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Polymer degradation principles - characterization challenges for sorption and transport phenomena

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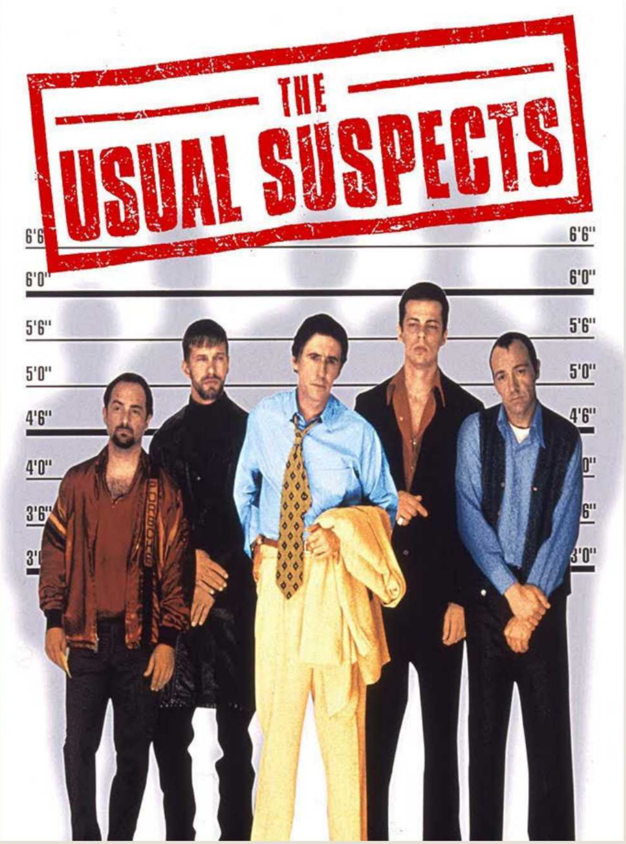
Do you know this movie?

Do these guys look suspicious?

Do you know this movie?



In applied polymer science the USUAL SUSPECT is often DIFFUSION
A variable that often explains our ‘real data’ and the anomalies

Motivation and Challenges

Polymer degradation and materials characterization often involves diffusion processes, reagent transport (O_2, H_2O) and exchange of small molecules

- Aging - Off-gassing - Compatibility
- Oxidative aging
- Hydrolytic aging
- Drying and best processing of materials
- Solvent loss, trapped species, delayed release
- Swelling and reversible stress states

Ongoing broad research goals to measure, model and predict sorption, diffusion and permeation processes

Goals: Improved diagnostic methods, time resolved spectroscopy, understanding material behavior, quantitative predictions, mechanistic evaluation, spatially and time dependent degradation chemistry

The Simple View

D	x	S	=	P
Diffusivity (diffusion constant)		Solubility		Permeability

- Specific material properties for polymer and penetrant

- Fick's law offers time and concentration relationships

- Guiding data are available in Polymer Handbook and Polymer Property text books

Whenever motion and TIME is involved we consider DIFFUSION
When we quantify reactions and masses we need PERMEATION

The Big Picture View

Basics

Diffusivity
Permeability
Solubility

Diffusion
Permeation
Sorption

Time
Fick's law
Slow
Transport

Rates
Diffusion constant
Dissolved species

Concentration
Non-linear
Small molecules

Square root
Migration

Complicating Extras

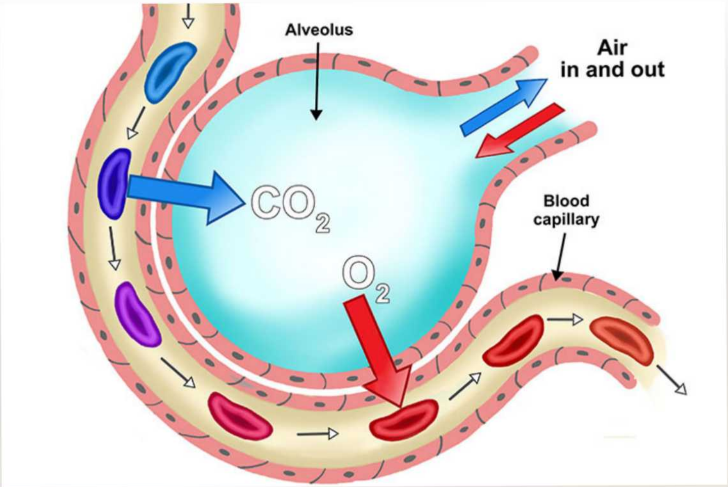
Depth
Tg
Mean free path
Mobility variations
Mean square collision diameter
Free volume
Polymer chain flexibility
Desorption
Differential equations
Gradient
Partial pressure

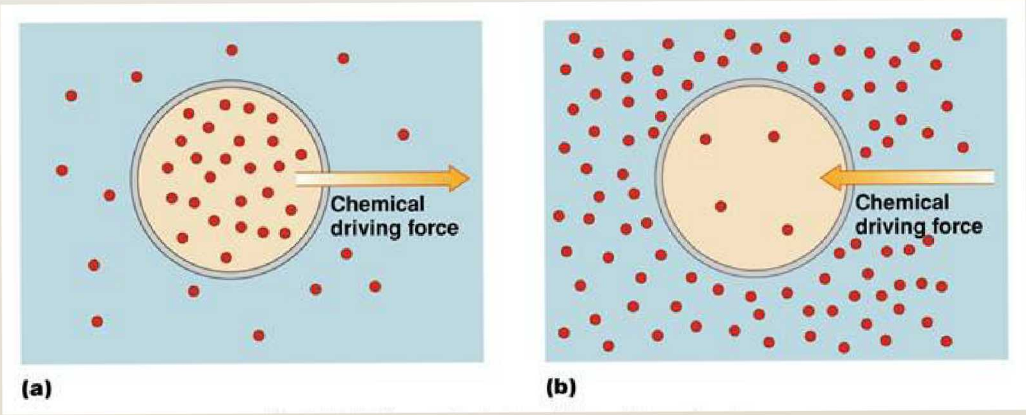
Consequences

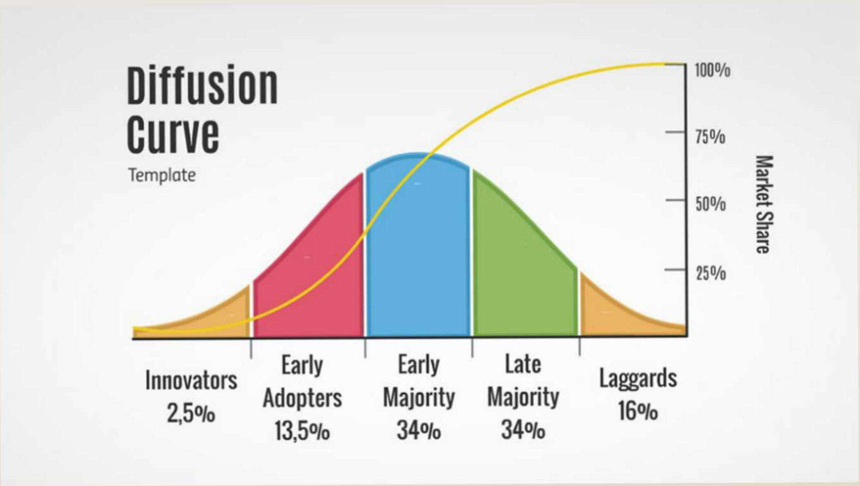
Diffusion profile
Diffusion control
Local properties
Local reactivity varies
Max. Penetration
Spatial dependence
Surface degradation
Permeative Flux
Trapped species
Quantitative off-gassing difficult

