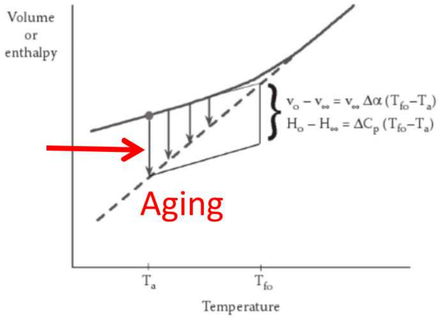
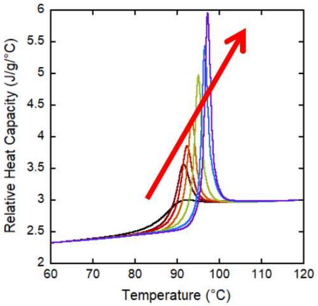
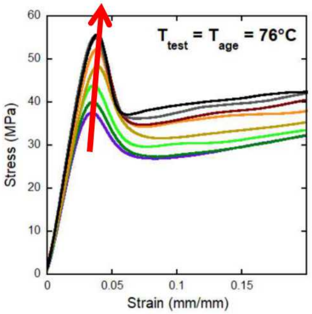
SAND2018-7264PE

Physical Aging in a Polyether-Amine Cured DGEBA Epoxy







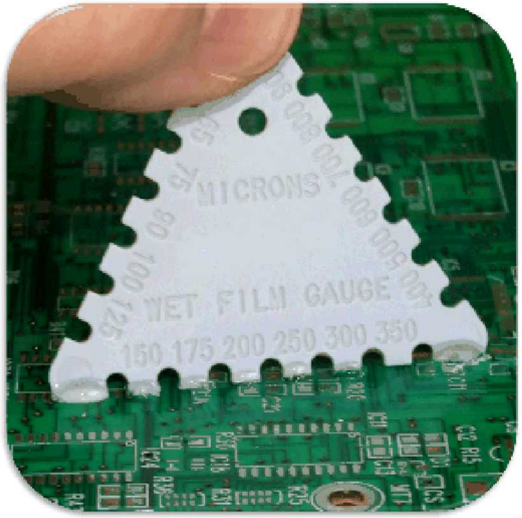
Kelsey Wilson

Outline

1. Introduction to Epoxies
2. Background
3. Previous Works
4. Procedure
5. Chemical Aging
6. Physical Aging
7. Composite Material (828/T-403/GMB)
8. Summary

Introduction to Epoxies

- Some applications include adhesives, coatings, and encapsulation
- Epoxies exist in a non-equilibrium state below Tg
    - Drive to evolve towards equilibrium
    - Evolution can result in changes in the material properties which impact the long-term performance of the epoxy



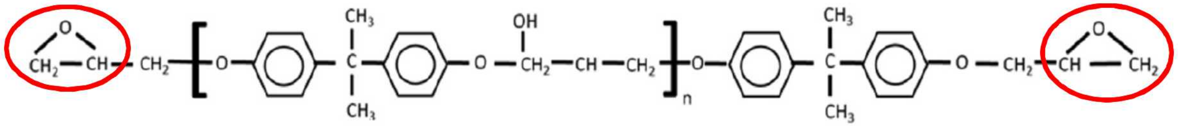
Objective: to obtain high fidelity data to track progression of an epoxy structure towards equilibrium, and how this progression affects the thermomechanical response

By Leehitchens - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=25305537

Background: Polymer Chemistry

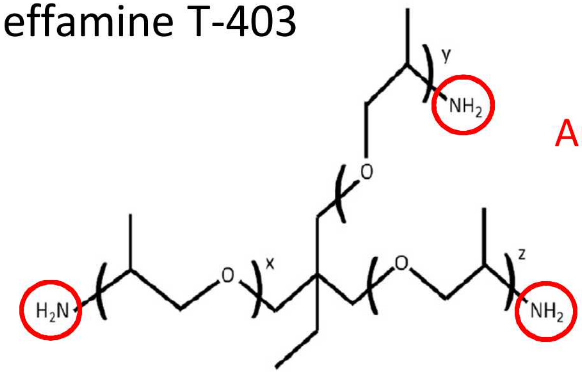
- EPON 828/Jeffamine T-403
  - Mix stoichiometrically: each amine-hydrogen group reacts with an epoxide group so that the full reaction occurs

DGEBA Resin—EPON 828



Epoxide group

Polyetheramine Hardener—
Jeffamine T-403

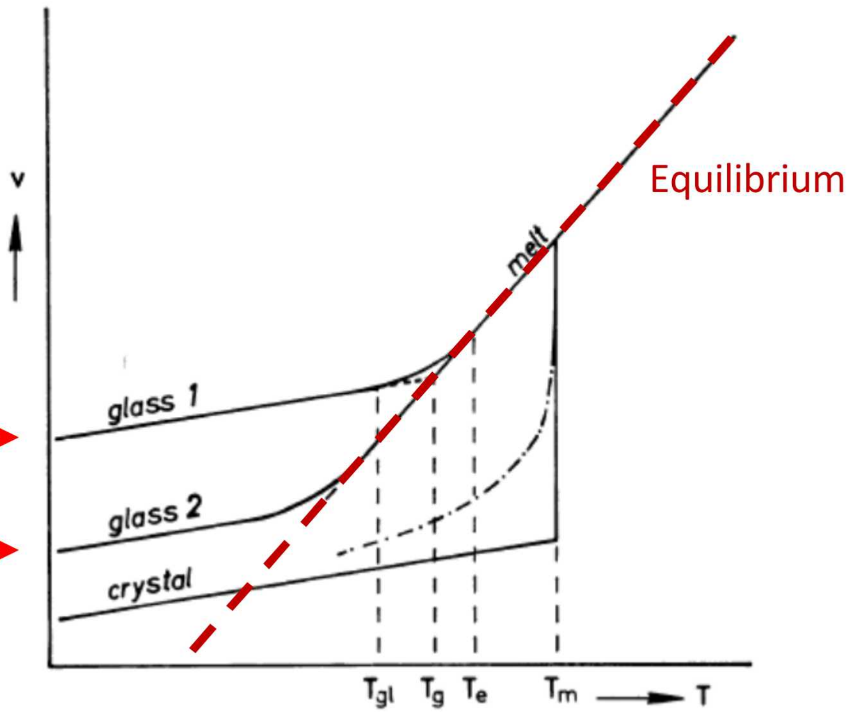


Amine group

Tg ~ 90°C

Background: Non-Equilibrium Glassy State

- The state of the glass depends on thermal history, e.g. cooling rate
  - Higher Tg results in a larger overall free volume, so more aging is possible

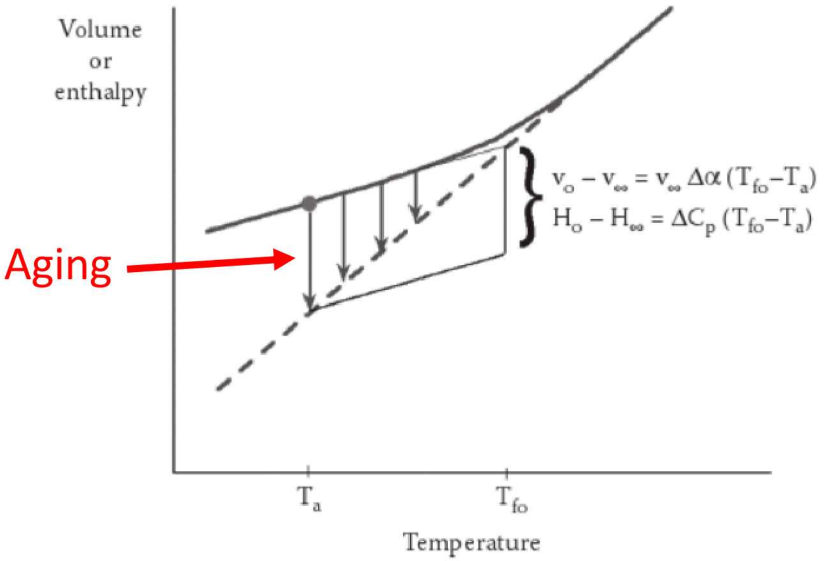


Faster cooling

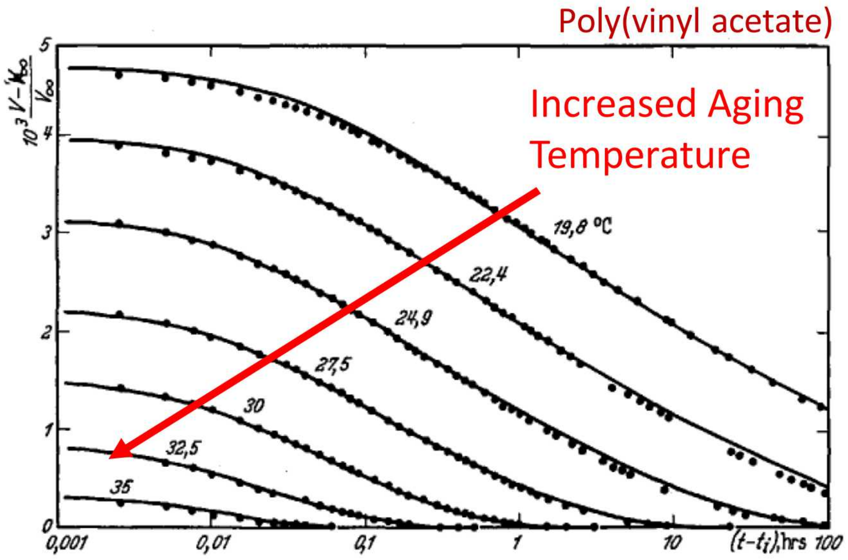
Slower cooling

G. Rehage and W. Borchard. (1997). Chaper 1 in *The Physics of Glassy Polymers*. Applied Publishers LTD. Springer.

Background: Structural Relaxation



Aging



Poly(vinyl acetate)

Increased Aging Temperature

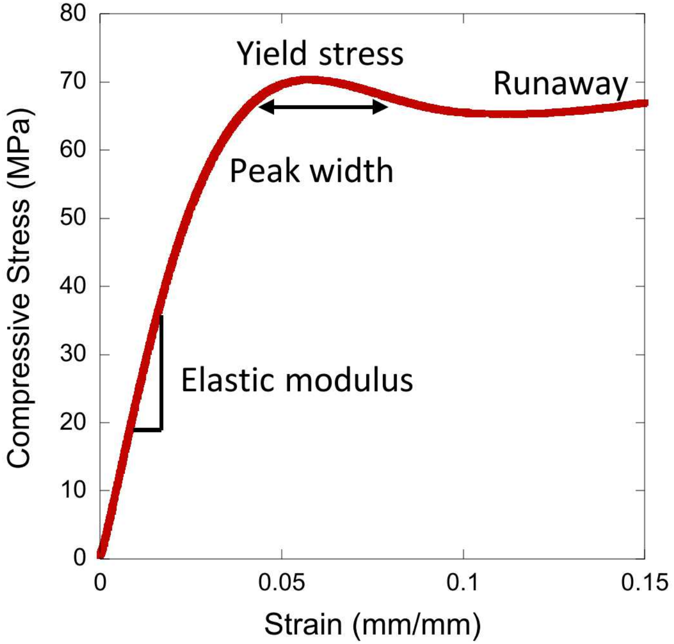
- Intrinsic isotherm experiment
  - Time to approach equilibrium depends on aging temperature
  - Can be used to assess both volume and enthalpy evolution

