Effect of Thermal-Oxidative Aging on Mechanical Properties of Epoxy Thermosets

SAND2018-12489D

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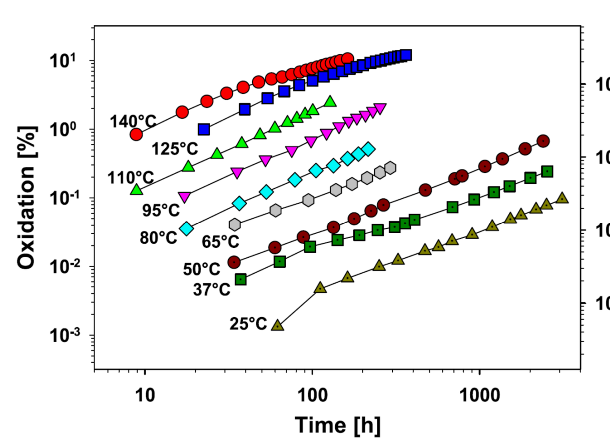
Why is Thermal-Oxidative Aging Important?

- Thermal oxidative aging of epoxies has been shown to have significant effects on mechanical response of the material, specifically leading to (1) decreased mechanical dissipation associated local motions within the polymer network and (2) an embrittlement observed as failure at lower strains during flexure tests.
- Detailed oxidation analyses of epoxies are limited, much less a coupling of this information with the mechanical effects of the oxidation.
- Here, we take a material (828/2049) for which detailed oxidation rates are available and perform a scoping experiment to determine whether significant changes are observed in the macroscopic stress-strain response.



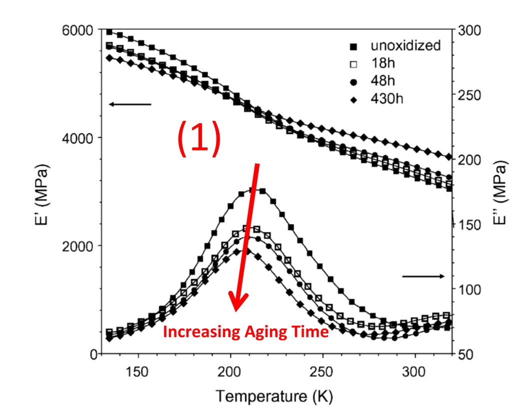
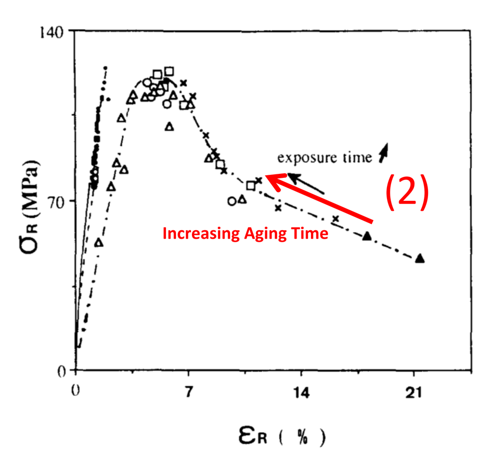
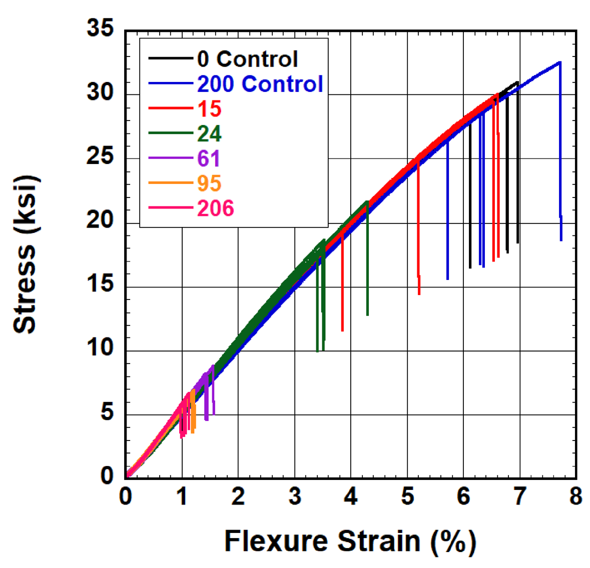


