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Oxygen Permeation and Thermoset Degradation with Temperature

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Approved for unlimited public release

Background and keywords

Research goals:

- Establish experimental capability to determine *P, D, S* for O_2 with T
- Accommodate reactive O_2 loss during permeation experiments
- Understand oxidative degradation of thermoset materials
- Develop models to predict spatial distribution of oxidative damage

Why do we need permeation parameters?

- Limited literature data
- Performance of environmental seals, transport processes
- Characterization of materials
- Predictive DLO models for degradation processes
- Kinetic model refinement explored by other R&D groups

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

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What are we dealing with?

- At elevated temperature polymers and films may act as an O2 barrier
- The underlying permeability is convoluted with degradation chemistry
- A parallel PHYSICAL and CHEMICAL process

Edge oxidation in high temperature composites

From Tandon GP, 2011, aging at 177°C

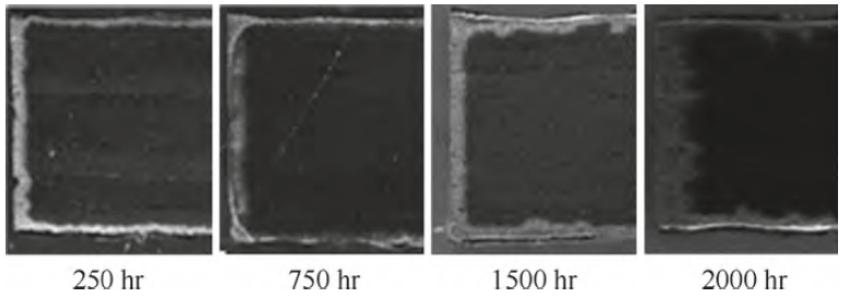

Fig. 9.9 Oxidation growth near the laminate edge in $[\pm 45]_{2S}$ laminate as a function of aging time

Laboratory accelerated thermal aging

Example of aged epoxy, degradation is limited to material surface

- **Edge effects complicate the prediction of bulk material aging**
- **O_2 Permeation experiments are similarly convoluted**

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.

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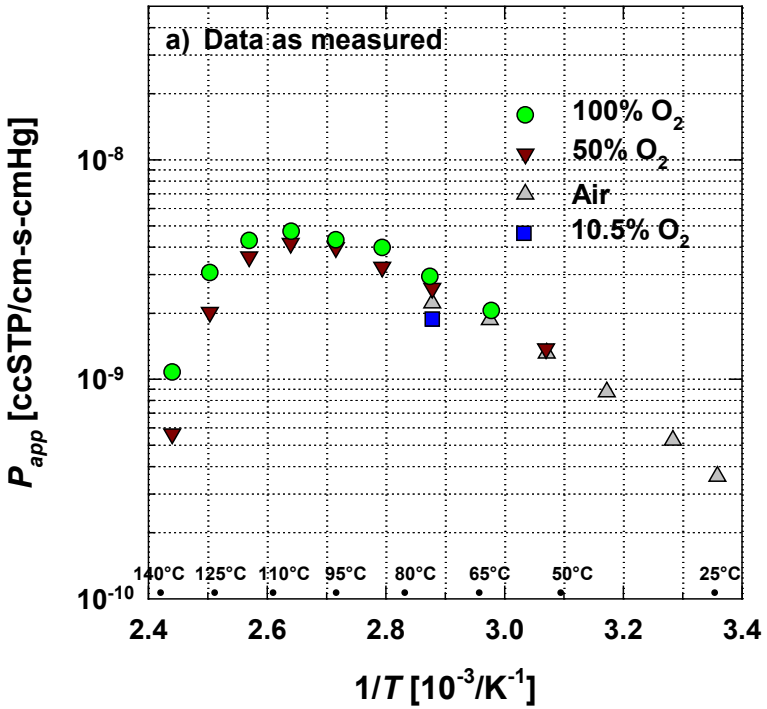
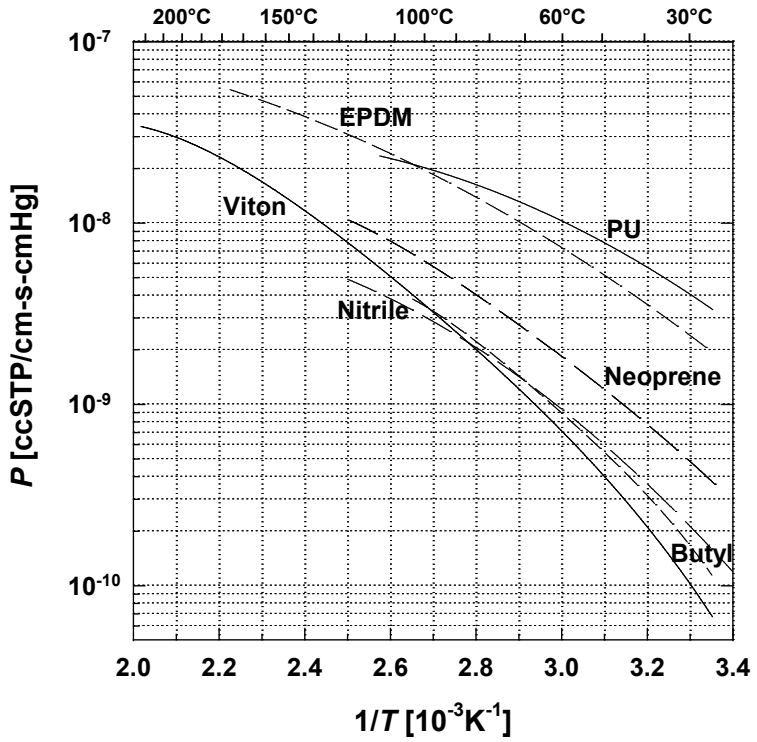
Permeation at elevated temperature

- Effective flux through polymers at high temperatures can be unexpectedly low due to reactive oxygen loss
- Determination of permeability as a 'material property' requires corrections





- Primary transport flux measurements do not always yield permeability
- Degradation chemistry interferes, but can be accommodated

Celina M, Gillen KT. Oxygen Permeability Measurements on Elastomers at Temperatures up to 225°C. Macromolecules 2005;38:2754

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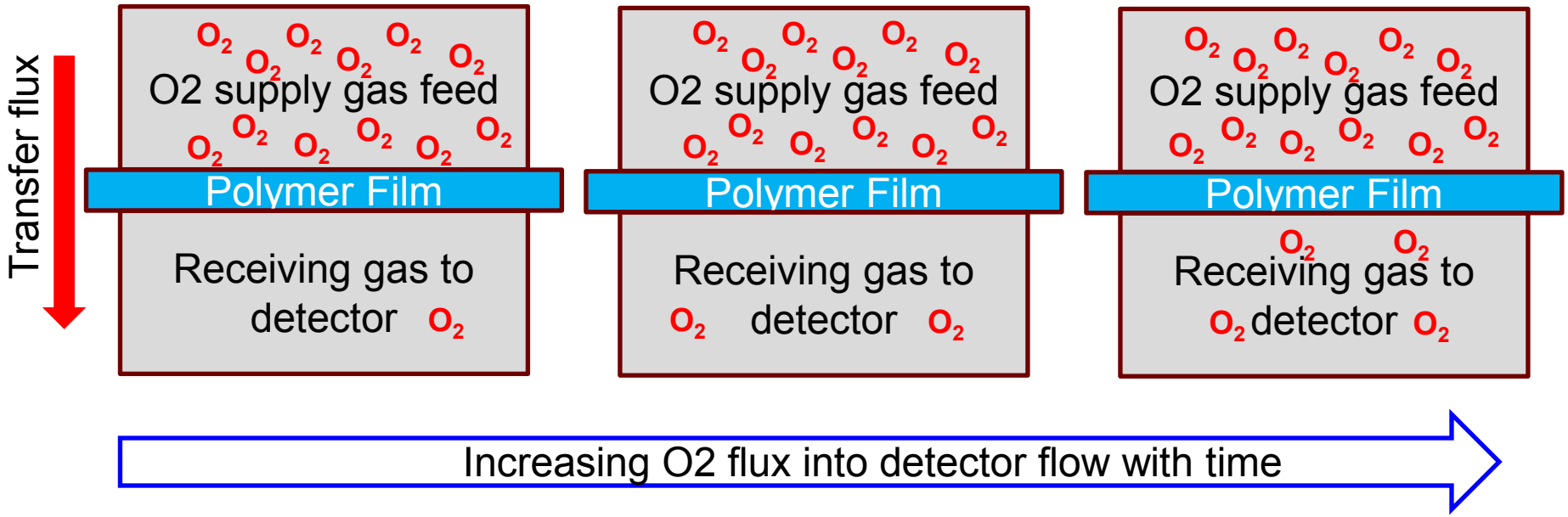
O_2 permeation through thin film

Thin film separation – Mass transport - Membrane characterization

In our case complicated by parallel oxidation because many polymers oxidize at high temperatures and have low permeability



Multiple variables need to be considered for successful determination of P, D, S and material characterization

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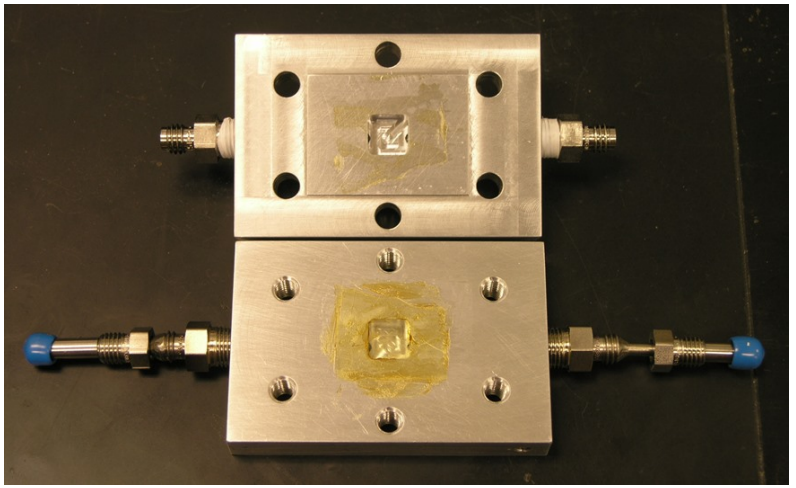
O2 permeation instrument

