Coupled Evolution of Damage and Oxidation in High Temperature Polymeric Matrix Composites

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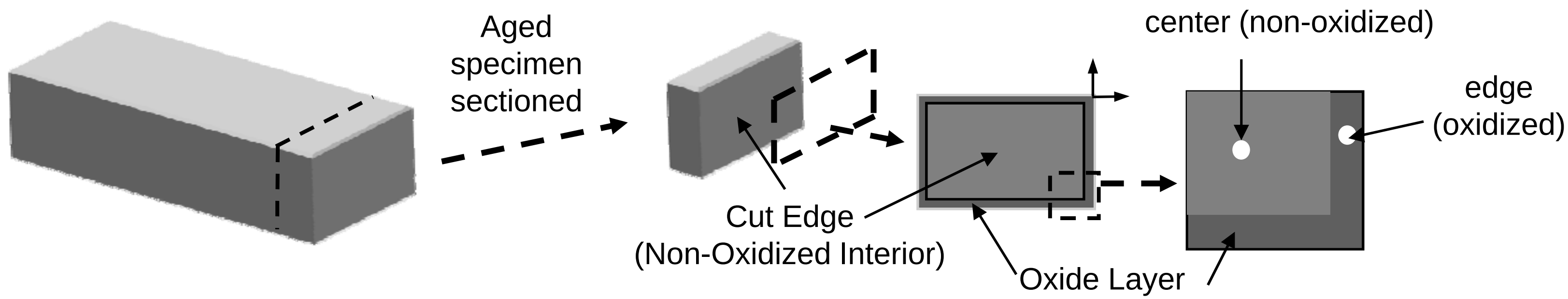
Experimental Methods for Oxidation Studies



Isothermally Aged in

Argon (Non-Oxidative) &

Air (oxidative) Environment

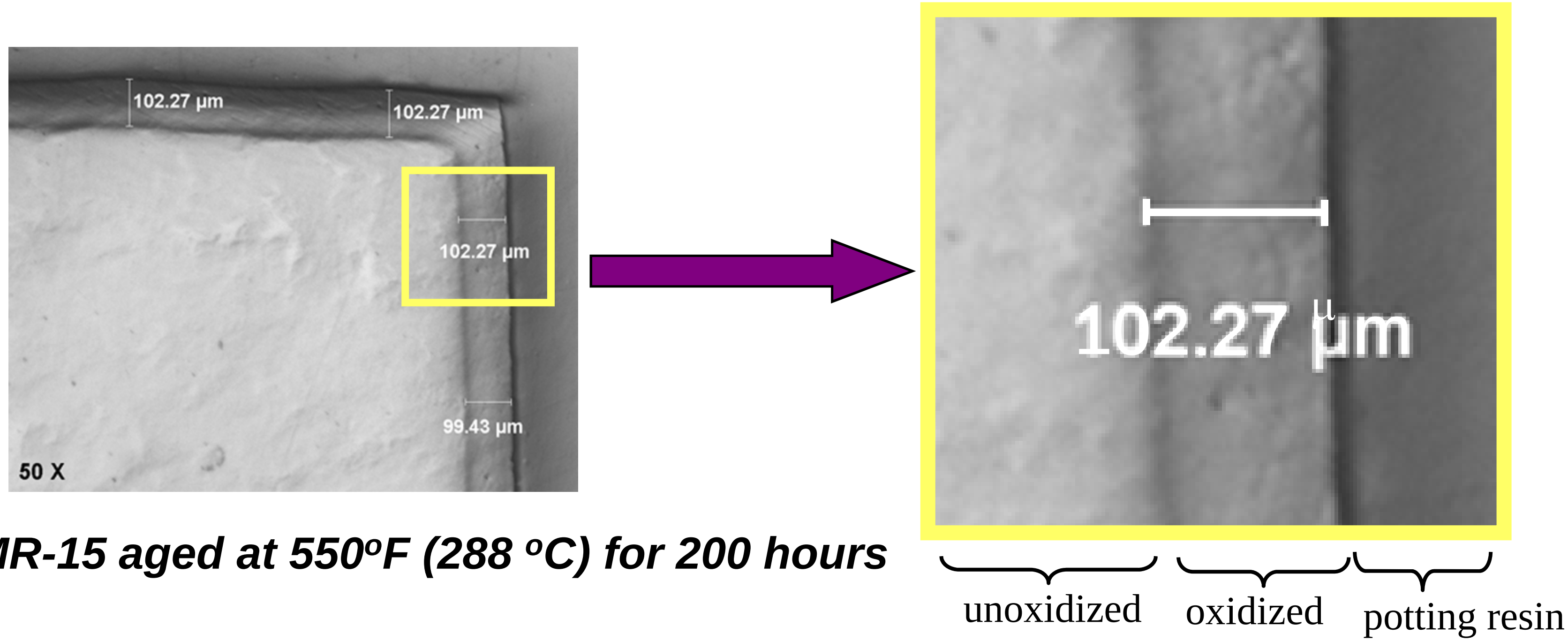
Specimen is weighed

Pieces are cut periodically from 10-3000+ hours of exposure and characterized using

A) Optical Microscopy
B) Nano-indentation
C) Other methods …

Oxidation of Neat Resins

Three-Resin Systems: PMR-15, BMI-5250/4* and AFR/PE-4*



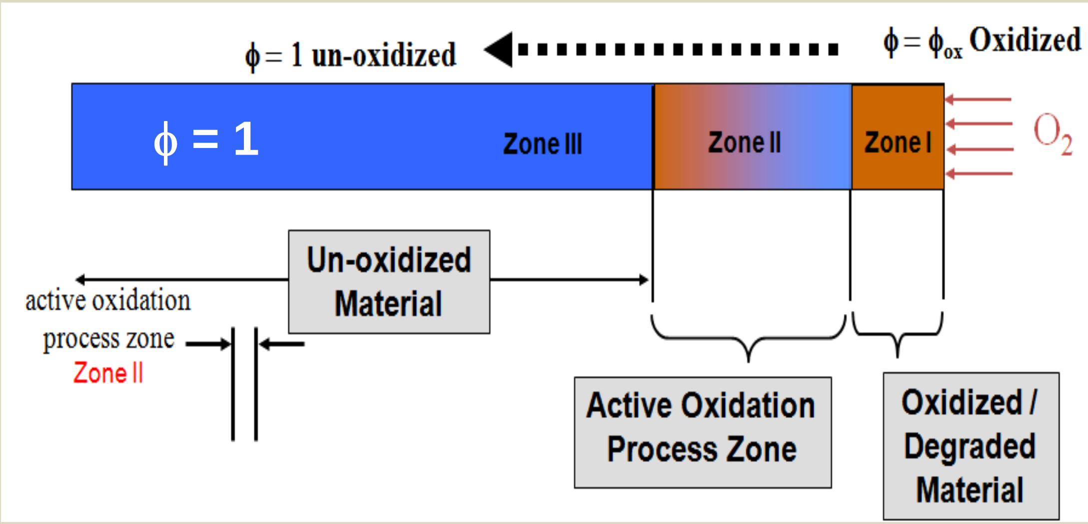
PMR-15 aged at 550°F (288 °C) for 200 hours

- **Microstructural changes due to oxidation can be observed with optical, SEM, nanoindentation (modulus changes) and X-Ray tomography.**
- **Oxidation in neat resins is controlled by diffusion in oxidized layers.**
- **A three-zone model can be used to understand the oxidative region development**

BMI/5250-4 and AFR/PE-4 oxidation data are under US ITA (export control) Restriction

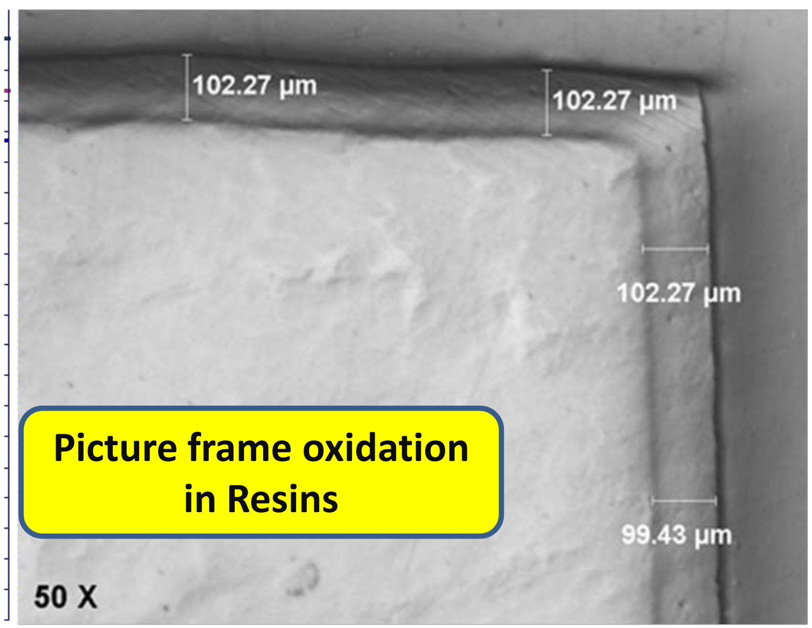
Oxidation in Neat Resin – Constituent Scale

Thermo-Chemical Model : Diffusion/Reaction/Conversion Simulations

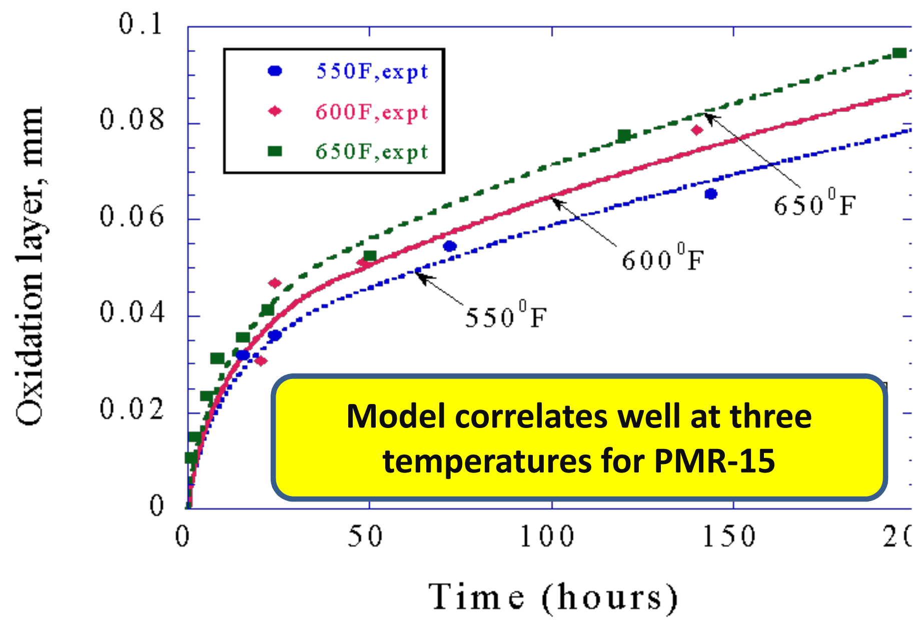


3-Zone Model with an Oxidation State Variable ϕ

[1] Pochiraju and Tandon, JEMT, 2006
[2] Tandon, Pochiraju, Schoeppner, PDS 2006
[3] Pochiraju, Tandon, Schoeppner, MTDM, 2008