S. L. Simon and G. B. McKenna. (2017). Chapter 2 in *Polymer Glasses.*

A J Kovacs. (1964). *Transition vitreuse dans les polymers amorphes...* Springer

Background: Physical Aging

- Physical aging is concerned with the effects of structural relaxation on the mechanical properties



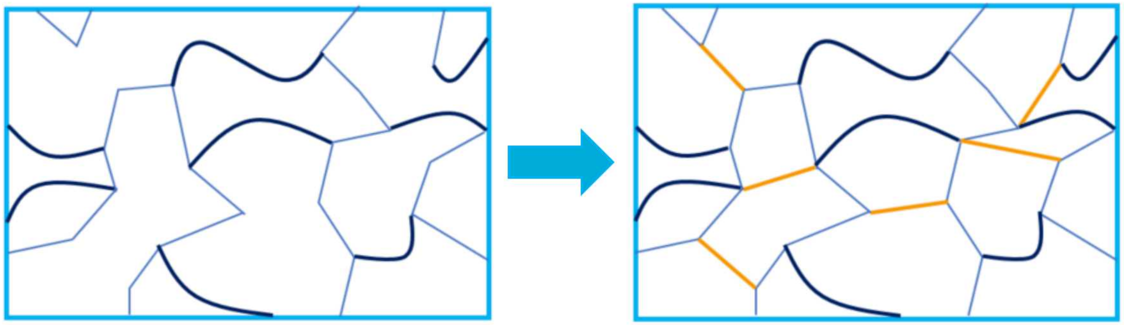
Changes in compressive stress-strain response include:

1. Increased yield stress
2. Peak sharpening
3. Increased elastic modulus
4. Increased runaway stress

WK31

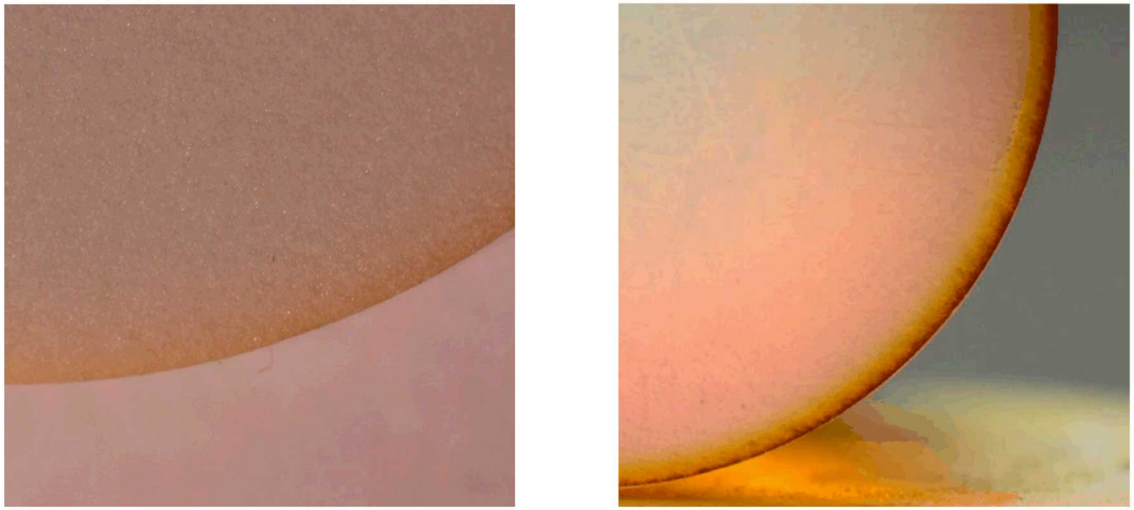
Background: Chemical Aging

Additional Crosslinking



Affects bulk properties

Diffusion Limited Oxidation



Affects surface properties

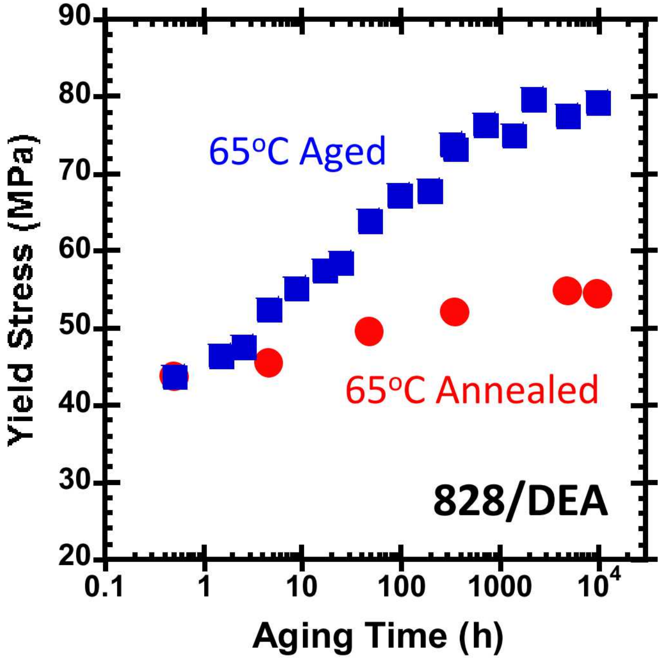
Slide 8

WK31 "For physical versus chemical aging contributions, I think it would be good to discuss this before even showing results. For example, what was seen with 828/DEA in Gabe’s work and how might things be different in 828/T403. Also, what testing is sensitive to chemical aging and what testing is not. Then when you get to the data that distinguishes these points, you can point it out and describe the role of chemical vs. physical aging."

Wilson, Kelsey, 6/27/2018

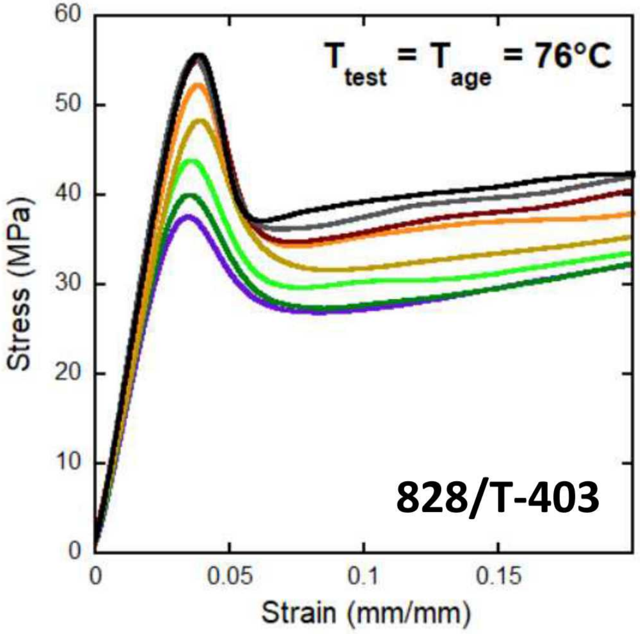
Chemical versus Physical Aging in Compression Cylinders

Chemical Aging



- Changes due to additional chemical crosslinks
  - Secondary chemical reaction occurs post-cure in 828/DEA

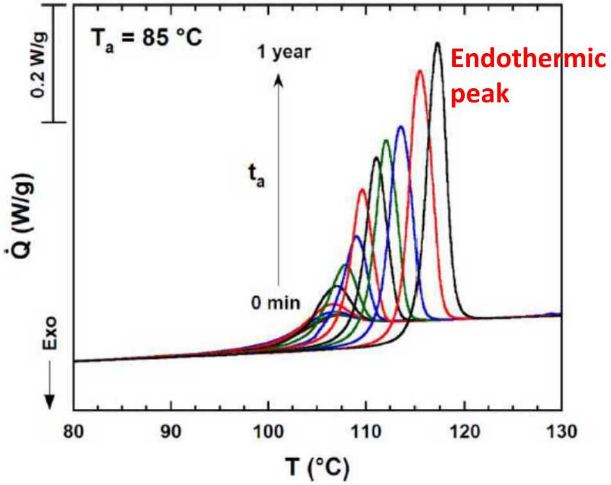
Physical Aging

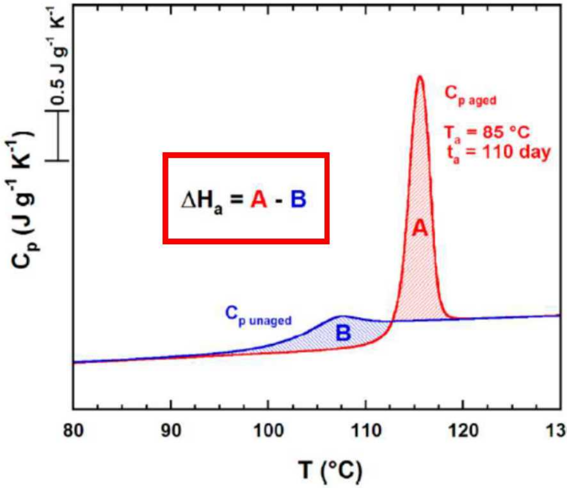


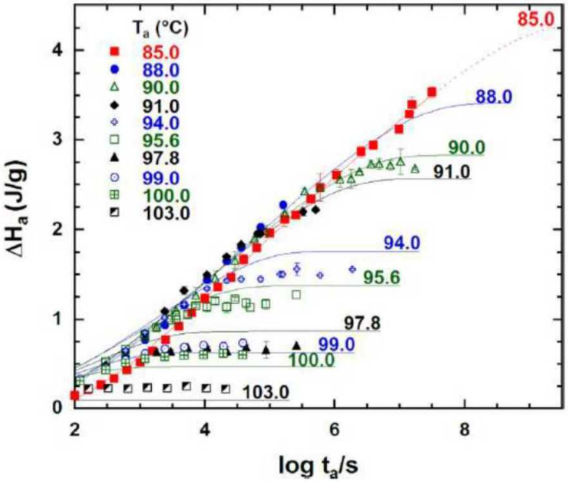
- Changes due to molecular relaxations
  - 828/T-403 is mixed stoichiometrically to reduce additional crosslinking post-cure

Arechederra, G. (2017). Evolution of Mechanical Properties During Structural Relaxation of the 828/DEA Epoxy Thermoset. Master's Thesis, NMT.

