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Challenges for Epoxy Cure Characterization and Long Term High Temperature Performance

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Epoxy Selection and Performance

- Degradation tendencies
- Depends on cure behavior and cure state evolution
- Elevated temperature performance

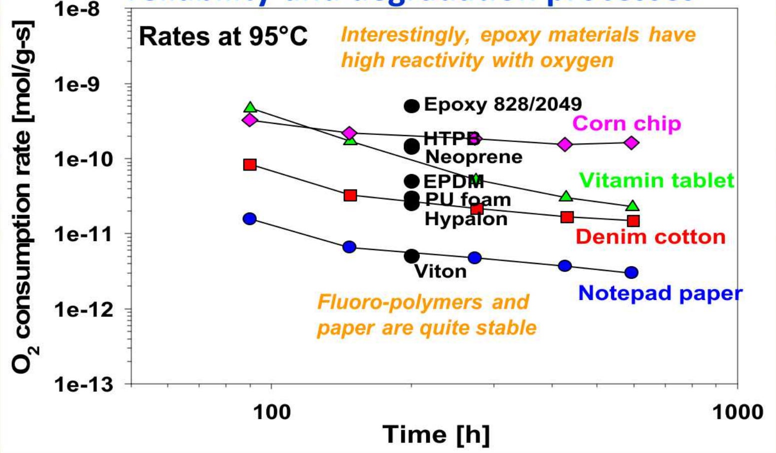
- Research goals and approach:
  - Spatially resolved oxidation chemistry
  - Understand cure behavior in epoxies
  - Identify reasons for unusual cure behavior in Epon 828/DEA
  - Better approaches for quantification of cure conversion states

  - High temperature epoxy degradation phenomena
  - Develop diagnostic tools and lifetime prediction models

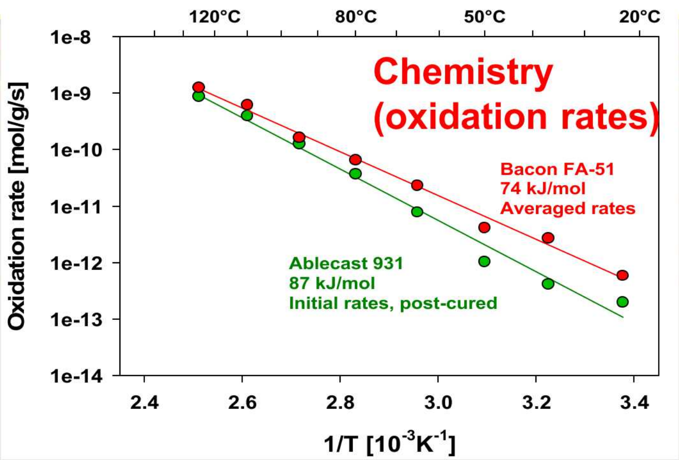
Key words: Materials Characterization, Spectroscopy, Mechanistic Evaluation

Reactive Diffusion Models Developed at SNL

Polymer oxidation relevant to reliability and degradation processes

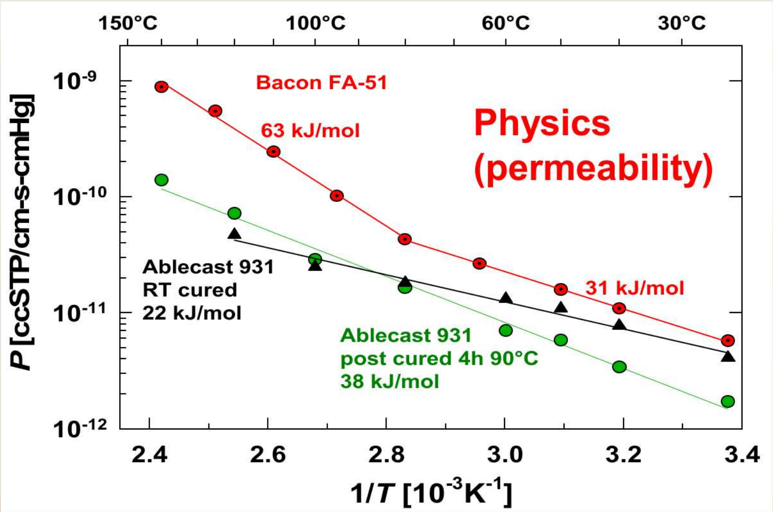


Measured intrinsic oxidation behavior for epoxies in Bell XI



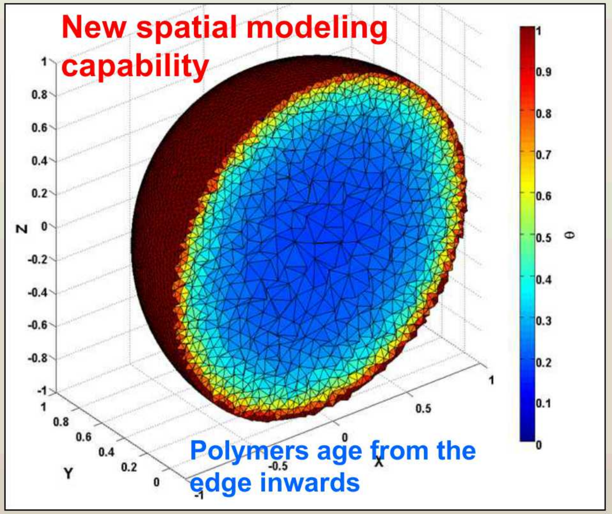
Celina MC, Dayile AR, Quintana A. A perspective on the inherent oxidation sensitivity of epoxy materials. Polymer 2013;54:3290.

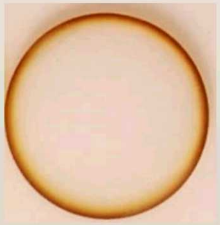
Measured oxygen permeation for epoxy materials in Bell XI



Celina MC, Quintana A, Giron N. Oxygen Permeation through Polymers. Polymer, in prep.

Applied Galerkin FEM DLO model capability for spatially resolved polymer degradation

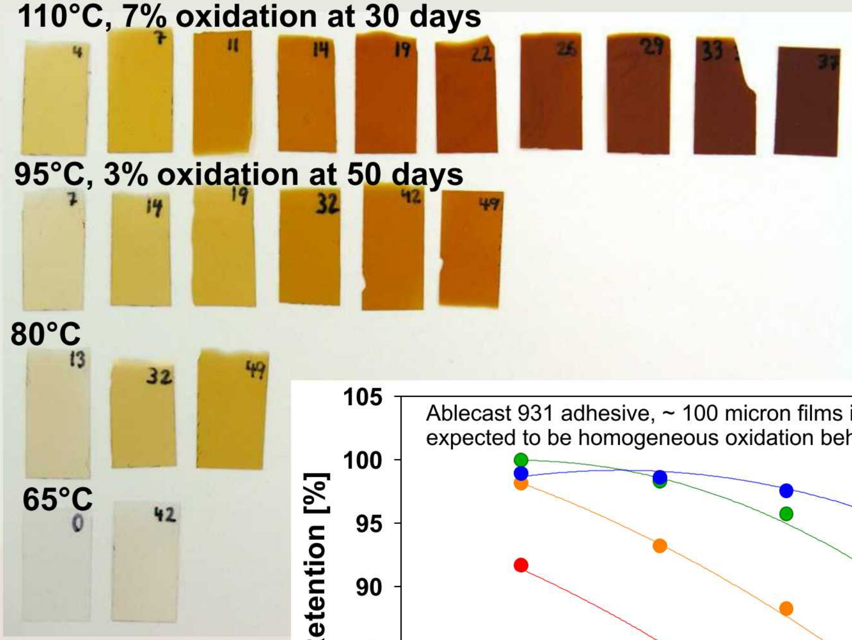


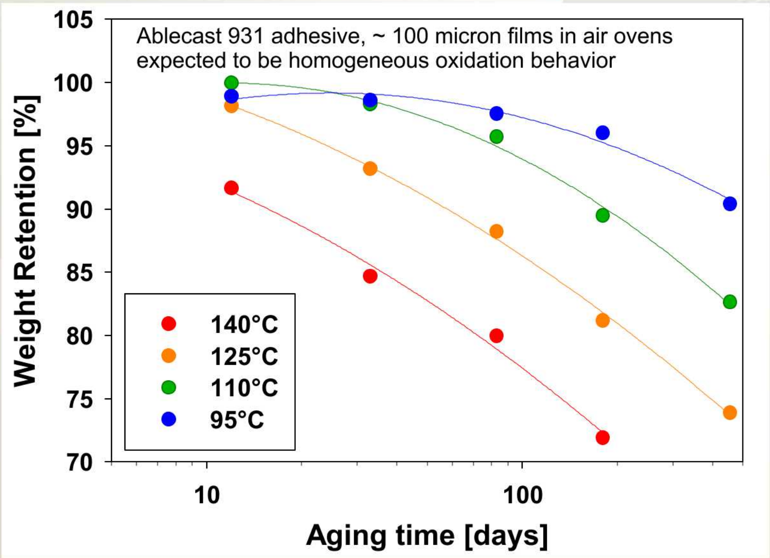


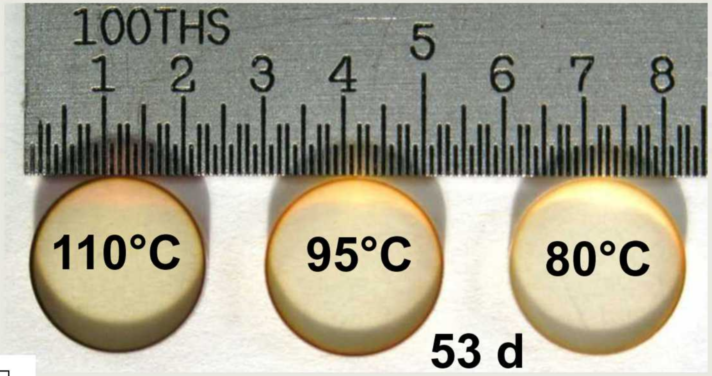
Exptl.