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

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Experimental conditions

- At high temperatures diffusivity is fast for thin films (flux changes in minutes)
- Thicker films may lose O2 through oxidation
- Low partial pressure will lower equilibrium permeation flux, but is also more sensitive to oxidation

- Film thickness
- Film area
- Transfer flux, detector overload
- Partial pressure of feed gas
- Detector sensitivity limit

Experimental range for ***P***

$$P = \frac{F \cdot l}{p_{O2}}$$

Permeability range: 9 orders of magnitude

P_{min} = 4.6e-16 ccSTP/cm-s-cmHg (0.01 ccSTP/m^2/day, 50 cm^2, 25 μm, 63 cmHg-O_2)

P_{max}= 1.7e-07 ccSTP/cm-s-cmHg (10000 ccSTP/m^2/day, 1cm^2, 1mm, 6.6 cmHg-O_2 (50/50 air/N2)

- Experiments require balancing/optimization of multiple parameters
- There are intrinsic experimental limits
- Additionally the material may oxidize during experiment

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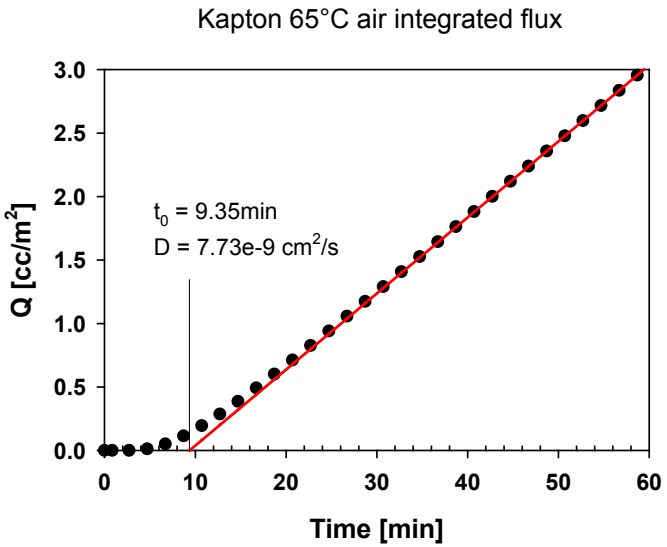
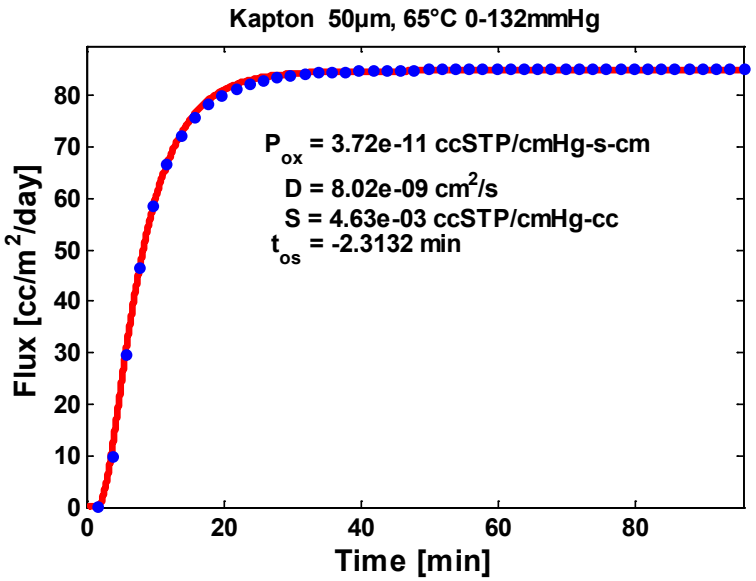
Analysis of flux curves to yield D

- **Traditionally a flux curve (non-equilibrium conditions) has been interpreted with boundary assumptions and simplification to extract D**





The X-intercept for the line is:

$$t_0 = \frac{L^2}{6D}$$

New method to extract *D*, fitted flux curve

Existing formula interprets slope of integrated flux curve

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Established mathematical approach

Traditionally a flux curve (non-equilibrium conditions) has been interpreted with boundary assumptions and simplification to extract *D*

Fick's second law in one dimension with specified boundary conditions for the experiment:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad C(x,0) = 0, \qquad \begin{matrix} C = f(x,t) \\ C(0,t) = C_1, \end{matrix} \qquad C(L,t) = 0$$

Solution through separation of variables and deriving the flux ($F = -D\frac{\partial C}{\partial x}$), the total O2 transmission is then specified:

$$Q(t) = \int_0^t F(L,\tau)d\tau$$

Then taking the limit:

$$\lim_{t\to\infty} Q(t) = \frac{DC_1}{L}\left(t - \frac{L^2}{6D}\right)$$

The X-intercept for this line is then:

$$\boldsymbol{t_0 = \frac{L^2}{6D}}$$

Existing formula interprets slope of integrated flux curve

Crank J. The Mathematics of Diffusion. 2d Ed. New York: Oxford University Press, 1975

New mathematical approach

Normalized Fick's Second Law with reactive term (oxidation), identical boundary conditions, application of finite difference approximations to both derivatives to derive the recursive matrix equation.

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\chi^2} - \underbrace{\frac{\alpha\theta}{\beta\theta+1}}_{\text{reactive term (oxidation)}} \approx \frac{\theta_{i+1,j}-\theta_{i,j}}{\delta\tau} = \frac{\theta_{i,j+1}-2\theta_{i,j}+\theta_{i,j-1}}{\delta\chi^2} - \frac{\alpha\theta_{i,j}}{\beta\theta_{i,j}+1}$$

$$\Downarrow$$

$$(a+2)\boldsymbol{\theta}_{i+1} = \mathbb{A}\boldsymbol{\theta}_i - R(\boldsymbol{\theta}_i)$$

$$\mathbb{A} \equiv \begin{bmatrix} a_1 & \cdots & & \cdots & 0 \\ 1 & a & 1 & \cdots & 0 \\ 0 & \ddots & \ddots & \ddots & 0 \\ 0 & \cdots & 1 & a & 1 \\ 0 & \cdots & & \cdots & a_N \end{bmatrix}, \qquad a = \frac{(\delta\chi)^2}{\delta\tau} - 2$$

$$a_1 = \frac{(\delta\chi)^2}{\delta\tau} + \frac{\alpha(\delta\chi)^2}{\beta+1}, \qquad a_N = 1$$

$$R(\theta_{i,j}) = \frac{\alpha\theta_{i,j}(\delta\chi)^2}{\beta\theta_{i,j}+1}$$

The flux is then calculated from this solution: $F_i = \dfrac{P_{ox}p_0\theta_{N-1,i}}{L(\delta\chi)}$

Flux with time is iteratively fitted to experimental data to extract *P*, *D* and *S*, oxidative term is accommodated

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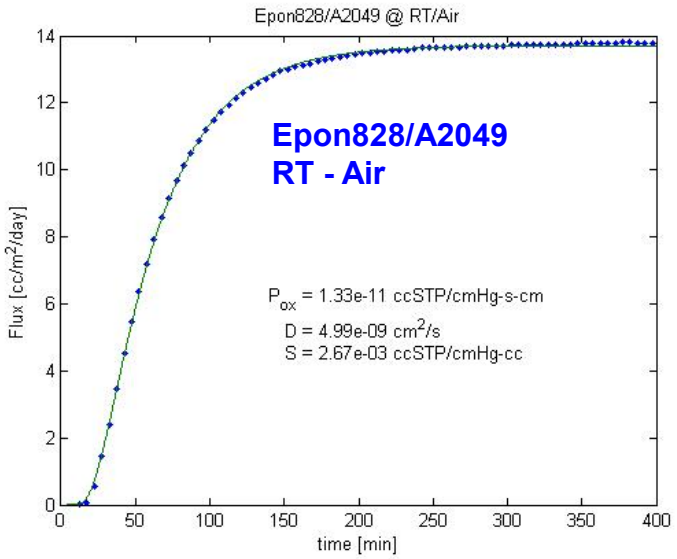
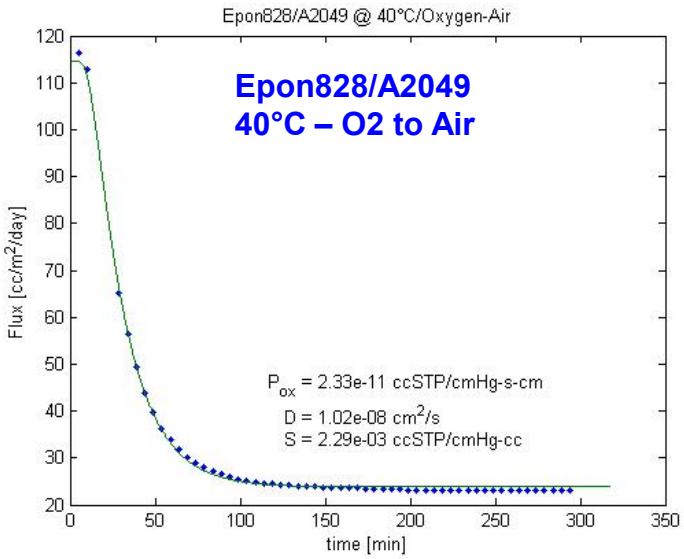
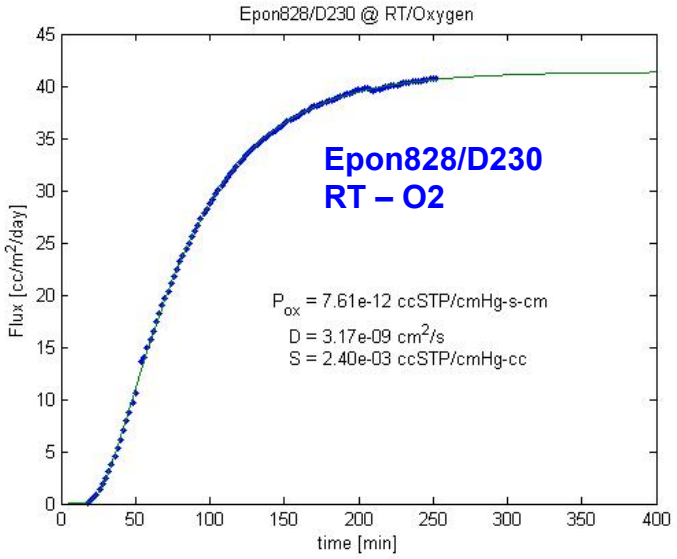
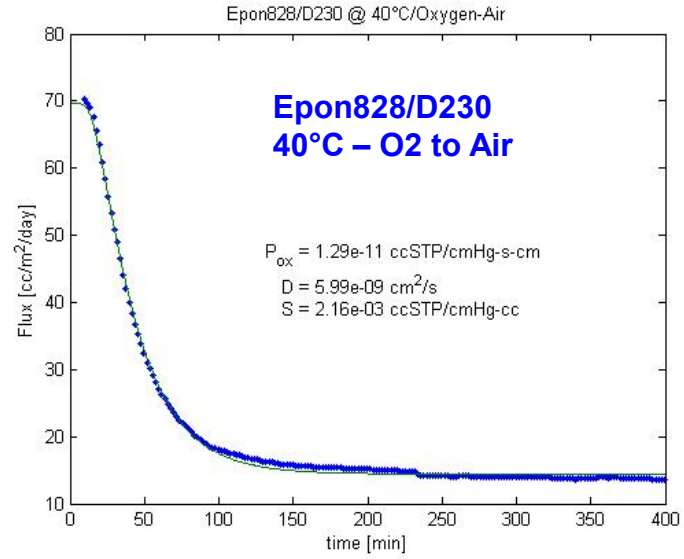
Examples of permeative flux experiments