Previous Work: Heat Capacity Evolution



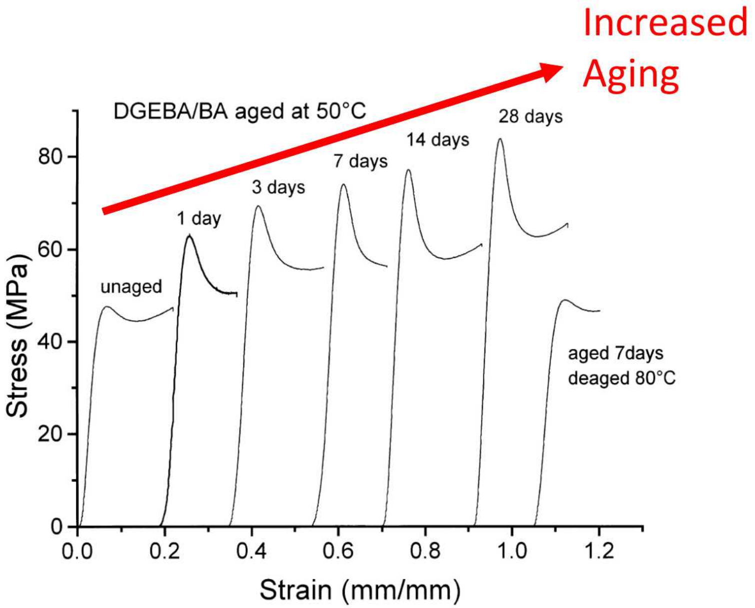


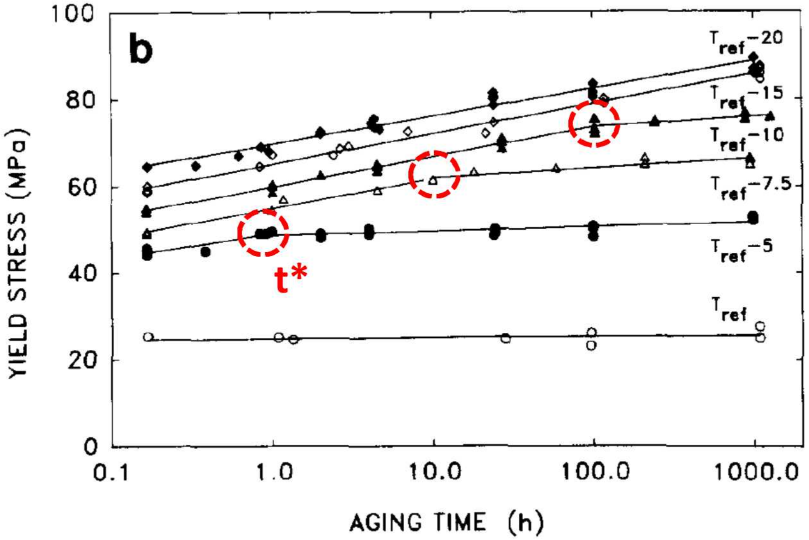


- Increased magnitude and location of the endothermic peak in heat capacity at longer aging times
- Reach enthalpic equilibrium in samples aged near Tg
- Method used to track enthalpic structural relaxation

Koh, Y. P. and Simon, S. L. (2013). Enthalpy Recovery in Polystyrene: Does a Long-term Aging Plateau Exist?. *Macromolacules, 46(14): 5815-5821*.

Previous Work: Mechanical Evolution





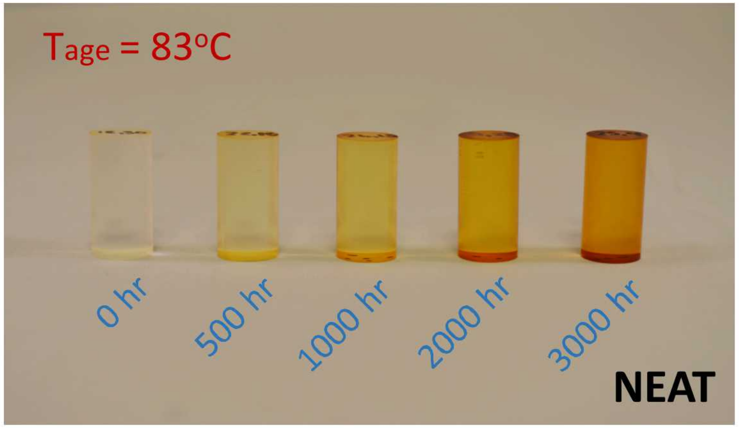
- Increase in: yield stress, modulus, and flow stress
- Peak narrowing/sharpening
- t* defined as point at which physical aging slows down or stops
- Method to observe **<u>effects</u>** <u>of structural relaxation (i.e., physical aging)</u>

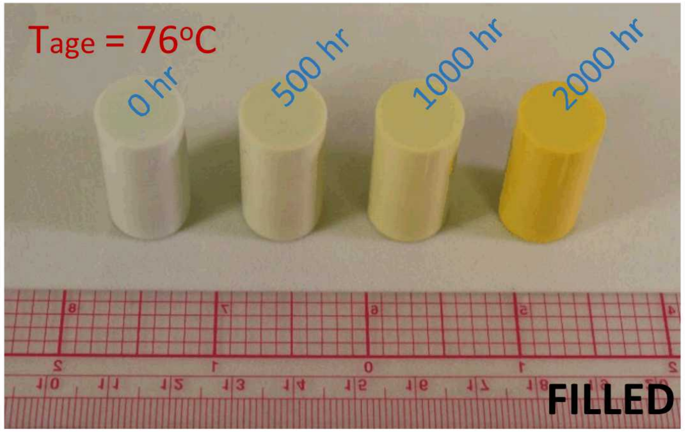
Cook, W. D., Mehrabi, M., & Edward, G. H. (1999). Ageing and yielding in model epoxy thermosets. *Polymer, 40*, 1209-1218.

G'Sell, C., & McKenna, G. B. (1992). Influence of Physical Aging on the Yield Response of Model DGEBA Poly(propylene oxide) Epoxy Glasses. *Polymer, 22*(10), 2103-2113.

Experimental Procedure

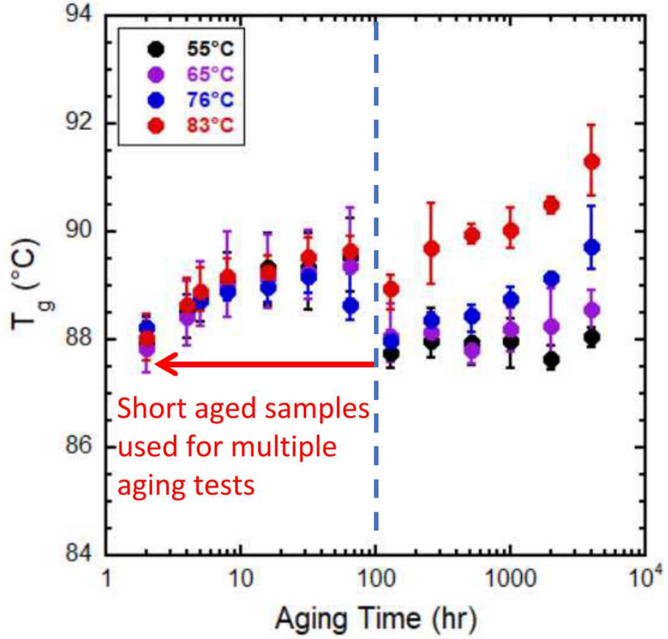
- Stoichiometric mixing 100:43 parts-by-weight 828:T-403, Tg~90°C
  - 828 g/eq = 185-192
  - T-403 g/eq = 81
- Compression cylinders
  - Section to obtain 2:1 L:W ratio—dia=0.56'', length = 1.12''
- Some material poured into 1mm thick plaques
- DSC samples
  - Liquid epoxy poured directly into Tzero aluminum pans for good contact
- Filled material
  - 3M D32 Glass Micro-balloons added to liquid mixture, 48% by volume



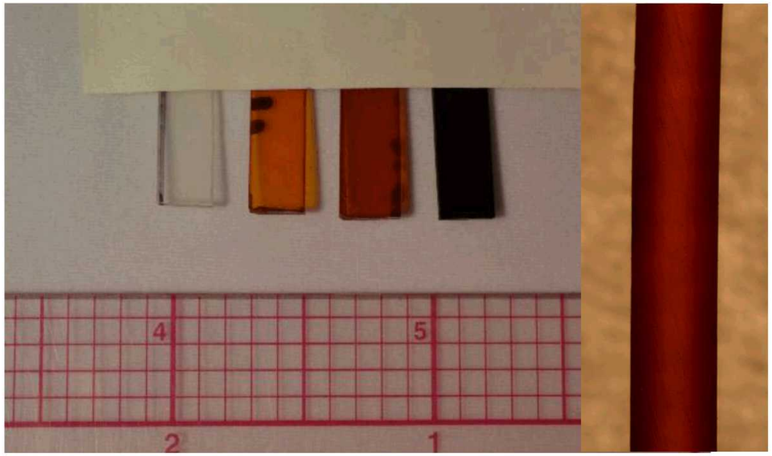


Results: Chemical Aging

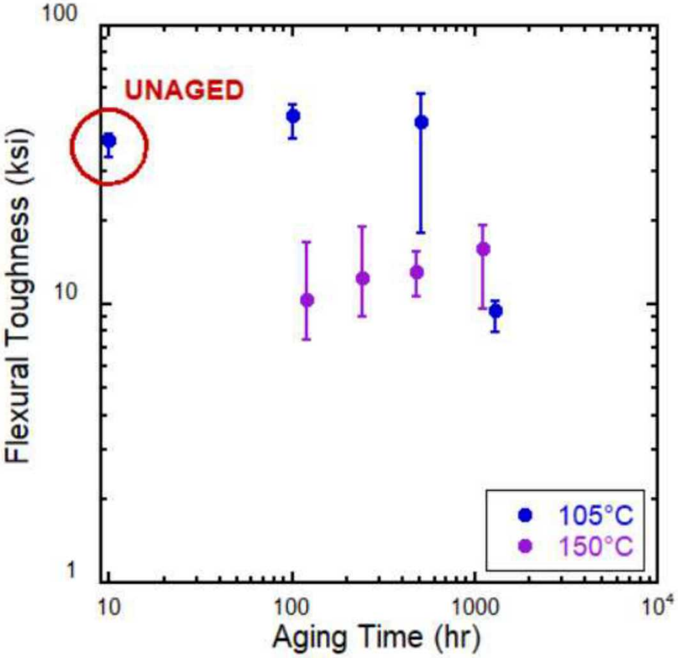
- Maximum Tg change ~+3°C at T = 83°C
- 3-point bend tests
  - Diffusion Limited Oxidation—occurs most prominently on outer surface
  - Toughness decreased by factor of 3



Short aged samples used for multiple aging tests



(left to right): 0, 100, 1300 hours at 105°C, 1100 hours at 150°C. Sectioned sample was aged at 105°C for 2000 hours.



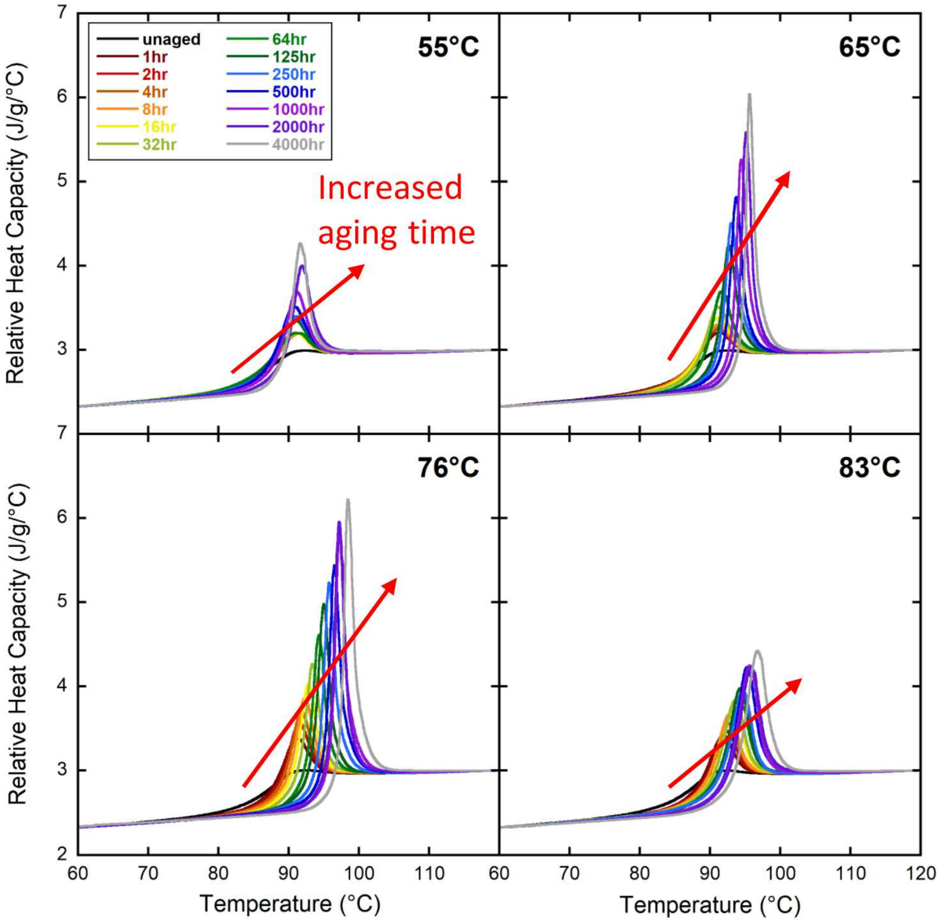
Slide 13

WK39 how aged was cross section?

