Measurements of Elastic and Viscoelastic Properties of Thermo-oxidized Polymer Composite Resins through Nanoindentation

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Introduction
Thermo-oxidized Polymer Matrix Composites

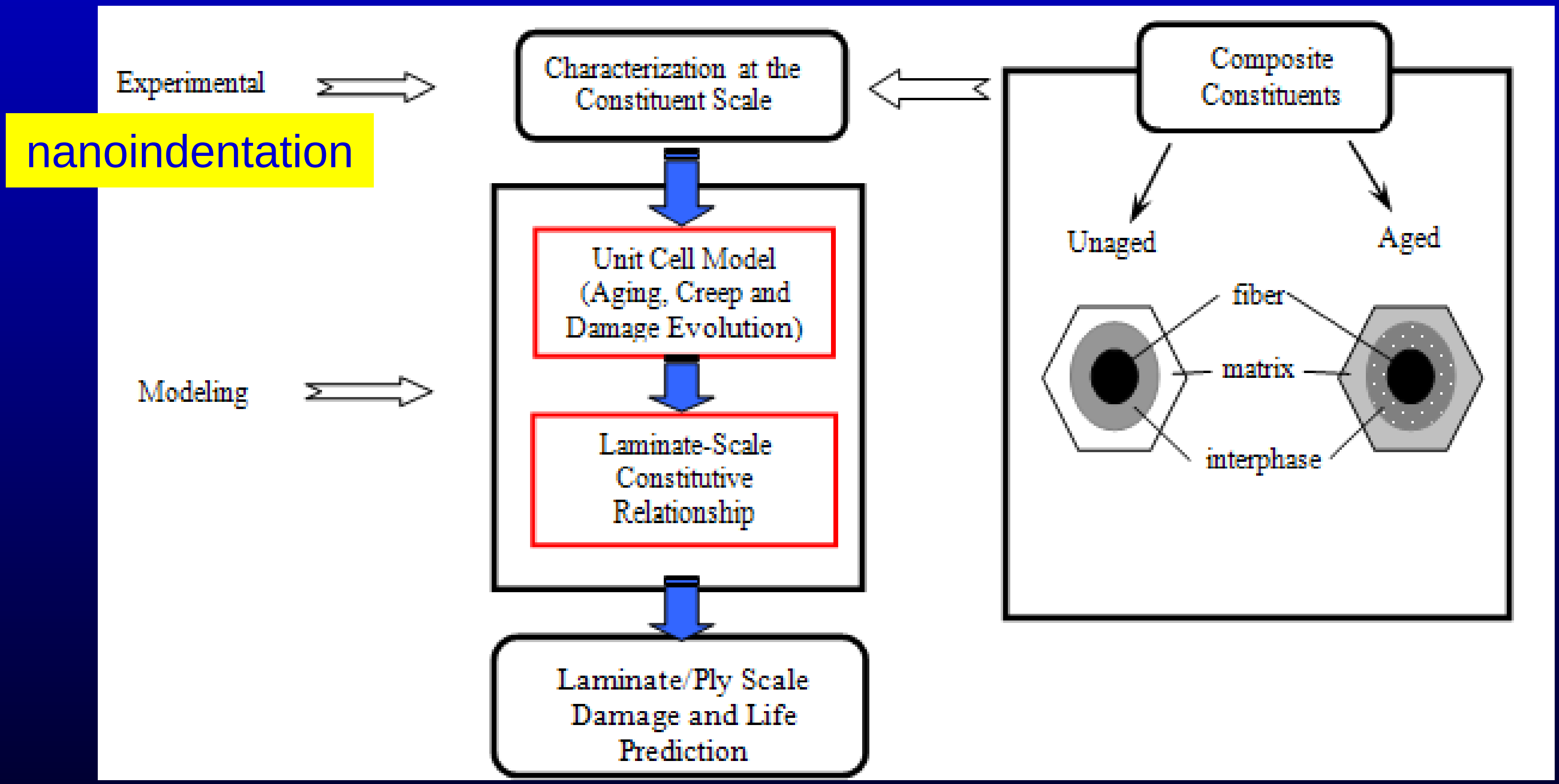
- Polymer matrix composites operating in high temperature environments (engine structures) undergo thermo-oxidative degradation.

- The oxidative degradation leads to the premature failures of the composites.

- It is very important to have a robust tool to measure the mechanical properties of oxidized materials so that the damage evolution can be predicted.

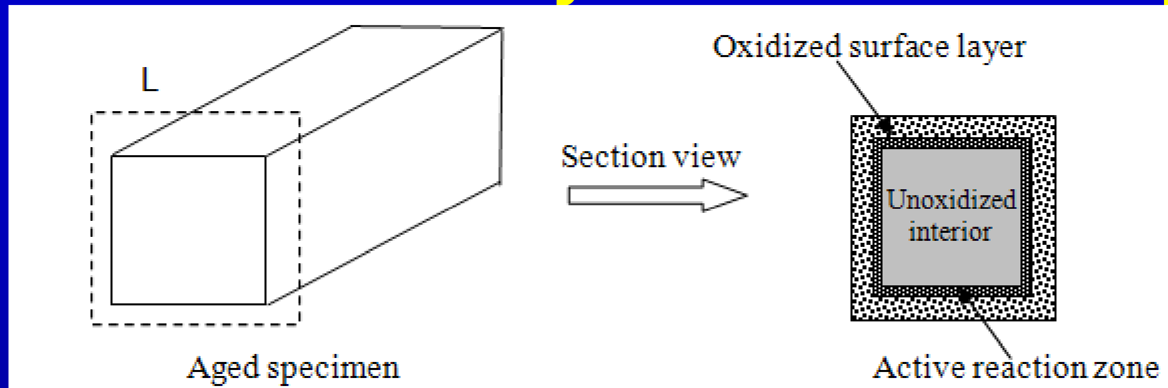
Introduction
Thermo-oxidized Polymer Matrix Composites

- <u>Mechanism-based design models </u>for predictinging the damage evolution and life expectance of HTPMCs.

