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Oxygen diffusion through polymers at elevated temperature

Mathew Celina, Adam Quintana, Nicholas Giron
Materials Characterization and Performance Dept. 1819
Sandia National Laboratories, Albuquerque, NM 87185-1411

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Background and keywords

Research goals:

- Establish experimental capability to determine *P, D, S* for O_2 with T
- Consider reactive O_2 loss during permeation experiments

Why do we need these 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: O_2 diffusivity, solubility, permeability, DLO, TOL, modeling

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

Edge oxidation in high temperature composites

From Tandon GP, 2011, aging at 177°C

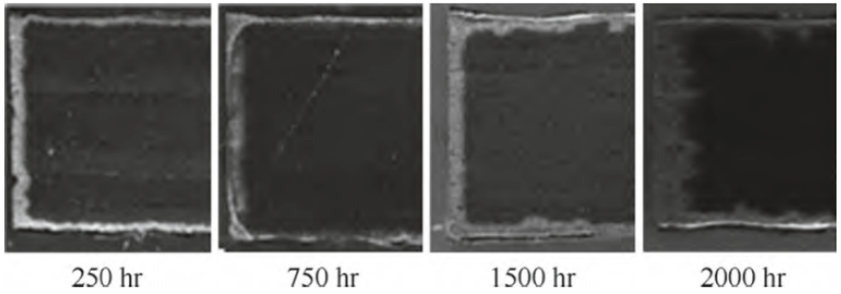


Fig. 9.9 Oxidation growth near the laminate edge in $[\pm45]_{2S}$ laminate as a function of aging time

Laboratory accelerated thermal aging

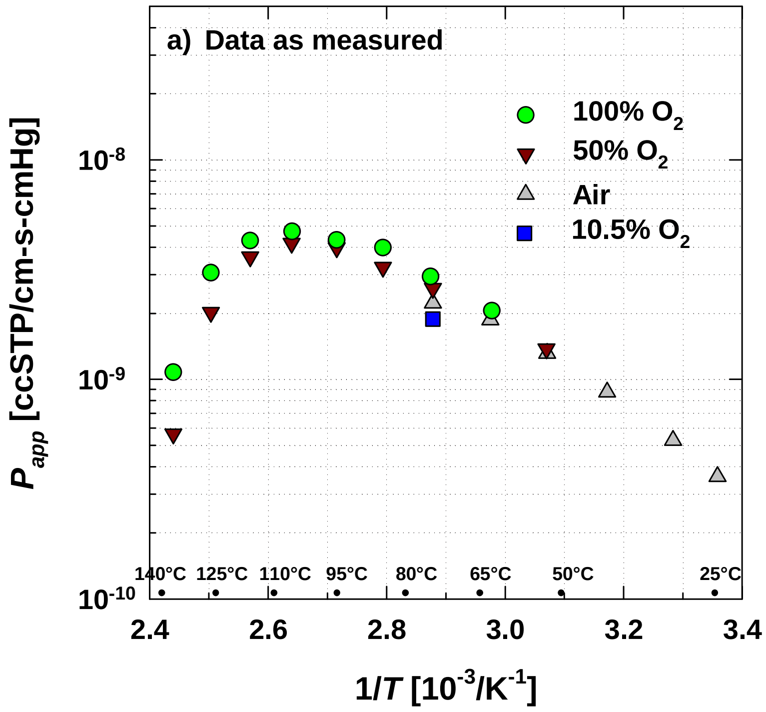
Example of aged epoxy, degradation is limited to material surface

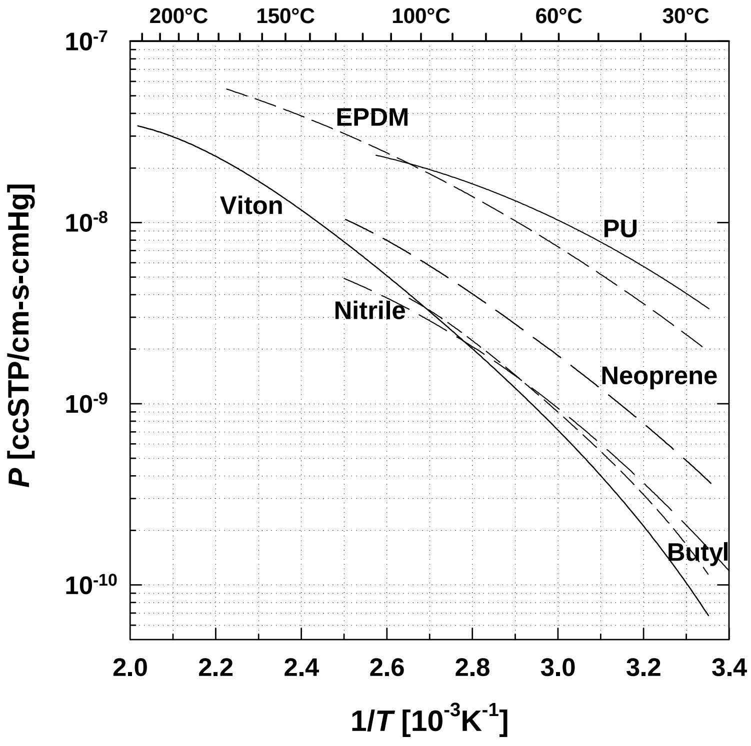
- **Edge effects complicate the prediction of bulk material aging**
- **O_2 Permeation experiments are similarly convoluted**

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.

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





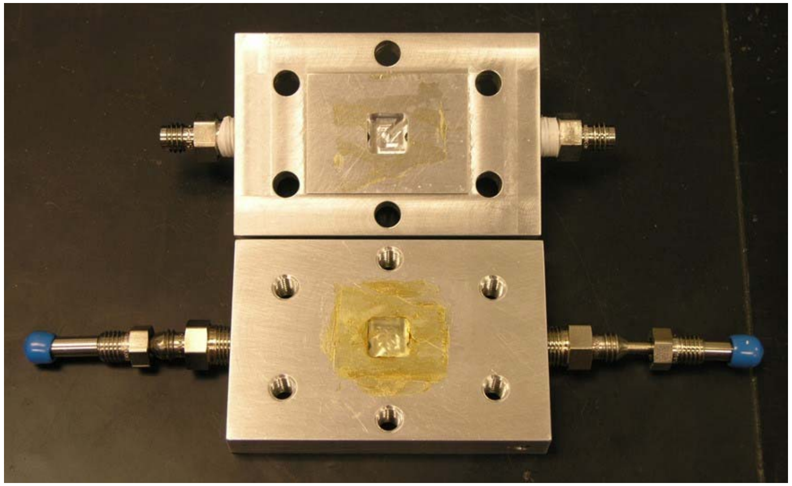
- **Primary transport flux measurements do not always yield permeability**
- **Degradation chemistry interferes but can be accommodated**

