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Rapid IR Flow-Through Method for Volatile Quantification in Thermoset Ageing used for Lifetime Predictions

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Epoxy Selection and Performance

Material properties:

- Cure behavior, cure state evolution, physical relaxation (Tg), degradation chemistry tendencies, elevated temperature performance, adhesion, wetting, viscosity

Broad research goals and approach:

- Cure behavior in epoxies
- Quantification of cure conversion states
- Spatially resolved oxidation chemistry
- High temperature epoxy degradation phenomena
- Degradation chemistry off-gassing characterization
- Develop diagnostic tools and lifetime prediction models

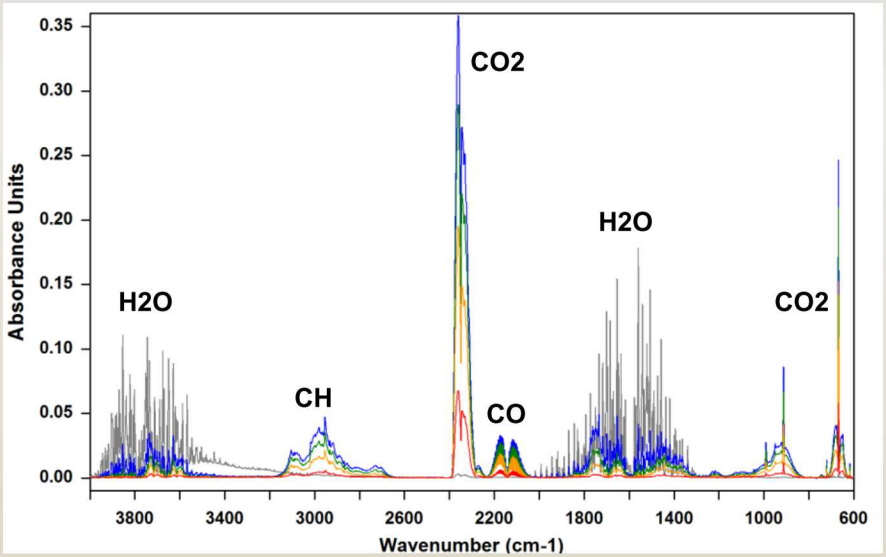
Application needs:

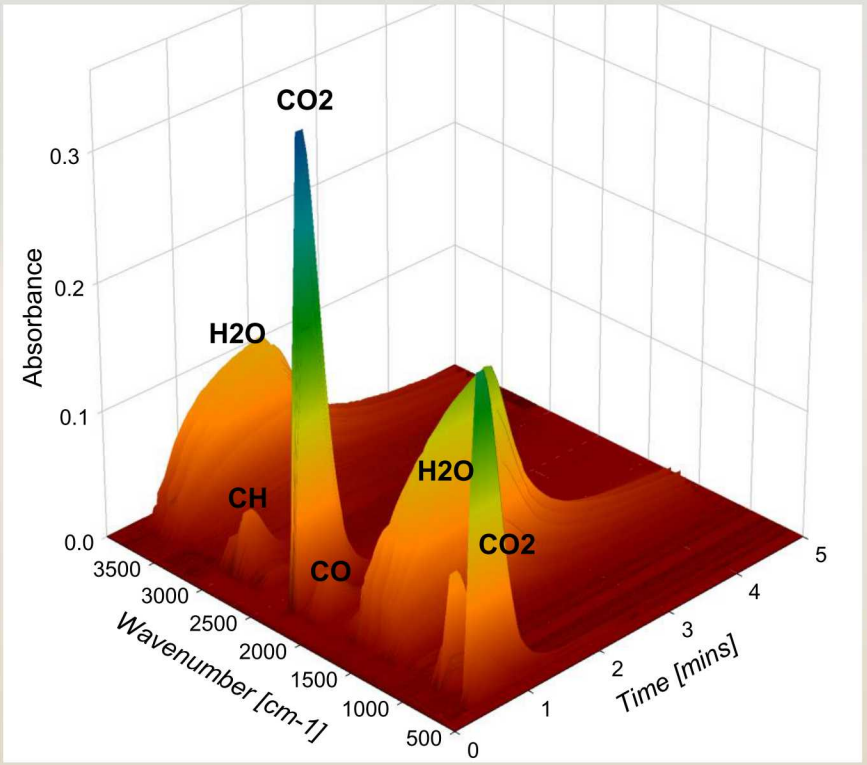
- Understand encapsulation materials and materials compatibility

Key words: Materials Characterization, Spectroscopy, Mechanistic Evaluation, Degradation Chemistry

High Temperature Performance of Epoxy

- Concern: Thermally induced decomposition (pyrolysis chemistry)
- Sealed ampoules, trapped gases, flow through approach, IR rapid scans
- IR based analysis of gaseous decomposition products





Quantification of H_2O and CO_2 yields via spectral and time integration

Giron N., Celina M., High temperature polymer degradation: Rapid IR flow-through method for volatile quantification. Polym Deg Stab 2017, in press

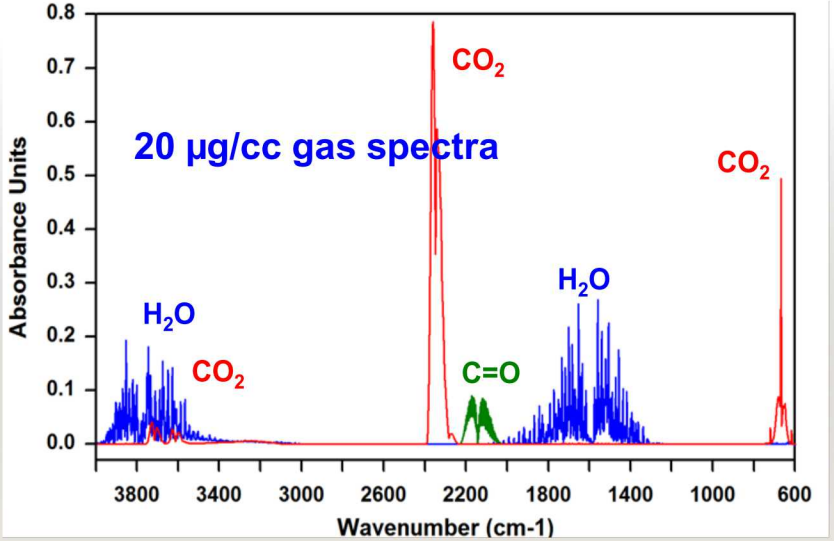
Analytical Methods

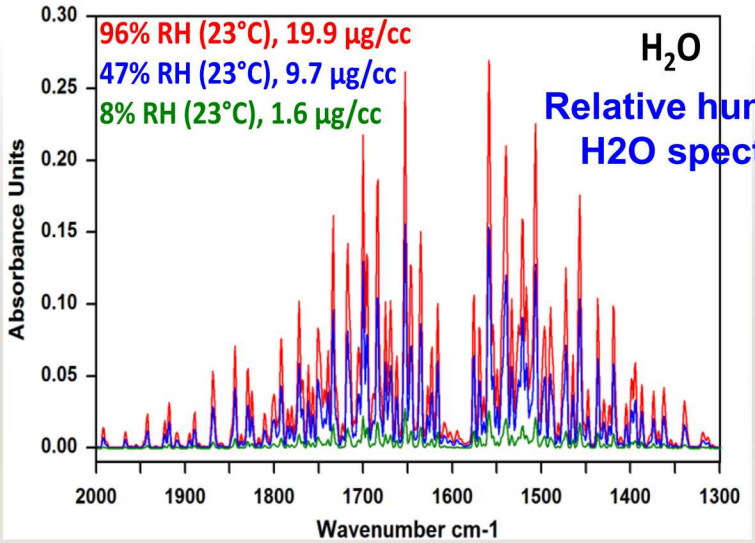
- **Considered multiple approaches (prior work in this area):**
- **MS or GC-MS is the method of choice for establishing exact mechanistic pathways through identification of volatiles. Some calibrated direct MS approaches have been accomplished .**
- **SPME (solid phase micro-extraction) may enable analysis of a large range of volatiles (often higher Mw) that can be individually identified through subsequent GC-MS, but does not easily capture H_2O, CO_2 or CO.**
- **GC (gas chromatography) requires individual head space sampling techniques and calibration efforts with temperature and pressure controls. Water analysis is usually challenging due to surface adsorption, particularly if needed in parallel with CO_2 and CO.**