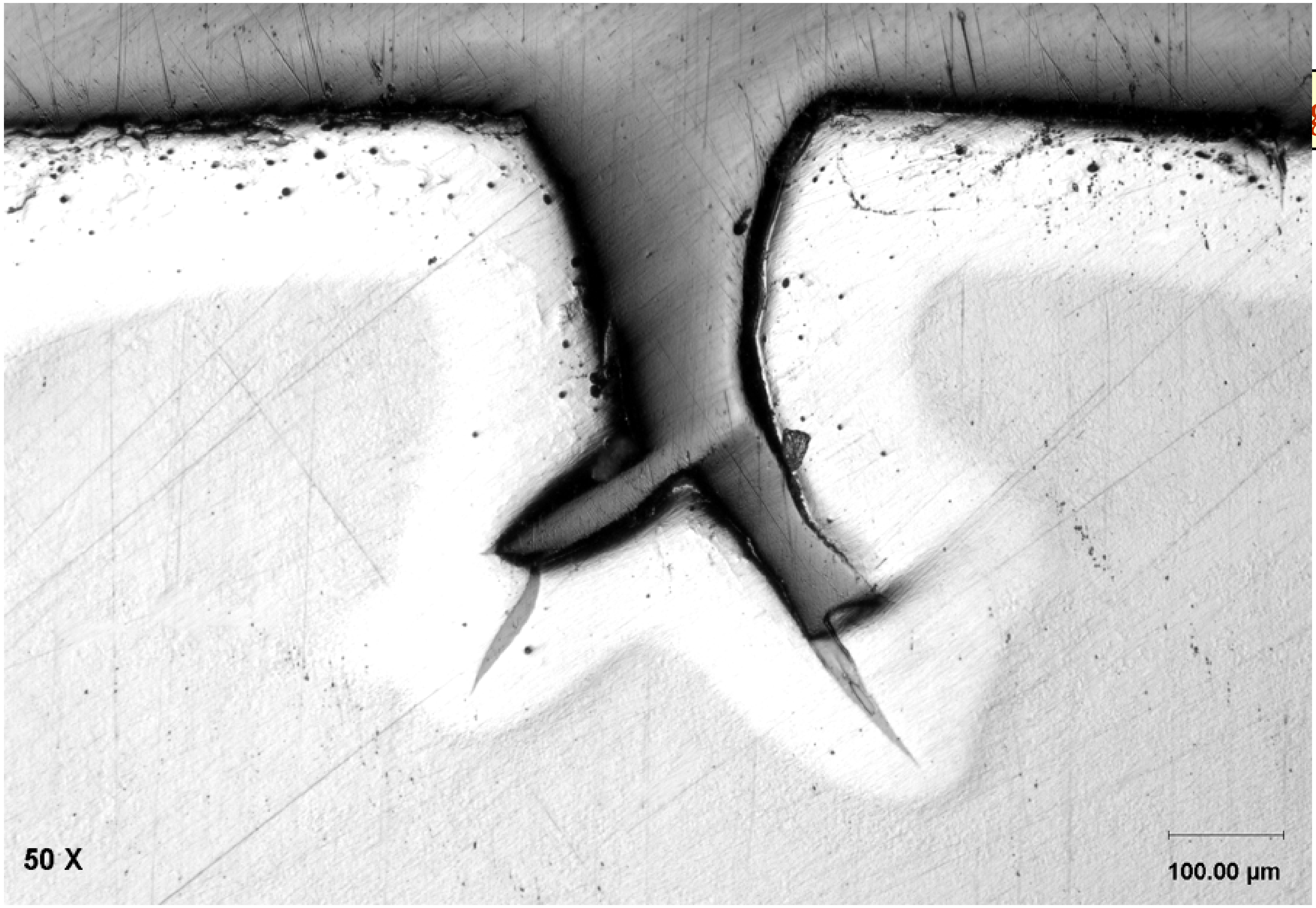


Picture frame oxidation in Resins



Model correlates well at three temperatures for PMR-15

Damage development during Thermo-Oxidation in Neat Resins



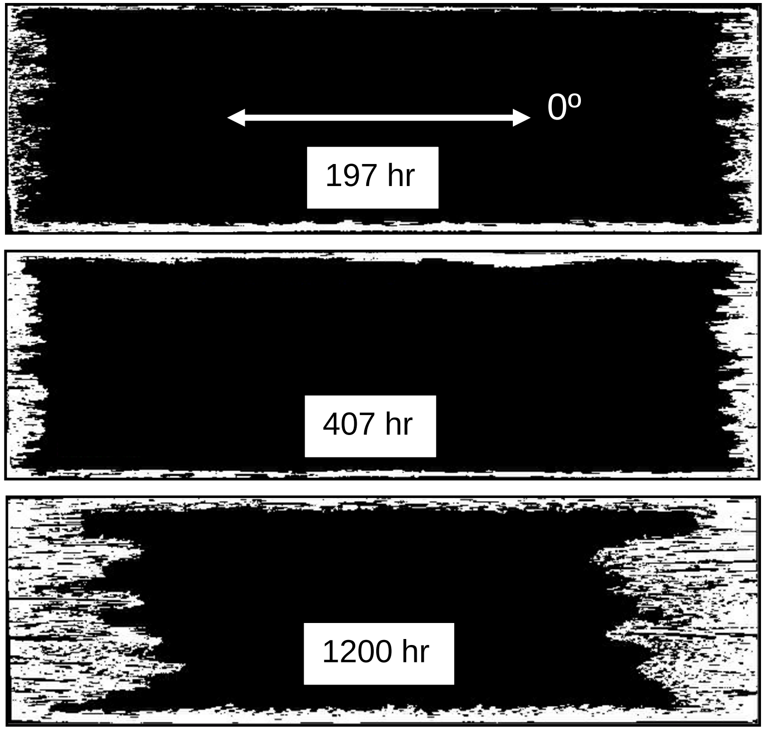
ged @ 343ºC

- ***Cracks first develop at ~ 200 hrs of aging***
- ***Extensive edge cracking, loss of material,***
- ***Cracks provide pathways for oxidation into the specimen interior***
- ***Oxidation accelerates due to sorption on crack-tips***

Oxidation in Composites

Unidirectional G30-500/PMR-15 aged at 288ºC

- Oxidized resin becomes lighter in color
- Development and growth of voids and microcracks into surface
- **<u>Preferential oxidation in axial direction</u>**

