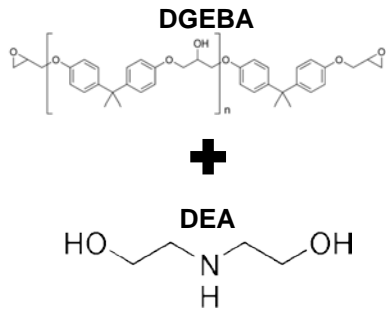


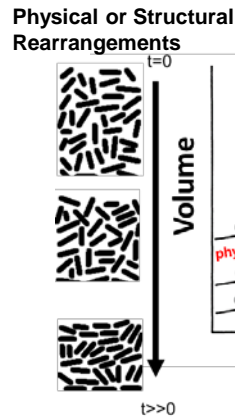
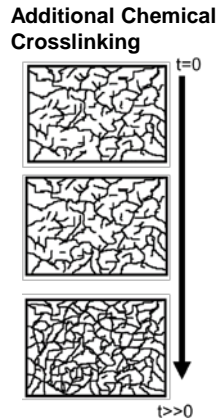
Exceptional service in the national interest



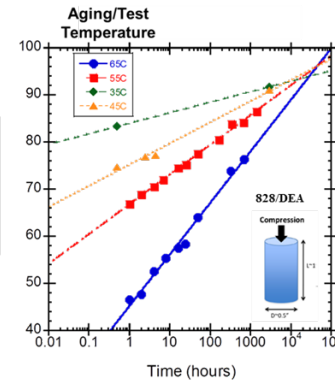
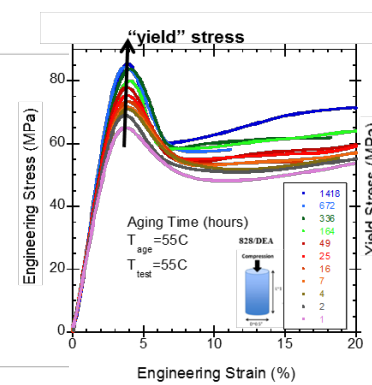
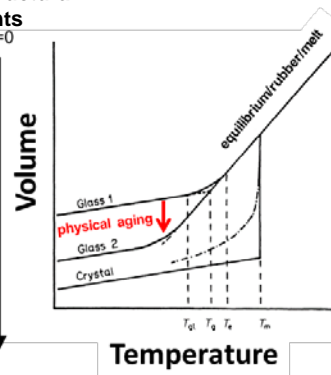
Materials



Chemical and Physical Aging



Thermal-Mechanical Response Changes



The interplay of chemical and physical aging in a DGEBA epoxy cured with DEA

Jamie M. Kropka, Gabriel K. Arechederra and John D. McCoy

2017 JOWOG 28 Main Meeting
AWE Aldermaston, Aug 29-Sep 01



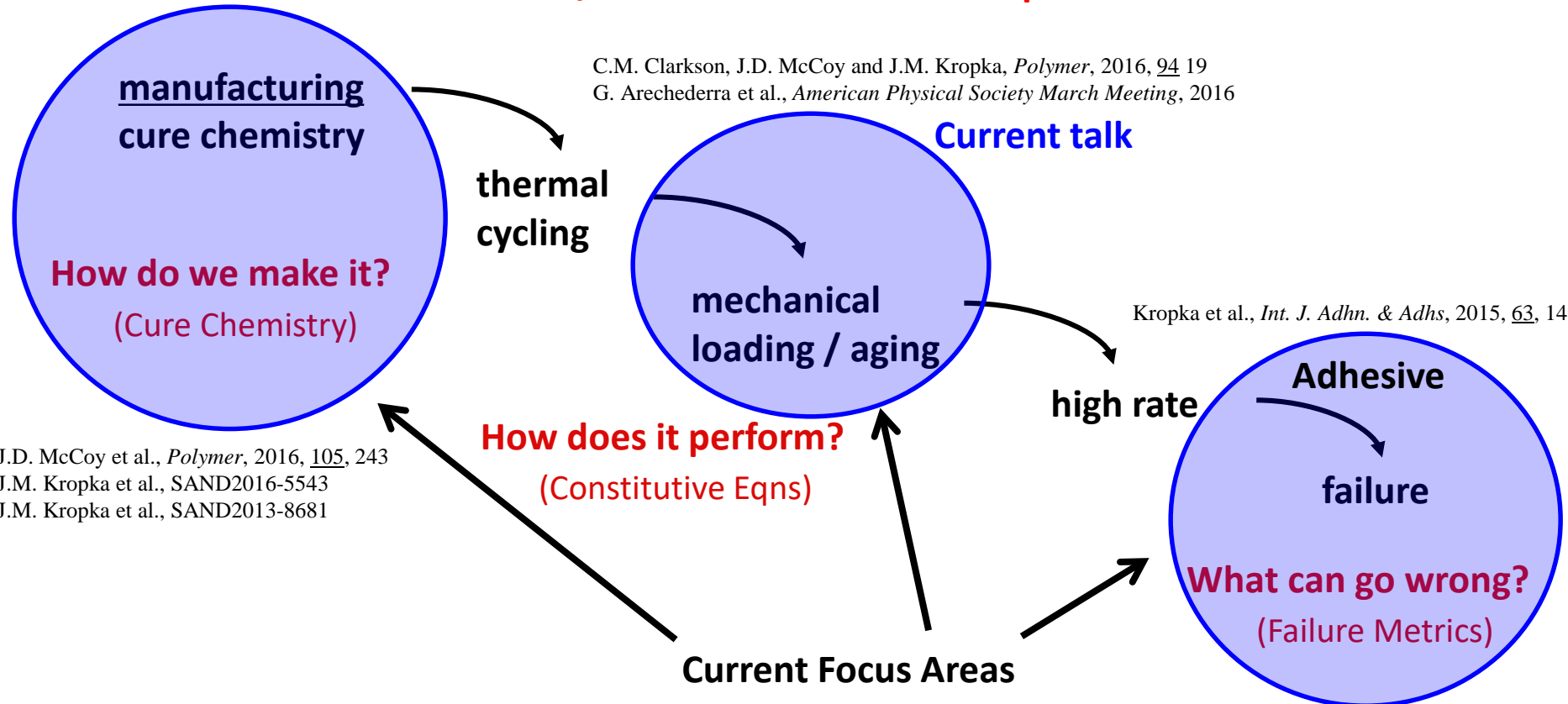
Our Vision: Validated Model-Based Lifecycle Engineering for Packaging Design