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

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

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

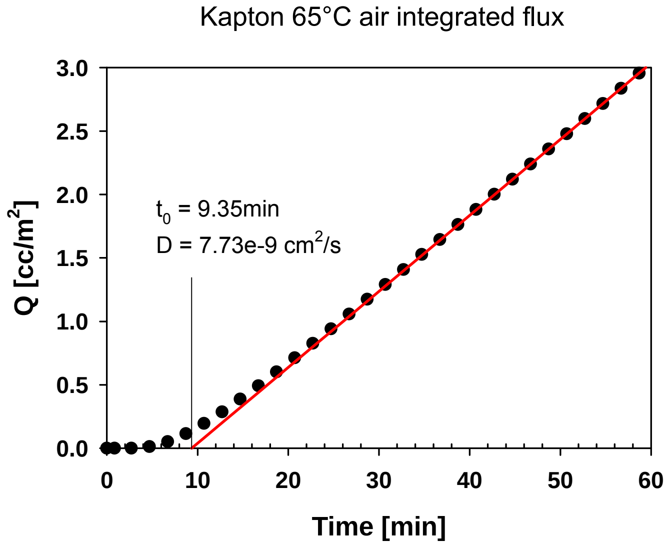
P_{min} = 4.6e-16 ccSTP/cm-s-cmHg (0.01 ccSTP/m^2/day, 50 cm^2, 25 µm, 63 cmHg-O_2)

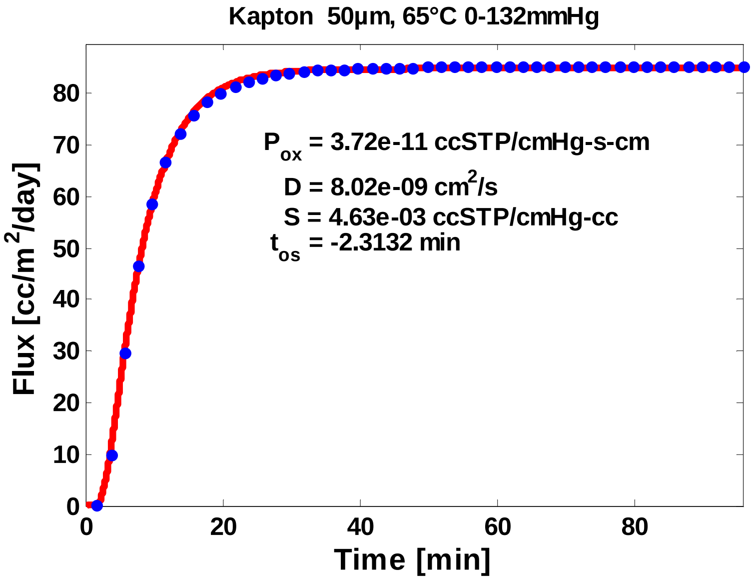
P_{max}= 1.7e-07 ccSTP/cm-s-cmHg (10000 ccSTP/m^2/day, 1cm^2, 1mm, 6.6 cmHg-O_2 (50/50 air/N2)

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

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 to interpret slope of integrated flux curve

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.

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\chi^2} - \frac{\alpha\theta}{\beta\theta+1} \approx \frac{\theta_{i+1,j}-\theta_{i,j}}{\delta\tau} = \frac{\theta_{i,j+1}-2\theta_{i,j}+\theta_{i,j-1}}{\delta\chi^2} - \frac{\alpha\theta_{i,j}}{\beta\theta_{i,j}+1}$$

reactive term (oxidation)

$$\Downarrow$$

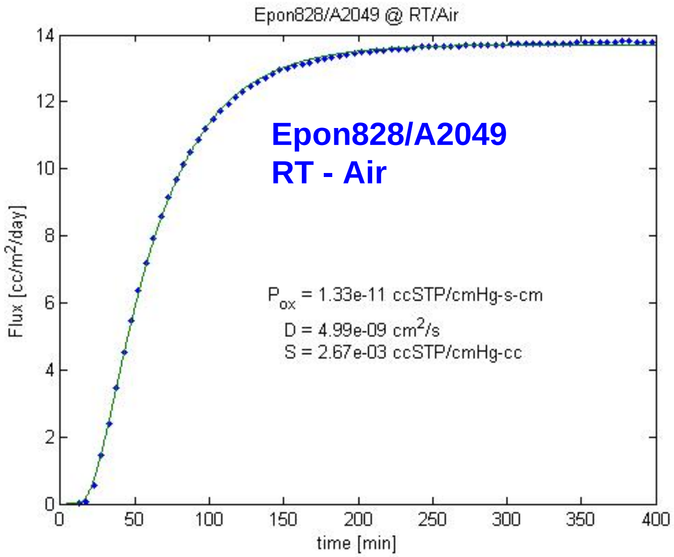
$$\boxed{(a+2)\boldsymbol{\theta}_{i+1} = \mathbb{A}\boldsymbol{\theta}_i - R(\boldsymbol{\theta}_i)}$$

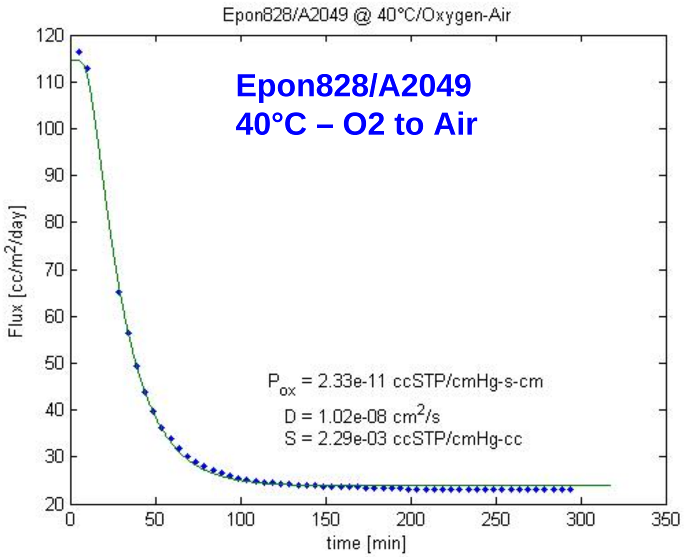
$$\mathbb{A} \equiv \begin{bmatrix} a_1 & \cdots & & \cdots & 0 \\ 1 & a & 1 & \cdots & 0 \\ 0 & \ddots & \ddots & \ddots & 0 \\ 0 & \cdots & 1 & a & 1 \\ 0 & \cdots & & \cdots & a_N \end{bmatrix}, \quad \begin{aligned} a &= \frac{(\delta\chi)^2}{\delta\tau} - 2 \\ a_1 &= \frac{(\delta\chi)^2}{\delta\tau} + \frac{\alpha(\delta\chi)^2}{\beta+1} \\ a_N &= 1 \end{aligned}, \quad R(\theta_{i,j}) = \frac{\alpha\theta_{i,j}(\delta\chi)^2}{\beta\theta_{i,j}+1}$$