Epoxy Oxidation is Real

- Oxidation level can be assessed using oxidation rates







5.6 mm diameter disks
DLO profile depth < 250 micron

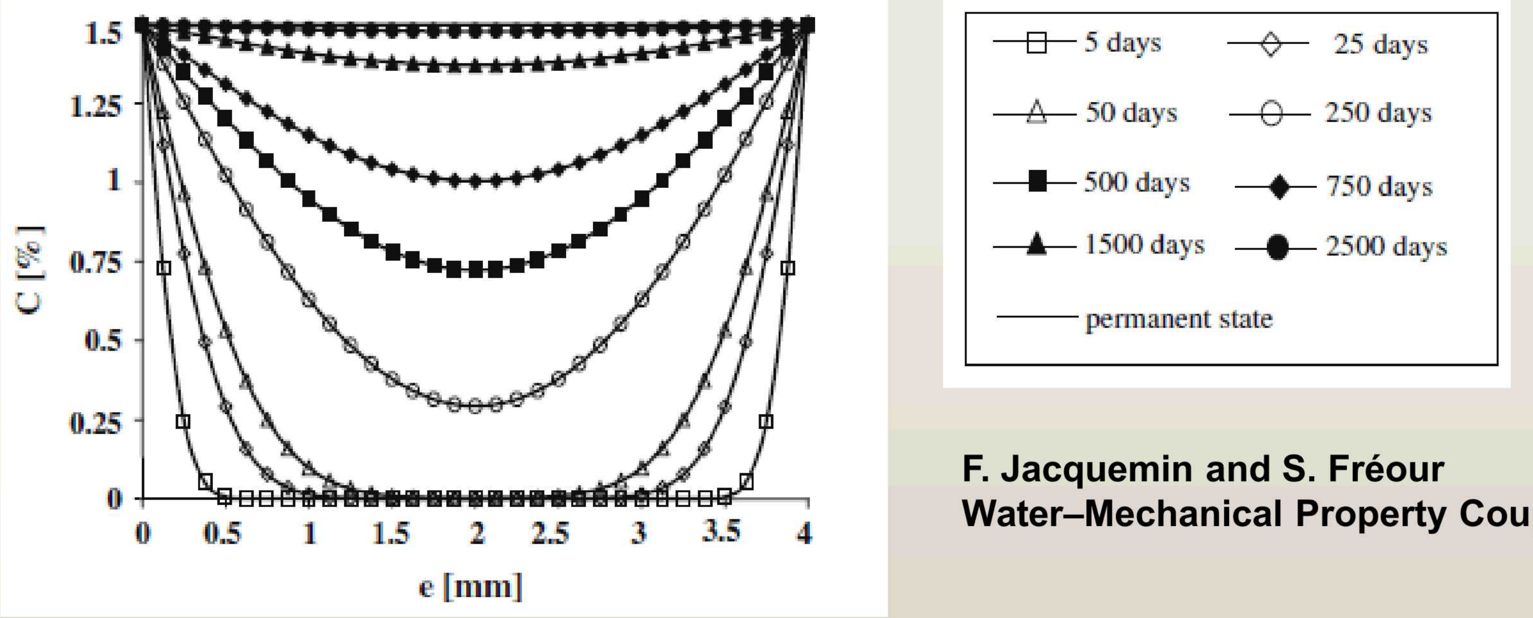
Weight Retention of homogeneously aged thin films (~110 micron)

Time	140°C	125°C	110°C	95°C
12 days	91.6%	98.1%	99.9%	98.9%
33 days	84.7%	93.2%	98.3%	98.6%
83 days	80.0%	88.2%	95.7%	97.5%
180 days	71.9%	81.2%	89.5%	96.0%
455 days		73.9%	82.6%	90.4%

- **At high temperature epoxy oxidation occurs in parallel with weight loss**
- **High temperature DLO depth is consistent with model predictions**

Diffusion Limited Water Profiles

- Water sorption important for mechanical performance, spatially dependent
- Humid environments result in moisture uptake, sorption kinetics
- Fickian and Langmuir sorption behavior
- Solid mechanics, swelling and cracking, Diffusion Controlled Hydrolysis

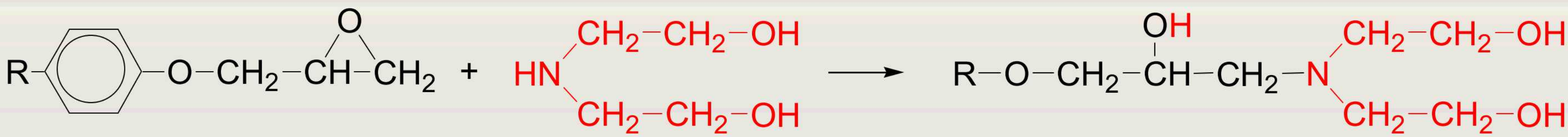


F. Jacquemin and S. Fréour
Water–Mechanical Property Coupling

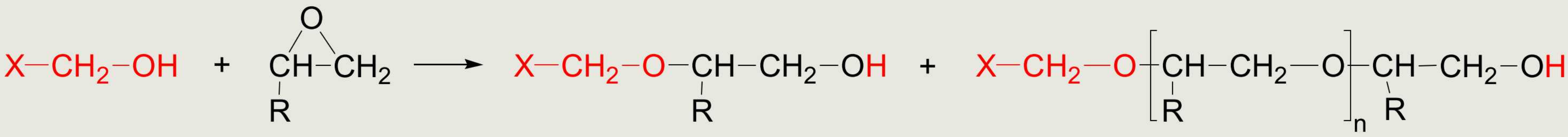
Chemistry: Hydrolysis kinetics as a function of [H2O] is needed

Davis Peter, Rajapakse Yapa. Durability of Composites in a Marine Environment, Springer, Vol. 208, 2014.

Epon 828 cured with DEA



Initial secondary amine addition

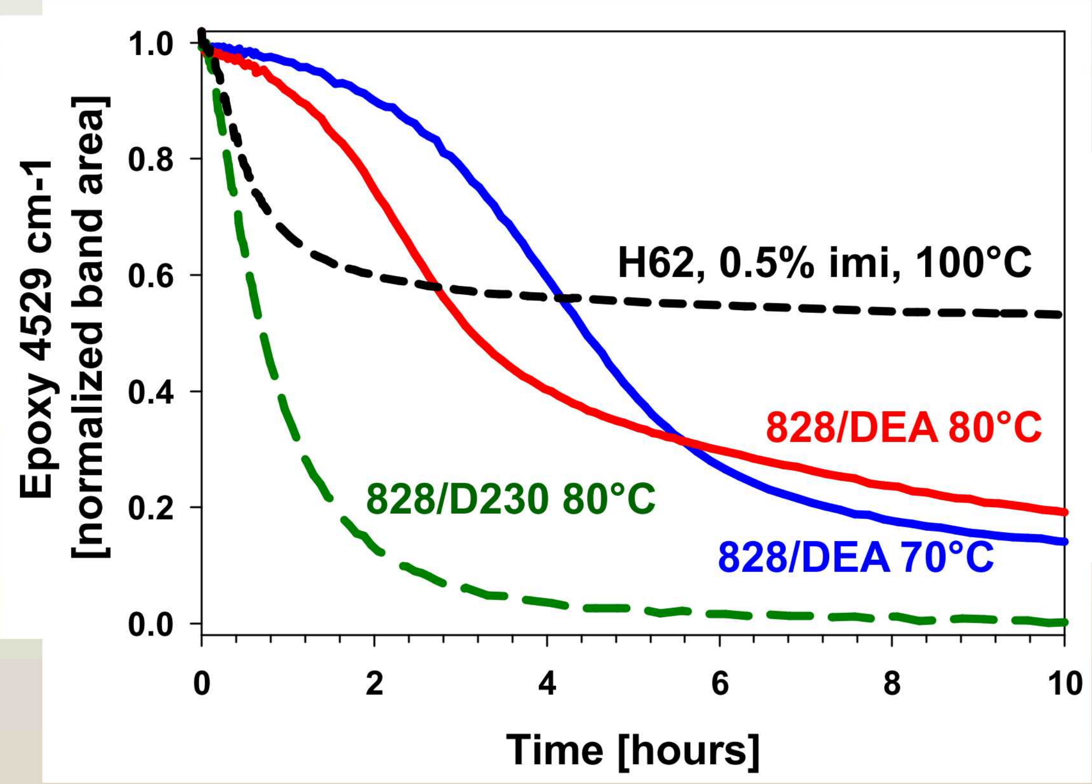


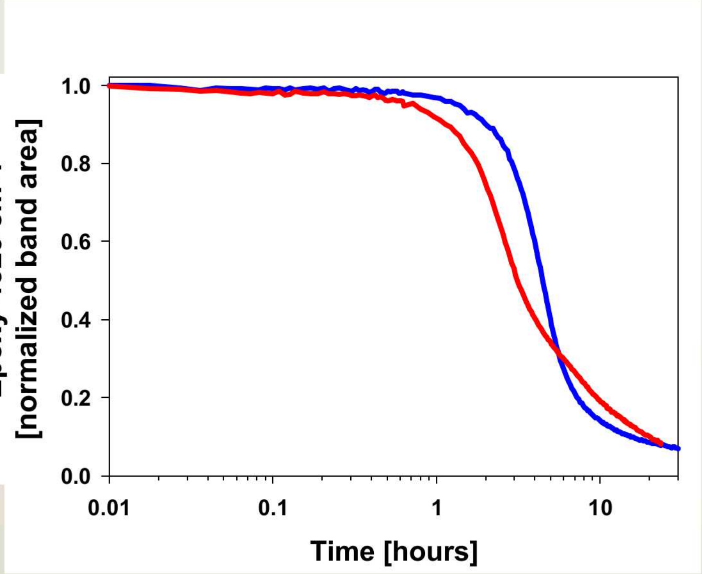
Hydroxyl addition plus parallel epoxy polymerization

- **Excess epoxy group reactions:**
- **A) Epoxy groups can homo-polymerize (exact mechanism unclear)**
- **B) Epoxy reactions with existing hydroxyl (ethanol and epoxy addition OH)**
- **Competitive chemistry, is either process dominant? Combination?**

Unexpected Reaction Kinetics in 828/DEA

- 828/DEA cure does not follow consistent Arrhenius behavior
- Expectation: Higher temperature should accelerate reaction and push cure conversion



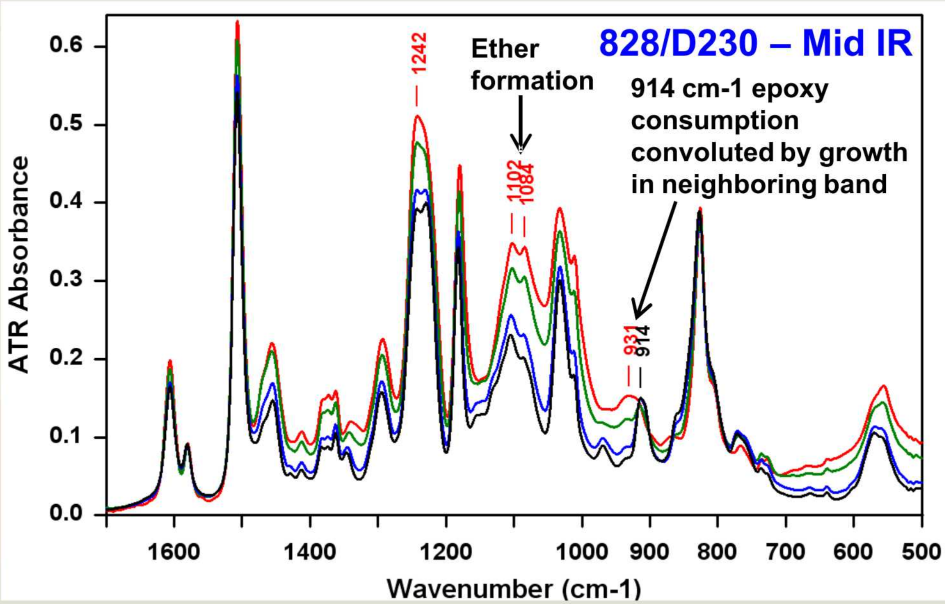


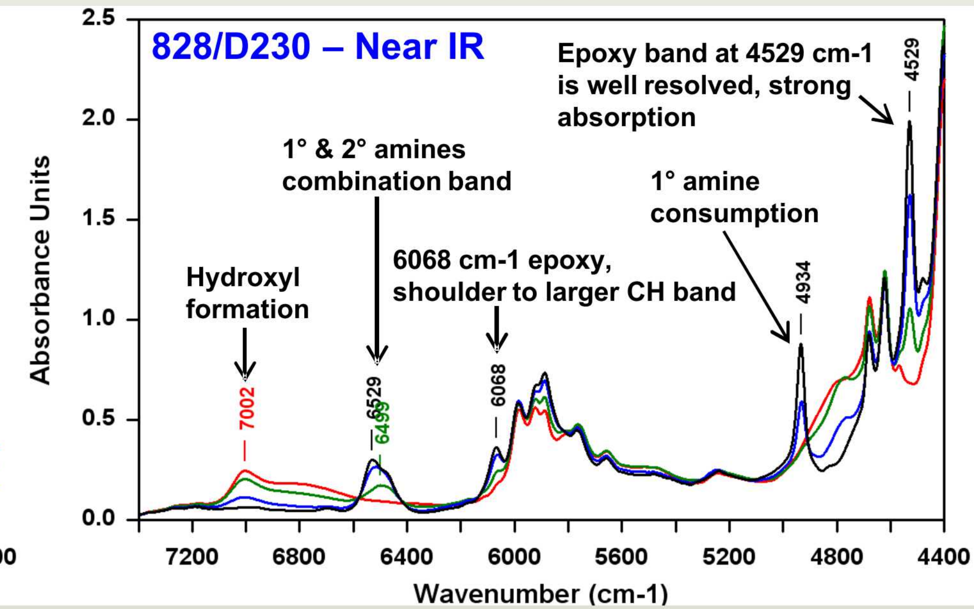
The cure reaction starts faster, but is then slower at higher temperature

