SAND2018-1985C

Exceptional service in the national interest

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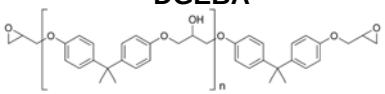
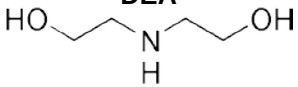
Materials

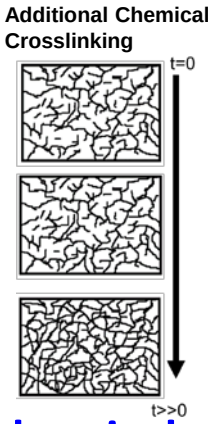
DGEBA

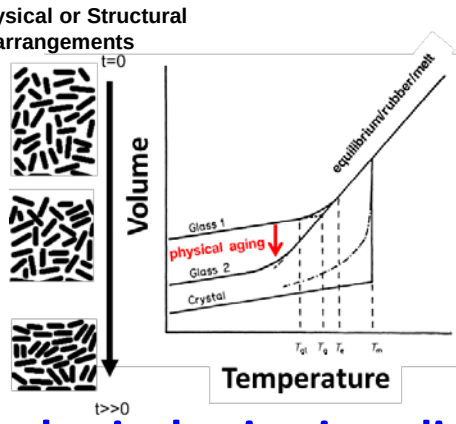


DEA

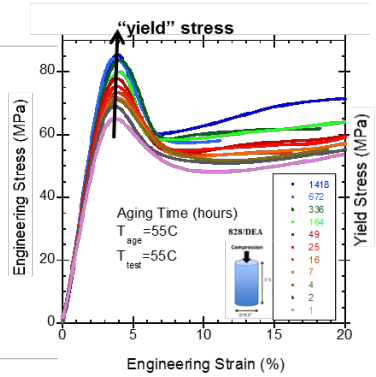


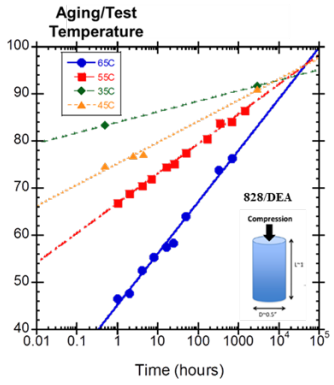
Chemical and Physical Aging





Thermal-Mechanical Response Changes





The interplay of chemical and physical aging in a diglycidylether of bisphenol A (DGEBA) epoxy cured with diethanolamine (DEA)

Jamie M. Kropka, Gabriel K. Arechederra, and John D. McCoy
Sandia National Laboratories, Albuquerque, NM

2018 Adhesion Society Annual Meeting, San Diego, CA February 27, 2018

U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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Polymer Physics, Characterization, Modeling and Processing Group

Experimentalists

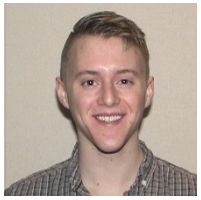
Materials Science & Engineering

Kelsey Wilson

Lindsey Hughes

Doug Adolf (retired)

Taylor Gabaldon



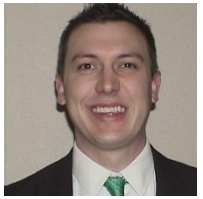
Rex Jaramillo

Mark Stavig

Nick Wyatt

Jamie Kropka

Cody Corbin



some past and present students

Jason Sharkey (NM Tech/SNL)

Caitlyn Clarkson (NM Tech/SNL)

Gabe Arechederra (NM Tech/SNL)

Jasmine Hoo (NM Tech)

Lara Draelos (NM Tech)

Maggie House (NM Tech)

Windy Ancipink (NM Tech)

Mat Celina

John McCoy (NM Tech)

Modelers

Bob Chambers (retired)

Kevin Long

Brenton Elisberg

Craig Tenney

Kurtis Ford

Matthew Neidigk (AFRL)

Main Contributors to Today's Topics

NNSA National Nuclear Security Administration

Sandia National Laboratories

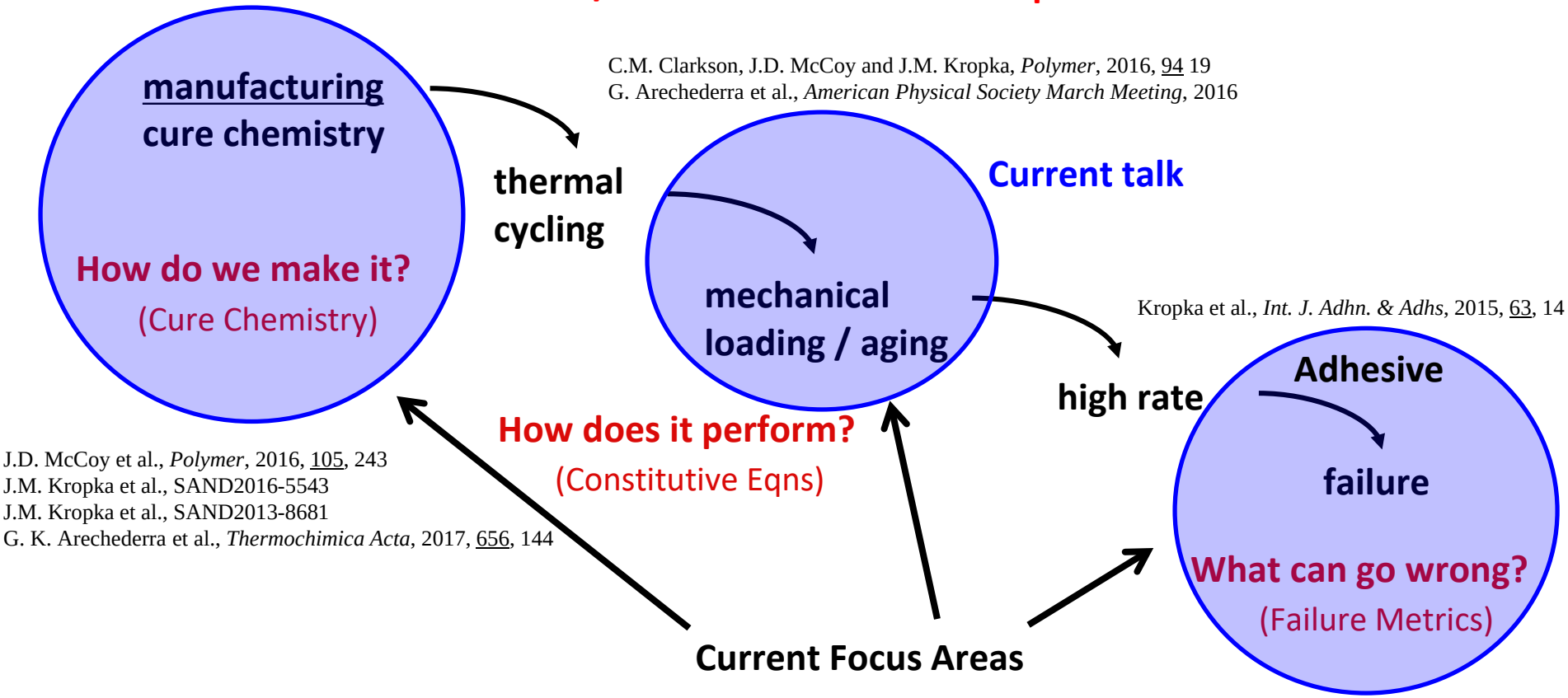
Our Vision: Validated Model-Based Lifecycle Engineering for Packaging Design

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

Polymer Nonlinear Viscoelastic (NLVE) Model

Predict Stress/Strain and Understand Impact on Performance

C.M. Clarkson, J.D. McCoy and J.M. Kropka, *Polymer*, 2016, 94 19
G. Arechederra et al., *American Physical Society March Meeting*, 2016