All the things that we didn't really study in 'physical chemistry'

Diffusion is Everywhere







Our creativity is hopefully also diffusing forward

Mathematical Description - Polymer Oxidation

MODEL CONCEPT - OXIDATION & DIFFUSION

Oxidation rate derived from the Basic Auto-Oxidation Scheme (BAS):

$$-r_{O_2} = \phi = \frac{k_a[O_2]}{k_b[O_2]+1}$$

Incorporation into Fick's second law:

$$\frac{\partial\theta}{\partial\tau} = \nabla^2\theta - \frac{\alpha\theta}{\beta\theta+1}$$

Pressure dependence of oxidation rate:

$$\frac{\phi}{\phi_0} = \frac{\beta+1}{\beta+{}^{1}/_{\theta}}$$

DLO model parameters:

$$\frac{\alpha}{\beta+1} = \frac{\phi_0 L^2}{P_{ox}p_0}$$

$$\alpha = \frac{k_1 L^2}{\boldsymbol{D}}$$

$$\beta = k_2 S p_0$$

$$\theta = {}^{p}/_{p_0}$$

$$\tau = \frac{t\boldsymbol{D}}{L^2}$$

$$\chi = {}^{x}/_{L}$$

$$\boldsymbol{P_{ox} = DS}$$

$[O_2] = \boldsymbol{S}p_0$ (Henry's Law)

MODEL PARAMETERS

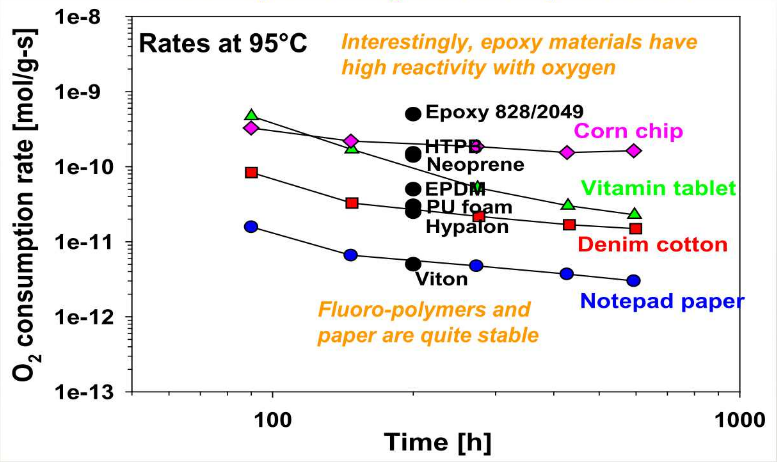
k_a, k_b . .	BAS overall rate constants
α, β. . . .	DLO model parameters
ϕ	Oxidation rate [mol/g/s]
θ	Relative oxygen partial pressure
$\boldsymbol{P_{ox}}$	Oxygen Permeability [ccSTP/cm/s/cmHg]
$\boldsymbol{D}$	Diffusivity [cm^2/s]
$\boldsymbol{S}$	Solubility [mol/cc/cmHg]
p_0	Oxygen partial pressure (reference) [cmHg]
χ	Relative position
L	Thickness (reference) [cm]
τ	Normalized time
t	Time [s]
Ω	Spatial integrator depending on dimension
φ	Simplex interpolation function

- **Many years of developmental work – SNL is a global leader**
- **Interdisciplinary material science is the foundation for aging models**

Gillen KT, Clough RL. Rigorous experimental confirmation of a theoretical model for DLO. Polymer 1992;33:4358.

Reactive Diffusion Models Development

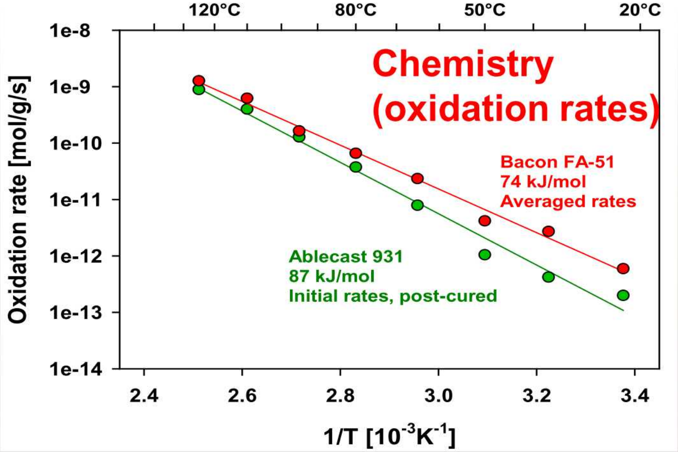
Polymer oxidation relevant to reliability and degradation processes



Interestingly, epoxy materials have high reactivity with oxygen

Fluoro-polymers and paper are quite stable

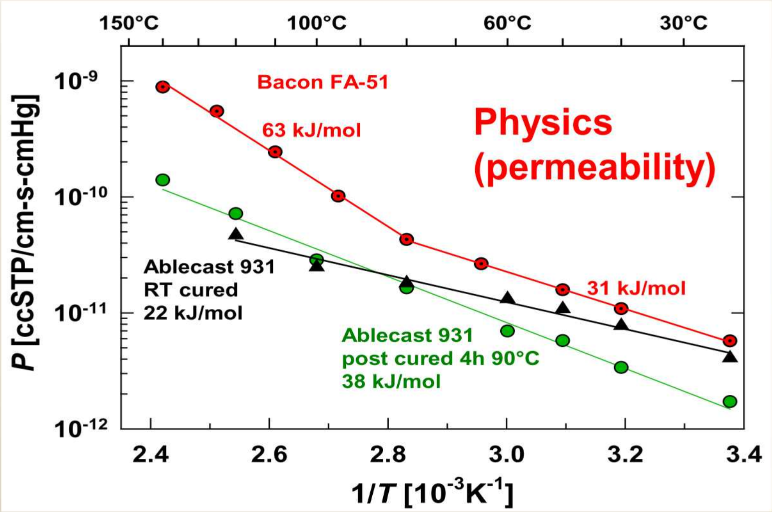
Measured intrinsic oxidation behavior for epoxies in Bell XI



Chemistry (oxidation rates)

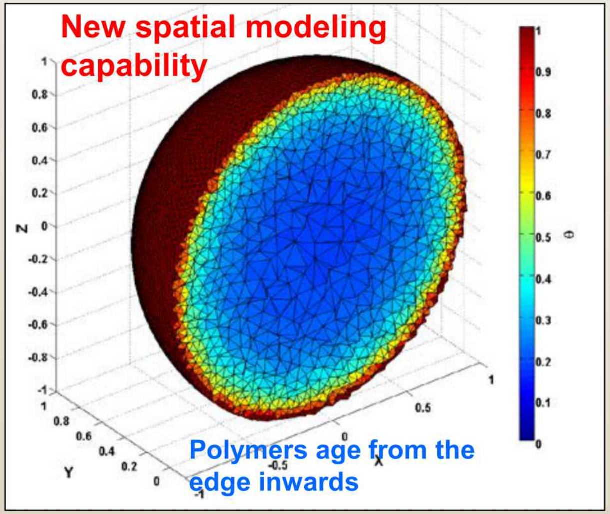
Celina MC, Dayile AR, Quintana A. A perspective on the inherent oxidation sensitivity of epoxy materials. Polymer 2013;54:3290.