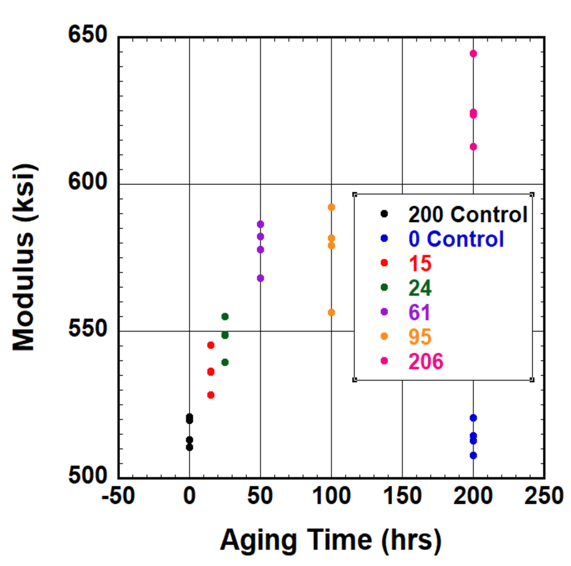
Fig. 1. β relaxation: storage modulus E′ and loss modulus E″ versus temperature at 1 Hz for increasing oxidation time at 423 K under oxygen pressure of 0.5 MPa.

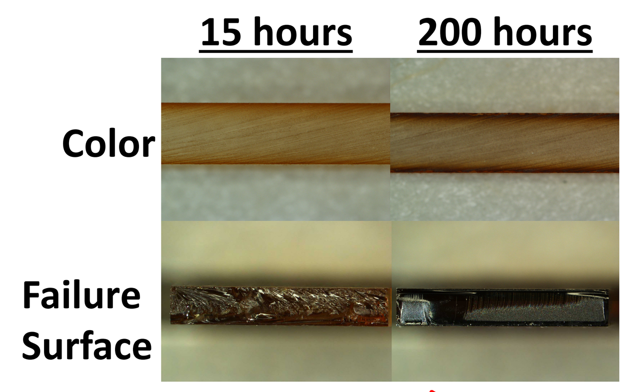


Results

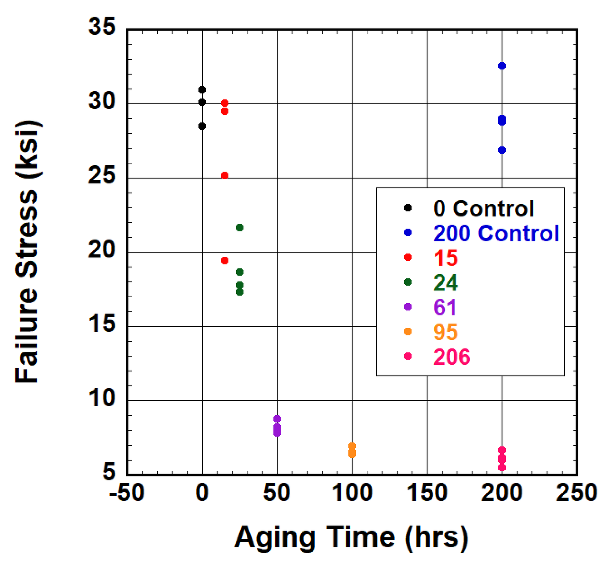
- At low aging times (e.g. 15 hours) distinguishing from control samples becomes hard.
- At higher aging time, Load (lbf) vs. Disp. (in), and Stress (ksi) vs. Flexure Stain (%) shift lower.
- Modulus of the material increases with aging times (140°C)