Mid IR – NIR 828/D230

- Epoxy band in some systems (ie. 828/DEA) is convoluted in mid IR (914)
- NIR offers better resolved epoxy absorbance at 6068 and 4529 cm-1

MIR and NIR spectra were acquired at ~8 seconds, 10 mins, 45 mins, and 15 hours at 80°C



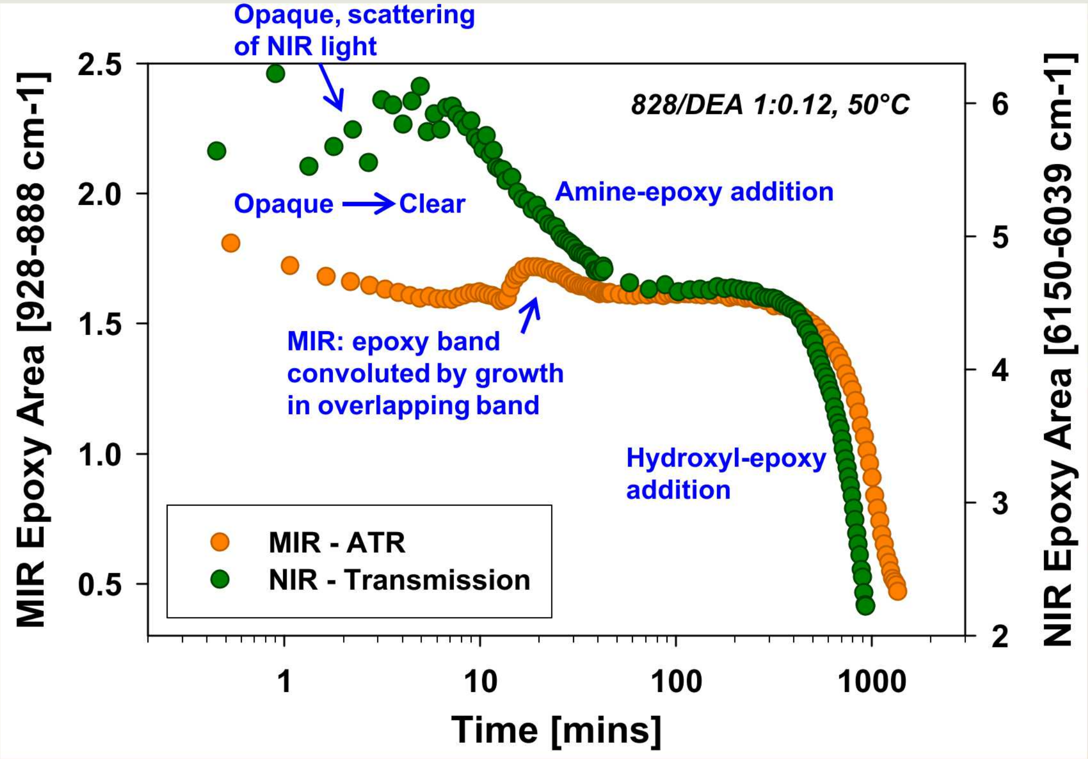


Epoxy as well as amine bands are resolved in NIR

E Duemichen, U Braun et al, Thermochimica Acta, 616 (2015) 49
'NIR monitoring of epoxy cure with variable heating rate'

Mid IR - NIR

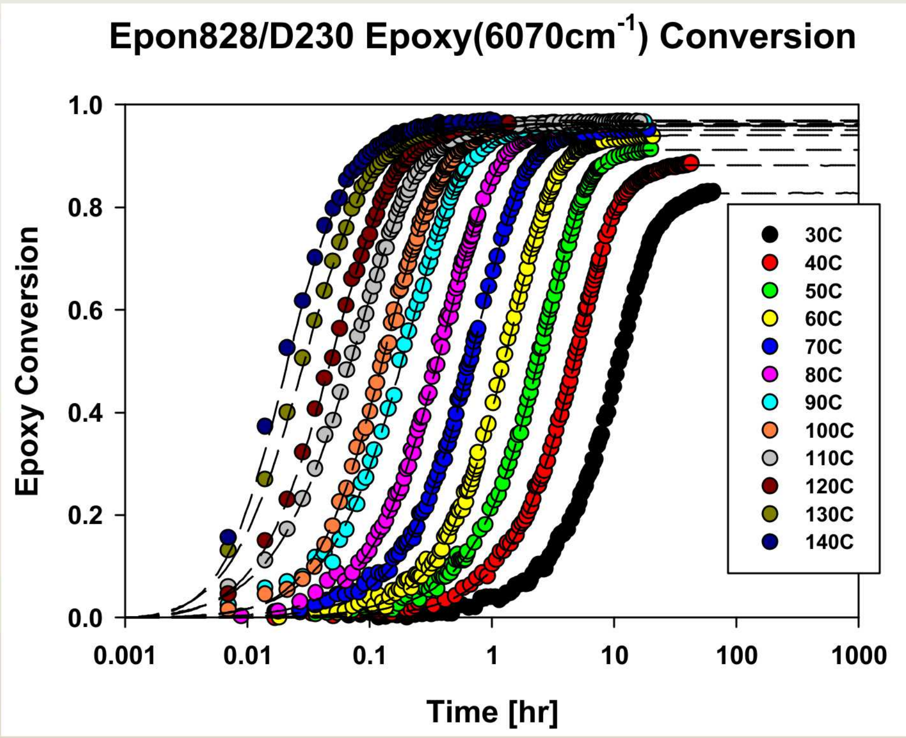
- Epoxy band consumption for 914 (mid-IR) and 6068 cm-1 (NIR) for 828/DEA cure at 50°C
- 914 is integrated between 928 and 888 (not deconvoluted)

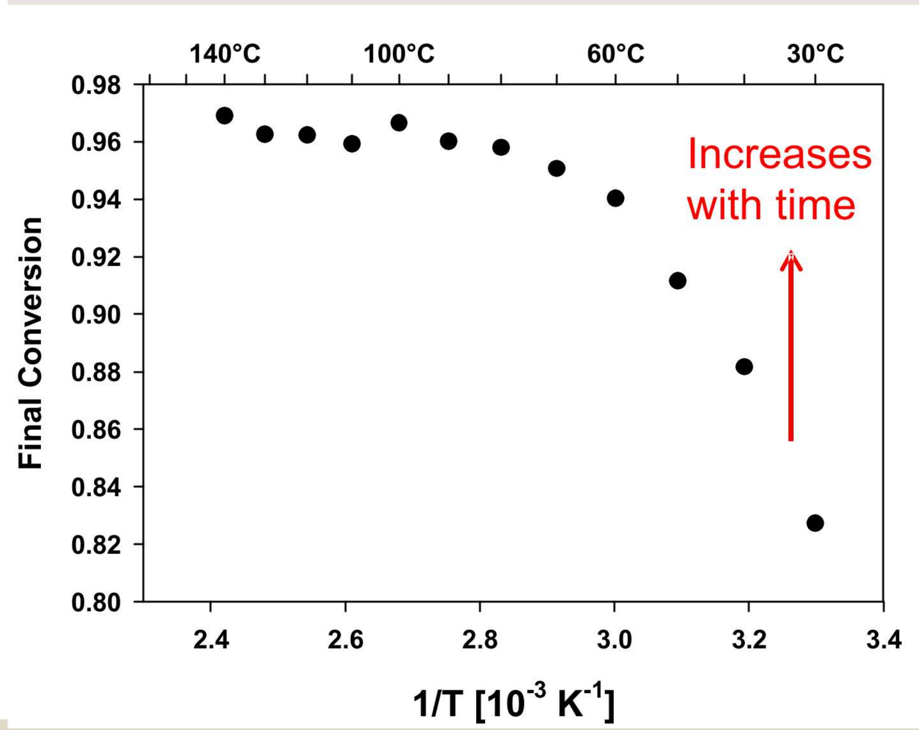


NIR also more easily picks up initial sec-amine epoxy addition

Epon 828/D230 t-T Cure Behavior

- Traditional epoxy cure
- Final conversion levels drop at lower T, but an ongoing power law driven cure reaction is evident

