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Challenges for epoxy cure characterization and long term high temperature performance

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Understanding Epoxy Performance

- Epoxy material selection and long term performance depends on cure behavior, cure state and possible degradation reactions

Research goals and approach:

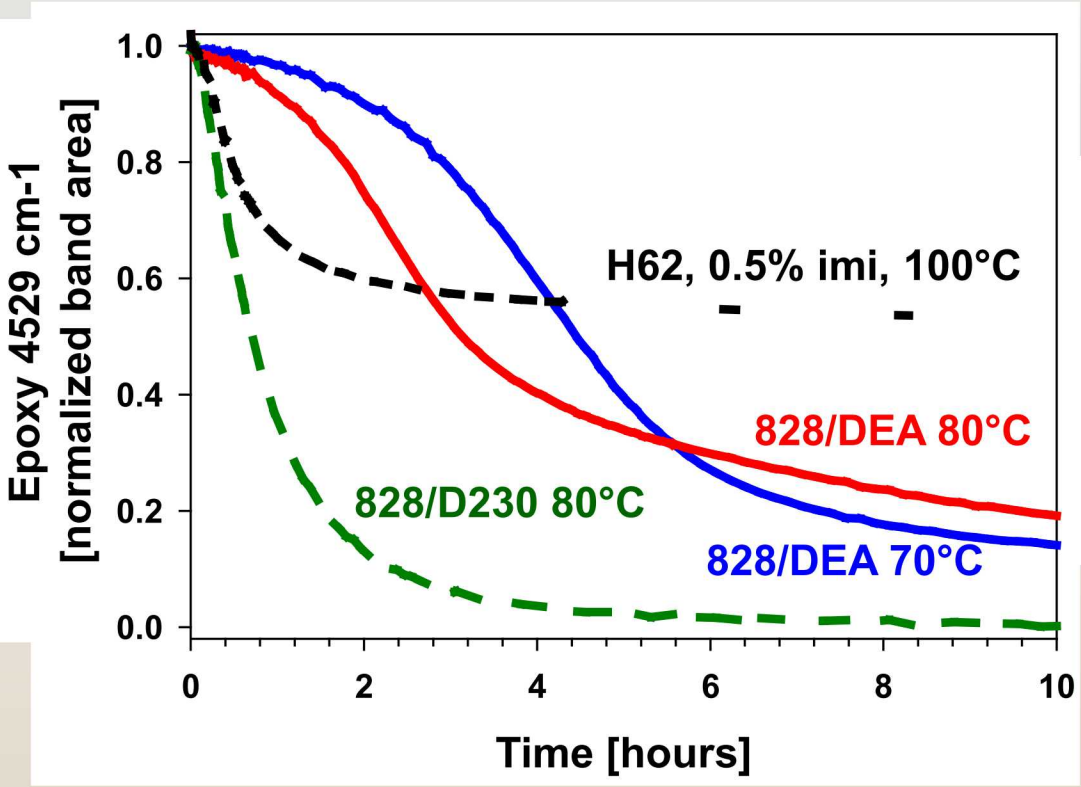
- Better understand cure behavior in epoxies
- Identify reasons for unusual cure behavior in Epon 828/DEA
- Develop approaches for quantification of cure conversion states

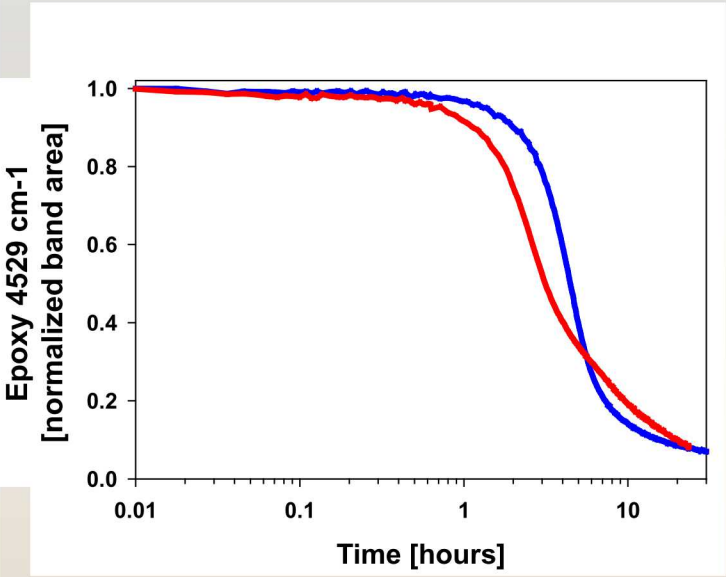
- High temperature epoxy degradation phenomena
- Develop diagnostic tools and lifetime prediction models

