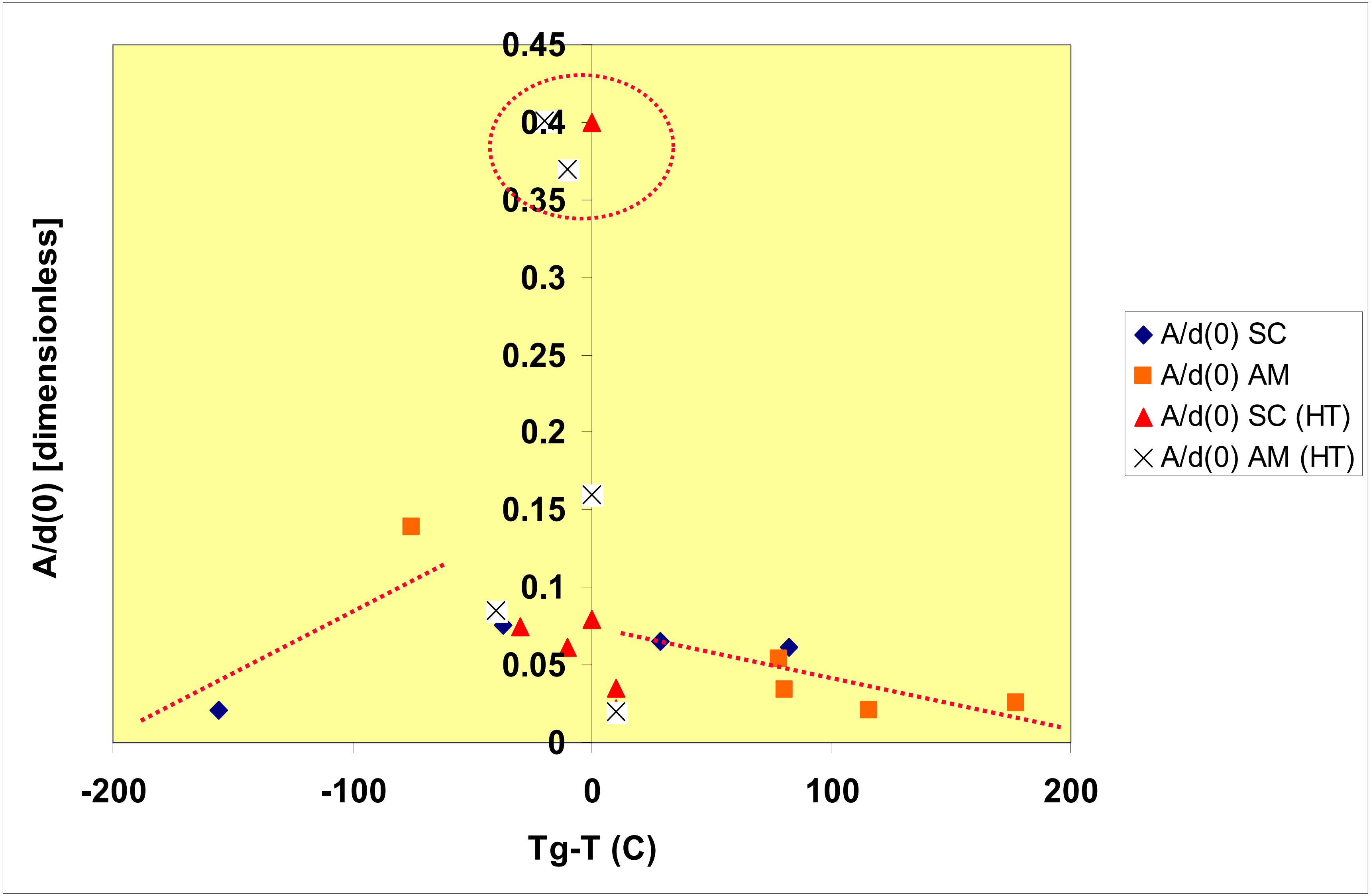
- **Fit to logarithmic creep equation in NanoTest s/w**
- **Creep parameter (A/initial depth) varies with temp ~ tan delta**