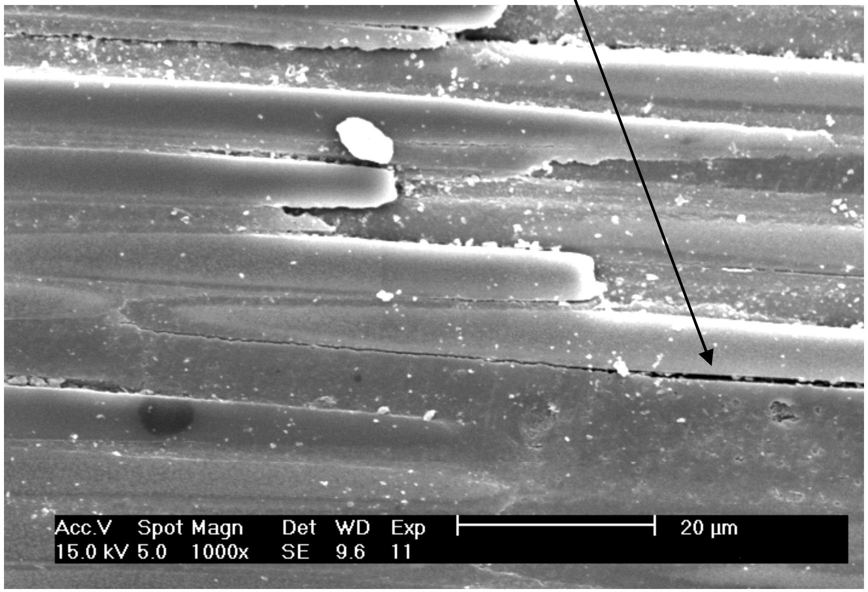


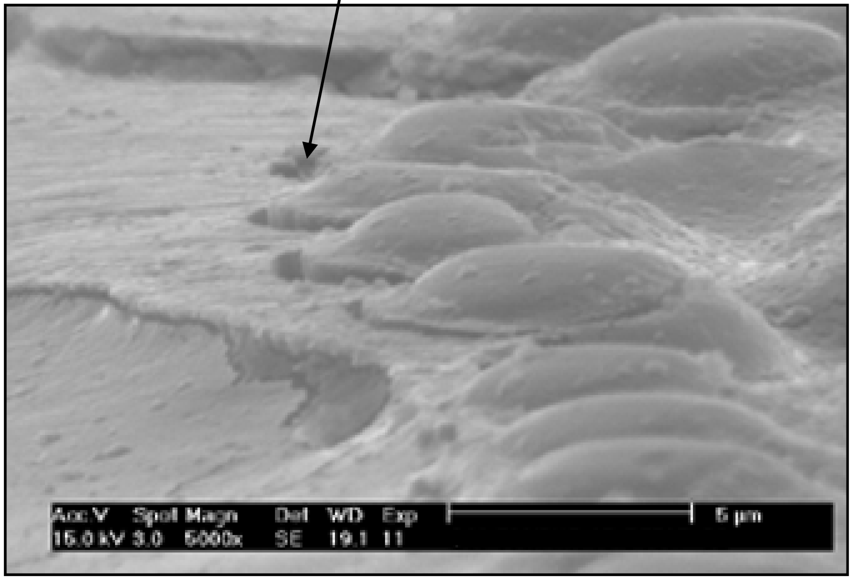
Characterizing Damage

G30-500/PMR-15
Composite Oxidation
@ 288 °C, 2092 hr

Development of damage at the fiber-matrix interface

Damage Development

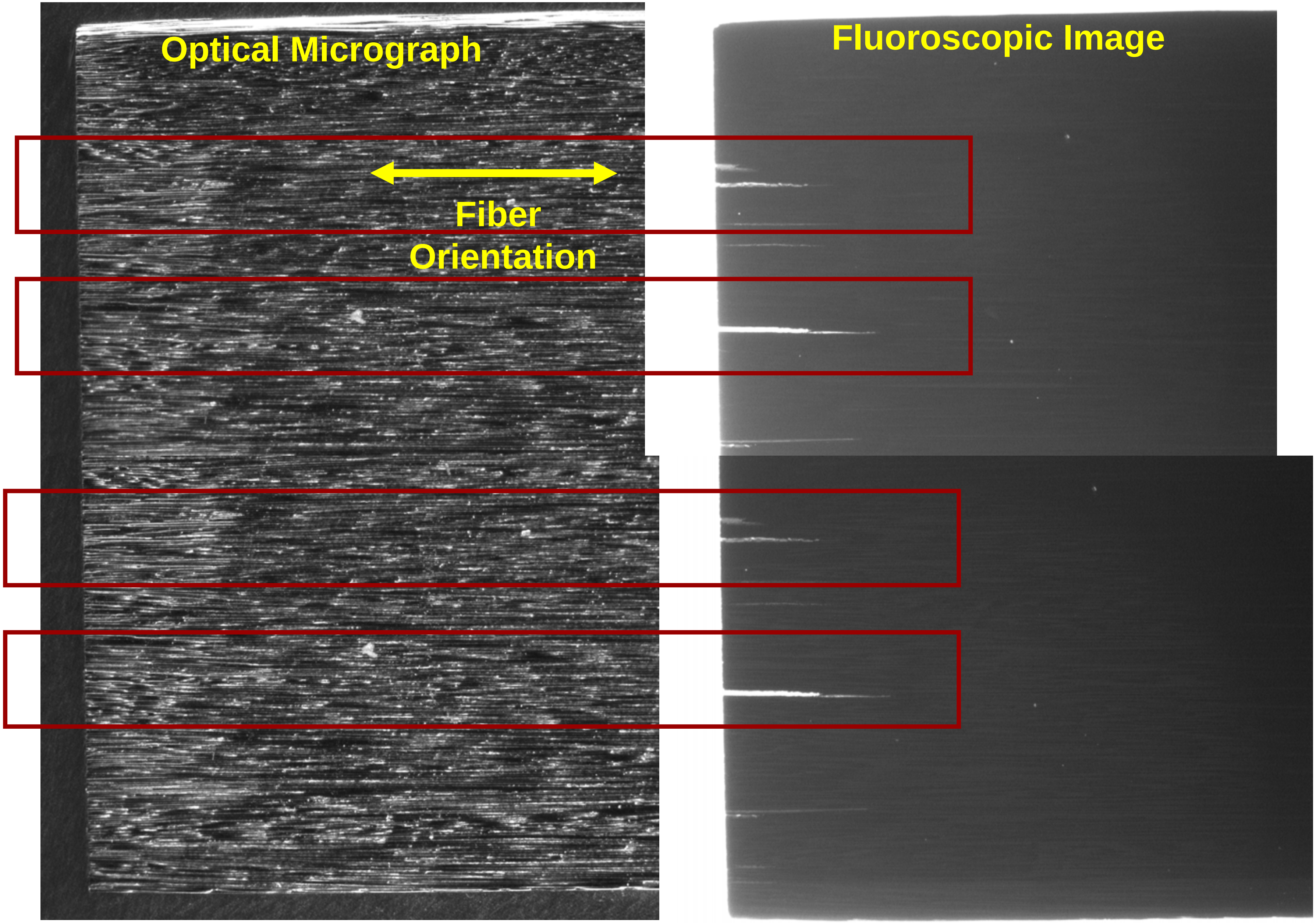




Close-up tilted view of the oxidized fiber end

•Debonding of fiber-matrix interface – embrittlement associated with oxidation

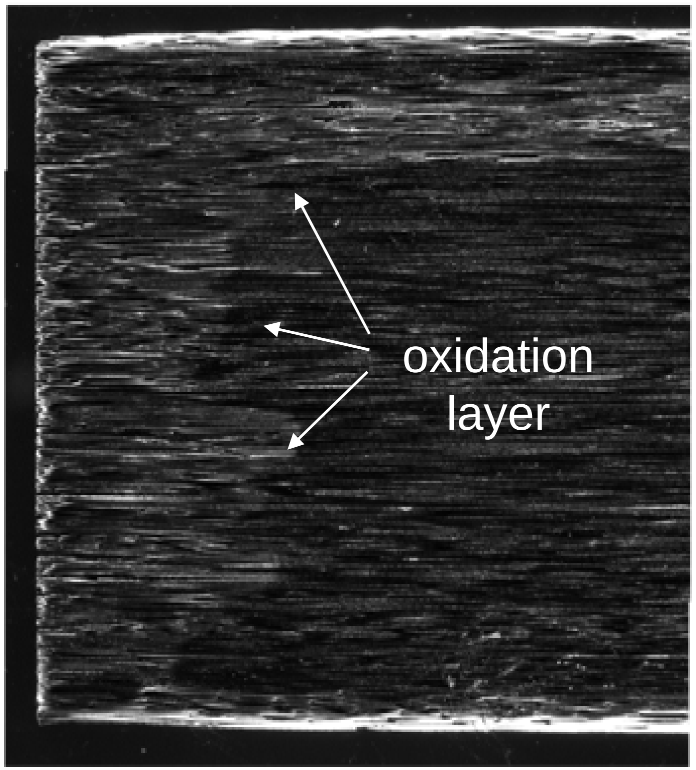
Cracks are seen in the Areas of Maximum Oxidation Depth

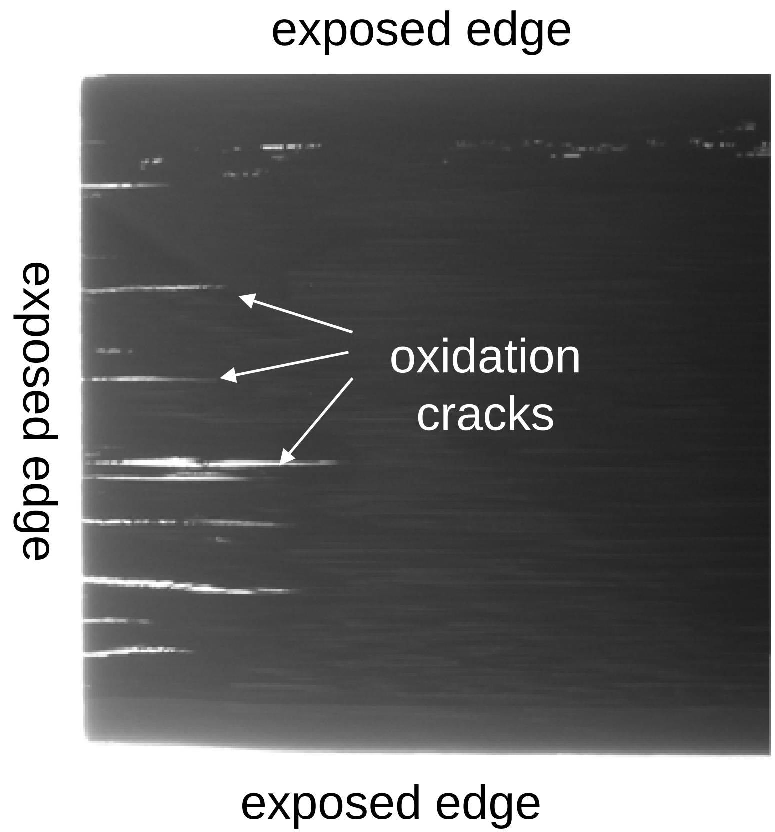


Aged at 288 ^{o}C 405 Hours

Axial Growth

668-hr aged specimen

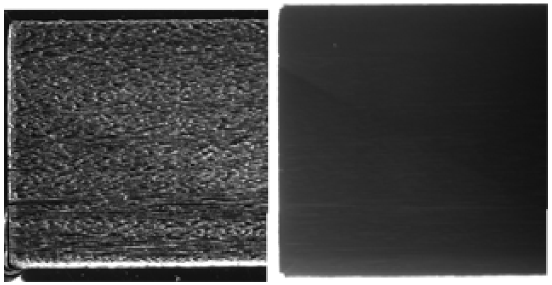




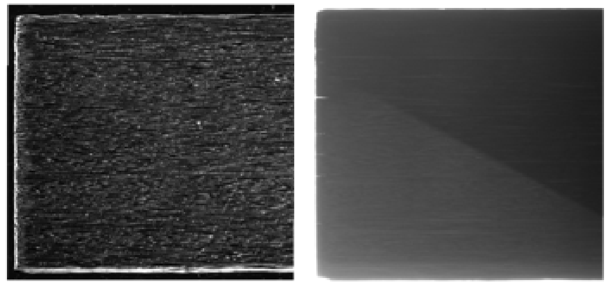
Dark-field image of oxidation

Fluorescence imaging of cracks

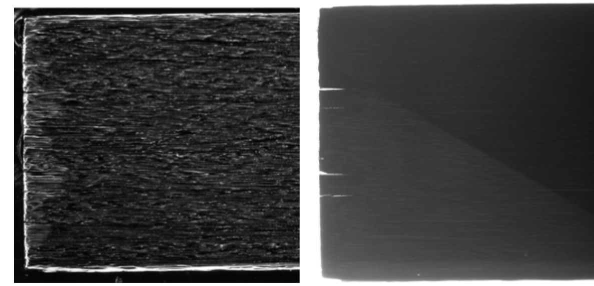
Summary of Axial Damage and Oxidation Growth