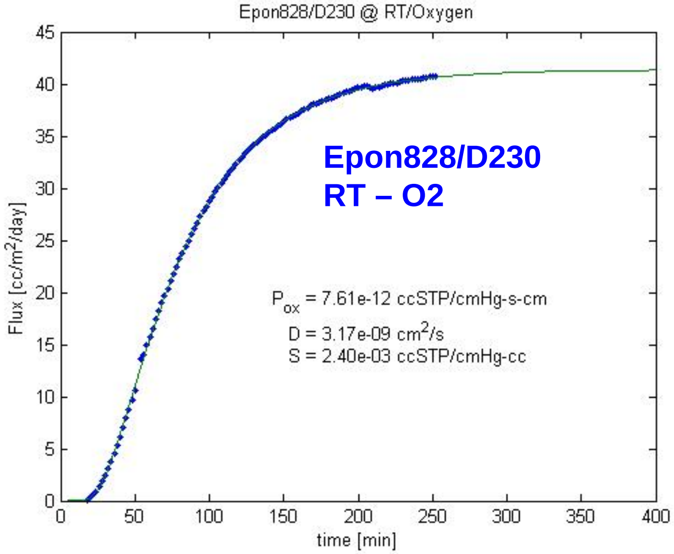
The flux is then calculated from this solution: $F_i = \dfrac{P_{ox}p_0\theta_{N-1,i}}{L(\delta\chi)}$

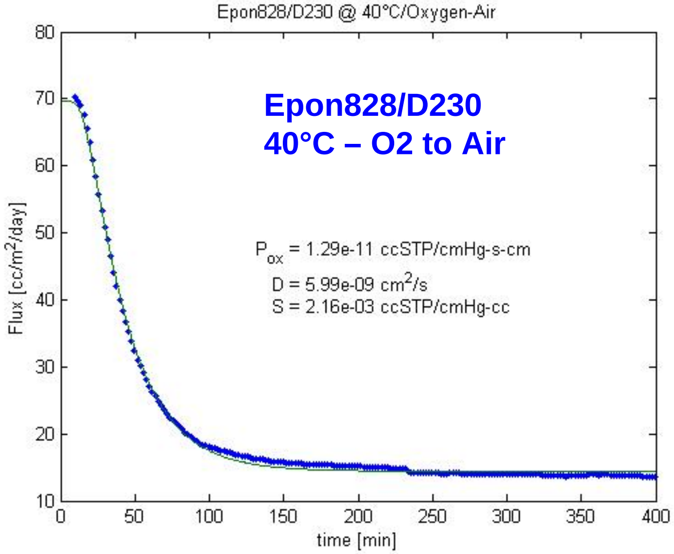
Flux with time is iteratively fitted to experimental data to extract *P*, *D* and *S*

Examples of permeative flux experiments



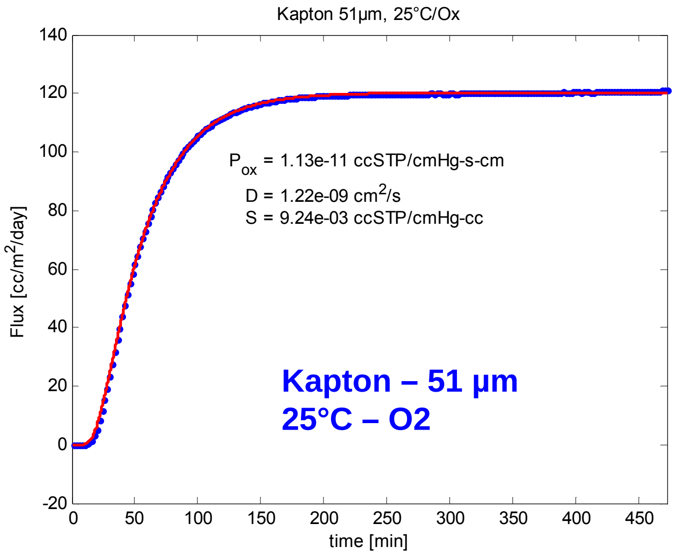






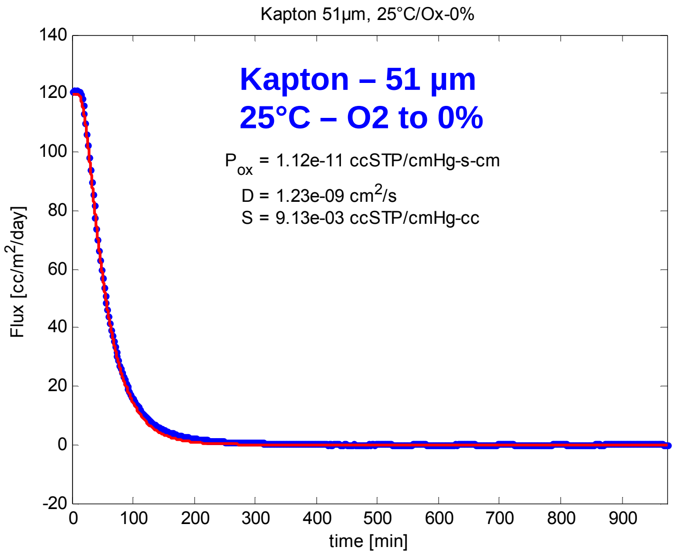
- **D, S available from decreasing and increasing flux and changing pressure experiments**
- **Flux changes modeled with Fickian diffusion behavior – perfect fits**