Key words: Materials Characterization, Spectroscopy, Mechanistic Evaluation

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



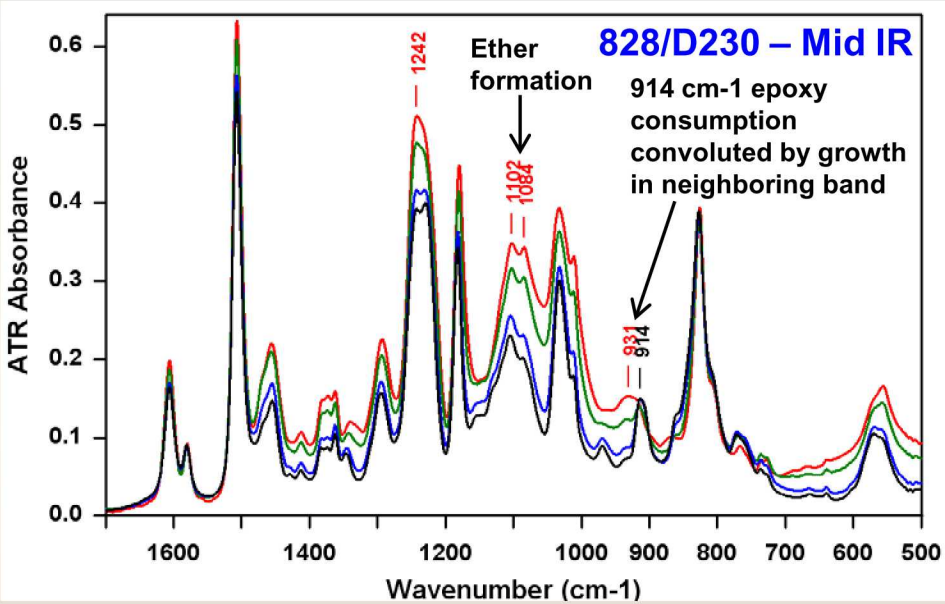


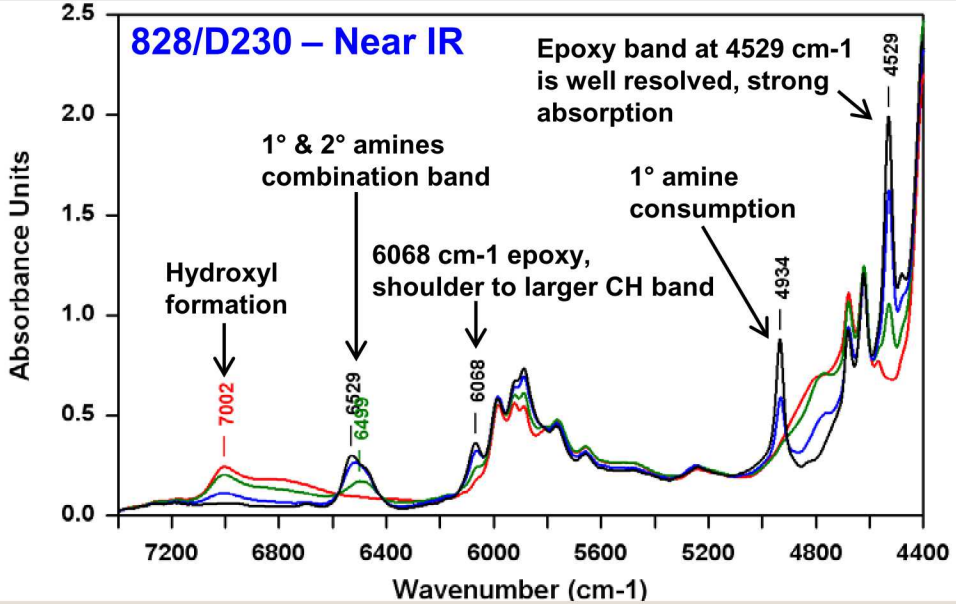
The cure reaction starts faster, but is then slower at higher temperature

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



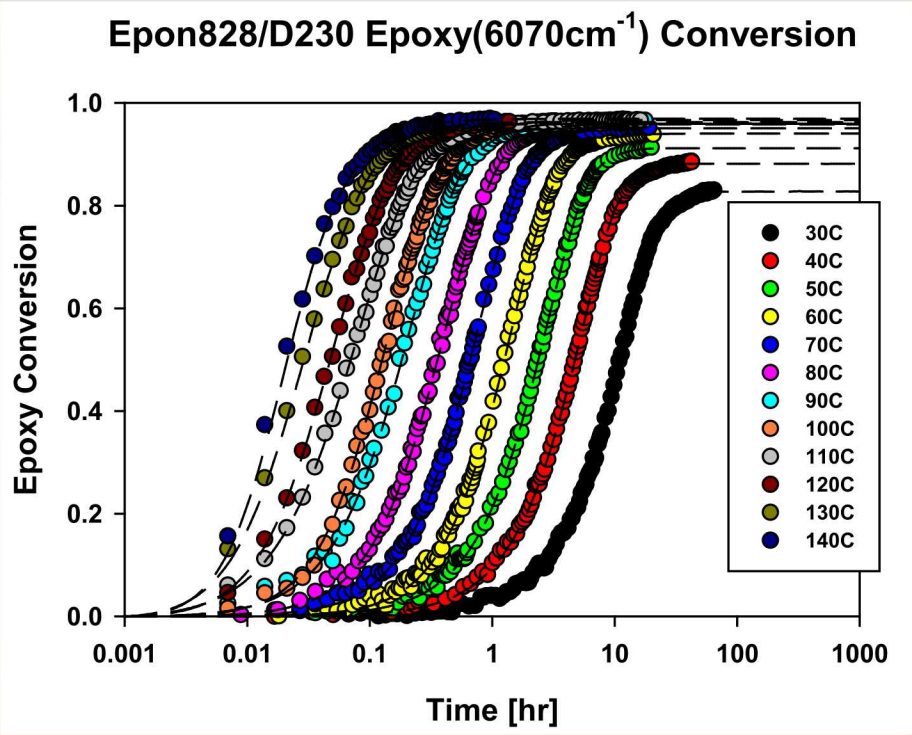


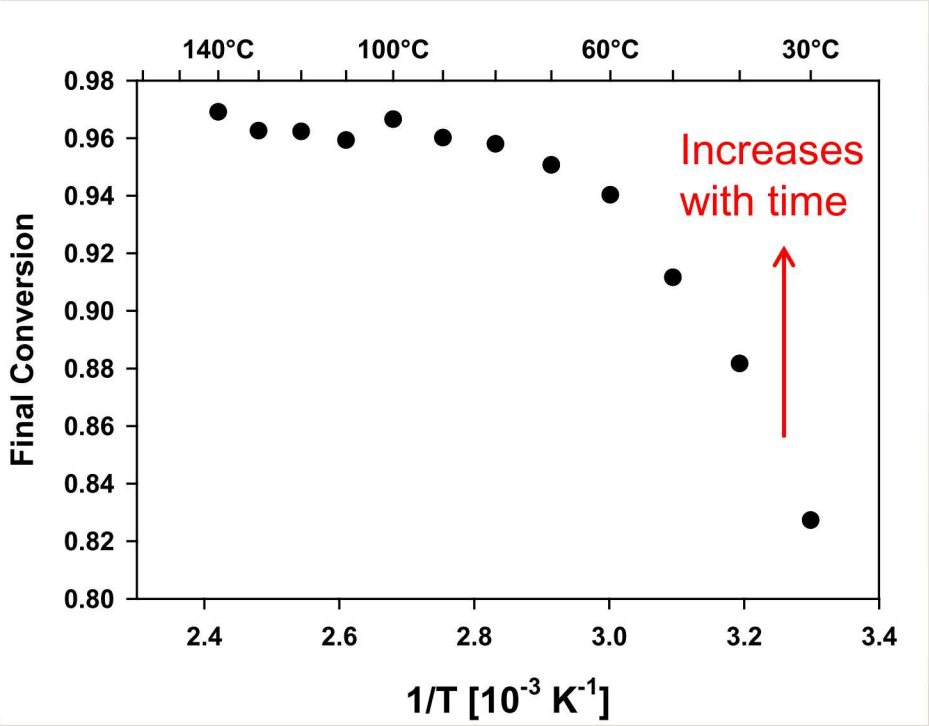
Epoxy as well as amine bands are resolved in NIR