- **Is there a feasible approach using a simple flush-out of the ampoule gases through an IR gas cell? Development of IR Flow-Through Volatile Quantification**
- **This was accomplished for CO_2 and CO gas evolution from epoxies using IR, but water was not considered. In situ IR gas evolution diagnostics was also applied to polymer pyrolysis or even fire gases.**

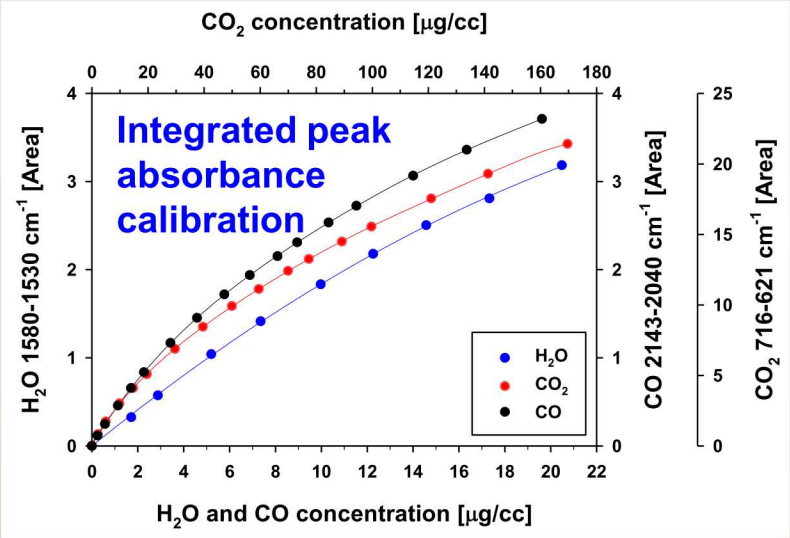
No perfect 'ready to go' method available

IR Based Gas Analysis





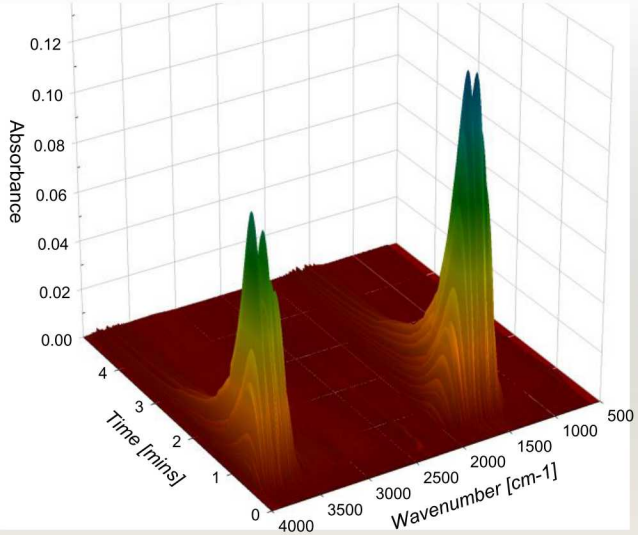
- Spectral signatures for H_2O, CO_2, CO do not overlap
- Calibration is non linear

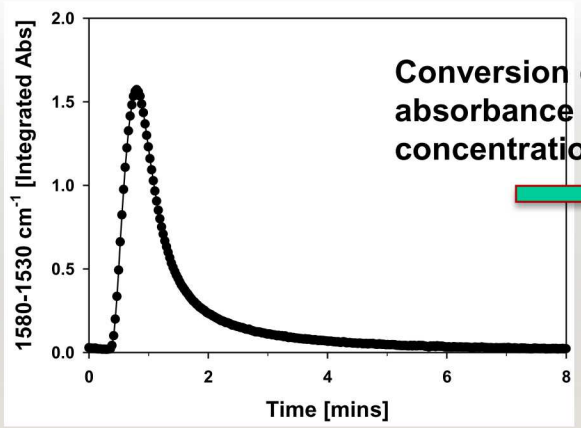


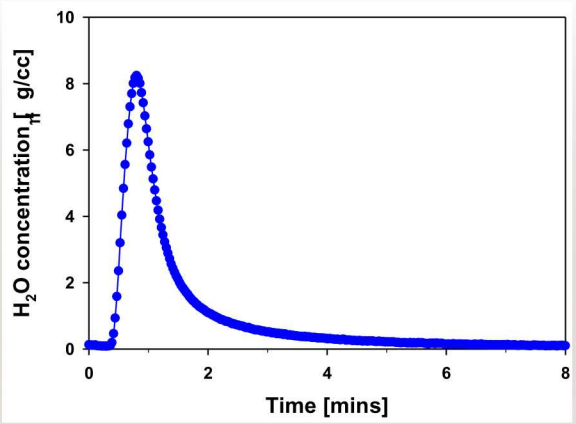
Good spectral response in concentrations of interest

Giron NH, Celina MC. High temperature polymer degradation: Rapid IR flow-through method….. Polym Degrad Stab 2017;145:93.

Successful Quantification of Water



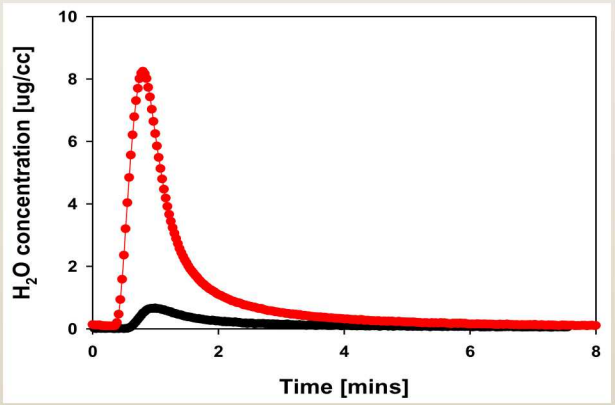




$$M = Q \times \int_{t1}^{t2} \left[F \int_{\nu 1}^{\nu 2} A(\nu)\, d\nu \right] dt$$

F = calibration factor [µg/abs]
A(v)=Absorbance at v
Q = flow rate [cc/min]

- **Spectral signatures for H_2O, CO_2, CO do not overlap**
- **Calibration is non linear**
- **0.01% of 1 gram of aging sample = 10 mg**



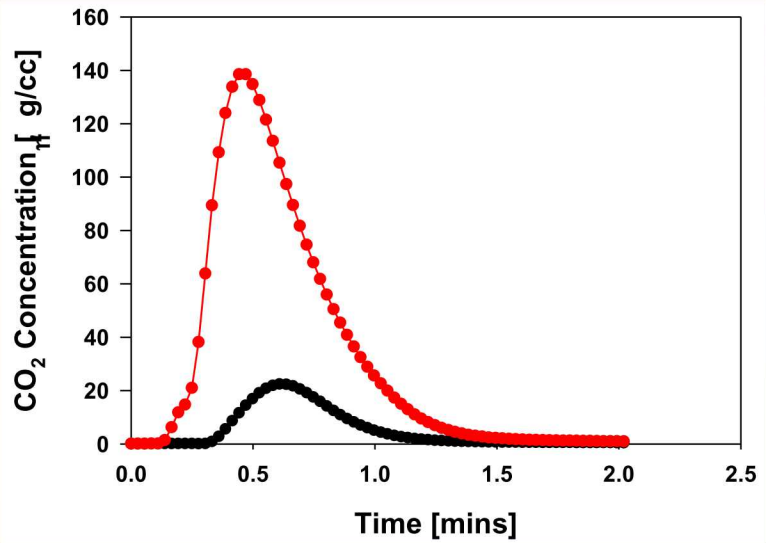
Theoretical: 70% RH at 25.5°C – (19.2 cc)(0.7*23.7 µg/cc) = 318.5 µg
Measured: (7.94 µg-min/cc)(40 cc/min) = 317.6 µg

Theoretical: 7.3% RH at 27.1°C – (19.2 cc)(0.073*26 µg/cc) = 36.4 µg
Measured: (1.155 µg-min/cc)(40 cc/min) = 46.2 µg