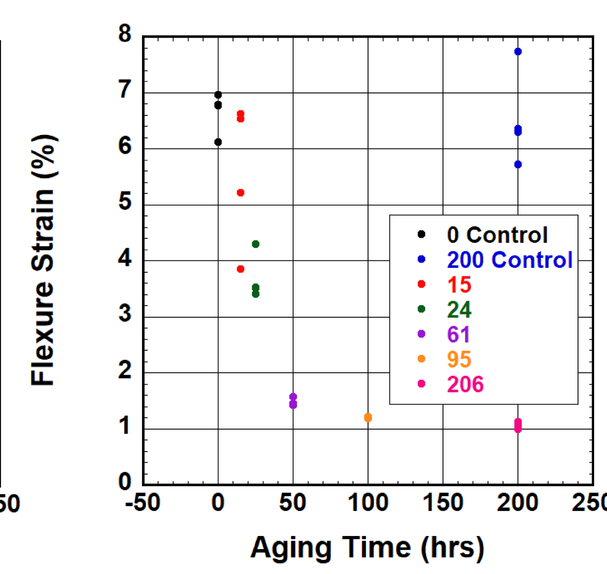


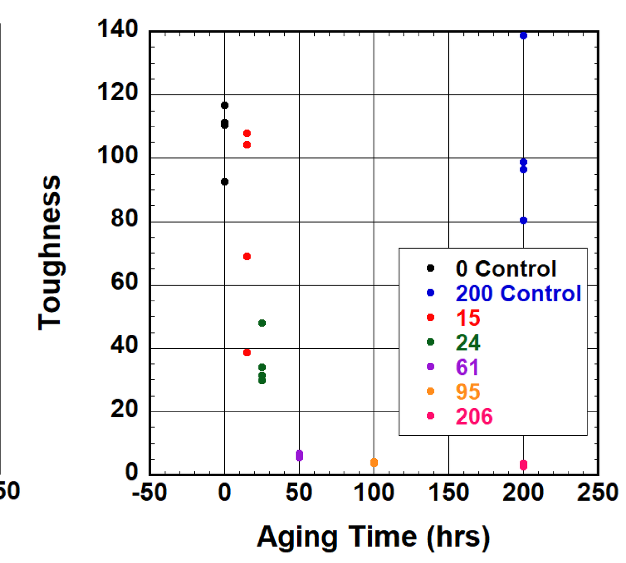


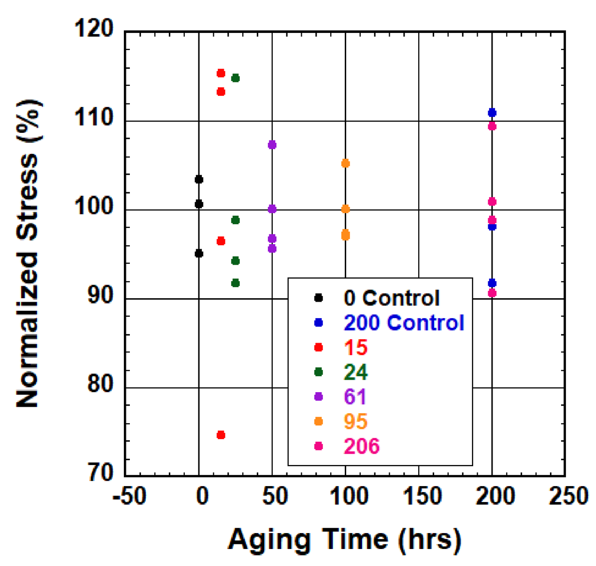


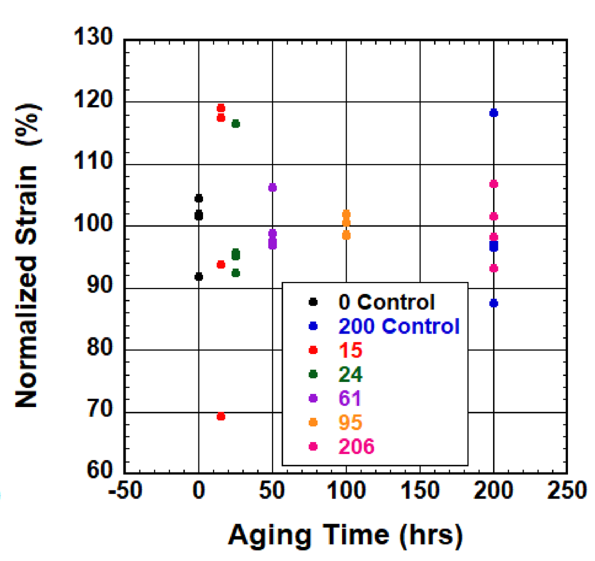
Failure Transition Occurs Between 24 and 61 hours

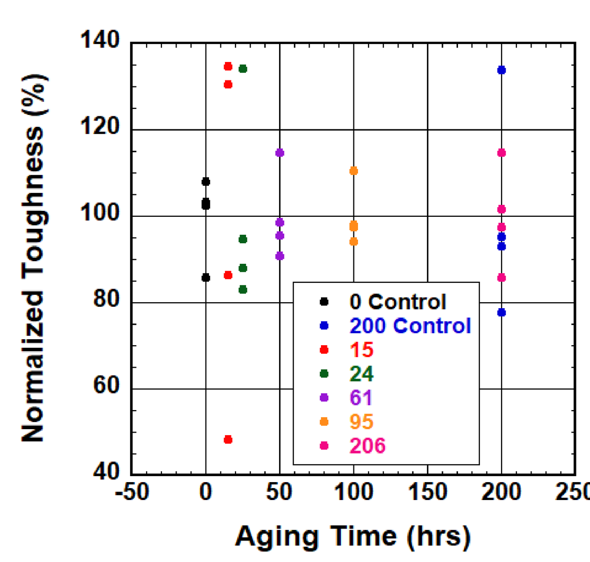