Wilson, Kelsey, 6/27/2018

Results: Heat Capacity Response

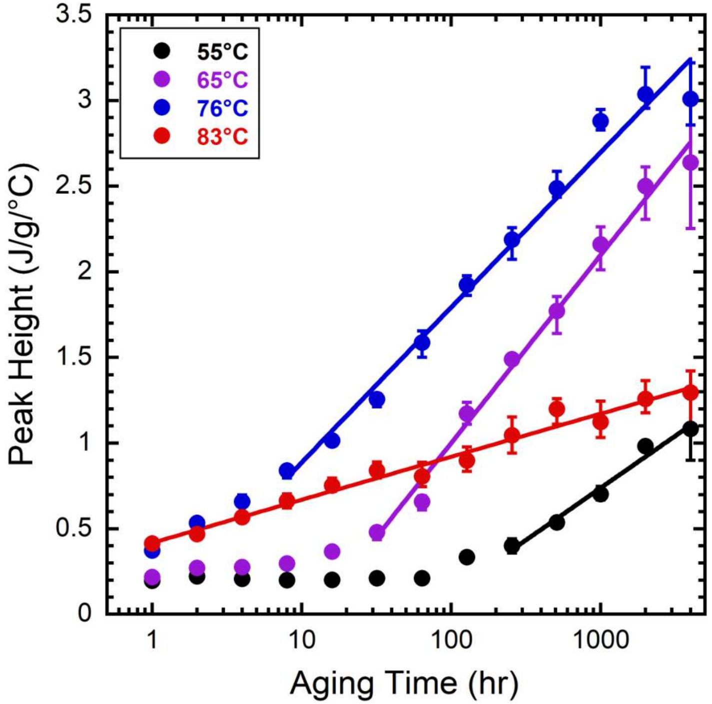
- Aligned all first and second heats
- Peak affected by aging temperature and time
- Competition exists between molecular mobility and distance from equilibrium



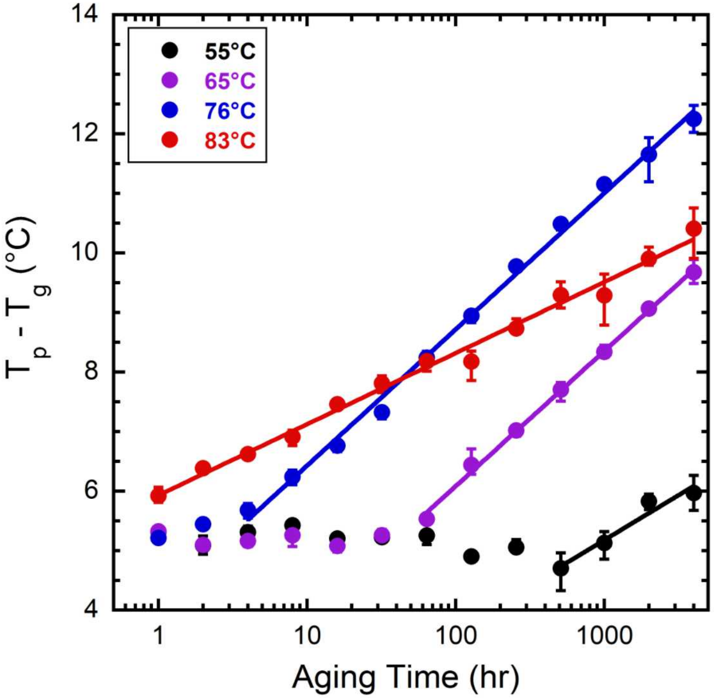
Increased aging time

Results: Evolution in Peak Properties

Peak Height vs Aging Time

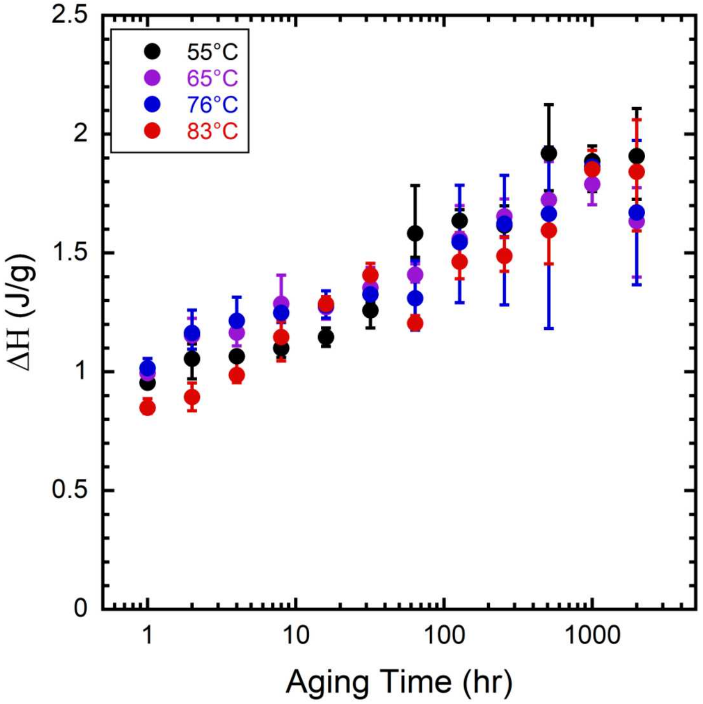


Peak Temperature vs Aging Time



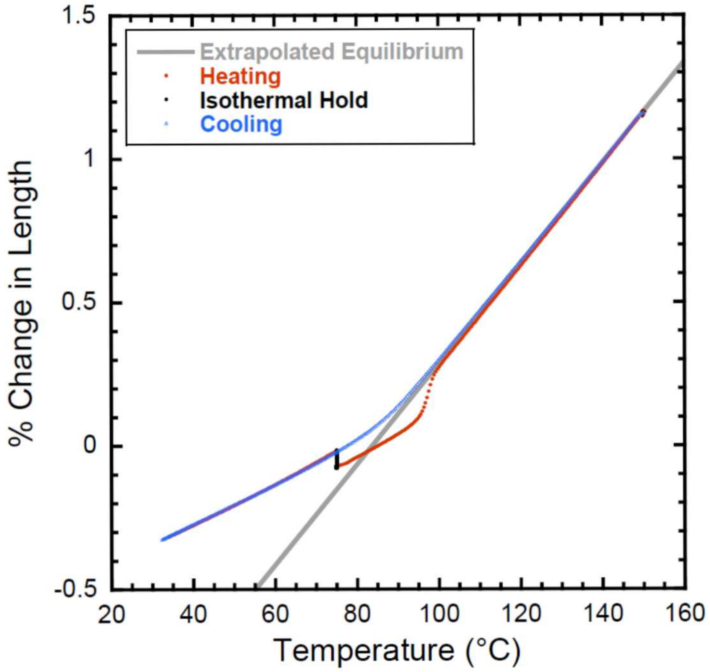
- Changes in properties are not significant enough to be tracked at shorter times—``induction time’’
- Peak height and peak temperature increase exponentially with aging time

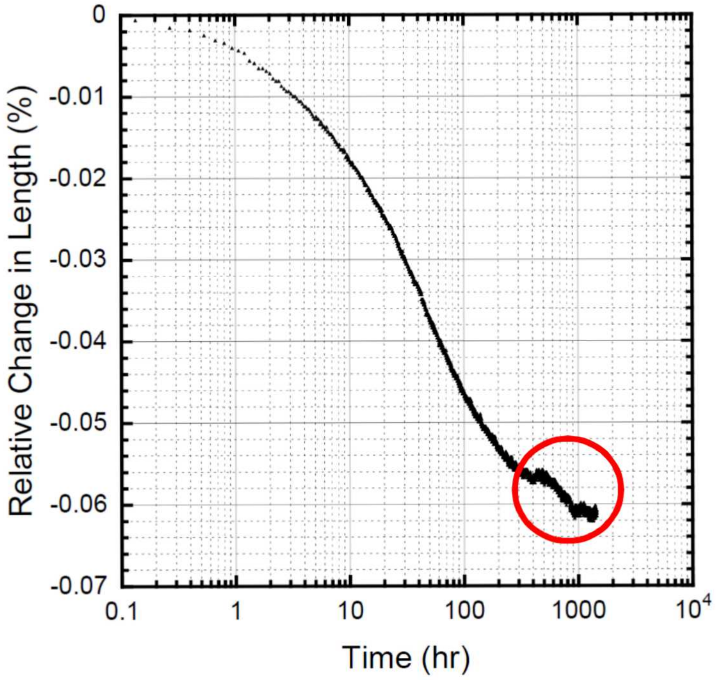
Results: Enthalpy Evolution



- Large error associated with calculation
- Unable to identify whether t* is reached at long times
  - Cp curves continue evolving at long aging times

Results: Optical Dilatometry



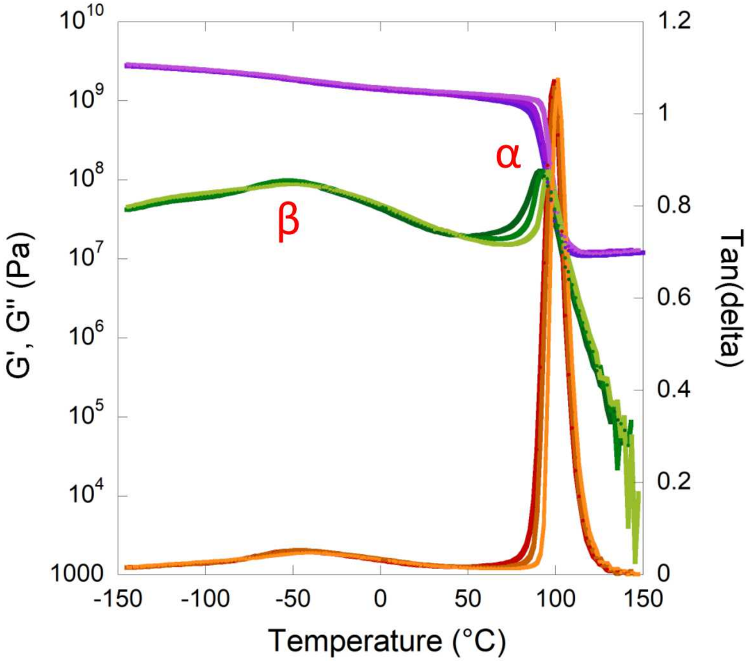


- Optical dilatometer used to observe volume relaxation
- Relaxation appears to stop evolving after ~1000 hours of aging at 75°C