Good spectral response in concentrations of interest

Successful Quantification of CO_2

- Similar approach for quantification of CO_2
- Method validation through analysis of ampoules with known amount
- Easy calibration and integration of flush out signal



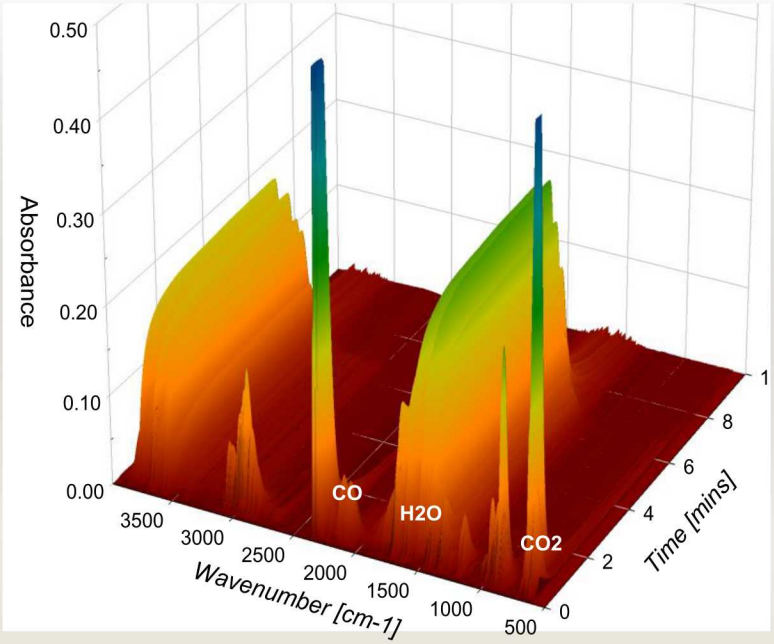
Theoretical: (700 Torr)(0.0863)(19.2 cc)/(62363 cc Torr K^{-1} mol^{-1})/(296.6 K)(44 g/mol)= 2759 µg
Measured: (68.2 µg-min/cc)(40 cc/min) = 2729 µg

Theoretical: (100 Torr)(0.0863)(19.2 cc)/(62363 cc Torr K^{-1} mol^{-1})/(296.6 K)(44 g/mol)= 395 µg
Measured: (10.48 µg-min/cc)(40 cc/min) = 419 µg

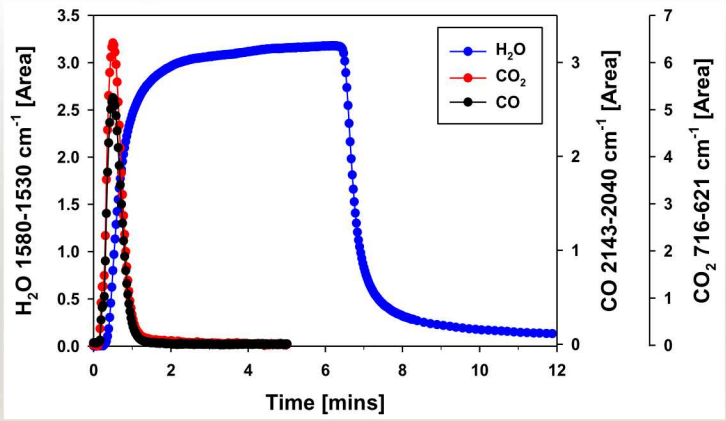
Flushing out of known amount validates this method

Aged Epoxy Test Specimen

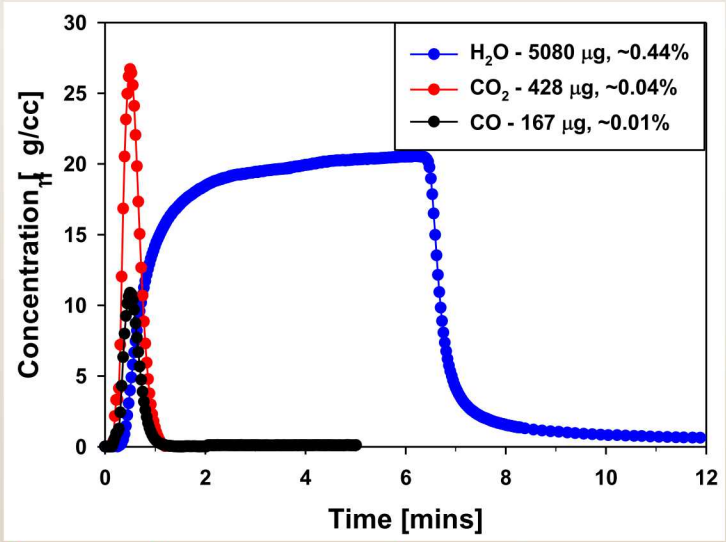
Primary IR spectral response over time



IR peak absorbance over time



Volatile concentrations over time

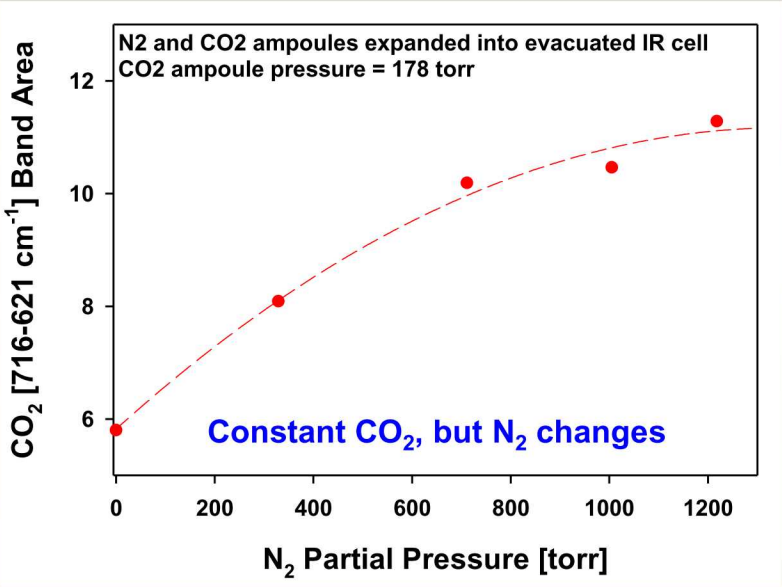


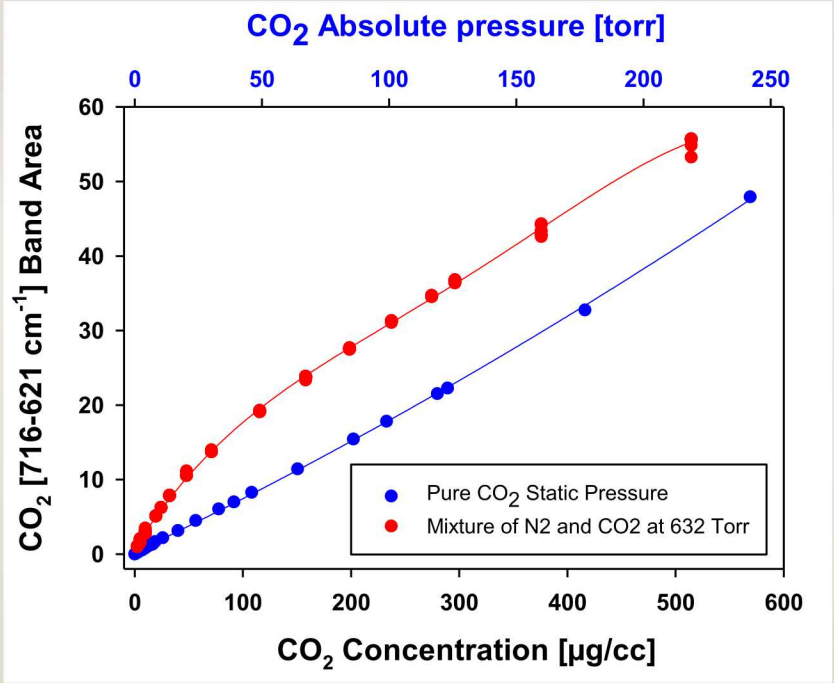
- ~ 1g sample was aged for < 1 d at 240°C
- Formation of 0.44 % H_2O, 0.04% CO_2, 0.01% CO during exposure
- Note: Extended H_2O detection