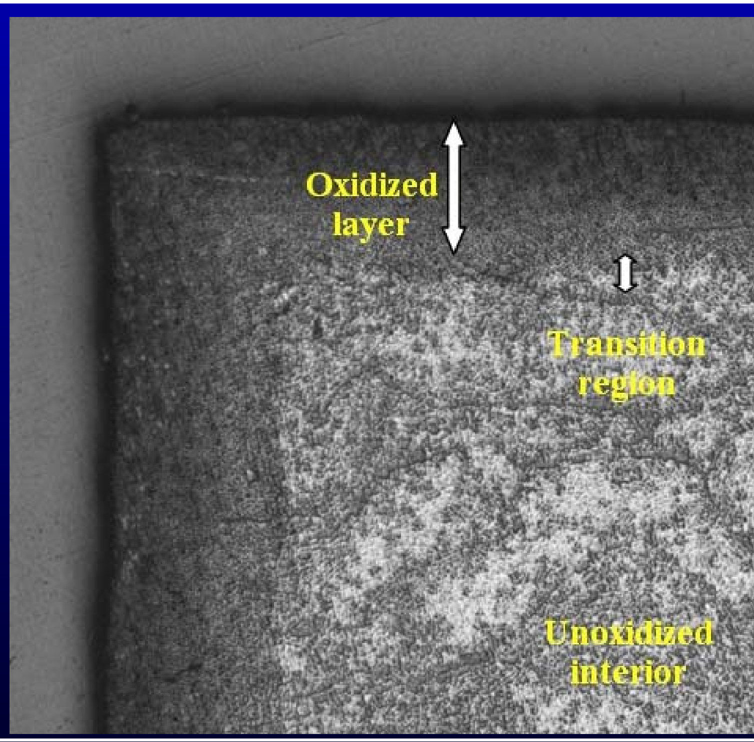


Introduction
Thermo-oxidized Polymer Matrix Composite

laboratory aged specimen

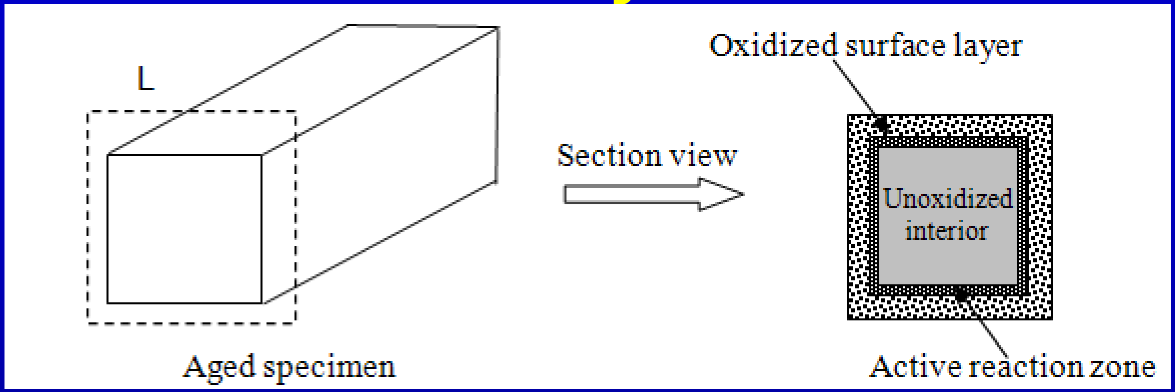


G30-500/PMR-15 composite aged at 288 ^{o}C for 3075 hr

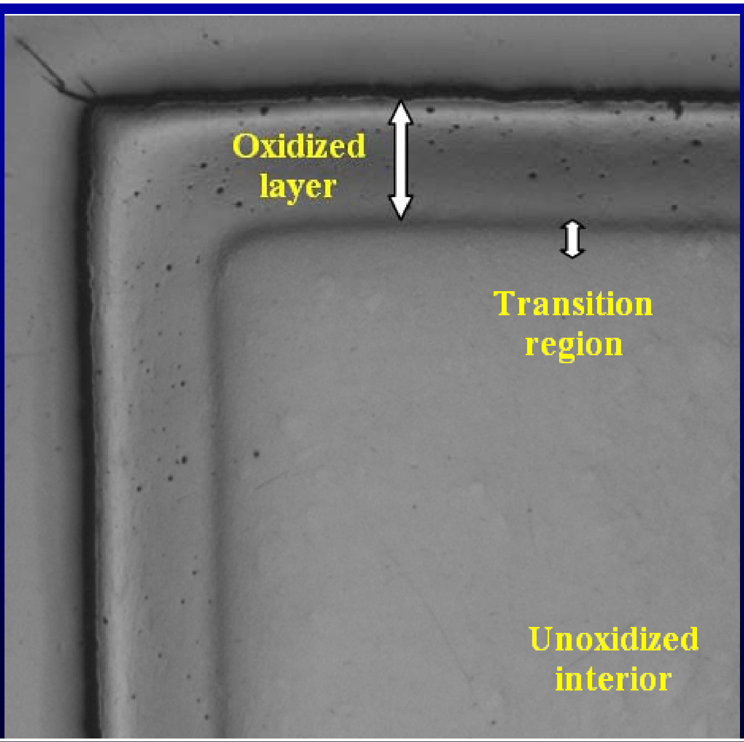


Introduction
Thermo-oxidized Polymer Matrix Resin

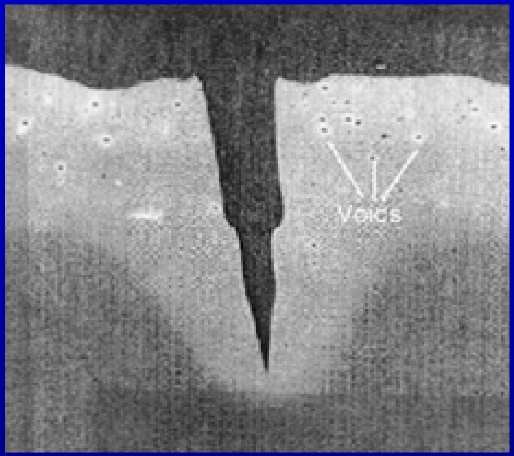
laboratory aged specimen

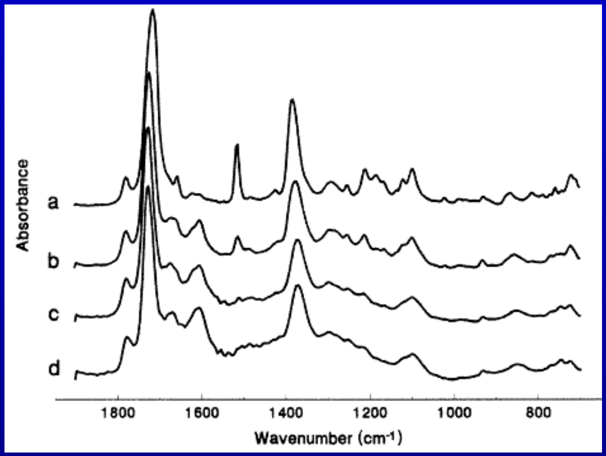


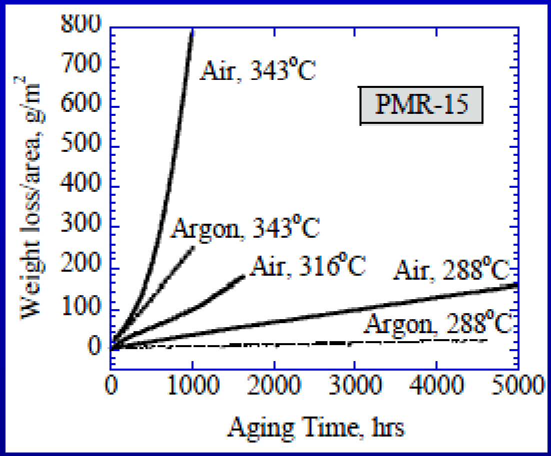
PMR-15 neat resin aged at 288 ^{o}C for 1518 hr



Introduction
Physical and Chemical Changes in Thermo-oxidized Polymer Resins



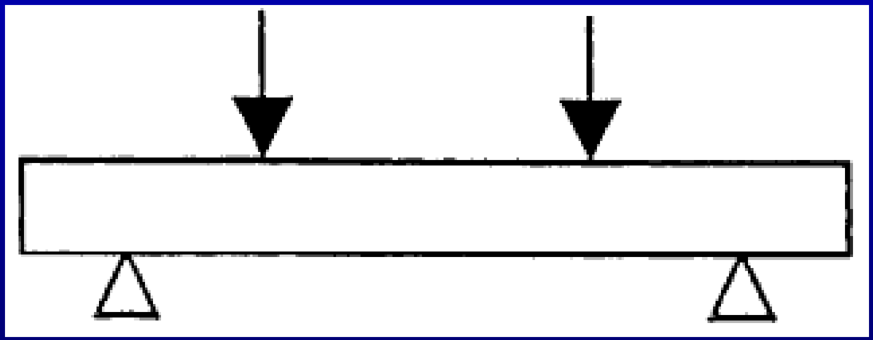




- **Lighter color**
- **Development and growth of voids and microcracks**
- **Chemical bond breakage**
- **Low-molecular weight species out-gassing**
- **Weight loss**

Introduction
Mechanical Properties
of Thermo-oxidized Polymer Resins

- **Traditional method: testing bulk specimens**

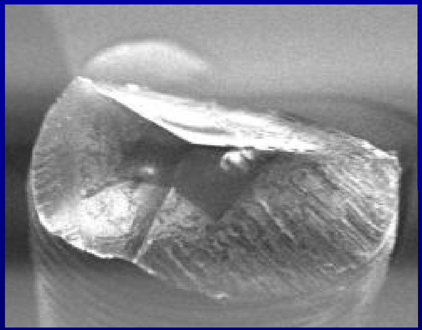


Problem:

The spatial variability in material response with oxidation may be ignored.

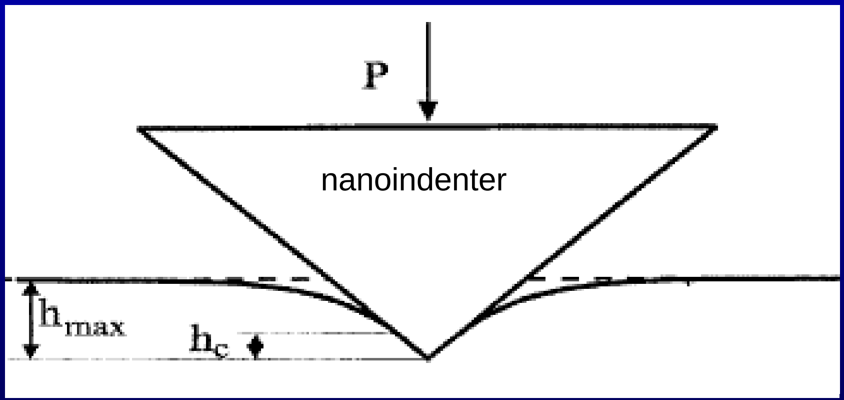
Introduction
Mechanical Properties
of Thermo-oxidized Polymer Matrix Resins

