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Oxidative Aging of Epoxy Materials

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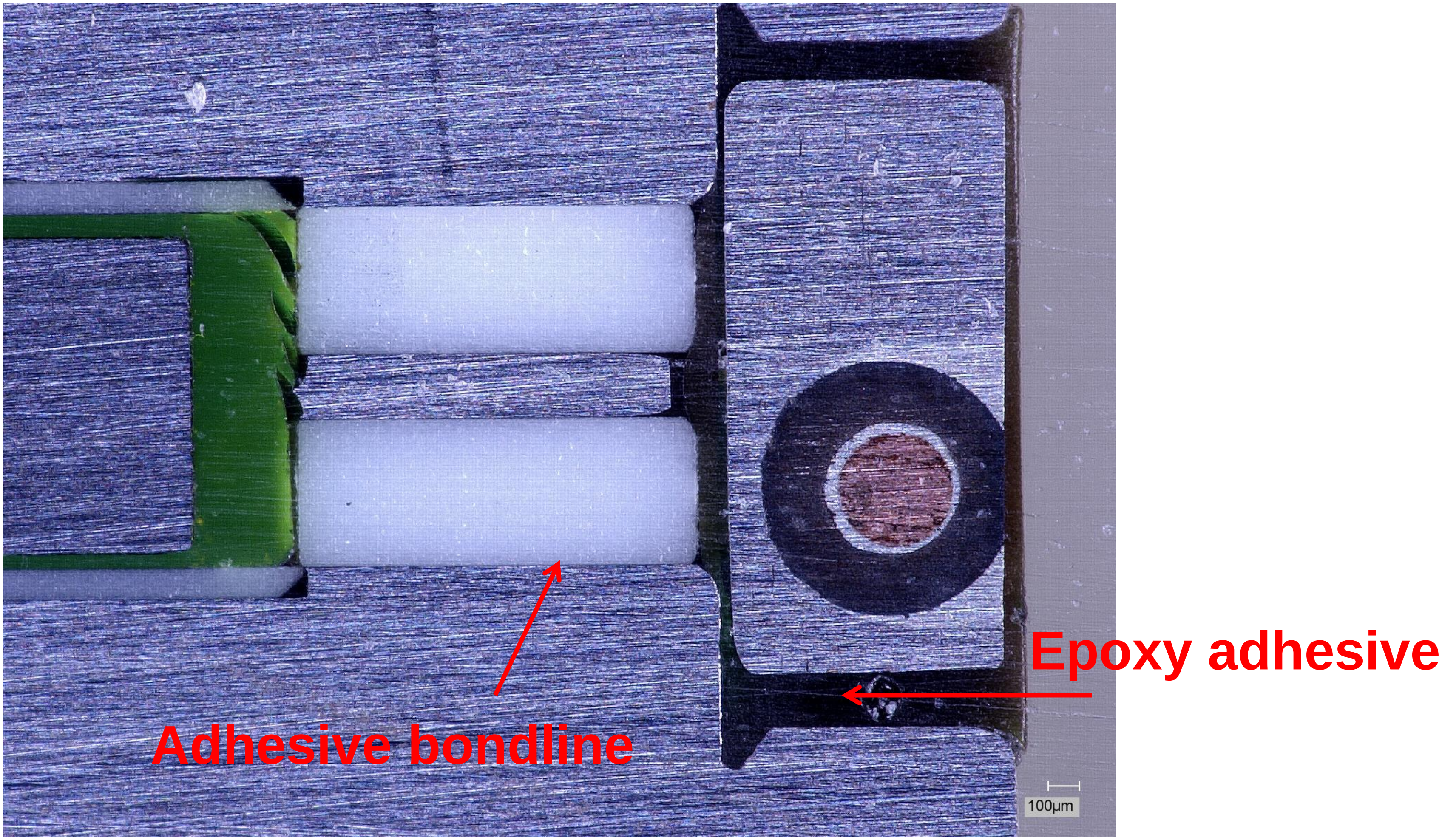
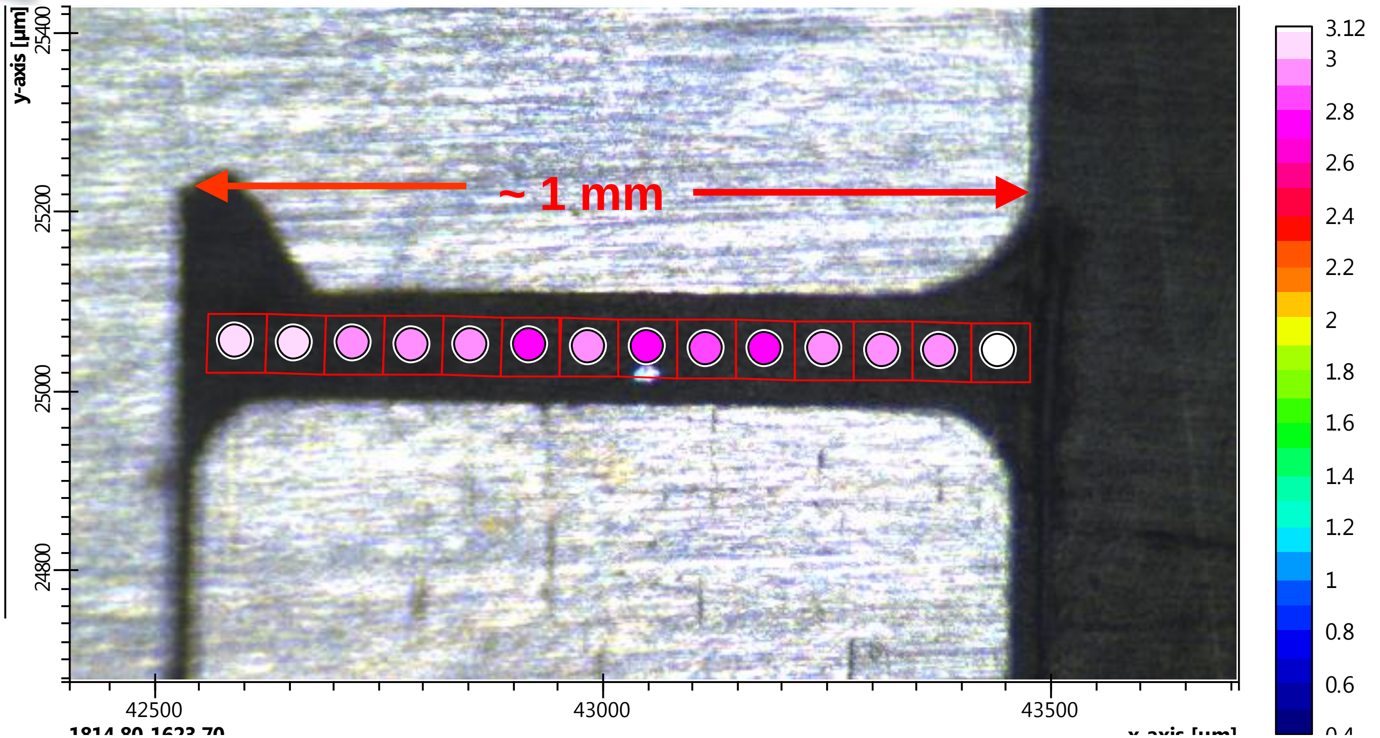
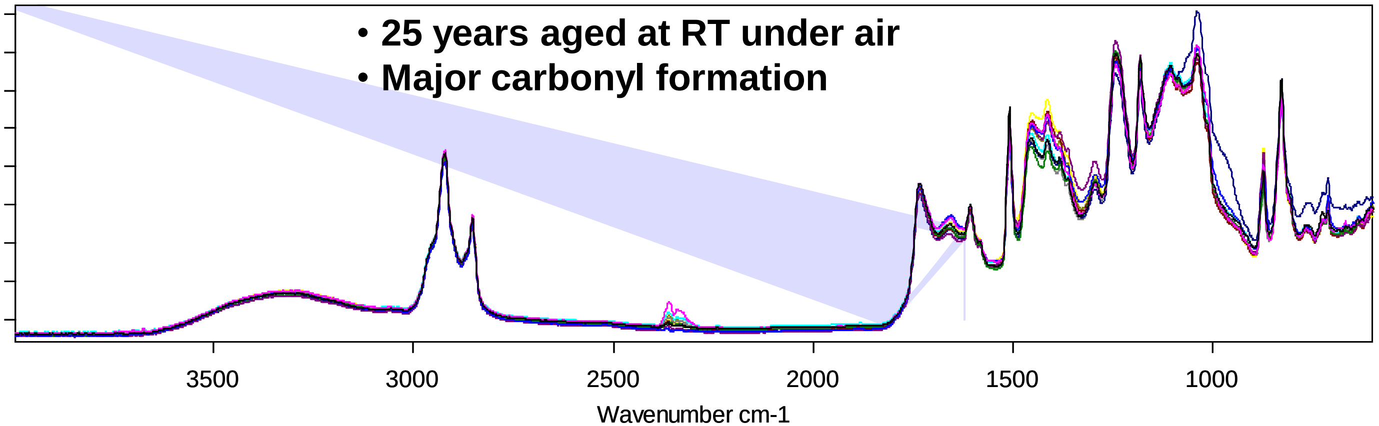
What is the Challenge?