Volatile analysis works for aging experiment

Complications - Calibrations

- Volatile (H_2O, CO_2, CO) absorbance depends on more than absolute P
- Absorbance depends on gas composition, collisional energy transfer?
- Calibration and volatile analysis need to have similar concentrations
- Could not use reduced P calibration; aging and analysis at 632 Torr N2

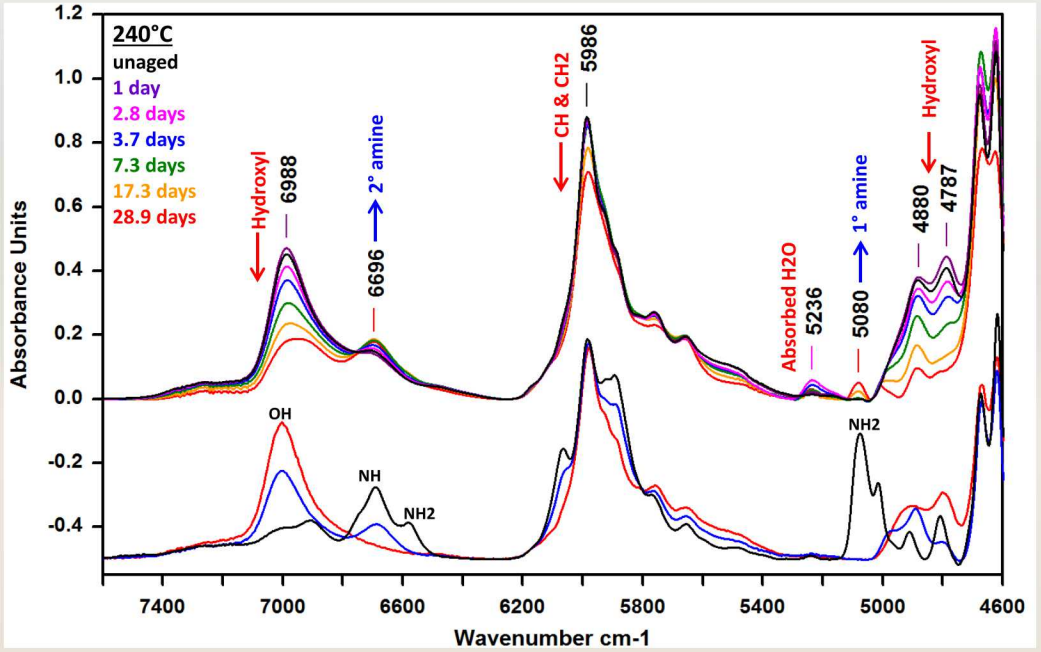


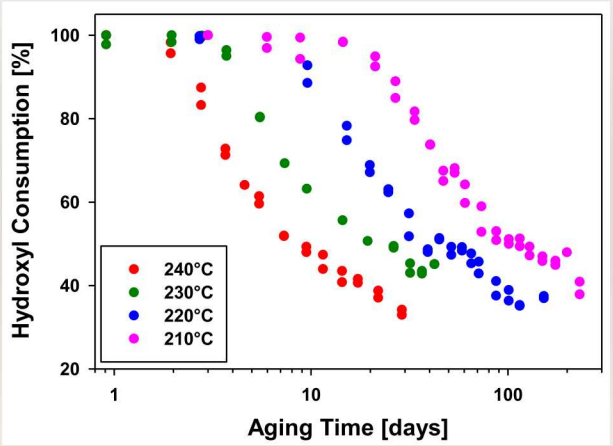


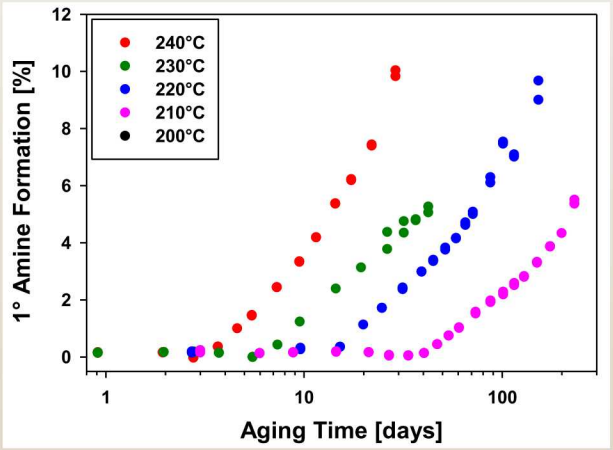
Single gas pressure based calibration is only approximate

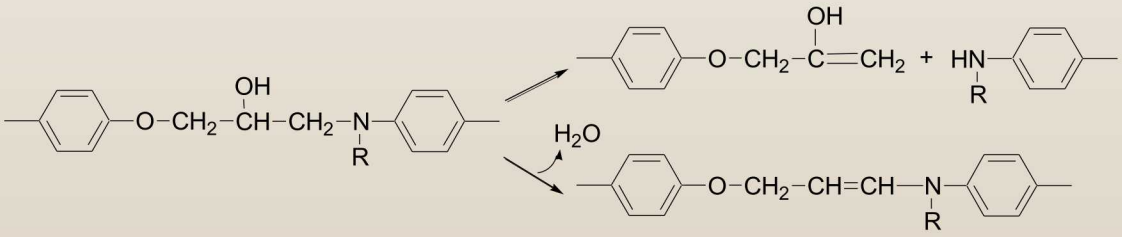
NIR Degradation Kinetics

- Changes in epoxy hydroxyl group (loss) with aging
- Formation of amine; must form carbonyls or unsaturation in parallel





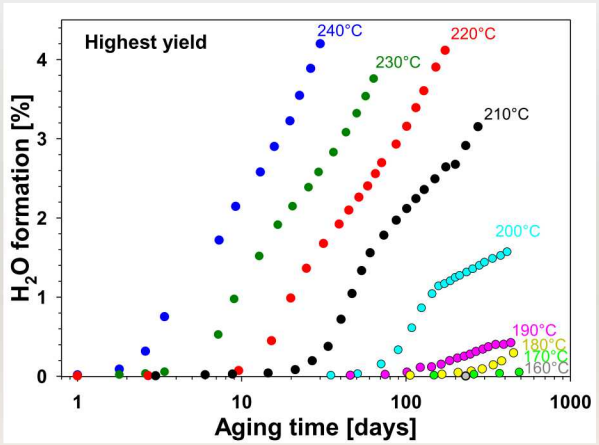


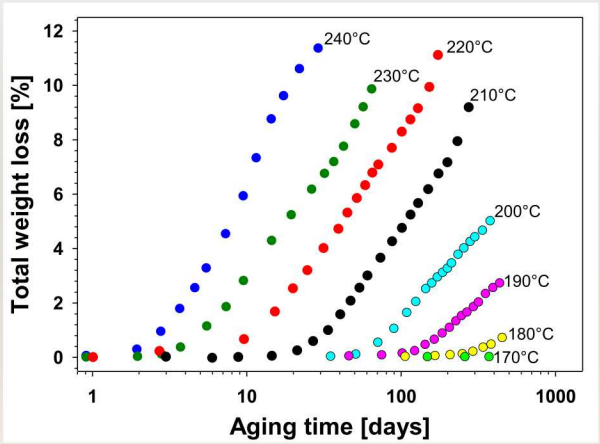


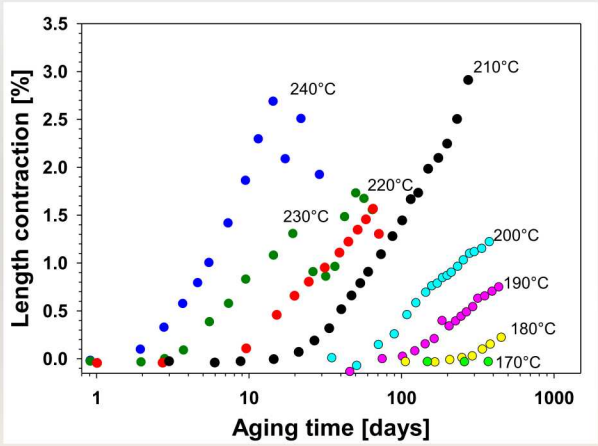
NIR epoxy response is consistent with 'aging chemistry'