High temperature creep



- Creep parameter (A/initial depth) varies with temp ~ tan delta

High values of A/d(0) only near Tg



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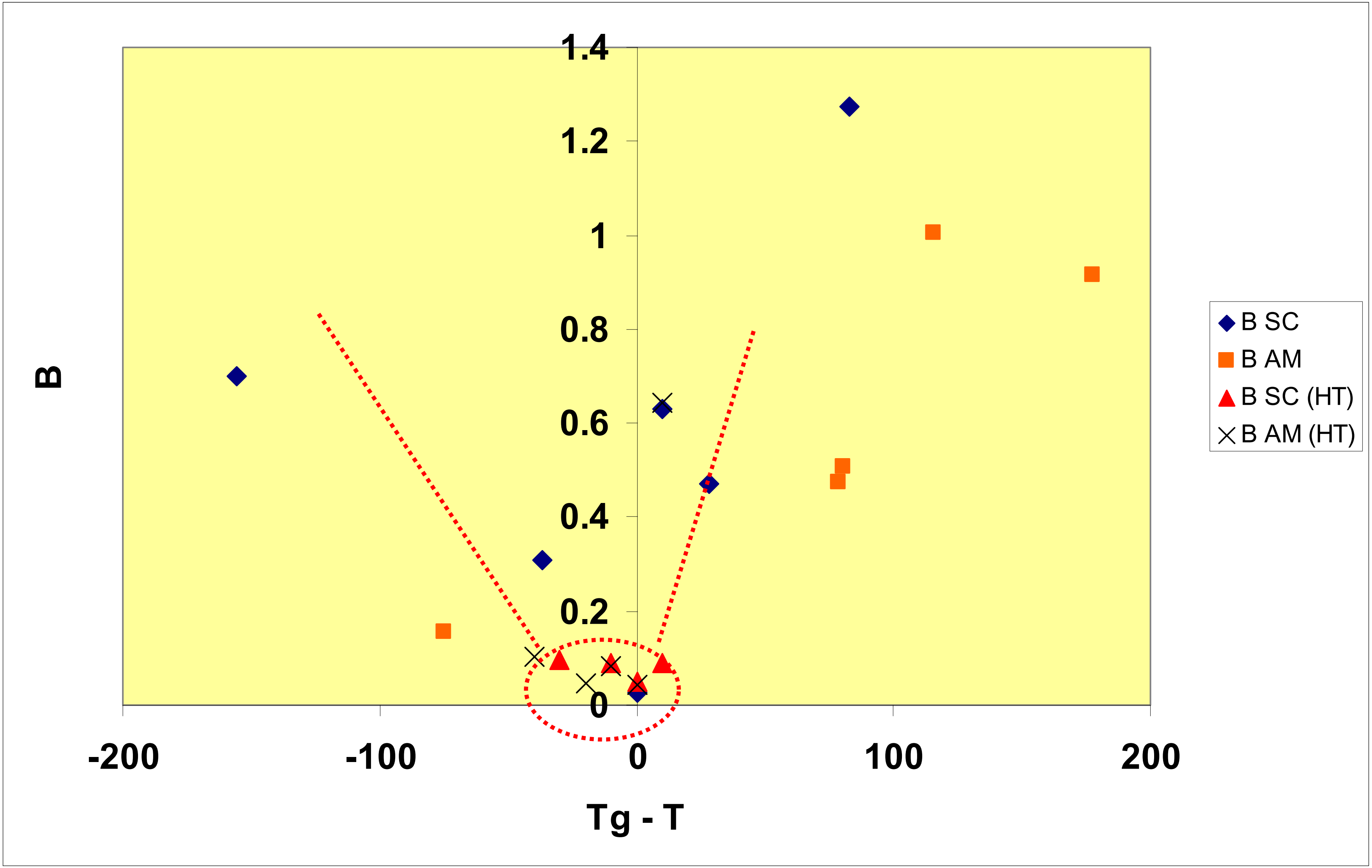
"Ultra-low" values of B only near Tg