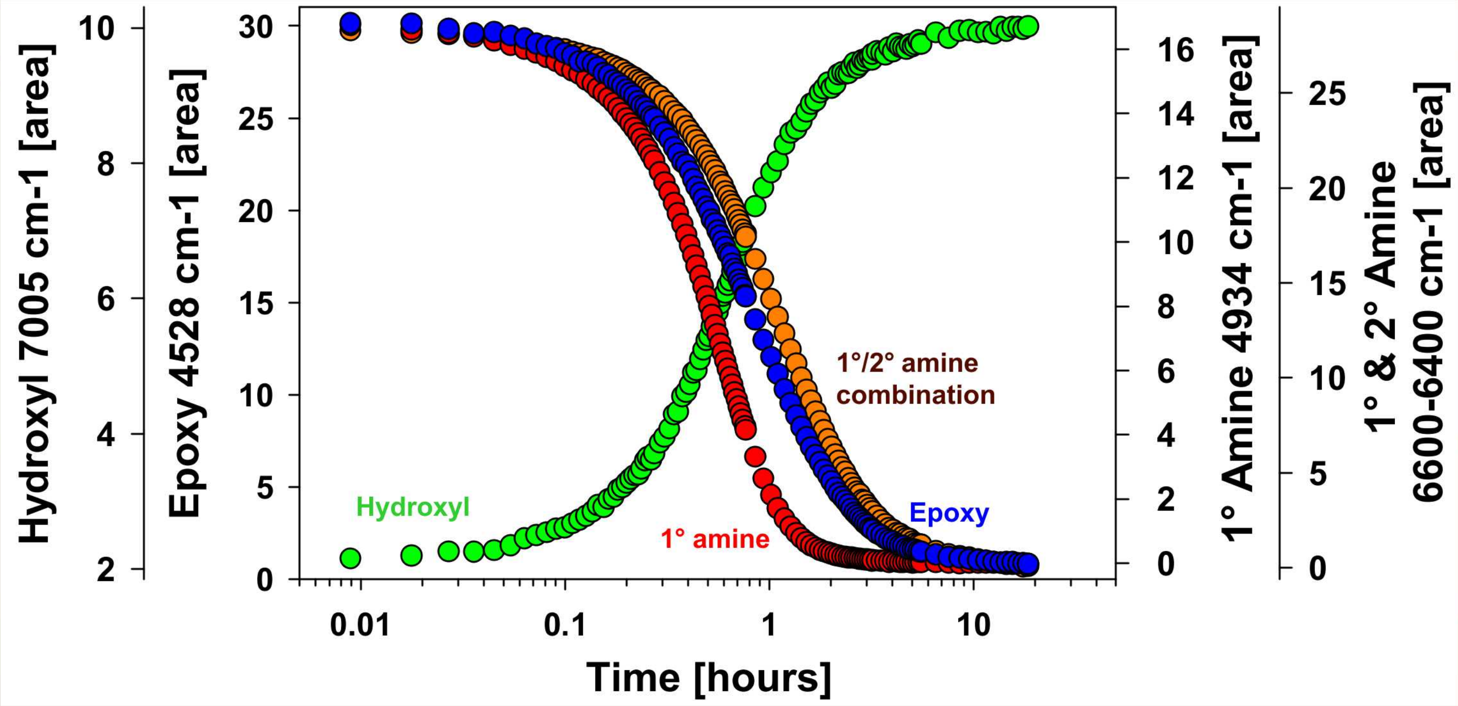




Cure speed increases and higher final conversion is obtained with T

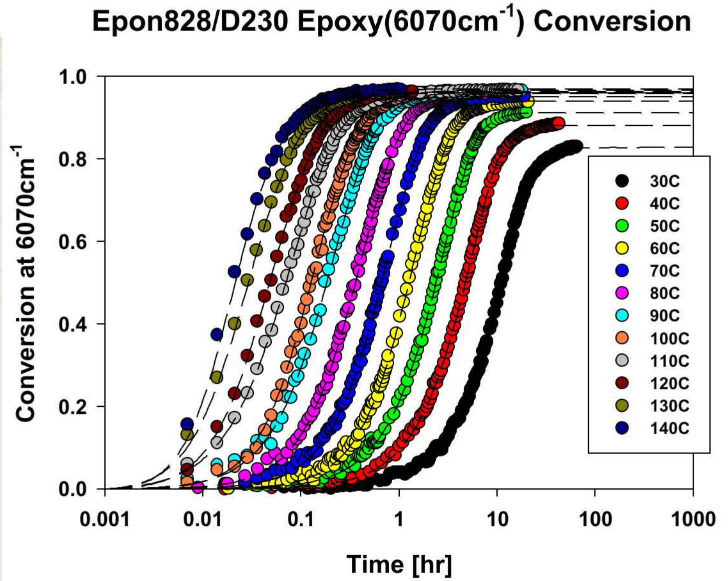
Epon 828 / D230 – 70°C Cure

- **Epoxy consumption can be compared with amine loss and hydroxyl formation**

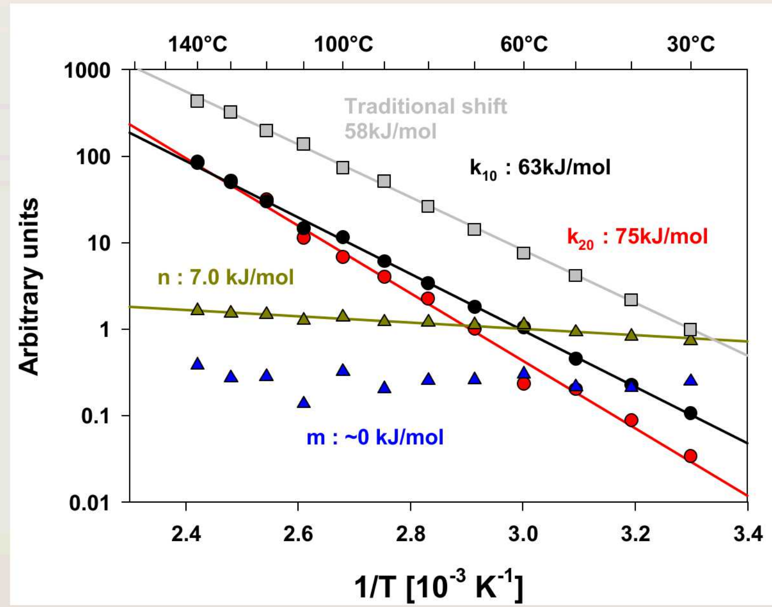


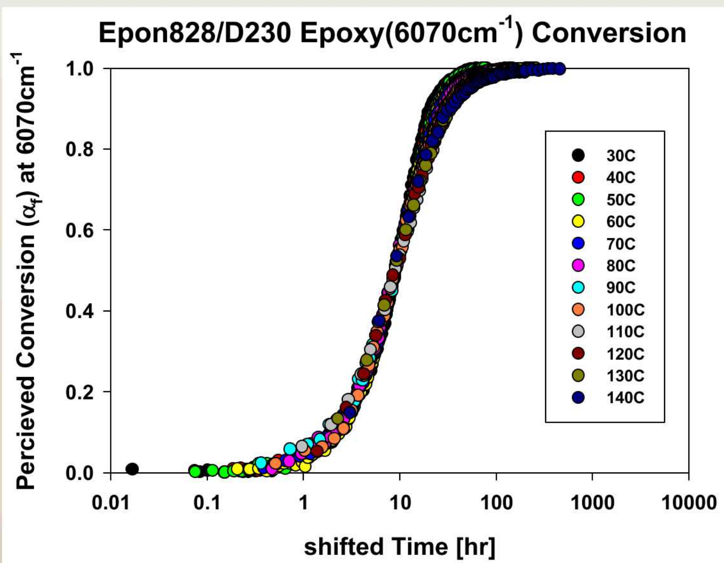
This system can be examined with multiple spectroscopy approaches

Epon 828 - D230



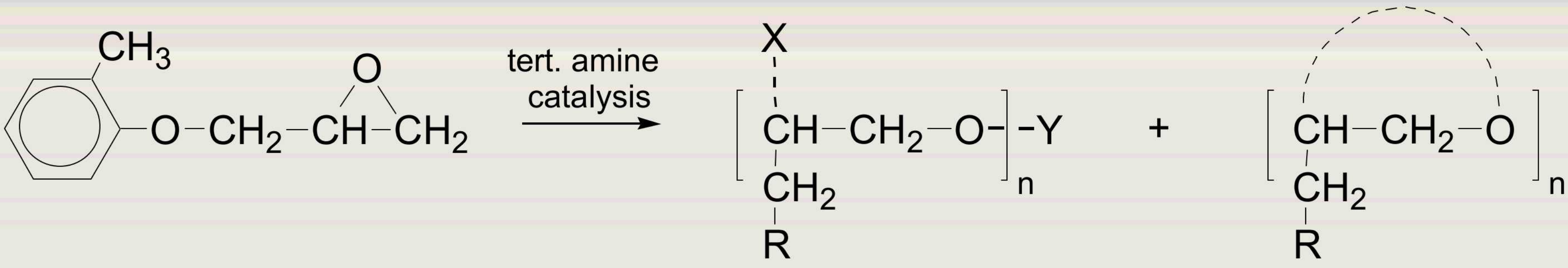
$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_f - \alpha)^n$$





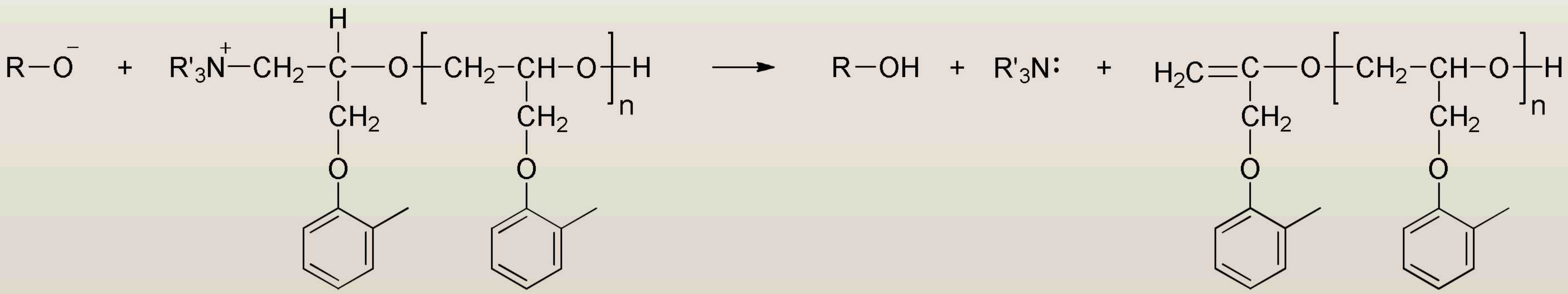
- Traditional shifting does not account for variance of kinetic regime at high conversion and is only available after data is corrected for final cure state (α_f)
- Kamal equation accounts for this with two modified rate constants and temperature dependent power.

Mono-functional Epoxy Polymerization



Polyether formation
Linear polymer requires some addition (initiation and termination)

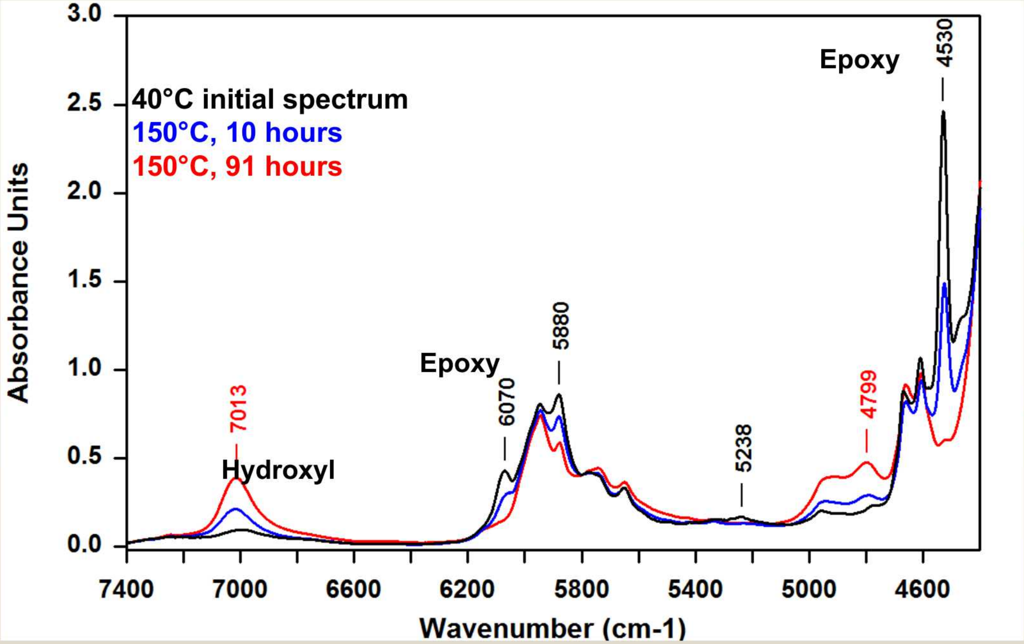
Cyclic-polyether?
Is this feasible?



How does this reaction proceed? What is conversion with time?
Can water interfere/contribute?