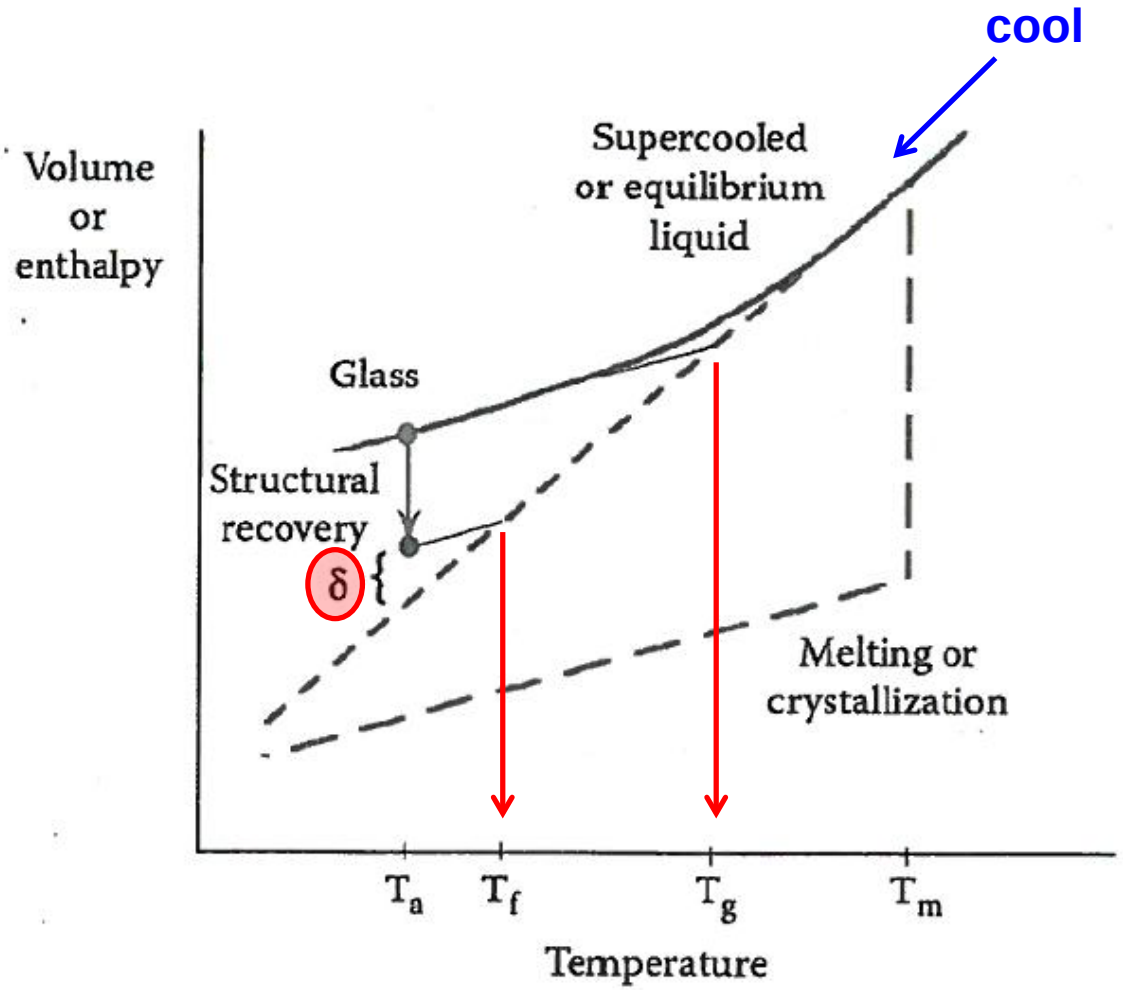
Kropka et al., *Int. J. Adhn. & Adhs*, 2015, 63, 14

J.D. McCoy et al., *Polymer*, 2016, 105, 243
J.M. Kropka et al., SAND2016-5543
J.M. Kropka et al., SAND2013-8681
G. K. Arechederra et al., *Thermochimica Acta*, 2017, 656, 144

Polymer Glass Aging Topics

- Background
  - Glass Formation and Structural Recovery/Relaxation
  - Signatures and Impact of Structural Recovery/Relaxation
  - What is lacking in our understanding and what is left to do?
- Our Current Efforts
  - Goals
  - Materials
  - Volume and mechanical response changes associated with aging
  - Assessment of impact of aging on stress and failure in application relevant geometries

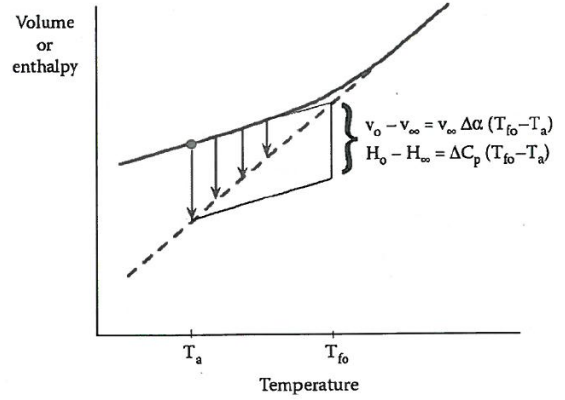
Glass Formation and Structural Recovery/Relaxation

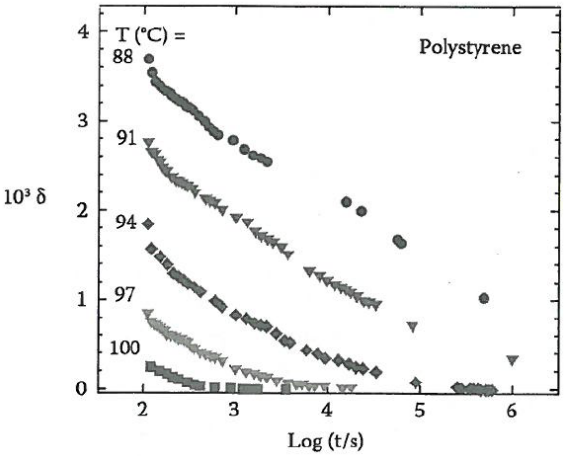


Simon and McKenna, Structural recovery and physical aging of polymeric glasses, in **Polymer Glasses**, 2017

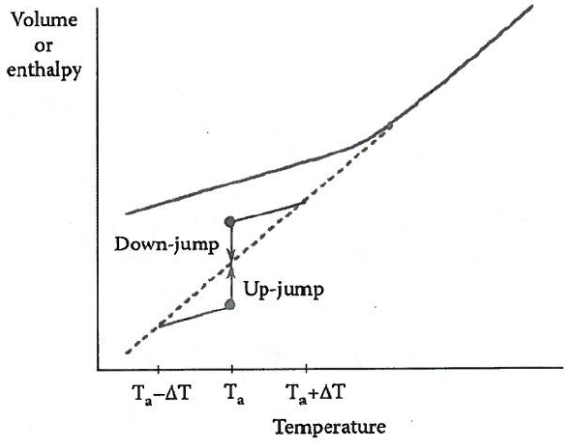
Signatures of Structural Recovery/Relaxation

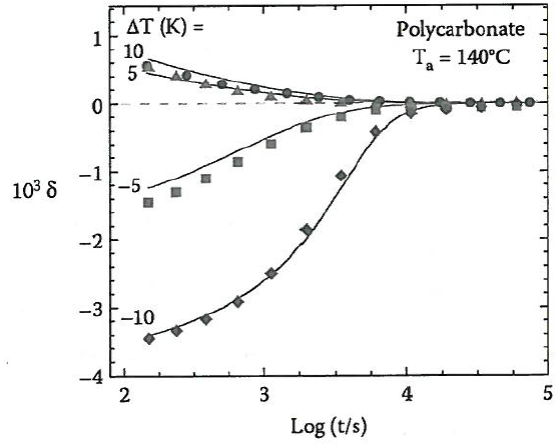
Intrinsic Isotherms



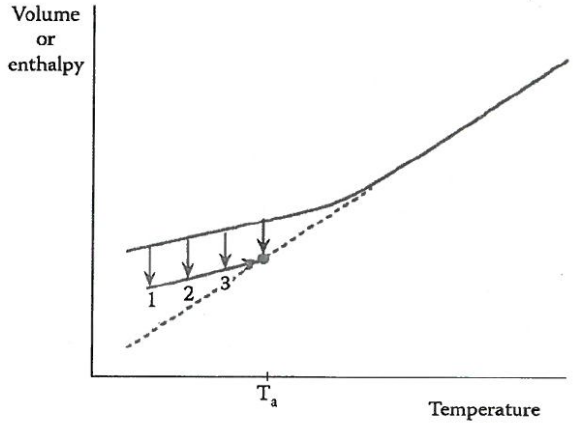


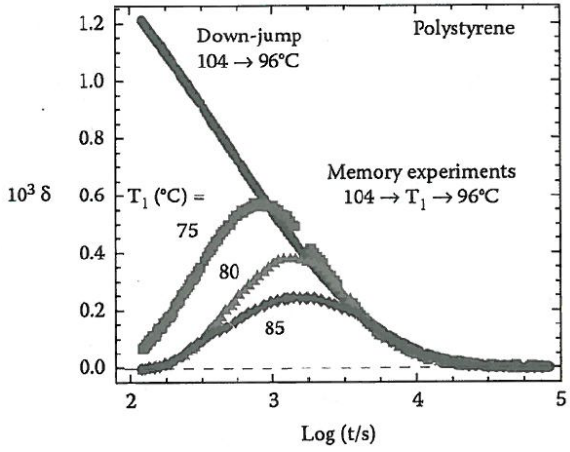
Asymmetry of Approach





Memory Effect





Relaxation Depends on Structure

Relaxation Depends on History

KAHR and TNM models capture qualitative features of glassy kinetics and the 3 signatures of structural recovery