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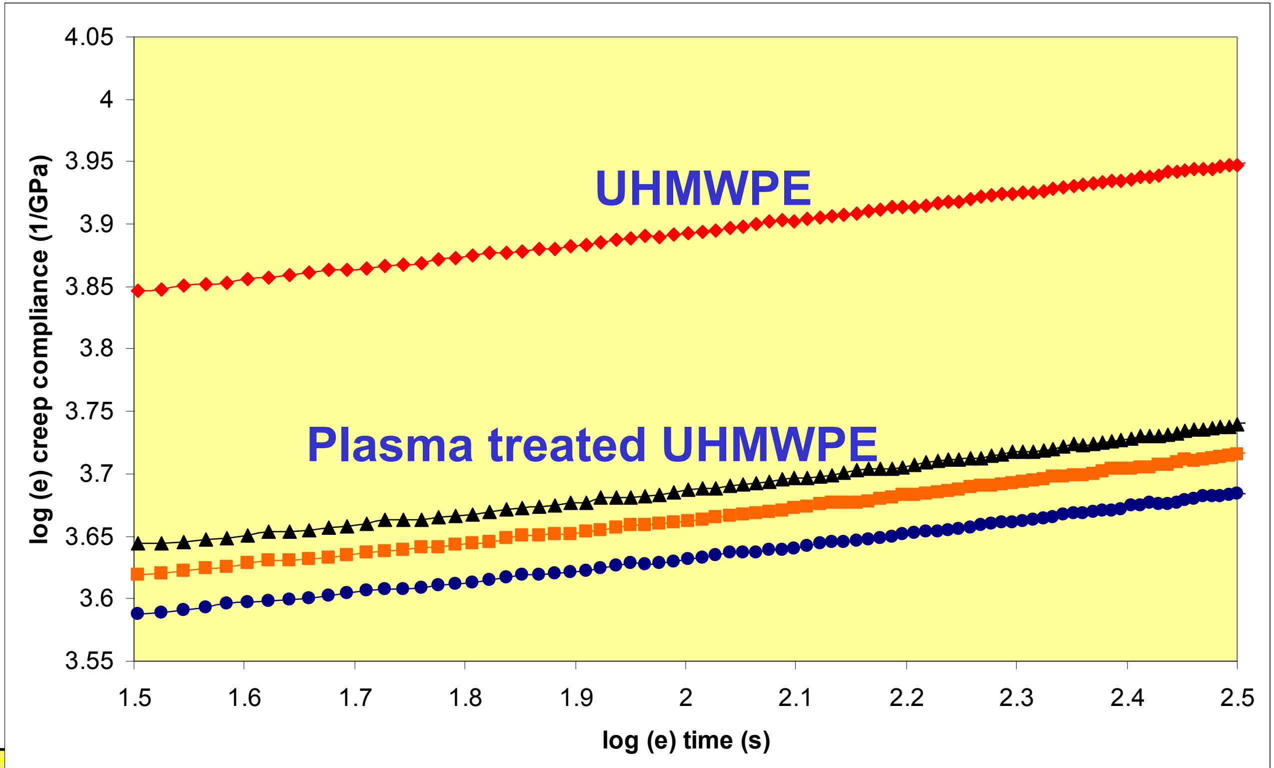
Creep compliance J(t) calculation

Can indentation be used to determine linear viscoelastic properties?



(t) α A(t)/(P_0 tan θ)