$$\sigma_{Norm.} = \frac{\sigma_n}{\left(\frac{\sigma_1+\sigma_2+\sigma_3+\sigma_4}{4}\right)}$$

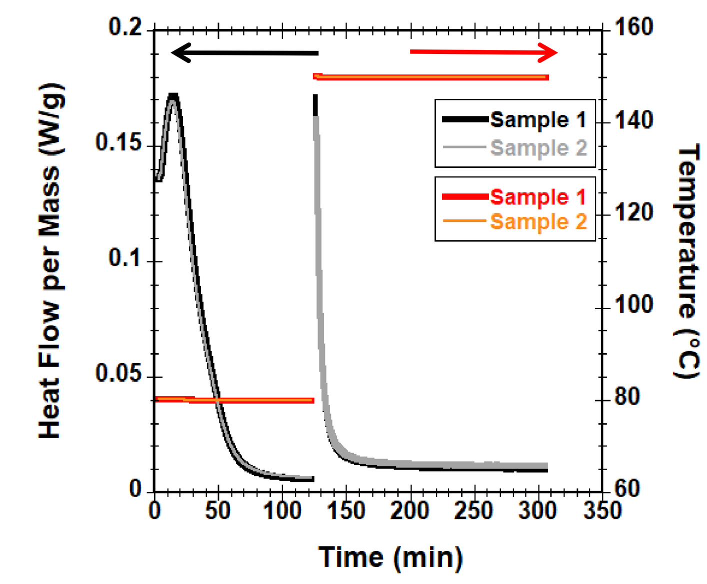
- Normalization of failure stress (ksi), flexure strain (%), and toughness using the above equation above, show that data distribution does not narrow or widen at higher aging times.