Polymer Nonlinear Viscoelastic (NLVE) Model

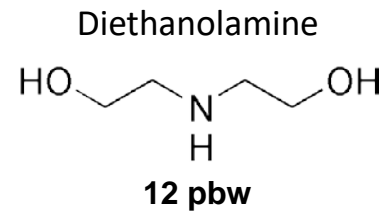
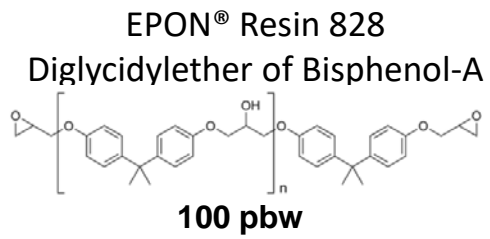
J.M. Caruthers, et al., *Polymer*, 2004, 45, 4577
 D.B. Adolf, et al., *Polymer*, 2004, 45, 4599
 D.B. Adolf, et al., *Polymer*, 2009, 50, 4257



Predict Stress/Strain and Understand Impact on Performance

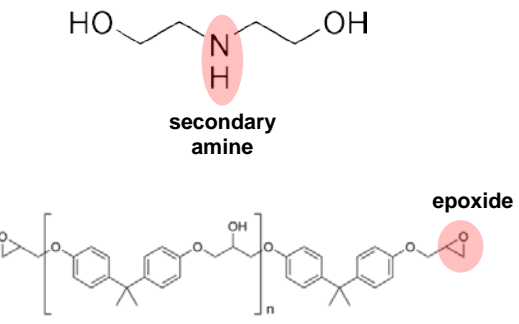


Material¹



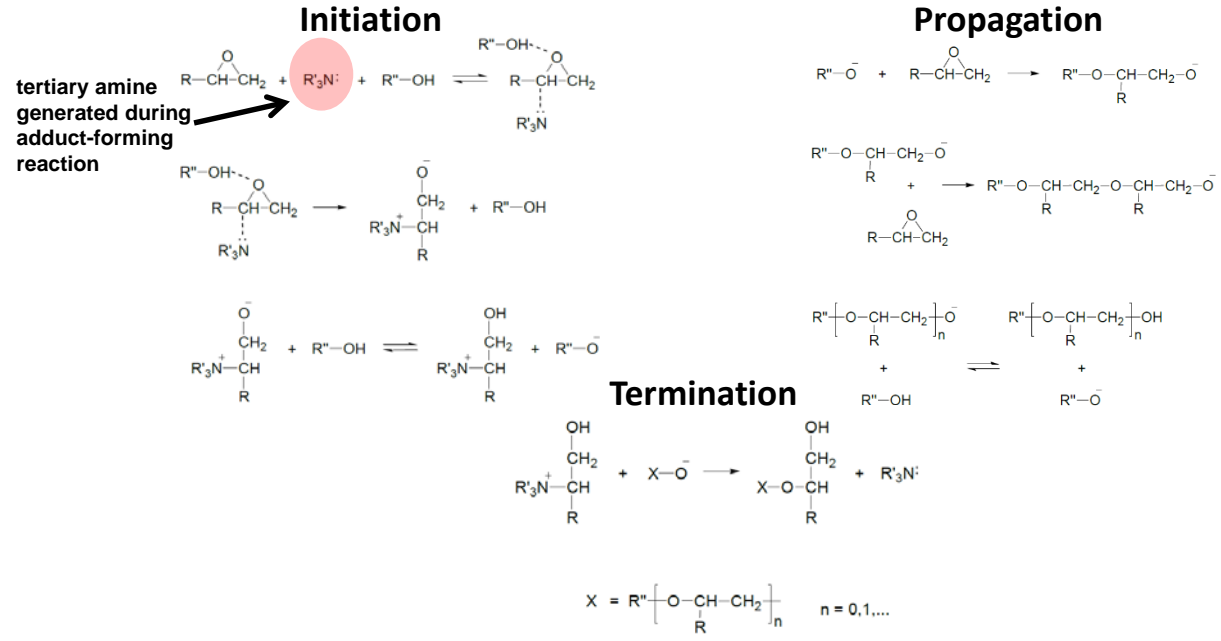
Polymerization at T = 70°C (the cure process before aging)

Adduct-Forming Reaction



All secondary amine is consumed in an addition reaction and excess epoxide remains

Proposed Gelation Reaction



Anionic Chain-Growth Polymerization Catalyzed by Tertiary Amine from Adduct-Forming Reaction

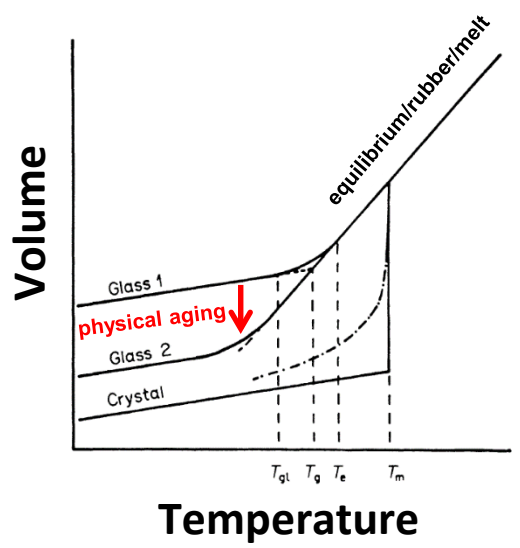
J.D. McCoy et al., *Polymer*, 2016, 105, 243