We need a perspective on aging state of epoxy adhesive in small assembly

Carbonyl Imaging of Epoxy





Strong carbonyl signature, highly aged (oxidized) epoxy adhesive at RT

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Science based Background
"Diffusion Limited Oxidation"

Research goals and approach:

- Develop models to predict spatial distribution of oxidative damage
- Understand oxidative degradation of thermoset materials
- Establish experimental capability to determine *P, D, S* for O_2 with T
- Use established methods to determine oxidation rates

We need O_2 permeation parameters

- Limited literature data
- Characterization of materials is the key to understanding of aging phenomena
- Input for predictive degradation DLO models

Keywords: Thermoset performance, O_2 diffusivity, solubility, permeability, DLO, TOL, degradation depth, spatial modeling

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What are we dealing with?

- **At elevated temperature polymers and films may act as an O2 barrier**
- **The underlying permeation is convoluted with degradation chemistry**

- **Parallel PHYSICAL and CHEMICAL processes**

Edge oxidation in high temperature composites

From Tandon GP, 2011, aging at 177°C

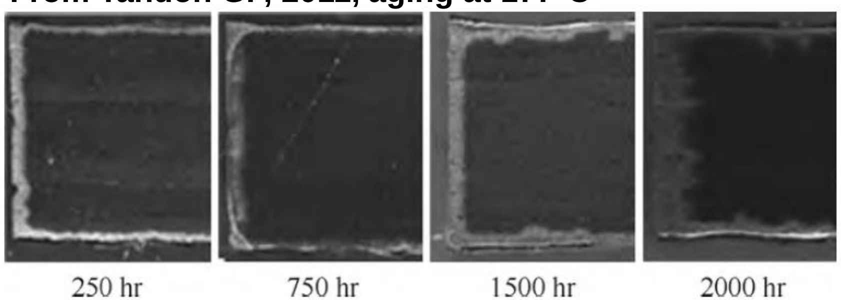


Fig. 9.9 Oxidation growth near the laminate edge in $[\pm 45]_{2S}$ laminate as a function of aging time

Laboratory accelerated thermal aging

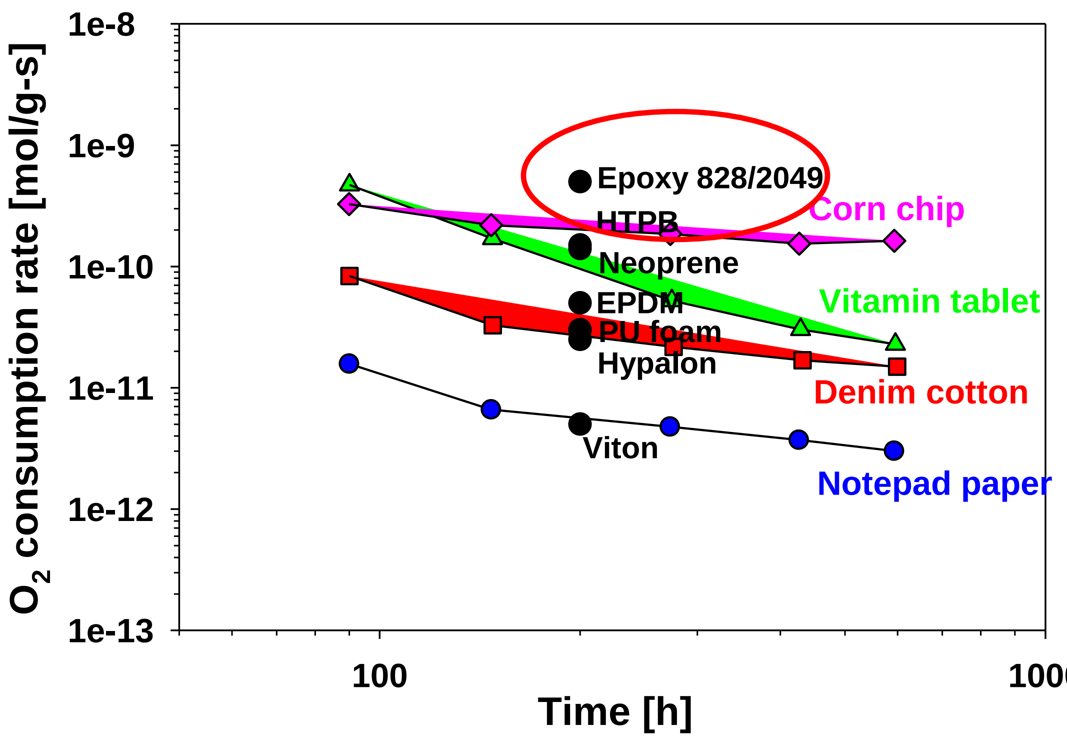
Example of aged epoxy, degradation is limited to material surface

- **Edge effects complicate the prediction of bulk material aging**
- **The same process applies for long-term aging at RT**
- **EPOXIES ARE OXIDATION SENSITIVE**

Tandon GP. Characterization of thermo-oxidation in laminated and textile composites. In: Pochiraju KV, Tandon GP, Schoeppner GA, eds. Long-Term Durability of Polymeric Matrix Composites. Springer Science + Business Media, 2011, p 345.

Epoxy Oxidation Behavior

- Epoxies are surprisingly reactive materials, but they tend to accommodate oxidation reasonably well. They do not embrittle at low levels of oxidation.



- **Epoxy oxidation rates are the at top of the range for many materials**
- **Above the activity of corn chips that turn rancid**

Celina MC, Dayile AR, Quintana A. A perspective on the inherent oxidation sensitivity of epoxy materials. Polymer 2013;54:3290

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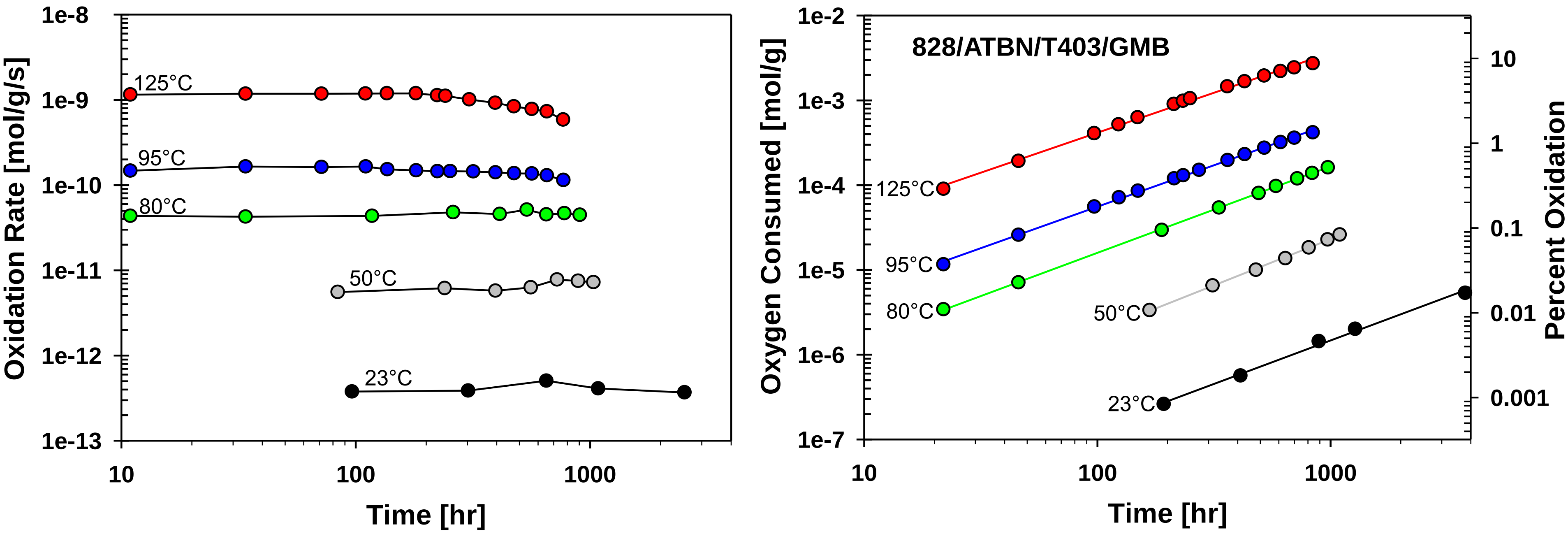
Oxidation Behavior with T - Example