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

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

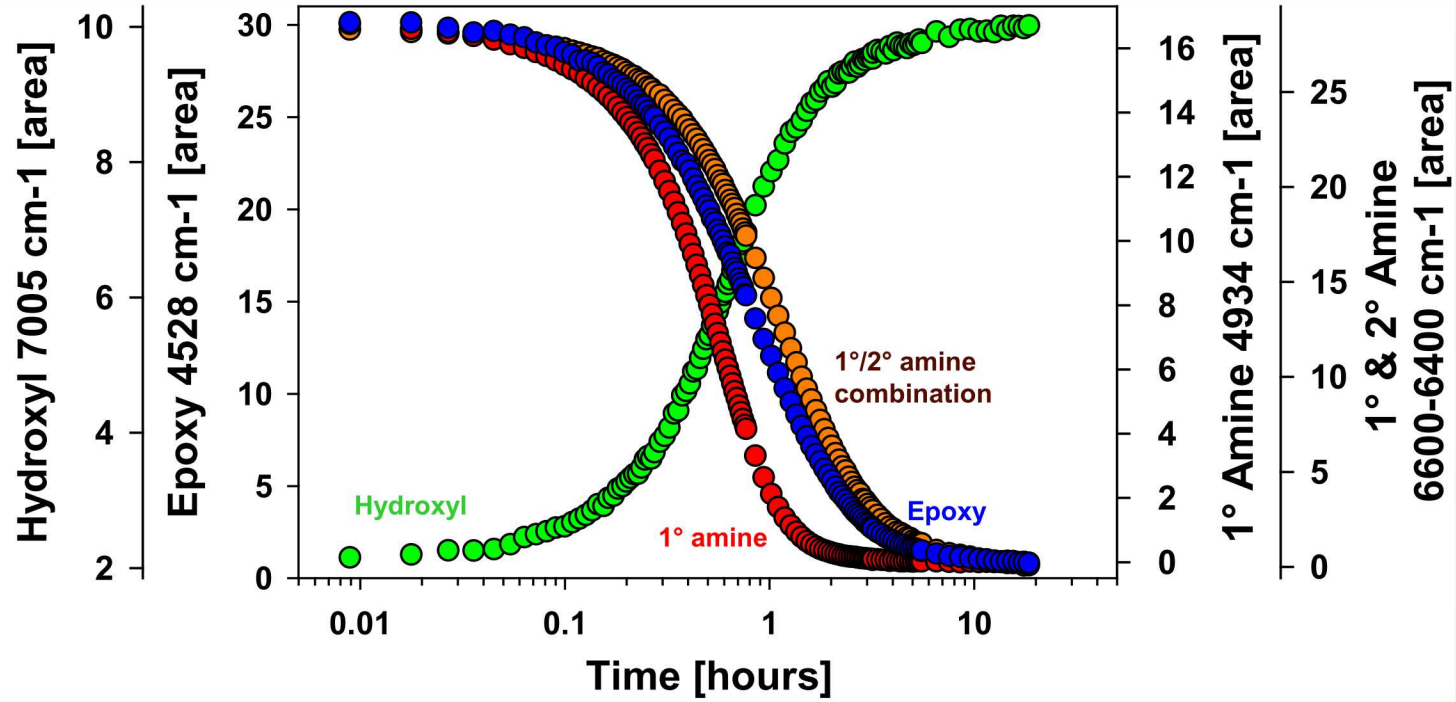




Cure speed increases and higher final conversion is obtained with T

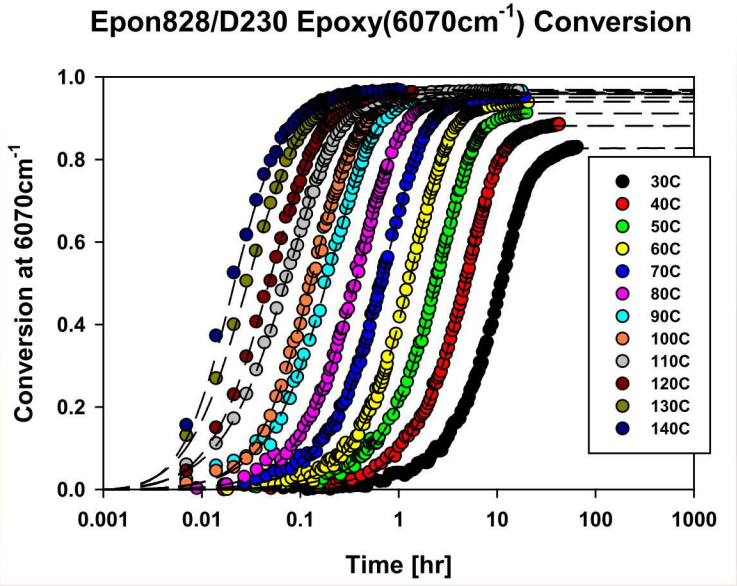
Epon 828 / D230 – 70°C Cure

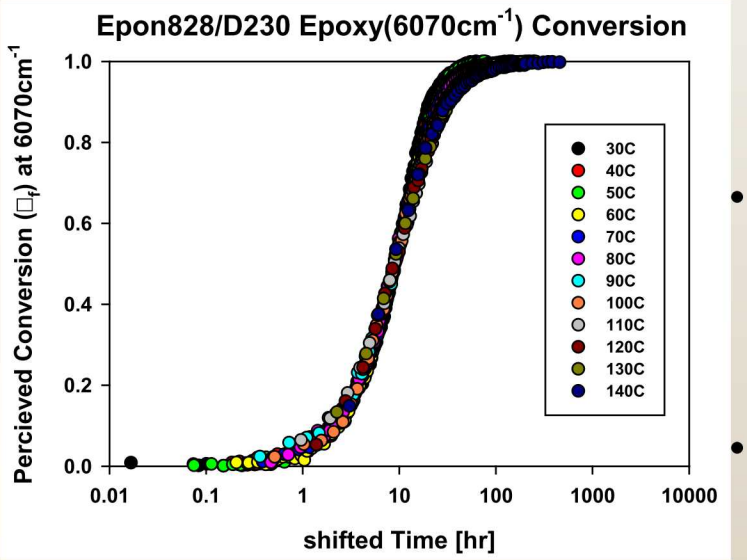
- Epoxy consumption can be compared with amine loss and hydroxyl formation



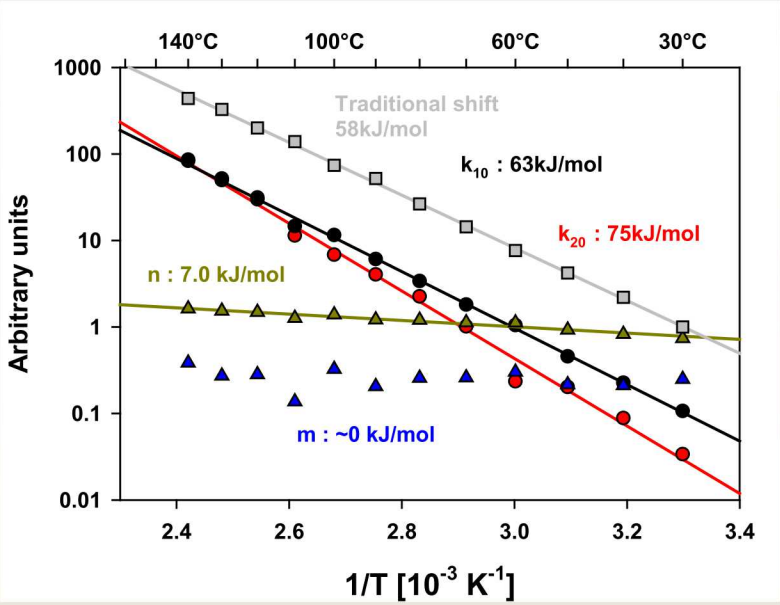
This system can be examined with multiple spectroscopy approaches