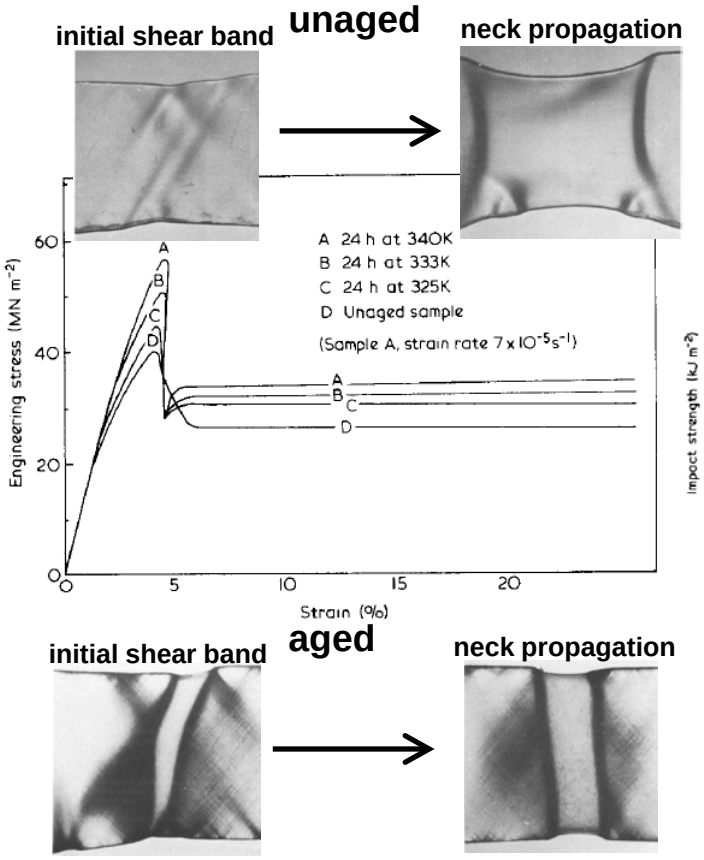
Simon and McKenna, Structural recovery and physical aging of polymeric glasses, in **Polymer Glasses**, 2017

Impact of Structural Recovery and Physical Aging

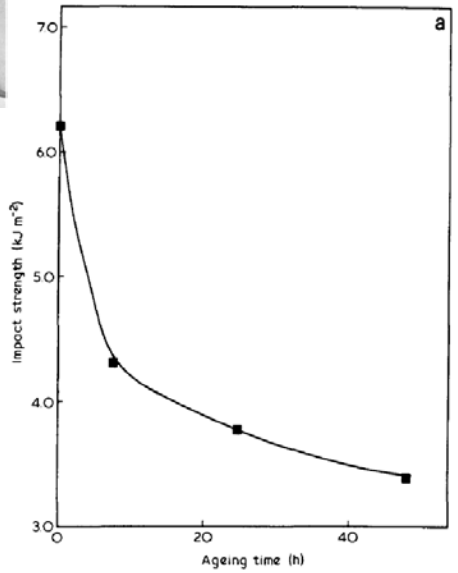
"Failure modes of polymers can change from ductile to brittle failure with aging"

S.L. Simon and G.B. McKenna, in *Polymer Glasses*, 2017, pg. 46

Tensile and impact tests of PET during isothermal "aging"



R.N. Haward et al., *Polymer*, 1983, 24 1245



Izod impact studies of PC during isothermal "aging"

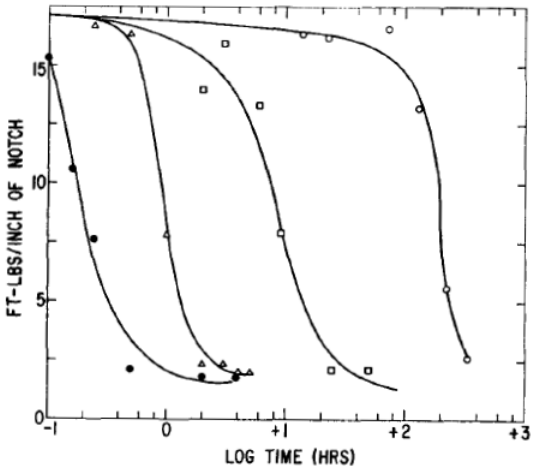


Fig. 3. Effect of annealing temperature on Izod impact data. ○) 100; □) 115; △) 125; ●) 130; [η] = 0.58.

D.G. Legrand, *J. Appl. Pol. Sci.*, 1969, 13 2129

These are thermoplastics, but the phenomena can occur in thermosets too

What is left to do?

"Further work and direct measurement of the volume and enthalpy along with the mechanical (physical aging) experiments should be undertaken on the same samples"

S.L. Simon and G.B. McKenna, in *Polymer Glasses*, 2017

- Currently probing epoxy volume/enthalpy relaxation plus changes in mechanical response AND using this information to design "strength" experiments in application relevant geometries

"…because the (KAHR and TNM) models do still exhibit some difficulties in quantitative prediction with model parameters showing a dependence on thermal history…" efforts are necessary to improve upon these models

S.L. Simon and G.B. McKenna, in *Polymer Glasses*, 2017

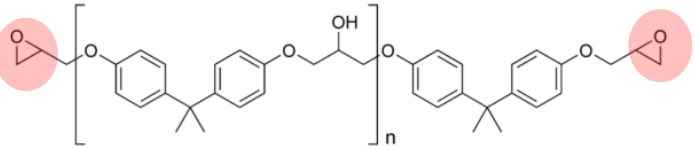
- Currently testing Sandia's non-linear viscoelastic modeling capabilities against aging data

Is physical aging a concern in terms of stress evolution in application designs?

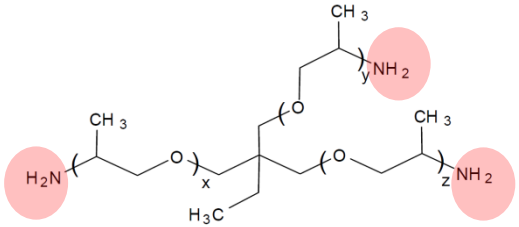
Materials

828/T403[1] and 828/GMB/T403

EPON® Resin 828
Diglycidylether of Bisphenol-A



Jeffamine® T-403 Polyetheramine



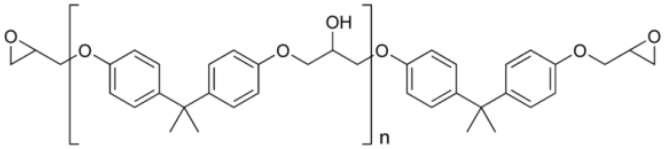
(x+y+z) = 5-6

3M D32 glass microballoons

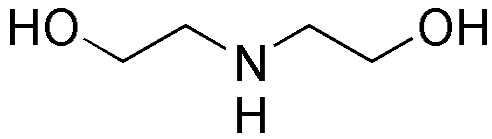
T_g ~ 90C
(when mixed stoichiometrically epoxy-amine)

828/DEA[2] and 828/GMB/DEA[3]

EPON® Resin 828
Diglycidylether of Bisphenol-A



Diethanolamine



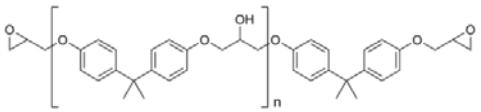
McCoy et al. *Polymer* **2016,** 105, 243-254.

T_g ~ 70C

[1]Mix ratio, cure schedule, and more can be found in SAND2013-8681
[2]Mix ratio, cure and typical properties can be found at: http://www.sandia.gov/polymer-properties/828_DEA.html
[3]Mix ratio, cure and typical properties can be found at: http://www.sandia.gov/polymer-properties/828_DEA_GMB.html

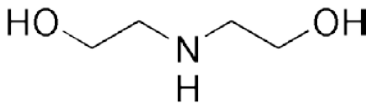
828/DEA[1]

EPON® Resin 828
Diglycidylether of Bisphenol-A



100 pbw

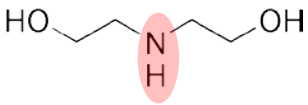
Diethanolamine



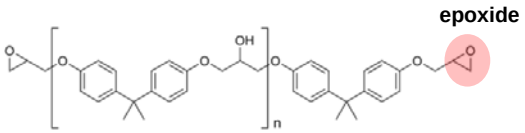
12 pbw

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

Adduct-Forming Reaction



secondary amine



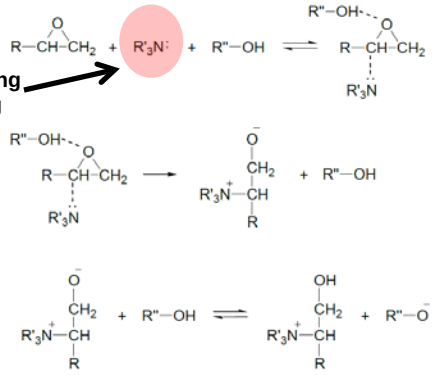
epoxide

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

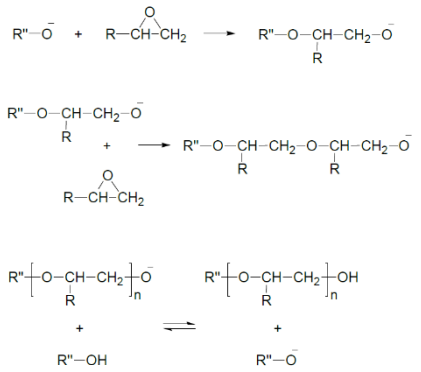
Proposed Gelation Reaction

Initiation

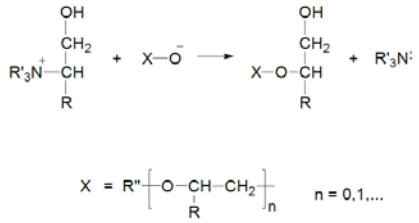
tertiary amine generated during adduct-forming reaction