Measured oxygen permeation for epoxy materials in Bell XI



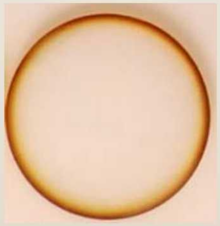
Physics (permeability)

Applied FEM DLO model capability for spatially resolved polymer degradation



New spatial modeling capability

Polymers age from the edge inwards



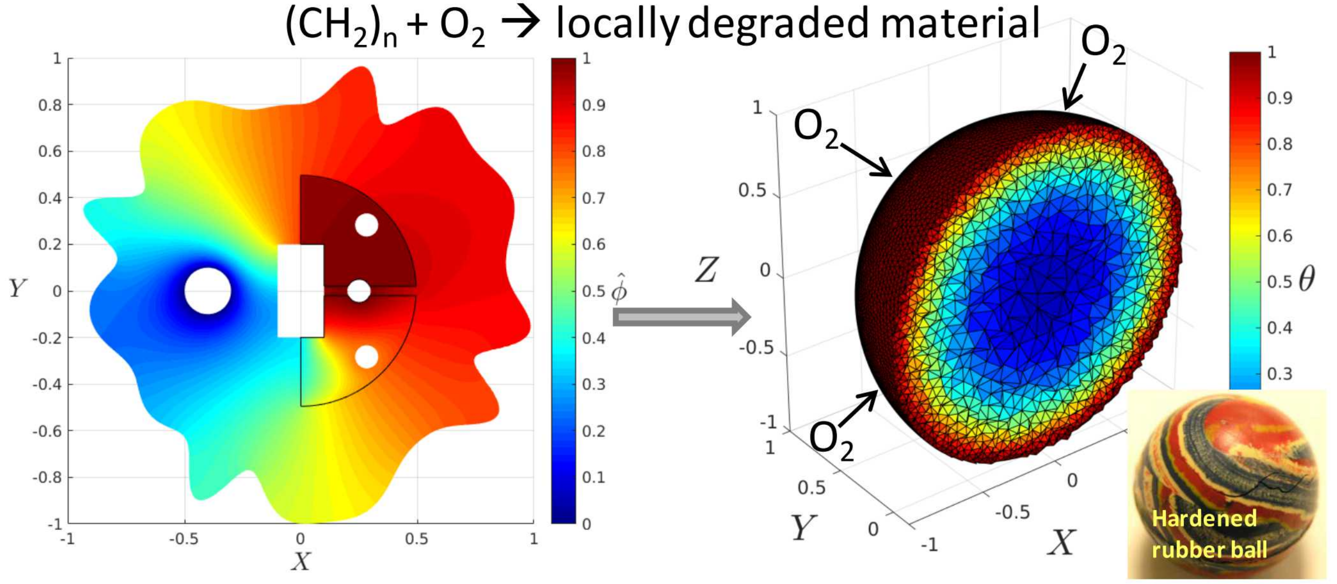
Exptl.
Aged epoxy

Polymer Aging and Predictive Behavior: Principles of Oxidative Polymer Degradation

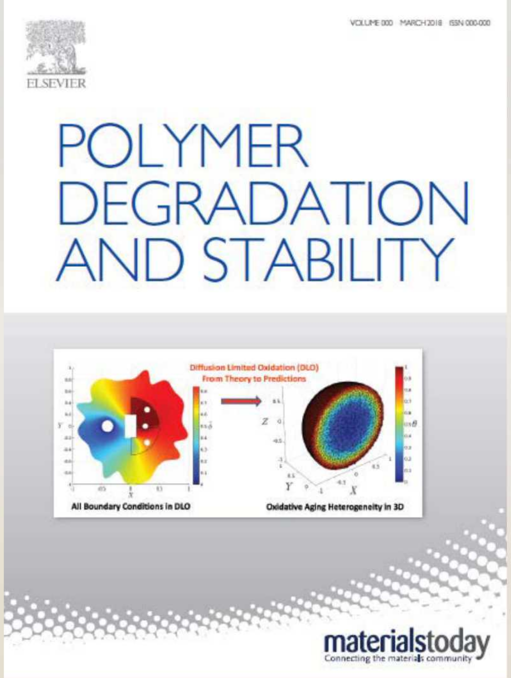
- Continuing SNL leadership with state of the art mathematical models
- Requires understanding of oxidation and reactive diffusion processes

Heterogeneous Polymer Degradation: **From the Theory of Oxidation to Predictions**
1D Definitions to describe 3D Surface Diffusion Limited Oxidation (DLO)

$(CH_2)_n + O_2 \rightarrow$ locally degraded material



All Boundary Conditions in DLO **Oxidative Aging Heterogeneity in 3D**



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ELSEVIER

POLYMER DEGRADATION AND STABILITY

Diffusion Limited Oxidation (DLO) From Theory to Predictions

All Boundary Conditions in DLO

Oxidative Aging Heterogeneity in 3D

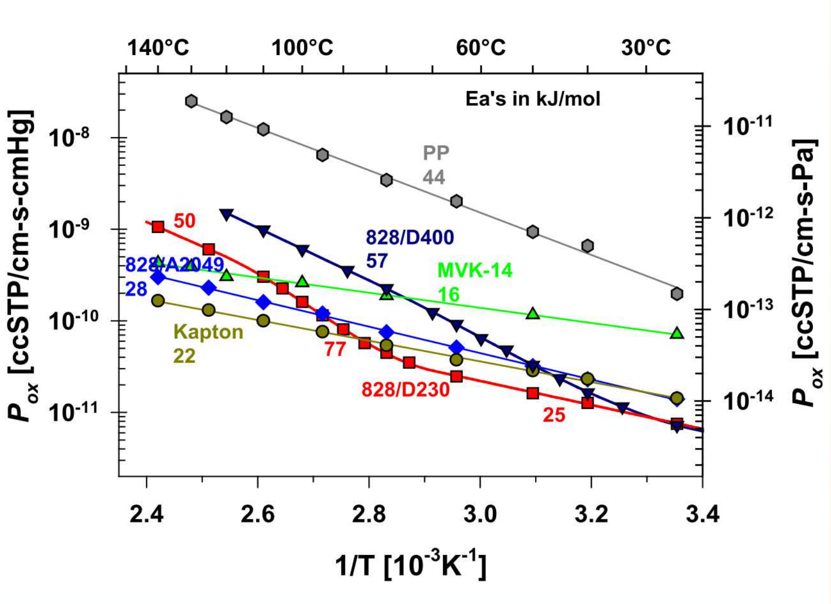
materialstoday
Connecting the materials community