$T_g \sim 70^\circ C$

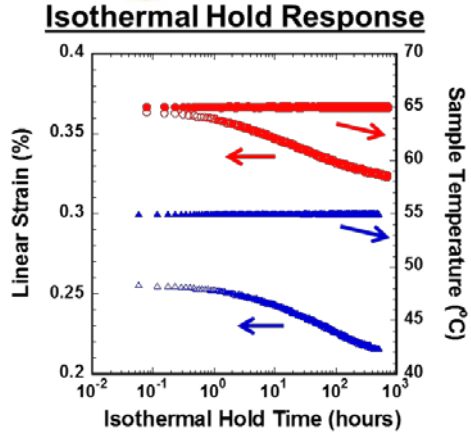
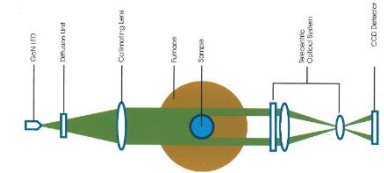
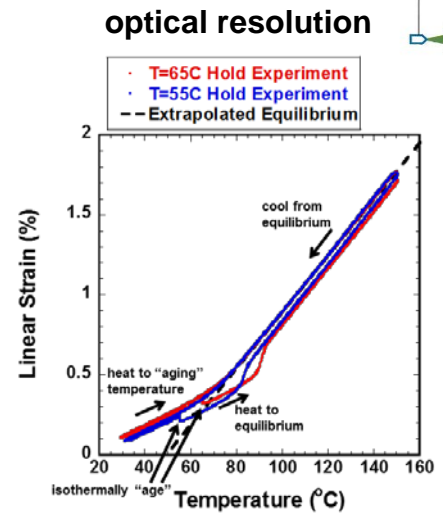
[when mixed 100:12 (pbw) 828:DEA and cured 24 hours at T=70°C]

¹Mix ratio, cure and typical properties can be found at: http://www.sandia.gov/polymer-properties/828_DEA.html

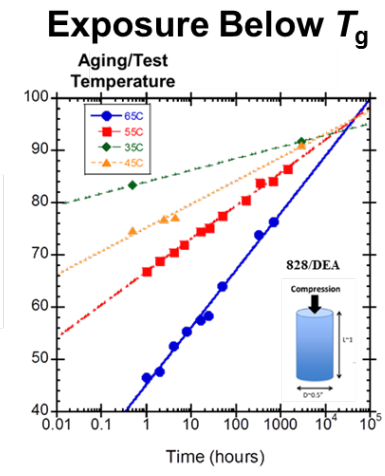
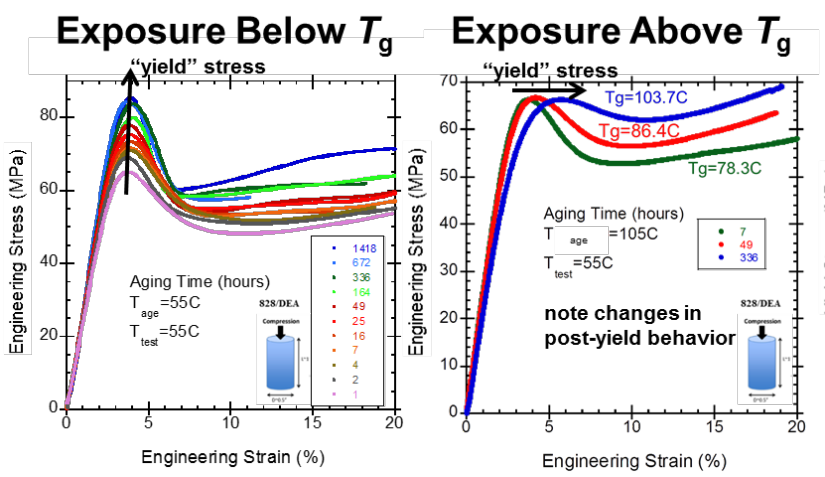
Polymer Glass Aging



Material Volume Changes



Material Mechanical Response Changes

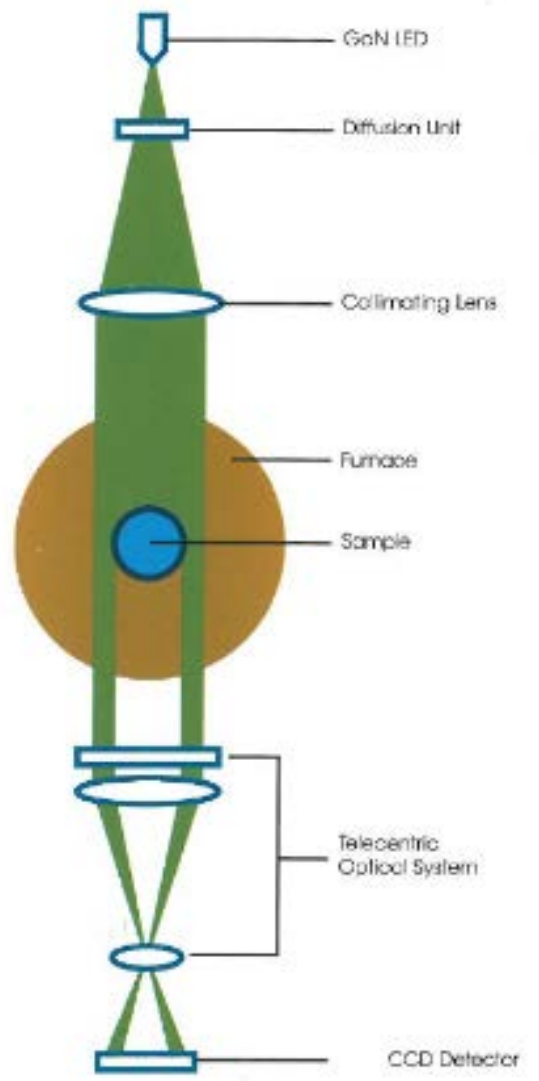


SNL NLVE polymer models (e.g., SPEC) have the framework to predict the aging behavior and should be tested against measurements