Propagation



Termination



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

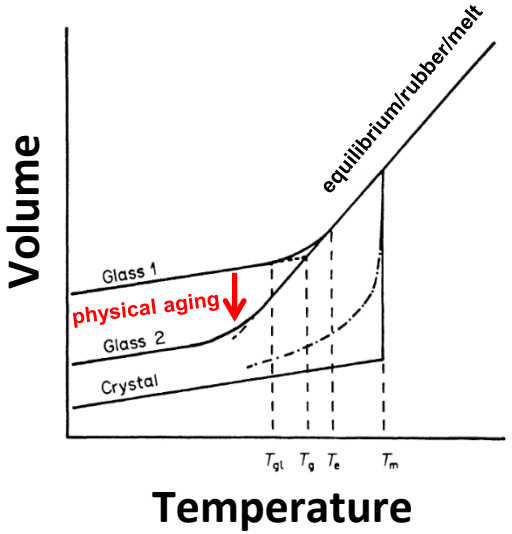
J.D. McCoy et al., *Polymer*, 2016, 105, 243

T_g ~ 70°C

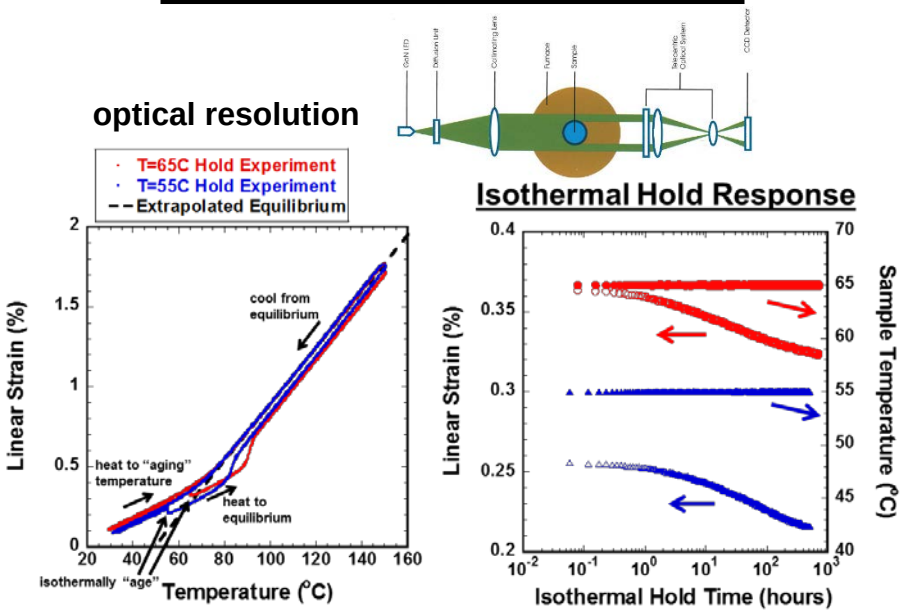
[when mixed 100:12 (pbw) 828:DEA and cured 24 hours at T=70°C]

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

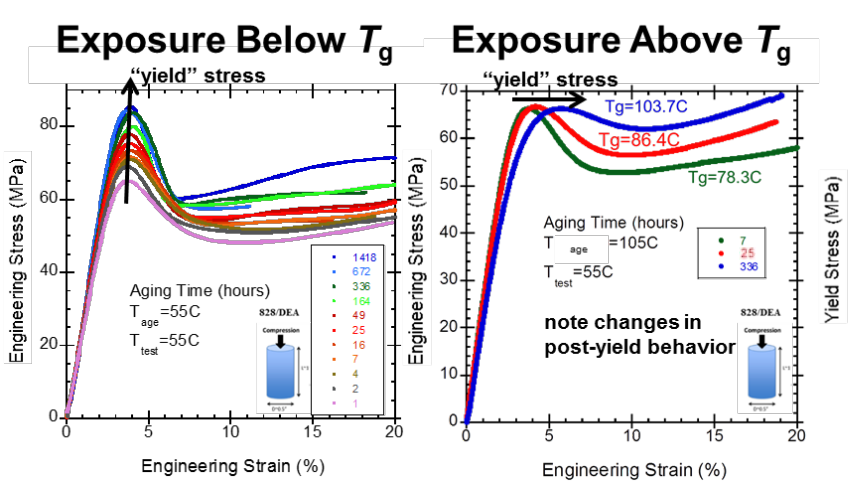
Polymer Glass Aging

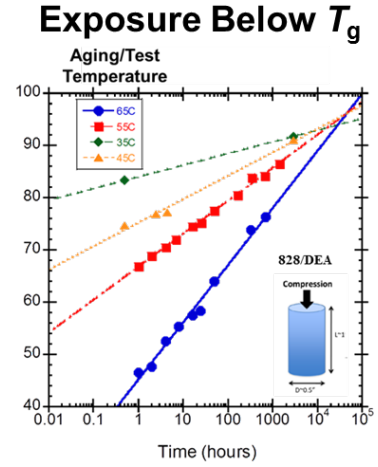


Material Volume Changes



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

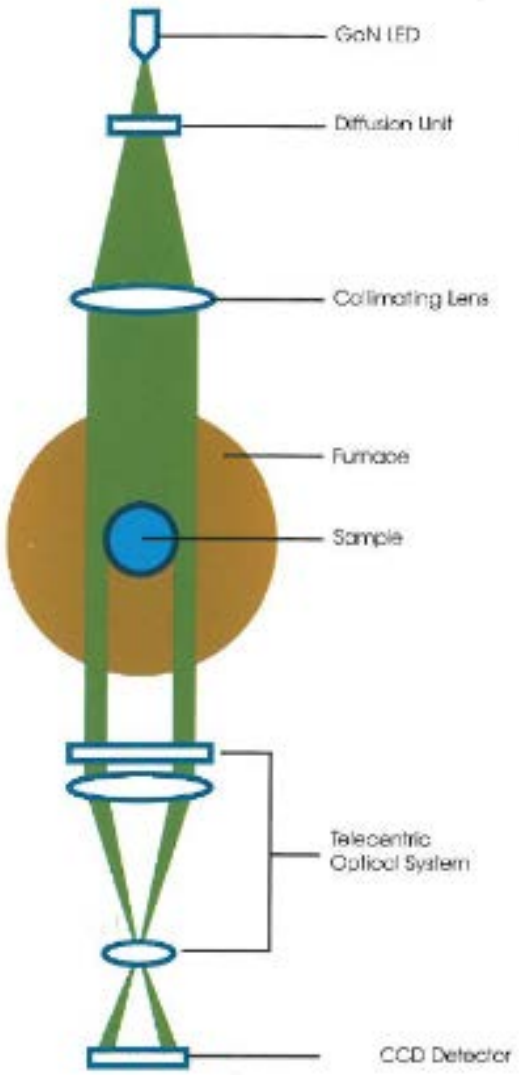
Clarkson, McCoy and Kropka, *Polymer*, 94 (2016) 19-30

Arechederra et al., APS 2016

Volume

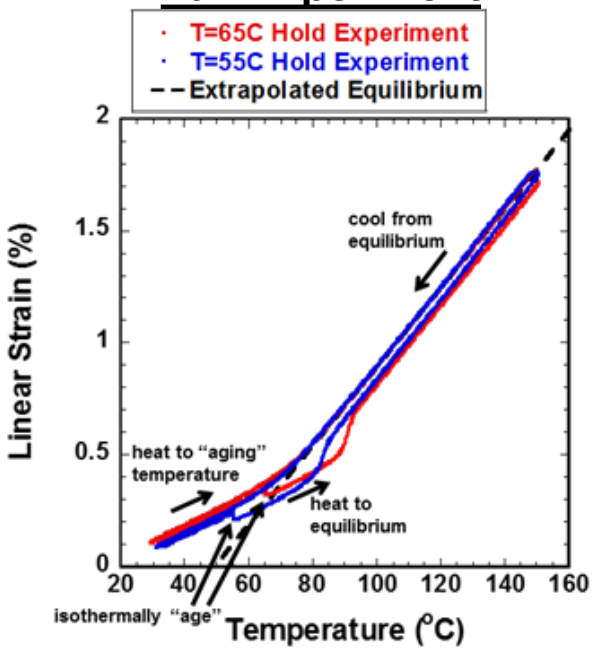
Measuring Volume Response Associated with Aging