Epon 828 - D230





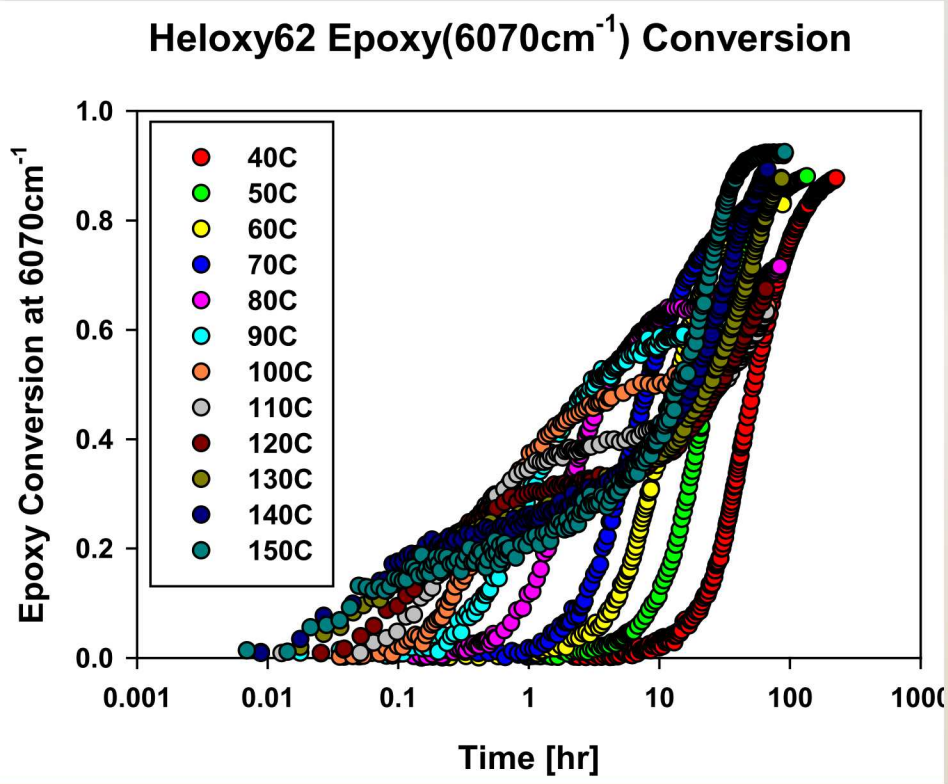
$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_f - \alpha)^n$$

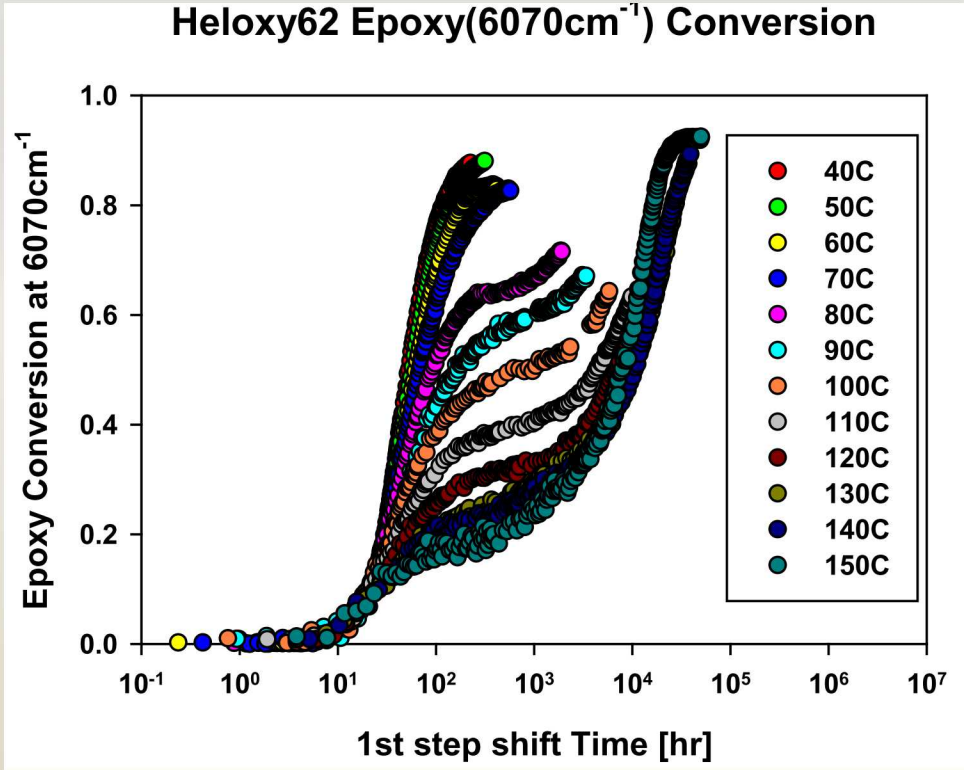


- **Traditional shifting does not account for variance of kinetic regime at high conversion and is only available after data is corrected for final cure state (α_f)**
- **Kamal equation accounts for this with two modified rate constants and temperature dependent power.**