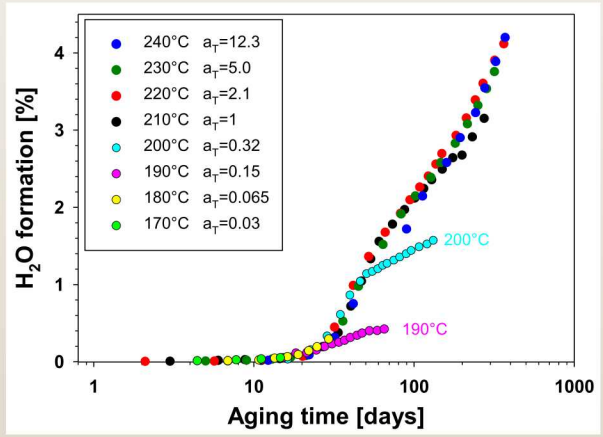
H_2O Yield - Weight Loss - Contraction

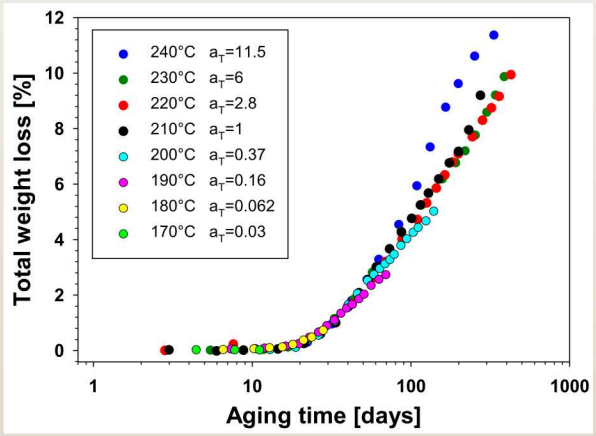
- Each property is monitored as part of extensive aging study
- t-T superposition to yield aging behavior with temperature

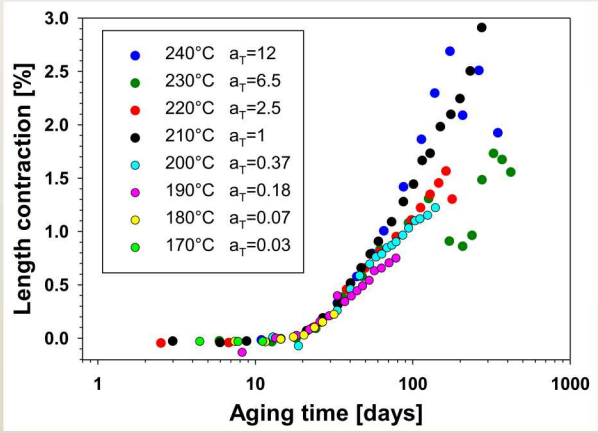








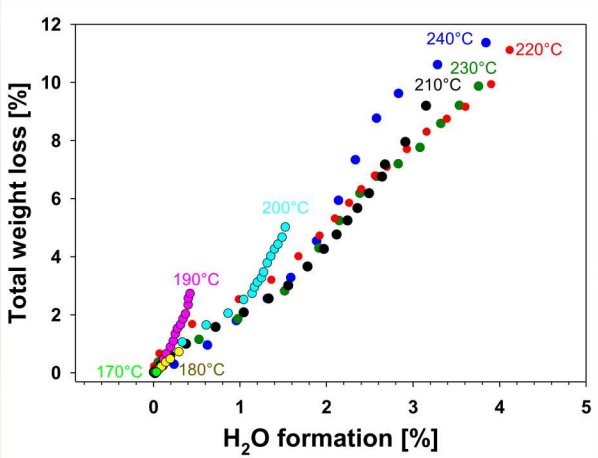


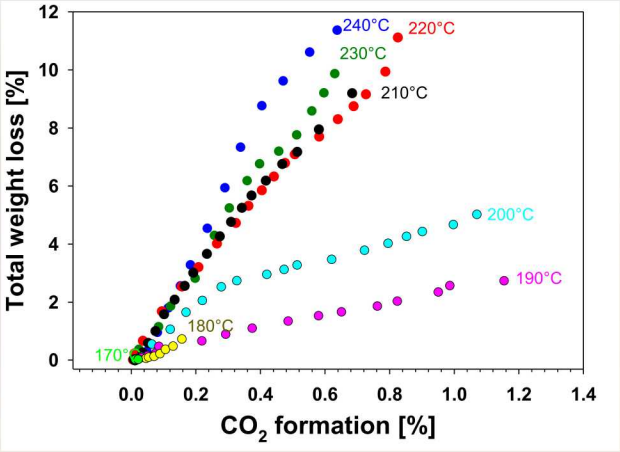


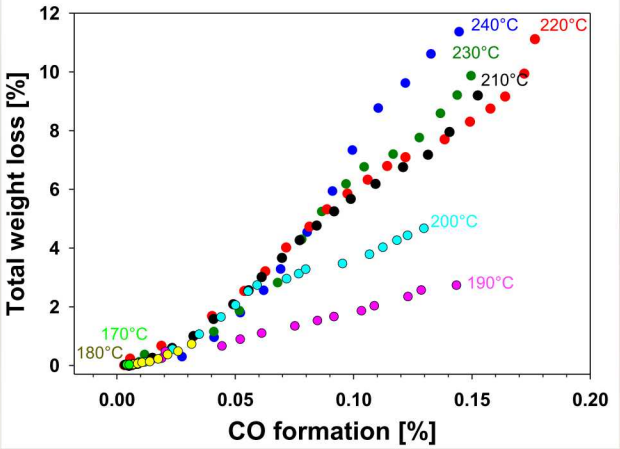
Aging chemistry and physical properties are coupled

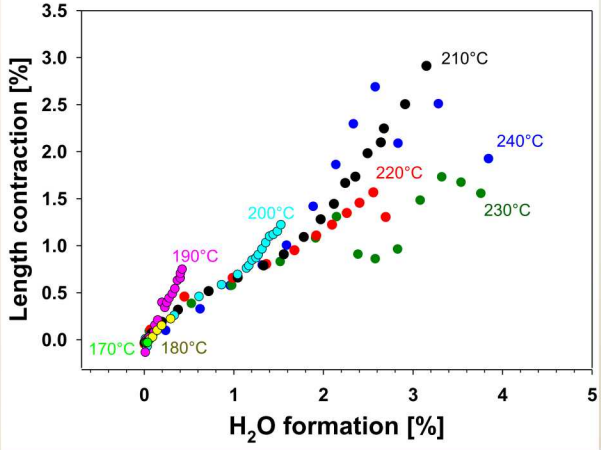
Volatile Formation with T

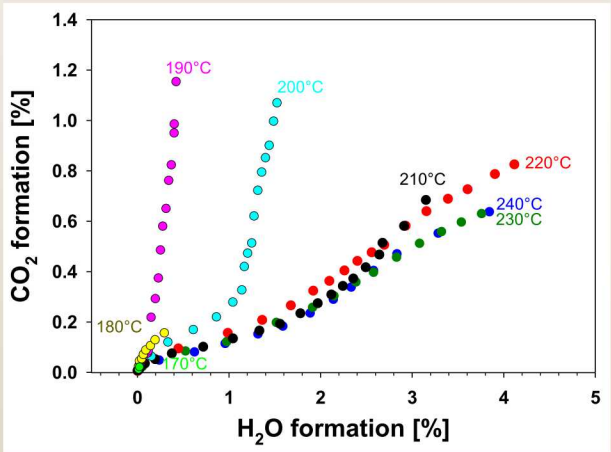
- Some subtle differences in volatile formation over large T range
- Cross-correlations are used to highlight mechanistic variations