Optical Resolution of Length*

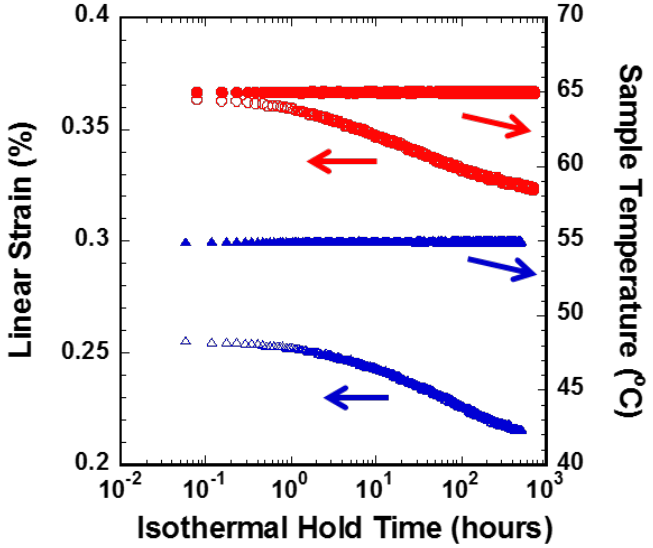


*for isotropic materials $\Delta V = 3\Delta L$

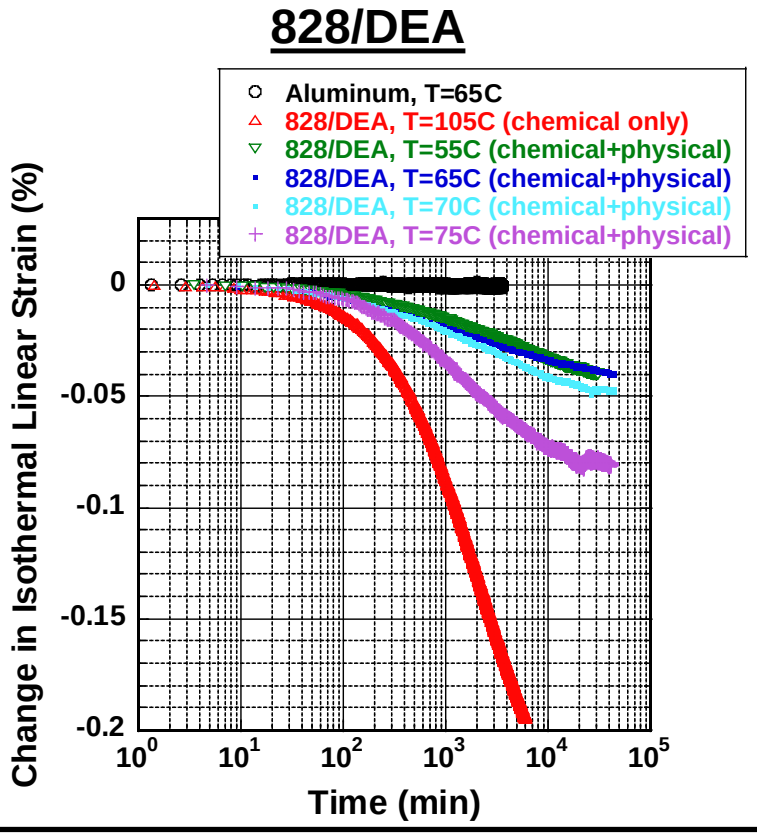
Full Experiment

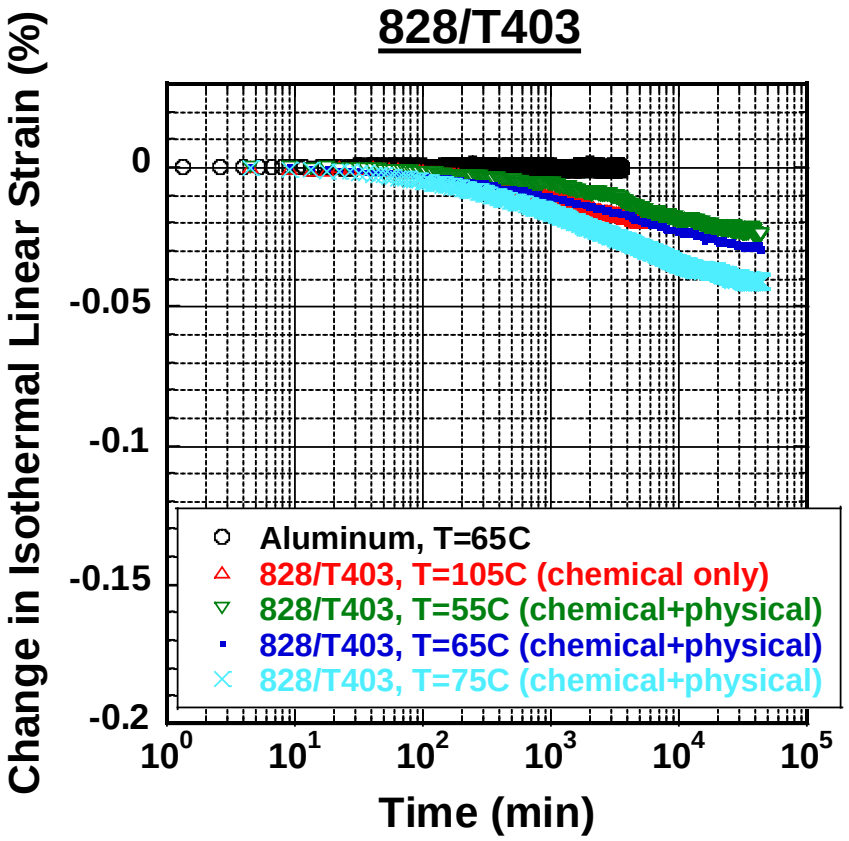


Isothermal Hold Response



Isothermal Volume Response for 2 Common Epoxy Thermosets

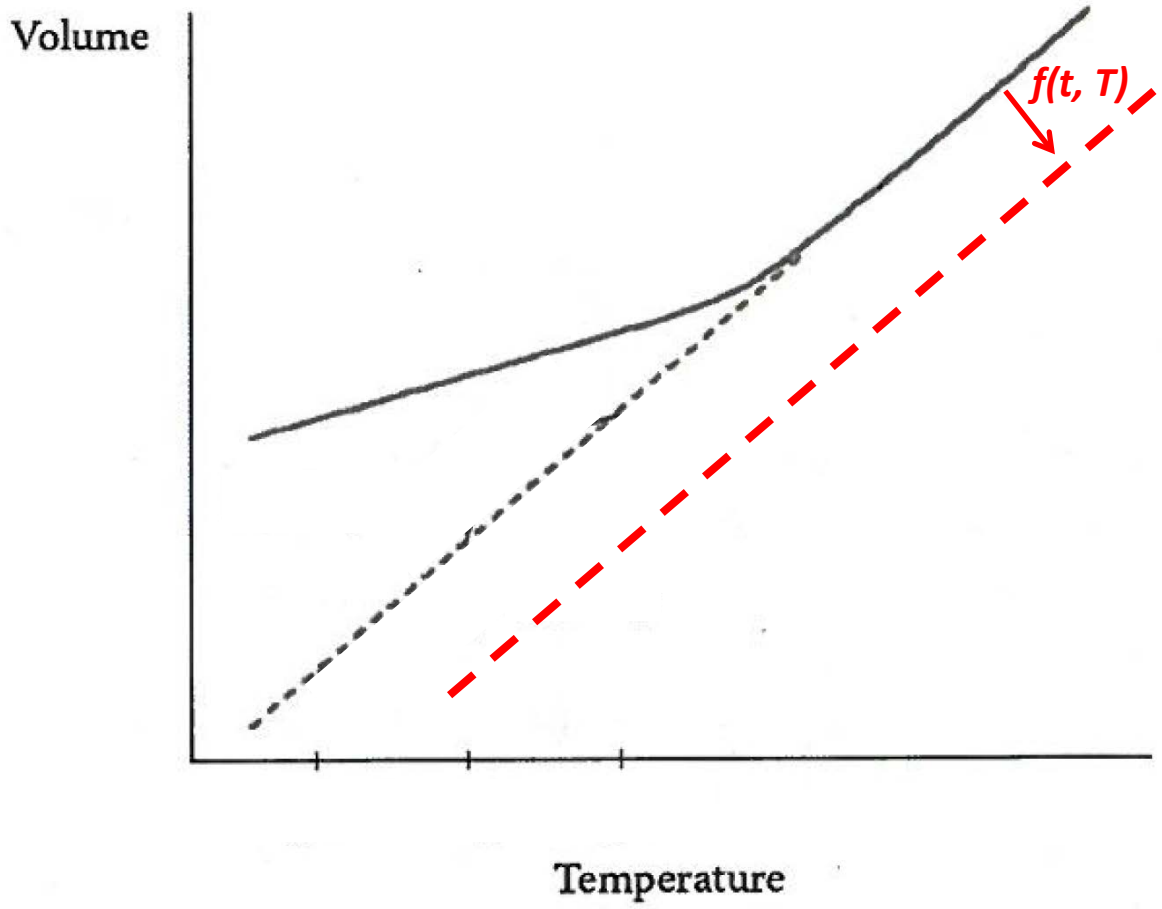




Note: Remaining reactive potential (excess epoxide groups in the case of 828/DEA) can play a significant role in total volume change