Examples of permeative flux experiments


Kapton 51µm, 25°C/Ox

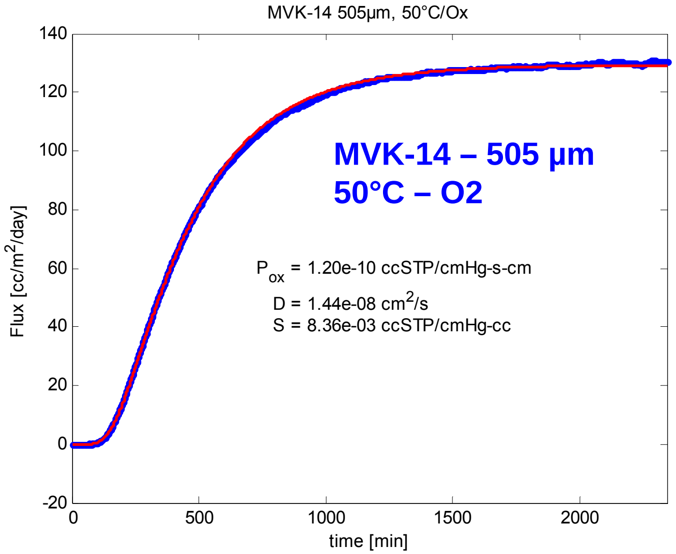
Kapton – 51 µm
25°C – O2

P_{ox} = 1.13e-11 ccSTP/cmHg-s-cm
D = 1.22e-09 cm^2/s
S = 9.24e-03 ccSTP/cmHg-cc


Kapton 51µm, 25°C/Ox-0%

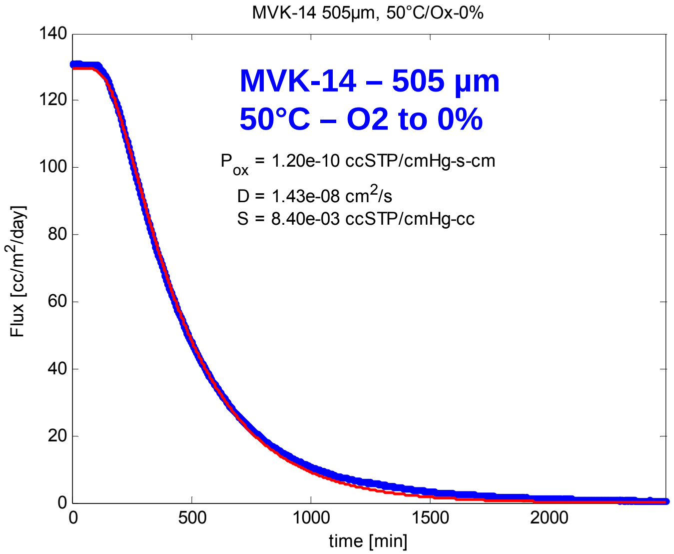
Kapton – 51 µm
25°C – O2 to 0%

P_{ox} = 1.12e-11 ccSTP/cmHg-s-cm
D = 1.23e-09 cm^2/s
S = 9.13e-03 ccSTP/cmHg-cc


MVK-14 505µm, 50°C/Ox

MVK-14 – 505 µm
50°C – O2

P_{ox} = 1.20e-10 ccSTP/cmHg-s-cm
D = 1.44e-08 cm^2/s
S = 8.36e-03 ccSTP/cmHg-cc


MVK-14 505µm, 50°C/Ox-0%

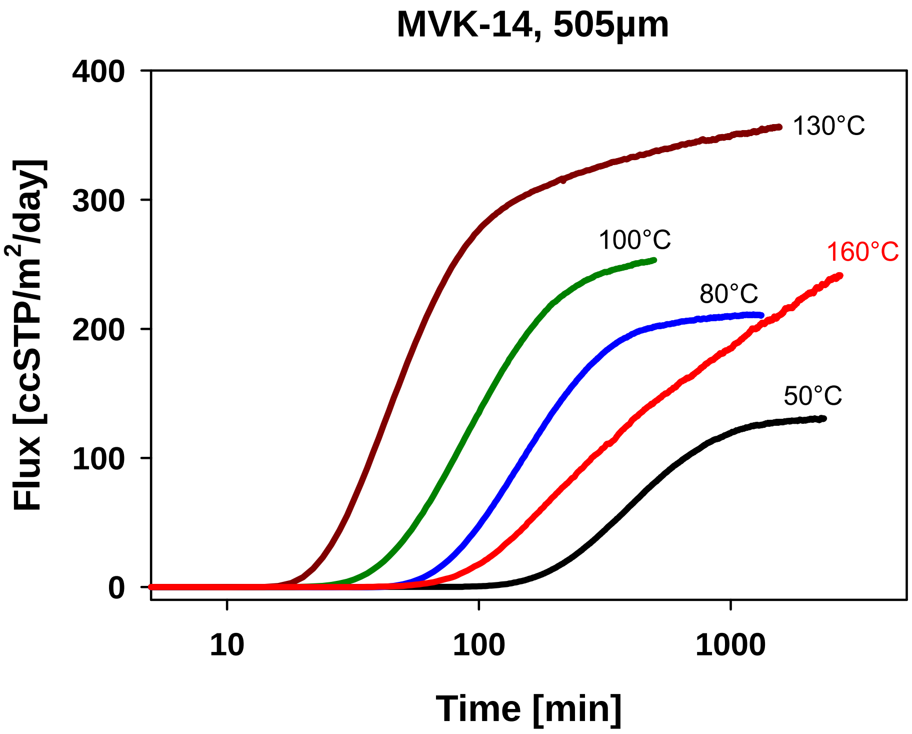
MVK-14 – 505 µm
50°C – O2 to 0%

P_{ox} = 1.20e-10 ccSTP/cmHg-s-cm
D = 1.43e-08 cm^2/s
S = 8.40e-03 ccSTP/cmHg-cc

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

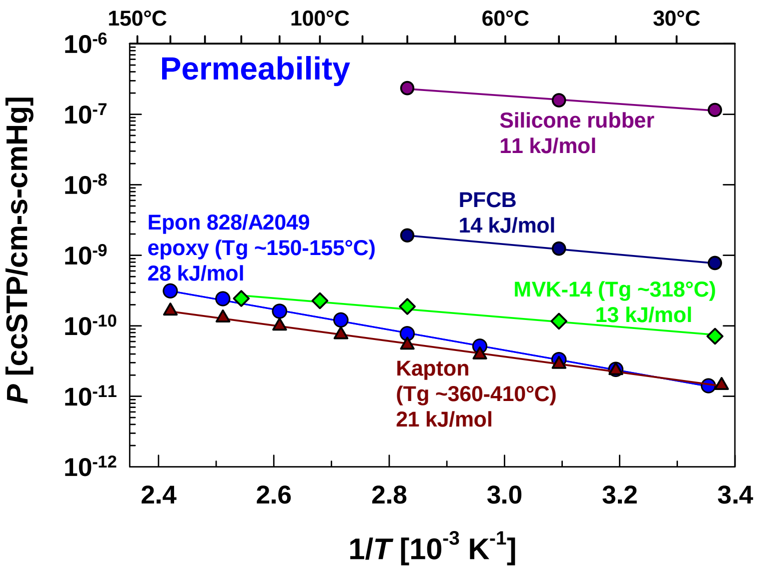