- **D, S available from decreasing and increasing flux and changing pressure experiments**
- **Flux changes modeled with Fickian diffusion behavior – perfect fits**

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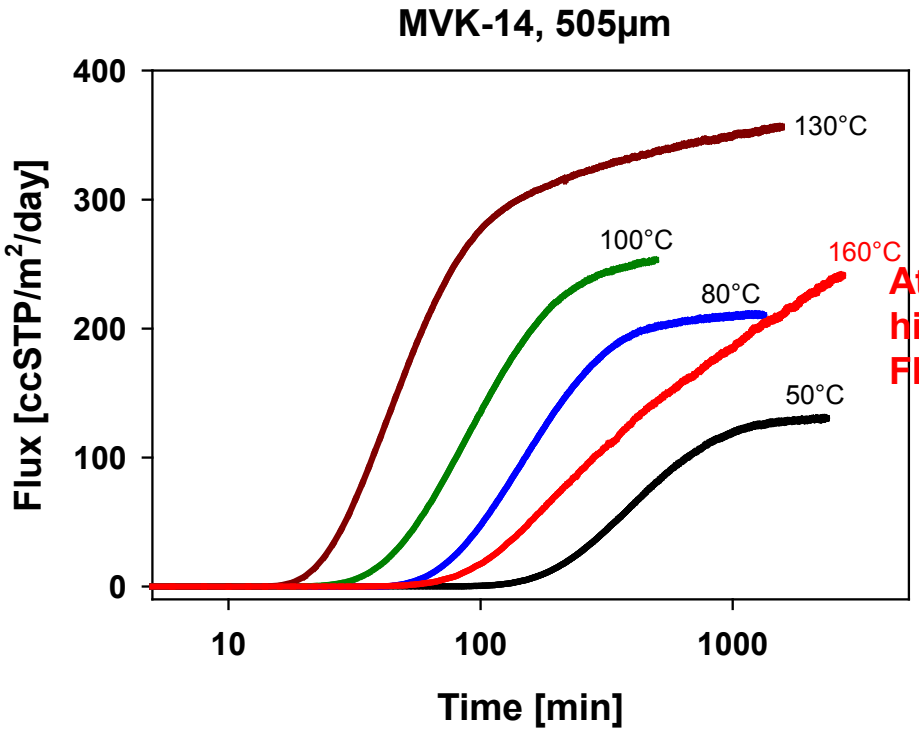
Oxidative reaction reduces flux

- Reactive oxygen loss results in creep at high temperature
- Effective flux is lower at high T



At 160°C this composite is highly reactive with O2. Flux is reduced.

High temperature permeation flux data require partial pressure checks and corrections for oxidation

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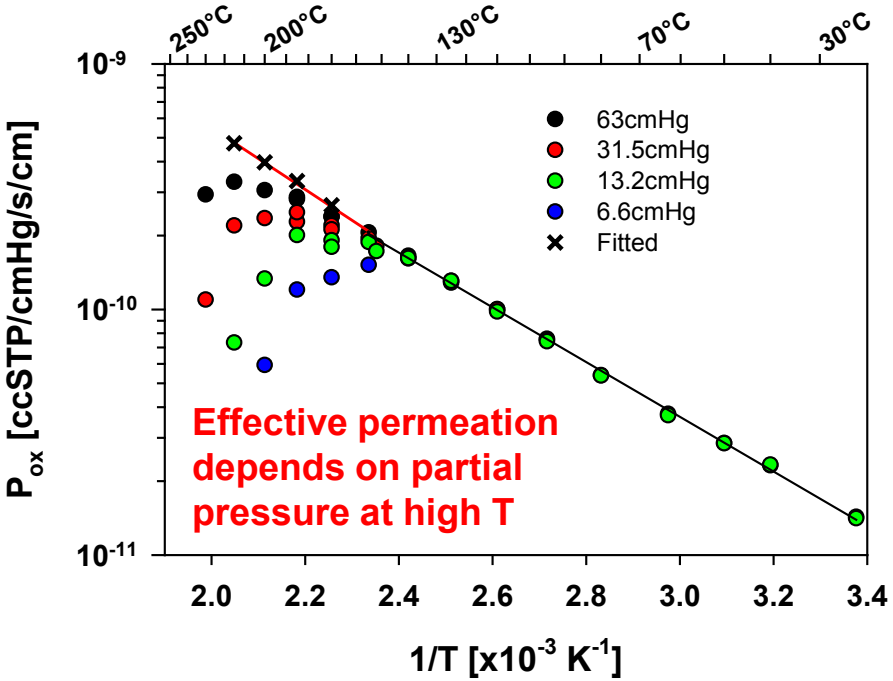
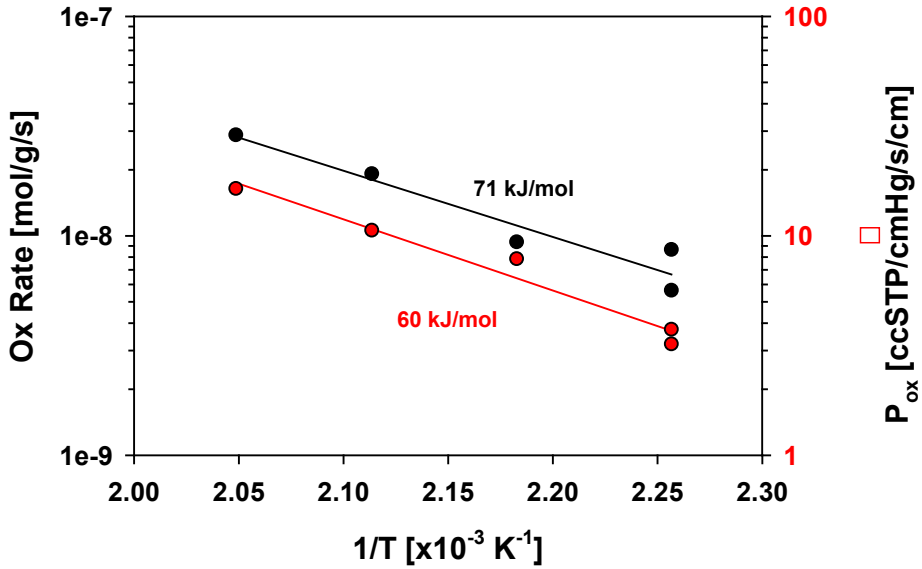
Flux reduction - Kapton

- 50 µm Kapton film
- At 150°C oxidation is visible in permeation measurements
- Permeation experiments allow to indirectly determine oxidation rate