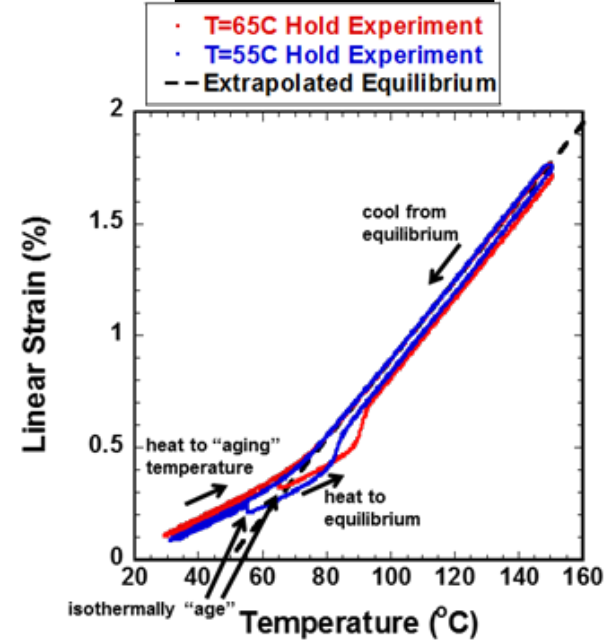
Volume

Measuring Volume Response Associated with Aging

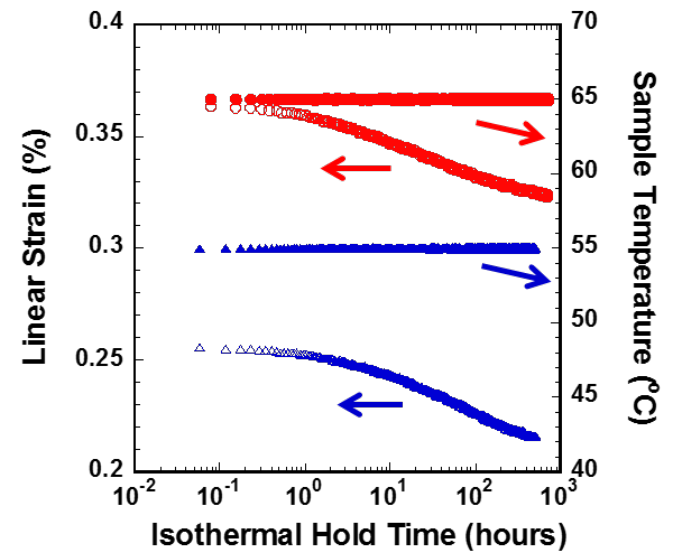
Optical Resolution of Length*



Full Experiment



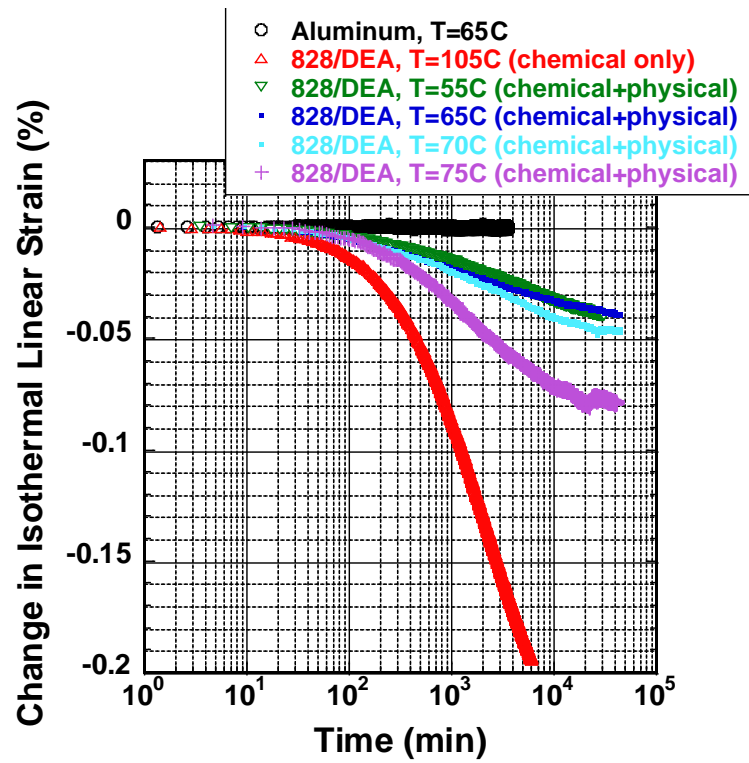
Isothermal Hold Response



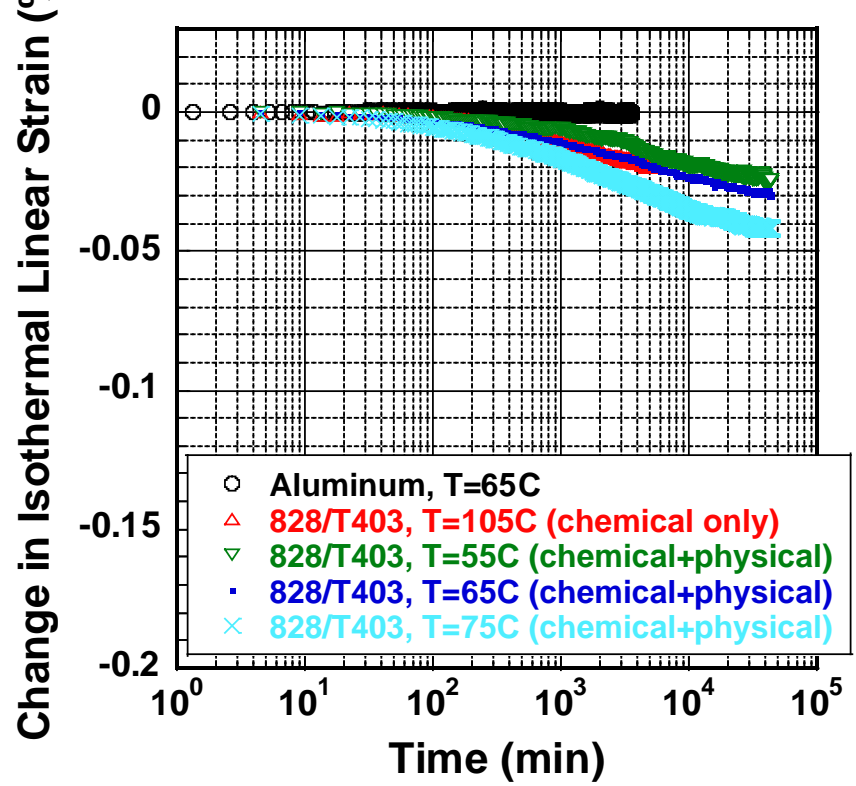
*for isotropic materials $\Delta V=3\Delta L$