Oxidative reaction reduces flux

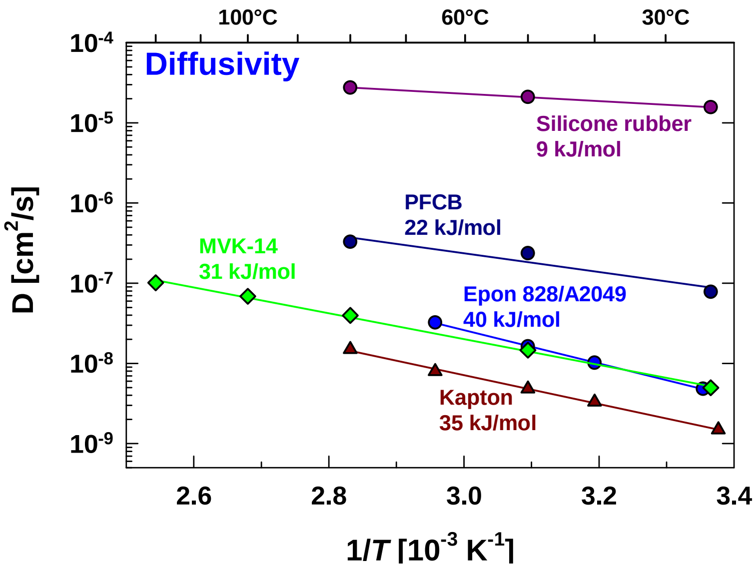
- Reactive oxygen loss results in creep at high temperature
- Effective flux is lower at high T



High T flux data require partial pressure checks and corrections for oxidation

O_2 Permeability – Diffusivity – Solubility

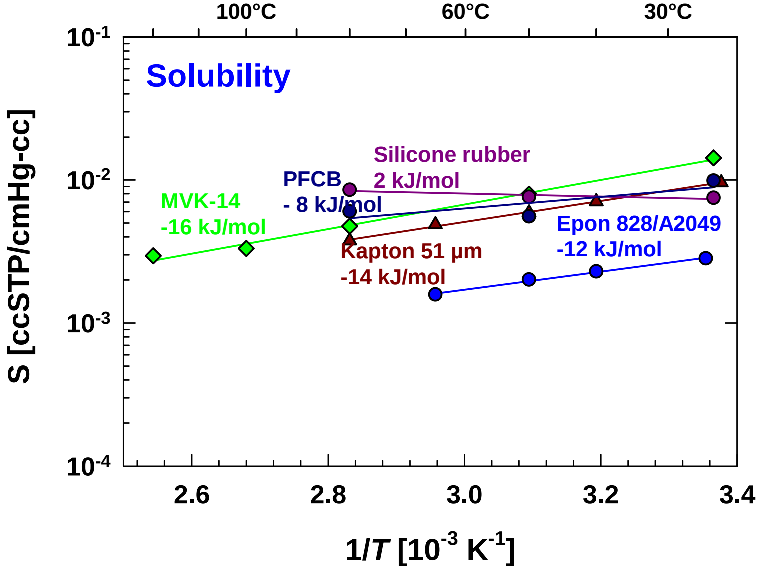




$$\boxed{P_{ox} = D \cdot S}$$

$$\boxed{E_P = E_D + E_S}$$

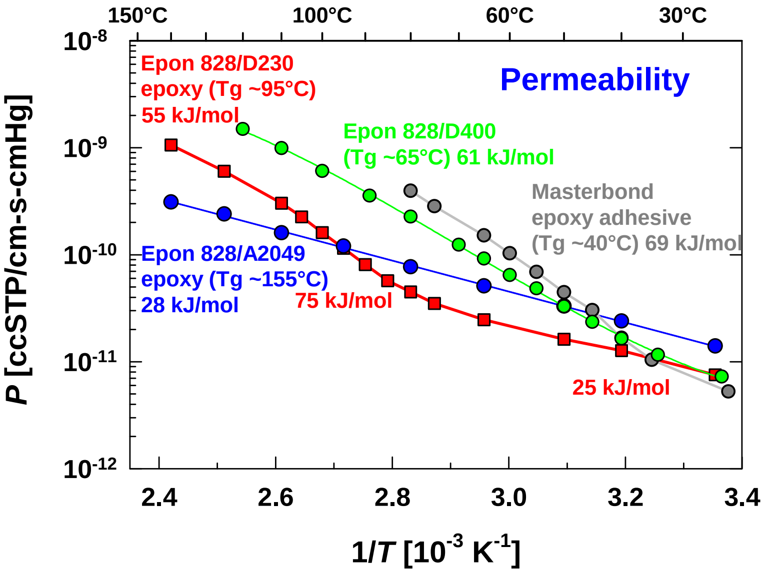
- Ea of 10 to 30 kJ/mol for *P*
- Ea of 10 to 40 kJ/mol for *D*
- Reduced solubility with increased T, up to -15 kJ/mol

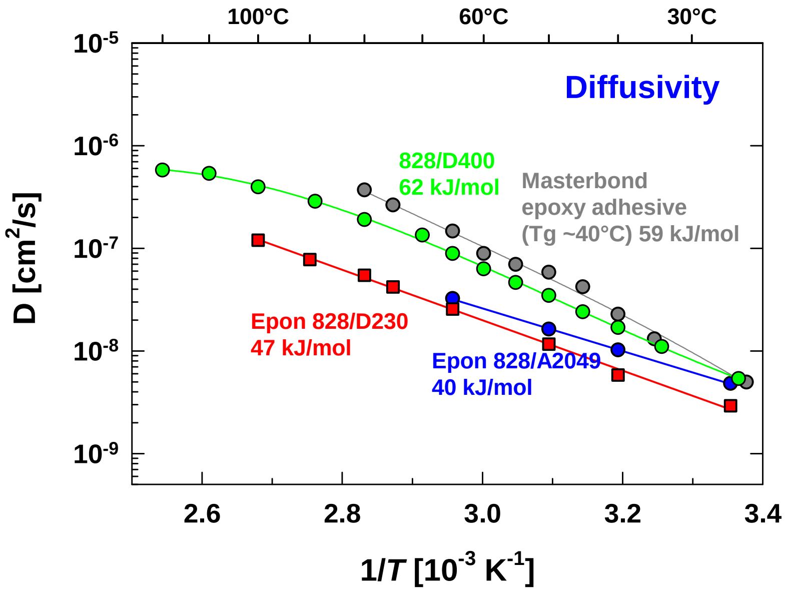


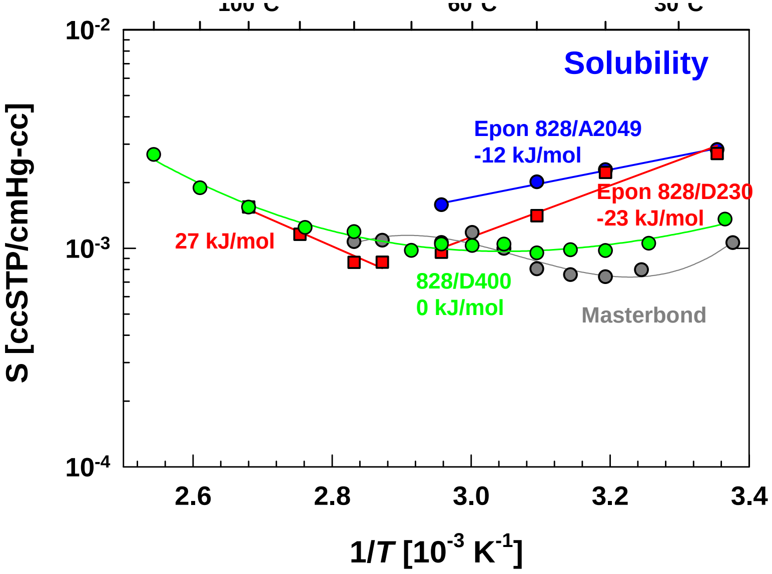
- **Succeeded to measure flux and determine *P, D, S* with temperature**
- **Excellent Arrhenius behavior below Tg and for silicone**