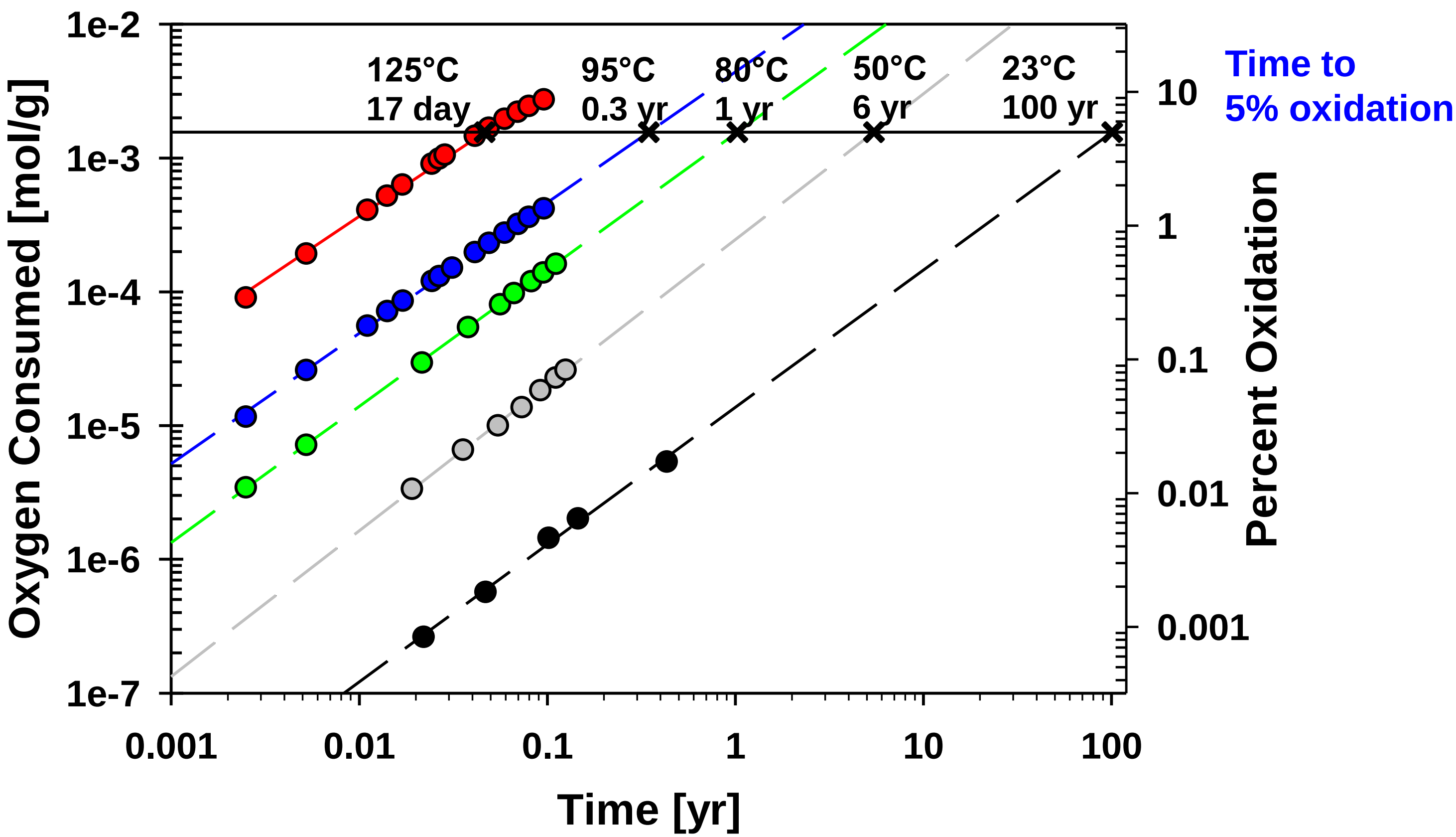
- **Approach: Use established oxygen consumption methods on thin films and quantify oxidation behavior**
- **Example: Epon 828 with ATBN, Jeffamine T403 and GMB**



Oxidation rates can be used for extrapolations of oxidation level

Oxidation Behavior - Predictions

- Approach: Use established oxygen consumption methods on thin films and quantify oxidation behavior
- Example: Epon 828 with ATBN, Jeffamine T403 and GMB



- Oxidation levels can be predicted
- Oxidation is expected to affect Tg, modulus and adhesion

Oxidation with Depth

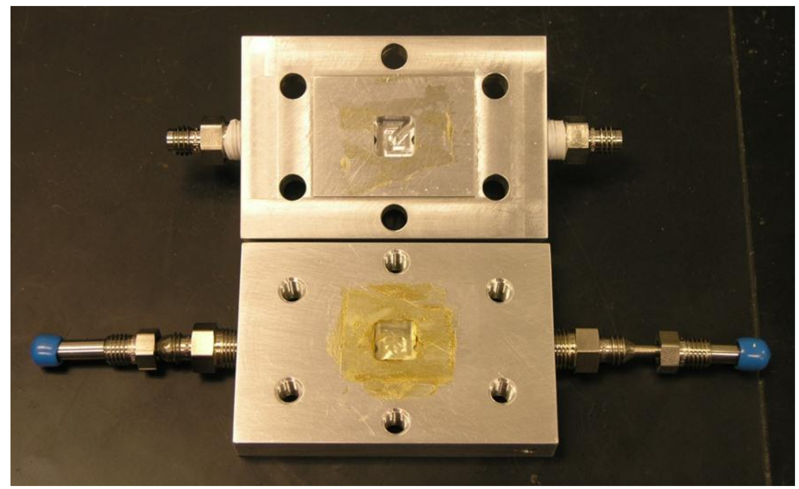
- **Oxidation rates enable predictions of surface oxidation level, but do not offer guidance for interior (keyword: DLO)**
- **Spatially resolved oxidation requires permeability**
- **Spatial degradation depends on the combined behavior of two epoxies**
- **Materials are intrinsically coupled**

- **Spatially dependent oxidation is a <u>reactive transport phenomenon</u>**
- **1D and 2D FEM DLO degradation models provide predictions (this is recognized SNL expertise)**

O2 Permeation Instrument

Application: Precision measurements of O2 permeability through polymer film materials using commercial sensing system
Optimized system: Customization with external feed composition and flow control, external temperature stage and permeation cell setup
Software: Unfortunately very limited for R&D, we use external data analysis

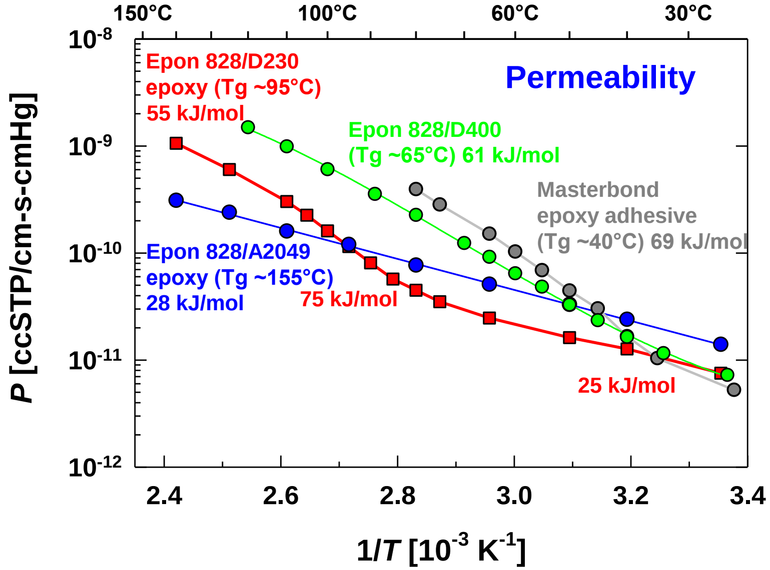
New more sensitive MOCON
Ox-Tran 2/21 permeation system