These experiments show Kapton as majorly oxidation sensitive above 200°C

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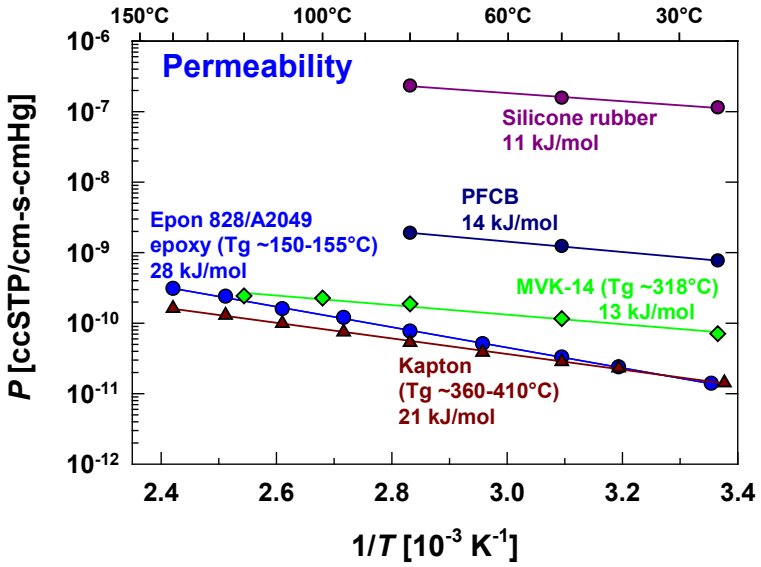
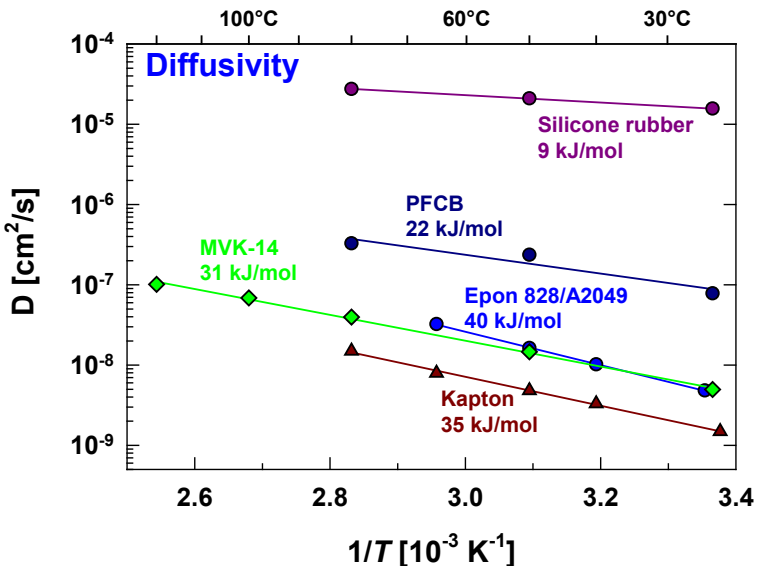
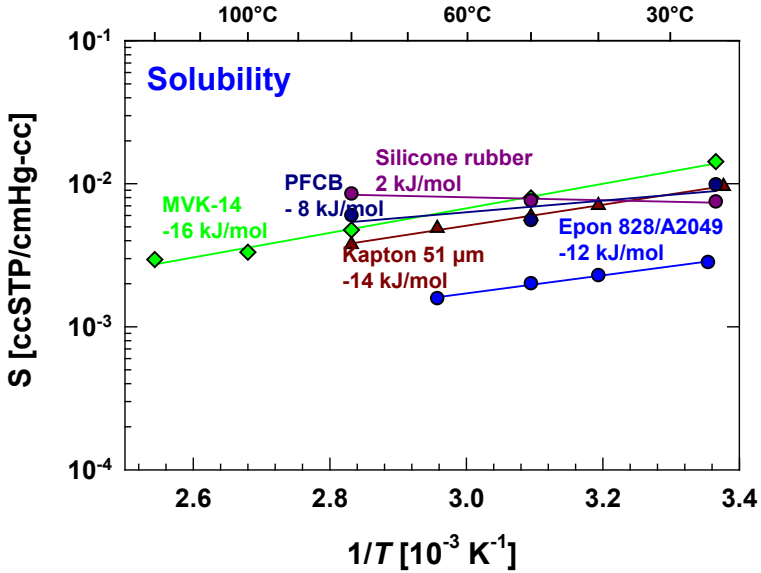
O_2 Permeability – Diffusivity – Solubility





$$P_{ox} = D \cdot S$$

$$E_P = E_D + E_S$$



- Ea of 10 to 30 kJ/mol for *P*
- Ea of 10 to 40 kJ/mol for *D*
- Reduced solubility with increased T, up to -15 kJ/mol

- **Succeeded to measure flux and determine *P, D, S* with temperature**
- **Excellent Arrhenius behavior below Tg and for silicone**

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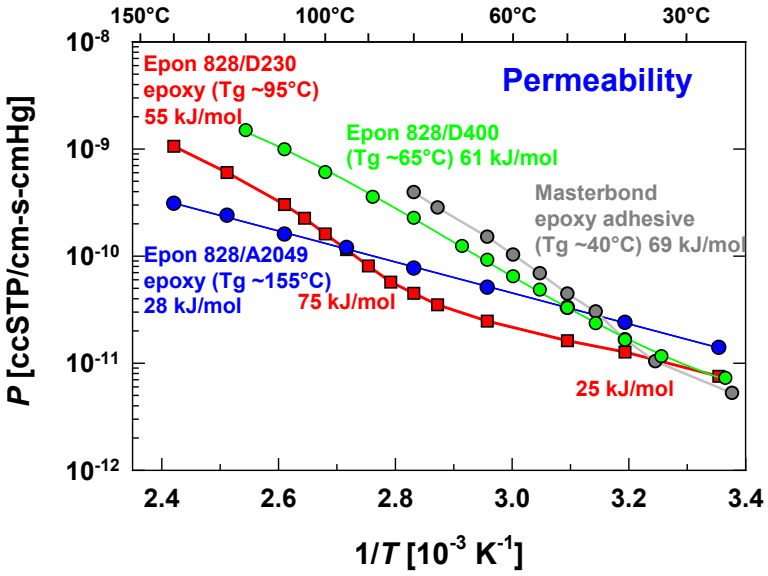
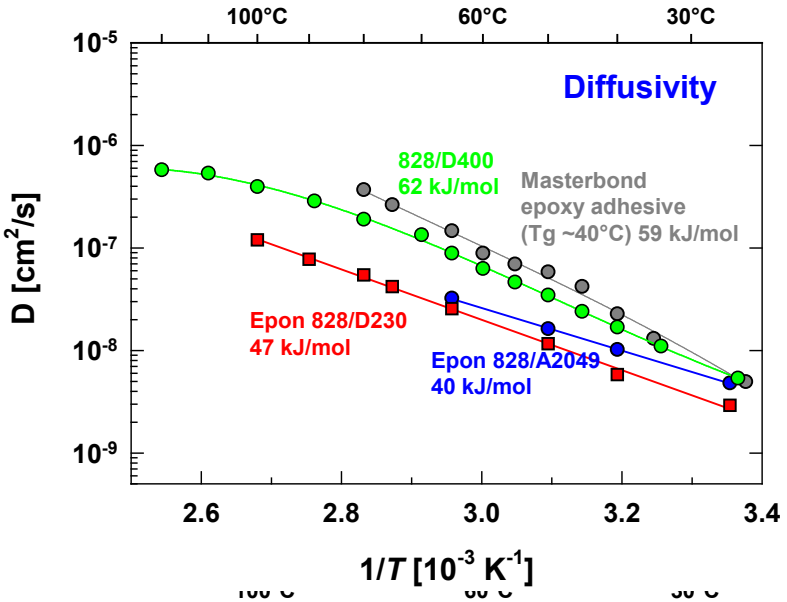
O_2 Permeability – Diffusivity – Solubility

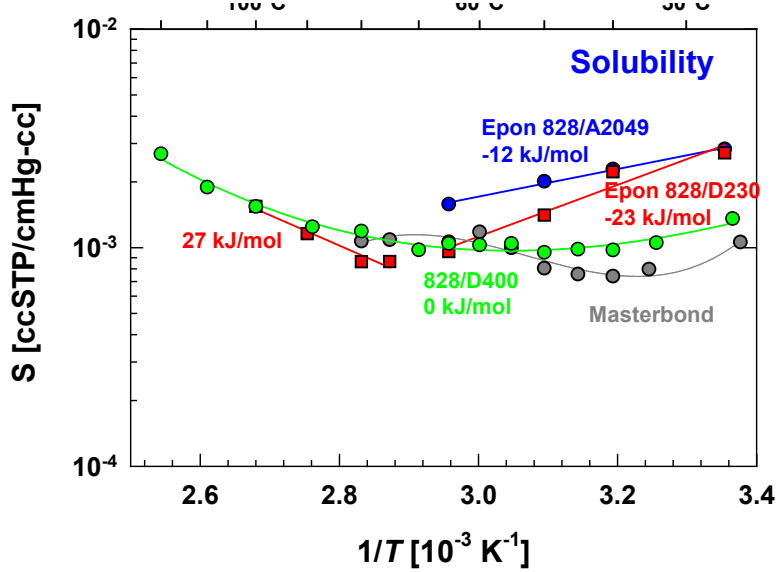
Epoxy systems





- 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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Applications?