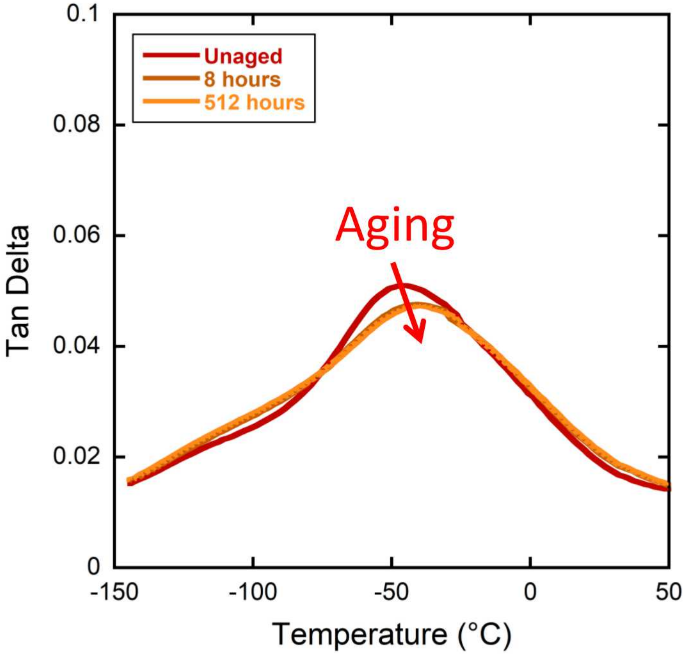
Optical dilatometry experiments performed by Dr. Jamie Kropka

Rheological Response with Aging

- Physical aging affects alpha peak more prominently than beta peak
  - α: Cooperative motion of many segments [9]
  - β: Crankshaft motion of hydroxyether and bisphenol A groups [9]



β-Relaxation Peak

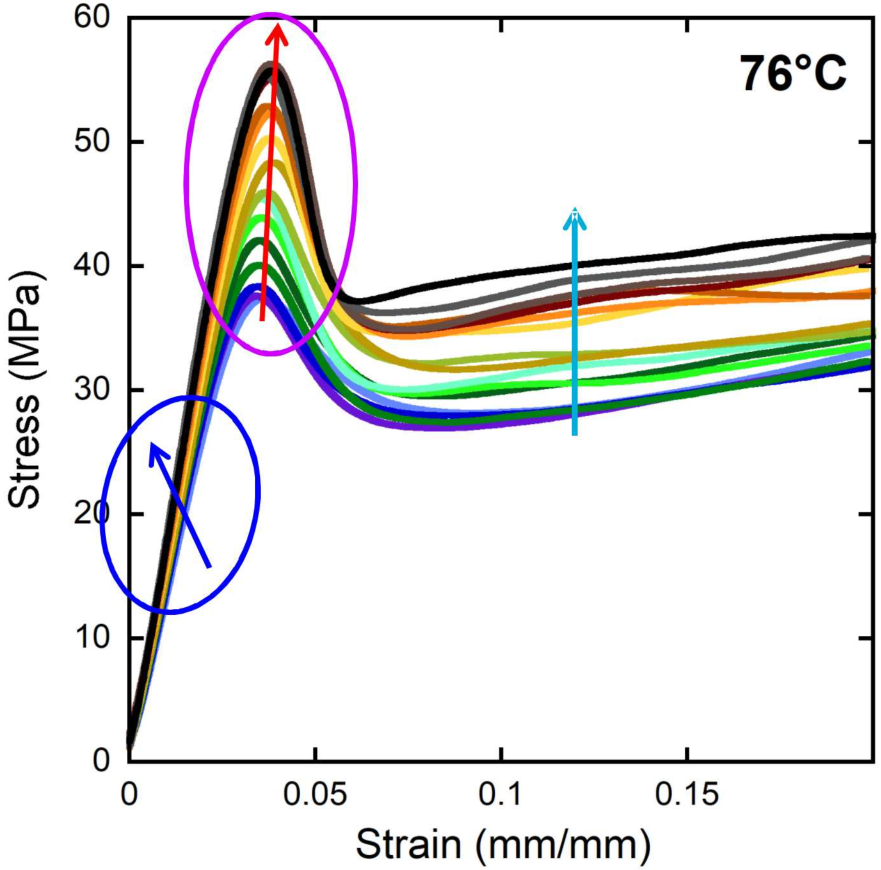


Slide 18

WK32 "You should address both of the conclusion additions in the defense presentation as well. First thoughts on how that might be done is to move the beta versus alpha peak effects from the appendix in the presentation to an earlier section. This could be done near the beginning when you talk about the intrinsic isotherm experiments, so you would be following it up with what motions are affected by the changes in the molecular packing during the isotherm experiment. Or, since you have T403 data specifically, you could put this information after talking about the volume data at 75C (maybe the best place). Explain what motions are attributed to the beta and alpha relaxation peaks too."

Wilson, Kelsey, 6/27/2018

Results: Stress-Strain Response

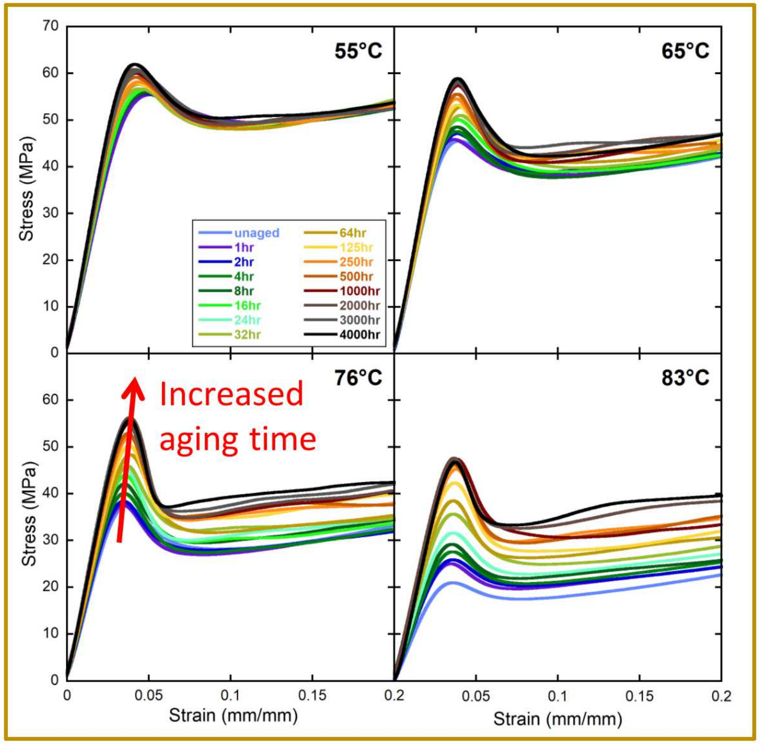


Key changes with increased aging:

1. Increase in yield stress
2. Increase in elastic modulus
3. Peak sharpening
4. Increased flow

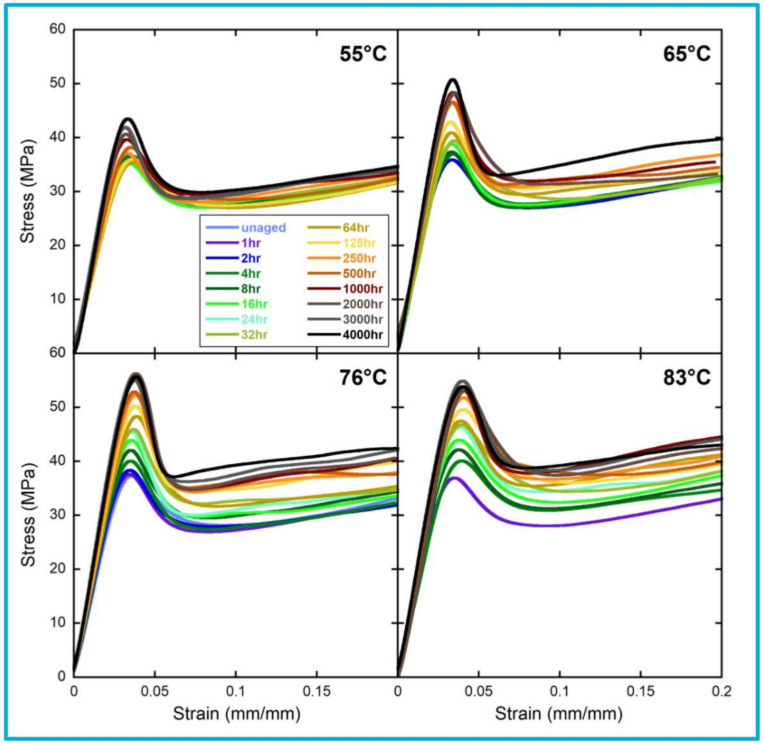
Results: Stress-Strain Response

$T_{test} = T_{age}$



Increased aging time

$T_{test} = 76^oC$



- Higher aging temperatures demonstrate greater changes in stress-strain response

- More changes evident in samples aged at 55°C, tested at 76°C.
- Fewer changes evident in samples aged at 83°C, tested at 76°C.

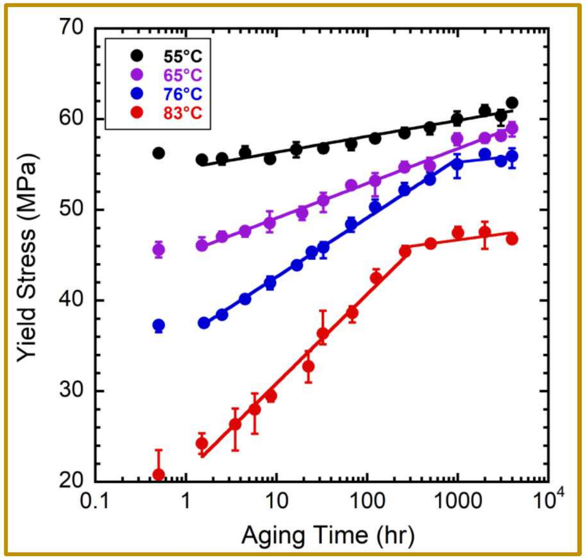
Higher temperature tests are more sensitive to changes in the yield stress

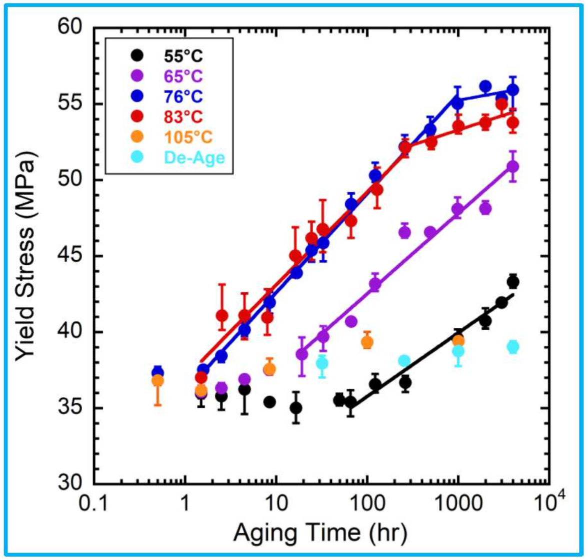
Slide 20

WK33 how do peak widths compare in samples tested at 76C, versus at different temperatures?