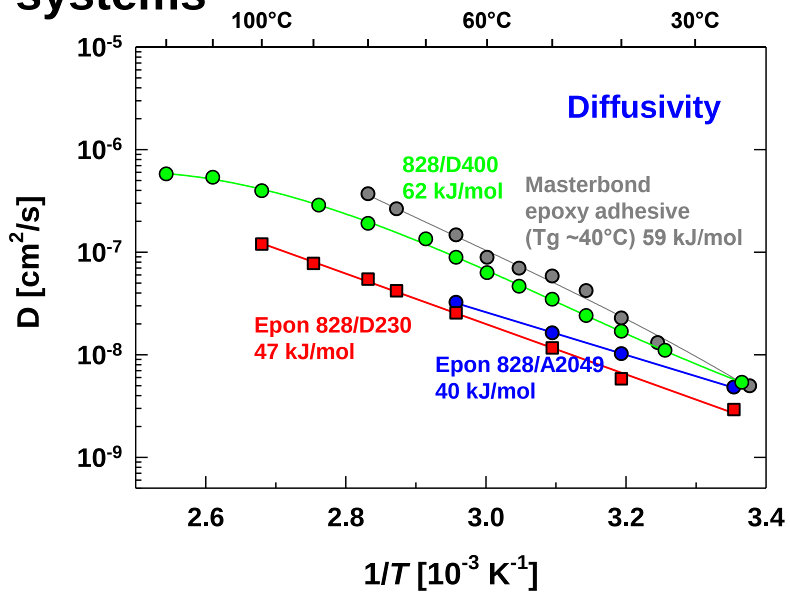


Instrument has high dynamic range but limits for *P, D* at high T due to the nature of these experiments

O_2 Permeability – Diffusivity – Solubility

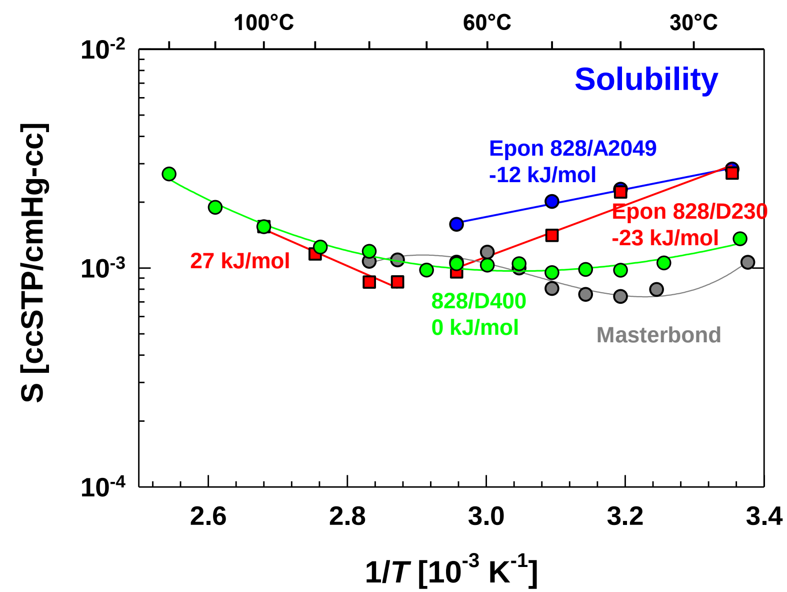
Epoxy systems





- Ea of up to 75 kJ/mol for *P*
- Ea of up to 60 kJ/mol for *D*
- Solubility increases above Tg

- Theoretical perspective:
- P is expected to curve at higher T because of non-Arrhenius changes in D and S
- D will curve at T>T_g from free volume theory
- S is expected to be a power function with T



P shows much higher Ea above Tg with reversal in solubility

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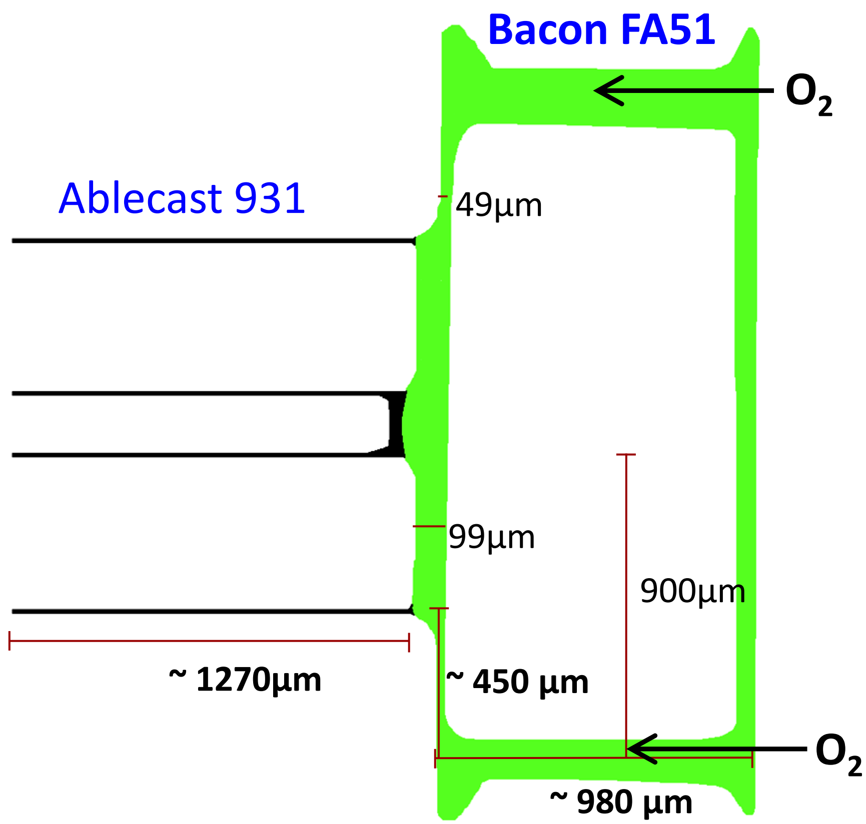
O2 Diffusion Pathways

- Bacon FA51 and Ablecast 931 epoxy adhesive are coupled in degradation behavior
- Oxidation of the Ablecast 931 can only occur if O2 passes through the FA51



- The interior Ablecast epoxy is behind ~ 1.5 mm of Bacon FA 51 adhesive

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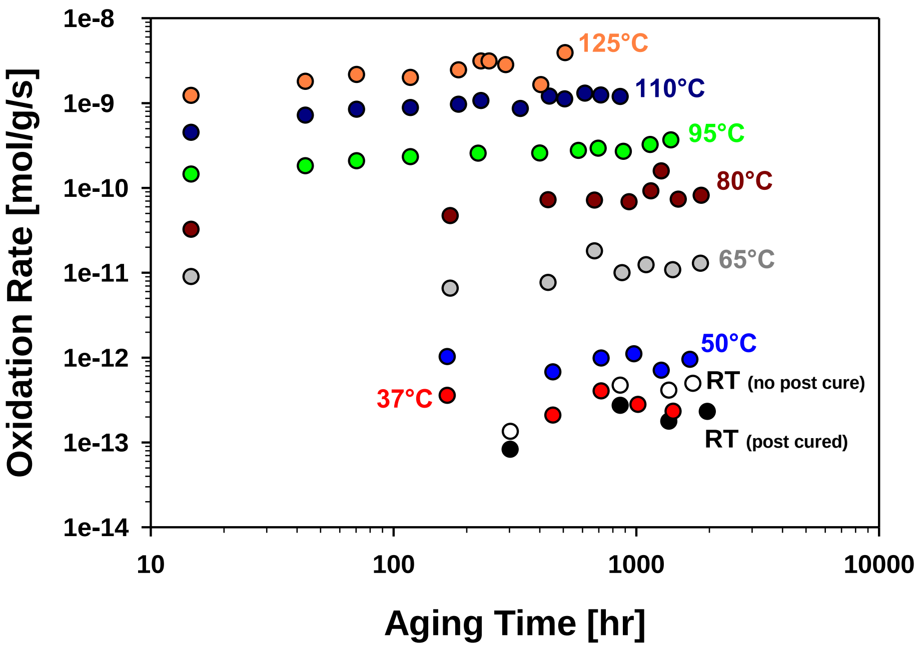
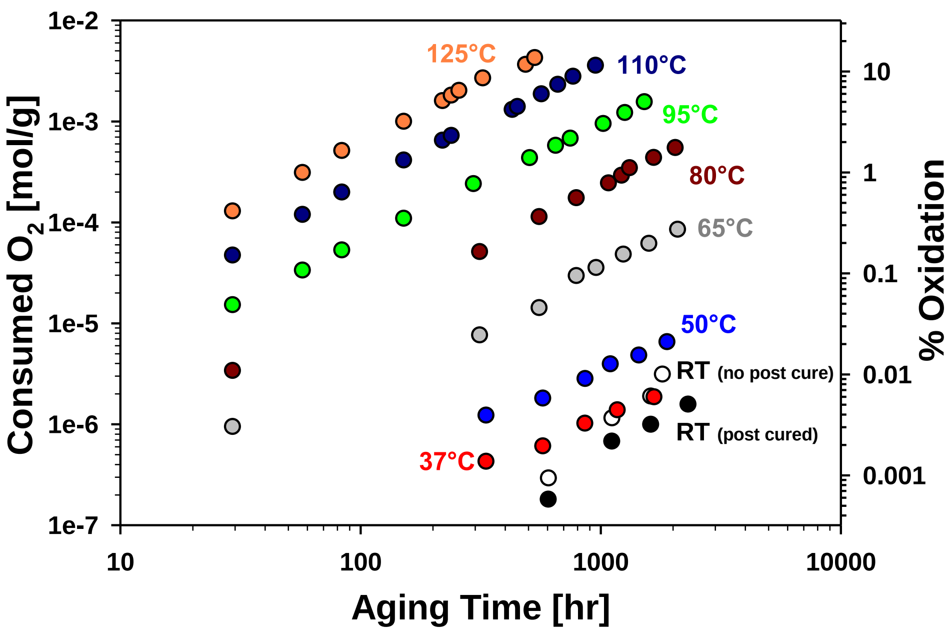
Ablecast Oxidation Behavior