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

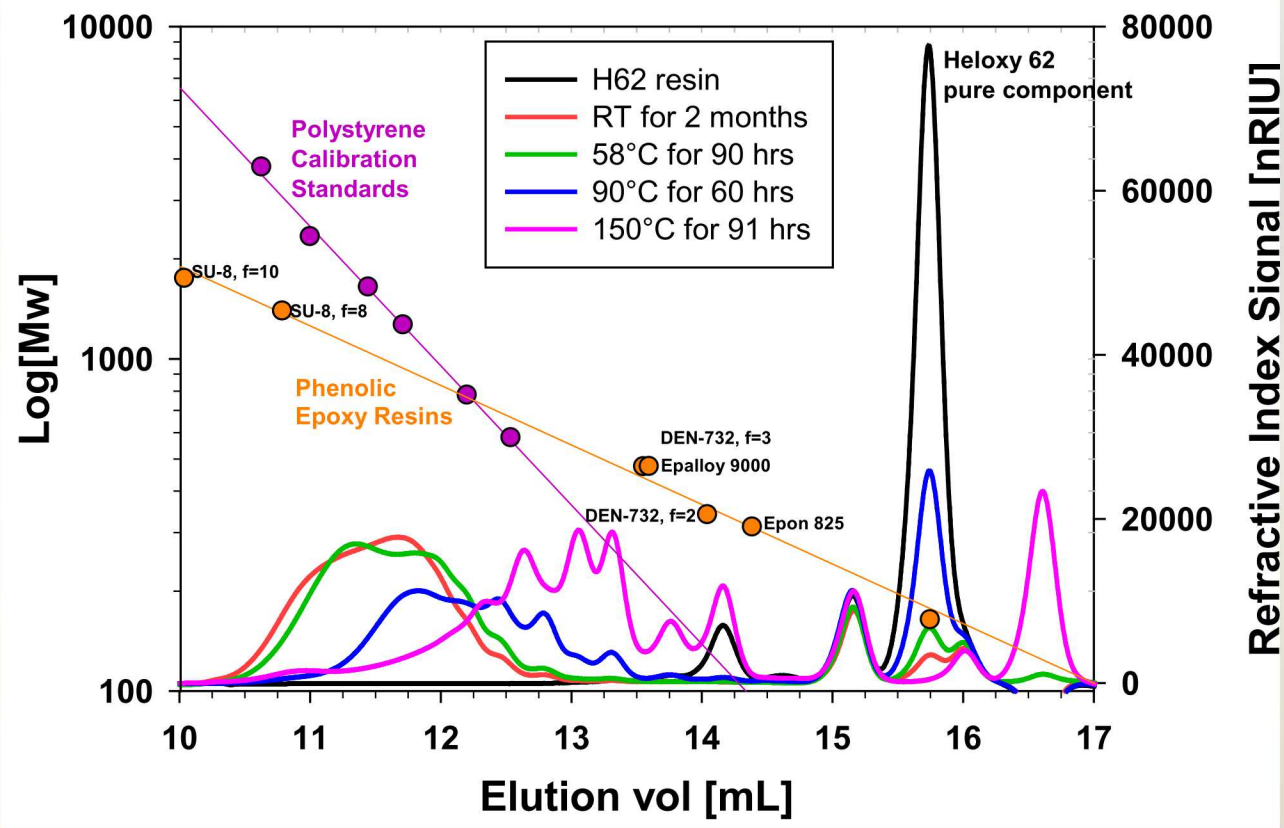




Delayed cure conversion at high temperatures
What do limited conversion states indicate?

Homopolymerization

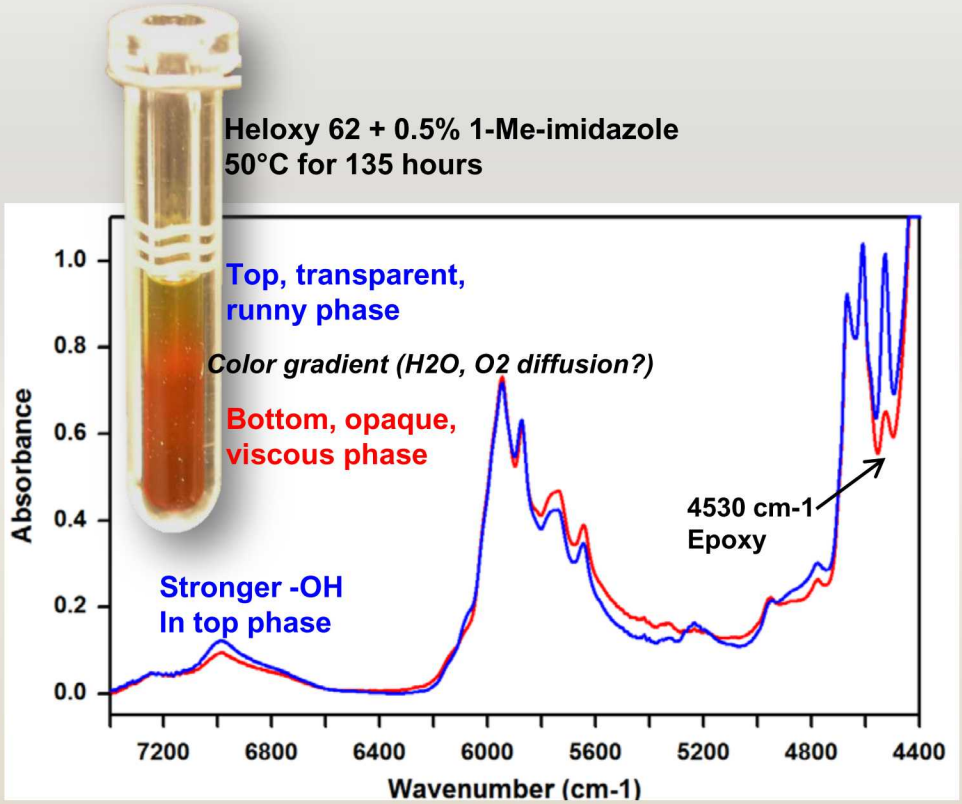
- Evidence for ‘ceiling’ temperature behavior
- What is Mw (polymerization degree) for linear polymerization?

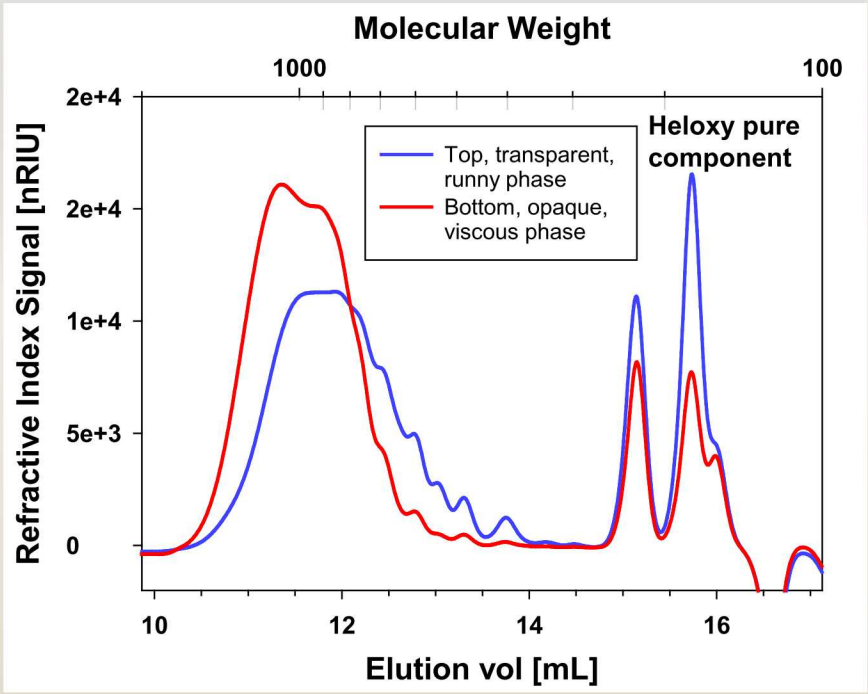


- GPC proves limited chain propagation behavior
- Higher Mw at lower temperatures