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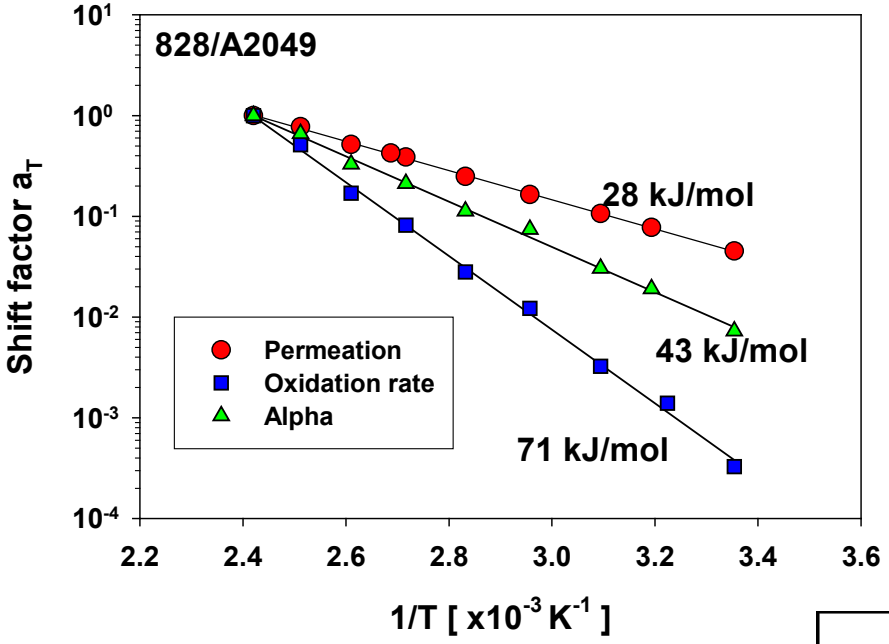
Combination of rate and permeability governs depth

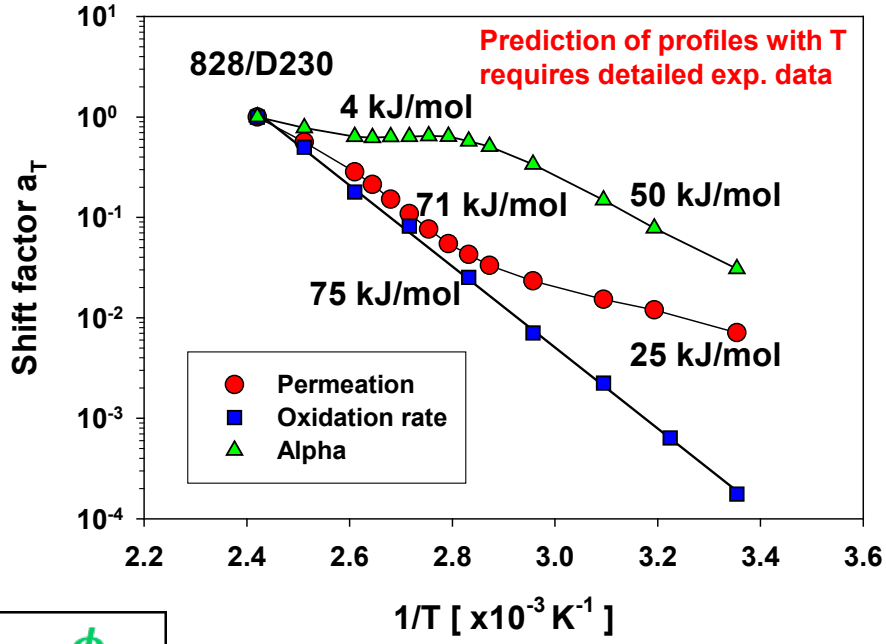
- Profile prediction involves the ratio of ***Φ/P***
- If oxidation rate and permeability decrease equally then the resulting profiles remain identical, yet different absolute oxidation levels evolve (governed by oxidation rate)



Well behaved epoxy
Linear Arrhenius behavior of Φ
and consistent change of P

$$\alpha \propto \frac{\phi}{P_{ox}}$$

$$E_\alpha = E_\phi - E_{P_{ox}}$$



Irregular behaved epoxy system
Linear Arrhenius behavior of Φ,
but Tg affects transition in P

First results showing that *Φ and P* can have similar Ea in a specific T range

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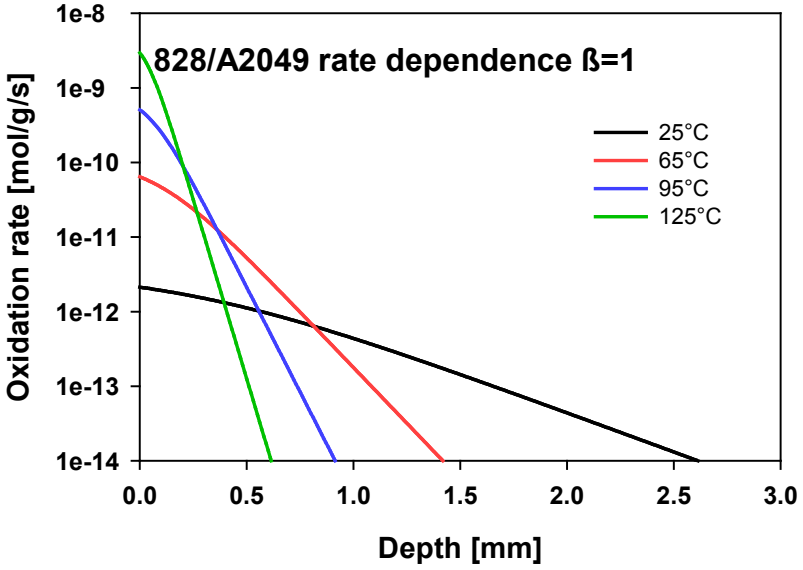
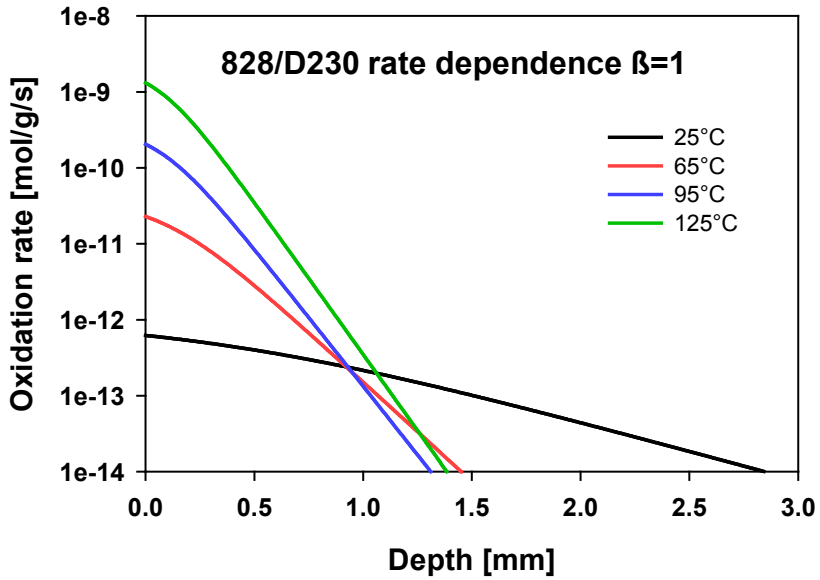
Oxidation profile formation – T dependence

- Profile prediction is possible when suitable parameters are available
- For lower temperatures oxidation rates and permeability drop, but oxidation rate decrease faster (higher Ea), resulting in more oxygen to diffuse deeper into material



Well behaved epoxy
Linear Arrhenius behavior of Φ and consistent change of P



Irregular behaved epoxy system
Linear Arrhenius behavior of Φ, but Tg affects transition in P

- Dynamics of *P*, *Φ* temperature dependence controls profile formation
- With lower T the profiles are generally less steep and deeper
- Tg and its impact on *P*, *Φ* can significantly affect profile shapes

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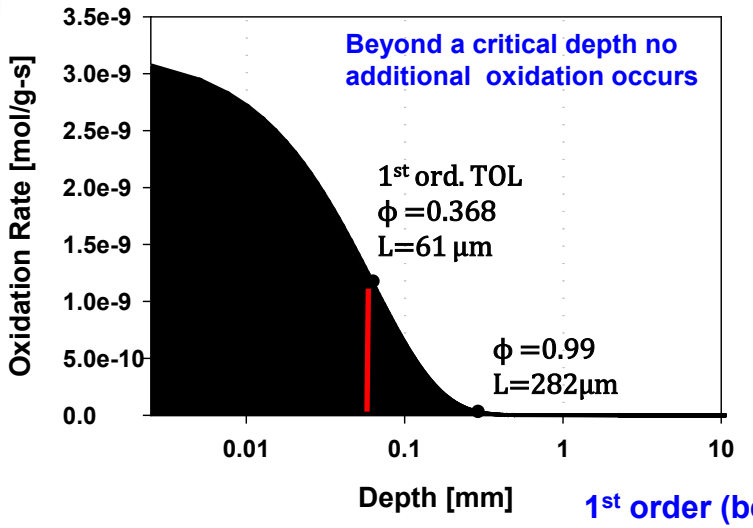
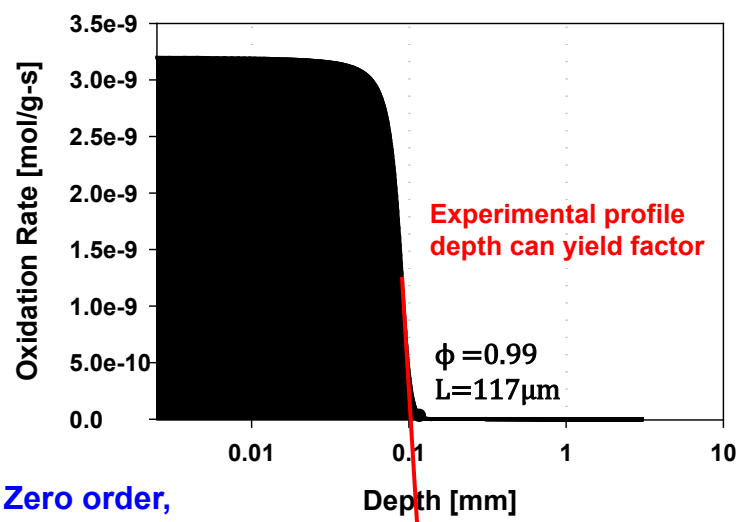
TOL – Total Oxidized Layer

Epon 828 / Ancamine 2049 at 125°C (□=0)



If P_{O2} is at kinetic saturation
β >> 1

Epon 828 / Ancamine 2049 at 125°C (□=100)



1st order (beta=0)

Zero order, steep and deep oxidized layer

$$\mathrm{TOL} \approx \left(\frac{D}{k_1}\right)^{1/2} = \left(\frac{P_{ox} p_0}{\phi}\right)^{1/2}$$