here

(t) = projected contact area at time t

= effective cone angle of indenter

= Creep load

P_0/A(t) α nominal indentation stress

1/tan θ α nominal indentation strain

J(t) α strain/stress

NanoTest dynamic compliance testing module

Dynamic mechanical compliance testing

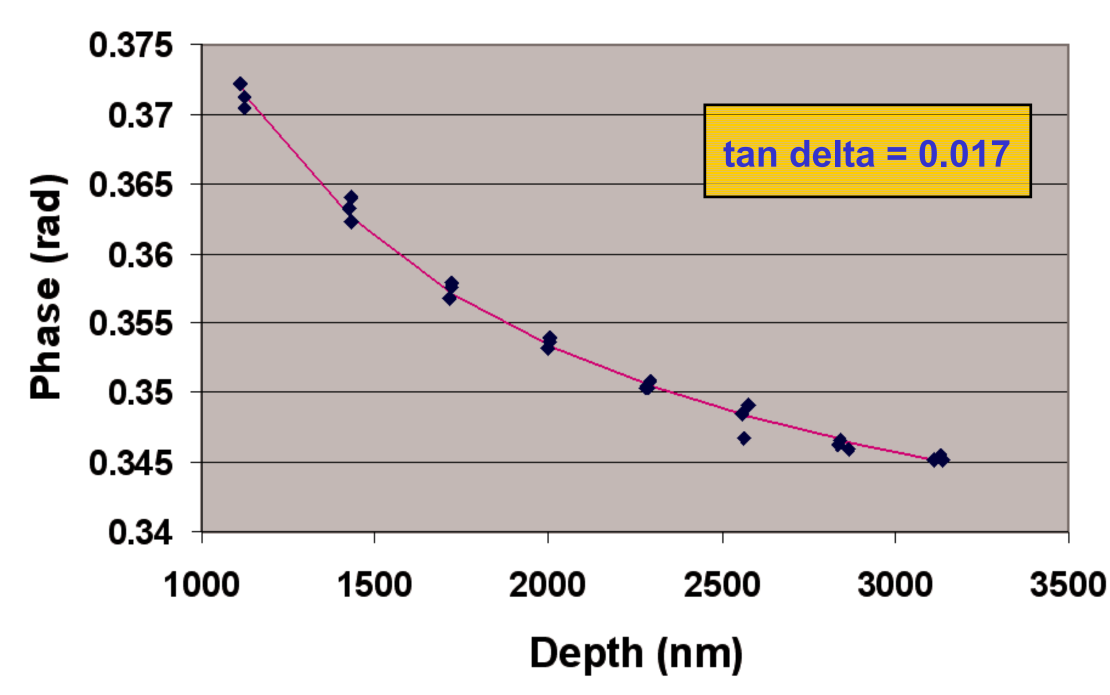
Includes lock-in amplifier and sample oscillation system to vibrate a sample and allow the compliance to be measured on a continuous basis

Nanoscale analogue of DMA

Collect raw phase angle data with spherical or pyramidal indenters

Analyse with a 4-element linear viscoelastic model

Determine loss and storage modulus, indentation complex modulus and tan delta



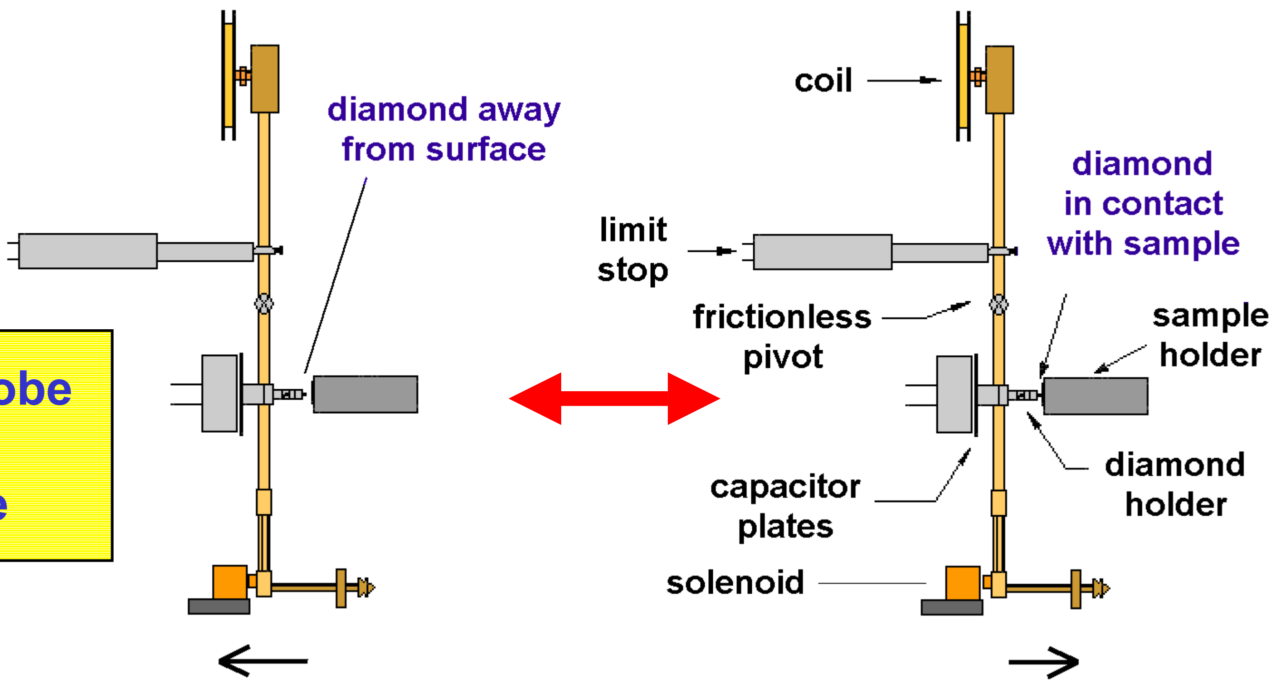
Variation in phase signal with indentation depth for three repeat tests on an epoxy sample.
Reproducibility of the data and its fit to the model is good