Heloxy Cure Inhibition - Water

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

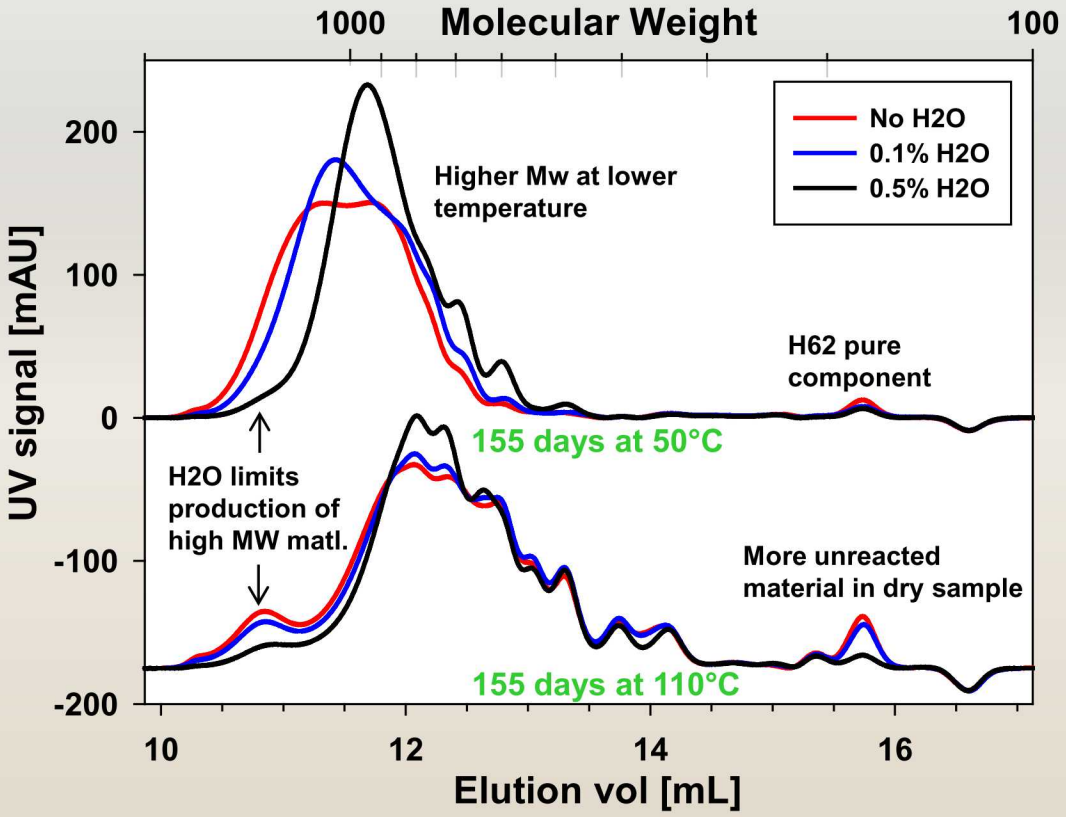




Clear evidence that atmospheric exposure affects cure behavior

Heloxy 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

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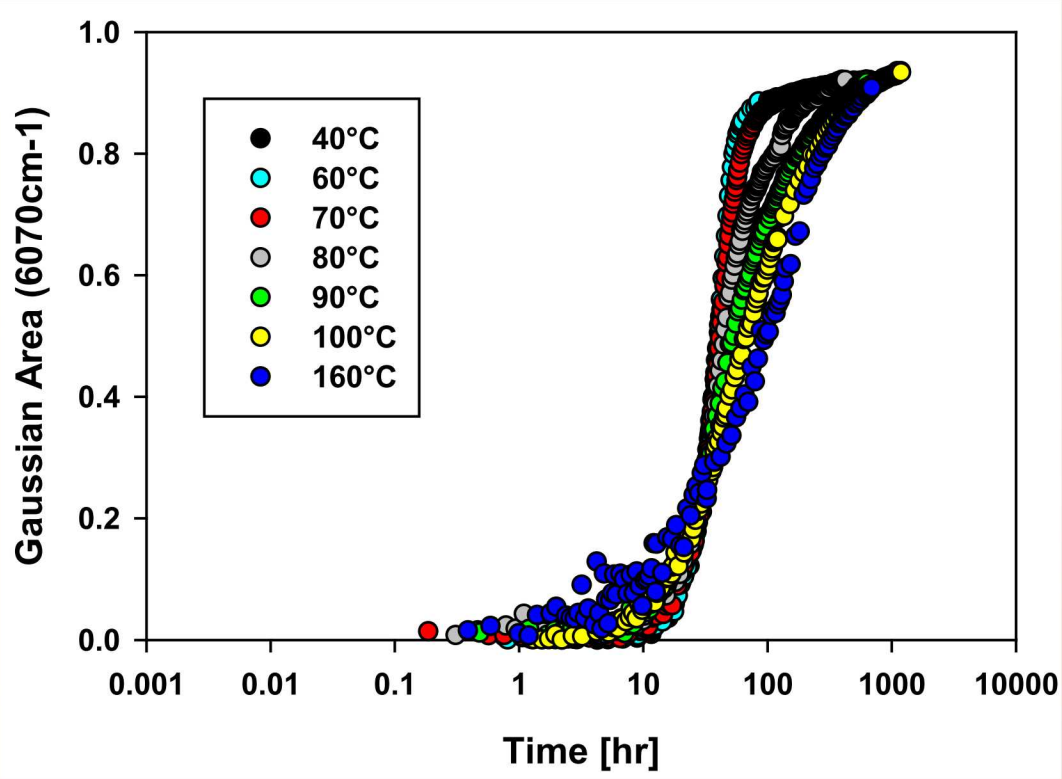
Epon 828/DEA Cure Behavior

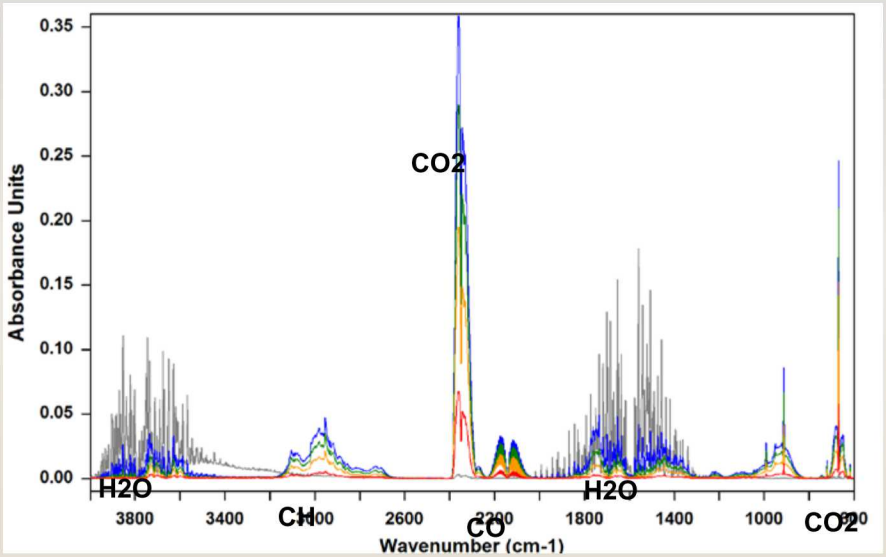
- Preliminary NIR data for t-T epoxy conversion (initial guidance)
- Peak quantification can be further optimized