NIR Epoxy Quantification Efforts

- Baseline and spectral correction for 'physics' T effects
- Band deconvolution with local baseline optimization (Matlab)
- Gaussian peaks with fixed peak position help the analysis
- Individual band integration and normalization for relative conversion
- Boundaries for conversion, initial reagent concentration (α =0), complete reaction from high T annealing above Tg (α =1)

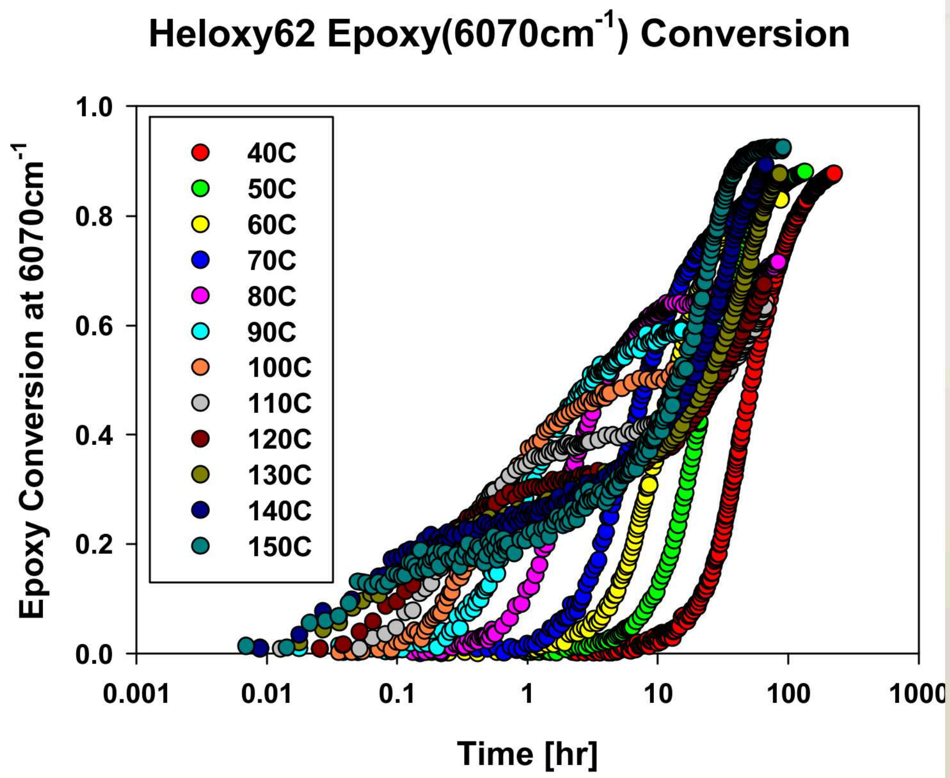


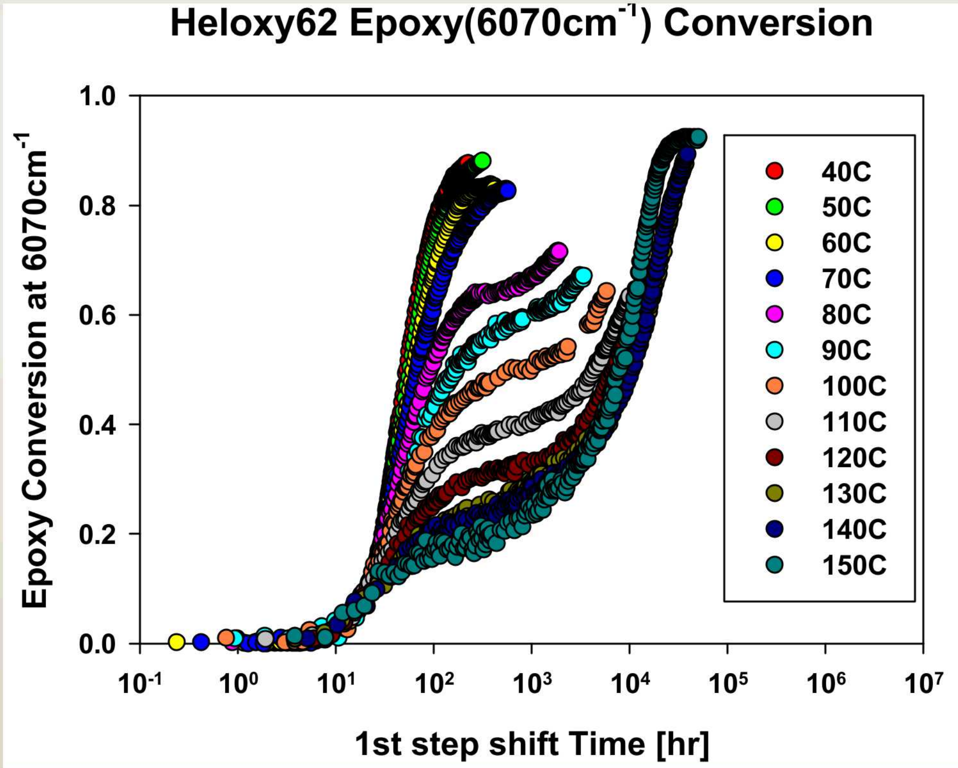
Homo-polymerization of Heloxy 62

Challenge is peak separation, integration, and conversion boundaries

Heloxy 62 – Complicated Cure Behavior

- No easy t-T superposition, highly complex cure behavior dependent on T
- Two cure stages result in complicated kinetic cure behavior and model
- Conversion state for transition between cure regimes depends on T

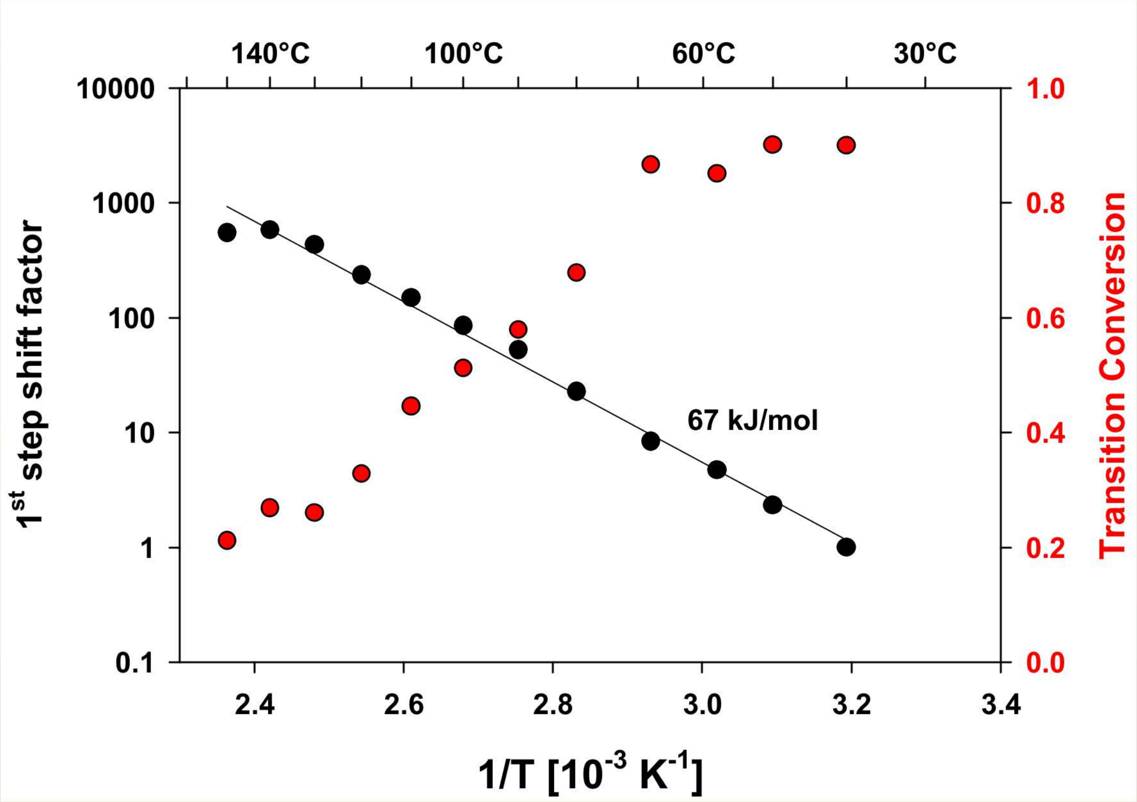




Delayed cure conversion at high temperatures
What do limited conversion states indicate?

Early Reaction Kinetics

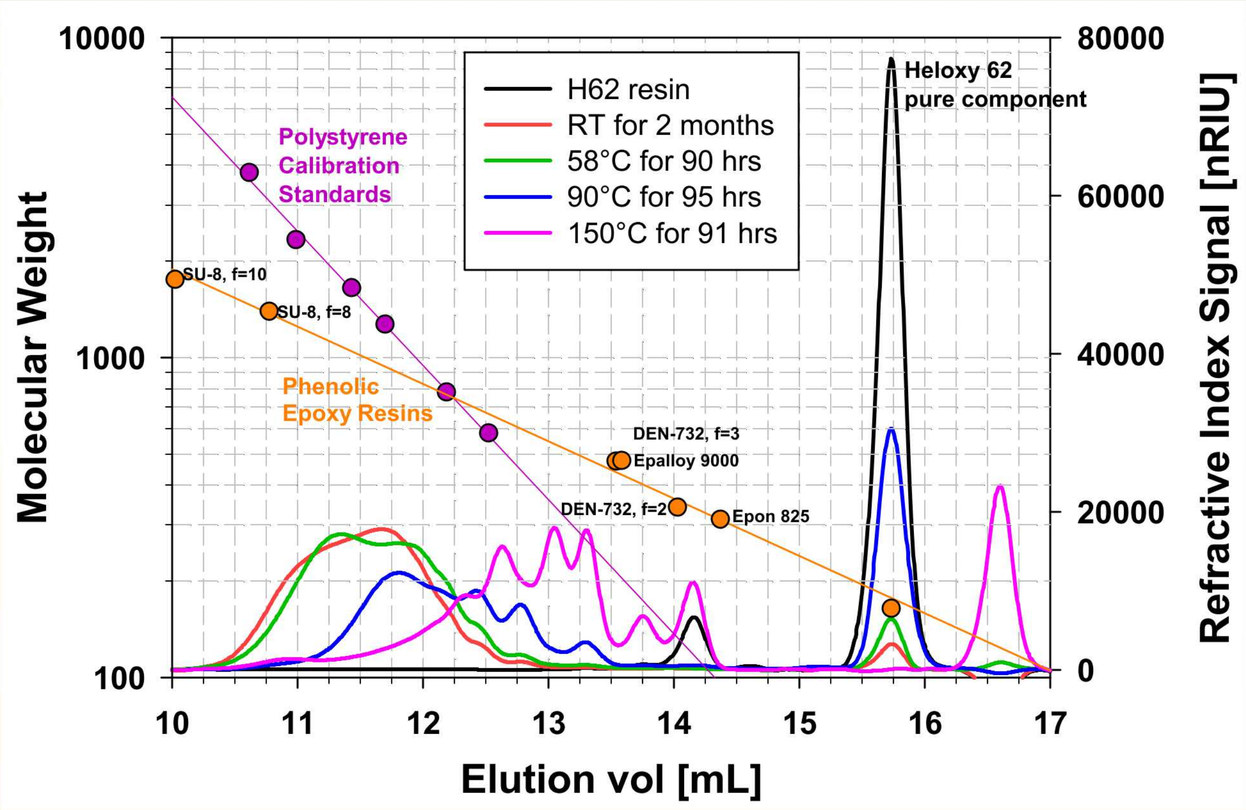
- **Early stage t-T superposition yields 67 kJ/mol over wide T range**
- **Is limited to specific conversion level, that decreases with T**



What do limited early conversion states indicate?

Homopolymerization

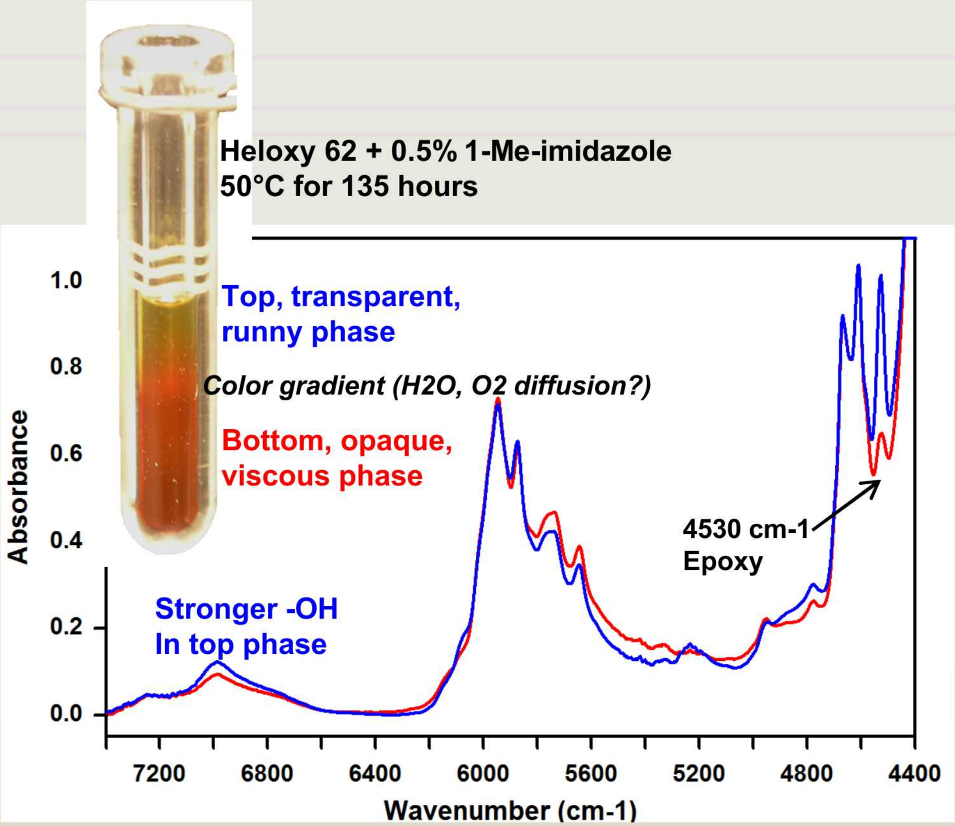
- Evidence for ‘ceiling’ temperature behavior
- What is Mw (polymerization degree) for linear polymerization?