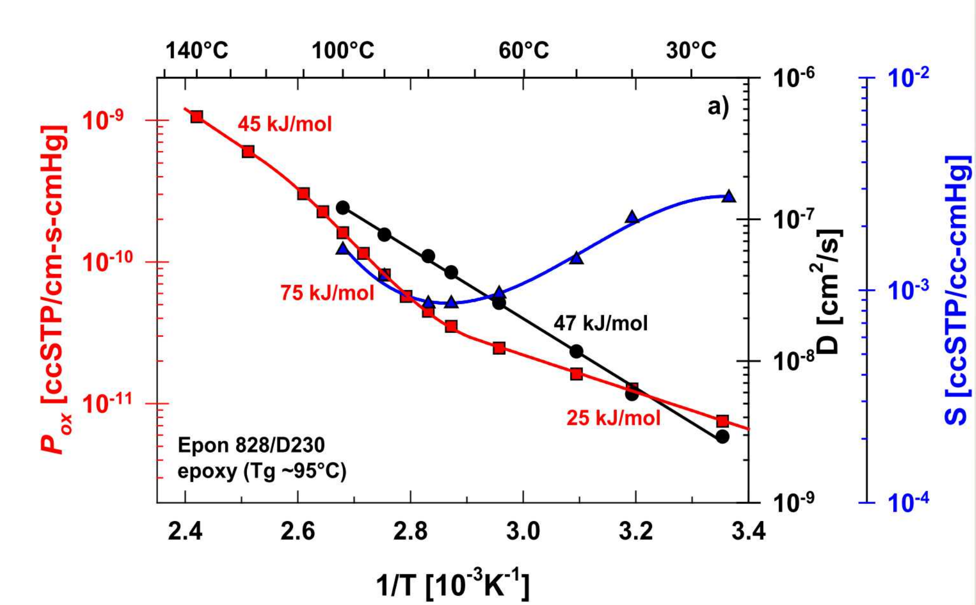
Published Review of Current Status in this Field, Added Innovative Mathematical Definitions and Concepts (PDST Inaugural Journal Cover)

Quintana A, Celina MC. Overview of DLO modeling and approaches to predict heterogeneous oxidative polymer degradation. Polym Degrad Stab 2018;149:173.

O2 Permeation and Diffusivity with T

- **Developed instrument and computational method to determine D from time dependent flux curves with temperature**
- **Systematic characterization for a few thermosets and PP**

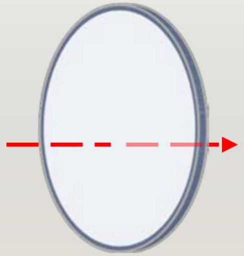




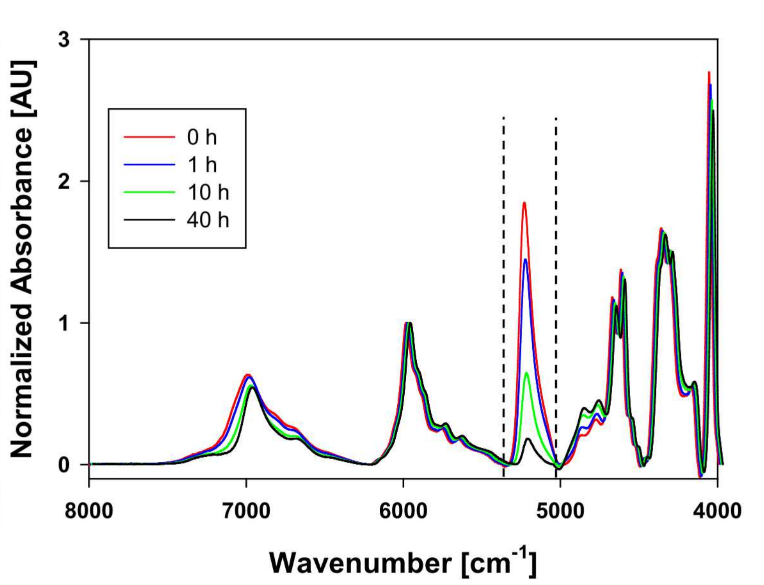
Tg induces change in free volume, <u>but does not affect Diffusivity</u> (solubility instead)
This is in contrast with the literature expectations (Cohen-Turnbull model)

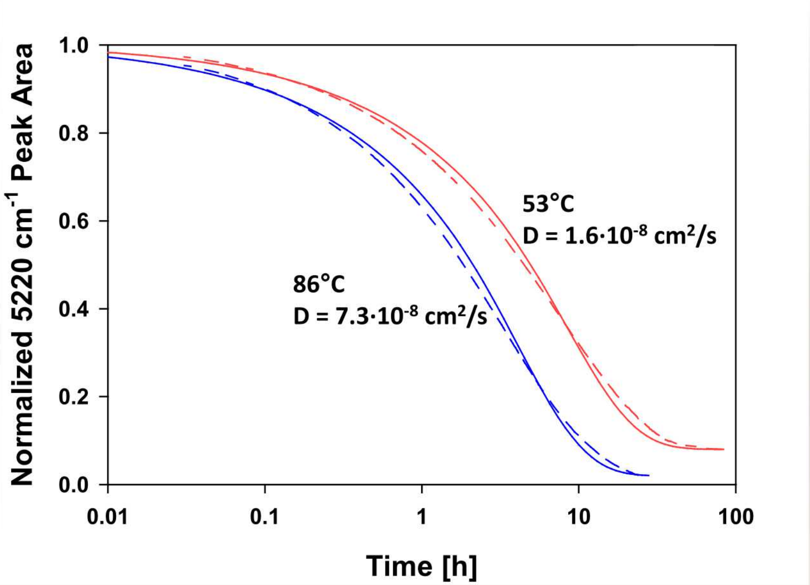
Celina MC, Quintana AD. Oxygen diffusivity and permeation through polymers at elevated temperature. Polymer 2018;in print.

