Exceptional service in the national interest

Sandia National Laboratories

Materials

DGEBA

+

DEA
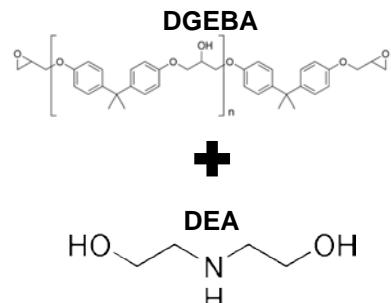
Chemical and Physical Aging

Additional Chemical Crosslinking

Physical or Structural Rearrangements
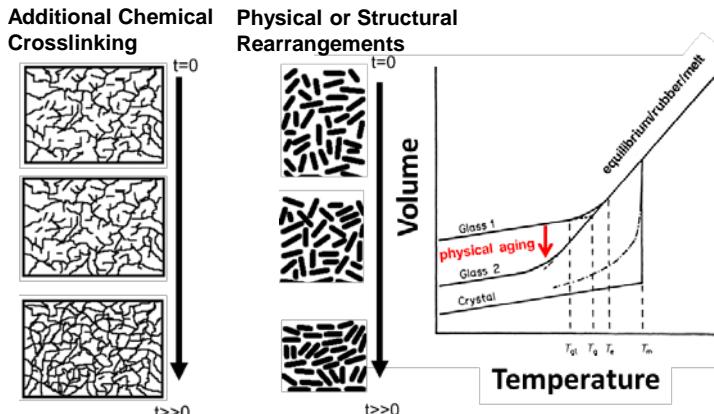
Thermal-Mechanical Response Changes
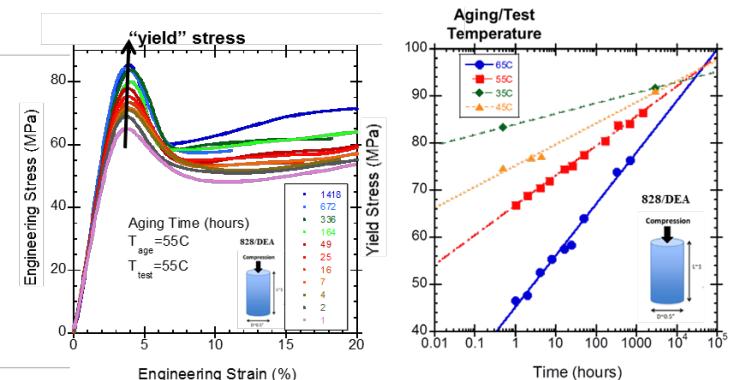
Understanding and Predicting the Evolution of Glassy Thermoset Polymers During Aging

Jamie M. Kropka, Sandia National Laboratories, Albuquerque, NM

Materials Engineering Graduate Seminar, New Mexico Tech, February 15, 2018

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Lara Draelos (NM Tech)

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Modelers

ENGINEERING SCIENCES CENTER

Bob Chambers (retired)

Kevin Long

Brenton Elisberg

Craig Tenney

Kurtis Ford

Matthew Neidigk (AFRL)

Main Contributors to Today's Topics

NNSA National Nuclear Security Adm

Sandia National Laboratories

How are Polymers Used at SNL?

- Encapsulants for:
  - structural integrity
    - impact
    - vibration
  - high voltage isolation

- Adhesives or Underfills for:
  - bonding materials
  - surface mount components

- Printed Circuit Boards:
  - orthotropic composites

thermosets

- Foams for:
  - energy dissipation
  - light constraints

- Plastic Parts for:
  - injection molded pieces

thermoplastics

- Gaskets and O-rings for:
  - sealing cavities

- Cushions, Pads, Coatings for:
  - stress relief
  - damping

elastomers
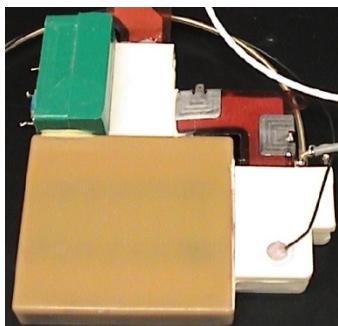
- Optimal use of polymers is not always obvious
- Poor choice of polymers can cause premature failures
- Modeling is important
- Must understand materials to represent them in models

Overpotting →   ← Coating
Electronic Part
Lead
Underfill
Printed Wiring Board (PWB)
Solder   Solder Pad
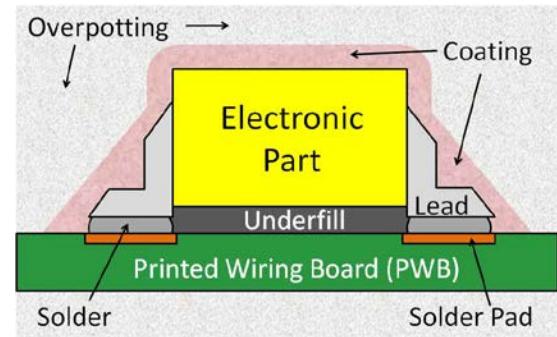
Polymers Are Complex Materials