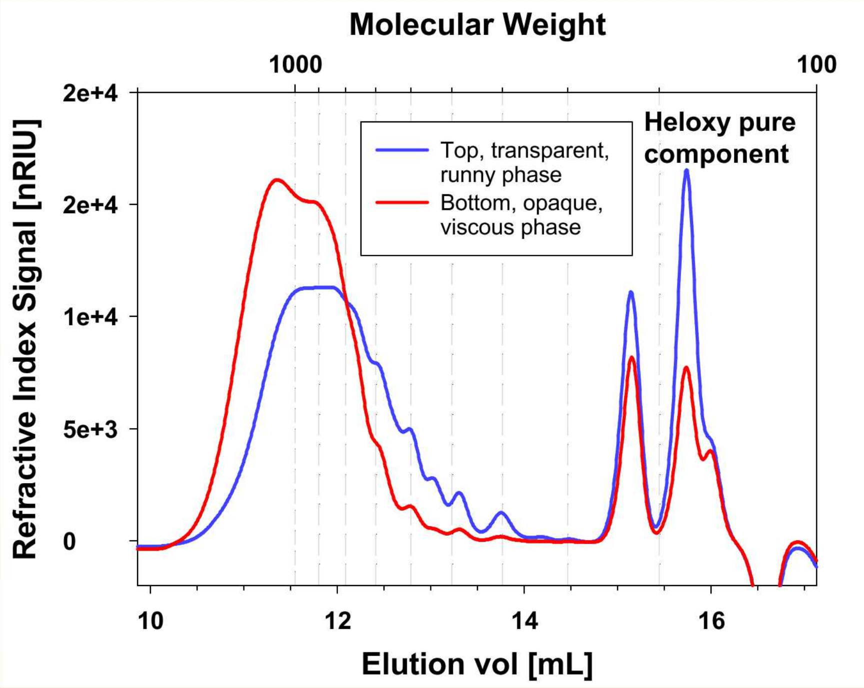


- GPC proves limited chain propagation behavior
- Higher Mw at lower temperatures

Cure Inhibition - Water

- Does water contribute?
- Can water favor linear polymers (recall addition needs)?

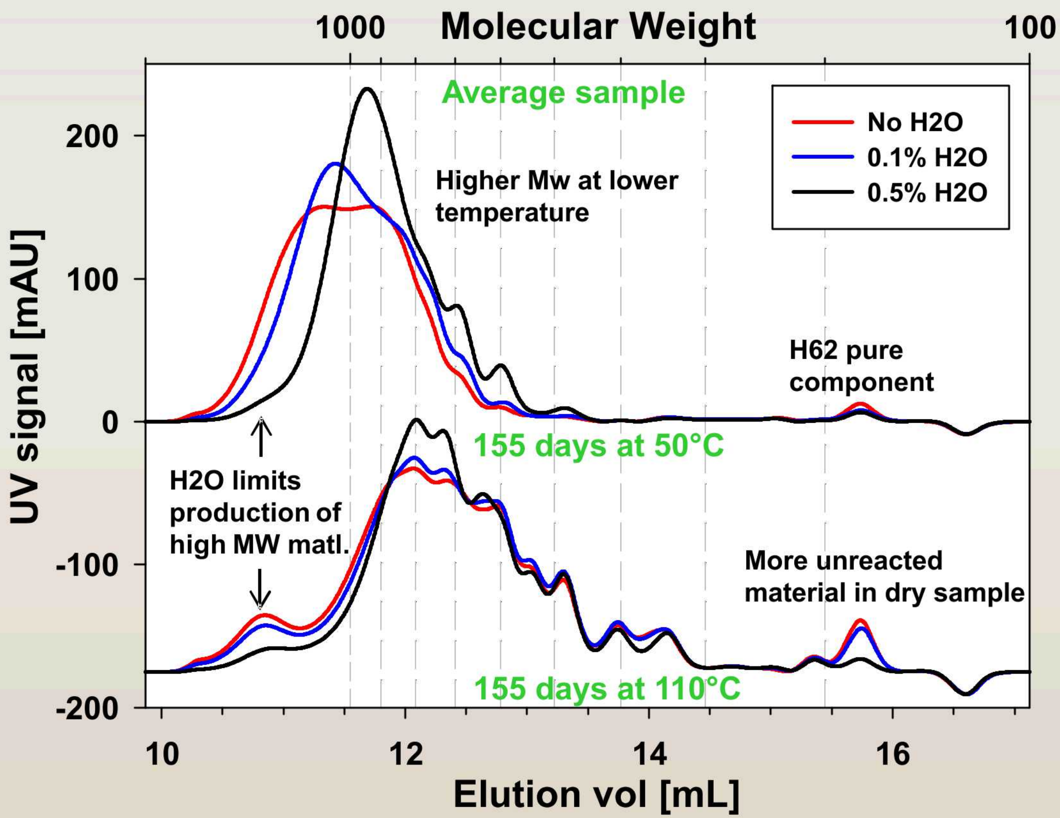




Perhaps evidence that atmospheric exposure affects cure behavior
Water loss or separation (density variance) during polymerization?

Cure Inhibition - Water

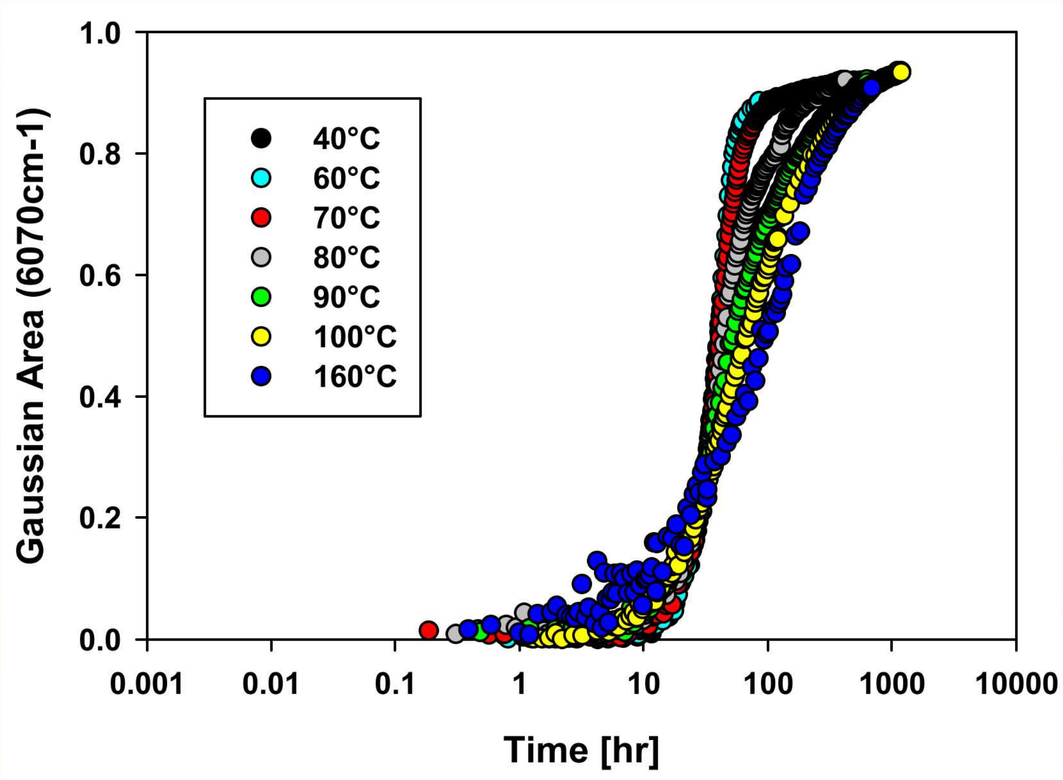
- 6 cure conditions: 0.1% & 0.5% H2O addition vs. control at 50°C & 110°C
- H2O is miscible with epoxy. Rxn carried out in sealed vials over 155 days.



- H2O lowers chain propagation or increases termination
- Much higher Mw formation at lower temperature

Epon 828/DEA Cure Behavior

- Preliminary NIR data for t-T epoxy conversion (initial guidance)
- Peak quantification can be further optimized



Influence of temperature (anomalous cure) is clearly apparent
Pure mathematical data superposition is not the best approach

Epon 828/DEA Cure Mechanisms

- **Extensive literature review with collaborator John McCoy – NM Tech**

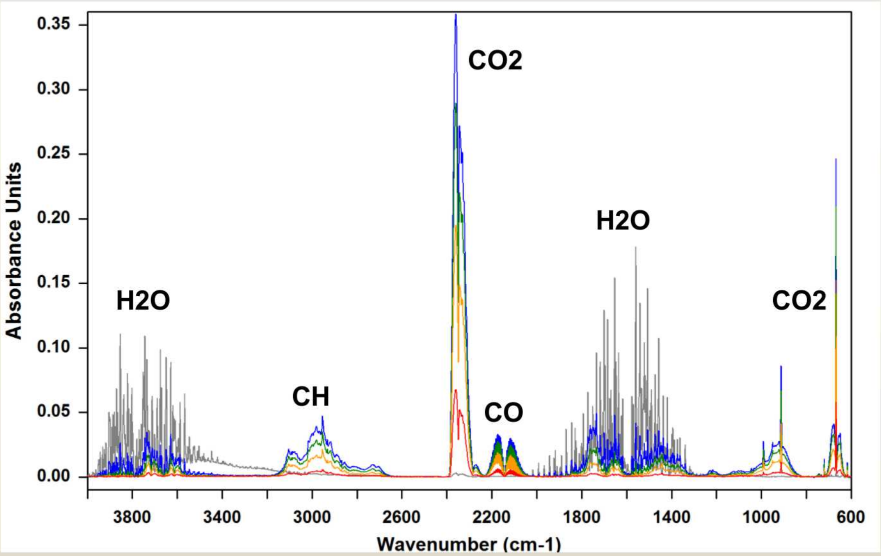
"Cure mechanisms of Diglycidyl Ether of Bisphenol A (DGEBA) Epoxy with Diethanolamine" John D. McCoy*, Windy B. Ancipink, Caitlyn M. Clarkson, Jamie M. Kropka**, Mathias C. Celina**, Nicholas H. Giron**, Lebelo Hailesilassie, Narjes Fredj, under review "Polymer"