Isothermal Volume Response for 2 Common Epoxy Thermosets

828/DEA



828/T403

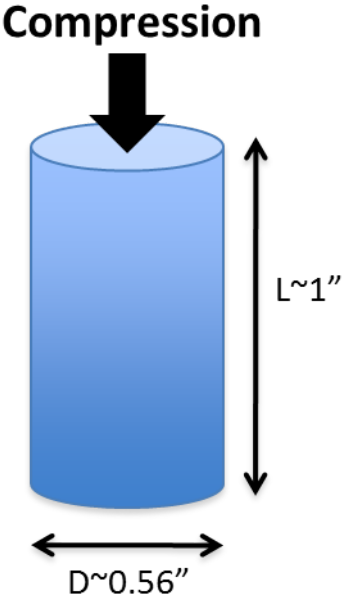
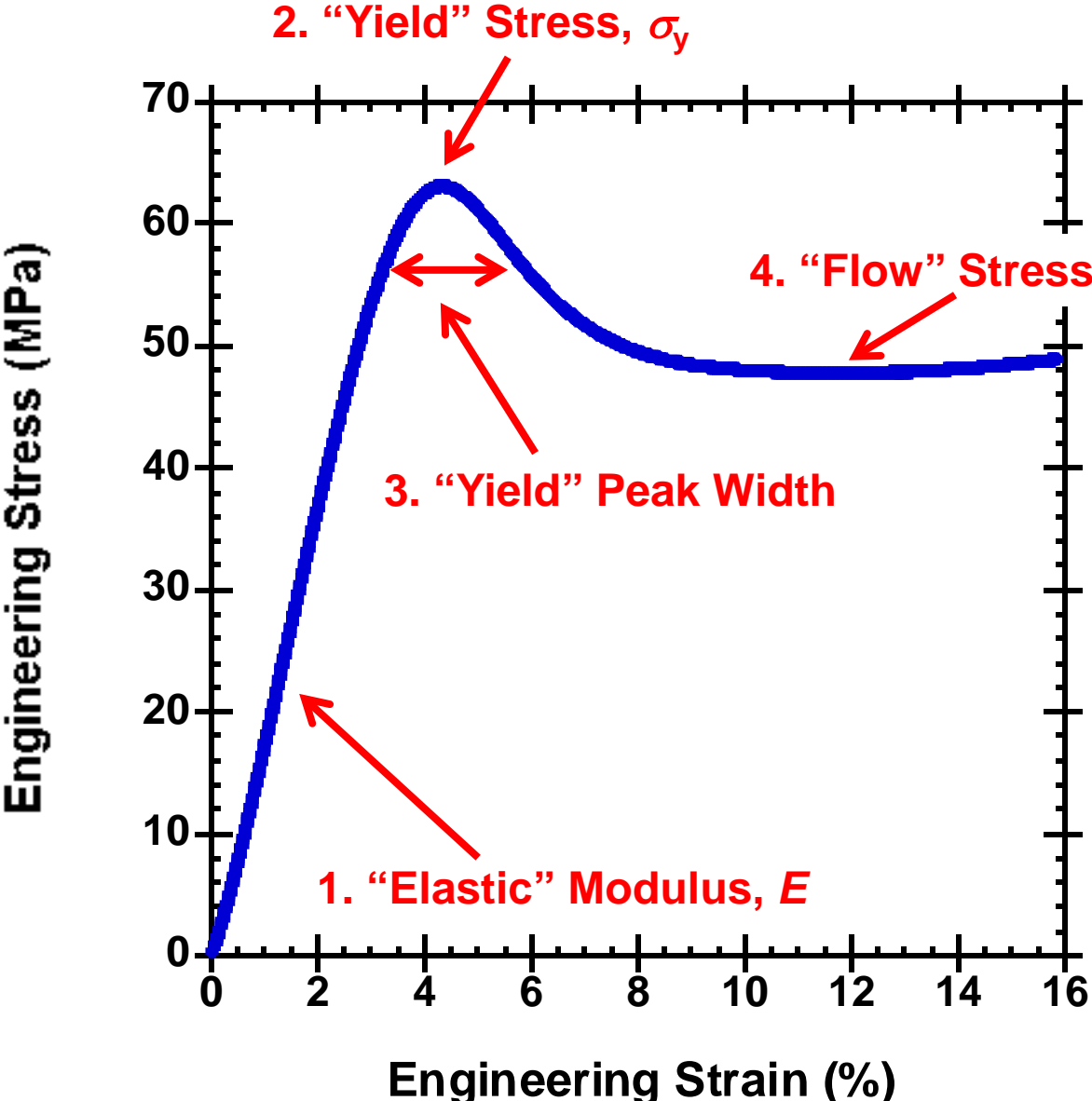


Note: Remaining reactive potential (excess epoxide groups in the case of 828/DEA) can play a significant role in total volume change