They respond differently than metals and ceramics
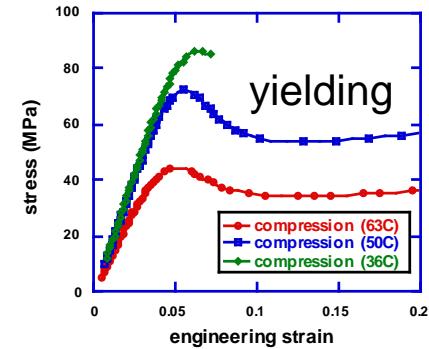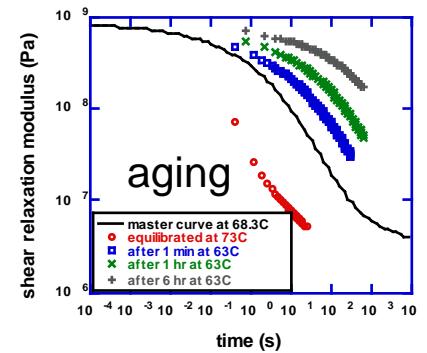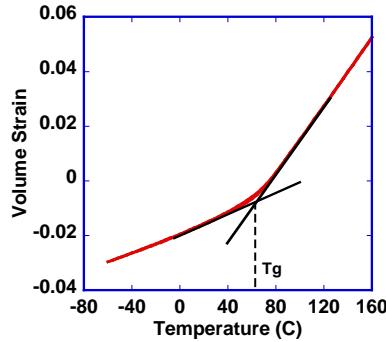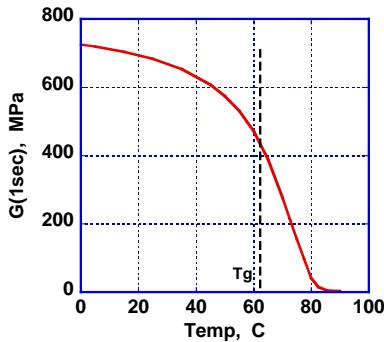
exhibit a glass transition:
- shear modulus can change by 2-3 orders of magnitude
- CTE can change by factor of 3

time dependent and nonlinear:
- relaxation rates vary with temperature and load

Behavior depends on thermal and strain histories

Performance predictions must be able to capture the full range of behavior for general thermo-mechanical loadings from manufacturing to failure.
- must be extensively validated
- computationally tractable

What We Do

1. Capability Development (relevant to Encapsulation and Bonding)
   a. Understanding of Polymer Material Structure-Processing-Properties Relationships
   b. Understanding of Stress in Polymers
2. Material Properties Analysis
3. Problem Solving

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

research	development	analysis
physics	tools	predictions

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

manufacturing
cure chemistry

How do we make it?
(Cure Chemistry)

thermal cycling

Current talk

mechanical loading / aging

How does it perform?
(Constitutive Eqns)

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

high rate

Adhesive

failure

What can go wrong?
(Failure Metrics)