- 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

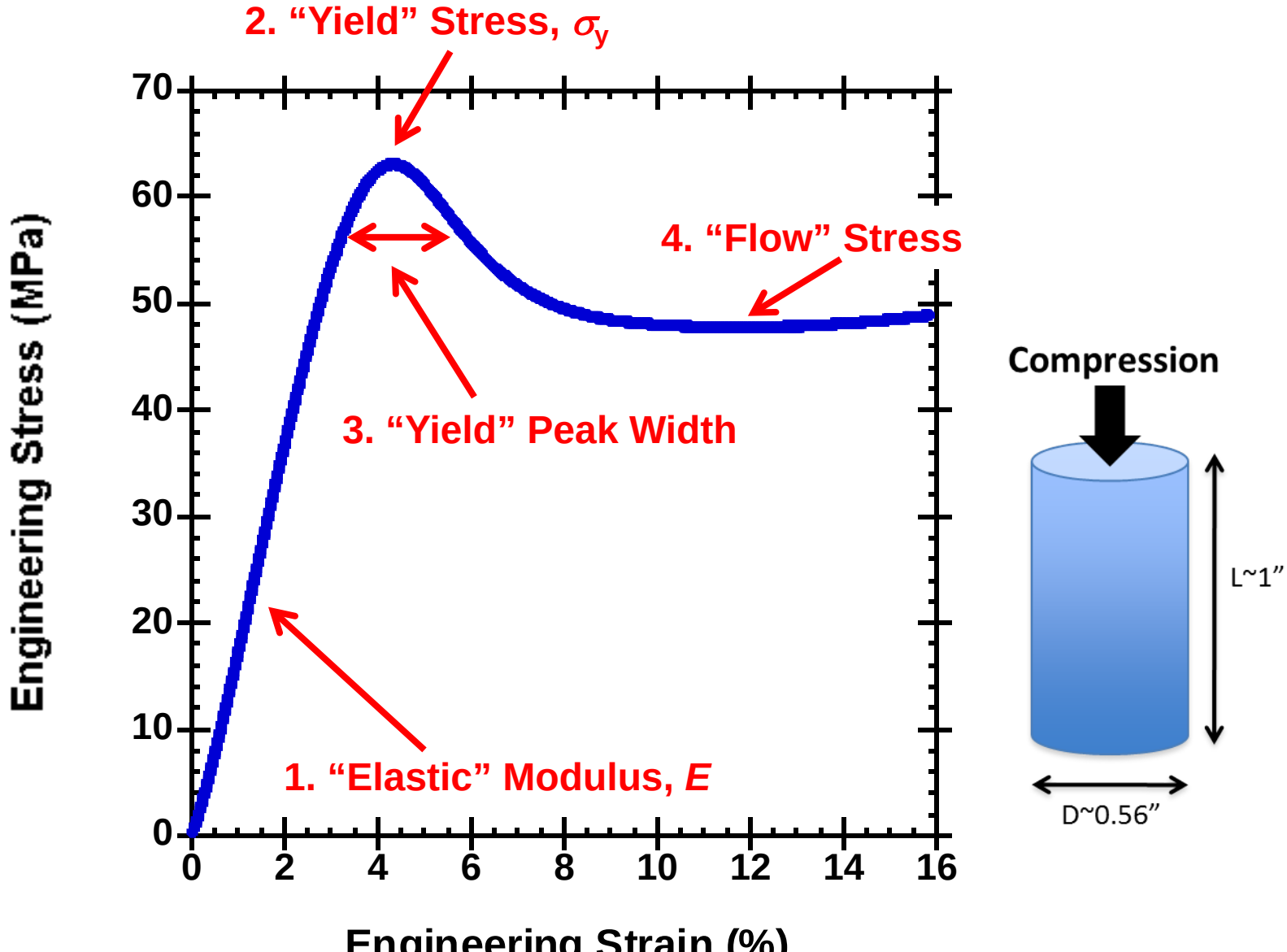
Challenges in Defining Equilibrium for 828/DEA



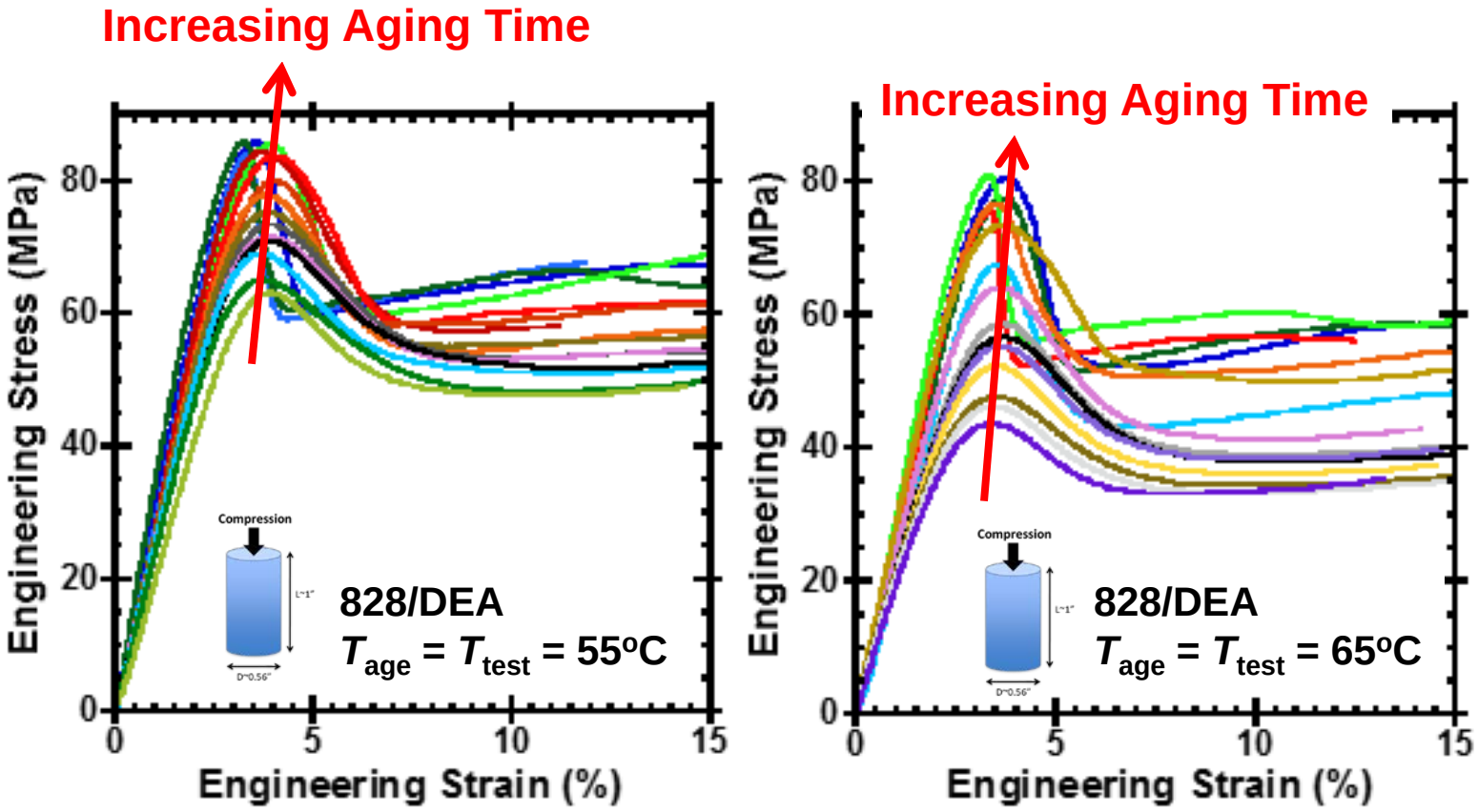
The rate of change of the equilibrium line (associated with continued epoxide cross-linking in 828/DEA) depends on the time and temperature history of the material and can only be determined for a particular history by re-equilibrating the material