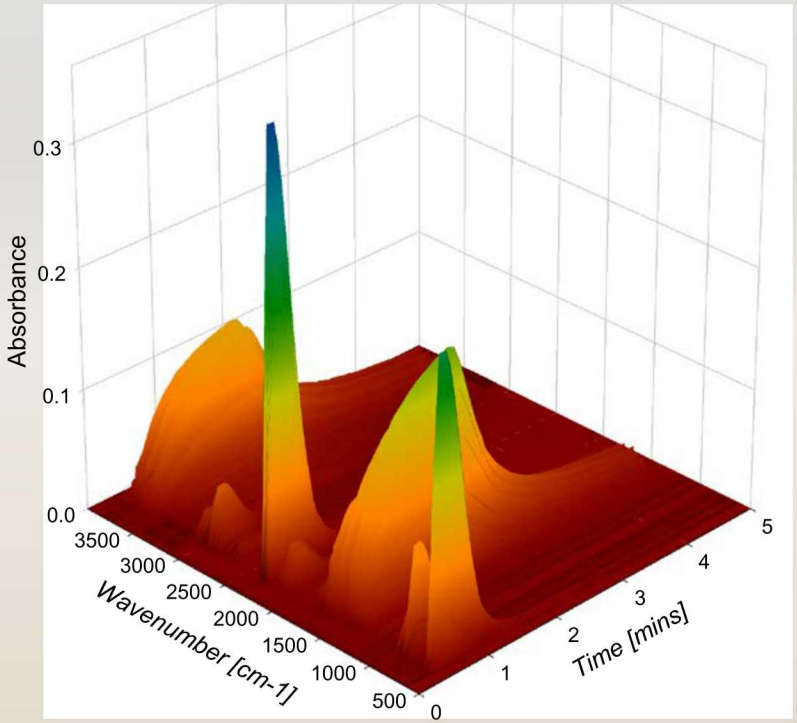


Influence of temperature (anomalous cure) is clearly apparent
Pure mathematical data superposition may not be the best approach

High Temperature Performance of Epoxy

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

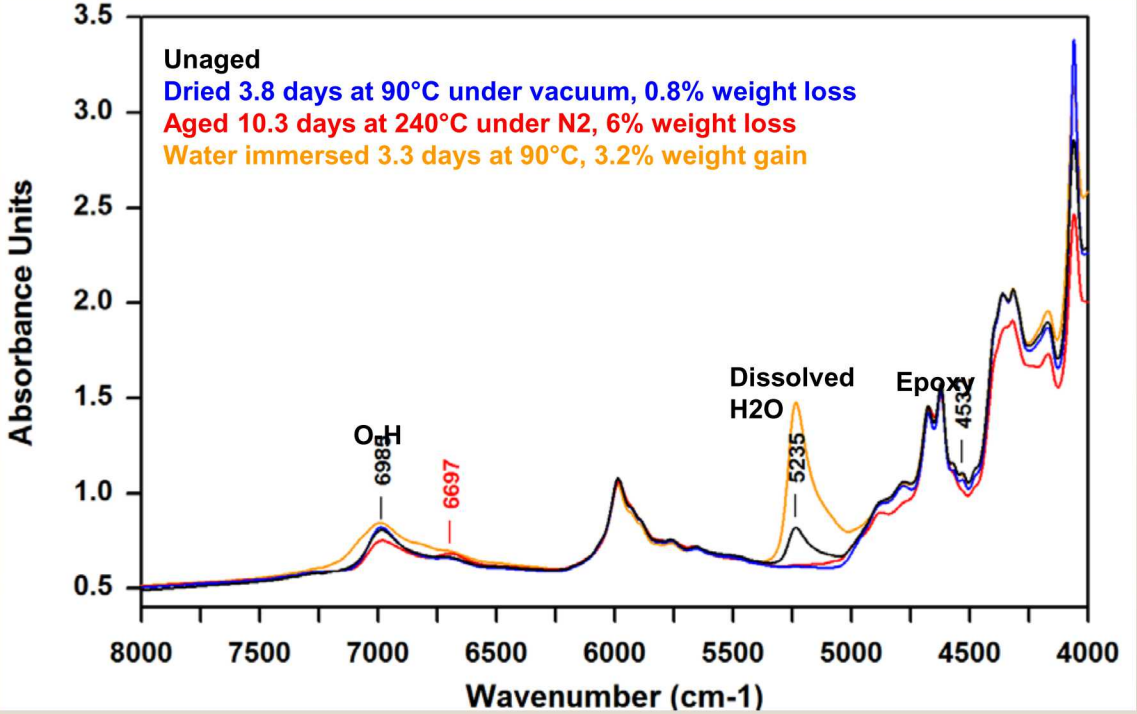




Quantification of H2O and CO2 yields via spectral and time integration

Physically Absorbed Water

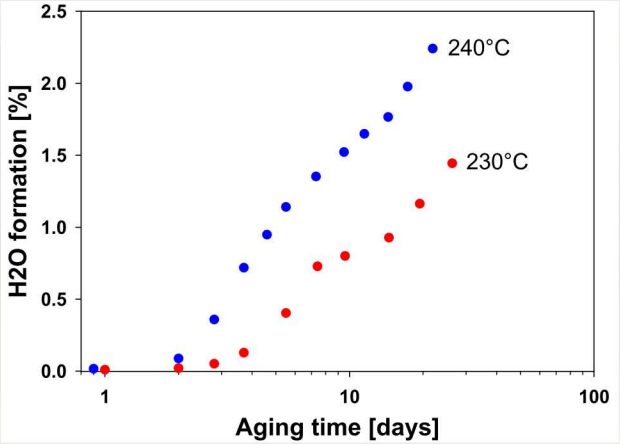
- Amine cured epoxy has a tendency to absorb water (somewhat hydroscopic)
- NIR can be used to quantify dissolved water in an epoxy
- Water uptake will depend on geometry and permeability (thin lab samples are expected to more easily pick up water)