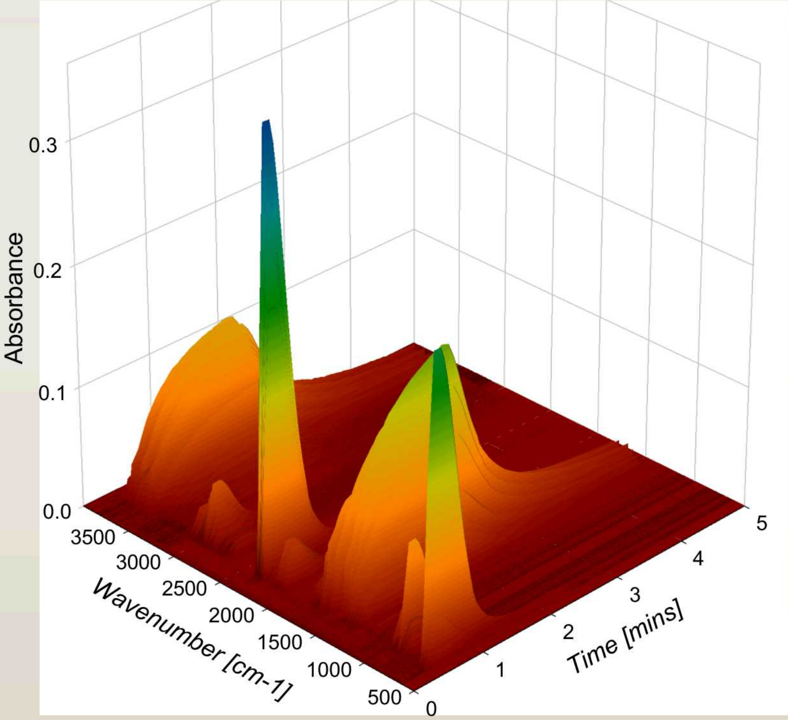
- At low temperature the DGEBA/DEA gelation reaction is "activated" (shows a pronounced induction time, similar to autocatalytic behavior) by the tertiary amine in the adduct.
- At high temperature, the activated nature of the reaction disappears.
- Upper stability temperature of the zwitterion initiator of the activated gelation reaction
- Reaction rate of epoxide consumption cannot be generically represented as a function only of temperature (*T) and degree of epoxy conversion (α)*

- **Requires specific consideration of the dilute intermediates in the reaction sequence**

High Temperature Performance of Epoxy

- Thermally induced decomposition (pyrolysis chemistry)
- IR based analysis of gaseous decomposition products
- Flow through approach, sealed ampoules, rapid scans

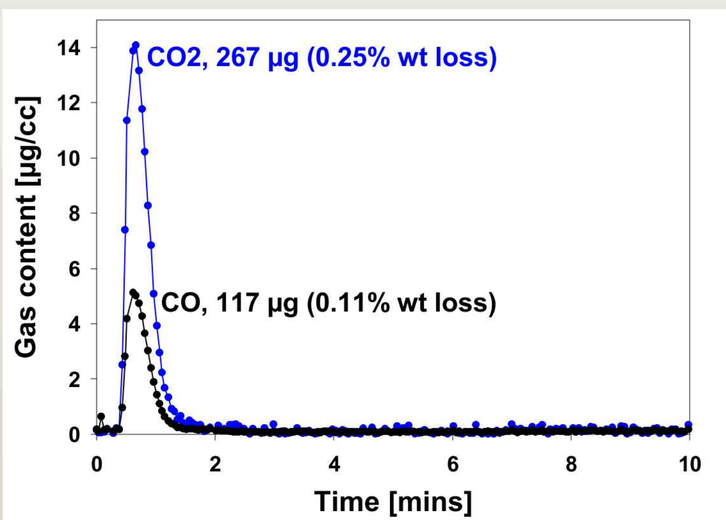


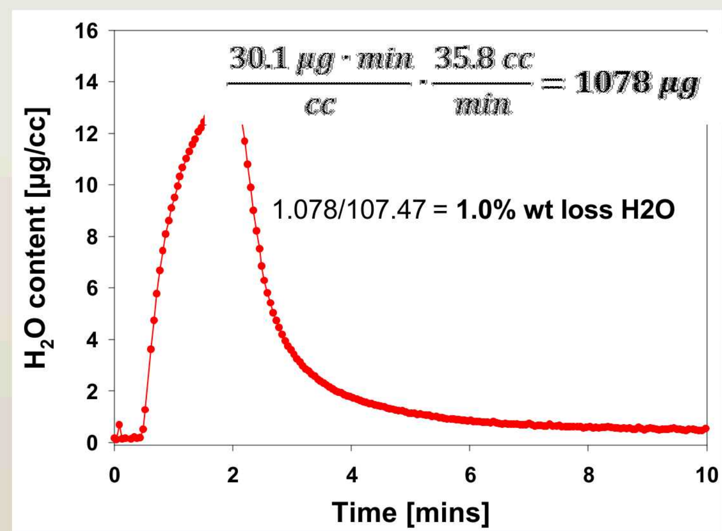


Quantification of H2O and CO2 yields via spectral and time integration

IR Analysis of Degradation Products

- Proof of principle epoxy aging test in sealed ampoule
- ~ 100 mg epoxy sample aged for 3.75 d at 240C,~ 1% expected weight loss
- Rapid IR spectral acquisition of flushed out gas with decomposition products
  - Evidence for significant water, plus some CO2 and CO as volatiles, some CH signatures
  - Integrate water peak between 1588 and 1518 cm-1
  - Use corrected calibration for limited water spectral range; content in µg/cc
  - Determined 1.078 mg H2O in sealed ampoule; actual weight loss was 2.4 mg (2.2%)

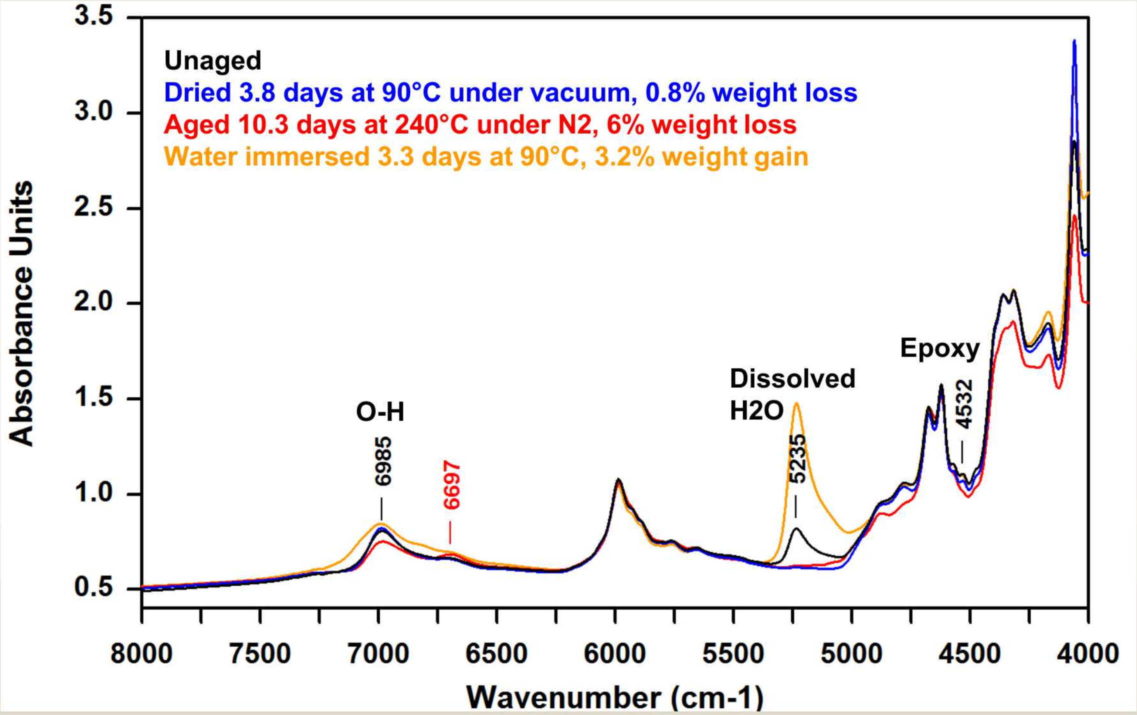




- **At 240C and early on, the epoxy yields ~ 45% weight loss as water**

Physically Absorbed Water

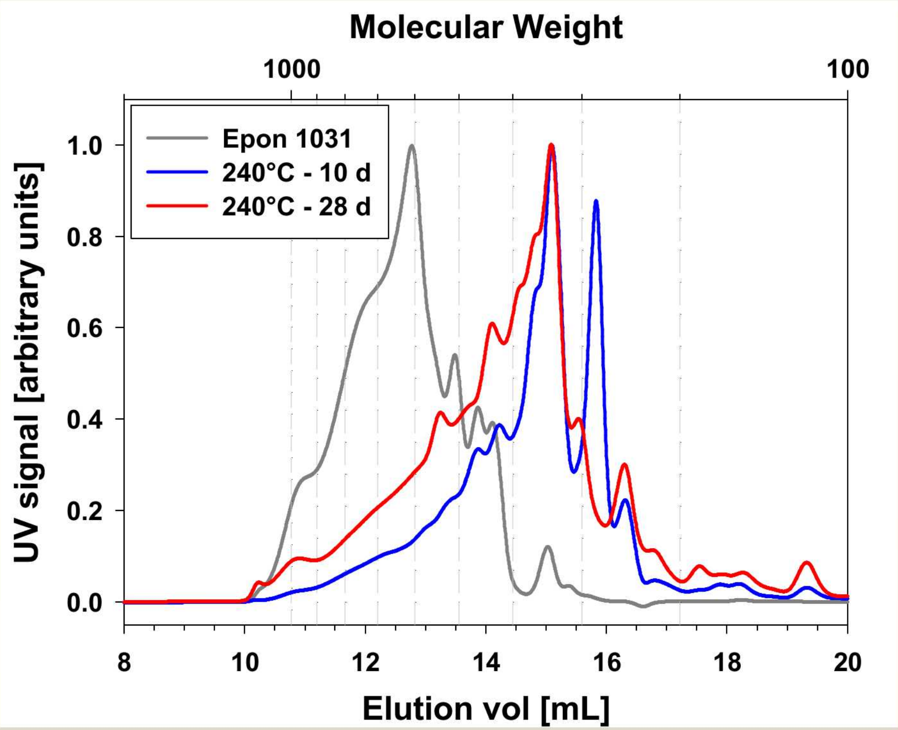
- Amine cured epoxy has a tendency to absorb water (somewhat hydroscopic)
- NIR can be used to quantify dissolved water in an epoxy
- Water uptake will depend on geometry and permeability (thin lab samples are expected to more easily pick up water)



Presence of dissolved water and its chemical formation

Liquid High T Products - Mw

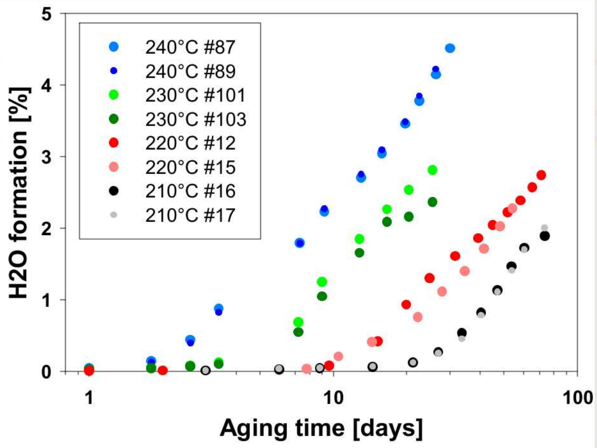
- Pyrolysis leads to some volatile material that can be liquid and solid upon cooling
- GPC was used for guidance on molecular weight of CDCl3 soluble residue
- Two samples: 240°C-10d and 240°C-28d