Chocinski-Arnault et al., *Mater Sci Eng A*, 2009, 521-522, 287
Le Huy et al., *Pol Degrad Stab*, 1993, 41, 149
Celina et al., *Polymer*, 2013, 54, 3290
Adolf, D. (2010). 828/2049. Retrieved 2018, from http://www.sandia.gov/polymer-properties/828_2049.html

METHODS AND ANALYSIS

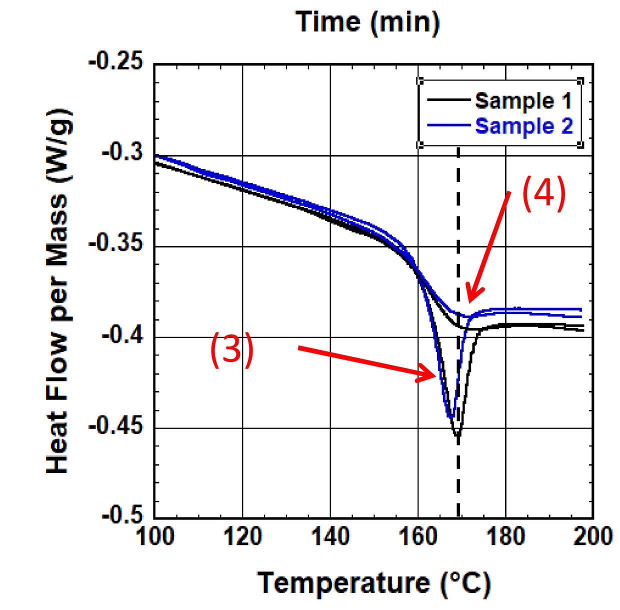
Sample Creation

- Stoichiometric ratio of 100 pbw diglycidyl ether of bisphenol A (Epon 828) to 32 pbw cycloaliphatic amine (Ancamine 2049)
- Aluminum plaque mold with a PTFE mold release spray: 6 in x 6 in x 0.05 in (W x L x T).
- ~40 samples were cut to the dimensions 0.25 in x 1.25 in x 0.06 in (W x L x T).
- Curing Schedule: 80°C for 2 hours and 150°C for 3 hours[1].

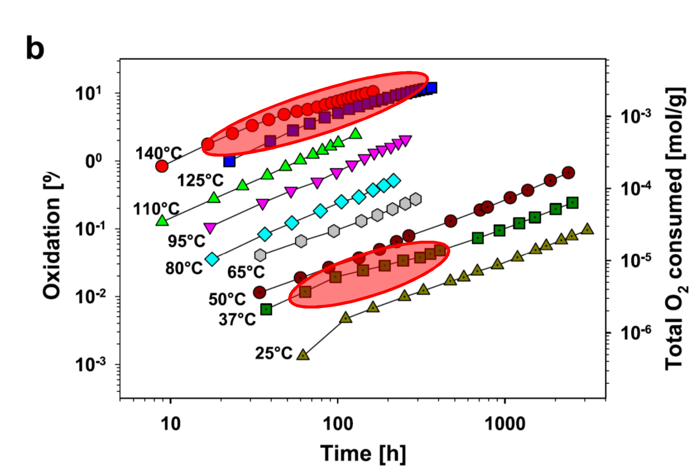


Curing Schedule

- Reaches equilibrium by ~170°C
- From cure schedule (<Tg) physical aging occurs. Thus from first heating cycle (3) there exist a large overshoot due to enthalpic recovery.
- Smaller overshoot during the second heating cycle (4) after erasing physical aging during first heating cycle.