Monitoring Water Content by NIR



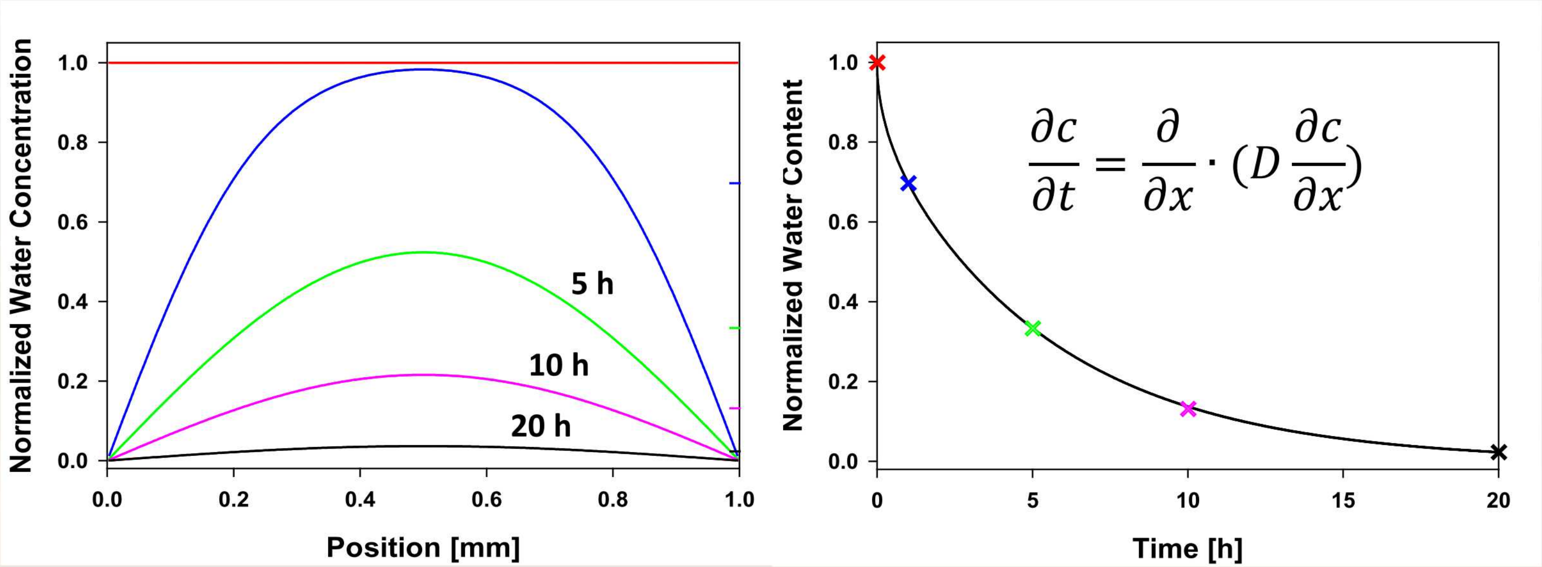
Diameter ≈ 40 mm
Thickness ≈ 1 mm





- **Transmission near IR spectroscopy monitors physically dissolved water content within a sample**
- **Changes in the 'water band' around 5220 cm^{-1} were used to follow the desorption kinetics from a disc-shaped sample**
- **Thin discs (thickness << diameter) allows for 1D simplification**

1D Fickian Diffusion

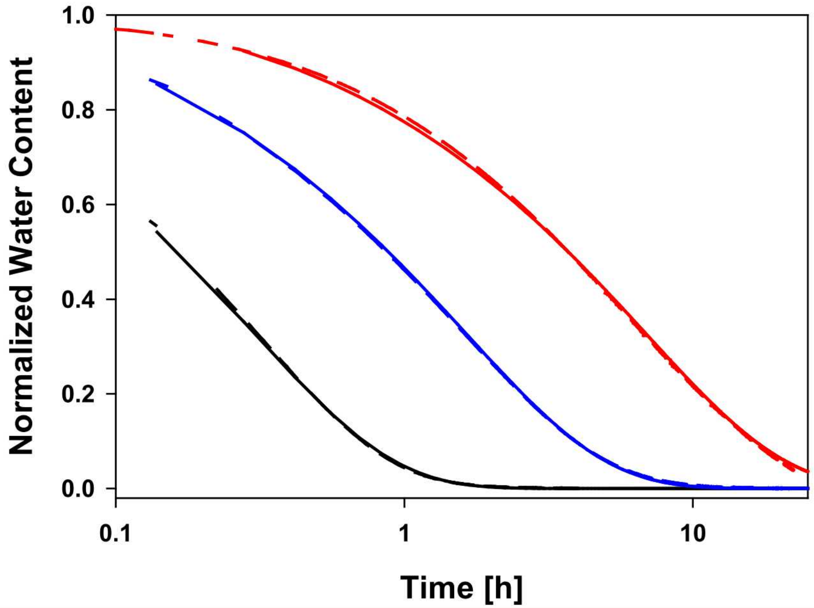


$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \cdot \left(D \frac{\partial c}{\partial x}\right)$$

- Desorption follows Fickian diffusion with a constant *D*
- A finite difference model was used yielding the spatial water distribution and average water content as a function of time
- *D* was obtained through fitting the simulated desorption curve with the experimental data