Displacement modulation based dynamic nanoindentation f viscoelastic material characterisation SP Singh, RP Singh and JF Smit

High strain rate nanoindentation "Nano-impact" testing

Experimental set-up for "pendulum impulse" nano-impact…

Pull probe from surface



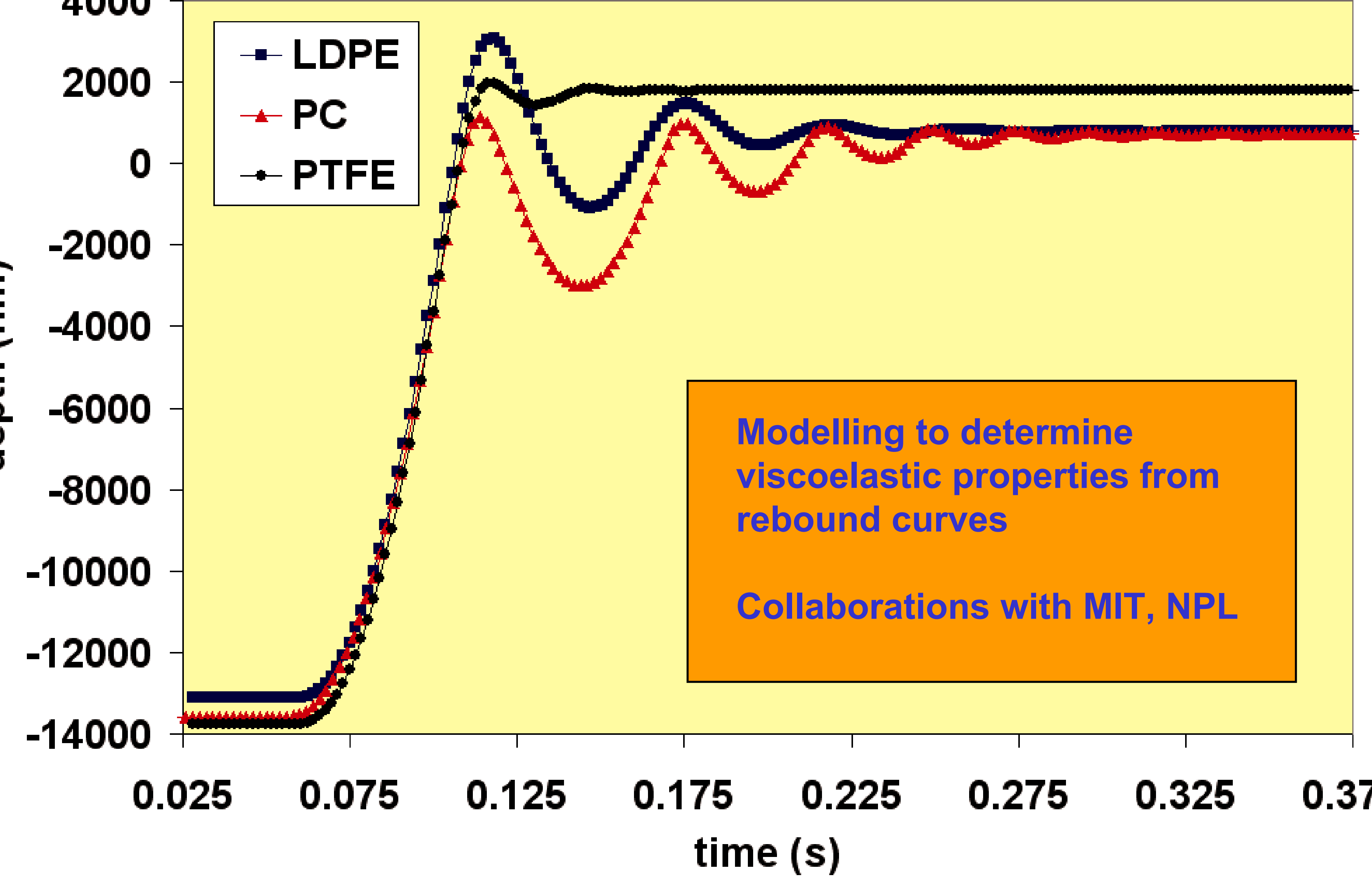
Ready for Impact

After Impact

Swing in and hit surface at high strain rate

- Repetitive impact is analogous to a woodpecker pecking at a tree!
- Nano-impact is an accelerated fatigue wear test