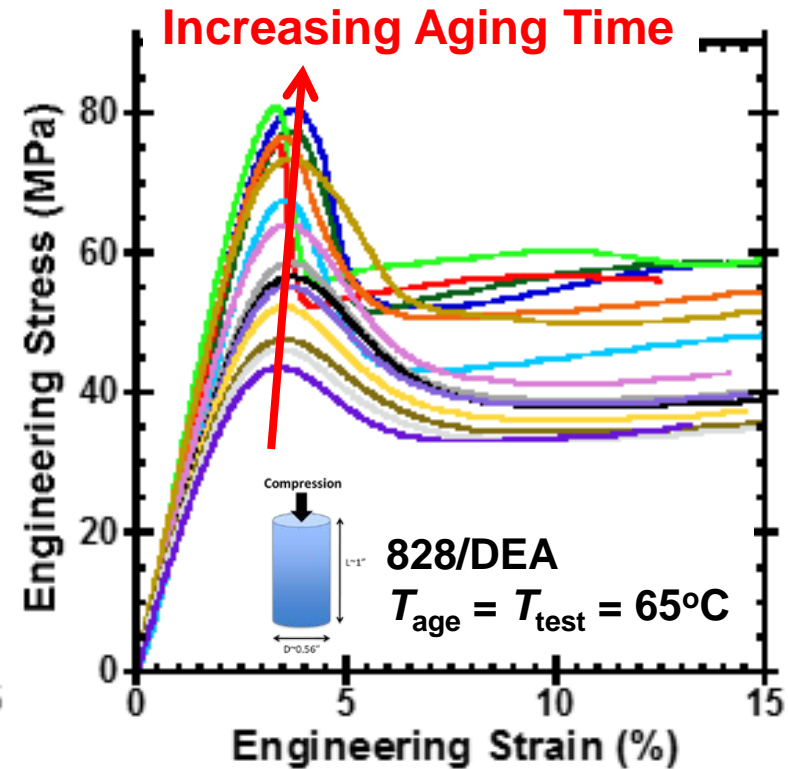
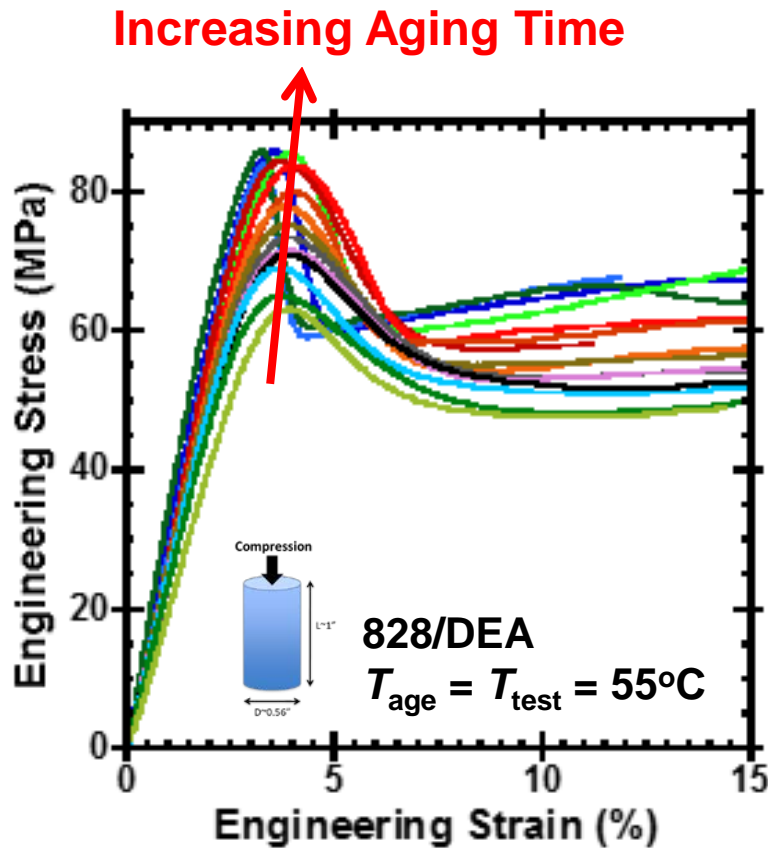
- The 50 nm instrument (length) resolution enables quantitative tracking of material length over time and provides the opportunity to resolve functionality [e.g., $l(t)$] that describes material behavior
- Minimizing potential for continued cure during “aging” by using “stoichiometric” epoxy thermosets (e.g., 828/T403) can have significant impact on material “shrinkage” magnitude

Mechanical

Anatomy of Compressive Stress-Strain Response of Glassy Polymers



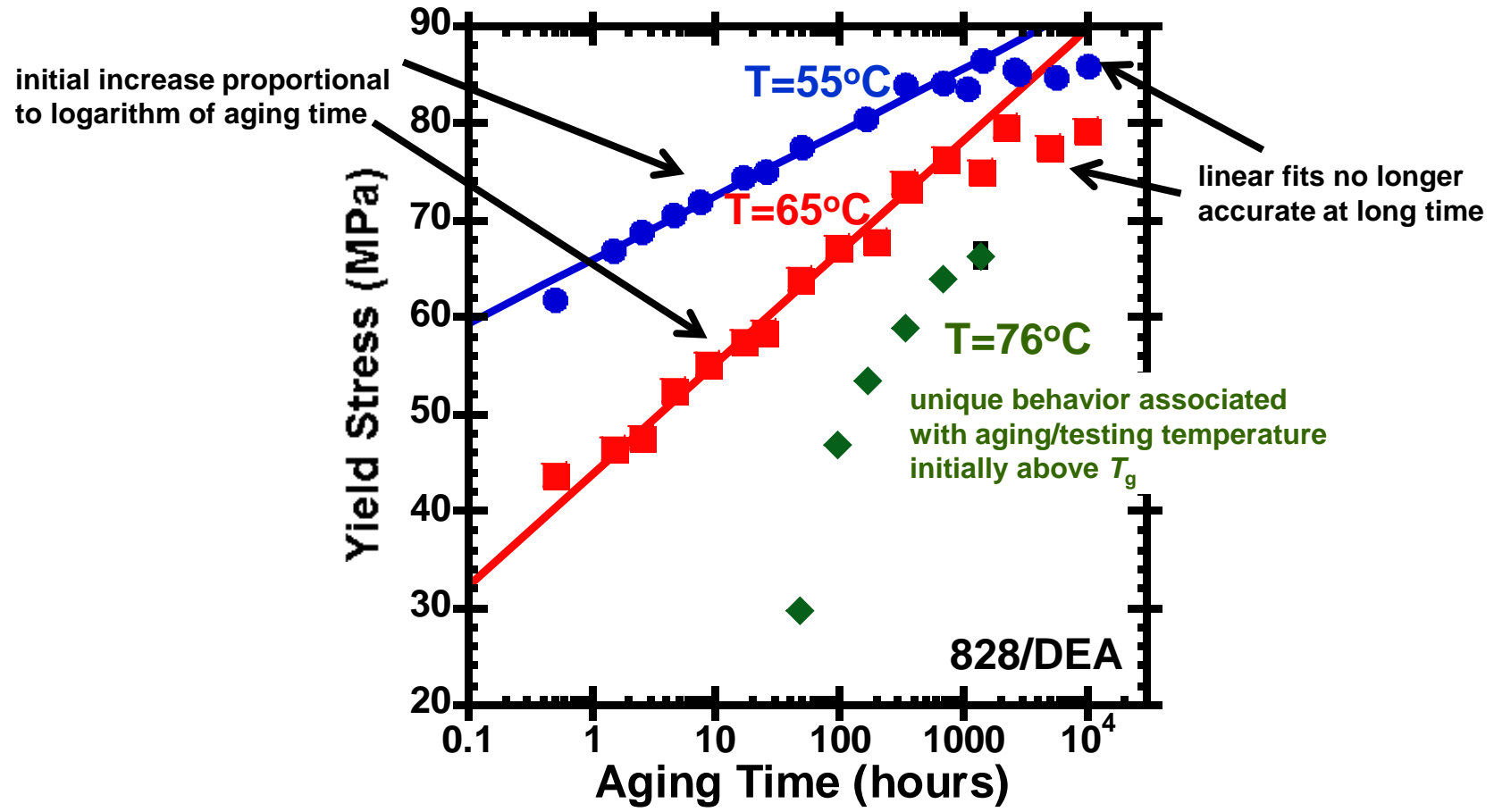
Changes in Compressive Stress-Strain Response Associated with Thermal Aging