- **Approach: We used established oxygen consumption measurements on thin films and quantified the oxidation behavior for this material**





- **Low rate at RT which depends a little on cure state**
- **Superposition of time - oxidation level yields 87 kJ/mol**
- **Relatively high E_a and low rate at RT**

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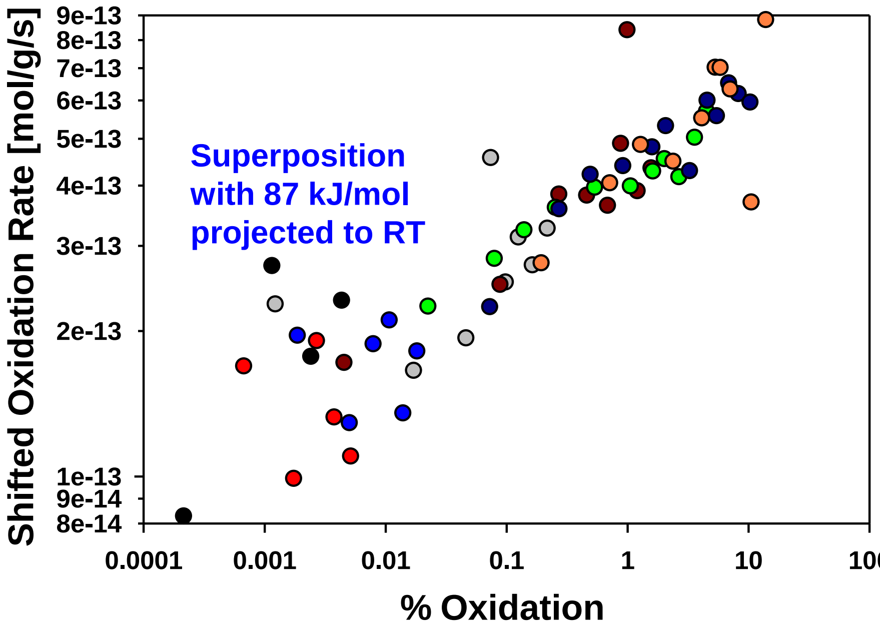
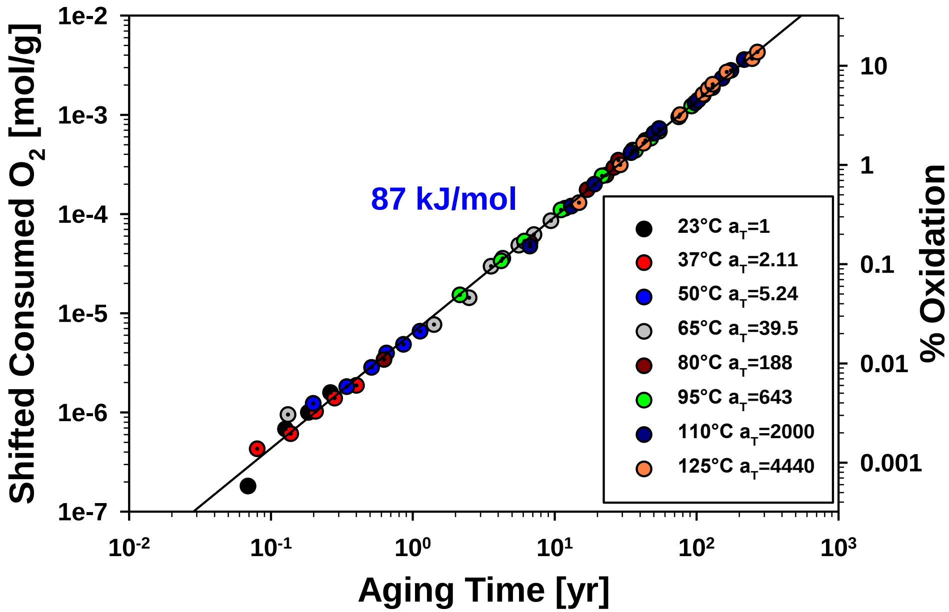
Ablecast Oxidation Behavior

- **Data analysis provides guidance for long term RT behavior**

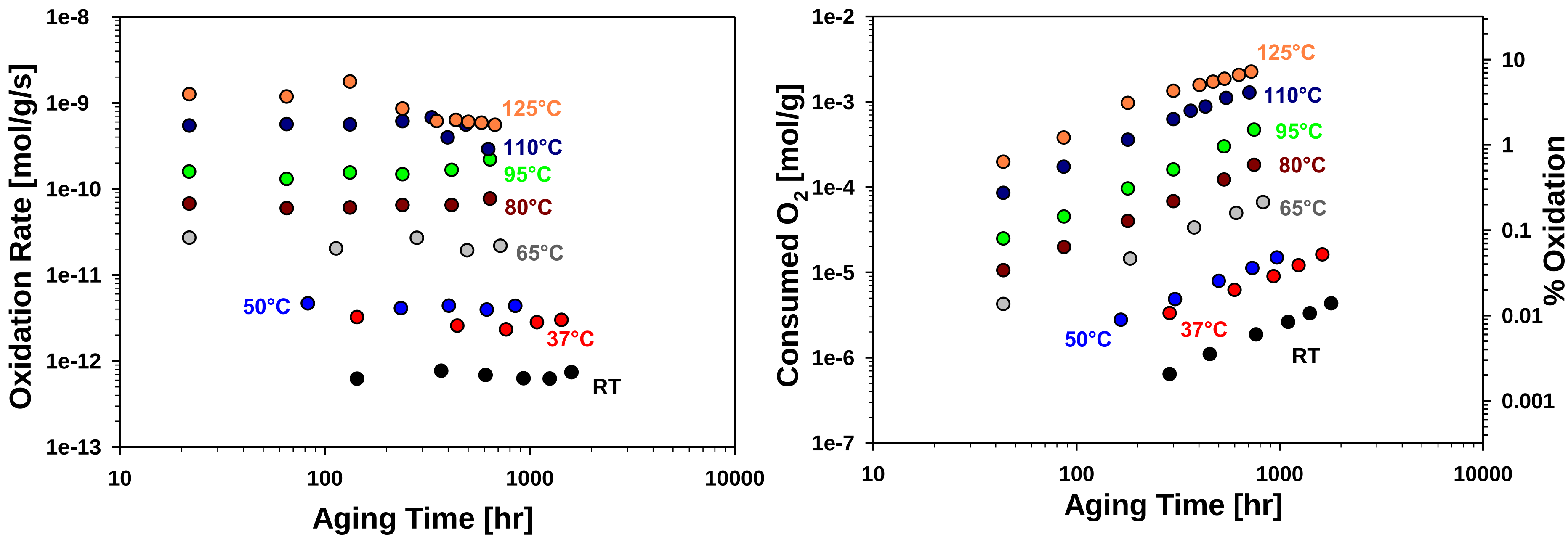




- **Oxidation rate increases as a function of oxidation level**

Bacon FA-51 Oxidation Behavior

- Approach: We used established oxygen consumption measurements on thin films and quantified the oxidation behavior for this material



- **Rate at RT is higher than for Ablecast**
- **Superposition of time – oxidation level yields 74 kJ/mol**
- **Rates and E_a are similar as for other epoxy materials**