- **New method: Nanoindentation**



Depth: nm ~ μm

Load: ~ μN



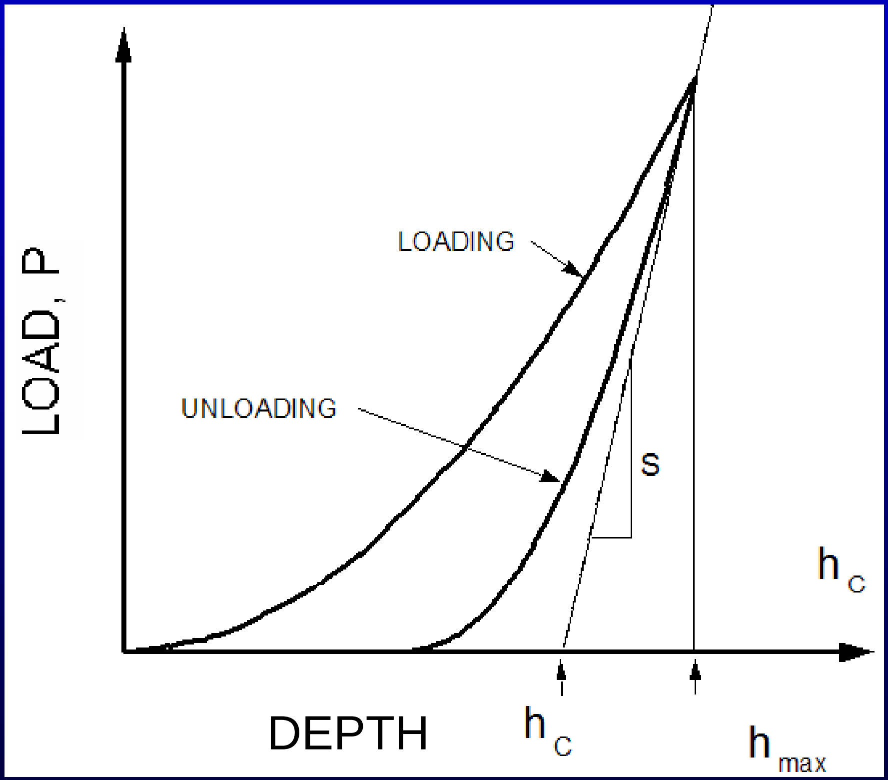
Determination of contact depth (h_c) is the key!

Advantage:

A nanomechanical testing method allowing to examine the localized mechanical properties.

Introduction
Principle of Nanoindentation Test

Big Assumption: initial unloading is pure elastic!



Sneddon formula

$$h_c = h_{max} - \frac{P_{max}}{S}$$

Oliver-Pharr formula

$$h_c = h_{max} - \beta \frac{P_{max}}{S}$$

$$A = C_0 \cdot h_c^2 + \sum_{i=1}^{n} C_i \cdot h_c^{1/2^i}$$

$$E_r = \frac{\sqrt{\pi}}{2 \cdot (1.034)} \frac{S}{\sqrt{A}}$$

Results
Mechanical Characterizations of Thermo-Oxidized Polymer Resins (PMR-15) Using Nanoindentation

(1) Elastic nanoindentation - modulus

(2) Visco-elastic nanoindentation - creep

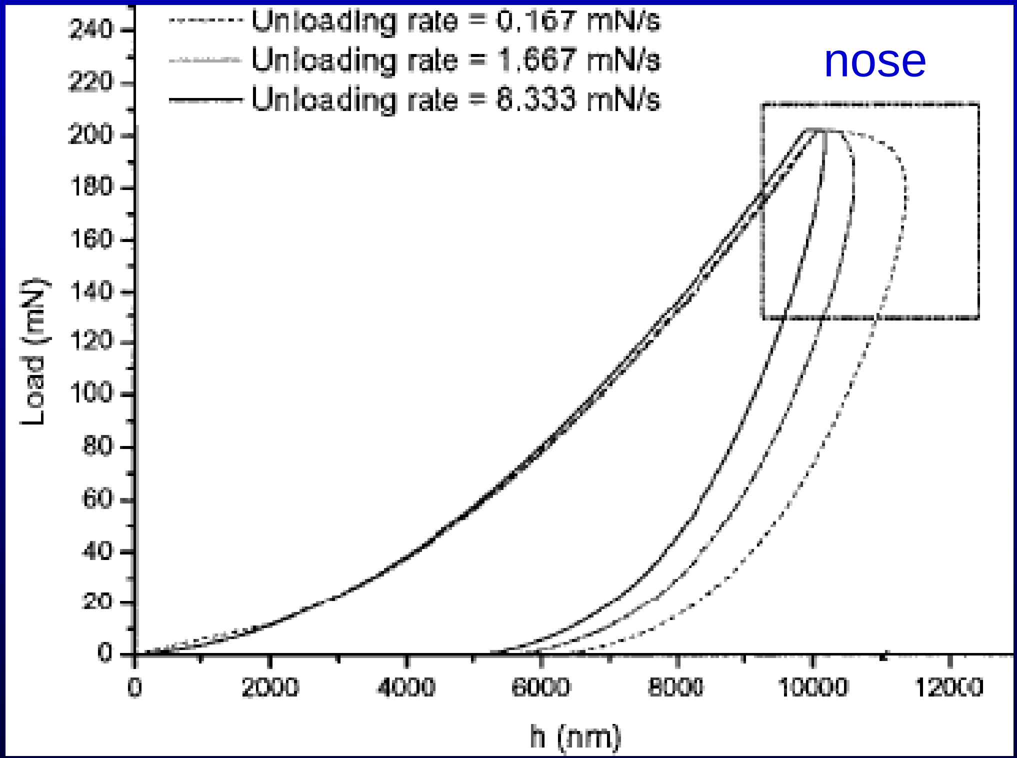
(1) Elastic nanoindentation - modulus

Challenge:

Visco-elastic effect on nanoindentation

Nanoindentation Test of Visco-Elastic Materials

Big Assumption: initial unloading is pure elastic! – not true!

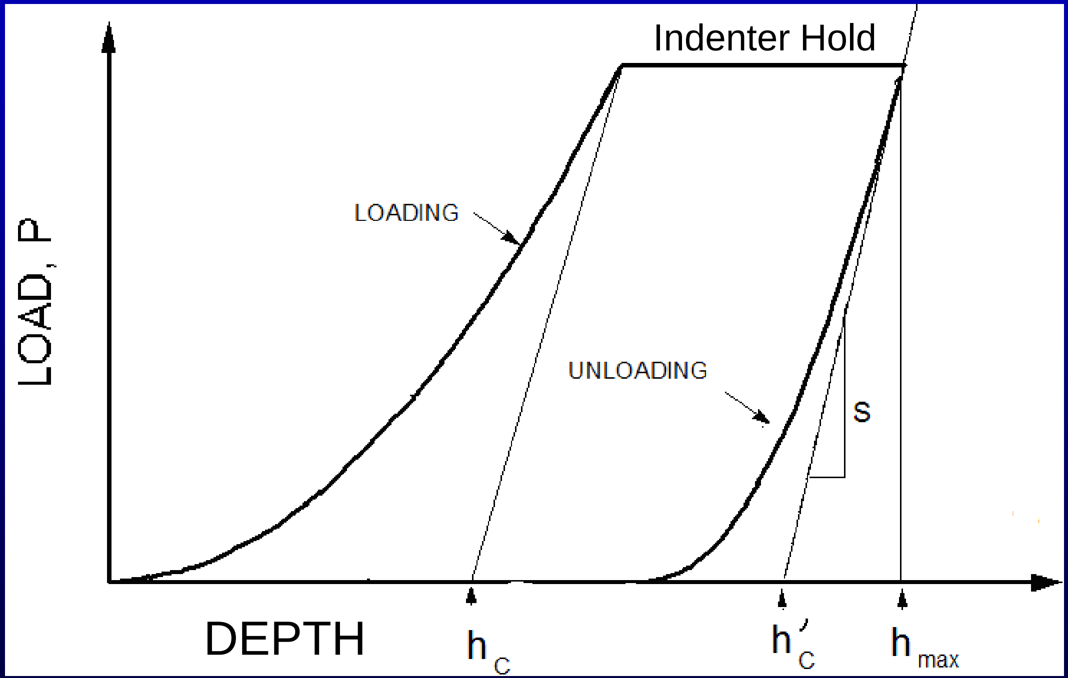


Viscoelastic effect:

- The initial unloading response is visco-elastic.
- A "nose" may occur.
- The stiffness (slope) becomes negative.