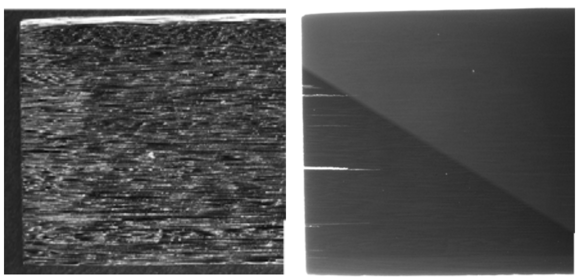
24 hr



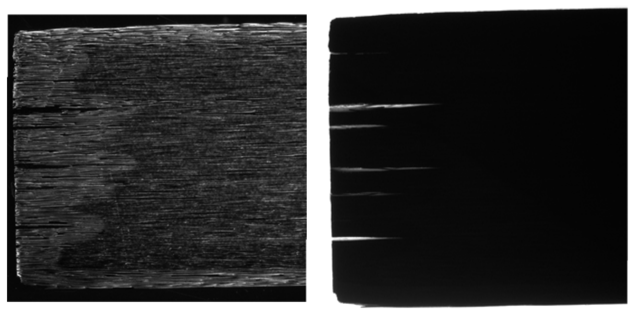
96 hr



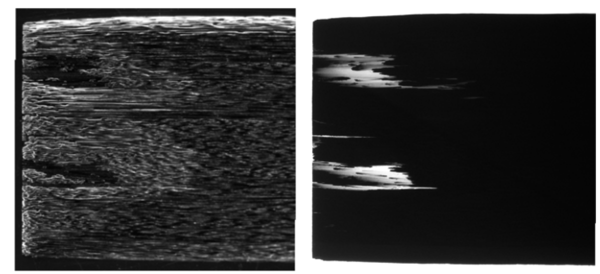
196 hr



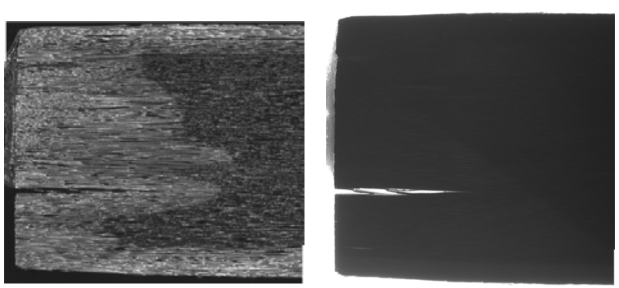
405 hr



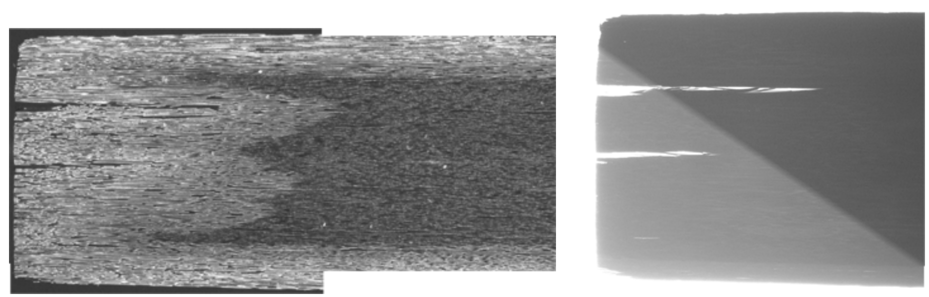
906 hr



1217 hr



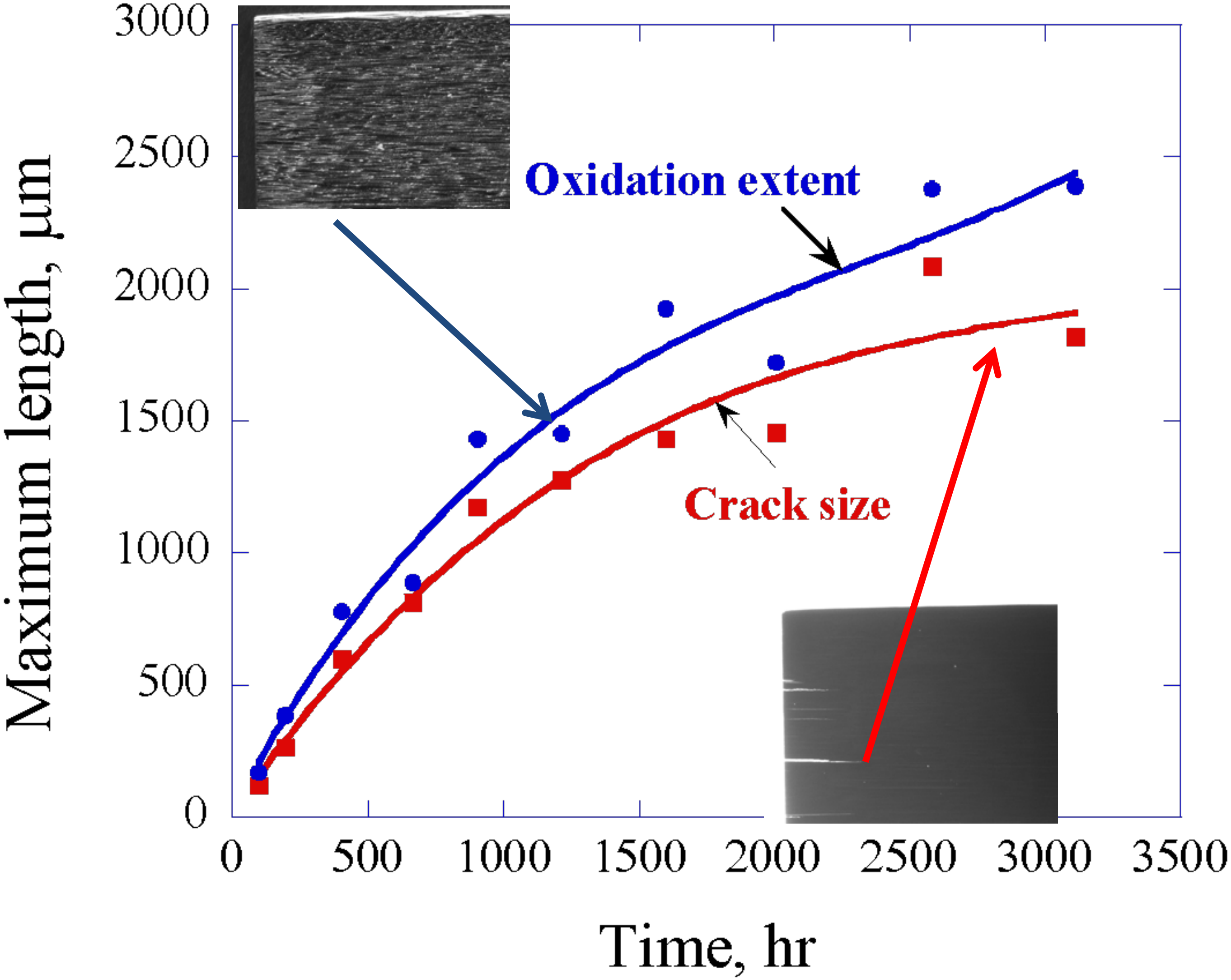
2009 hr



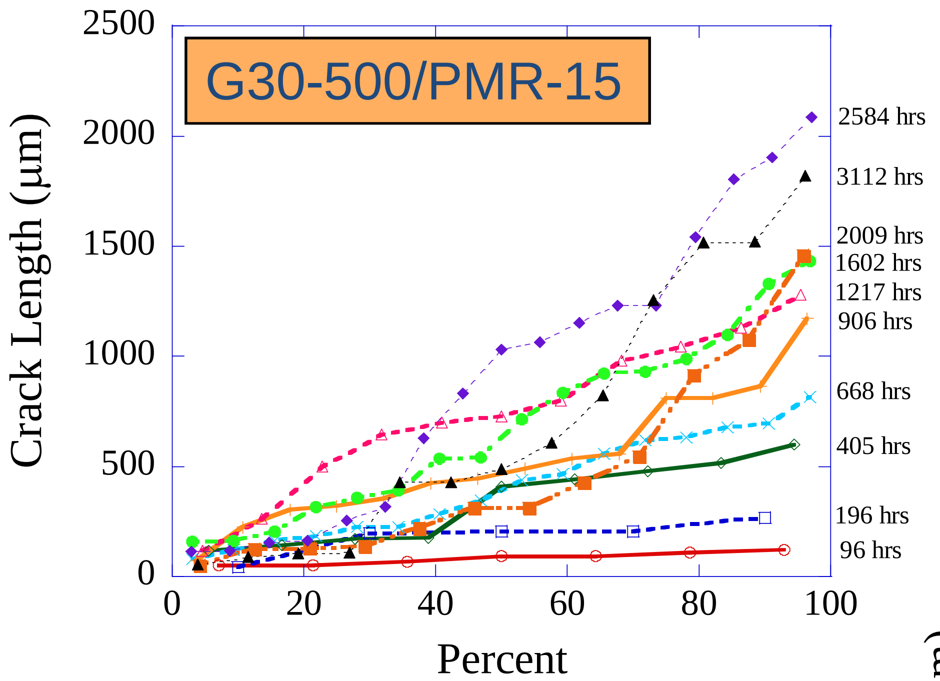
3112 hr

G30-500/PMR-15

Axial Oxidation and Damage Growth



Distribution of
Axial Crack Lengths and Oxidation Extent

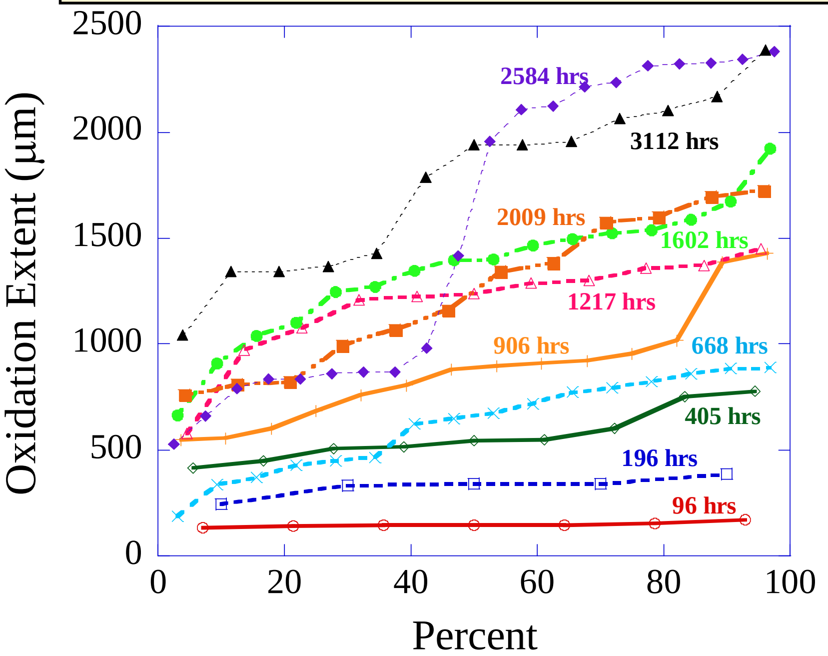


Short Aging Times

- Up to 668 hours, linear crack growth indicating a uniform distribution of crack length
- Deterministic representative single cell micromechanics models can be used to describe the effective oxidation behavior of the unidirectional composite.

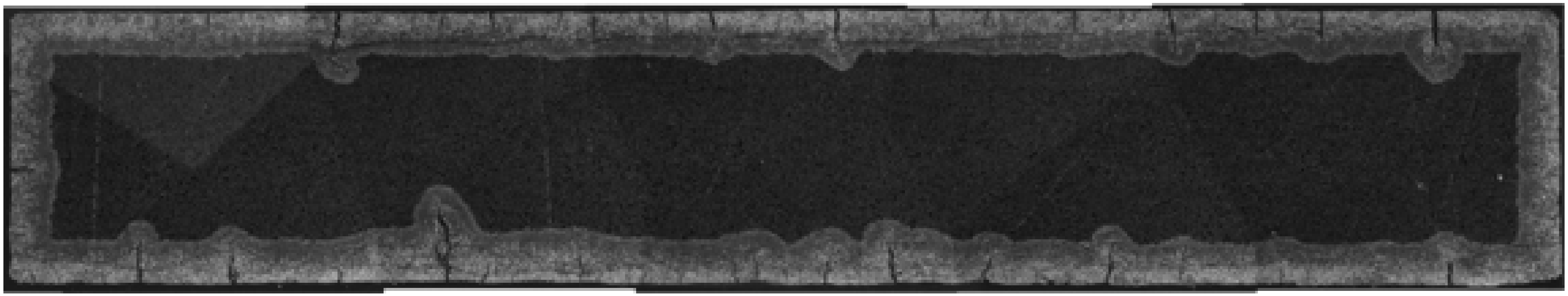
Long Aging Times

- Crack length data less reliable at longer aging times since crack coalescence occurs and the oxidation extent and crack lengths become highly nonuniform
- Damage propagation will likely require a stochastic modeling scheme to predict the material behavior.