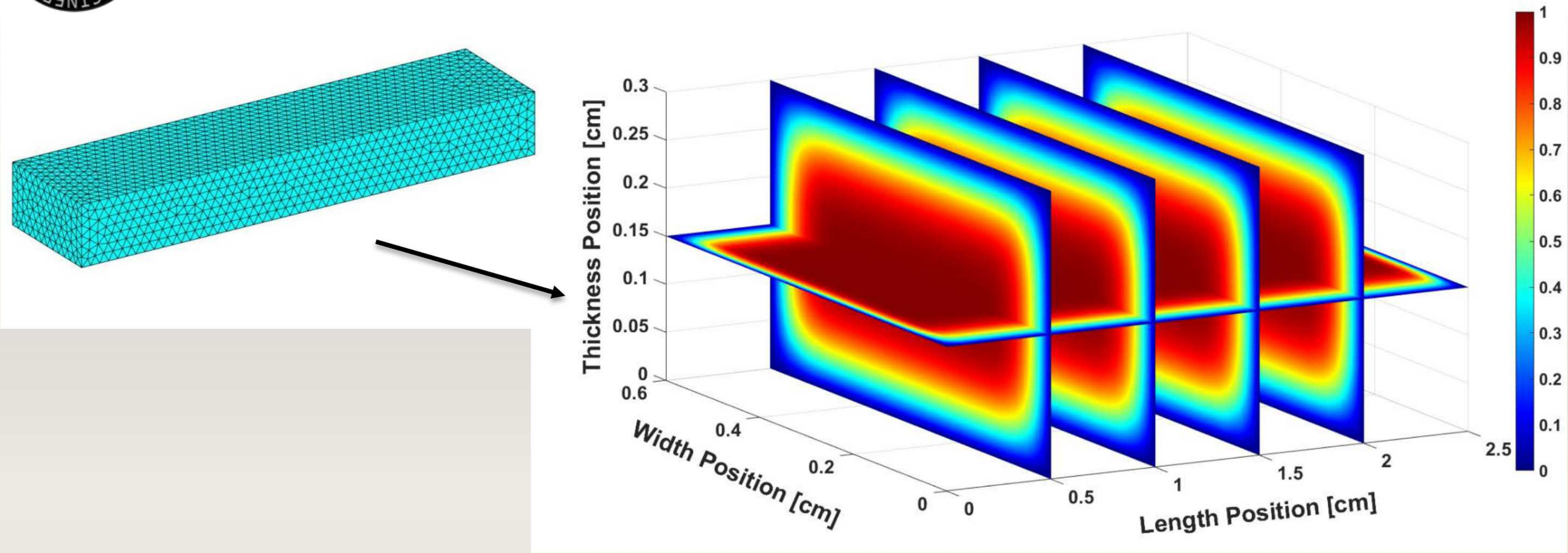
Weight Loss Kinetics by TGA

25 x 6 x 3 mm



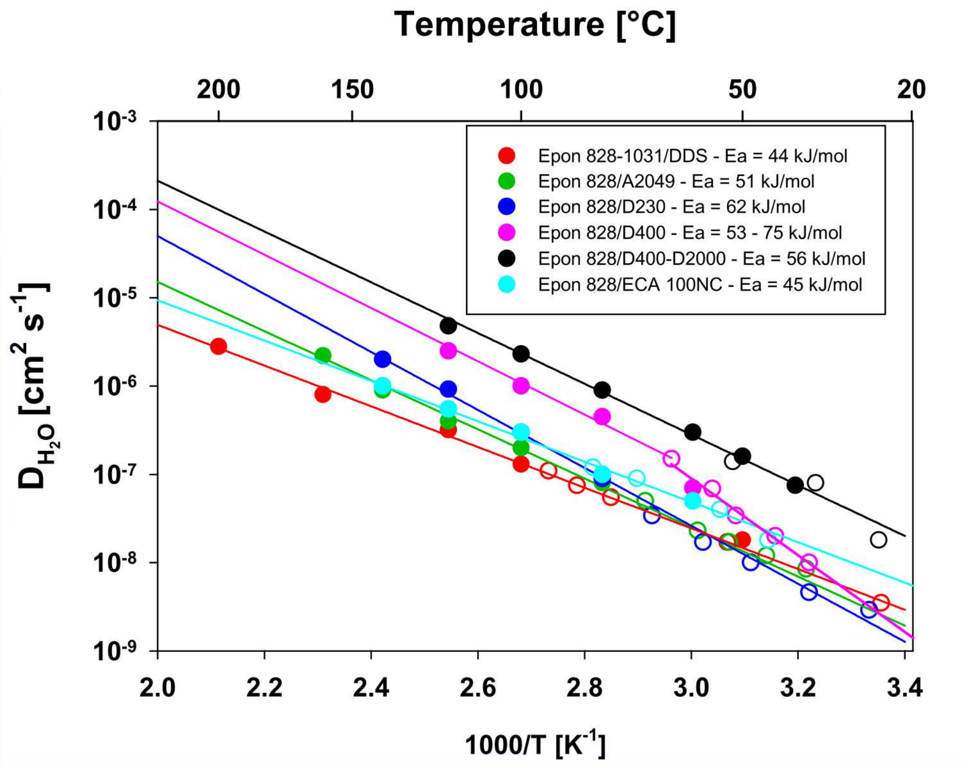
- **TGA enables measurements at higher temperatures**
- **The mass loss follows Fickian diffusion**
- **The samples dimensions require 3D modeling to extract *D***

3D Finite Element Model



- The 3D finite element model is used to extract *D* based on average water content given by the TGA drying curve
- Simulations yield the spatially and temporally resolved water concentration in the material

D as a Function of T



- **Most materials show a single *E_a for* diffusivity over the investigated temperature range (linear Arrhenius)**
- **One material, Epon 828/D400, shows a change in *E_a* at *T_g* (~ 65°C), from 53 kJ/mol below to 75 kJ/mol above *T_g***
- **For most materials *T_g* has no influence on *E_a* of *D***

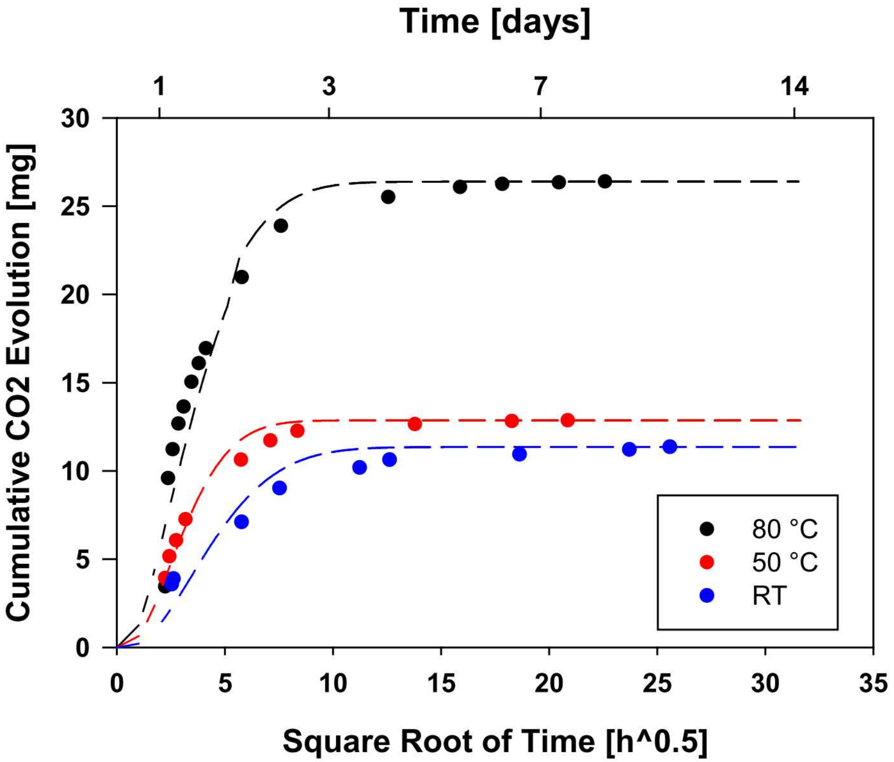
Linde E, Giron NH, Celina MC. Water Diffusion with Temperature Enabling Predictions for Sorption and Transport Behavior in Thermoset Materials. Polymer 2018; in revision.

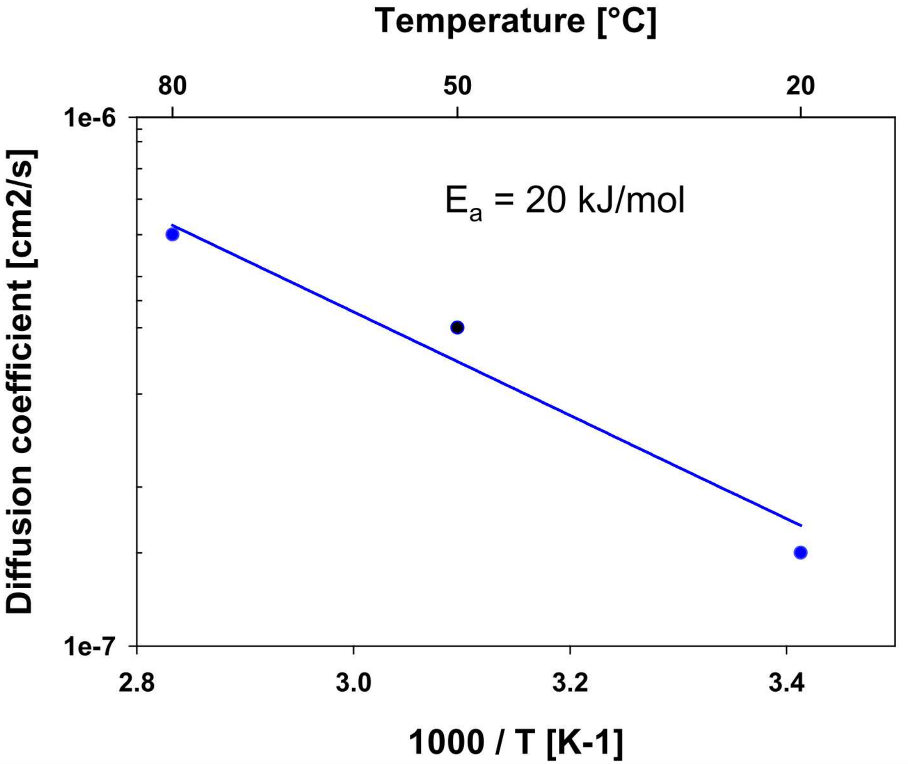
Volume Increase – Free Volume

	Measured uptake [100·g_{H2O}/$cc_{polymer}$]	D 65°C [cm^2/s]	$E_{a,D}$ [kJ/mol]	Ideal volume increase without free volume [%]	Measured volume increase [%]	Fraction of water occupying free volume [%]
E828 –E1031/DDS	5.8	3.0*10^{-8}	44	5.8	4.2	28
E828/A2049	2	3.2*10^{-8}	51	2	1.3	35
E828/D230	3.3	3.5*10^{-8}	62	3.3	2.0	39
E828/D400	3.6	1.3*10^{-7}	<65°C: 75 >65°C: 53	3.6	2.4	33
E828/D400- D2000	3.8	3.7*10^{-7}	56	3.8	N/A	N/A
E828/ECA 100NC	1.6	6.1*10^{-8}	45	1.6	0.8	50