*Pseudo 1st order: $\phi = k_1 C_s$

$$\mathrm{TOL} \approx v \left(\frac{D}{k_1}\right)^{1/2}$$

*0th order approx: $v = \left(2\left(1 - \frac{C_c}{C_s}\right)\right)^{1/2}$

- **Discussion of mathematical basis:**
- Audouin L, et al. Role of oxygen diffusion in polymer aging: kinetic and mechanical aspects. J Mater Sci 1994;29:56
- Kiryushkin SG, Shlyapnikov YA. Diffusion-controlled polymer oxidation. Polym Degrad Stab 1989;23:18
- **Used for discussion of aging in elastomers, thermosets and thermoplastics:**
- Audouin L, et al. "Close Loop" mechanistic schemes for hydrocarbon polymer oxidation. J Polym Sci, Part A: Polym Chem 1995;33:92
- Colin X, Verdu J. Strategy for studying thermal oxidation of organic matrix composites. Comp Sci Tech 2005;65:411
- Devanne T, et al. Radiochemical ageing of an amine cured epoxy network. Part II: kinetic modelling. Polymer 2005;46:237
- Rincon-Rubio LM, et al. A theoretical model for the diffusion-limited thermal oxidation of elastomers. Rubber Chem Technol 2003;76:460
- Richaud E, etal. Diffusion-controlled radiochemical oxidation of bisphenol A polysulfone. Polym Int 2011;60:371
- **Lc90 used by Gillen et al.** (Emphasis on maximum thickness to achieve homogeneous oxidation in accelerated aging)
- **TOL requires expt. data for aging models; Lc90 & profiles can be predicted based on oxidation rates and permeation**

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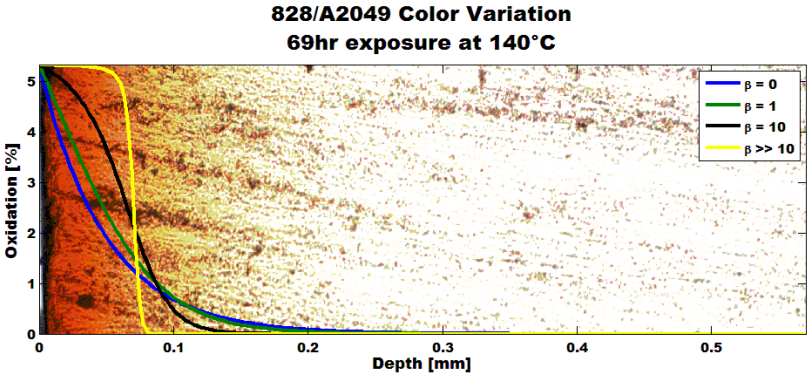
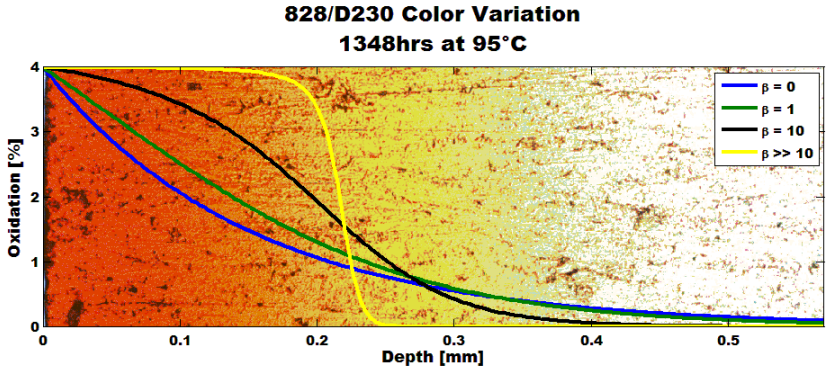
TOL – Total Oxidized Layer - Examples

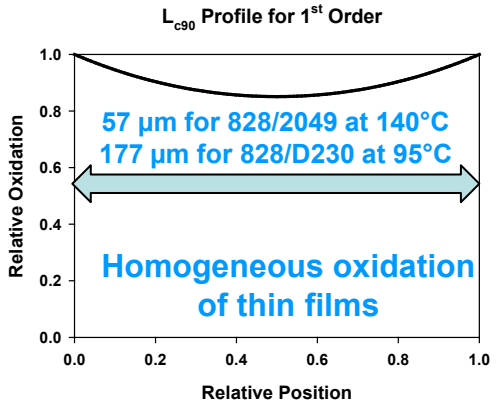
- Actual (discoloration) and predicted oxidation profiles (DLO modeling) are available for epoxy



P_{ox} [ccSTP cm^{-1} $cmHg^{-1}$ s^{-1}]	φ [mol g^{-1} s^{-1}]	ρ [g cc^{-1}]
3.10E-10	6.70E-09	1.134
TOL 1st order(beta =0)	49 µm	
TOL zero order (beta=100)	70 µm	
Lc90 (Gillen definition)	57 µm	



P_{ox} [ccSTP cm^{-1} $cmHg^{-1}$ s^{-1}]	φ [mol g^{-1} s^{-1}]	ρ [g cc^{-1}]
1.15E-10	2.57E-10	1.148
TOL 1st order	152 µm	
TOL zero order	248 µm	
Lc90 (Gillen definition)	177 µm	



TOL depends on kinetic regime, at high O_2 pressure the profile is steeper

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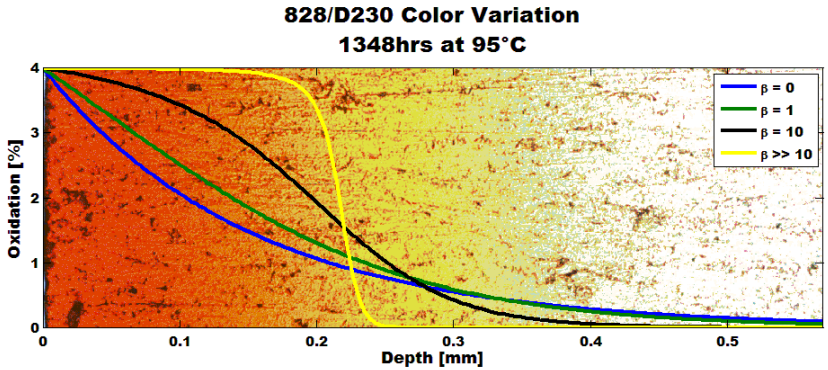
TOL – Total Oxidized Layer - Examples

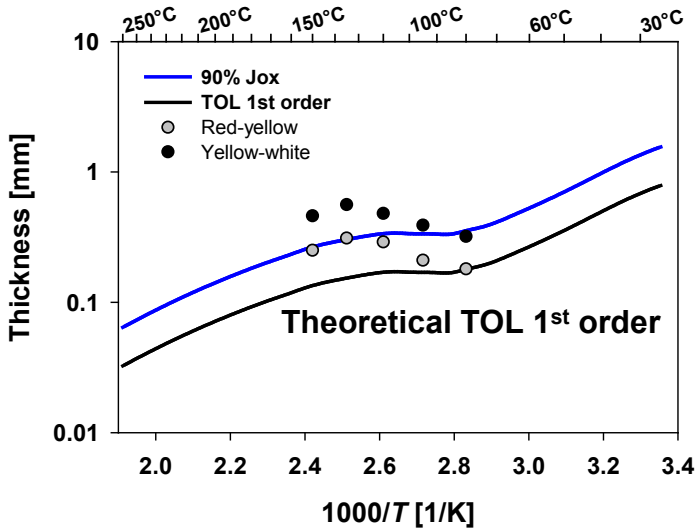
- **Degradation gradients and predicted oxidation profiles (DLO modeling) are available for epoxy**



$$\mathrm{TOL} \approx v\left(\frac{D}{k_1}\right)^{1/2}$$ 0 order

$$\mathrm{TOL} \approx \left(\frac{D}{k_1}\right)^{1/2} = \left(\frac{P_{ox}p_0}{\phi}\right)^{1/2}$$ Pseudo 1st order

TOL for 828/D230



P_{ox} [ccSTP cm^{-1} cmHg^{-1} s^{-1}]	φ [mol g^{-1} s^{-1}]	ρ [g cc^{-1}]
1.15E-10	2.57E-10	1.148
TOL 1st order	152 µm	
TOL zero order	248 µm	
Lc90 (Gillen definition)	177 µm	