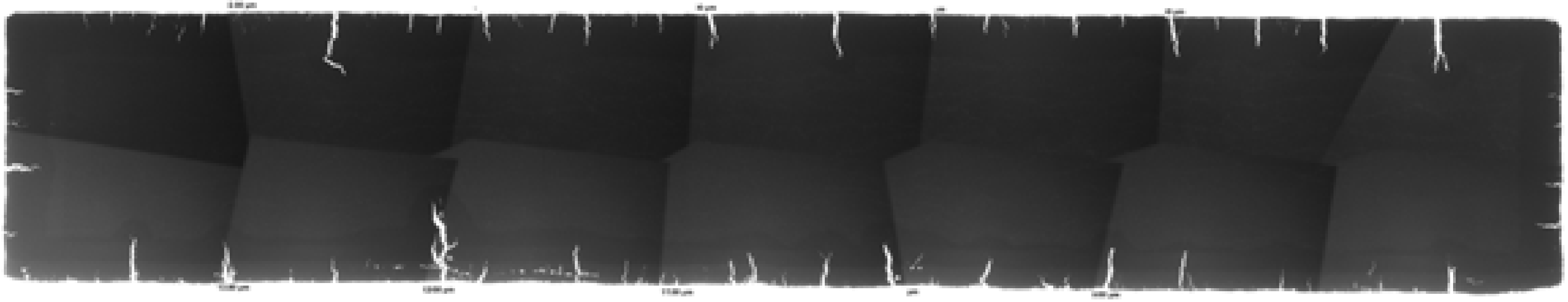


Transverse Growth

3112-hr aged specimen



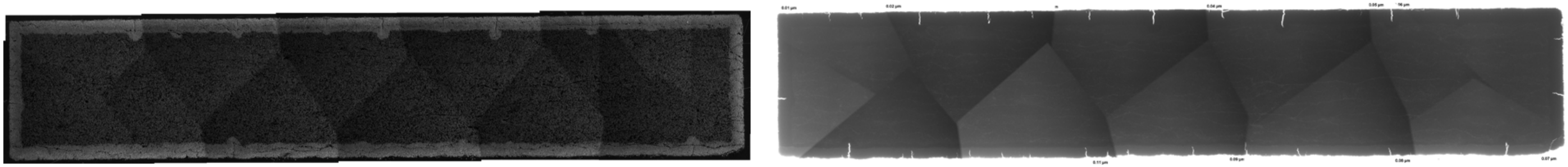
Dark-field image of oxidation



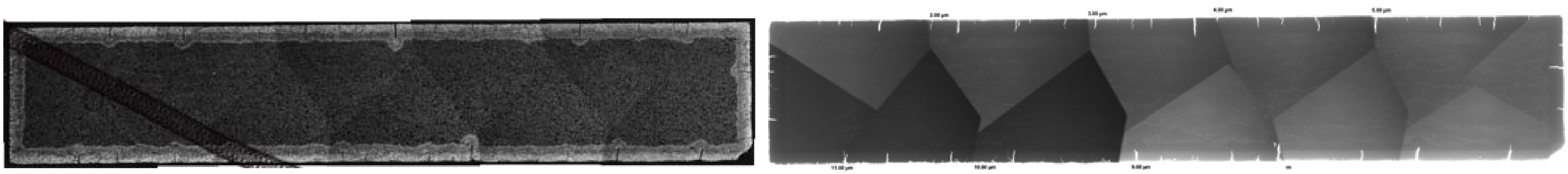
Fluorescence imaging of cracks

Summary of Transverse Damage and Oxidation Growth

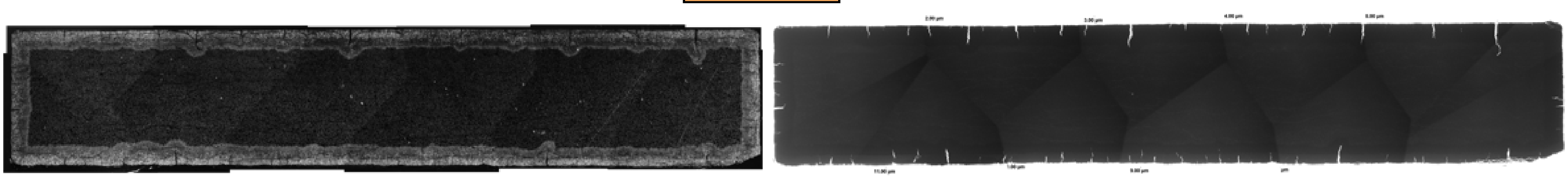
G30-500/PMR-15



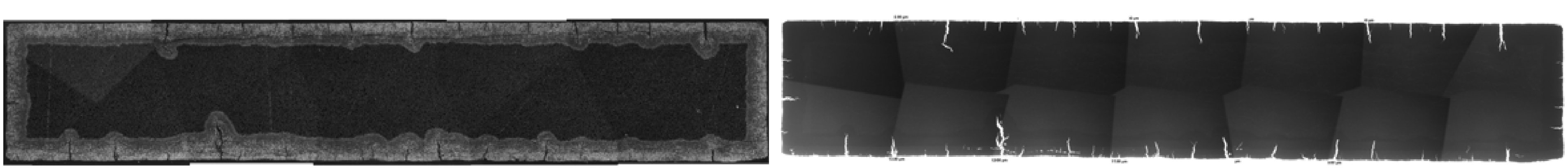
1602 hr



2009 hr



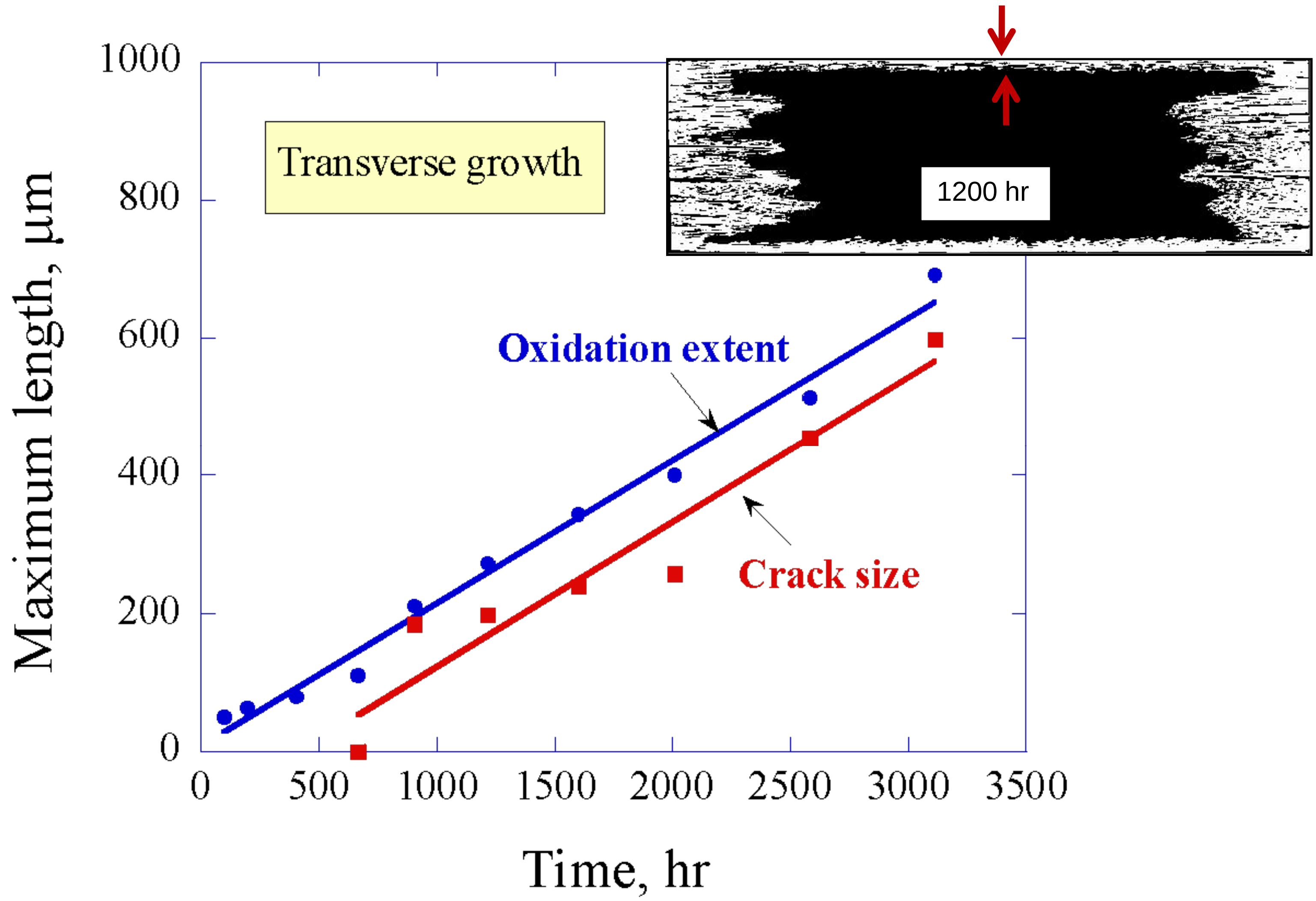
2584 hr



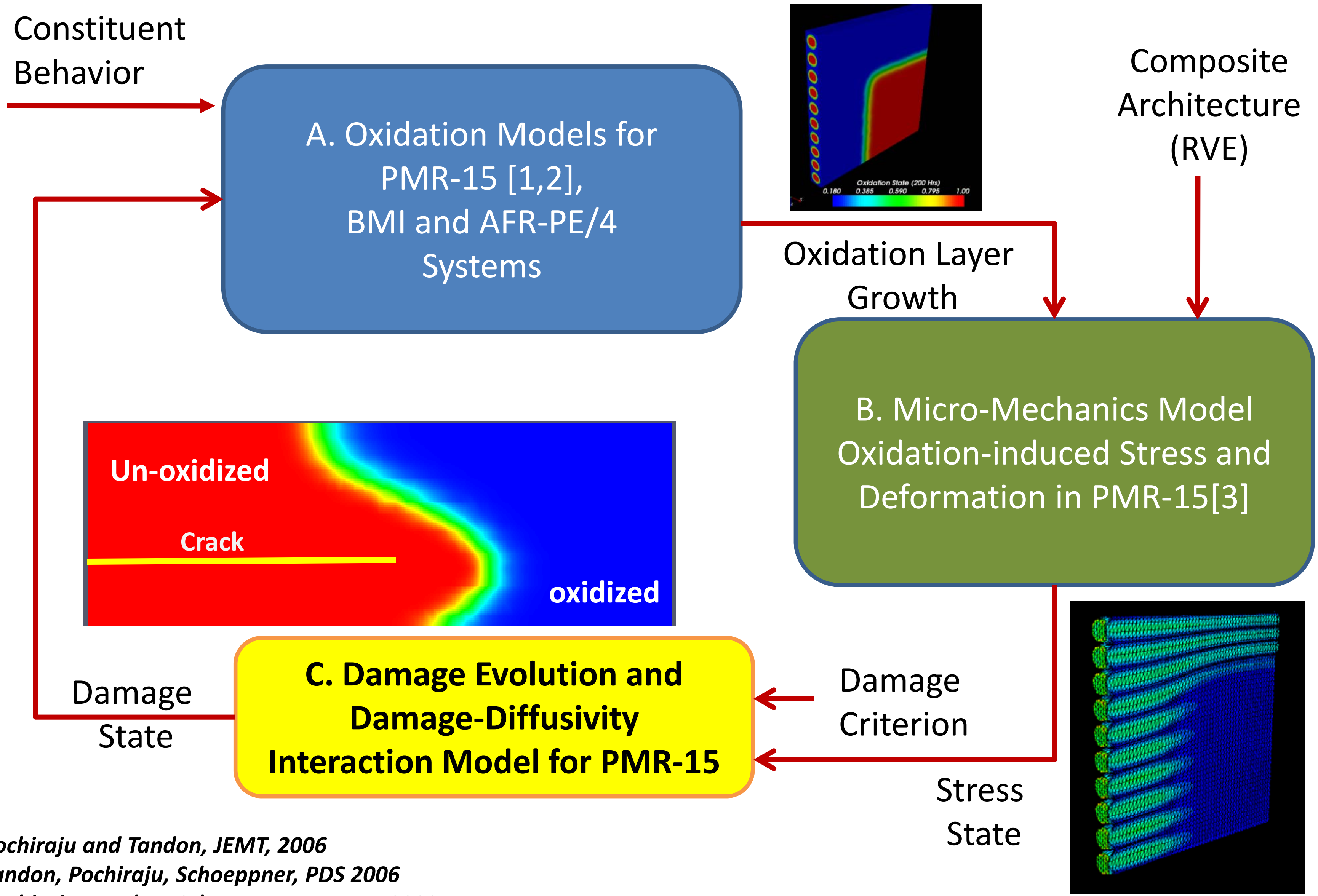
3112 hr

Oxidation **Damage**

Transverse Oxidation and Damage Growth



Thermo-oxidation Modeling Framework



[1] Pochiraju and Tandon, JEMT, 2006
[2] Tandon, Pochiraju, Schoeppner, PDS 2006
[3] Pochiraju, Tandon, Schoeppner, MTDM, 2008

Modeling – Stress / Diffusion Coupling

$$\frac{\partial C}{\partial t} = D_{MM} \nabla^2 C$$

Mass Diffusion due to concentration gradients
D_{MM}- Fickian Diffusion Coefficients

$$+ D_{MT} \nabla^2 T$$

Diffusion due to thermal gradients
D_{MT} – Soret Factors

$$+ D_{ME} \nabla^2 \varepsilon_{ij}$$

Stress Assisted Diffusion
D_{ME} – Coupling Coefficients

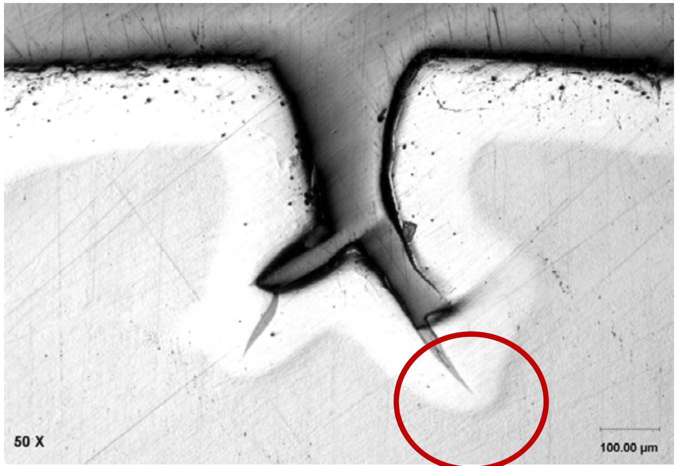
$$- R(C)$$

Oxidation Reaction Rates

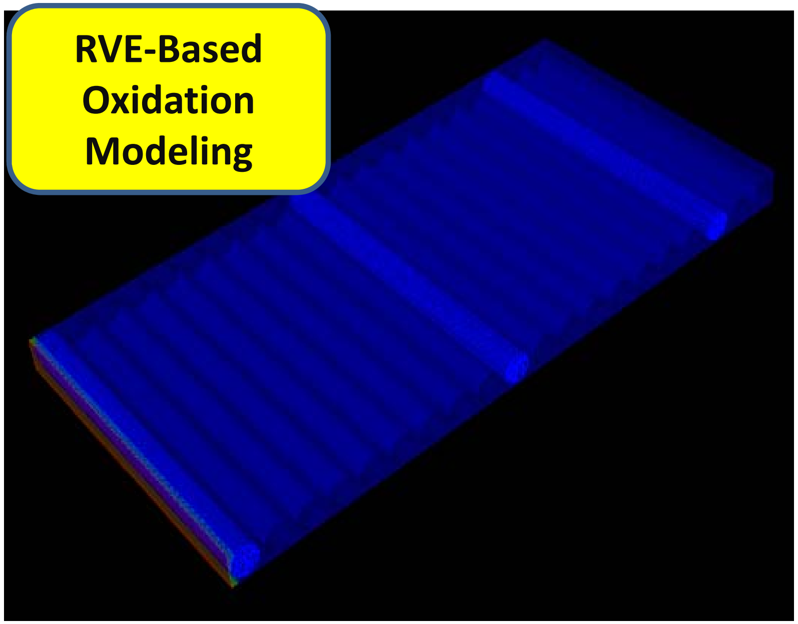
Equilibrium Equation with
concentration coupling