O_2 Permeability – Diffusivity – Solubility

Epoxy systems







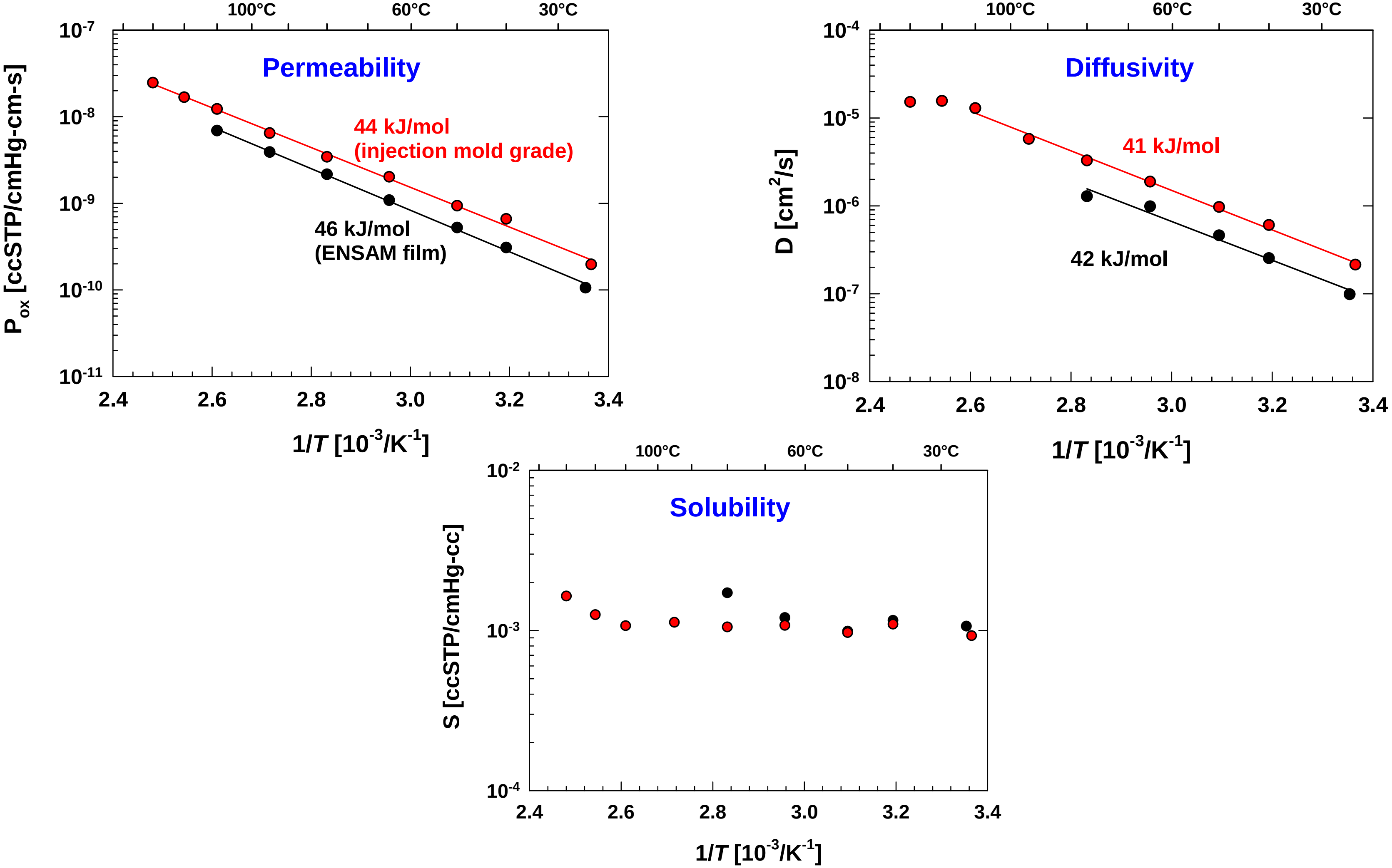
- Ea of up to 75 kJ/mol for *P*
- Ea of up to 60 kJ/mol for *D*
- Solubility increases above Tg

- 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

Polypropylene

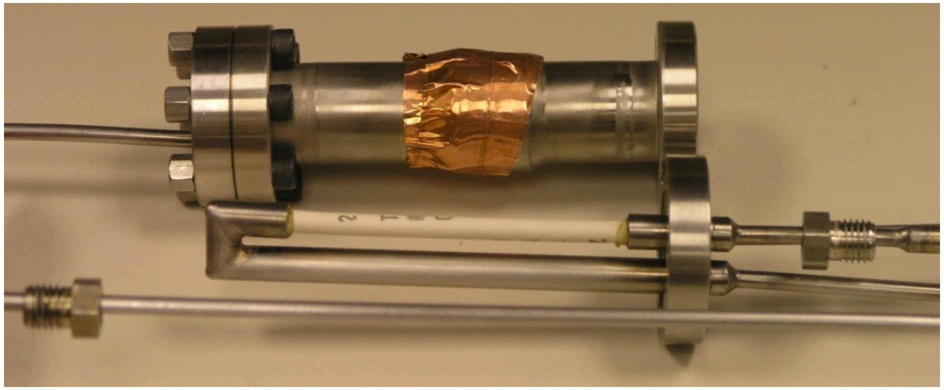
- Parameters needed for extensive kinetic degradation models
- Previous literature data are limited to 50°C