TOL may be useful for steep profiles, generally is conservative

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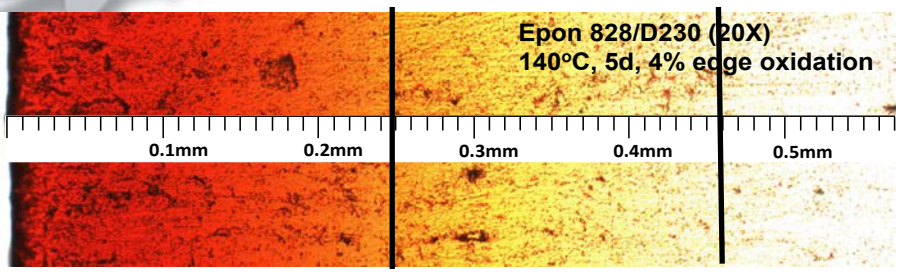
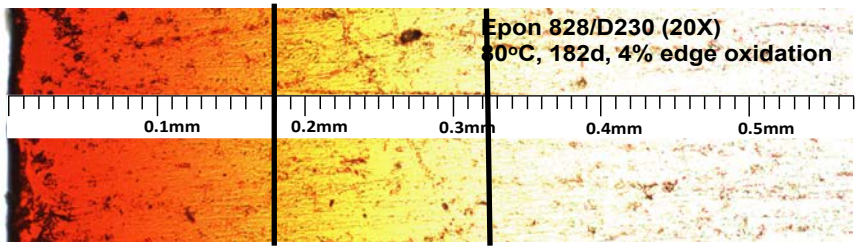
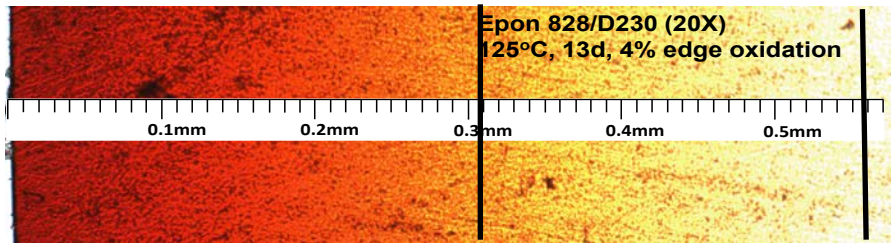
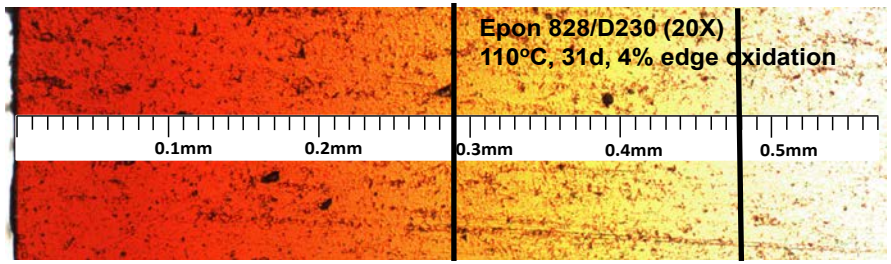
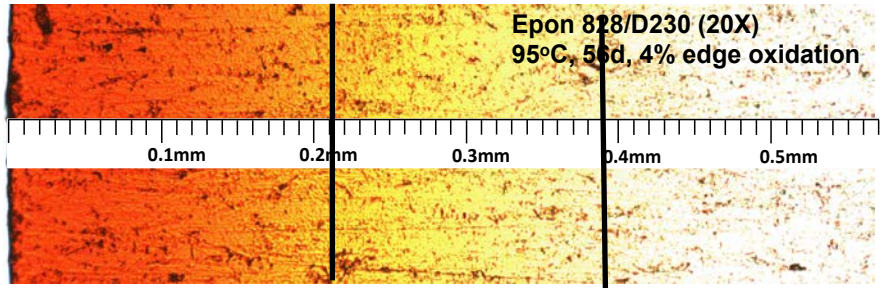
Visual degradation in 828/D230 system 140 - 80 °C











828/D230 system to ~ 4% edge oxidation (20X)

T [°C]	L1 [mm]	L2 [mm]
140	0.25	0.46
125	0.31	0.56
110	0.29	0.48
95	0.21	0.39
80	0.18	0.32

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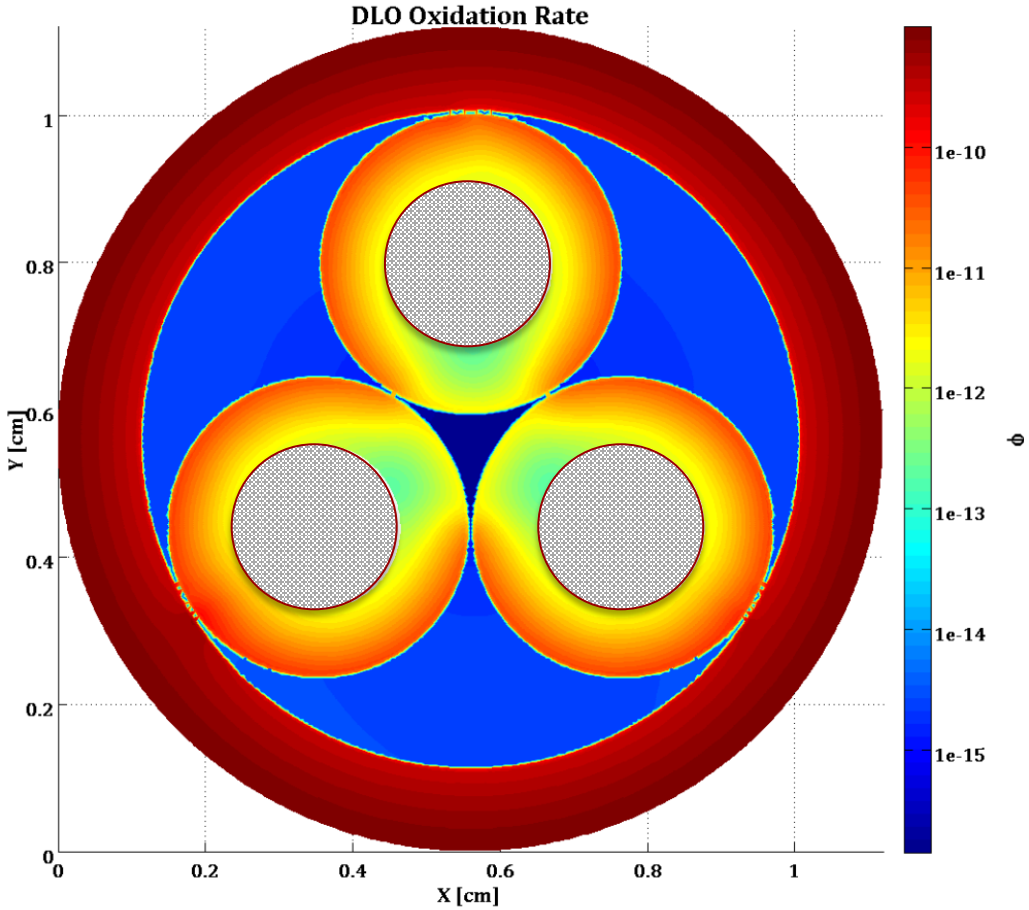
Modeling of cable assembly degradation

Permeability is key input into FEM codes



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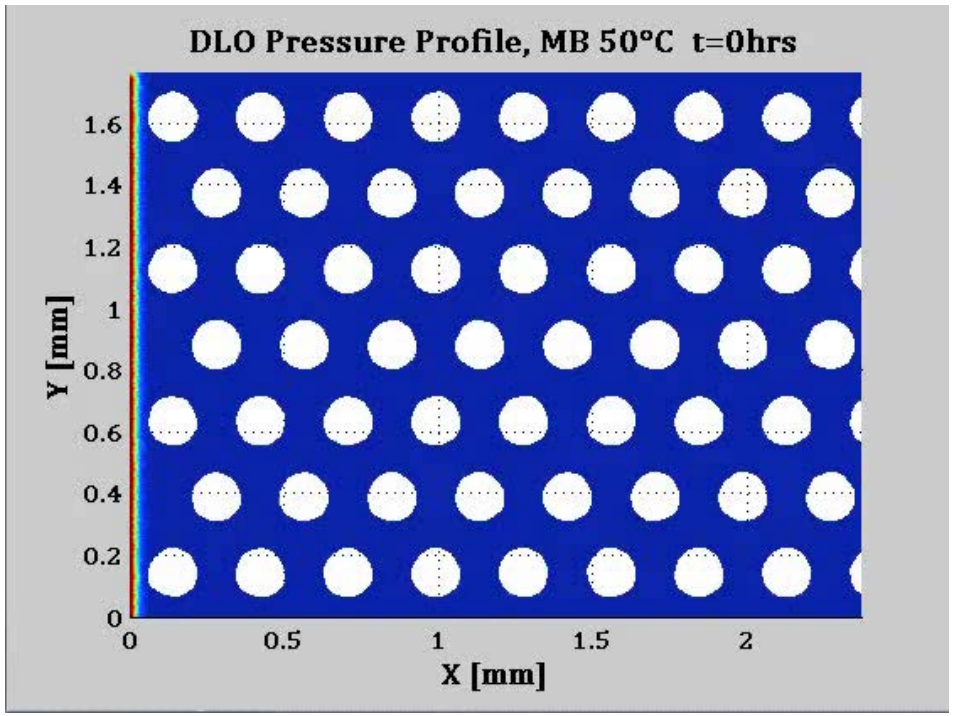
Modeling of DLO evolution