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

Current Focus Areas

Capability Development: Evolution of Constitutive Representation of Polymers

Linear Elasticity → **Linear Viscoelasticity** → **Nonlinear Viscoelasticity**

Linear Elasticity

E, ν, α
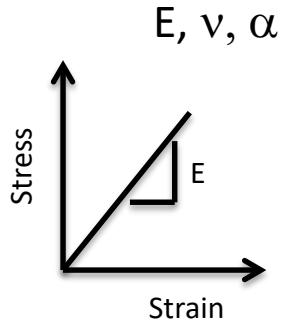
+ temperature dependencies

Linear Viscoelasticity

Glass Transition
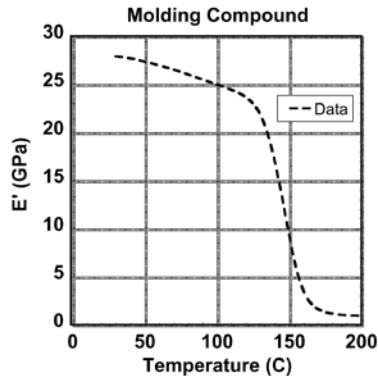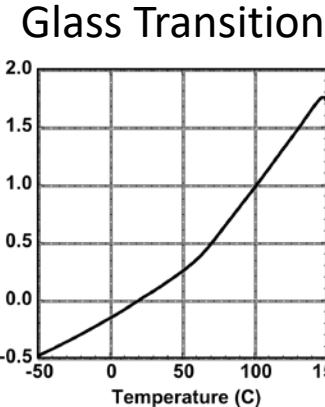
Stress Relaxation
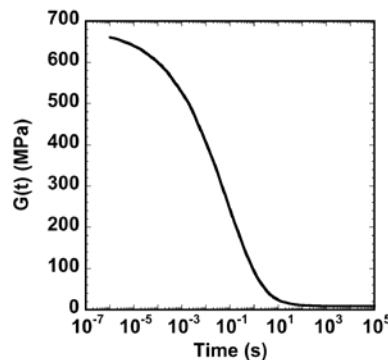
Nonlinear Viscoelasticity

Yielding
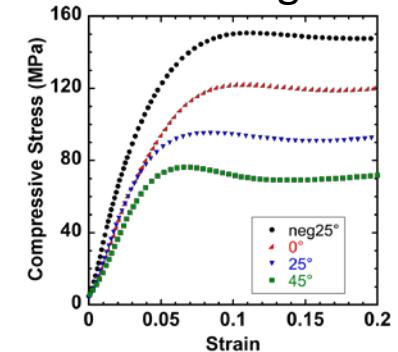
Creep
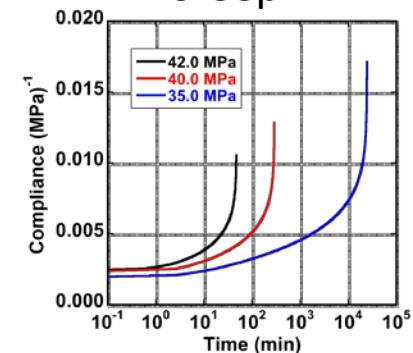
+ manufacturing
+ aging
+ failure metrics

Hierarchy of Polymer Material Characterization for Modeling Nonlinear Viscoelasticity (NLVE)

| Other Options not Possible	Material Evaluations	Critical Encapsulants/Adhesives
Bare Bones Approach	**Quick and Dirty Approach**	**The Whole Shebang**
Measure: 1. calorimetric Tg 2. filler volume fraction	**Measure:** 1. filler volume fraction 2. thermal strain versus temperature 3. elastic shear modulus versus temperature	**Measure:** 1. filler volume fraction 2. thermal strain versus temperature 3. elastic shear modulus versus temperature 4. compressive stress-stain through yield at multiple temperatures 5. shear mastercurve 6. glassy volume relaxation 7. creep at multiple temperatures and stress levels 8. Material evolution during cure
Model Parameterization: Estimate NLVE response based on universal properties and rule of mixtures approach	**Model Parameterization:** Estimate NLVE response based on universal properties and rule of mixtures approach. Compare predictions to data. Ability to tweak relaxation spectra and prefactors to better match predictions to data.	**Model Parameterization:** Populate material specific SPEC NLVE model
Limitations/Potential Errors: • Must be rigid fillers (e.g., alumina, silica, mica…) • Breadth of relaxation spectra • Nonlinear material clock	**Limitations/Potential Errors:** Lack definition of clock for nonlinear relaxations	**Advantage:** Model can now predict yielding AND (physical) aging with more confidence

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
  - Simple structural response tests validate predictive tools