Experimental variables include static force, impact angle,



Modelling to determine viscoelastic properties from rebound curves

Collaborations with MIT, NPL

- **Single impacts for dynamic hardness, yield stress and viscoelastic properties**

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High throughput for combinatorial testing

COMMUNICATIONS

ADVANCED MATERIALS

Combinatorial Material Mechanics: High-Throughput Polymer Synthesis and Nanomechanical Screening**

By *Catherine A. Tweedie, Daniel G. Anderson, Robert Langer*, and *Krystyn J. Van Vliet**

1. **Nanoindentation on 576 polymers in only 24 hr**
2. **Rapid nanoindentation without loss of precision**
3. **Nano- and micro-mapping is now possible**
4. **MIT evaluate photocrosslinkable and degradable polymers for drug-delivery and tissue-engineering scaffold applications**

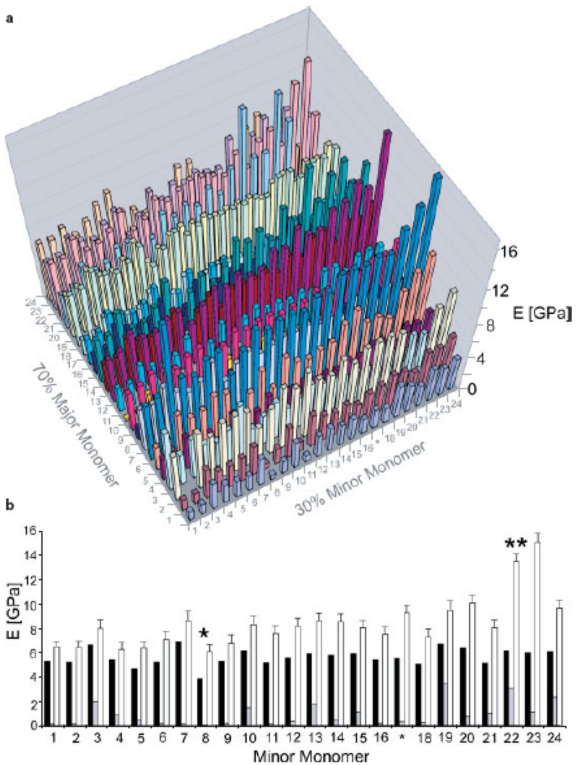

Figure 3. Automated array-nanoindentation determination of elastic modulus *E* for entire 576-element polymer library. a) Nanoindentation data were acquired and analyzed in 24 h of instrument time, with high precision and accuracy. b) Subarrays of major monomer 8 (black); major monomer 11 (gray); and major monomer 22 (white). Error bars represent the maximum observed standard deviation of 7.5% among the triplicate subarrays (shown only on major monomer 22 data for clarity). Large asterisks depict polymer spots of minimum *E* (30% monomer 8) and maximum *E* (30% monomer 19 or 22) within a given subarray. Values of *E* are comparable to the range for macroscopic, crosslinked polymers characterized by uniaxial testing [25].

"the absence of piezo-crystal actuation of the indenter used herein resulted in frame compliance and load/displacement signals that were extremely stable and repeatable." Adv Mater 17 (2005) page 2604

A Tweedie et al, Adv Mater 17 (2005) 2599-2604
G Anderson et al, Adv Mater 18 (2006) 2614-2618

Summary

Advances in nanomechanics instrumentation mean that it is possible to obtain reliable raw data

Several interesting approaches to determine viscoelastic properties

Some work to be done!

Where NPL can help?

1. **Provision of reliable tan delta information**
2. **Development of models suited to nanoindentation data**
3. **Joint development of new techniques (e.g. nano-impact)**
4. **Cross-correlation with other techniques**