- **Max water uptake for epoxies is ~ 15 to 60 mg$_{H2O}$/cc$_{Polymer}$**
- **The volume increase is smaller than the sum of the volume of polymer and the volume of absorbed water**
- **Some absorbed water occupies the free volume ranging from 28% (DDS cured) to 50% (ECA 100NC cured)**
- **Solubility and diffusivity are independent parameters**
- **Despite some free volume and glassy state, the materials swell significantly even at RT**

CO_2 Evolution Curves from PU



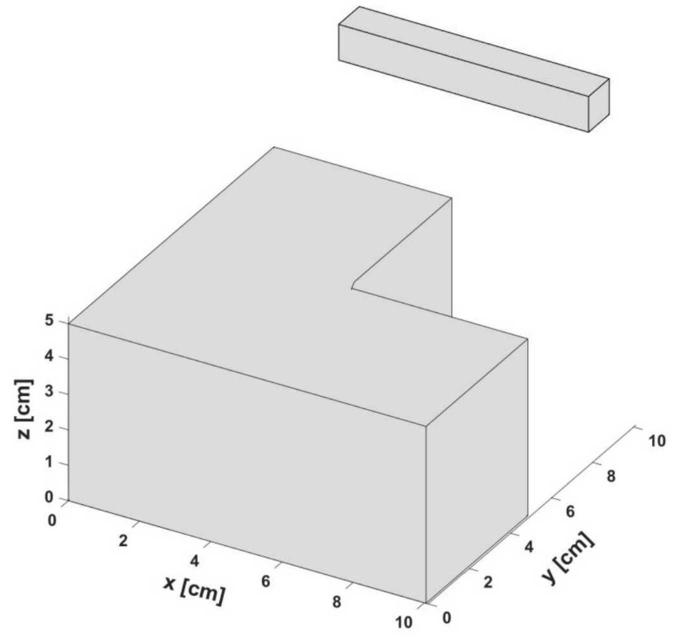


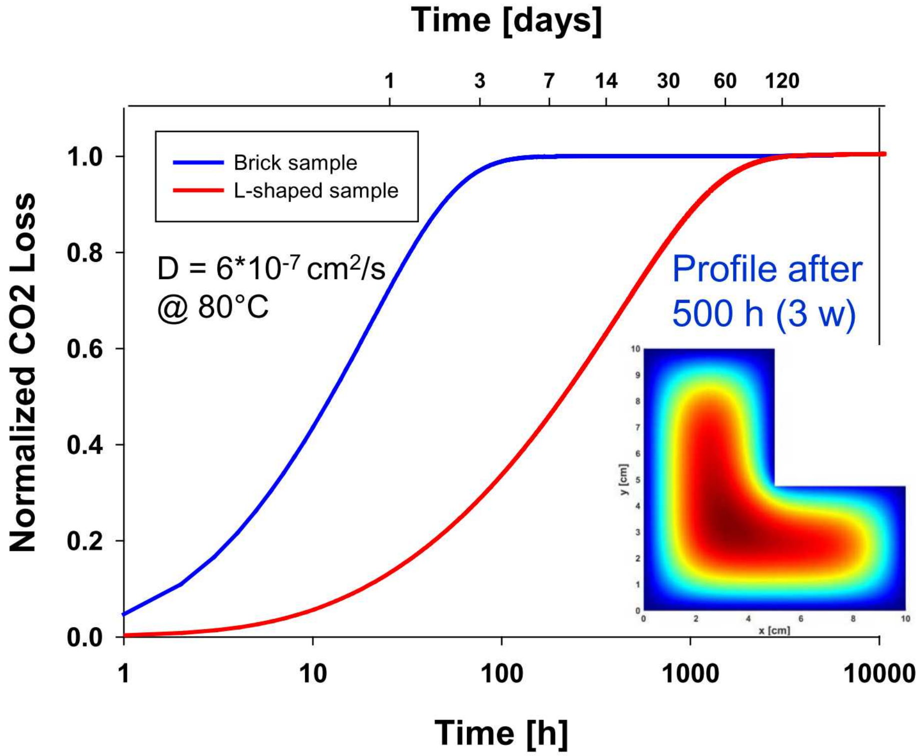
- CO_2 mass loss was fitted with a single D FEM model for that specific geometry.
- A diffusion coefficient also defines the initial linear slope of CO_2 yield in a plot against square root of time; a higher D leads to a higher slope.
- The value of the Ea (20 kJ/mol) for D is of similar magnitude as observed for other diffusion phenomena, such as water in epoxies.

Note: D cannot be determined from these primary yields curves as sample geometry must also be taken into account