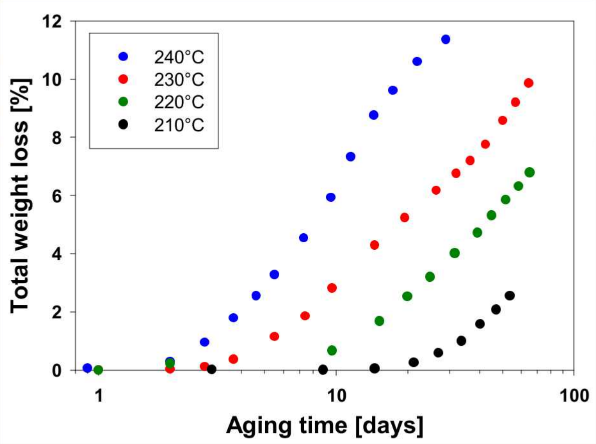


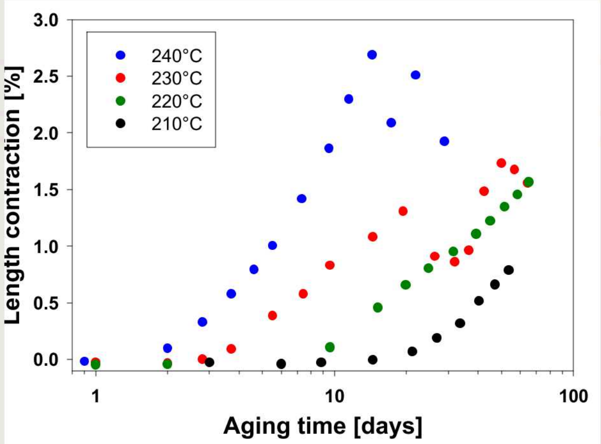
- **High T pyrolysis products yield 'organic material' in 10^2-10^3 Mw range**

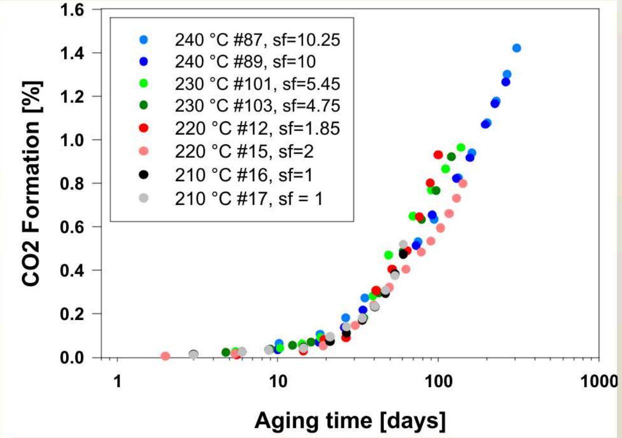
Volatile Yields - Weight Loss - Contraction

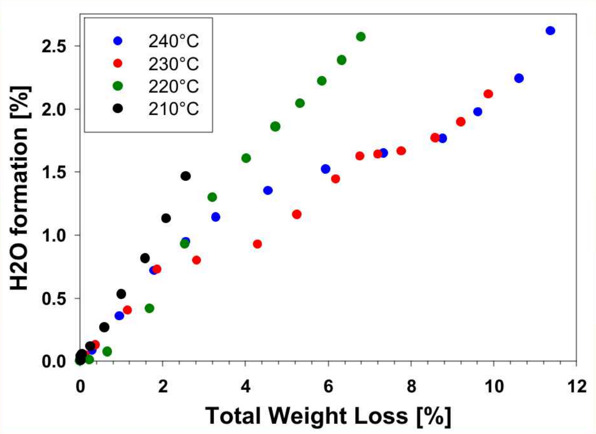
- **Weight loss – Water formation – Material Contraction**
- **Stress and changes in local chemical environment**

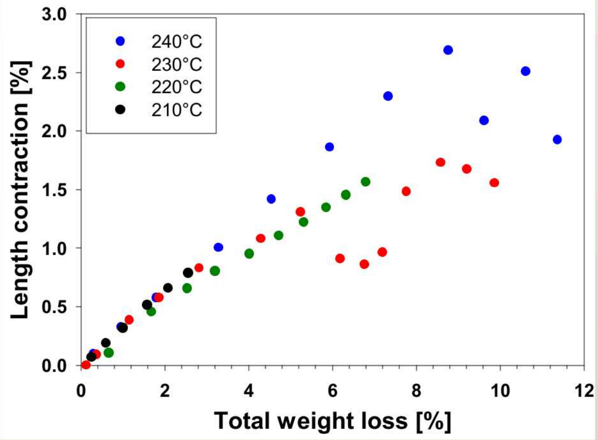








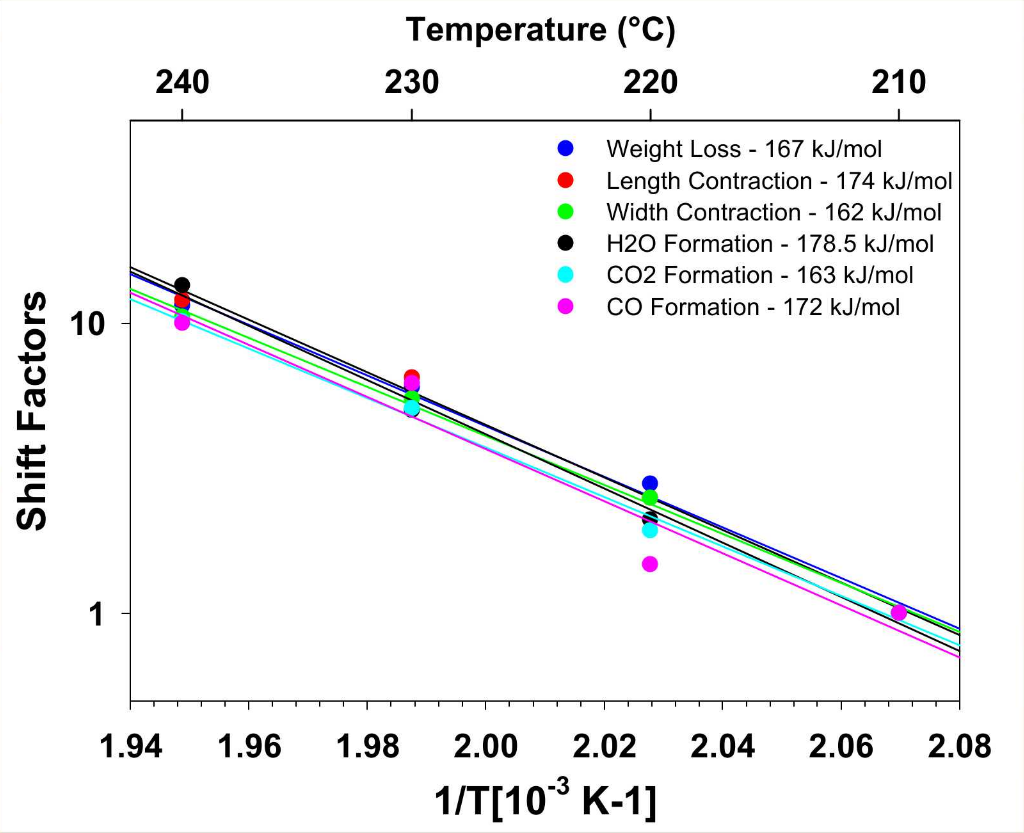




Aging studies to be continued at lower temperature – Arrhenius ?

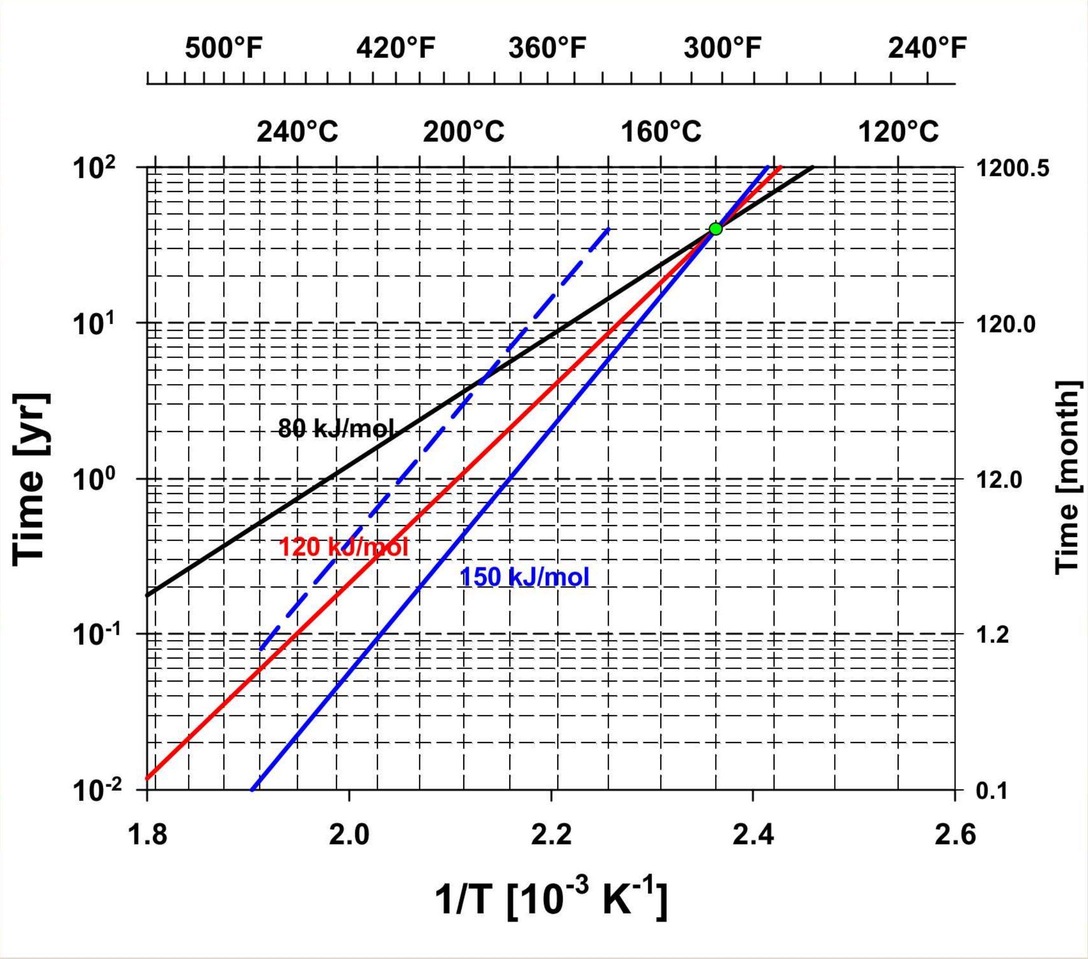
Kinetic Models – Basis for Extrapolations

- **Shift factors were determined by time–temperature superposition of multiple properties referenced to 210°C**



Initial trends: activation energies range from 162-179 kJ/mol.

Lifetime Prediction Models



Need to establish Ea for high temperature epoxy degradation processes through extensive t-T data sets, establish relevant Ea

Summary

- Never disregard polymer aging phenomena

- NIR coupled with mid-IR spectroscopy are excellent cure monitoring tools
- Epoxy polymerization can be unexpectedly complex
- 828/DEA contains excess epoxy and shows anomalous cure behavior
- Elevated temperature may not favor rapid increased cure-conversion
- Small amounts of water can mechanistically interfere

- High temperature applications (>150°C) will induce epoxy degradation
- Issues are volatile formation, weight loss and material contraction (stress)

- Ongoing work: Extensive aging studies for lifetime prediction studies

- Impact: Improved methods for cure characterization and aging characterization