Nanoindentation Test of Visco-Elastic Materials

Reducing the visco-elastic effect – indenter holding time



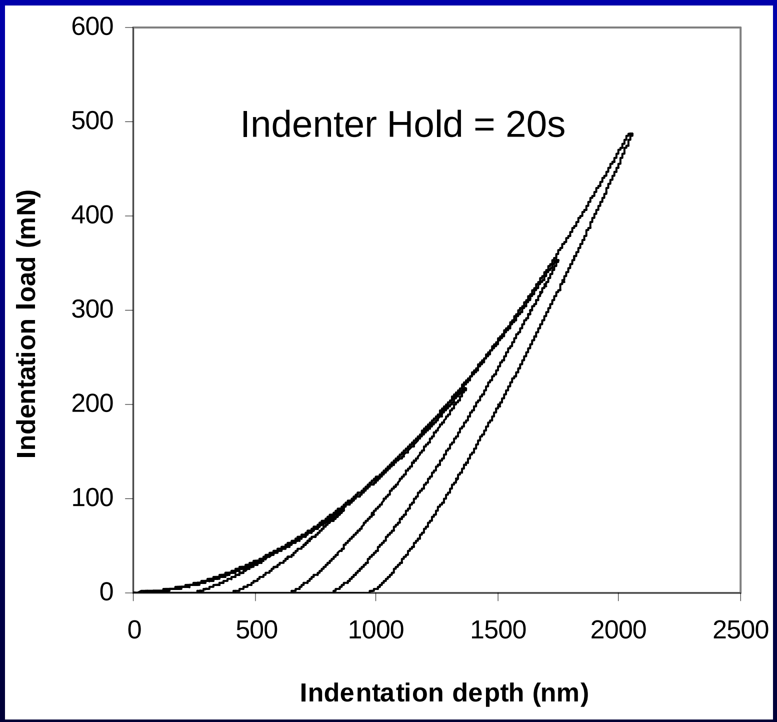
Modified Oliver-Pharr formula

$$h_c = (h_{max} - h_{creep}) - \beta \frac{P_{max}}{S}$$

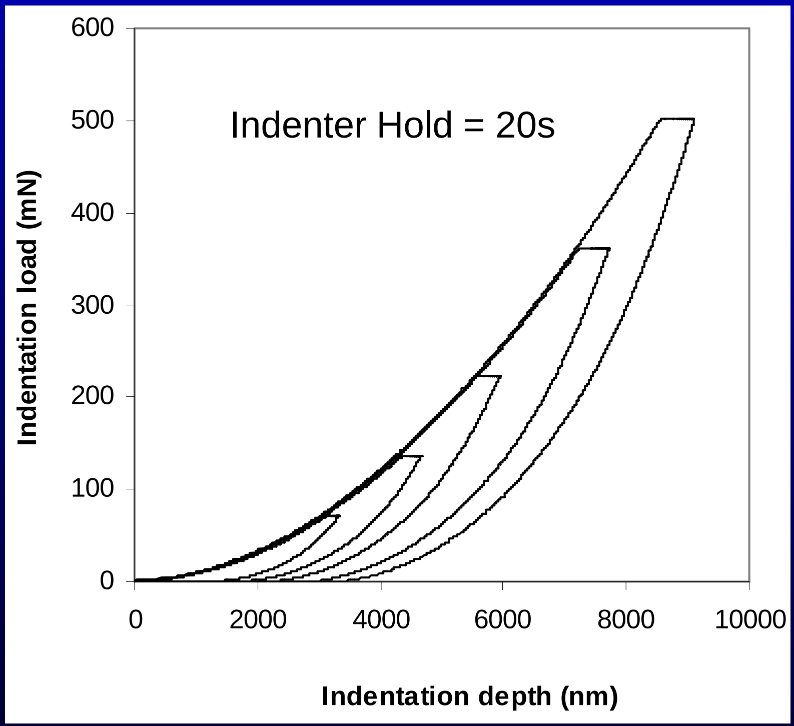
$$\frac{1}{S} = \frac{1}{S_e} + \frac{1}{S_t} = \frac{1}{S_e} + \frac{\dot{\varepsilon}}{\dot{P}} h$$