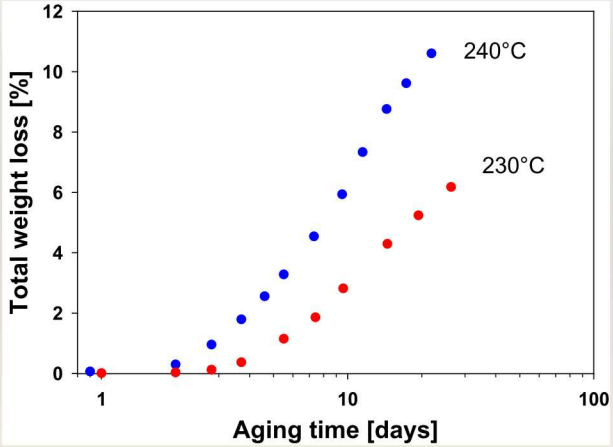


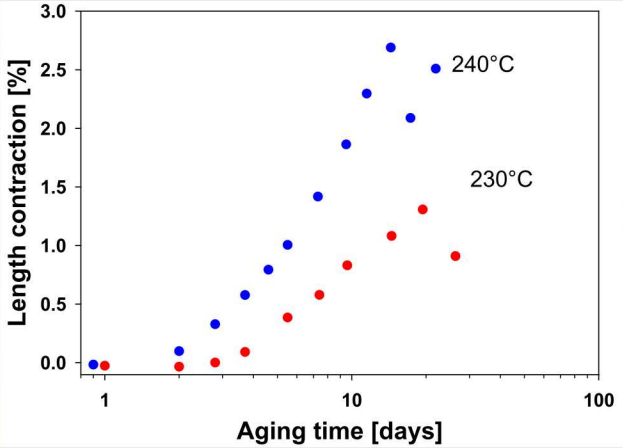
Presence of dissolved water and its chemical formation

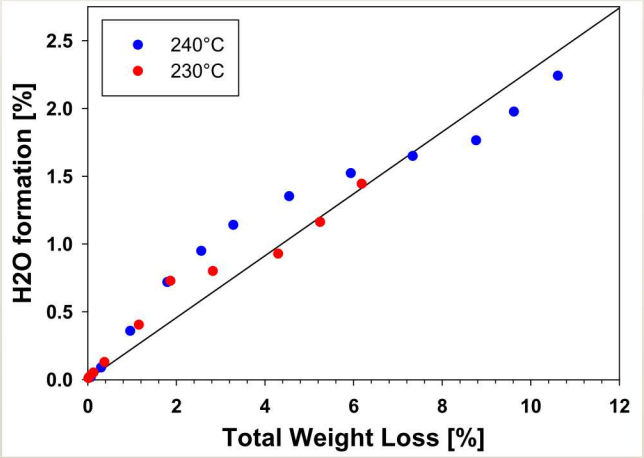
Volatile Yields - Weight Loss - Contraction

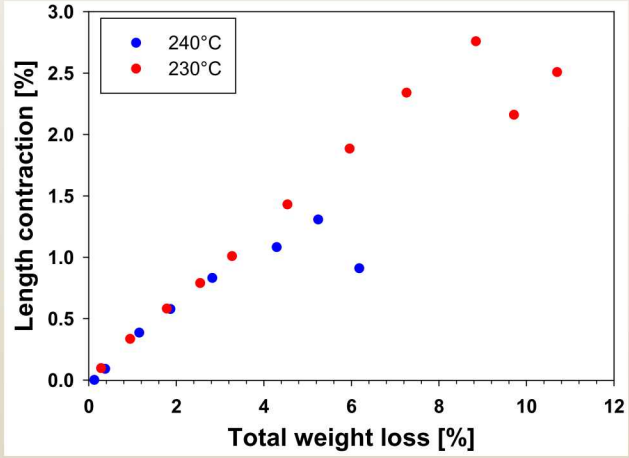
- Weight loss – Water formation – Material Contraction
- Stress and changes in local chemical environment





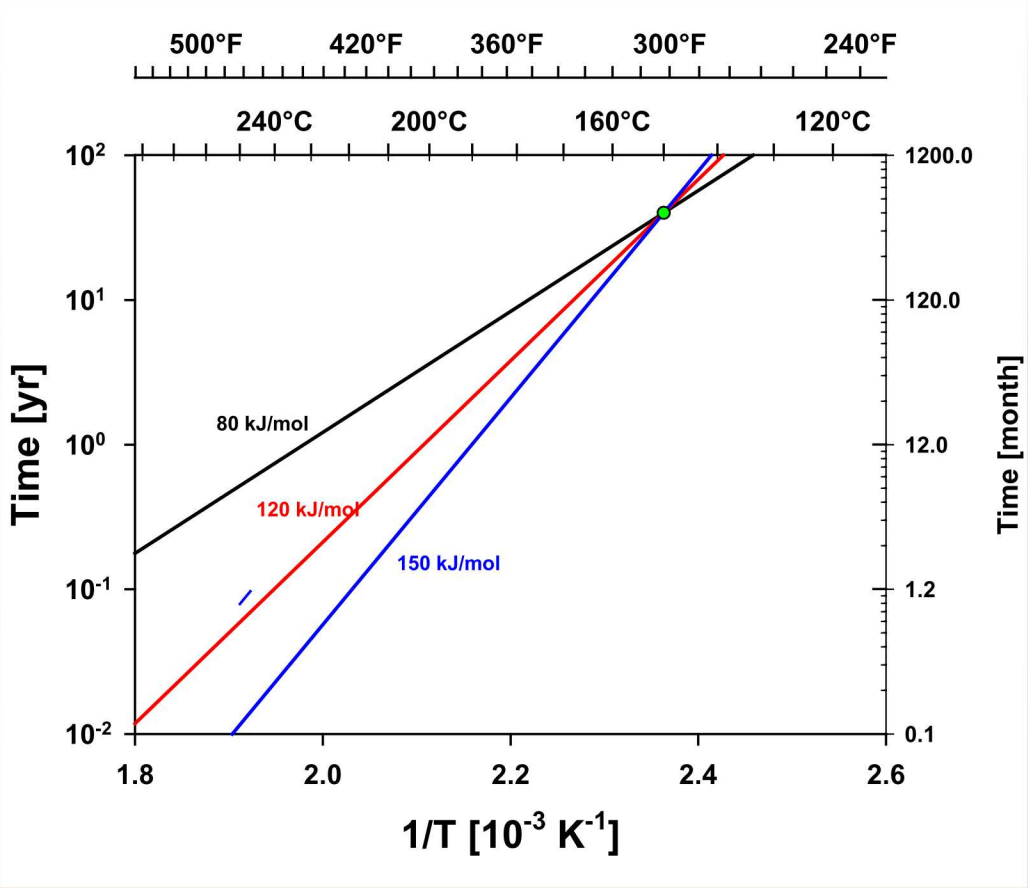






Aging studies to be continued at lower temperature – Arrhenius ?

Lifetime Prediction Models



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

Summary

- 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)

- Outstanding work: Extensive aging studies for lifetime prediction studies

- Impact: New methods for cure characterization and aging characterization