Wilson, Kelsey, 6/27/2018

Results: Yield Stress Evolution


$T_{test} = T_{age}$


$T_{test} = 76^oC$

1. Initial linear increase in yield stress with log(t)
2. No induction time obviously seen in samples aged at lower temperatures
3. Slope of linear fit increases with increasing temperature
4. t* approached at higher temperatures
5. Unaged yield stress varies with temperature

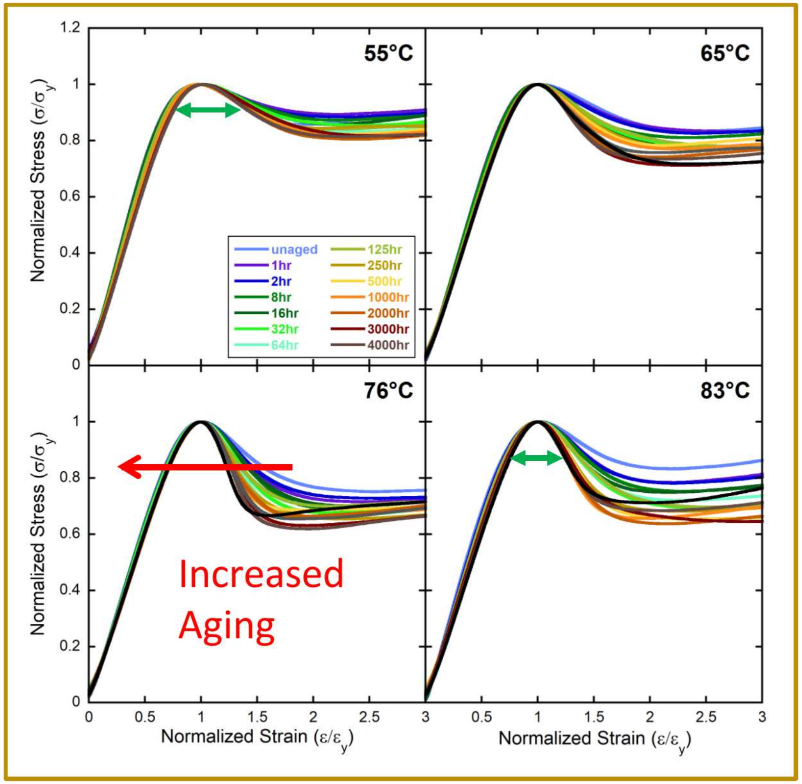
1. Initial linear increase in yield stress with log(t)
2. Linear slope at lower temperature does not intersect the zero-time condition
3. Slope of linear fit is indistinguishable between temperatures
4. t* approached at higher temperatures
5. Unaged yield stress approaches same value for samples aged at different temperatures

Slide 21

WK34	why isn't induction time seen in Ttest = Tage samples? sis osme 65C data missing? Wilson, Kelsey, 6/27/2018
WK35	point 5, should i take out and just talk about induction time? Wilson, Kelsey, 6/27/2018

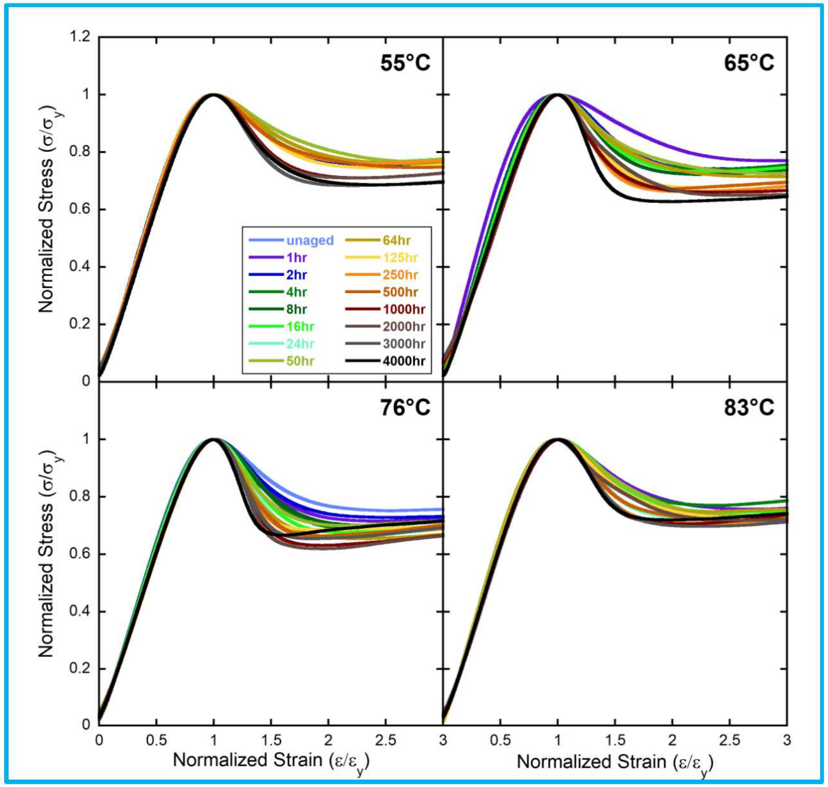
Results: Other Properties of Stress-Strain Response

$T_{test} = T_{age}$



Increased Aging

$T_{test} = 76^oC$



- Increased aging results in more localized deformation
  - ``Shear Banding''
- Peak width in samples aged and tested at lower temperatures (e.g., 55^oC) changes significantly less than at higher temperatures (e.g., 83^oC)

Slide 22

WK36 76C peak width vs 83C peak width at both conditions??

Wilson, Kelsey, 6/27/2018

Results: DSC versus Compression Testing

Method	Aging Temperature (°C)	t* (hr)
Optical Dilatometry	75	1000
828/T-403 Yield stress evolution (Current Work)	55	--
	65	--
	76	1000
	83	250
DGEBA/PPO Yield stress evolution (G'Sell&McKenna 1992)	$T_g - T_a = 5$	1
	$T_g - T_a = 10$	100
	$T_g - T_a = 20$	1000

Method	Aging Temperature (°C)	t* (hr)
828/T-403 Peak Height & Peak Temperature (Current Work)	55	--
	65	--
	76	--
	83	--
Polystyrene Enthalpy evolution (Koh&Simon 2011)	$T_g - T_a = 4.4$	3
	$T_g - T_a = 10$	300
	$T_g - T_a = 15$	8800

t* in volume relaxation comparable to yield stress

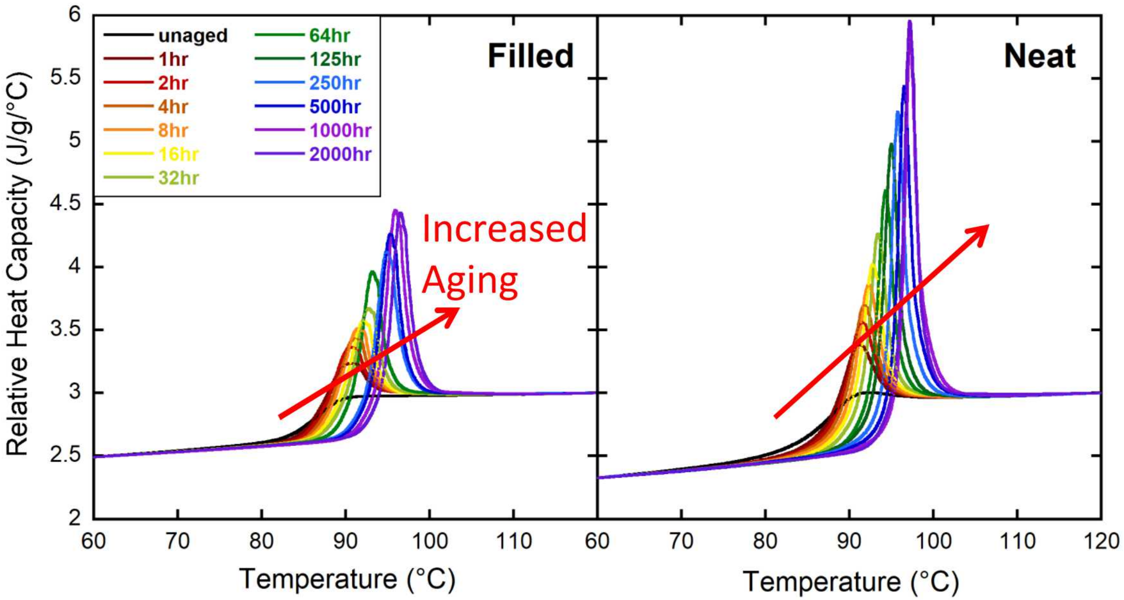
Yield stress ceases (t*) in current work comparable to other work (G'Sell&McKenna 1992)

Enthalpic equilibrium reached in different study at similar amount of undercooling

- Volume relaxation does not entirely account for enthalpy relaxation
- Different systems can physically age at different rates
  - Chain flexibility, crosslink density, extent of branching

Results: Composite Heat Capacity

T_{age} = 76°C



- Endothermic peak height evolution slower once filler is introduced
  - Need to separate glass micro-balloon response from that of the neat epoxy!

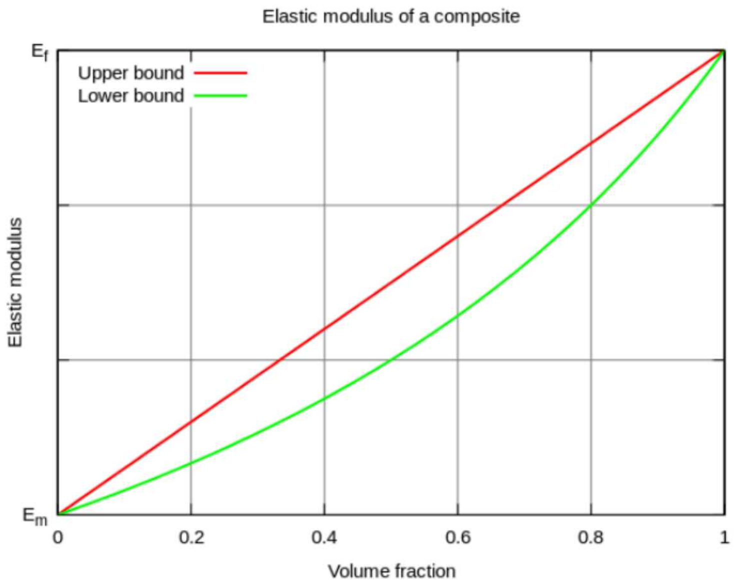
Results: Composite Rule of Mixtures

$$Series : P_c = f(P_f) + (1-f)P_m$$

$$Parallel : P_c = \left(\frac{f}{P_f} + \frac{1-f}{P_m}\right)^{-1}$$

$$Log : \ln P_c = f \ln P_f + (1-f) \ln P_m$$

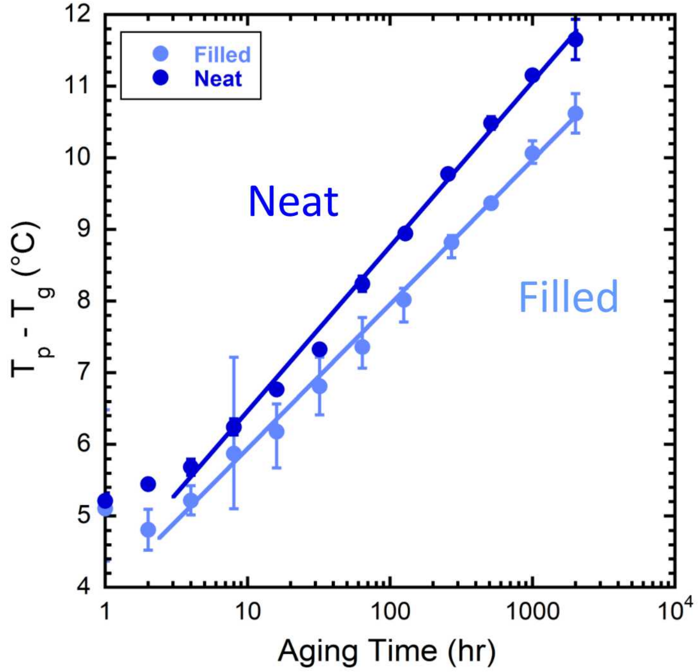
Pc, Pf, and Pm is the property being investigated of the composite, filler, and matrix, respectively.