Glass Formation and Structural Recovery/Relaxation
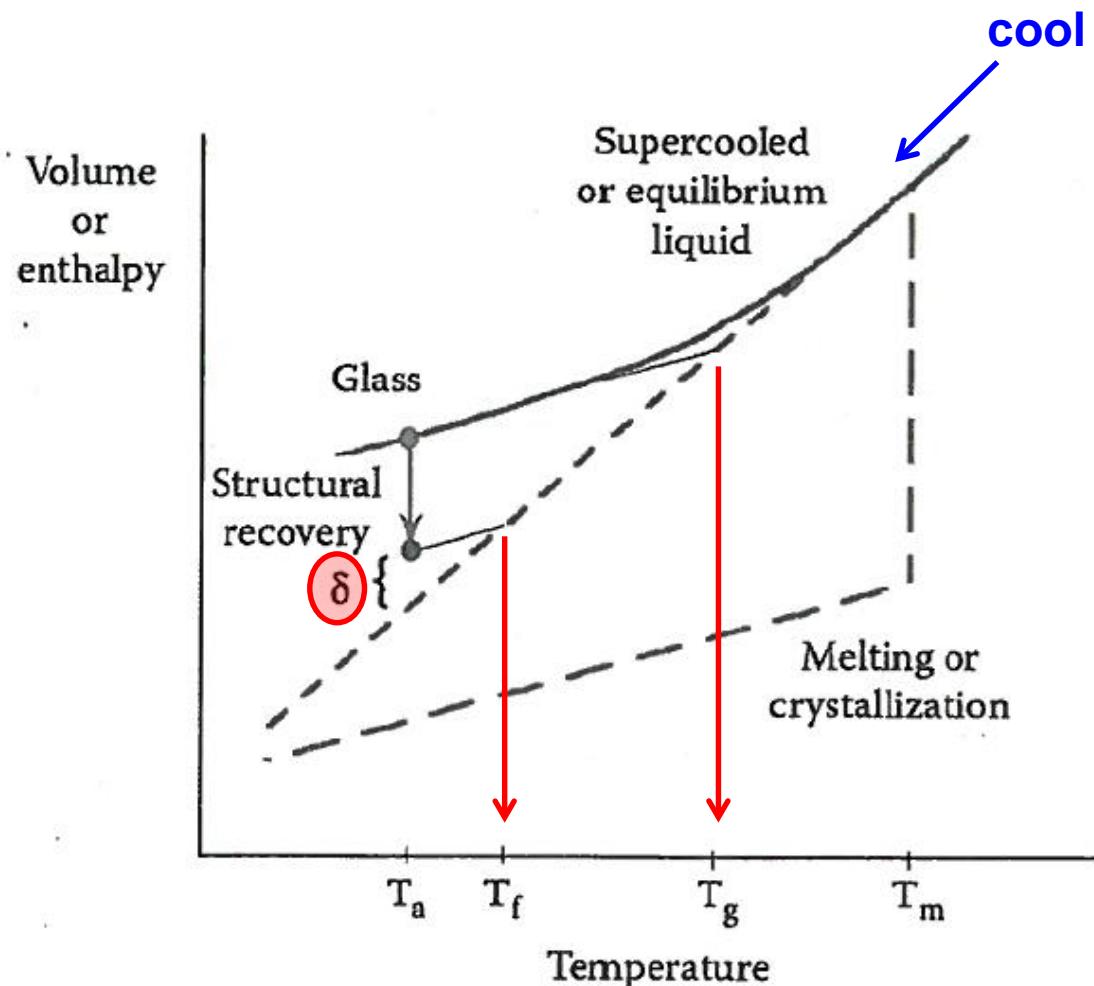
Signatures of Structural Recovery/Relaxation

Intrinsic Isotherms

$$v_o - v_\infty = v_\infty \Delta\alpha \, (T_{fo} - T_a)$$
$$H_o - H_\infty = \Delta C_p \, (T_{fo} - T_a)$$
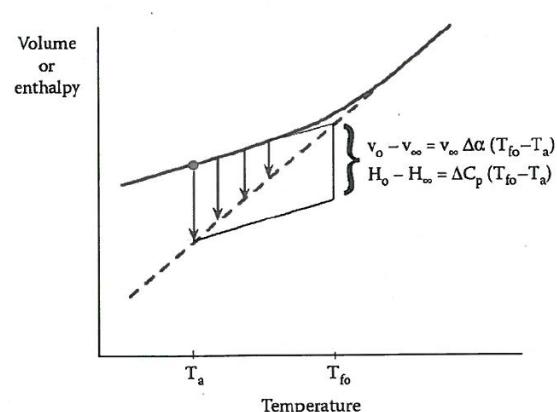
Asymmetry of Approach
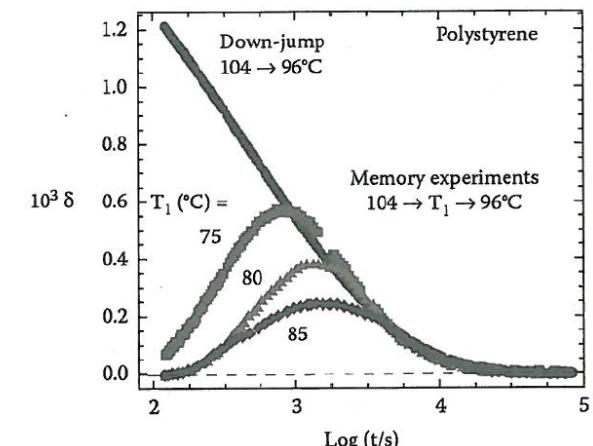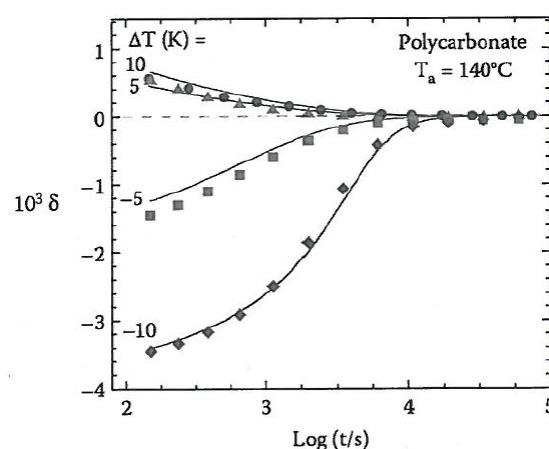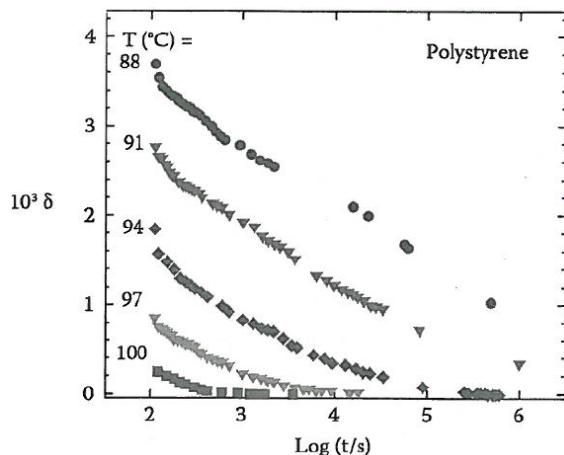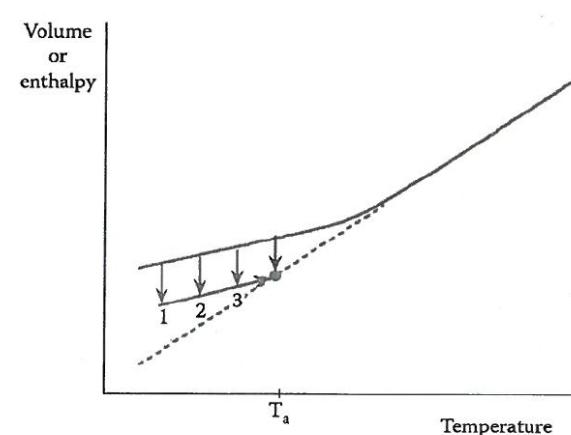
Relaxation Depends on Structure