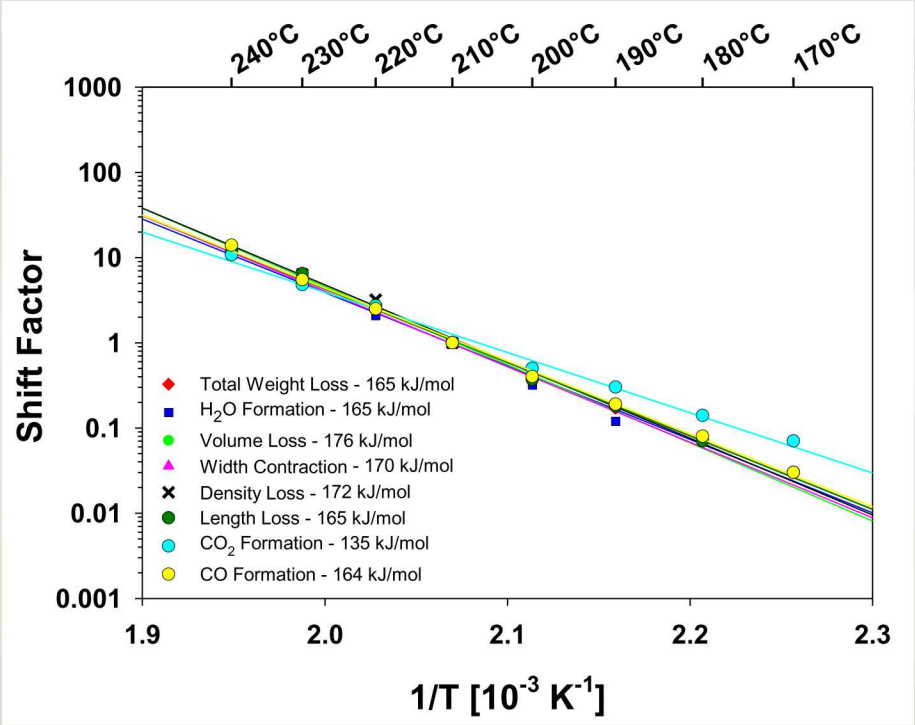
Towards lower T

- Less water
- More CO_2/CO
- Also, more acetic acid as seen by IR

Ongoing aging studies towards lower temperatures – Arrhenius?

Kinetic Models – Basis for Extrapolations

- Shift factors were determined by time–temperature superposition of multiple property changes referenced to 210°C
- Still significant uncertainty in shift factors for 180-160°C range

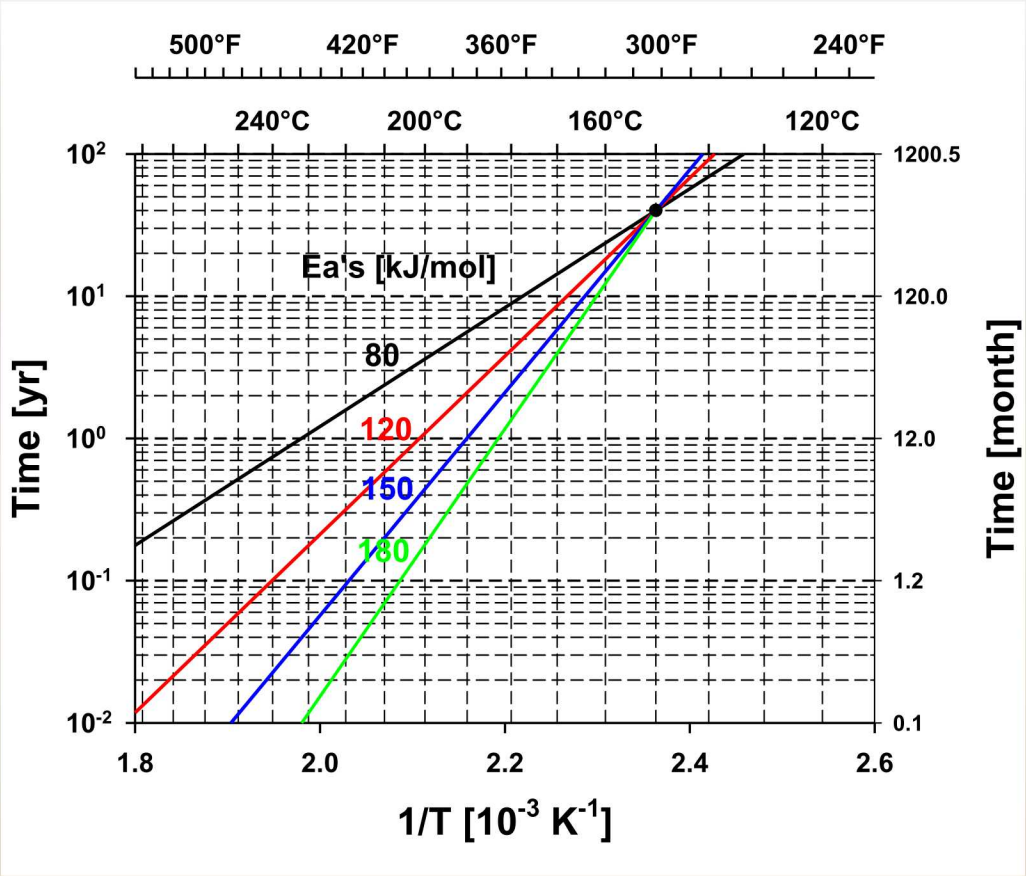


- CO_2 generation appears to be developing as a separate process with different Ea and divergence at lower T
- This subtle change in the dominant chemistry does not affect total weight loss and contraction
- Average Ea close to 170 kJ/mol

Trend: Activation energies range from ~140-180 kJ/mol

Lifetime Prediction Models

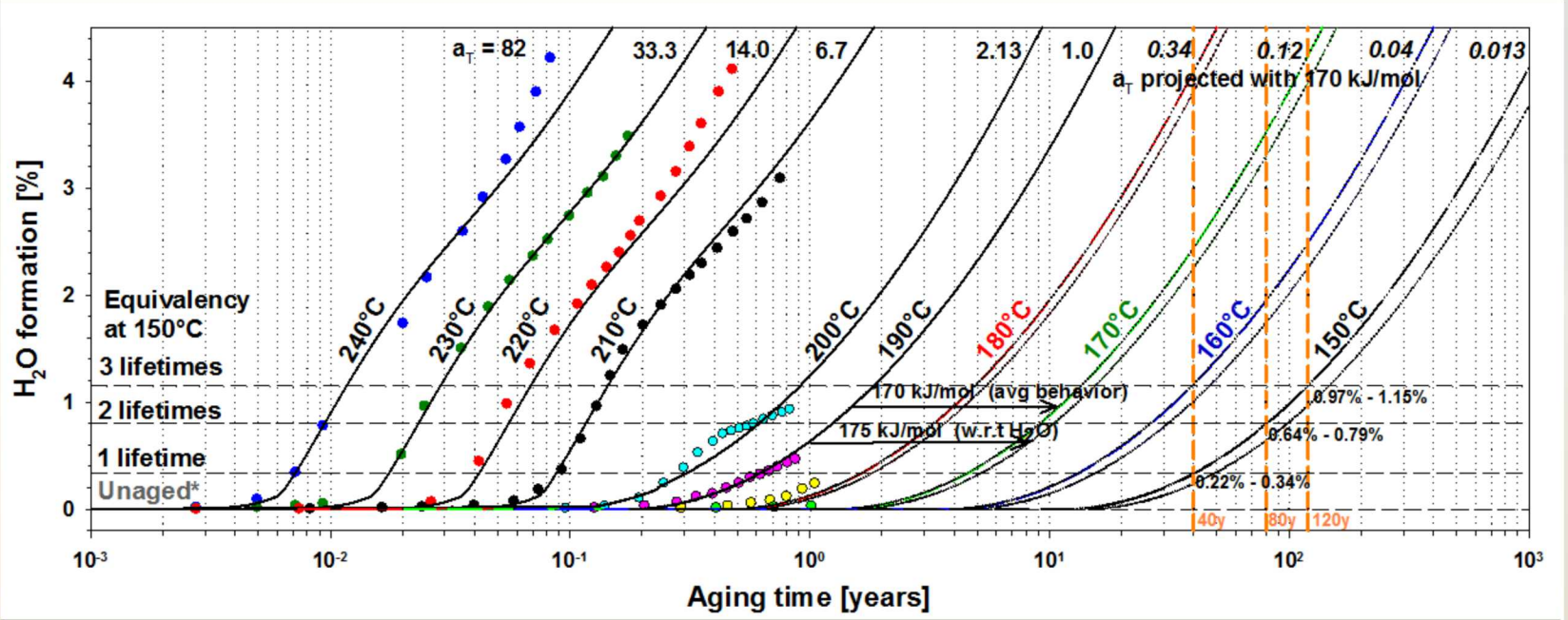
- Arbitrary performance expectations for t-T