Excellent Arrhenius behavior for *P* (RT - 130°C), *S* essentially constant

Cable insulation

Parameters needed to predict DLO under various degradation conditions

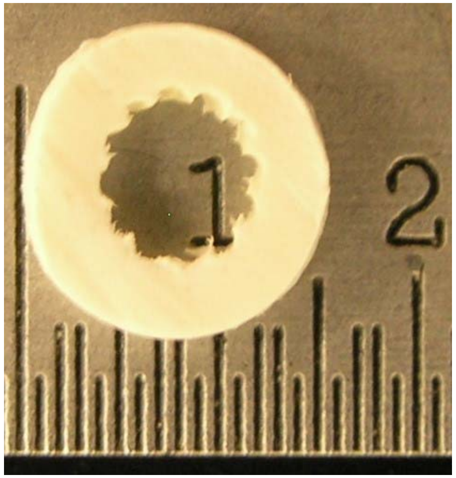


Experimental chamber for feed and detector flow

$$F_{ox} = P_{ox} p_0 \frac{1/\ln {}^{d_{out}}/_{d_{in}}}{{}^{d_{in}}/_{2}}$$

$$\Updownarrow$$

$$P_{ox} = \frac{F_{ox} d_{in}}{2 p_0} \ln \frac{d_{out}}{d_{in}}$$

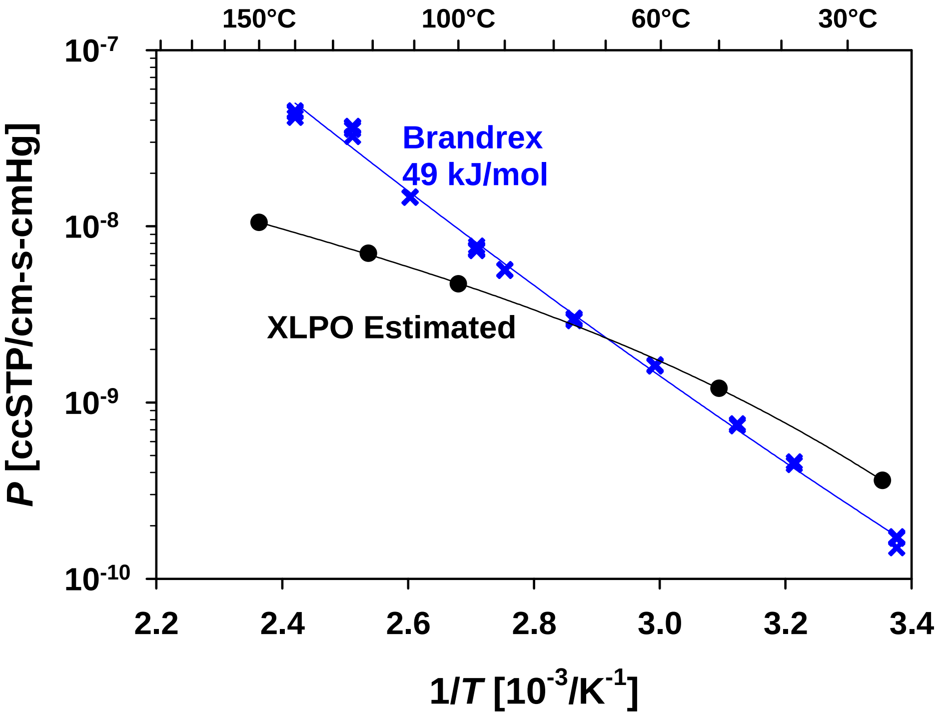


NPP Brandrex cable insulation
Each tick mark = 1/100 inch
External diameter: 3.87 mm
Internal diameter: 2.0 mm
Thickness: 0.94 mm
Length is 58mm

- **Mathematical solution for cylindrical geometry to extract *P* from equilibrium flux**
- **Extraction of *D* much more challenging**