Memory Effect


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"

initial shear band **unaged** **neck propagation**

initial shear band **aged** **neck propagation**

A 24 h at 340K
B 24 h at 333K
C 24 h at 325K
D Unaged sample

(Sample A, strain rate 7 x 10⁻⁵s⁻¹)
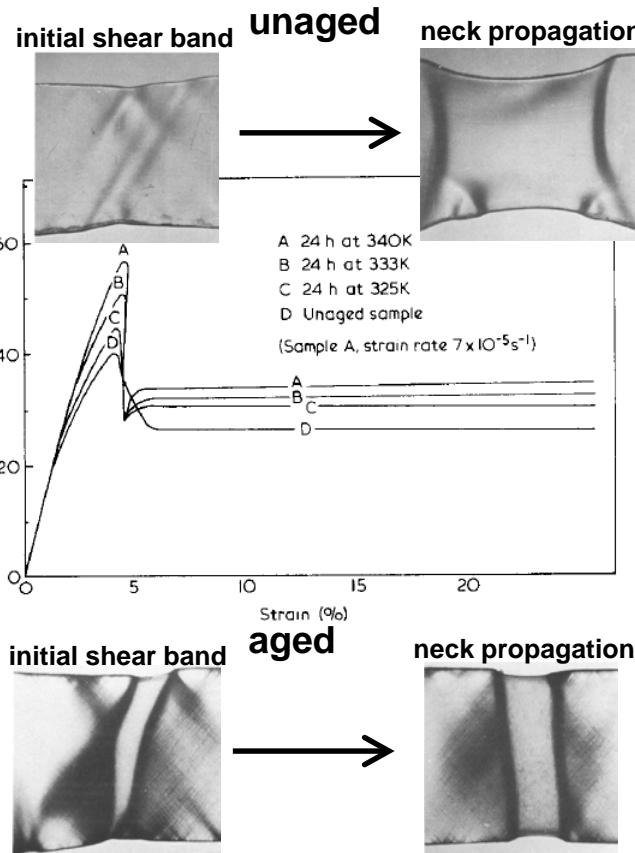
Izod impact studies of PC during isothermal "aging"
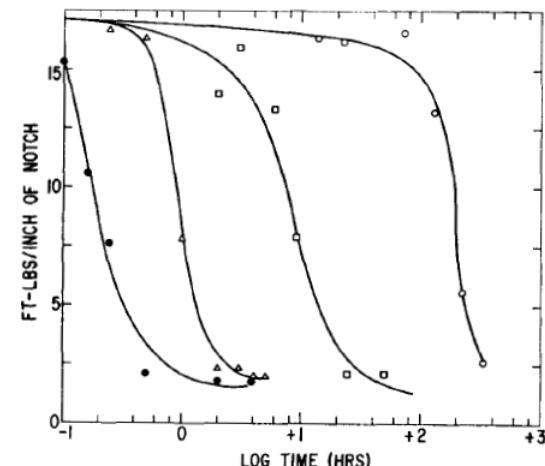
Fig. 3. Effect of annealing temperature on Izod impact data. ○) 100; □) 115; △) 125; ●) 130; [ηi] = 0.58.