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

Projections based on Current Ea

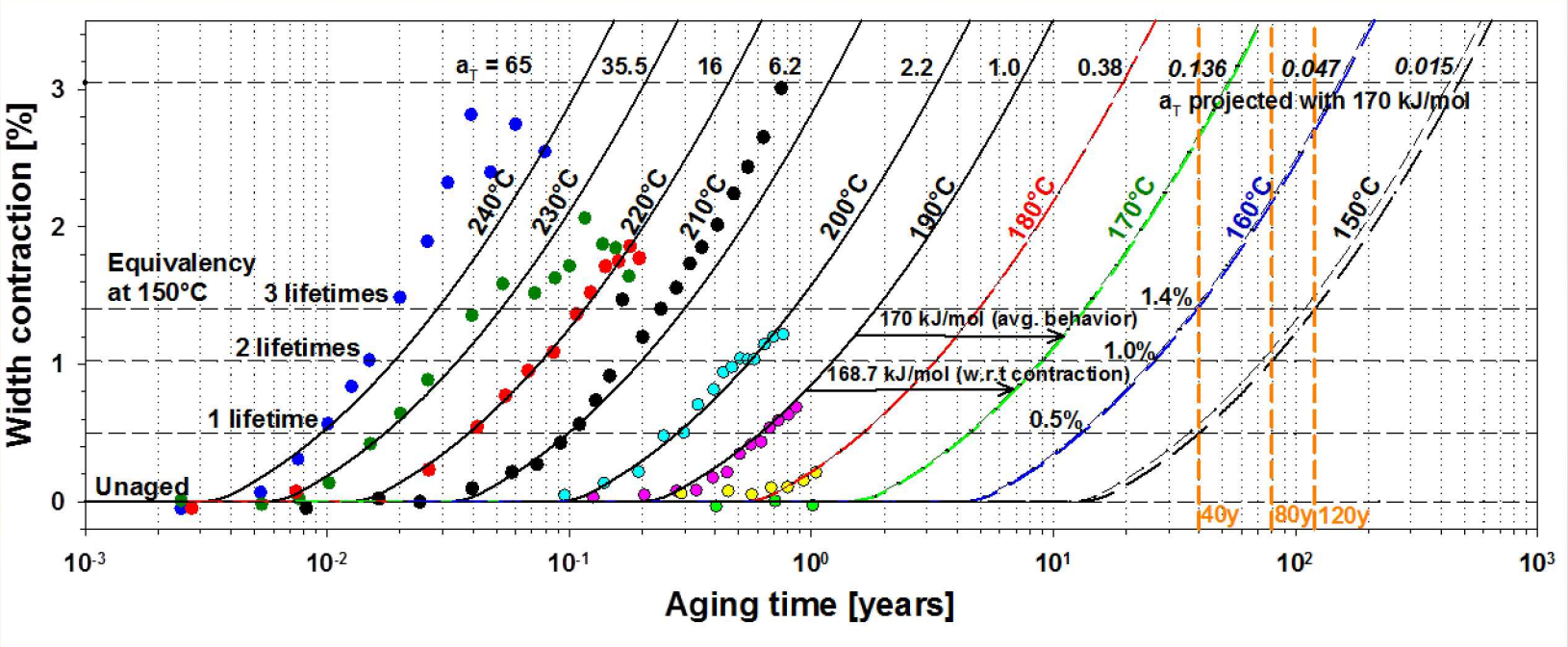
- Average Ea for degradation chemistry and physical property changes is ~ 170 kJ/mol
- Specific performance expectations of 40 years at 150 -160°C
- How much water may evolve?



Worst case water generation predicted as between 0.2 – 1.2% in target t-T range (40 years at 150 -160°C)

Predictions for Material Contraction

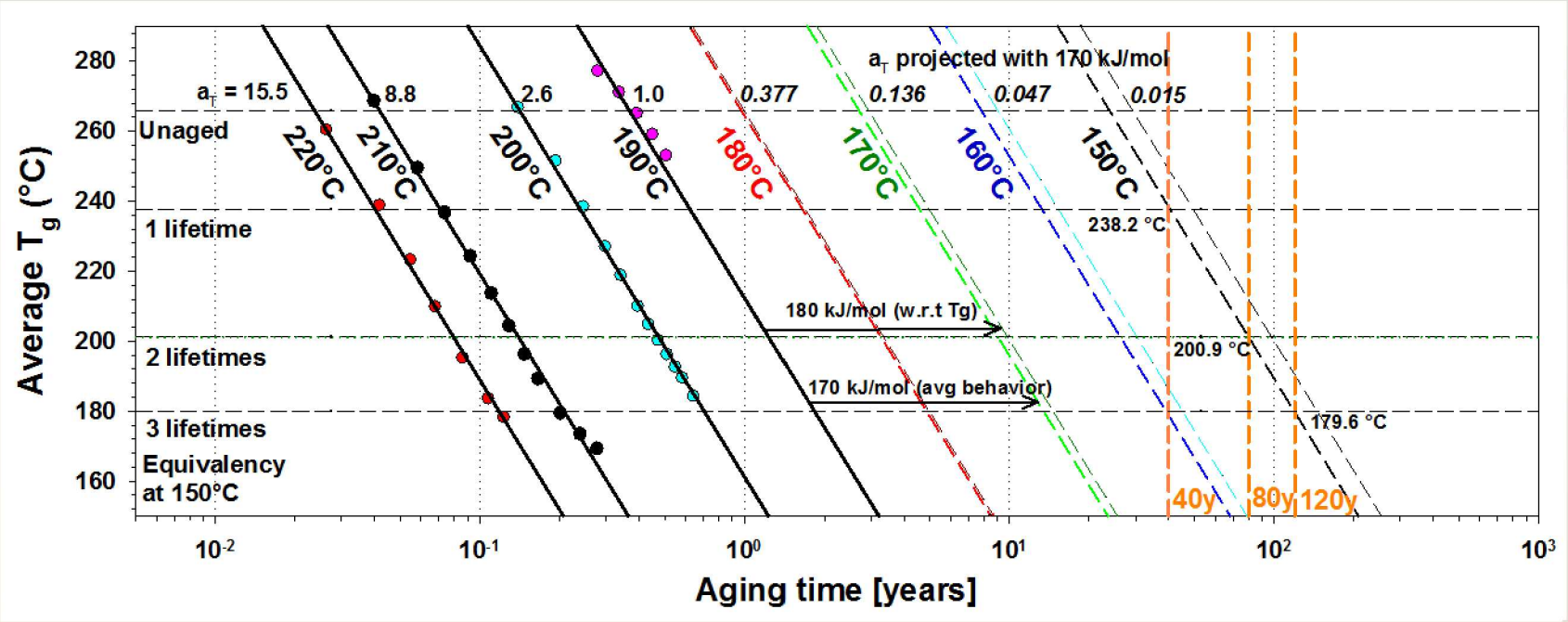
- At accelerated aging condition where data are available (180-220°C), shrinkage correlates very well with primary degradation chemistry
- No evidence for limits in predictability based on existing data



- Despite subtle mechanistic changes in degradation chemistry, all evidence supports the average Ea enabling suitable predictions
- Shrinkage ~ 0.5 – 1.4% in target t-T range (40 years at 150 -160°C)