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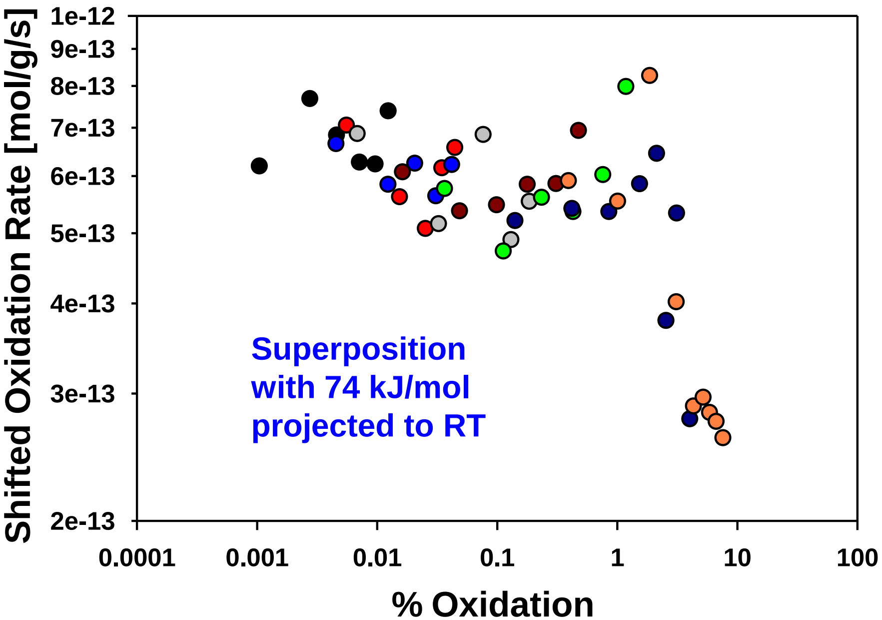
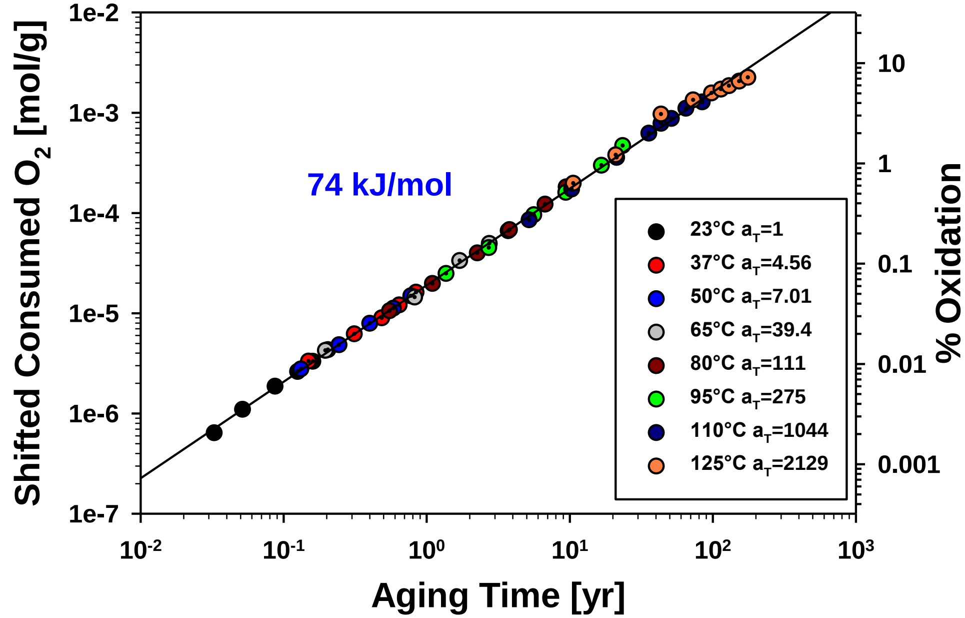
Bacon FA-51 Oxidation Behavior

- Data analysis provides guidance for long term RT behavior





- Oxidation rate at RT is projected to drop slightly above ~ 3% oxidation level

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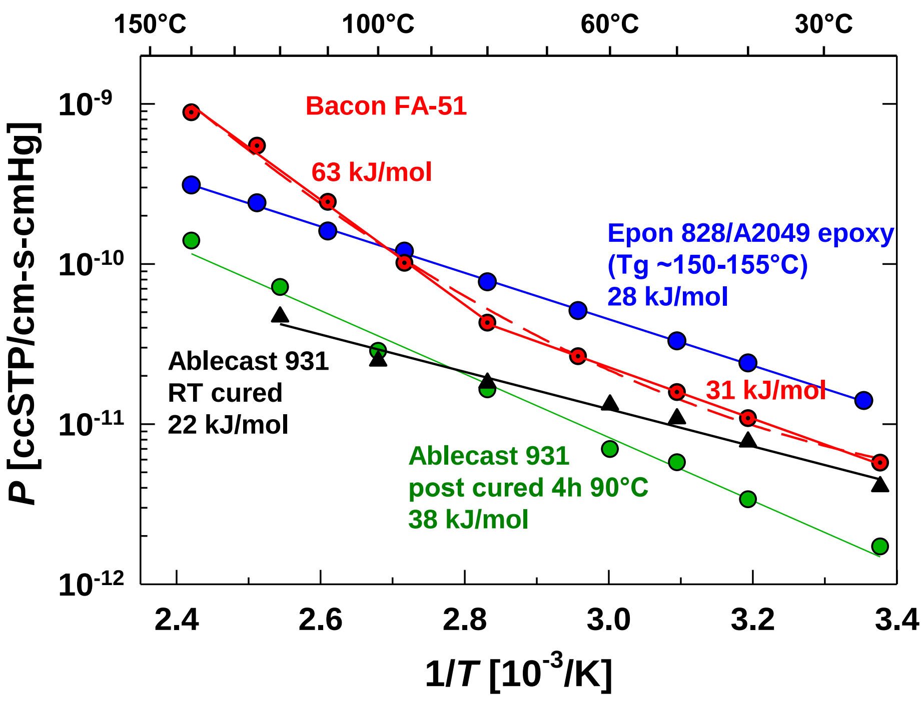
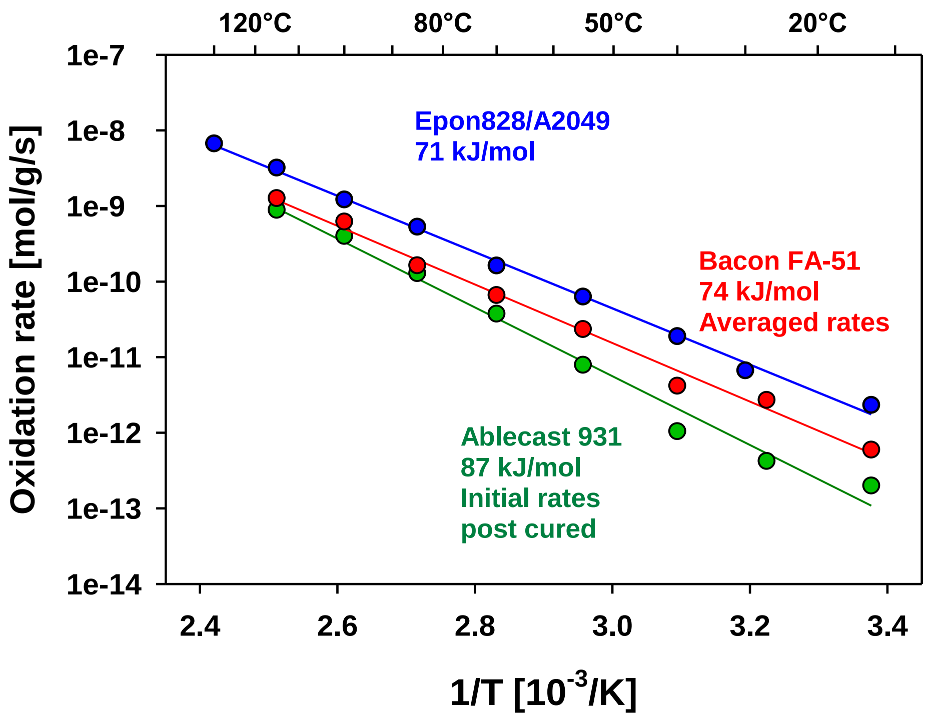
O2 Permeation for FA-51 & Ablecast 931