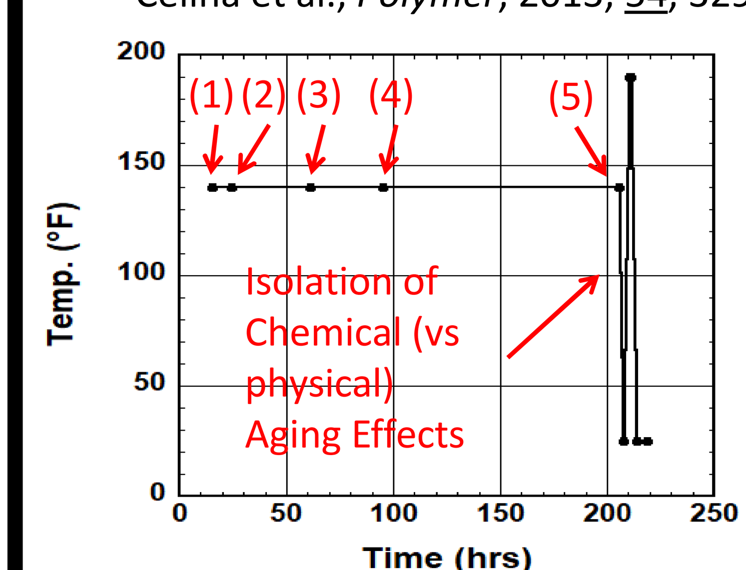


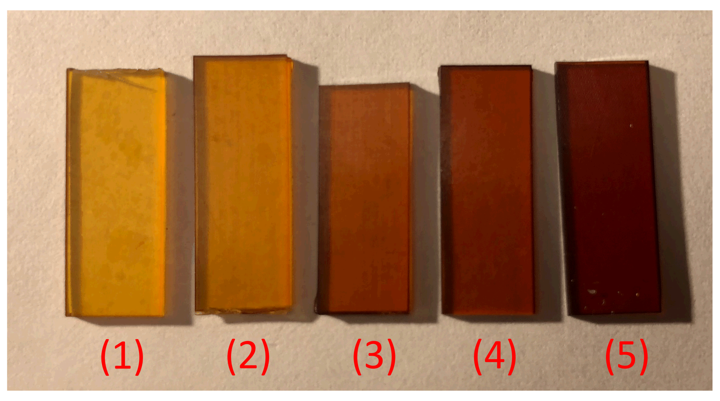
Aging Profile & Isolation of Chemical (vs physical) Aging Effects



Celina et al., *Polymer*, 2013, 54, 3290

Samples (#)	Actual Aging Time (hrs)	Aging Temp. (°C)
1-4	0	25
5-8	200	25
9-12	15	140
13-16	24	140
15-20	60.8	140
21-24	95	140
25-28	205.7	140

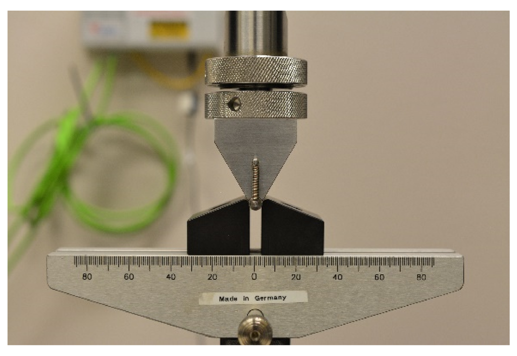




Aging Time (hrs): 15 24, 60.8, 95, 205,7

3-POINT-BEND-TEST

- Ramp-load-to-failure experiment.
- 0.5” support span, displacement rate of 0.1 in./minute.
- Ductile and brittle fracture surfaces of 15 and 200 hour samples, respectively (8) (Ductile to brittle transition across 24 and 61 hours).



Conclusion

- The effect of thermal-oxidative aging on the failure of the 828/2049 epoxy thermoset is apparent.
- Flexural strain decreases from 7-1 (%).
- Stress decreases from 30-5 (ksi).
- Data suggests an abrupt change in failure between 24 and 61 hours.

Future Steps

- Collect more data within the 24-60 hour regime and correlate this with what is going on chemically within the material.
- Test a wider range of aging temperatures, and use additional thermo-mechanical test methodologies to discriminate, or discern the origin of, “mechanical weakening” (becoming more brittle) of the material.
- Put a known defect (crack) along each samples to determine how thermal-oxidative mechanical properties change.

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