Mechanical

Anatomy of Compressive Stress-Strain Response of Glassy Polymers



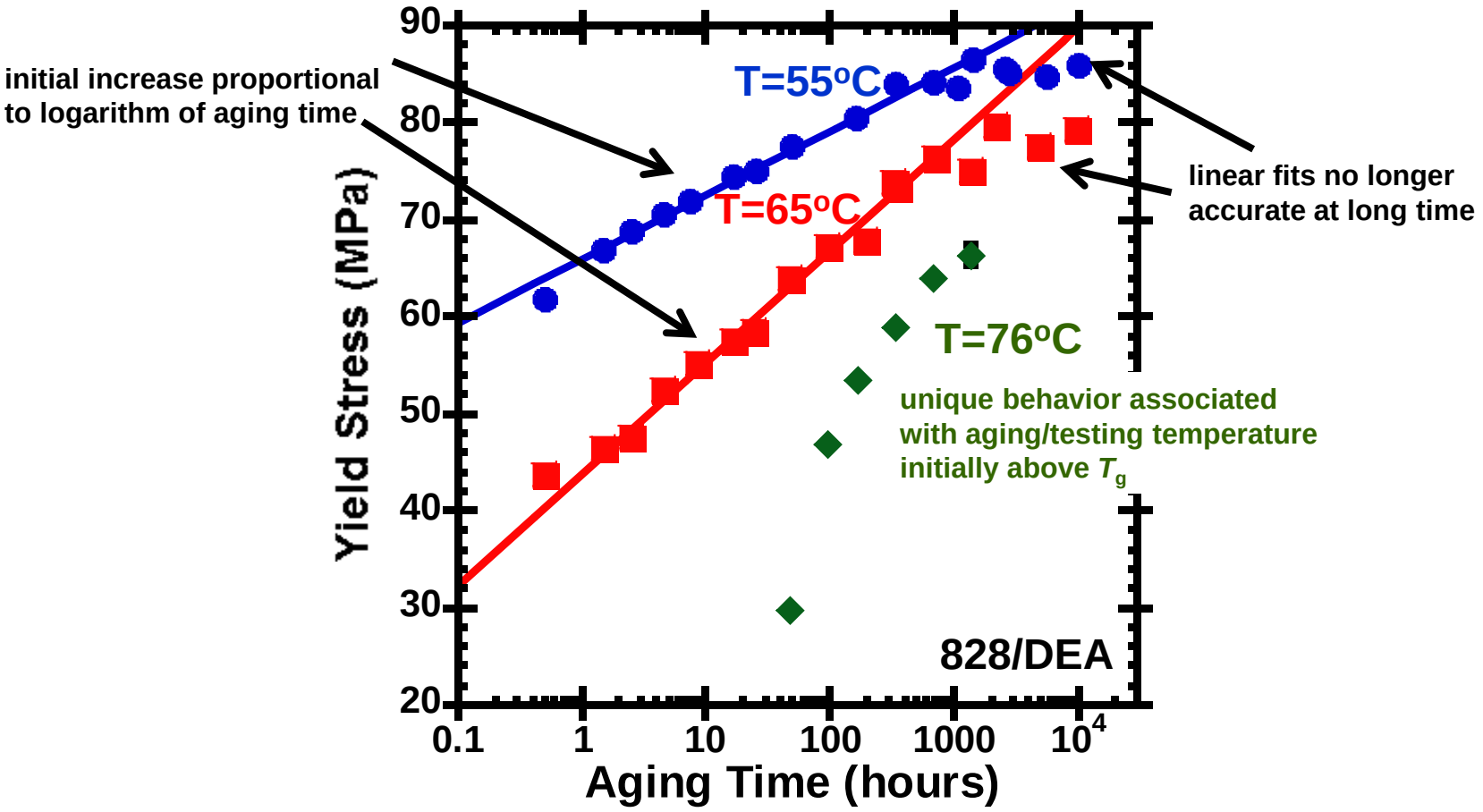
Changes in Compressive Stress-Strain Response Associated with Thermal Aging



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



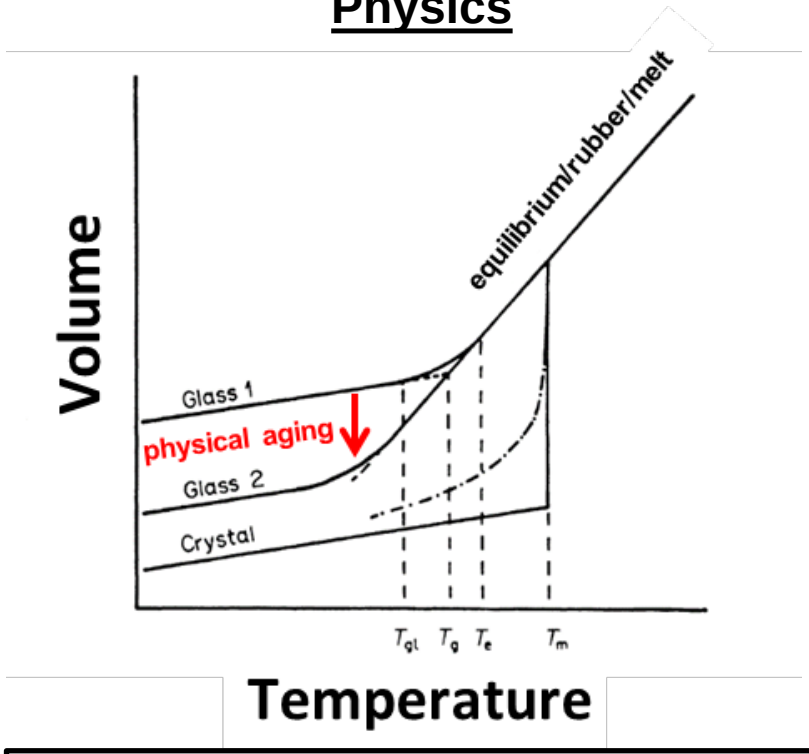
Focusing on T = 55°C and 65°C datasets for now:

- 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?

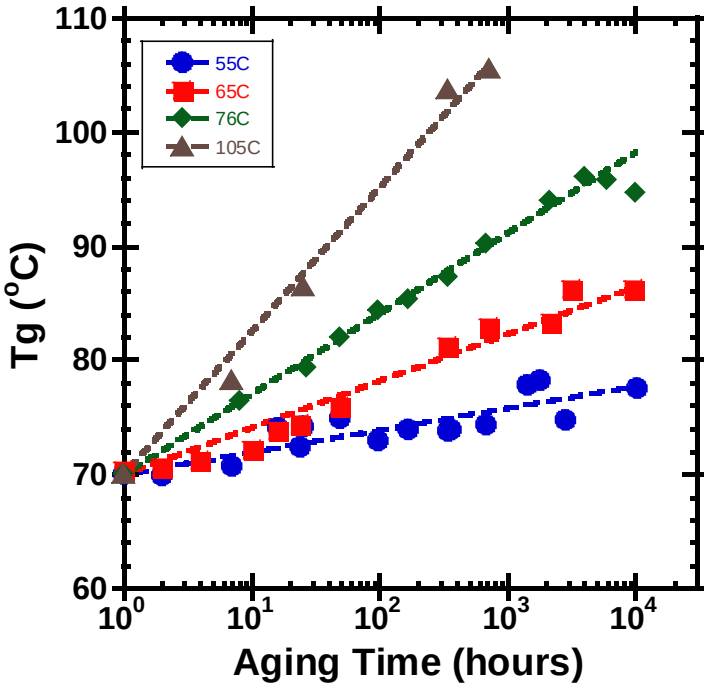
Mechanisms Driving Evolution of Yield Stress during Thermal Aging

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



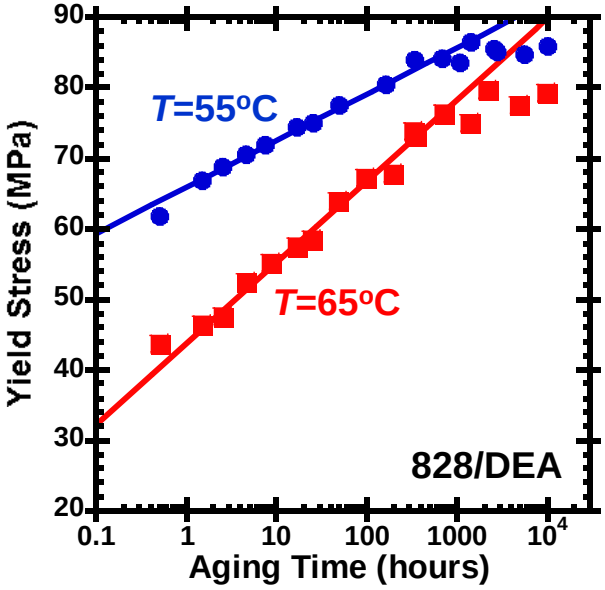
Continued chemical crosslinking increases the glass transition temperature of the material. This also slows molecular motions in the polymer chain (at a given temperature below T_g) and contributes to an increase in the observed yield stress in the compressive stress-strain response

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

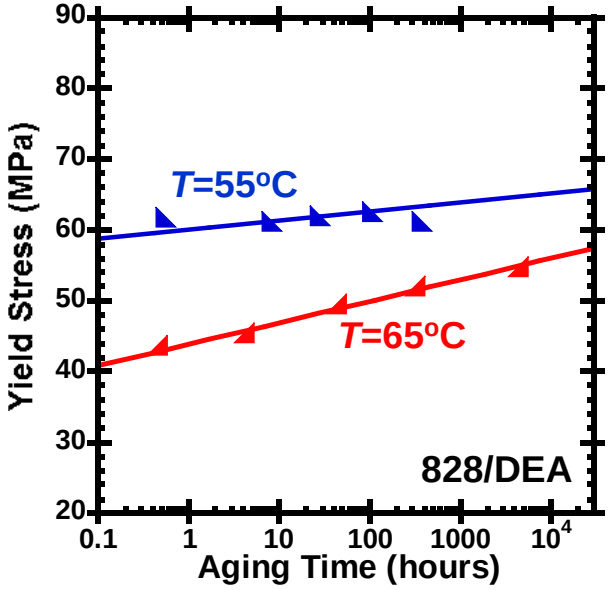
Anneal → Age → Test

Chemical + Physical (Measured)