Elastic properties of thermo-oxidized PMR-15 polyimide

Load-unloading curves of fused silica
- No sign of creep

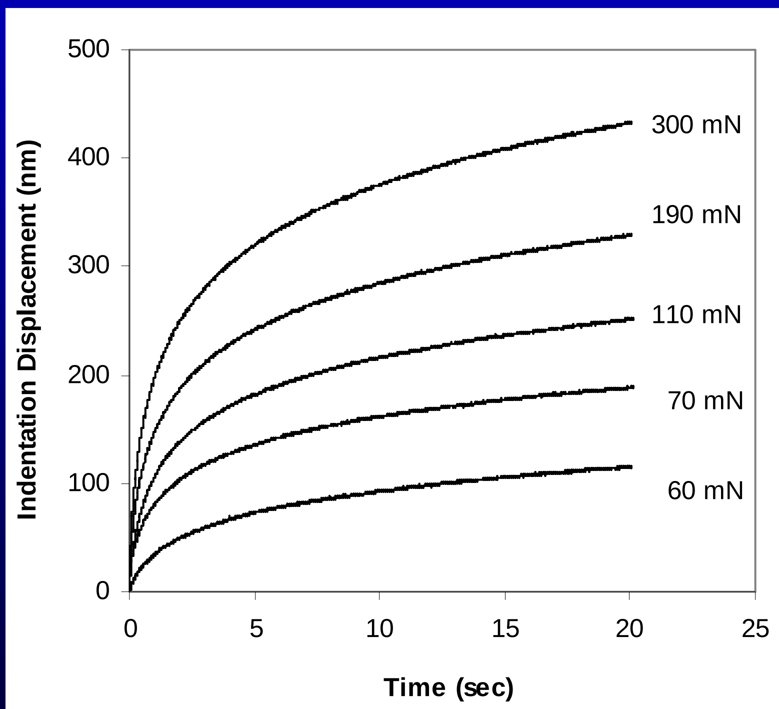


Load-unloading curves of PMR-15
-Creep occurs during holding period

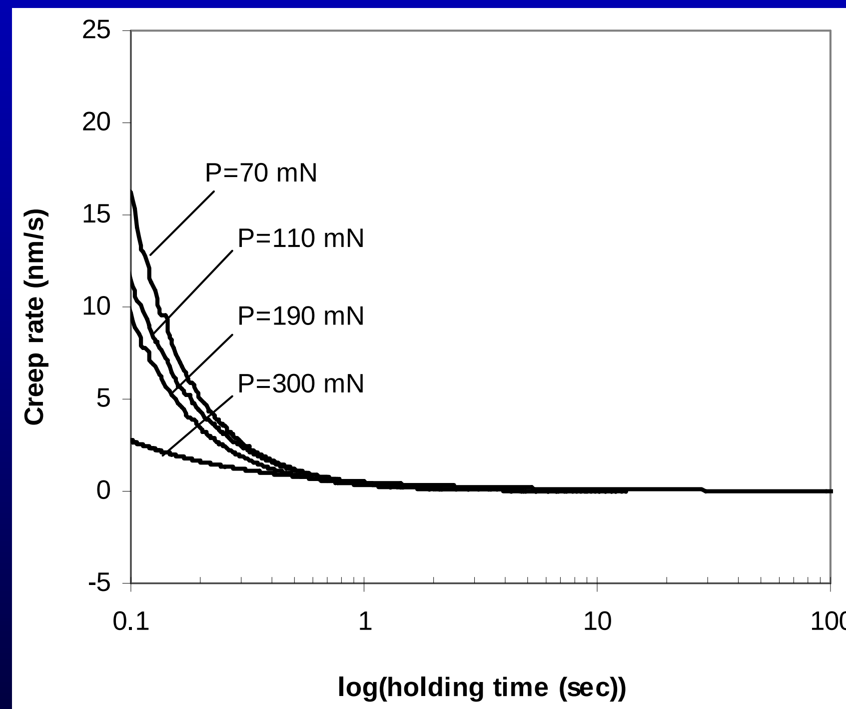


Elastic properties of thermo-oxidized PMR-15 polyimide

Creep response during holding period

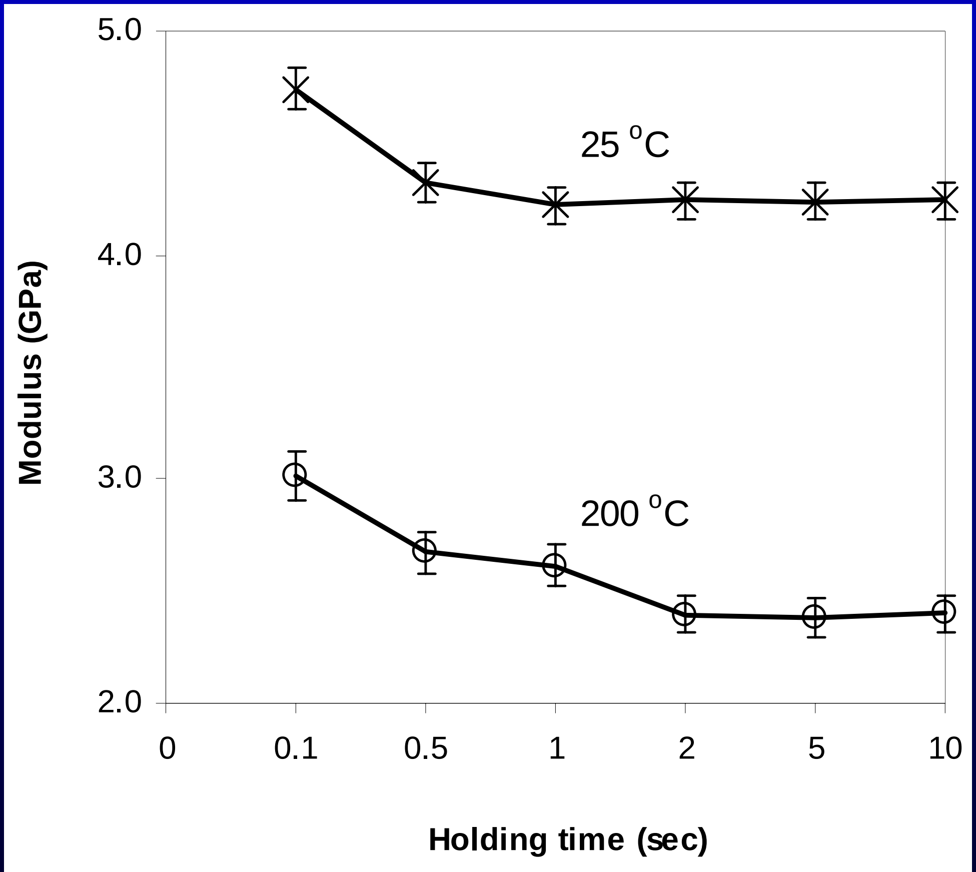


Creep rate *versus* holding time

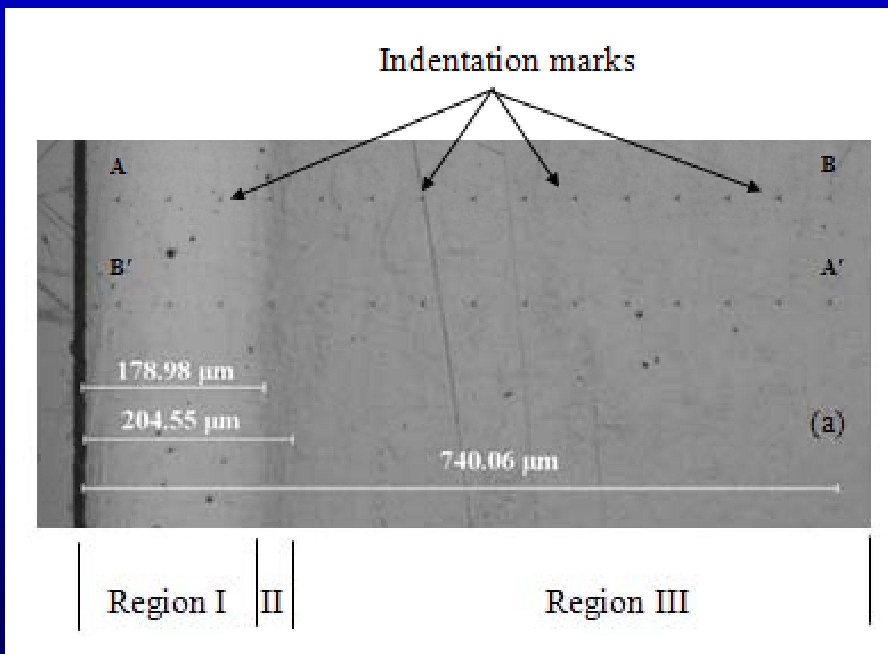


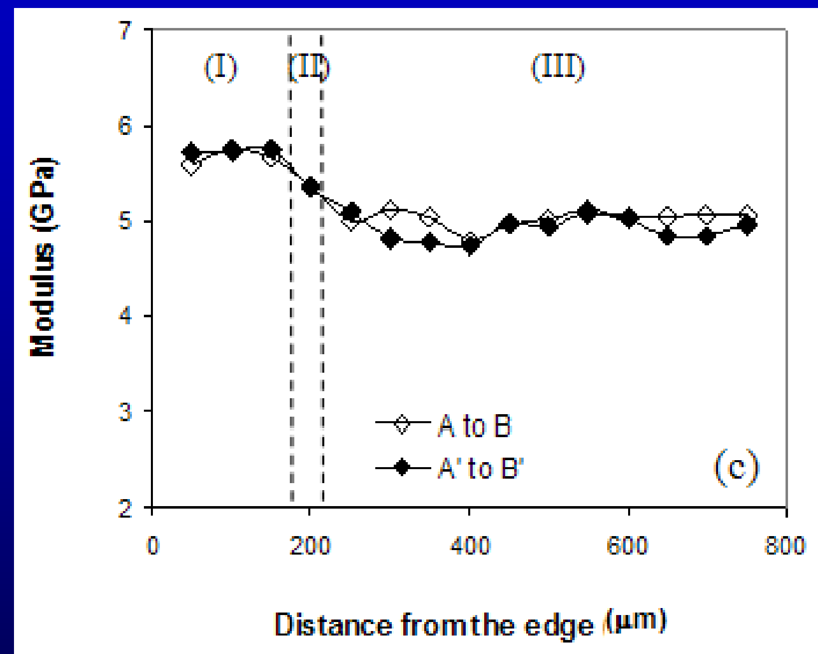
Elastic properties of thermo-oxidized PMR-15 polyimide