- Measured for RT and post-cured 100 µm thin films



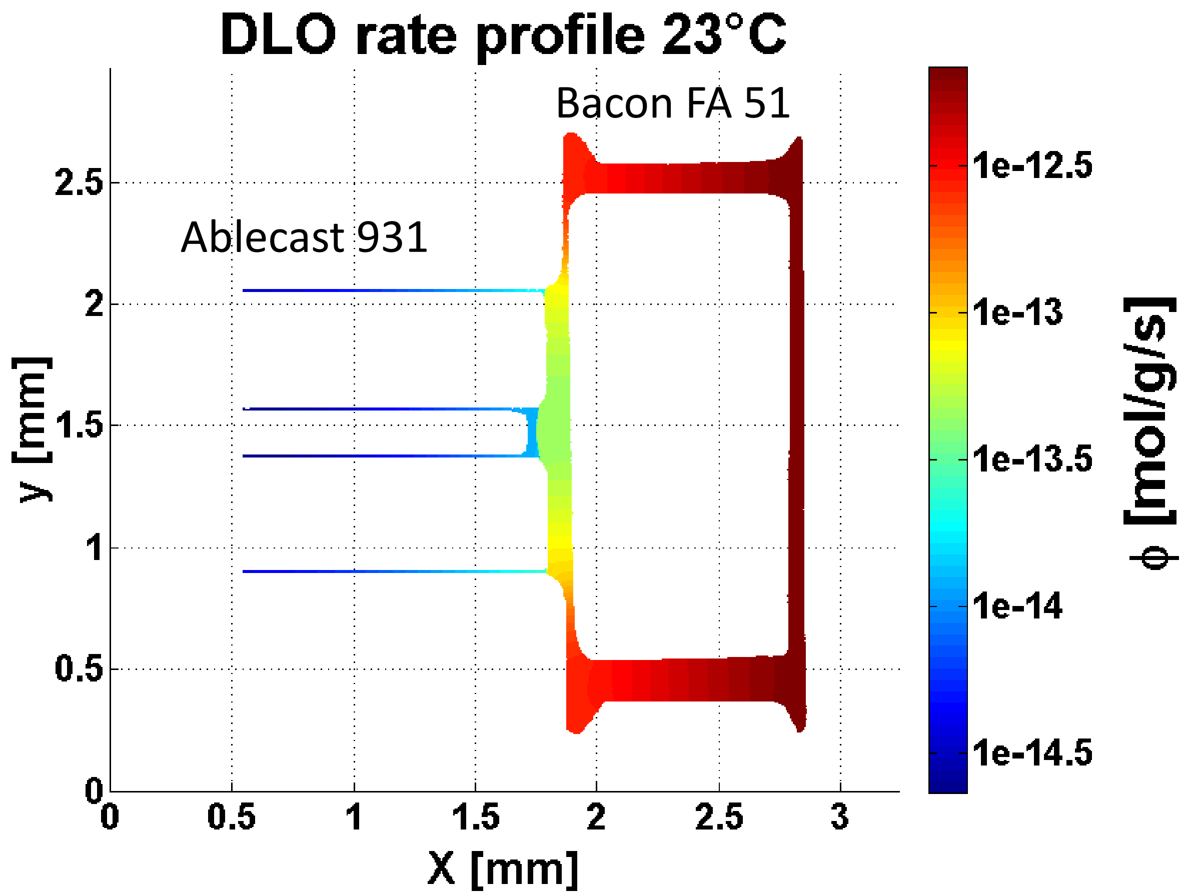


- Bacon adhesive has higher permeability than Ablecast
- Unusually low O2 permeation for Ablecast 931 material, high E_a (post-cured)
- Also, low ox-rate for Ablecast at RT

Predicted Spatially Dependent Oxidation

- Local oxidation rate depends on O2 diffusion into material under reactive conditions
- Model requires O2 permeability and oxidation rates for both epoxies at RT
- This model uses an average rate for the two Ablecast materials at 23°C

All model predictions were conducted for β=1 in the auto-oxidation chemistry (rate – P_{O2} correlation)



- **Initial FEM model projections show a significantly reduced 'oxidation activity' of the embedded Ablecast 931 material**

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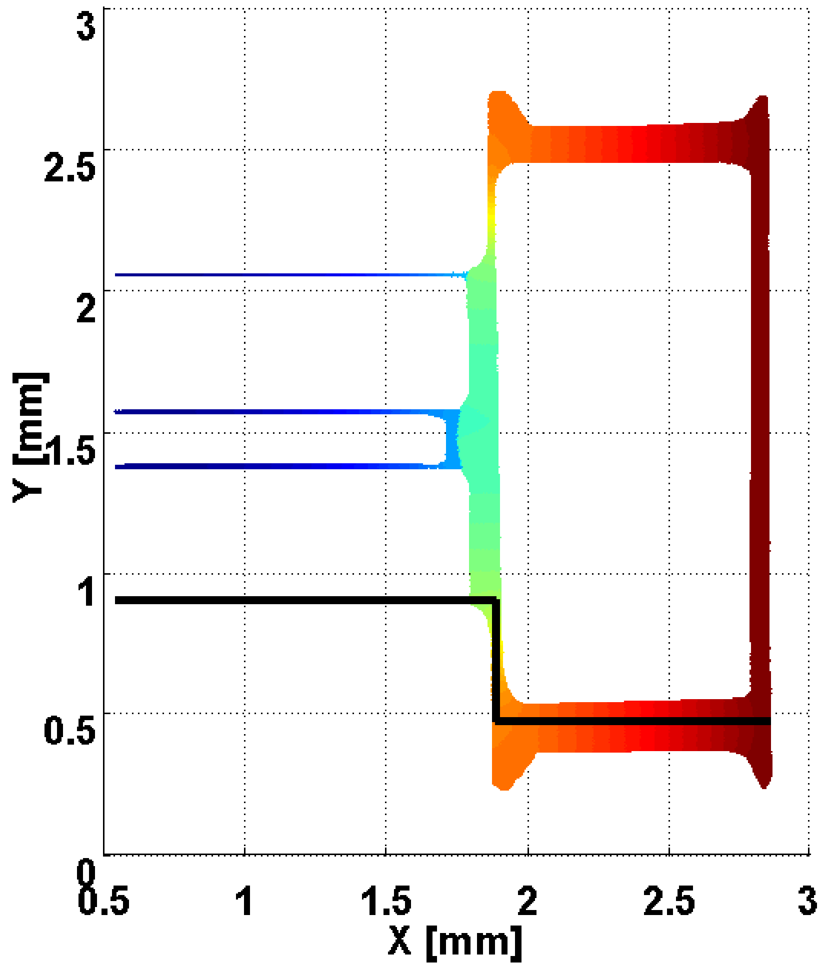
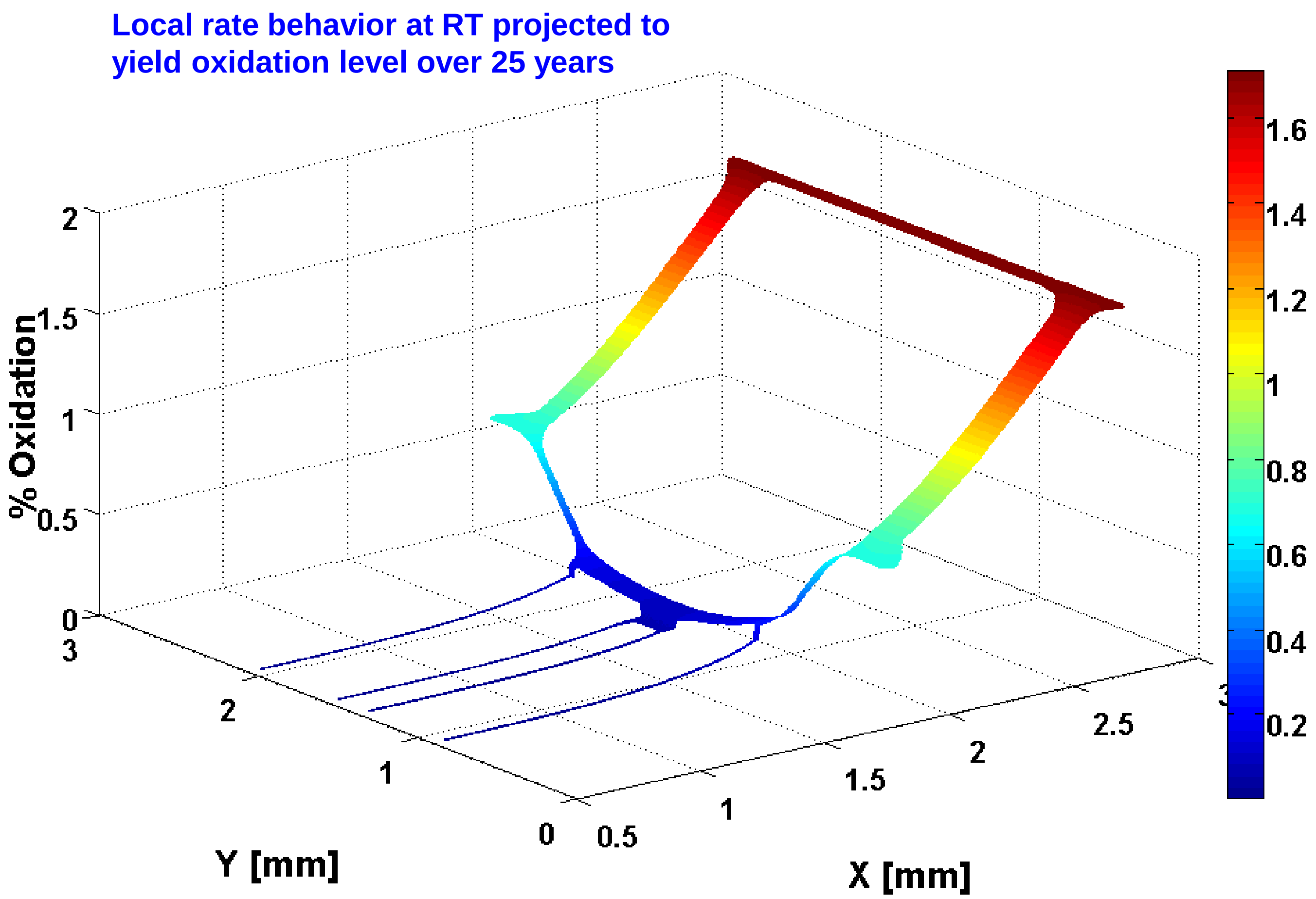
Predicted Spatially Dependent Oxidation