D.G. Legrand, *J. Appl. Pol. Sci.*, 1969, <u>13</u> 2129

R.N. Haward et al., *Polymer*, 1983, <u>24</u> 1245

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

Approach to Understanding/Predicting Epoxy Aging

- Identify material aging mechanisms and their impact on material physical behavior (**current efforts and results**)
- Develop/augment science-based modeling tools to predict material aging behavior with high fidelity
- Demonstrate impact of aging on stress in application relevant geometries (**scoping tests**)
- Validate predictive tools in application relevant geometries (**scoping tests**)

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
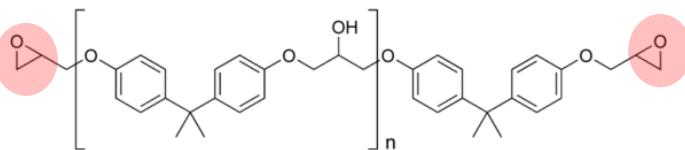
Jeffamine® T-403 Polyetheramine

$(x+y+z) = 5-6$
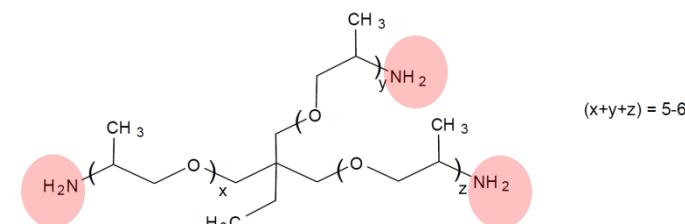
828/DEA[2] and 828/GMB/DEA[3]

EPON® Resin 828
Diglycidylether of Bisphenol-A
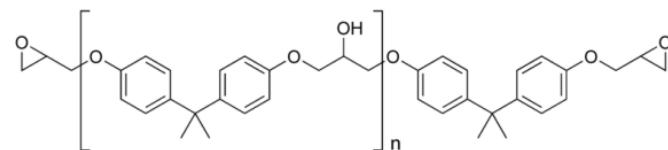
Diethanolamine
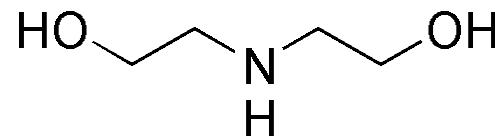
McCoy et al. *Polymer* **2016,** 105, 243-254.

3M D32 glass microballoons

$T_g \sim 90C$
(when mixed stoichiometrically epoxy-amine)

$T_g \sim 70C$

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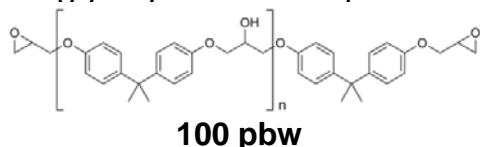
Polymerization at T = 70°C (the cure process before aging)

Adduct-Forming Reaction

secondary amine
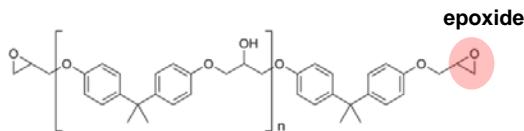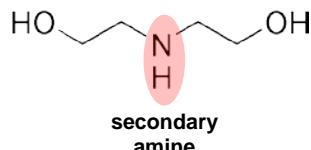
epoxide

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

Proposed Gelation Reaction

Initiation

Propagation

tertiary amine generated during adduct-forming reaction
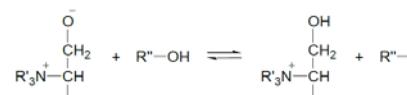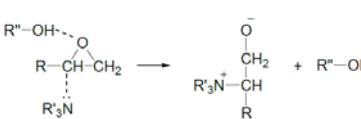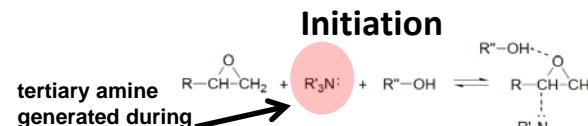
Termination
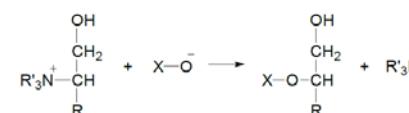
$X = R''{-}[O{-}CH{-}CH_2{-}]_n$ n = 0,1,...