Effective holding time



Elastic properties of thermo-oxidized PMR-15 polyimide

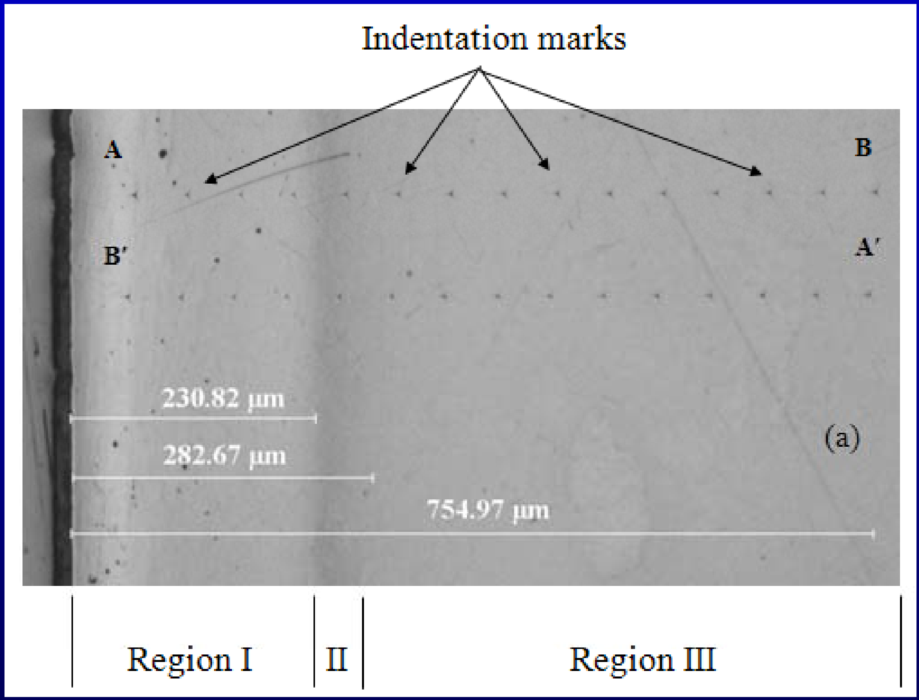


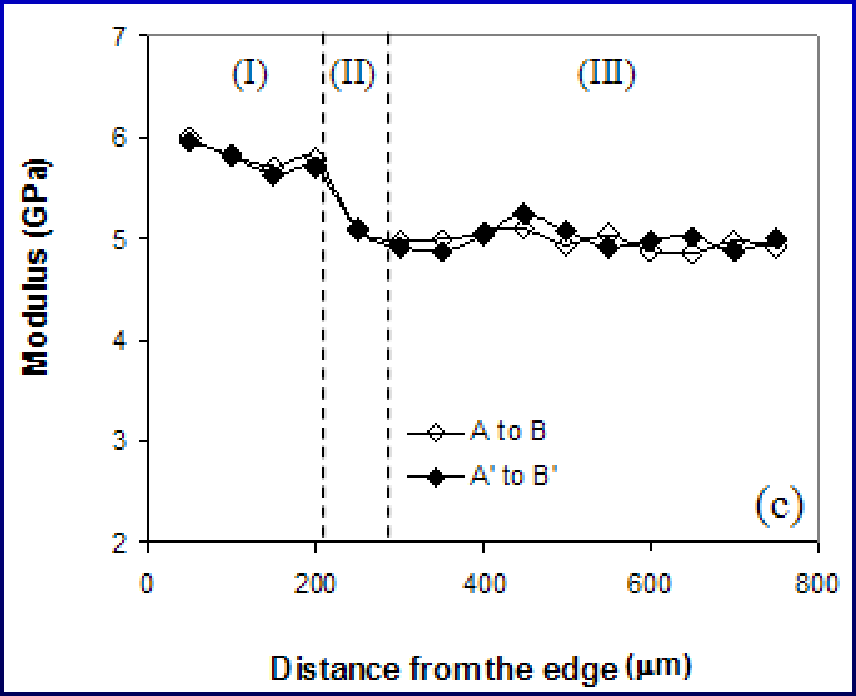


Modulus mapping of thermo-oxidative PMR-15

- aged at 288 ºC for 651 hr in 0.414 MPa pressurized air

Elastic properties of thermo-oxidized PMR-15 polyimide

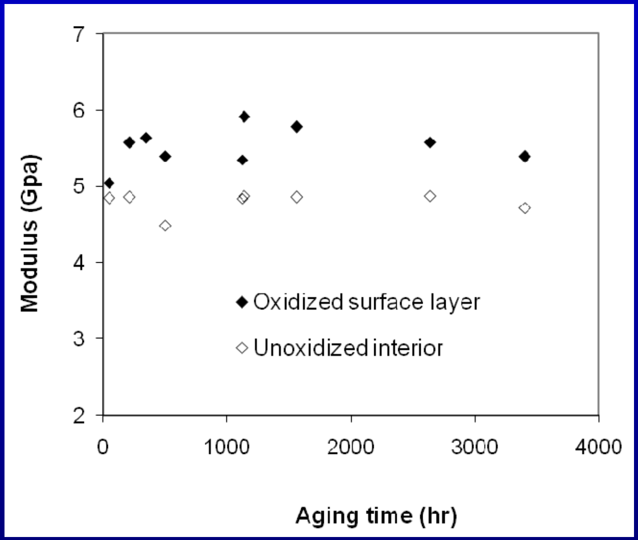


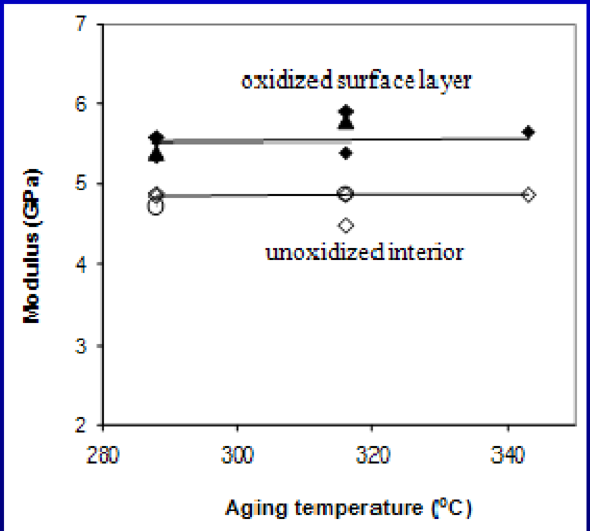


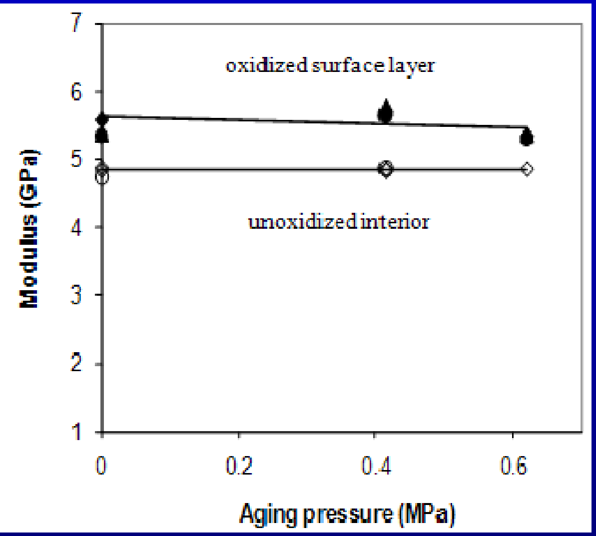
Modulus mapping of thermo-oxidative PMR-15

- aged at 288 ºC for 1518 hr in 0.414 MPa pressurized air

Effects of environmental conditions on modulus of thermo-oxidized PMR-15 polyimide







- The moduli in oxidized surface layers are consistently higher than those in unoxidized interiors.
- Once passing the initial aging stage, the modulus becomes insensitive to the environmental conditions.

(2) Visco-elastic nanoindentation - creep

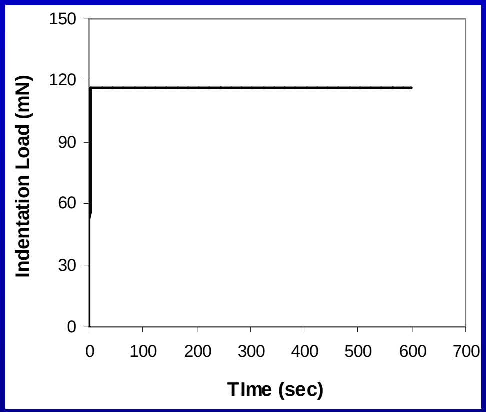
Challenge:

No constant stress during nanoindentation creep (since the contact area keeps decreasing)

Creep properties of thermo-oxidized PMR-15 polyimide

Indentation creep:

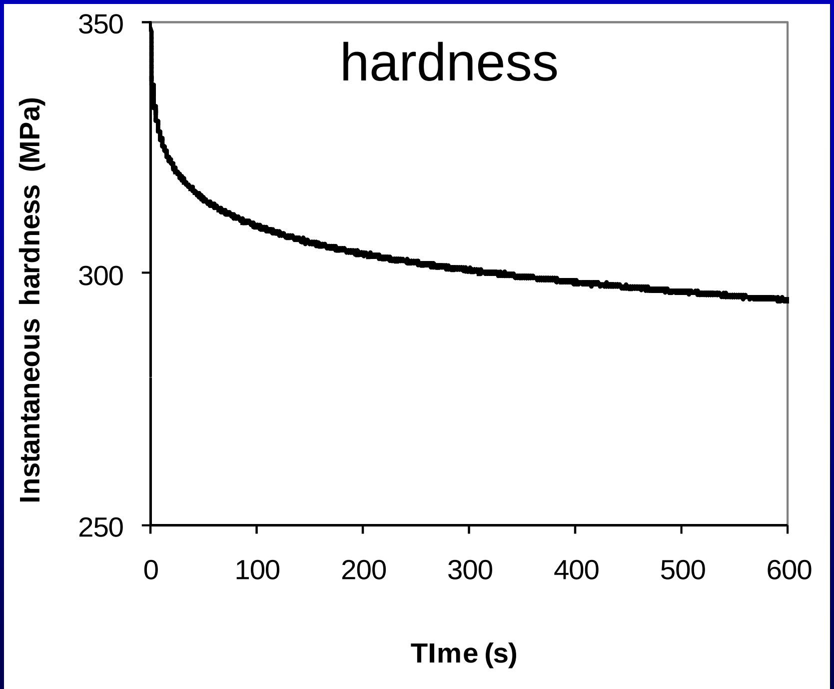
Constant-displacement-rate ($\dot{h}$) experiment:

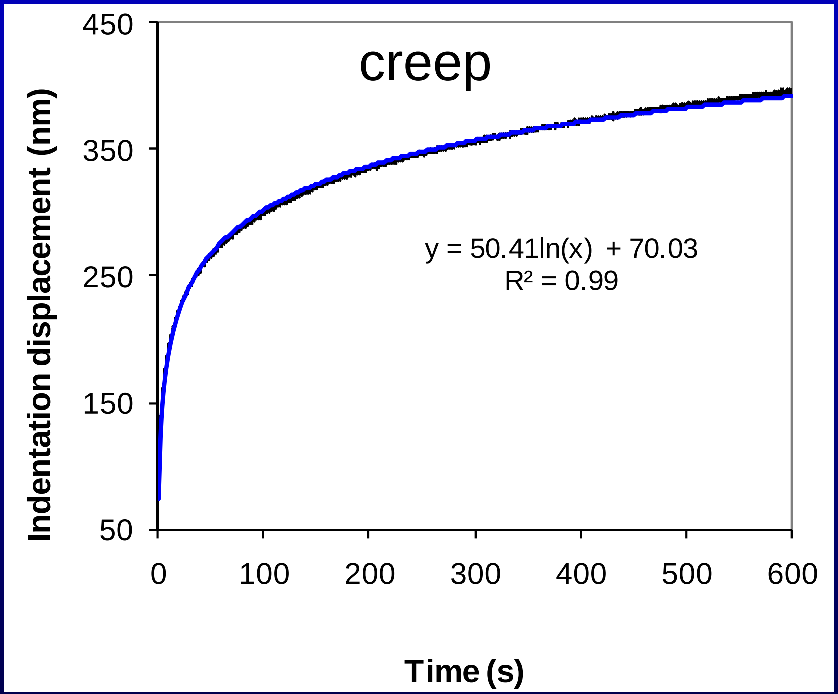


$$H = (b\prod_{\gamma})(\frac{\dot{h}}{h})^{m}$$

m: strain rate sensitivity (creep exponent)