Local rate behavior at RT

- 2D FEM predictions can be interpolated to extract center line behavior for comparing multiple material parameters

Predicted Spatially Dependent Oxidation



- **Visualization shows reduced activity in the center epoxy bondline area**

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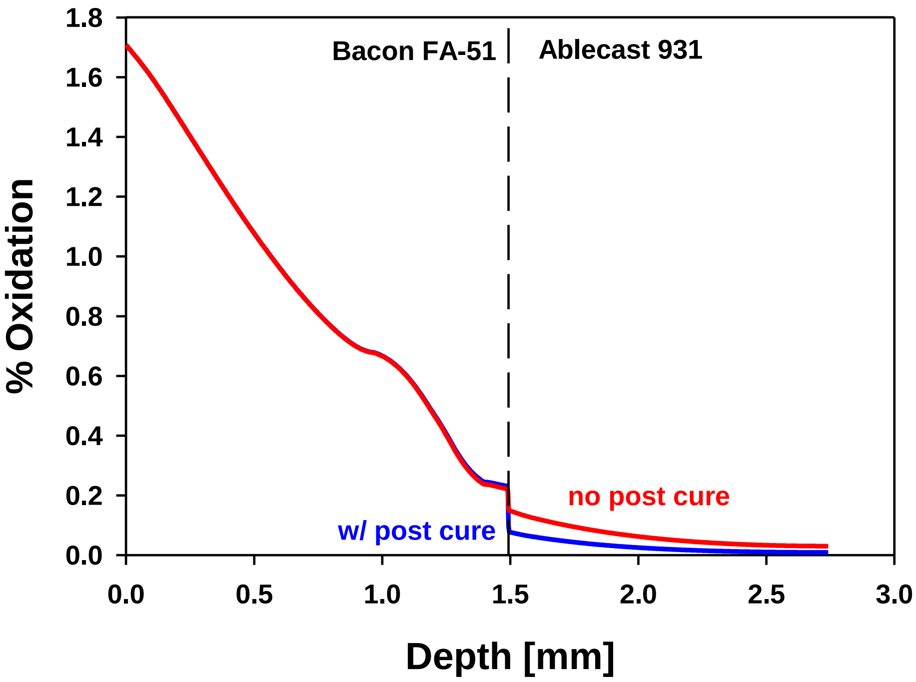
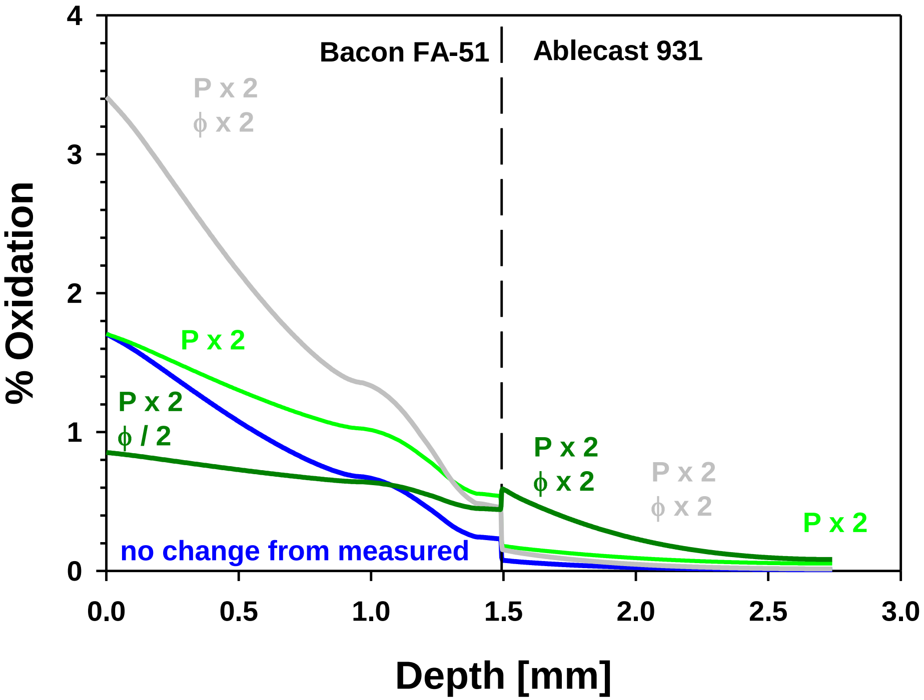
Local Oxidation – Material Variations

- Interpolated center line from 2D FEM model is used to visualize dependence on variations in permeability (*P*) and oxidation rate (*Φ*)
- % oxidation projection to 25 years





- **Even if material parameters moderately change during aging, the center material remains protected by the Bacon Adhesive cover.**

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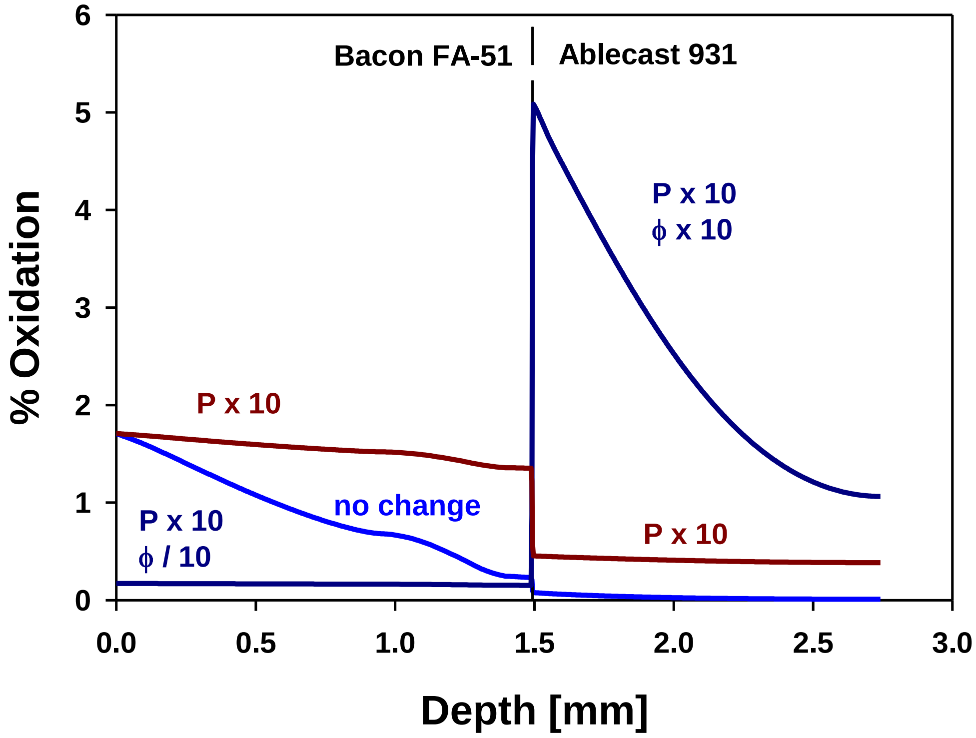
Local Oxidation – Material Variations

- **2D FEM model allows user to probe under which scenarios a significantly enhanced oxidation of center material could occur**
- **Exterior Bacon Adhesive would have to display considerably lower *Φ* and higher P, whereas the interior would need to have a higher *Φ* and higher P**



- **The exptl. observed decrease in rate for the Bacon adhesive with aging level is insufficient to change overall system aging behavior as long as the Ablecast maintains its low oxidation rate**

Conclusions - Summary

- **Defined approach to understand combined epoxy aging in small assembly**
- **Characterized two epoxies with measured ox-rate and permeability features**
- **Developed 2D FEM oxidative aging model for assembly**
- **This model yields aging projections and can be used to quantify/visualize the dependence of aging behavior on variances in material parameters**
- **Material parameters could change moderately without changing projected assembly behavior**

  - **Impact: Developed capability to predict spatial material oxidation behavior in complex geometries. Demonstrated that exterior epoxy provides significant protection for interior Ablecast bondline in assembly geometry.**
  - **Outstanding: Degradation chemistry – mechanical/adhesive property correlations.**