Simulating CO_2 Loss from Other Shapes

Size comparison of the brick sample run at 80 °C and a simulated L-shaped sample



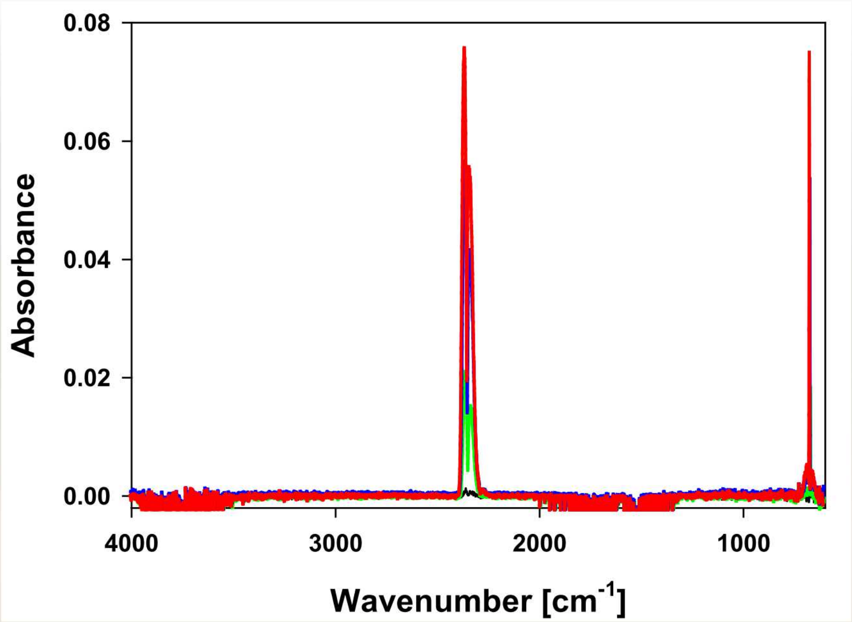


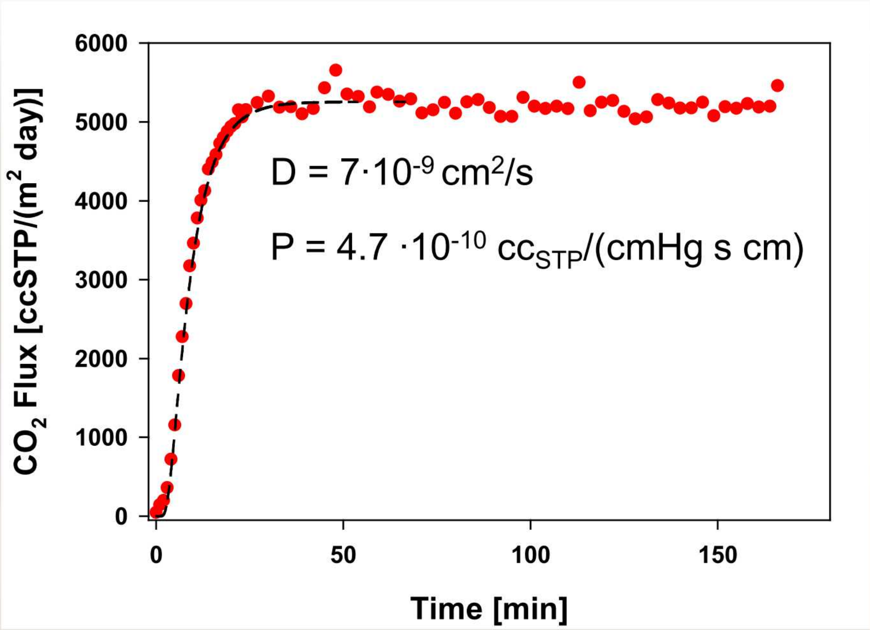
D = 6*10^{-7} cm^2/s @ 80°C

Profile after 500 h (3 w)

- By using the values of D obtained from the experimental data, the behavior of other, more complex shapes can be assessed.
- Long-term physical desorption at RT can be predicted.

Gas Transport Quantification with mid-IR



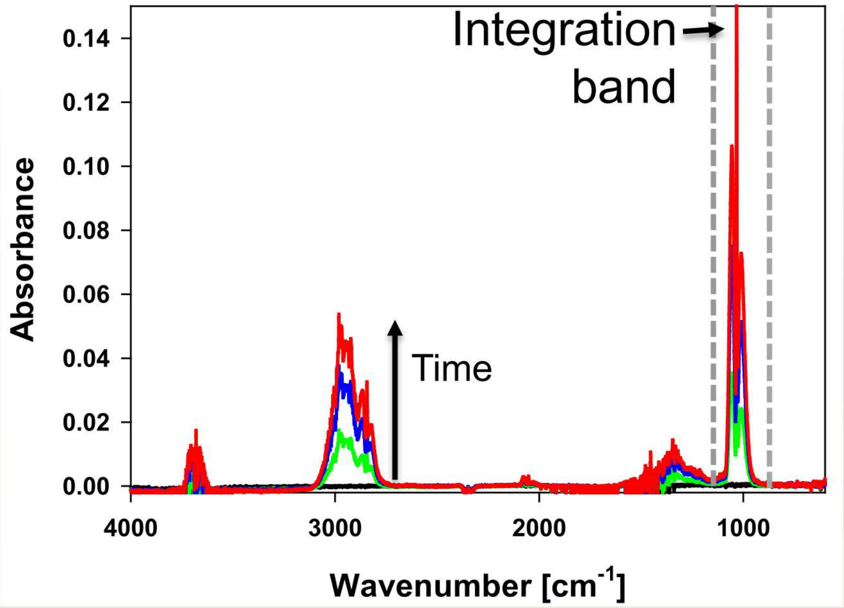


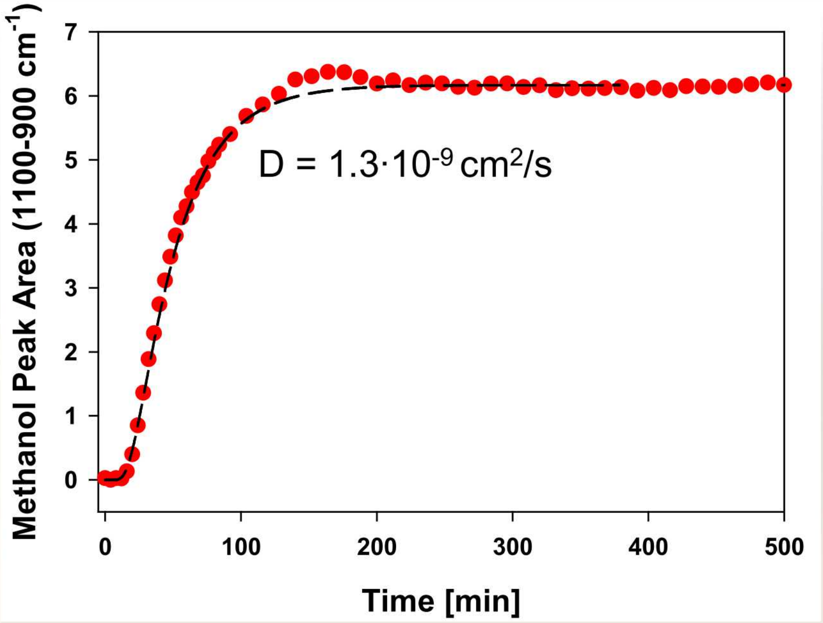
$D = 7 \cdot 10^{-9}\ \mathrm{cm^2/s}$

$P = 4.7 \cdot 10^{-10}\ \mathrm{cc_{STP}/(cmHg\ s\ cm)}$

- **Goal: Proof of principle to monitor organic vapor diffusion using mid-IR**
- **Permeation of CO_2 through a 50 μm Kapton film at 100°C determined using a newly developed mid-IR based method**
- **Quantification used spectral integration at 672–665 cm^{-1}**
- **Permeability can be obtained using Fick's first law, and diffusivity is obtained from the time-lag**

Organic Vapor Transport through Films





- **Goal: Monitor organic vapor diffusion using IR gas spectroscopy**
- **Permeation of methanol through a 50 µm Kapton film at 50°C**
- **The permeate is detected in IR cell by a flow of dry N_2 at 10 cc/min**
- **The time-dependent flux matches theory for Fickian diffusion**
- **Methanol causes significant swelling, which likely increases effective *D***
- **Calibration is required to obtain permeability**

CONCLUSION

- Established principles of water sorption and permeation for encapsulation, adhesives and thermosets. Quantification enables guidance throughout SNL
- We lead the aging community through understanding and quantification of O_2 transport through polymers and its local reactivity
- We have started to measure volatile diffusion and are exploring appropriate methods to help SNL community for compatibility and off-gassing
- **IMPACT:**
- **Our science basis has enabled diagnostics and helped material requalification**
- **We have recommended improved processing conditions for specific materials**
- **We assist with material selection and identification of concerns for continued use of materials or replacements**

- **Publications:**
- Overview of DLO modeling and approaches to predict heterogeneous oxidative polymer degradation. Quintana A, Celina MC. Polym Degrad Stab 2018;149:173.
- Oxygen diffusivity and permeation through polymers at elevated temperature. Celina MC, Quintana AD. *Polymer* 2018; accepted.
- Water Diffusion with Temperature Enabling Predictions for Sorption and Transport Behavior in Thermoset Materials. Linde E, Giron NH, Celina MC. Polymer 2018; in revision.

Conclusions

Impact on Service Life Prediction, Polymer Aging Phenomena:

- **Despite high T_g glassy epoxy materials absorb water at RT and expand, leading to dynamic mechanical stress that can be an additional concern for reliability and long-term performance**

- **Accelerated aging studies that involve water, hydrolytic degradation, and weathering must take transport kinetics into account in order to obtain better predictive data (surface wetting vs. partial water uptake or full saturation)**