4 Distinguishable Changes in Compressive Stress-Strain Response Include:

- Increase in “elastic” compressive modulus
- **Increase in “yield” stress**
- Narrowing of “yield” peak
- Increase in “flow” stress

Evolution of Yield Stress during Thermal Aging



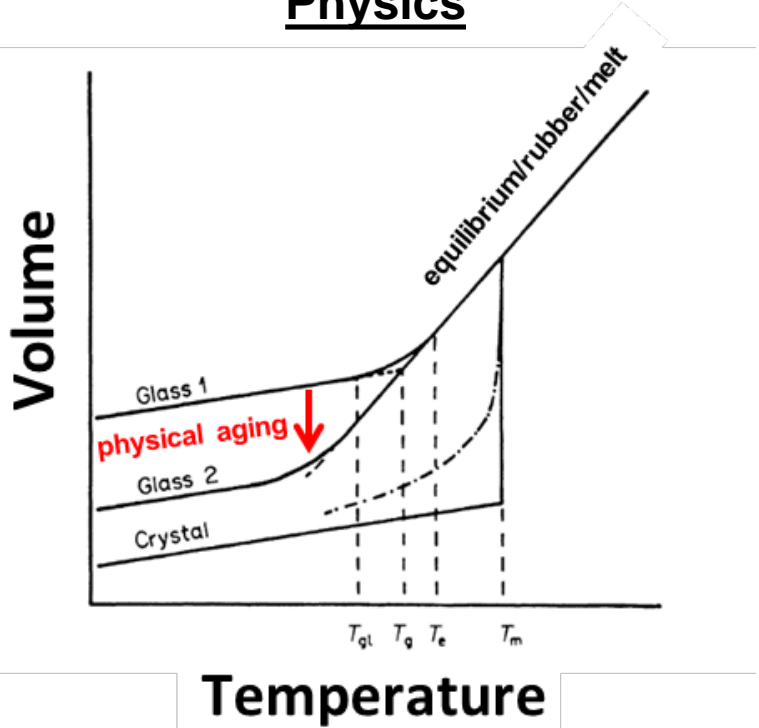
Focusing on $T = 55^\circ\text{C}$ and 65°C datasets for now:

- Changes in yield stress are substantial—as high as 82%
- The evolution of yield stress with time changes (or possibly stops) after ~30 days

What is the mechanism(s) driving this change?

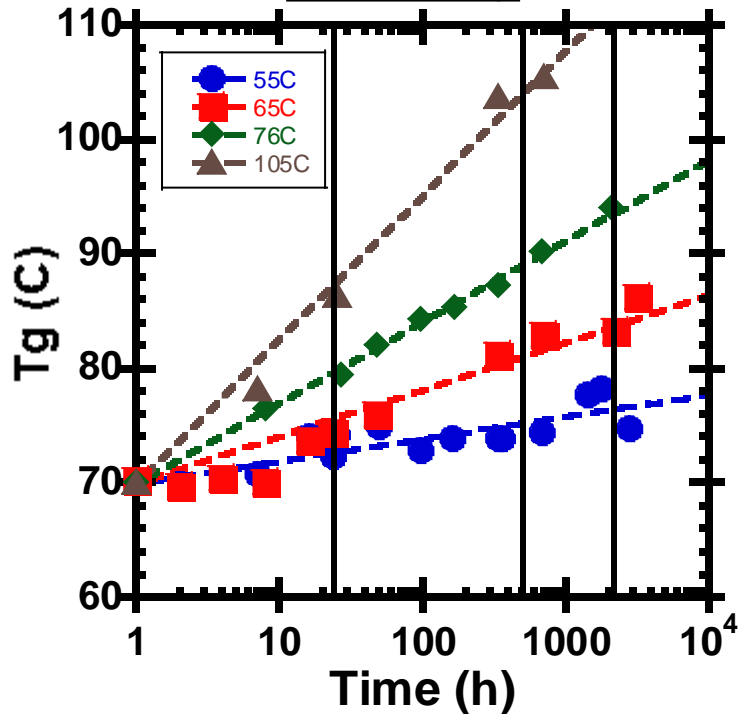
Mechanisms Driving Evolution of Yield Stress during Thermal Aging

Physics



Volume relaxation (densification) of the material slows molecular motions in the polymer chain and this contributes to an increase in the observed yield stress in the compressive stress-strain response