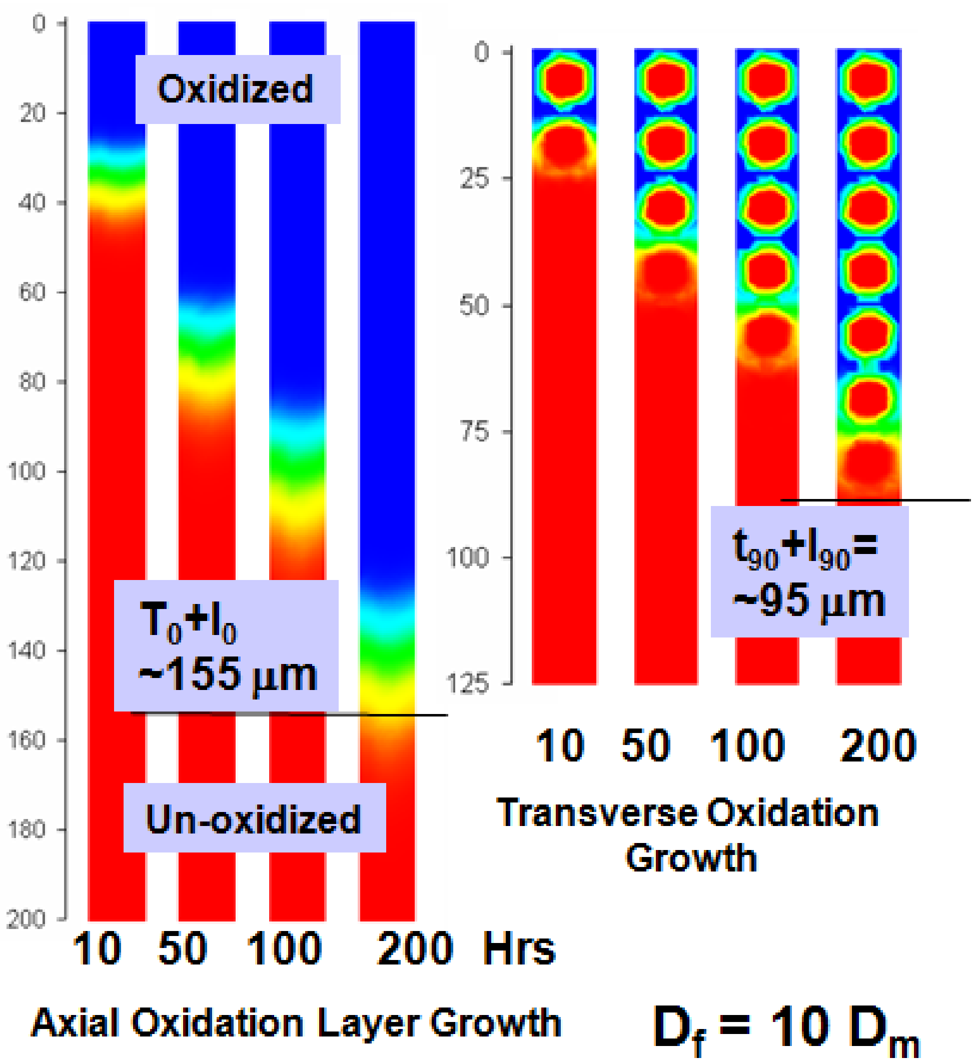
$$-C_m \frac{\partial C}{\partial t} + (\lambda + \mu) \frac{\partial \varepsilon_{kk}}{\partial x} + \mu \frac{\partial^2 u}{\partial x^2} = 0$$

Stress-concentration coupling (~body force term)



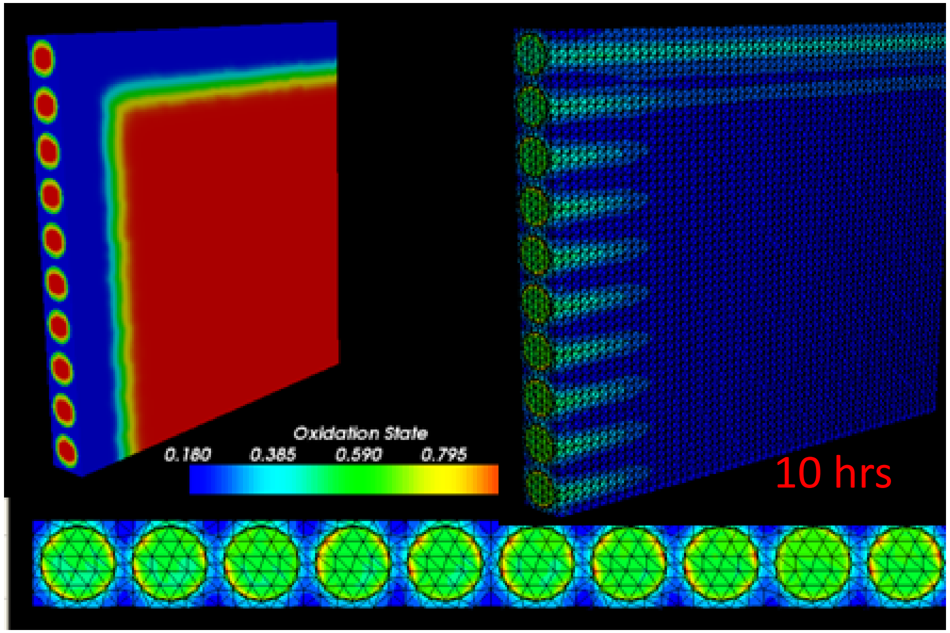
Oxidation Orthotropy due to Diffusive Fiber-Interphases Assemblages





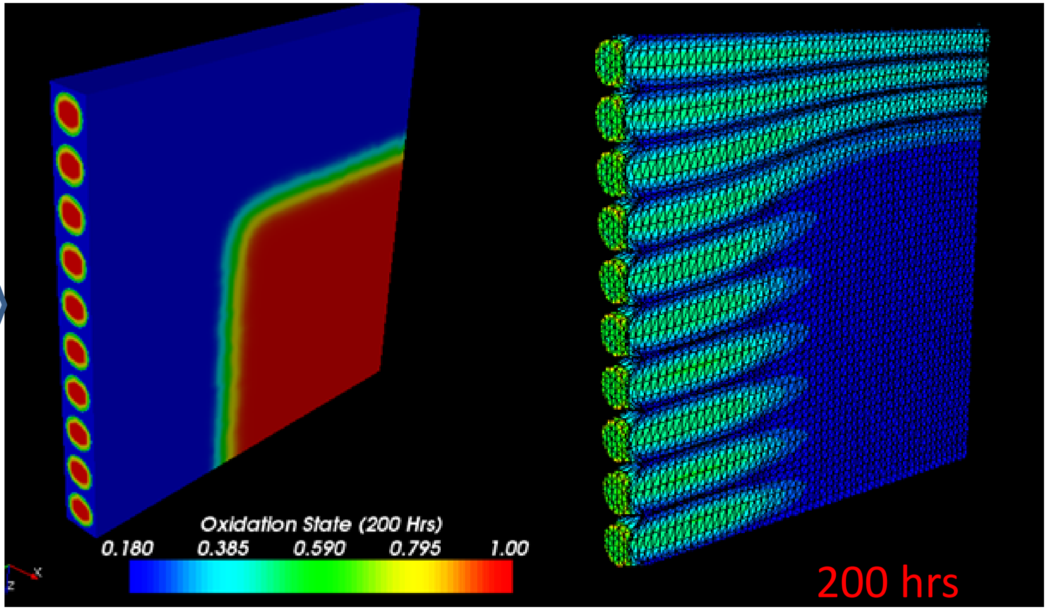
- Representative Volume Elements with explicit fiber, matrix and interphase domains
- 3-D coupled Finite Element Technique with Parallel Solvers.
- 200 Hours of Aging Time Simulations
- Oxygen concentration and oxidation state simulations

B. Evolution of Stress During Oxidative Aging

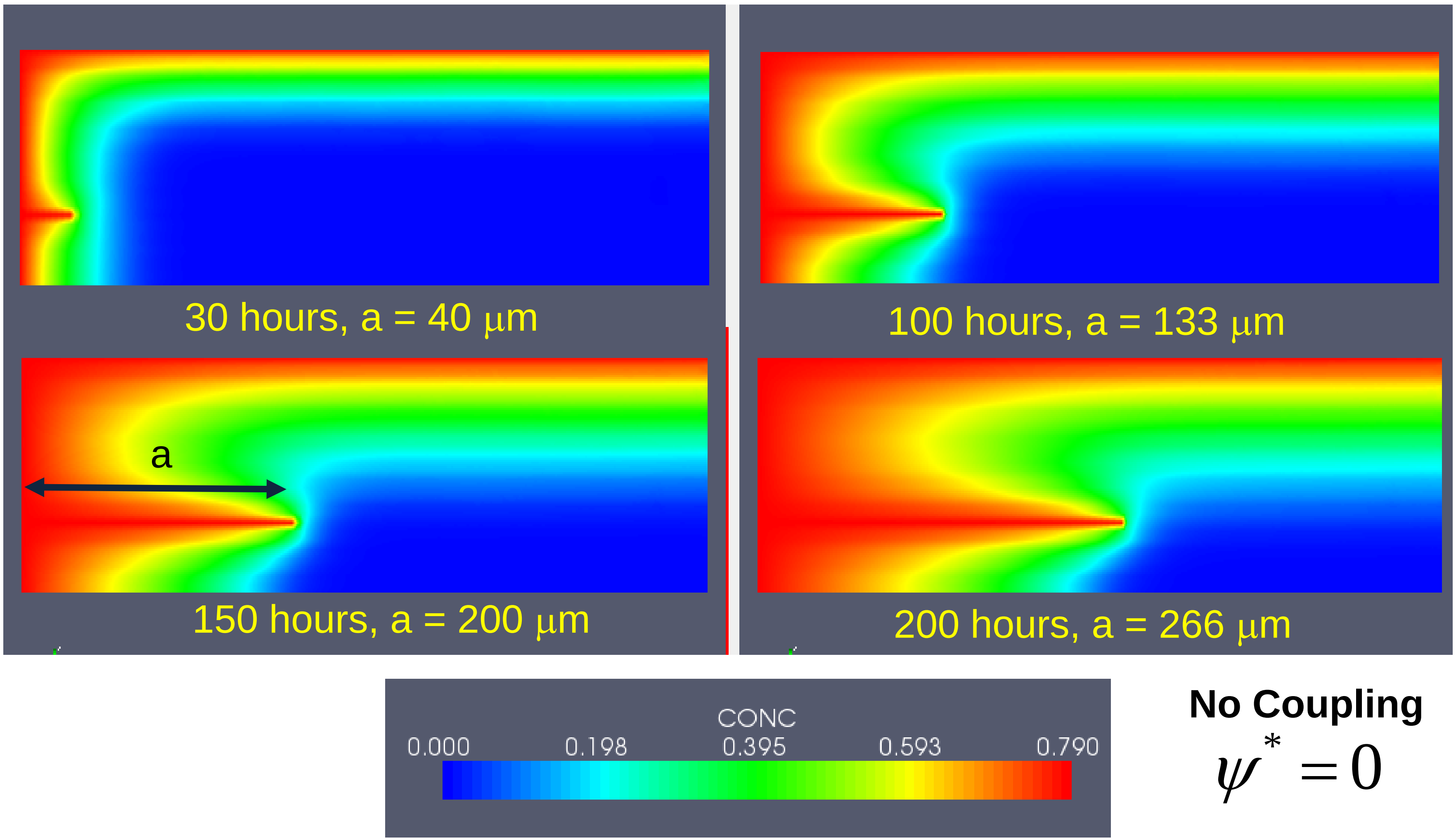


- Oxidation Layer (Left) and stress fields (right) after 10 Hours of aging.
- The peak Von Mises effective stresses (2.4 MPa) are at the fiber matrix interface and near the free edge (below)
- Average interstitial matrix stresses are at 0.4 MPa and in fiber is 2.4 MPa

- Oxidation Layer (left) shown at 200 hours
- Average peak stress near the free edge is 47.3 MPa
- Average interstitial matrix stresses are at 1.2 MPa
- Average fiber stress = 25 MPa
- Matrix strength ~ 41MPa @288 C



Oxygen Concentration Profiles with Prescribed Crack Growth: 1.33 μm/hour Without Stress-Diffusion Coupling