Approach towards non-equilibrium conditions



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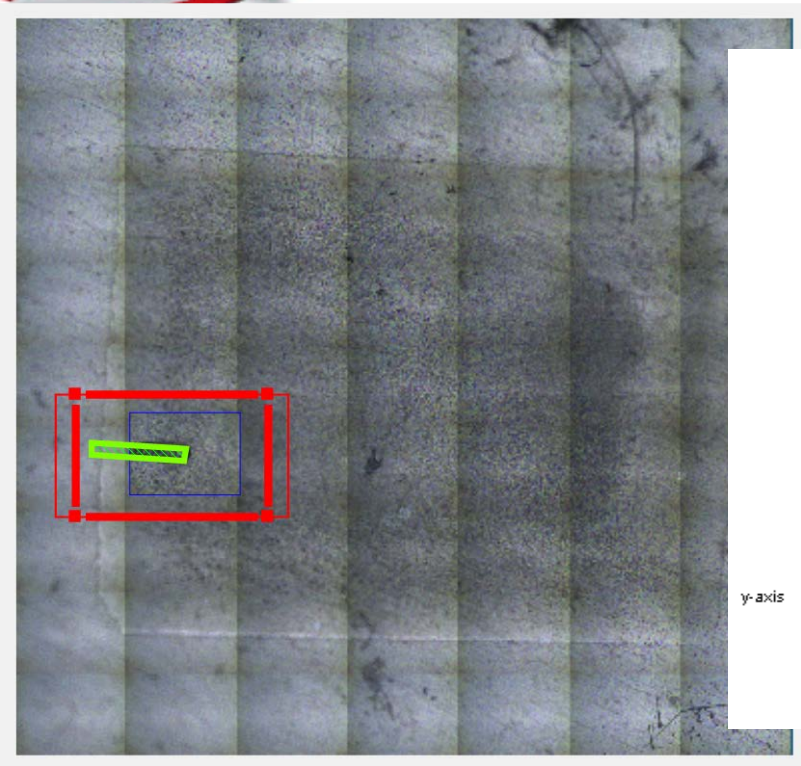
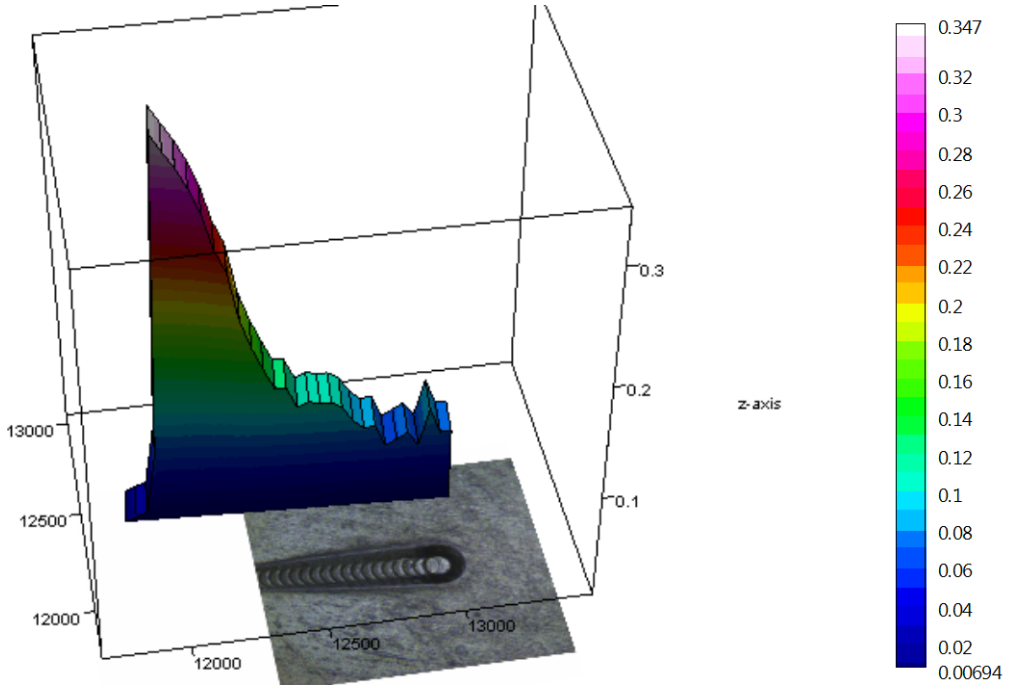
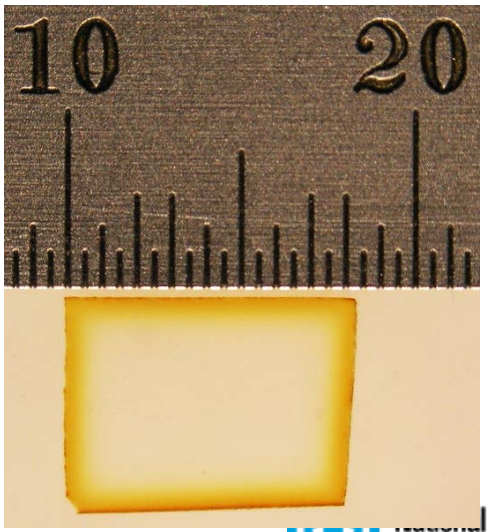
Carbonyl imaging, epoxy adhesive



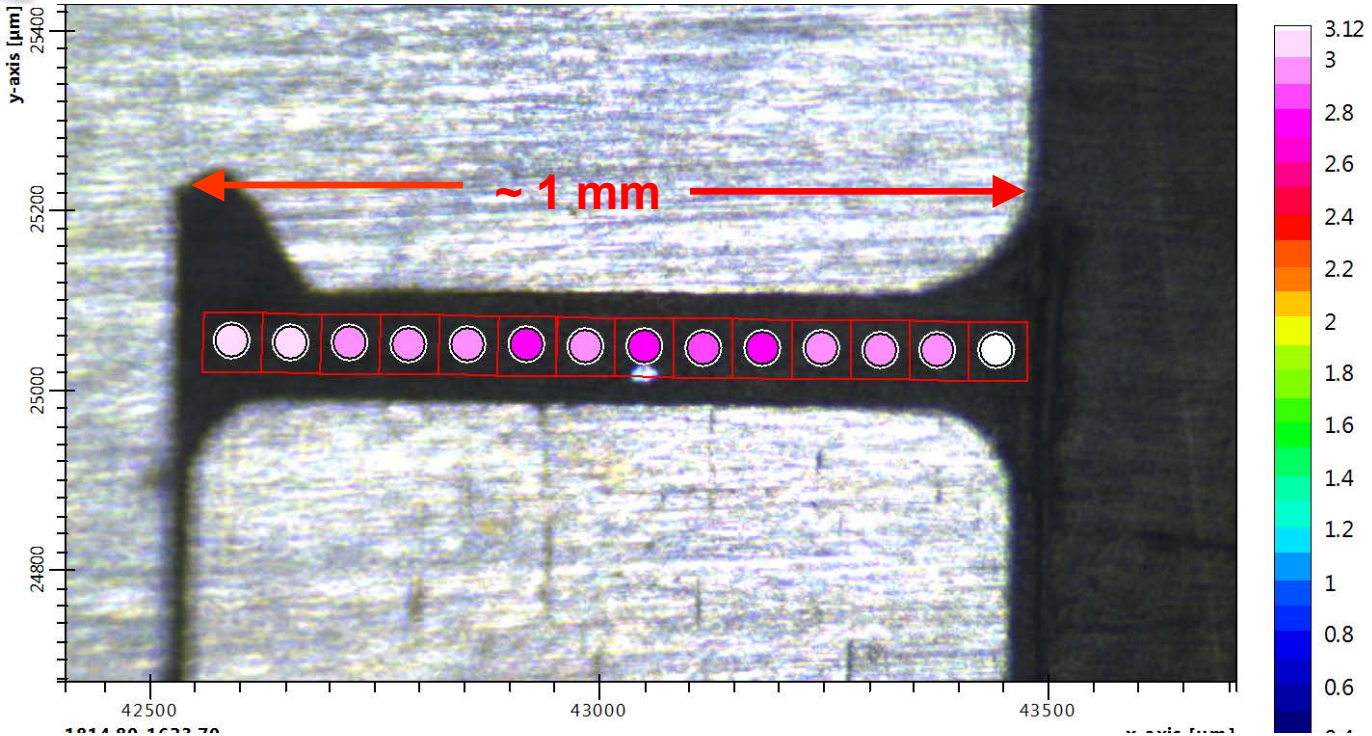


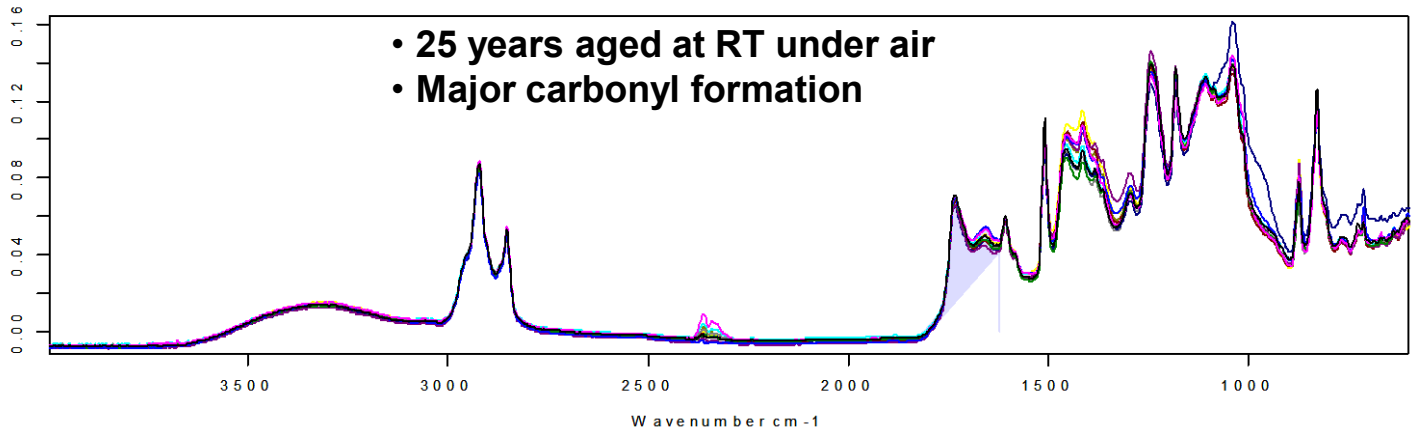
- Master bond adhesive, aged 30 days at 105°C
- DLO profile less than 1mm, significant carbonyl decay in 500 micron
- IR picks up ‘chemical’ degradation profile which correlates with color



Thermo-oxidatively aged epoxy adhesive specimen

Carbonyl imaging of epoxy bond line





Highly aged (oxidized) epoxy adhesive at RT

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Summary

- Customized commercial detector system for high T experiments
- New flux data analysis with reactive term for diffusion mathematics
- Obtained extensive *P* data set for multiple thermoset materials
- Extracted *D* and *S* where possible
- Tg appears to affect solubility more than diffusivity

- We have obtained input parameters for advanced DLO degradation models
- We better understand oxidative aging of thermosets

- Impact: Ability to predict material oxidation behavior in complex geometries

Instrumental range

• Detector sensitivity,	film area,	thickness,	partial pressure
• 0.0035 ppm	1 cm2	20 µm	6.6 cmHg (0.5*air)
• 70 ppm	50 cm2	2 mm	63 cmHg (O2)
• Factors:			
20000	50	100	10

Total 10^9

~ 9 orders of magnitude

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