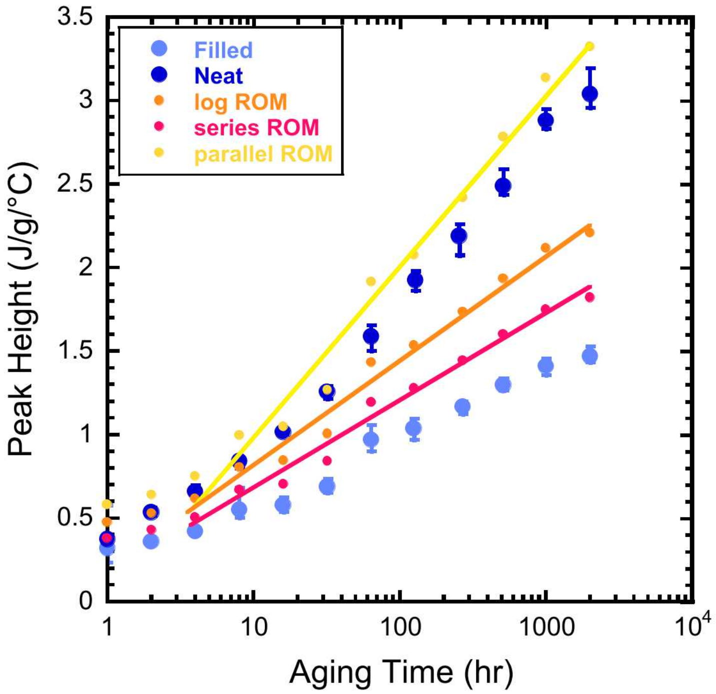


- Assumed that the effect of aging on the properties of GMB were much less than the effect of aging on the epoxy
  - Initial GMB properties can then be calculated using known values of the epoxy and the composite at time zero.

https://en.wikipedia.org/wiki/Rule_of_mixtures

Results: Composite DSC Tests

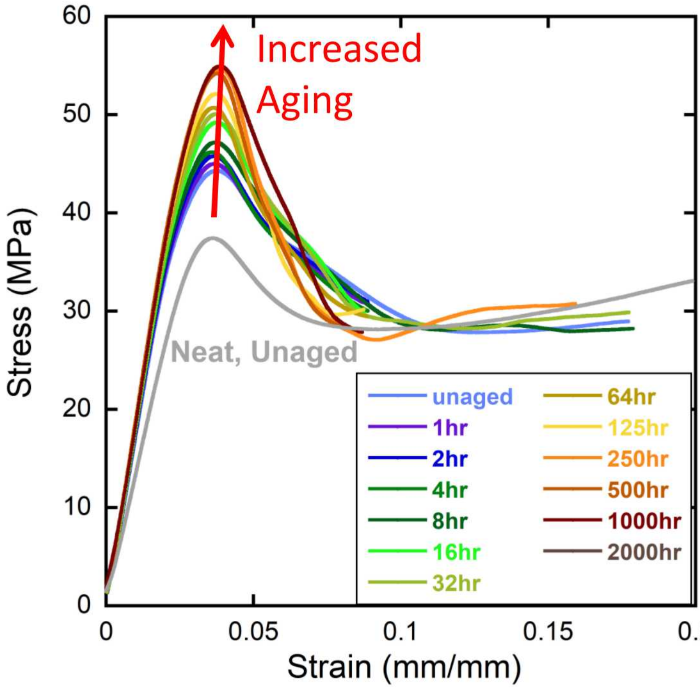


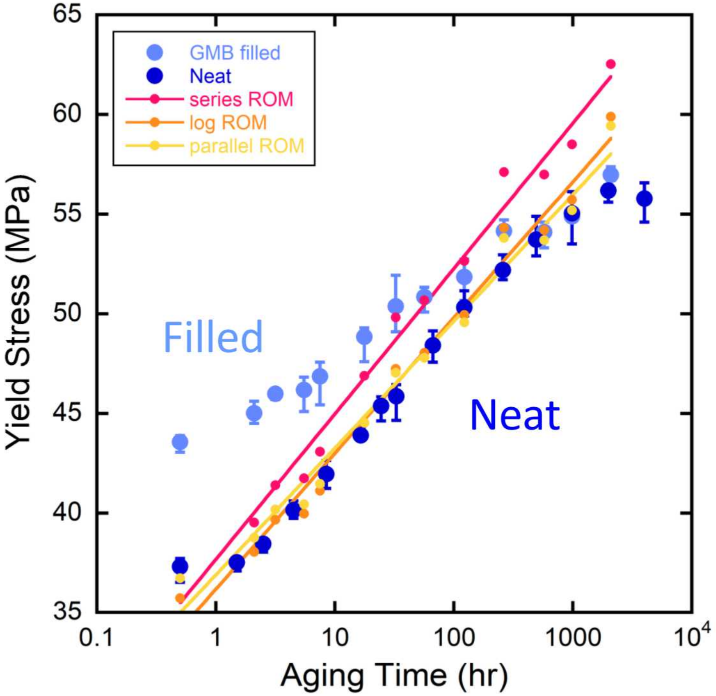


- Peak temperature evolves at a similar rate in filled and neat material
- Use ROMs to evaluate epoxy peak height evolution
  - Filled versus unfilled epoxy height evolution are similar

Results: Composite Compression Tests

Reported crush strength with 80-90% survival rate: 31MPa [10]
Calculated ranged from 51-54MPa depending on ROM used





- Yield stress evolution of filled and neat materials is similar
    - The addition of a filler does not affect the aging rate of the 828/T-403 material

Summary

- Physical aging dominates changes seen in the stress-strain response.
- In samples aged at 76°C and 83°C, a time was reached where the yield stress evolution dramatically slowed down after 1000 and 250 hours, respectively.
- The use of optical dilatometry illustrated that physical aging is an effect of structural relaxation.
- Physical aging is highly dependent on the temperature that the samples are aged at.
- Differences in the time to reach equilibrium between compression and DSC tests indicate that volume changes do not completely account for enthalpy changes.
- Addition of filler does not affect physical aging in 828/T-403, at least outside of the sensitivity of the current experiments.

Acknowledgements

- Dr. Jamie Kropka, Dr. John McCoy, and Dr. Dave Burleigh
- SNL employees
- NMT Polymers Group

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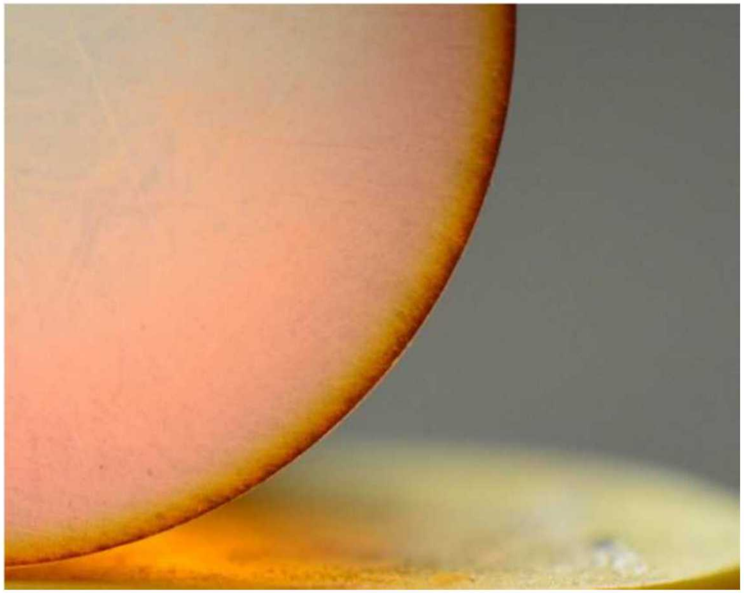
Appendix: Some Images

GMB-filled sample compressed to 10% strain at 76°C

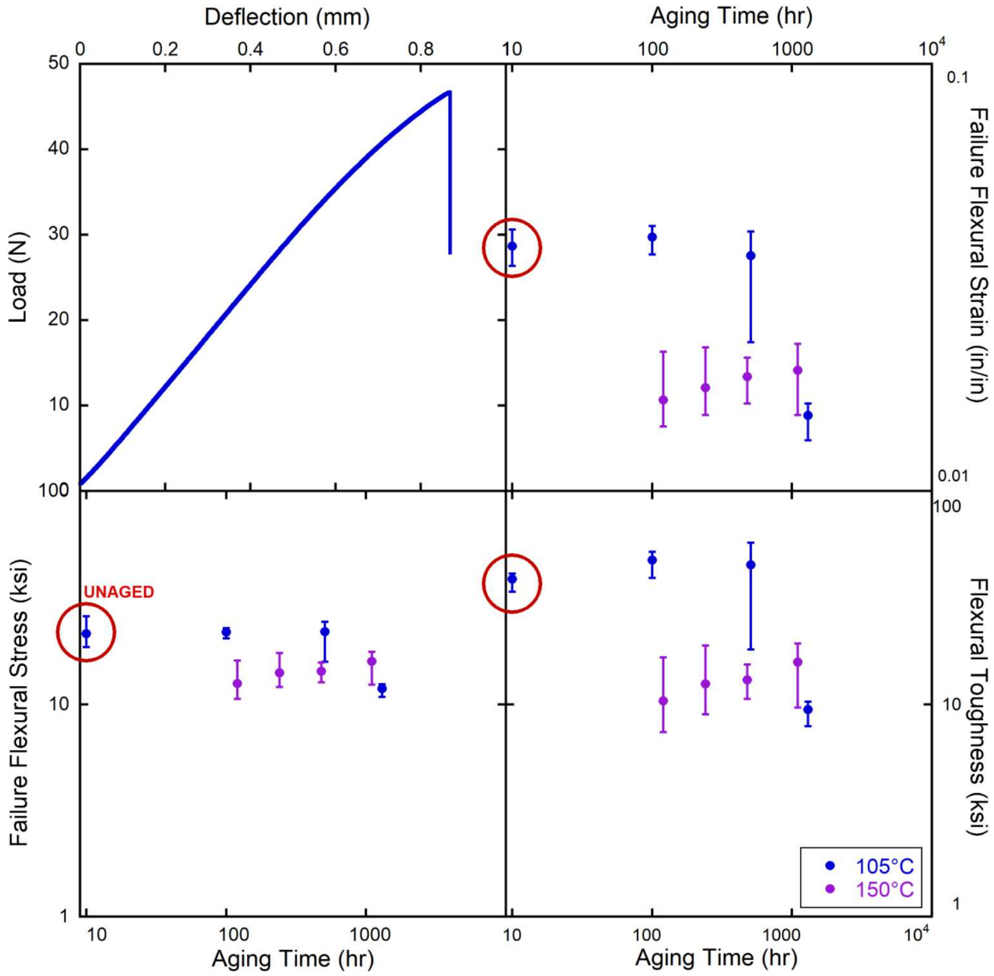


Cross-section of samples aged for 1000 hours at 105°C. DLO is visually evident.