Chemistry

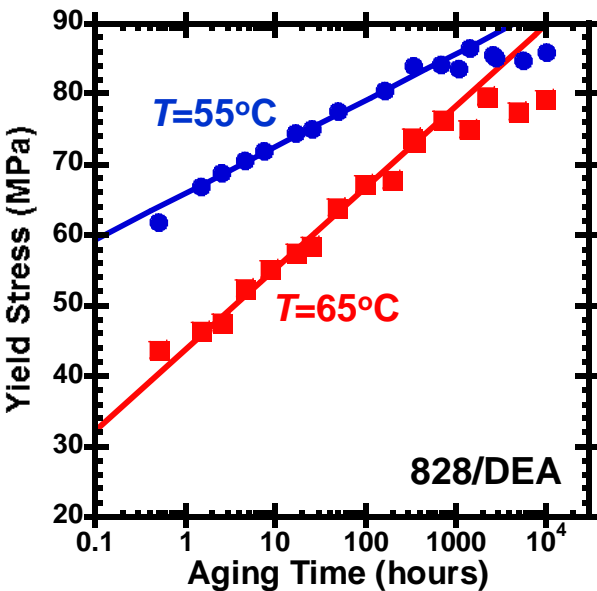


Continued chemical crosslinking increases the glass transition temperature of the material. This also slows molecular motions in the polymer chain (at a given temperature below T_g) and contributes to an increase in the observed yield stress in the compressive stress-strain response

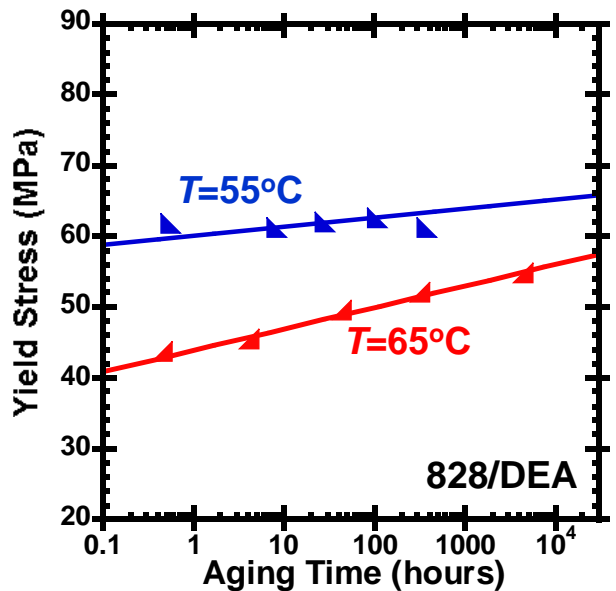
Can these contributions to the overall increase in yield stress be separated?

Chemical and Physical Contributions to the Evolution of Yield Stress during Thermal Aging

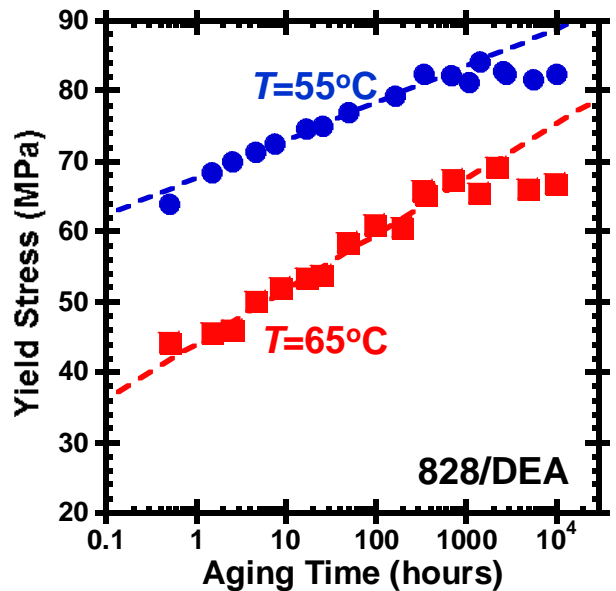
Chemical + Physical (Measured)



Chemical Only (Measured)



Physical Only (Calculated)



By thermally annealing the samples above the glass transition temperature (after aging), the physical history of the sample is erased and the chemical-only contributions to the evolution of the yield stress are resolved. Physical-only contributions are calculated by subtracting the chemical-only contributions from the total change in yield stress.

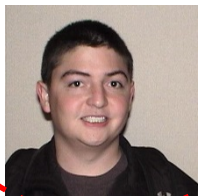
Summary

- **Demonstrated ability to resolve in-situ material dimensional changes associated with isothermal aging under no mechanical load**
- **Illustrated differences in dimensional changes between materials associated with the specifics of a given material (e.g., remaining reaction potential that can occur under the aging conditions)**
- **Resolved substantial changes in the compressive yield stress (as high as 80%) of the 828/DEA material over relatively short times (~30 days) when aged and tested below, but near, the glass transition temperature (e.g., $T_g-10^\circ\text{C}$, $T_g-20^\circ\text{C}$)**
- **Resolved the apparent attainment of equilibrium (volume), at which time there is no further change (associated with physics) in yield stress**
- **Discriminated between the chemical and physical contributions to the evolution of the yield stress during isothermal aging**

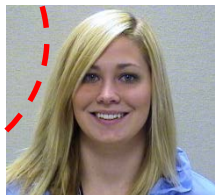
Polymer Chemistry/Physics, Characterization, Modeling and Processing Group

Experimentalists

Gabe Arechederra



Lindsey Hughes



Scott Spangler (retired?)



Rex Jaramillo



Nick Wyatt



Jamie Kropka



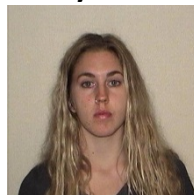
Doug Adolf (retired)



Mark Stavig



Kelsey Wilson



Mat Celina



John McCoy (NM Tech)



Modelers



Bob Chambers (retired)



Kevin Long



Brenton Elisberg



Kevin Troyer



Kurtis Ford



Matthew Neidigk



some past and present students

Jason Sharkey (NM Tech/SNL)

Caitlyn Clarkson (NM Tech/SNL)

Windy Ancipink (NM Tech)

Jasmine Hoo (NM Tech)

Lara Draelos (NM Tech)

Maggie House (NM Tech)