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

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

$T_g \sim 70°C$

[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

Volume vs Temperature: equilibrium/rubber/melt, Glass 1, physical aging, Glass 2, Crystal. T_{gl}, T_g, T_e, T_m.

Material Volume Changes
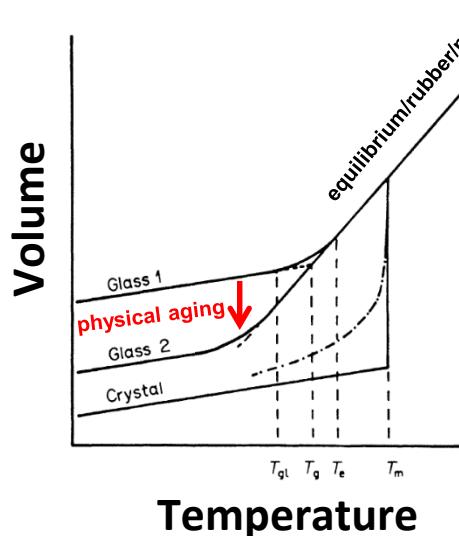
optical resolution

- T=65C Hold Experiment
- T=55C Hold Experiment
- Extrapolated Equilibrium

Linear Strain (%) vs Temperature (°C): cool from equilibrium, heat to "aging" temperature, heat to equilibrium, isothermally "age"

Isothermal Hold Response

Linear Strain (%) / Sample Temperature (°C) vs Isothermal Hold Time (hours)
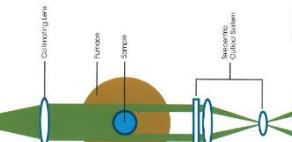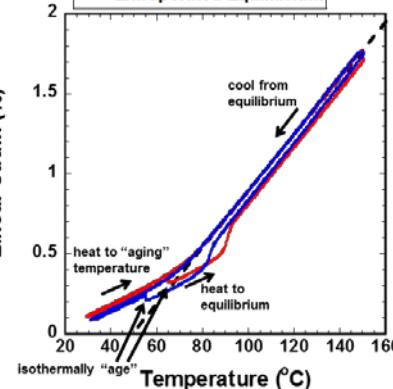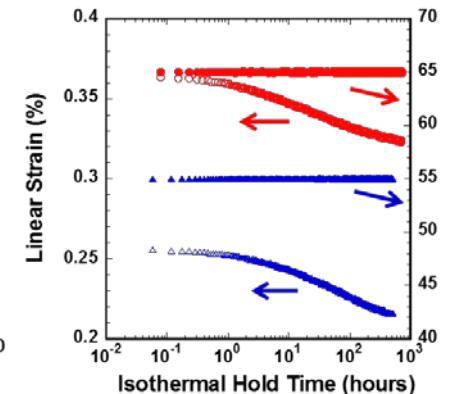
Material Mechanical Response Changes

Exposure Below T_g

"yield" stress. Engineering Stress (MPa) vs Engineering Strain (%).
Aging Time (hours), T_{age}=55C, T_{test}=55C, 828/DEA Compression
1418, 672, 336, 164, 49, 25, 16, 7, 4, 2, 1

Exposure Above T_g

"yield" stress. Engineering Stress (MPa) vs Engineering Strain (%).
Tg=103.7C, Tg=86.4C, Tg=78.3C
Aging Time (hours), T_{age}=105C, T_{test}=55C
7, 25, 336
note changes in post-yield behavior 828/DEA Compression

Exposure Below T_g

Aging/Test Temperature. Yield Stress (MPa) vs Time (hours).
65C, 55C, 35C, -45C. 828/DEA Compression