Appendix:

$$flexural\, stress = \frac{3 * P * S}{2 * w * t^2}$$

$$flexural\, strain = \frac{6 * d * t}{S^2}$$



- Toughness found by taking integral of the flexural stress versus flexural strain curve.
- Overall changes are less than a factor of 3

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WK37 add stuff about celina paper?

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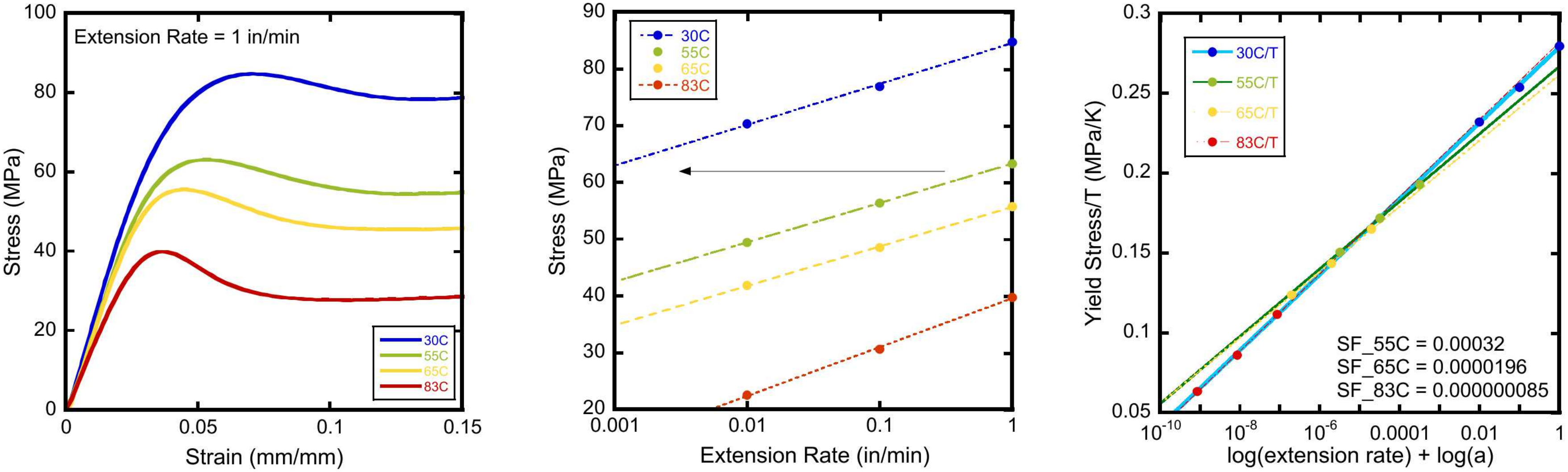
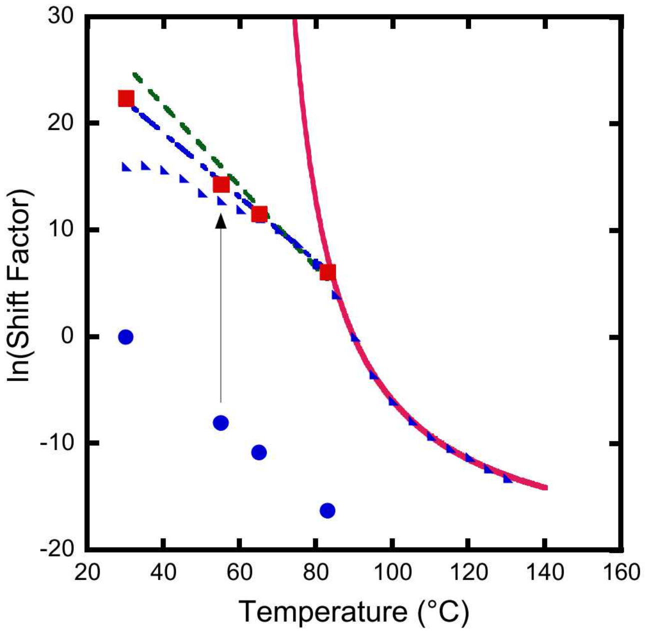
Appendix: Yield Stress Dependence on Strain Rate and Temperature (1)

- Test compression cylinders at different temperatures and strain rates
- Plot yield stress versus extension rate, and obtain shift factors for master curve



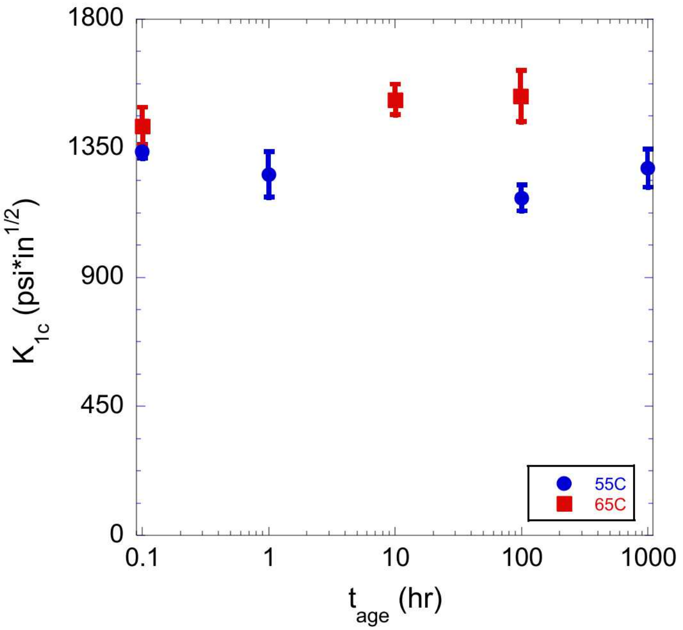
Appendix: Yield Stress Dependence on Strain Rate and Temperature (2)

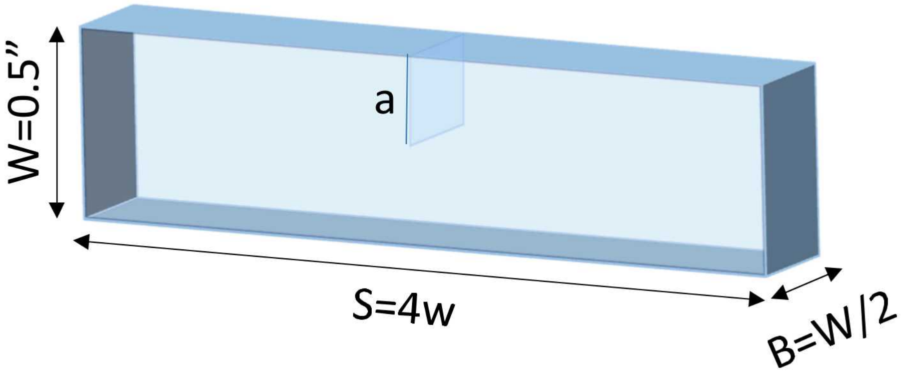
- From Clarkson 2016 [11]
- Use shift factors from previous slide to match the KAHR model (blue dashed line) which predicts that the logarithm of the shift factor will be linear with temperature



Appendix: Fracture Toughness

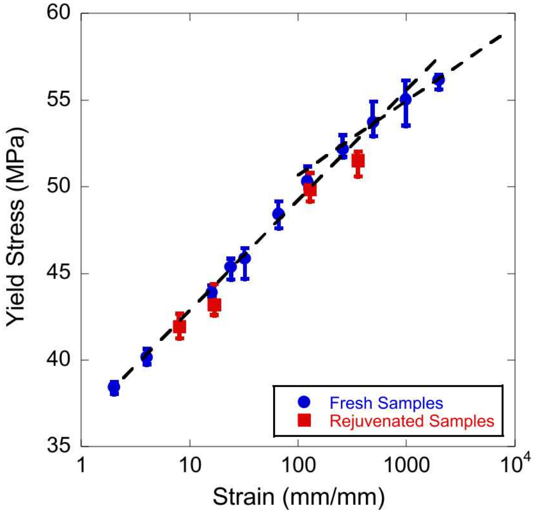
- Scoping study to investigate changes in fracture toughness with aging
- Significant changes not seen under the present testing conditions

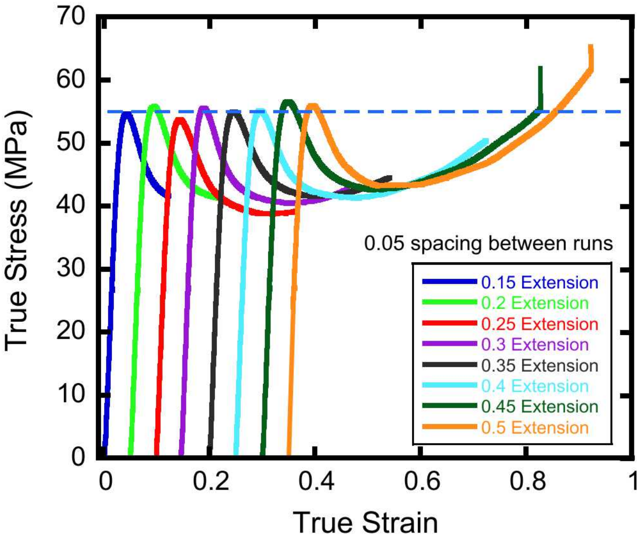




Appendix: Rejuvenation

- Cracks in samples occurred after ~0.4 strain
- It was concluded that samples can be safely reused when strained up to 0.2 strain





Appendix: Maxwell Model

s = stress
ε = strain
έ = strain rate
E = elastic modulus
η = viscosity

$$s_{dp} = s_{spring}$$

$$E\varepsilon_{spring} = \eta\acute{\varepsilon}_{dp}$$

$$\acute{\varepsilon} = \frac{\dot{s}}{E} + \frac{s}{\eta}$$

With some manipulation, integrate to solve for *s*

$$s = \acute{\varepsilon}\tau E\left(1 - e^{-t/\tau}\right) , \qquad \tau = \frac{\eta}{E}$$

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WK38 Use latex equations?

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Appendix: KAHR Model

Model relaxation time in molecules

$\delta = the\ deviation\ from\ equilibrium, which\ gets\ smaller\ with\ time$:

$\frac{d\delta}{dt} = \frac{-\delta}{\tau} \rightarrow \delta = \delta_o e^{-t/\tau}$ slowly decays to 0, this is the relaxation constant

$\frac{d\delta}{dt} = Cp\Delta T$ for constant degree of aging.

- Doolittle: $\eta \approx e^{v_o/v_f}$ $> Tg, WLF\ (both\ occupied\ and\ free\ volume)$