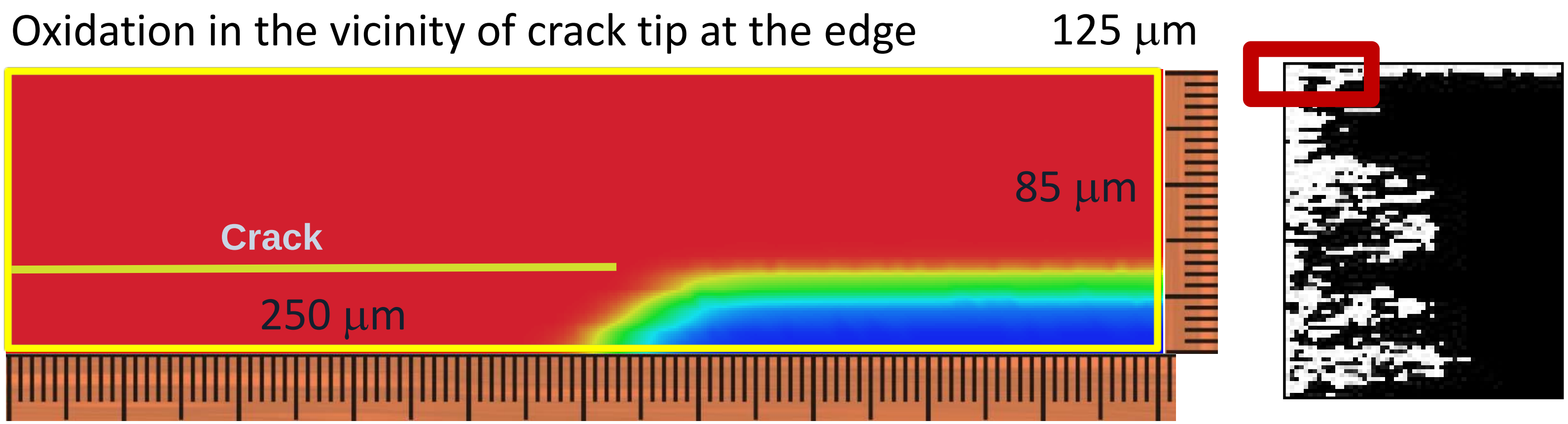


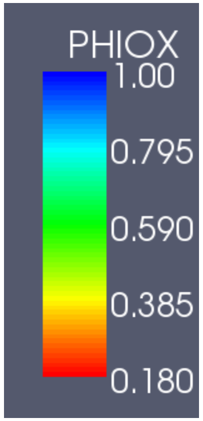
No Coupling

$$\psi^* = 0$$

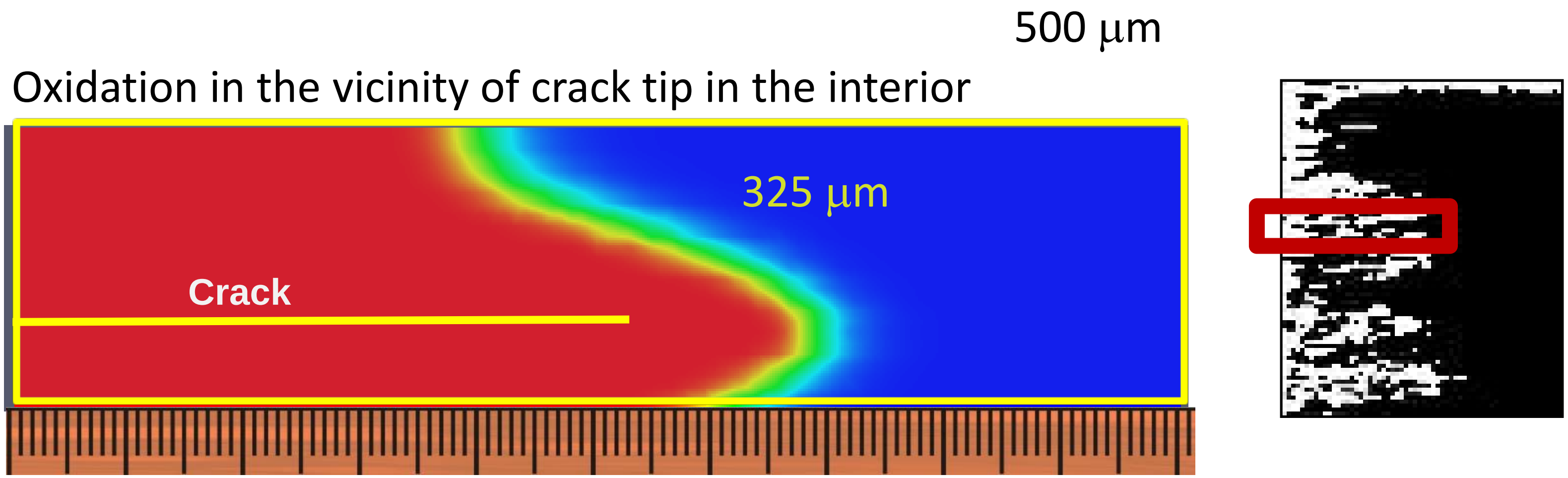
Oxidation Layer Measurements with Damage

Oxidation in the vicinity of crack tip at the edge





Oxidation in the vicinity of crack tip in the interior

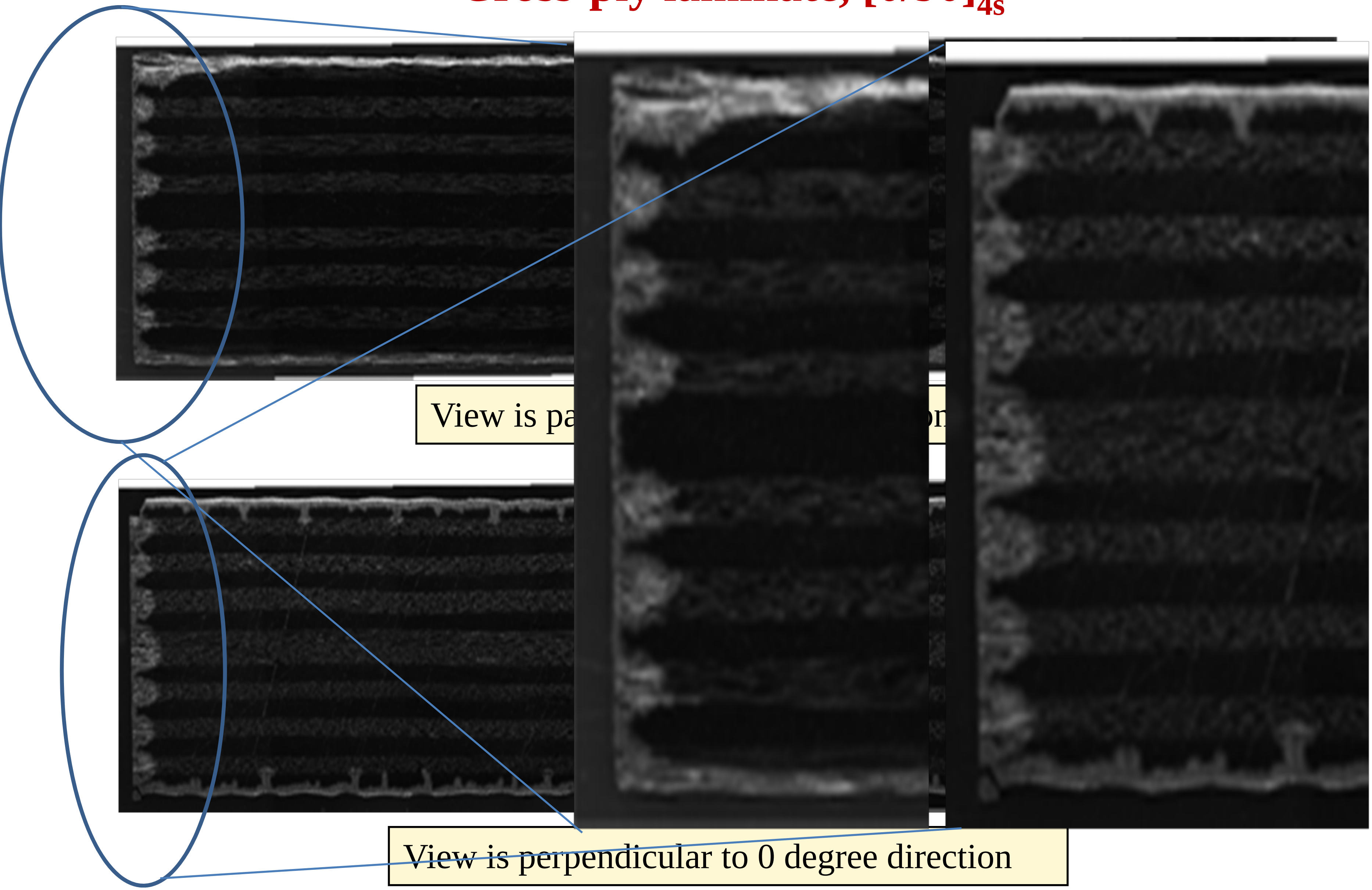


G30-500/PMR-15
@ 196 Hours

<u>Damaged Areas (266 μm crack)</u>
Axial: 385 μm
Transverse: 63.09 μm
Ratio: 6.1