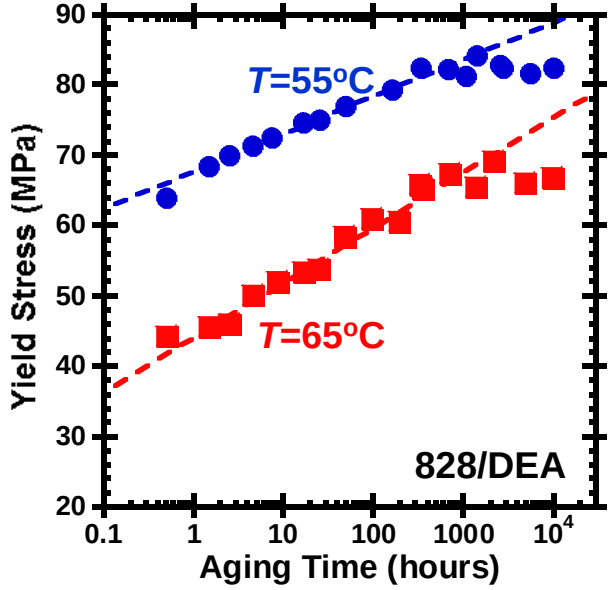


Anneal → Age → Anneal → Test

Chemical Only (Measured)

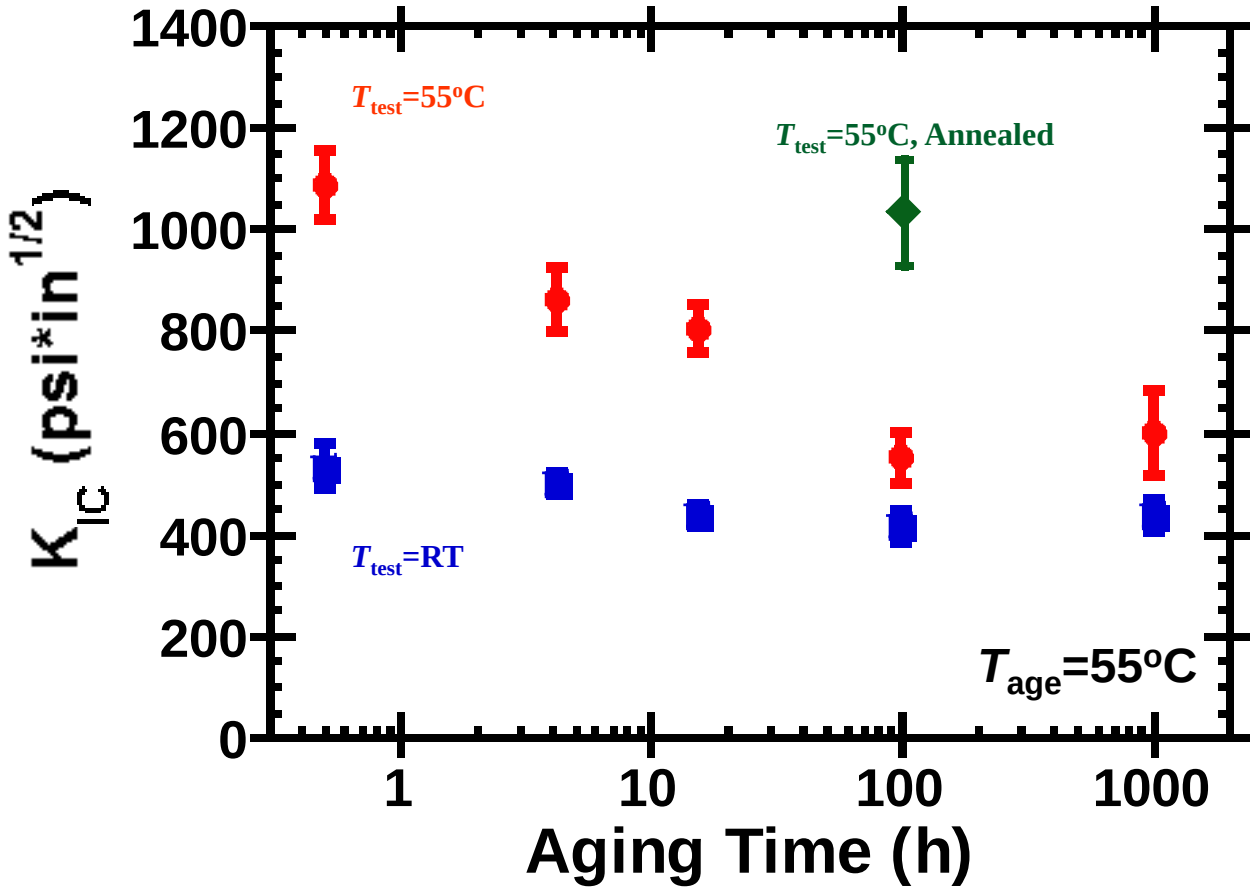


Physical Only (Calculated)



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.

Fracture Toughness Changes with Aging Too



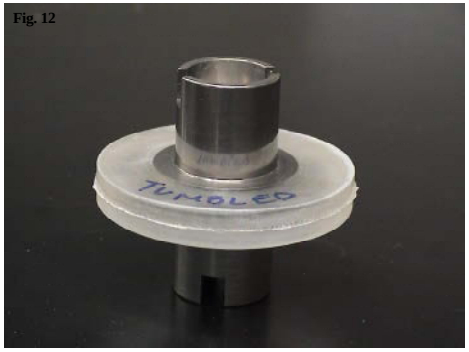
Fracture Toughness Changes Occur Over the Same Timescale and are Associated with Structural Relaxation

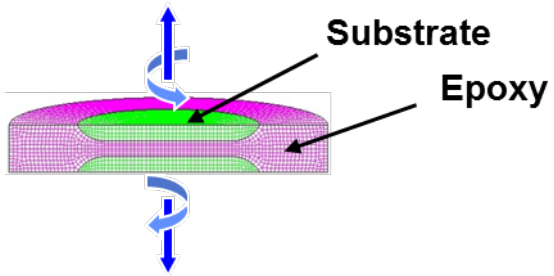
Summary

- **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^{o}C, T_g-20^{o}C)**
- **Resolved the apparent attainment of equilibrium, 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**

Impact of Aging in Application Relevant Geometries

Saucer Test Geometry

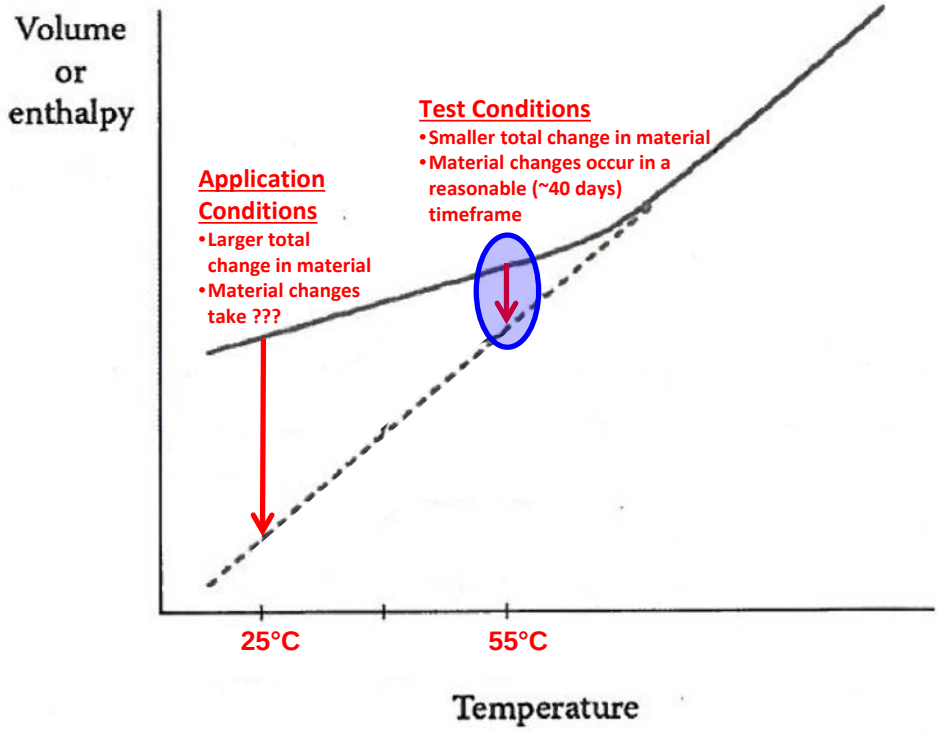




- Max stresses do not reside at an air interface (failure at "embedded interface")
- Max stresses are smooth functions, not "spiked"

Initial focus on tensile loading only (it may be the most sensitive to aging)

Aging Conditions



Results Coming Soon

Final Remarks

- We are actively examining structural recovery (volume, enthalpy) and physical aging (e.g., compressive stress-strain, fracture toughness) together in epoxy thermosets
  - Dimensional changes monitored at a high resolution
  - Significant changes in mechanical response (yield stress, fracture toughness) are observed to accompany structural relaxation
- Based on what is learned from materials testing, we are designing structural tests to examine the impact of materials aging on application designs
- More work is necessary to assess predictive capabilities of materials aging in order to build confidence in the tools to examine the impacts of application designs and environments