Predictions for T_g Changes

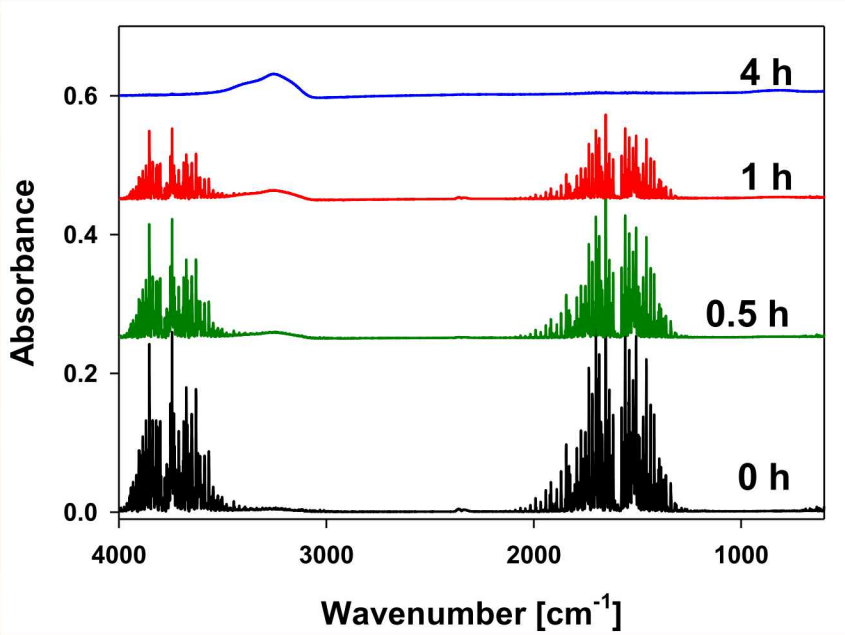
- Significant drop in Tg during accelerated aging
- Tg is expected to level off

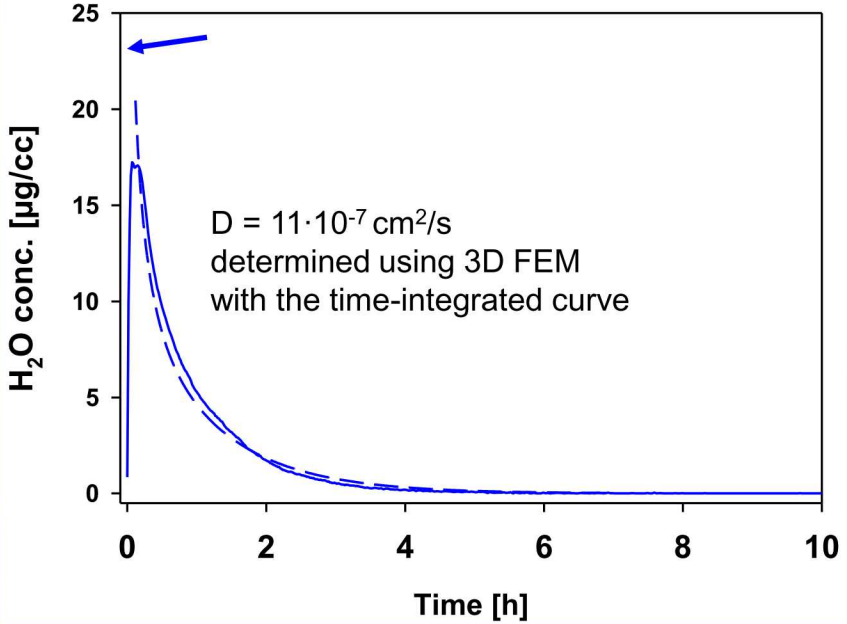


Drop in Tg not expected to approach application temperature during expected timeframe for performance

Desorption Kinetics – Flow Through IR

- Epon828/D400-D2000 (25x4x3mm, 300 mg) placed in heated ampoule at 80°C
- Evolved vapor is flushed through IR cell with dry N_2 at 10 cc/min
- Yields momentary mass loss – The time-integrated curve is used to determine *D* through 3D FEM; Flow through desorption yields D = $11 \cdot 10^{-7}$ cm^2/s compared to $9 \cdot 10^{-7}$ cm^2/s from TGA results

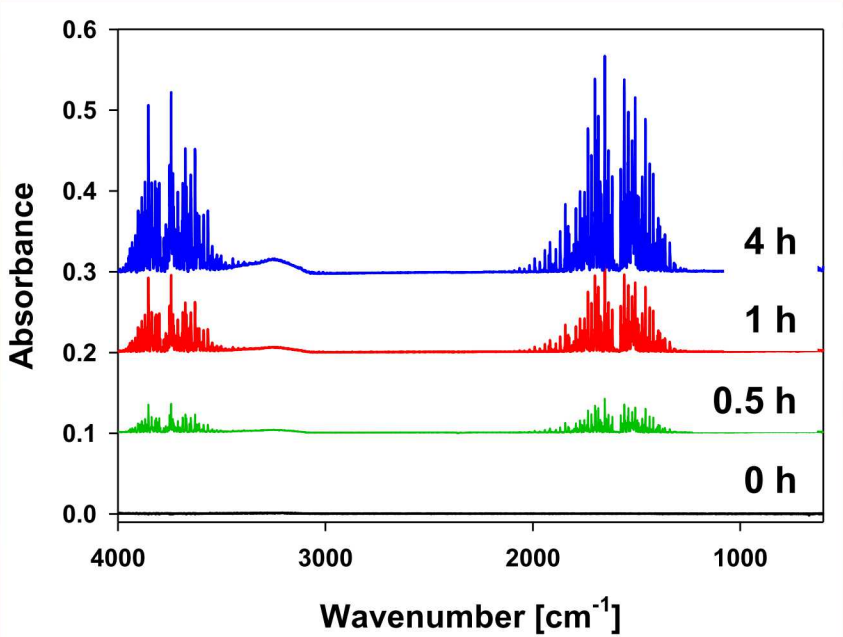


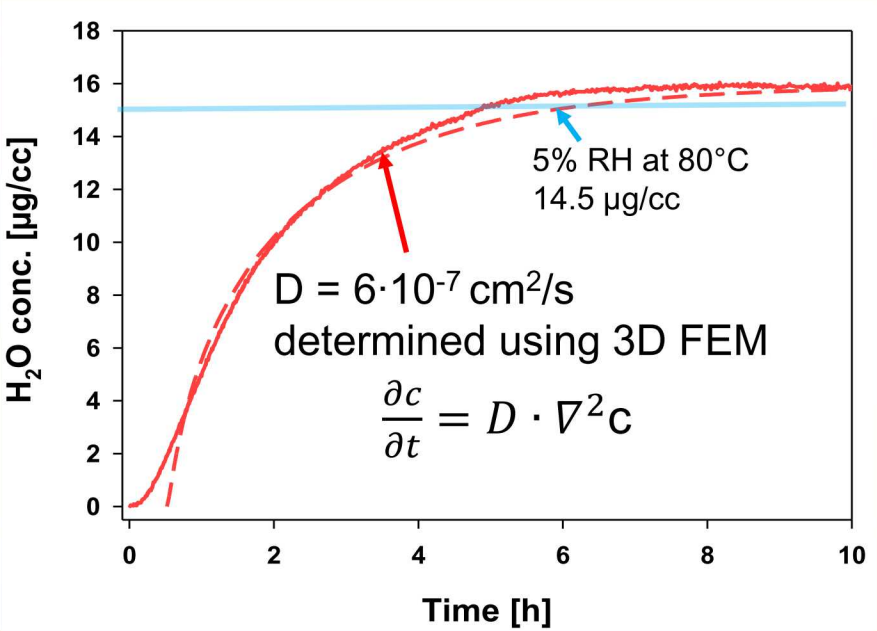


Using calibration IR quantifies momentary water yields from sample

Desorption Kinetics into Static IR cell

- Epon828/D400-D2000 (4x5x3 mm, 60 mg) was sealed in ampoule connected to IR gas cell (volume of system ≈ 110 cc, T = 80°C)
- D was determined using FEM using Fick's second law
- Quantification uses spectral integration at 3910–3790 cm^{-1}; Static water accumulation yields D = $6 \cdot 10^{-7}$ cm^2/s, compared to $9 \cdot 10^{-7}$ cm^2/s from TGA





Water evolution in sealed system can be measured for D, but generates some partial pressure that changes boundary

Summary

- Established a new IR based volatile identification and quantification method for accelerated aging studies of thermosets
- Method is amenable to successive aging exposures, cumulative data
- Determination of H_2O, CO_2 and CO in presence of some methane, toluene, phenol, acetone, isopropylene is possible
- Such data can be coupled with other measurements, such as shrinkage and total weight loss to obtain guidance on material behavior
- Excellent correlation between degradation chemistry and physical property changes, only subtle mechanistic variations
- Impact: Systematic volatile analyses as degradation chemistry signatures are being used for lifetime prediction purposes
- Enables in-depth understanding of thermoset performance