Cable insulation

- **Previous literature data are limited to 50°C with estimations**

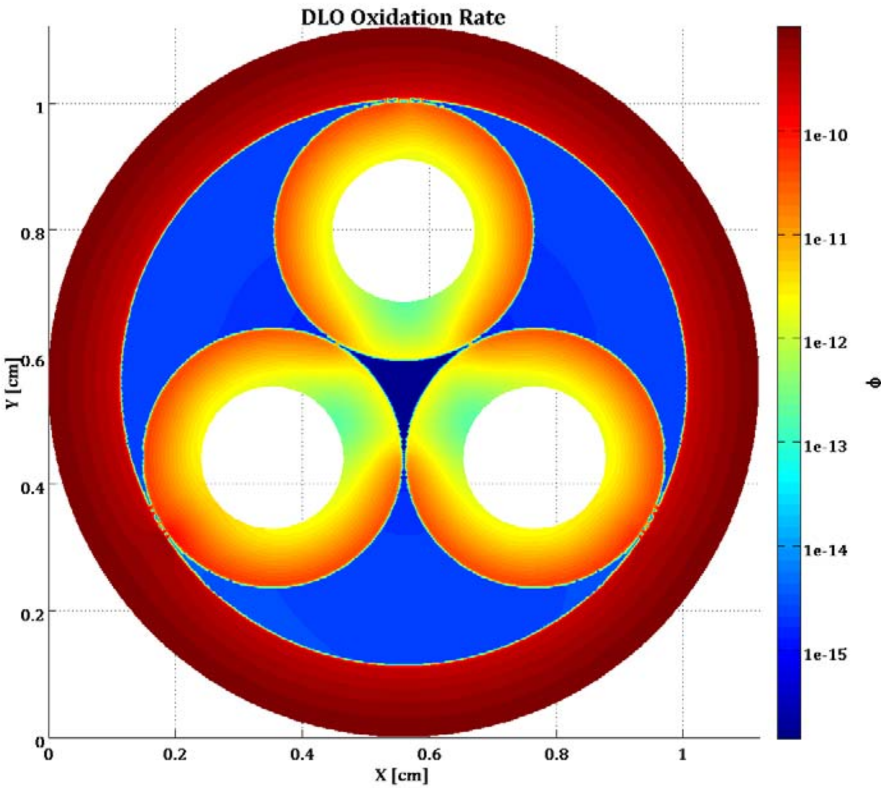


Linear Arrhenius based on first data set for actual cable insulation compound

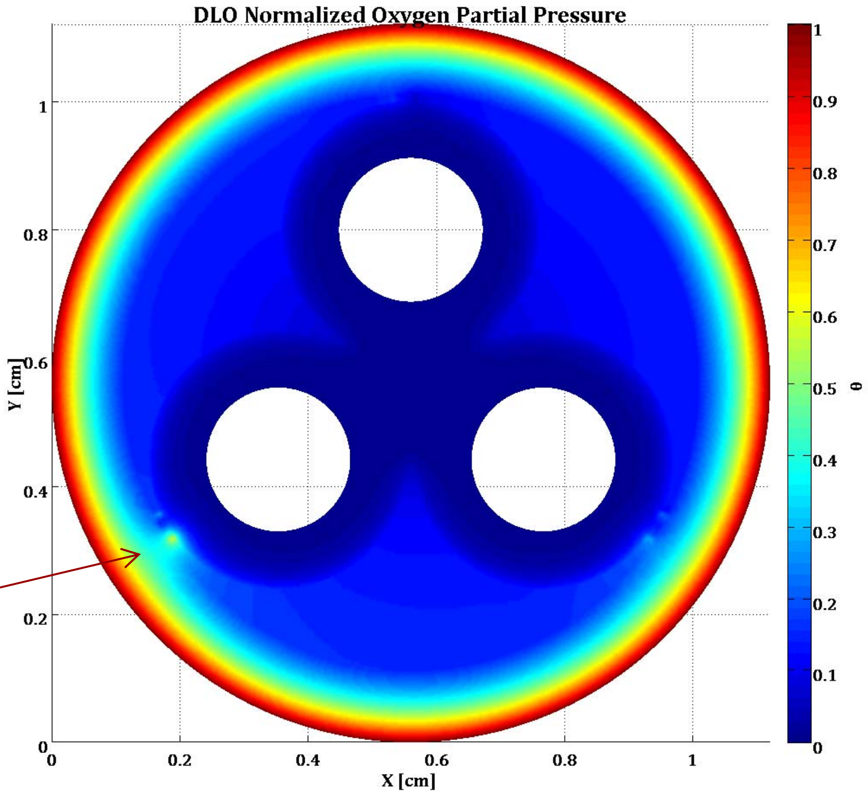
Applications?

Modeling of cable assembly degradation

Permeability is key input into FEM codes



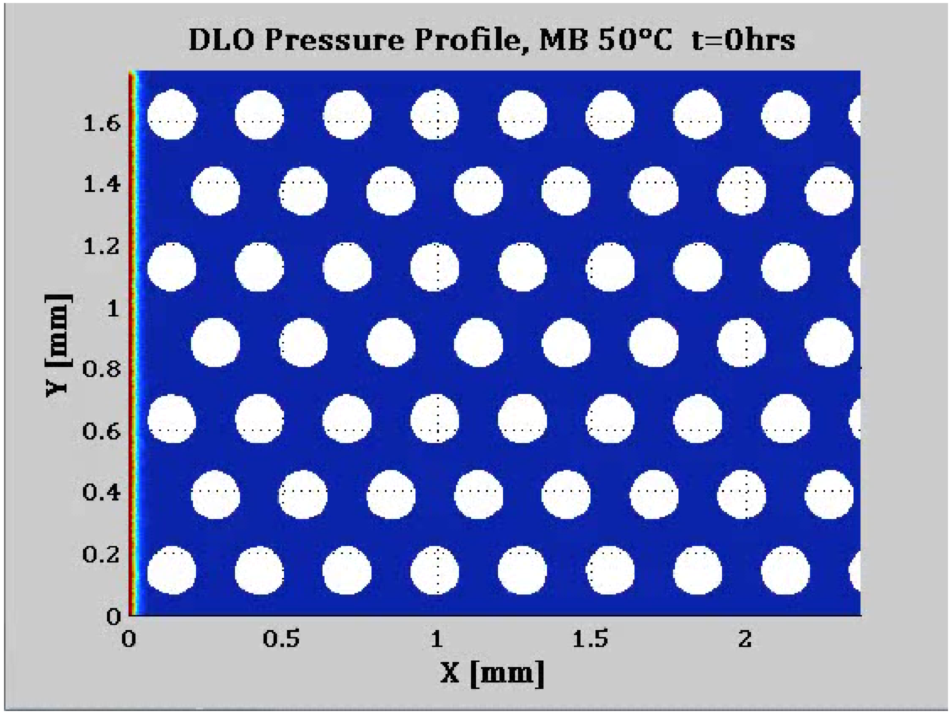
Modeling of cable assembly degradation



Some models unexpectedly show localized HETEROGENEITY

Modeling of DLO evolution

Approach towards non-equilibrium conditions



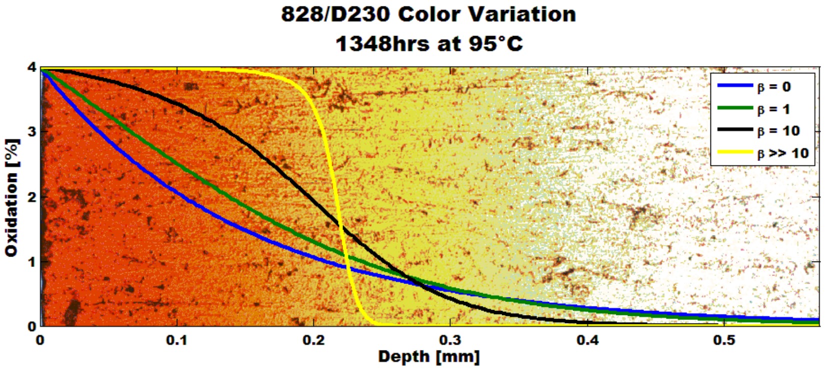
Summary

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

Impact: Predict material oxidation behavior in complex geometries
Have obtained input parameters for advanced DLO degradation models

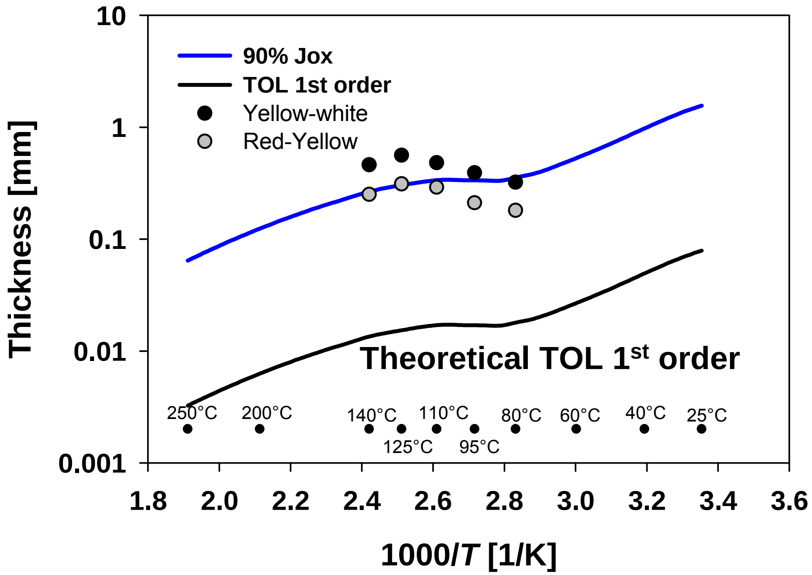
TOL – Total Oxidized Layer - Examples

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



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

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



Theoretical TOL 1st order

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, but does not easily provide the true ratio of diffusivity and oxidation rate, or is very conservative