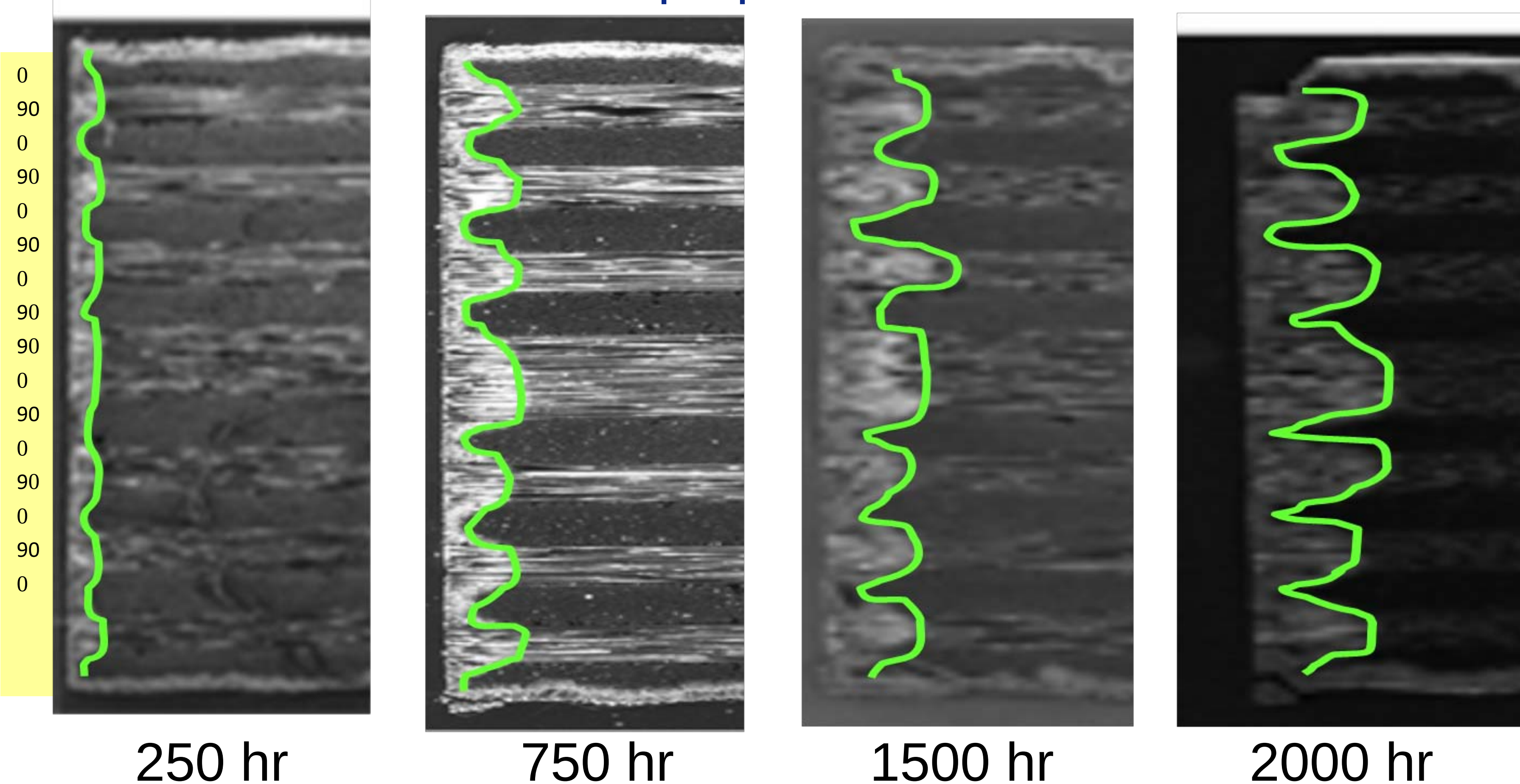
Oxidation at the Laminate Scale

Cross-ply laminate, $[0/90]_{4s}$



Cross-ply laminate, $[0/90]_{4s}$

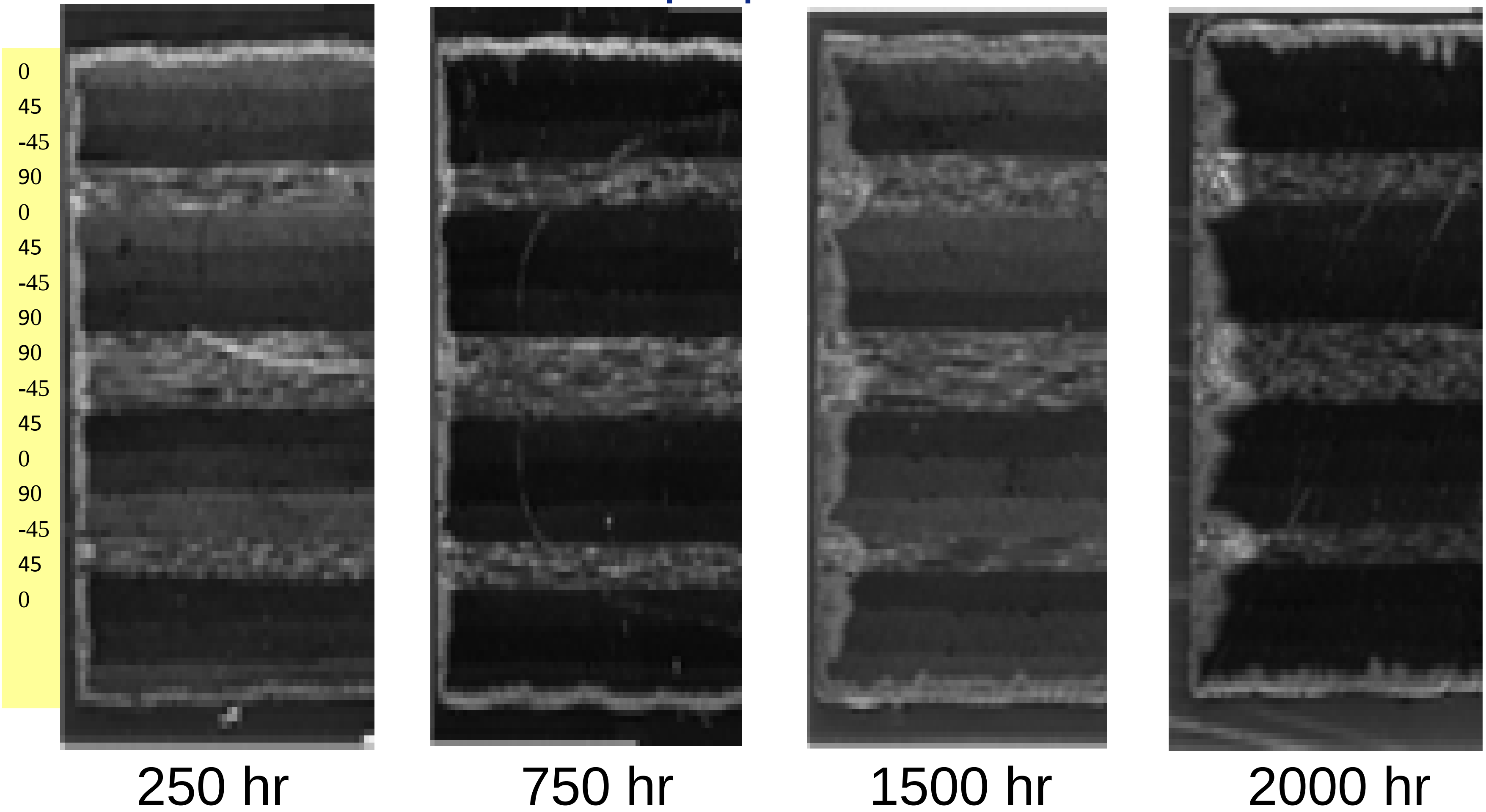
View is of cross-section perpendicular to 0º direction



- Preferential oxidation growth along the fiber paths for the cross-ply laminate
- Maximum/minimum oxidation extent occur at the plies midplane

Quasi-isotropic laminate, $[0/\pm45/90]_{2S}$

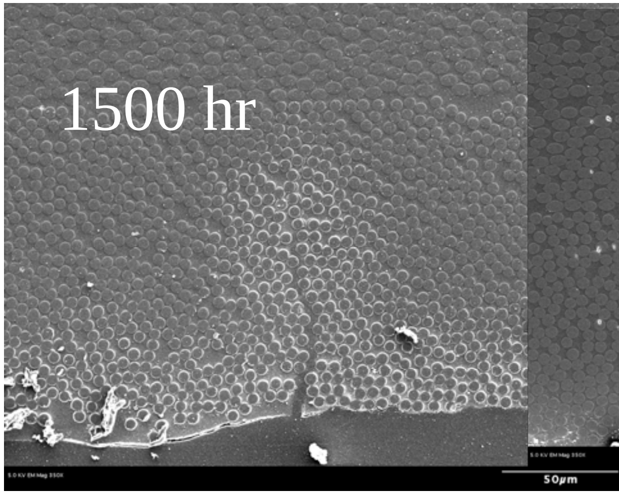
View is of cross-section perpendicular to 0º direction

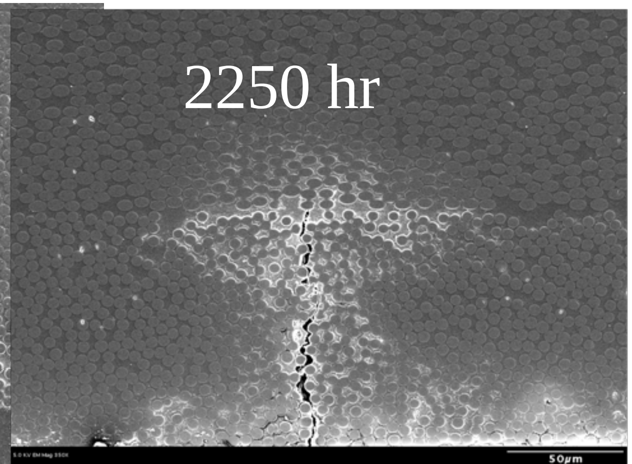


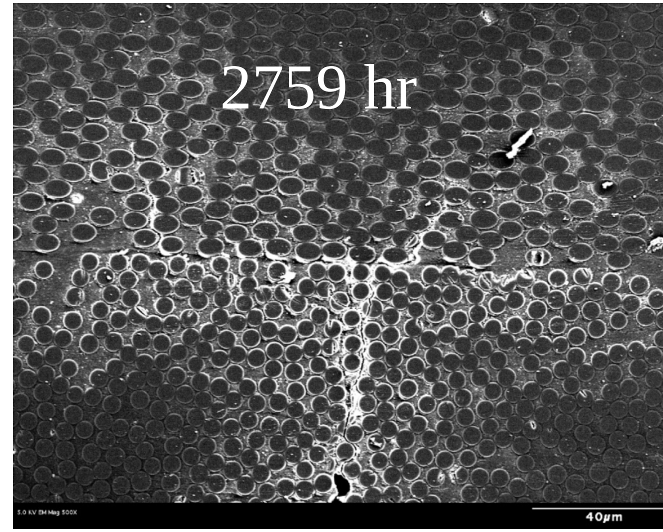
- Maximum/minimum oxidation extent do not occur at the plies midplane
- Ply oxidation extent is strongly influenced by the orientation of its neighboring plies

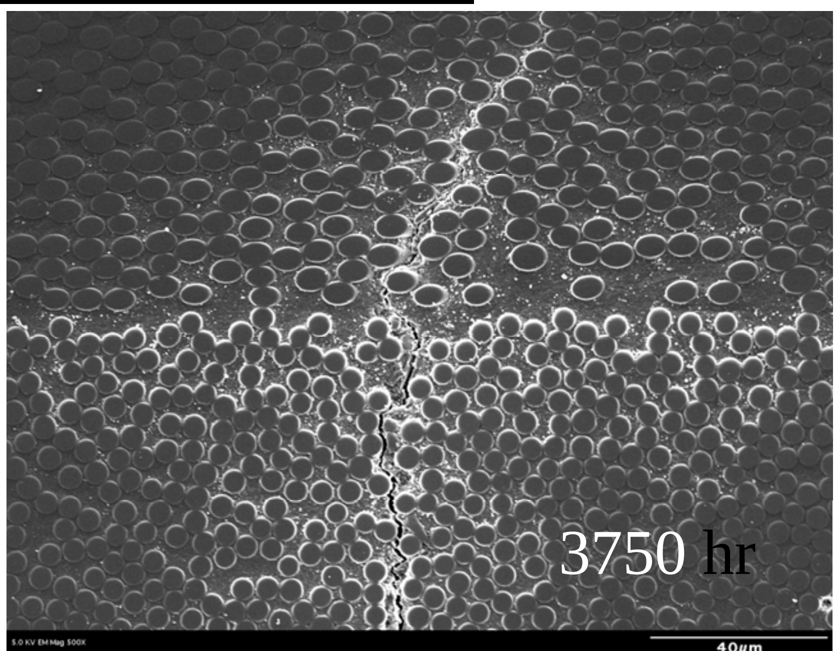
Oxidative Damage Propagation

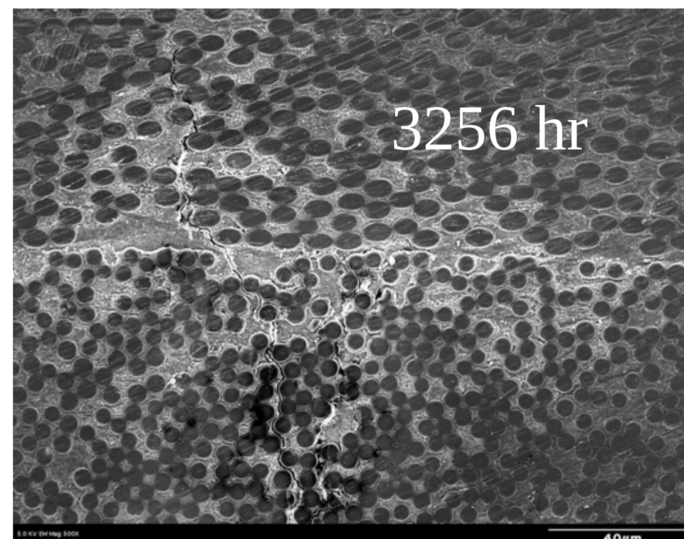
$[0/\pm45/90]_{2S}$











Concluding Remarks

- Using the mechanistic oxidation reaction models, a comprehensive model for oxidation evolution in neat polymers has been created.
  - A three-zone diffusion-reaction-oxidation model was created and validated for PMR-15 neat resins (Pochiraju and Tandon, JEMT, 2006)
  - Parametric studies based on the model were conducted to characterize the unknown parameters from iso-thermal aging studies (Tandon, Pochiraju, and Schoeppner, Polymer Degradation and Stability, 2006)
  - Determined the parameters for BMI-5250/4 from the aging studies (Tandon, Pochiraju and Schoeppner – SAMPE 2006 – Closed Session ITAR Restricted)
- Based on dimensional measurements, the oxidation-induced shrinkage of neat resins has been quantified.
- A chemo-mechanics model has been implemented to determine the oxidation induced stress states in a UD Composite. (*Pochiraju, Tandon and Schoeppner; Mechanics of Time Dependent Materials, 2008*)
- Effect of discrete damage on the oxidative layer growth at the laminate scale is currently being studied.