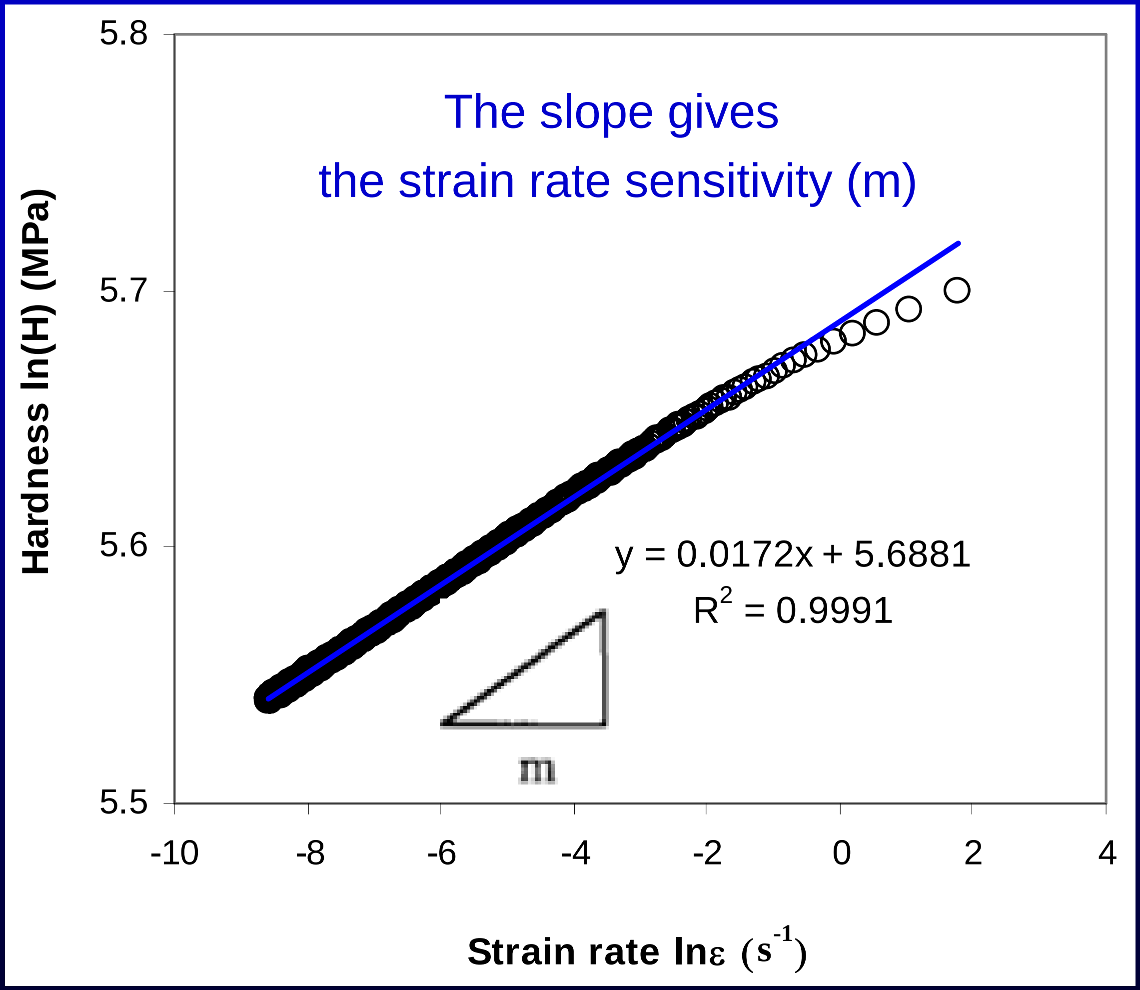
Creep properties of thermo-oxidized PMR-15 polyimide





$$\dot{h} = \partial h / \partial t \qquad \dot{\varepsilon} = \dot{h} / h$$

Creep properties of thermo-oxidized PMR-15 polyimide



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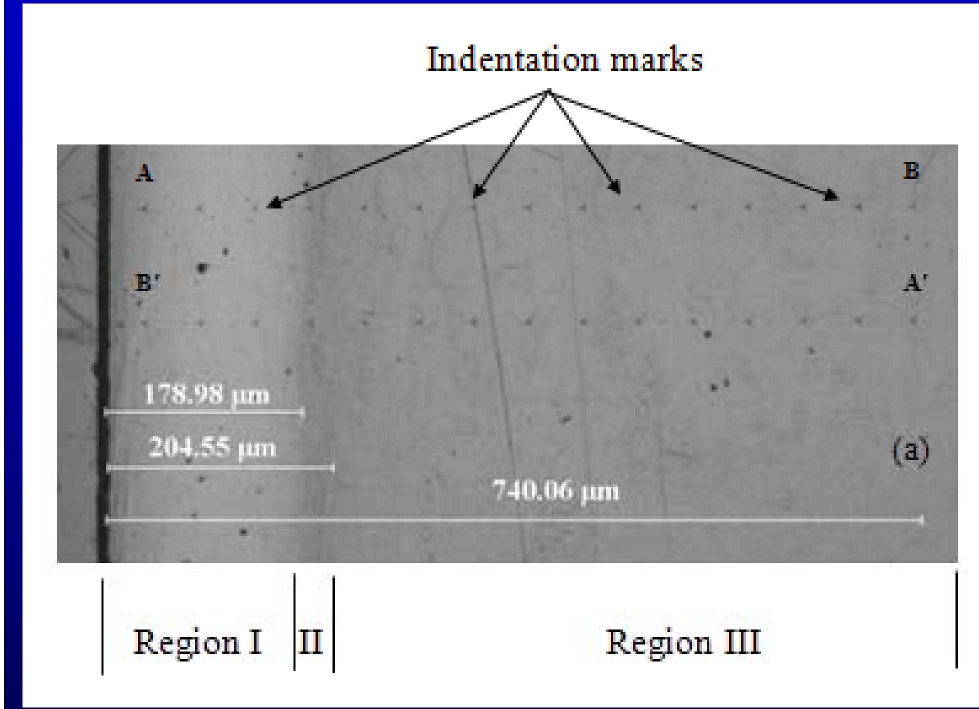
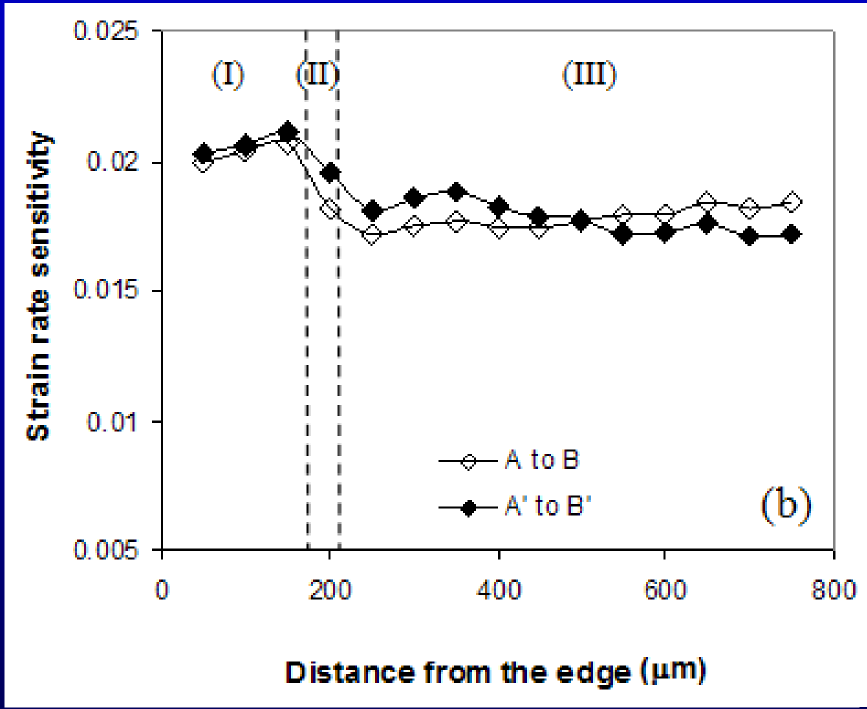
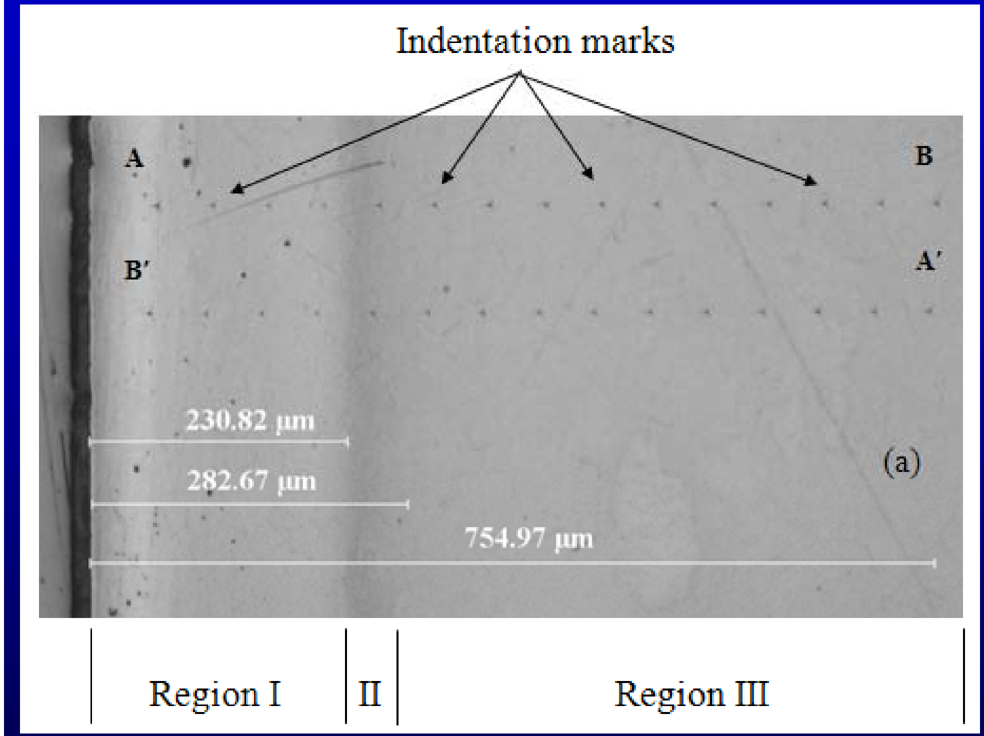
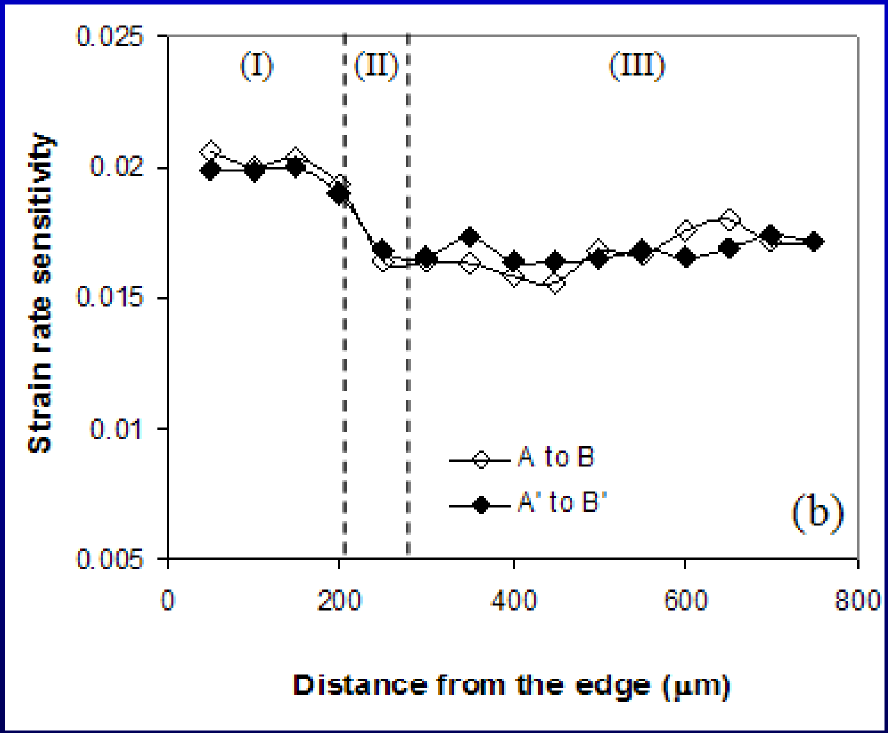




Strain rate sensitivity mapping of thermo-oxidative PMR-15
- aged at 288 ^{o}C for 651 hr in 0.414 MPa pressurized air

Creep properties of thermo-oxidized PMR-15 polyimide





Strain rate sensitivity mapping of thermo-oxidative PMR-15

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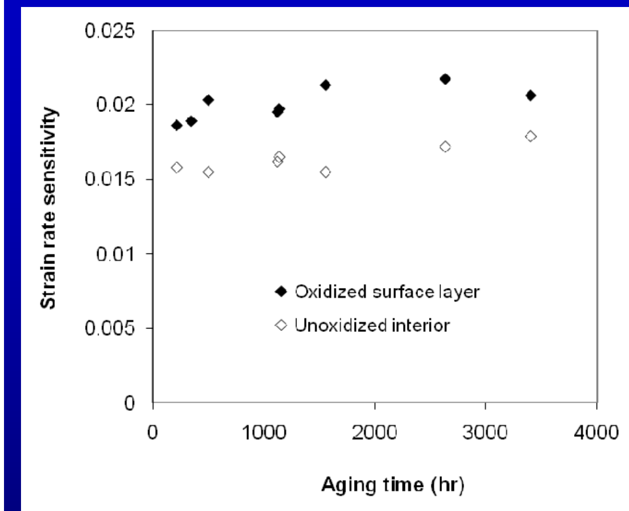
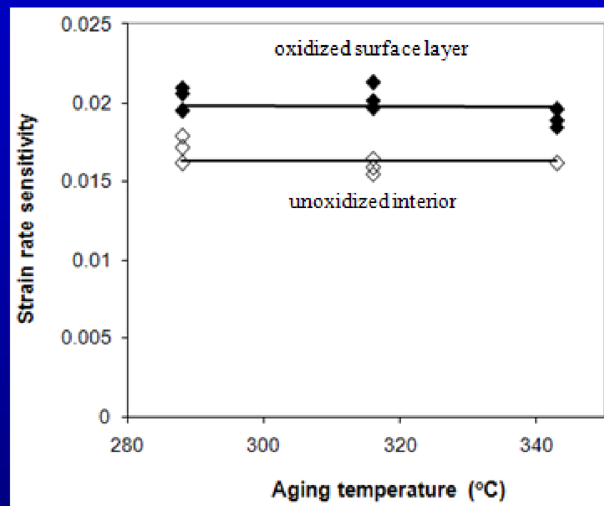
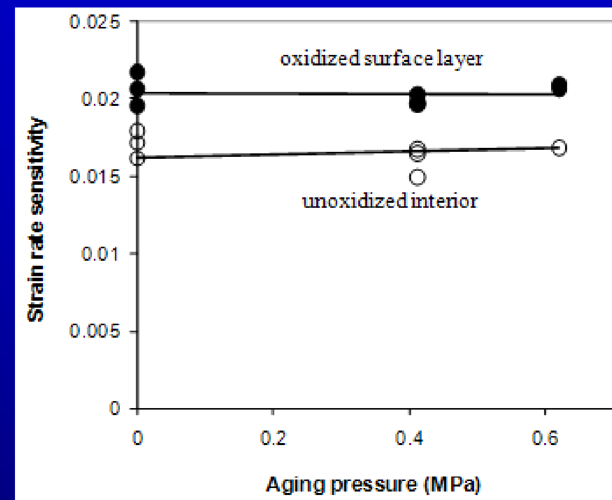
Effects of environmental conditions on creep of thermo-oxidized PMR-15 polyimide







- The strain rate sensitivities in oxidized surface layers are consistently higher than those in unoxidized interiors.
- Once passing the initial aging stage, the strain rate sensitivity becomes insensitive to the environmental conditions.

Summary

- Nanoindentation techniques have been used to characterize the elastic and visco-elastic properties of thermo-oxidized polymer matrix resins.
- Results are useful as inputs in mechanistic material design models to predict the life expectance of the composite components.