**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

Volume

Measuring Volume Response Associated with Aging

Optical Resolution of Length*

GaN LED

Diffusion Unit

Collimating Lens

Furnace

Sample

Telecentric Optical System

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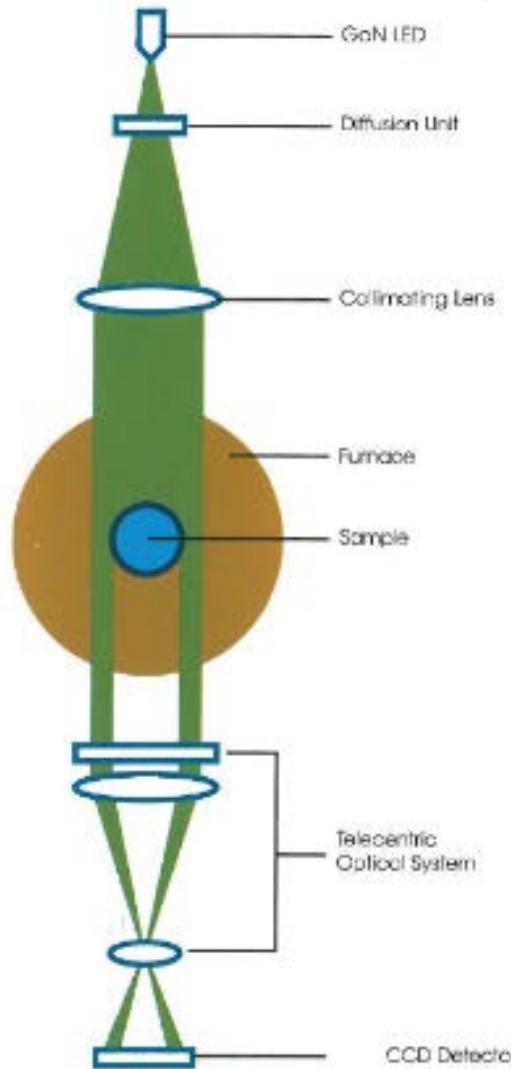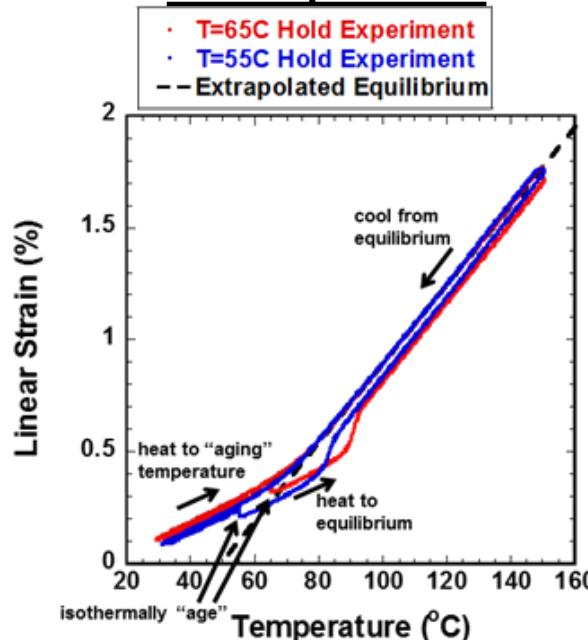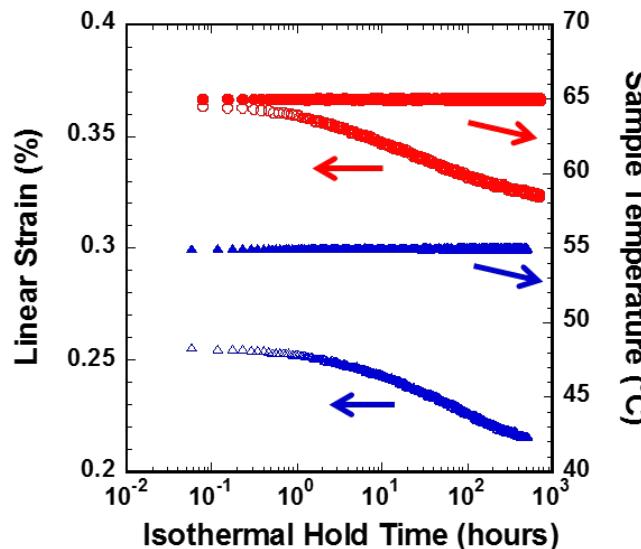
*for isotropic materials $\Delta V = 3\Delta L$

Full Experiment

- T=65C Hold Experiment
- T=55C Hold Experiment
- Extrapolated Equilibrium

Linear Strain (%) vs Temperature (°C)

cool from equilibrium

heat to "aging" temperature

heat to equilibrium

isothermally "age"

Isothermal Hold Response

Linear Strain (%) / Sample Temperature (°C) vs Isothermal Hold Time (hours)

Isothermal Volume Response for 2 Common Epoxy Thermosets

828/DEA

- ○ Aluminum, T=65C
- △ 828/DEA, T=105C (chemical only)
- ▽ 828/DEA, T=55C (chemical+physical)
- ▪ 828/DEA, T=65C (chemical+physical)
- ▪ 828/DEA, T=70C (chemical+physical)
- + 828/DEA, T=75C (chemical+physical)

828/T403

- ○ Aluminum, T=65C
- △ 828/T403, T=105C (chemical only)
- ▽ 828/T403, T=55C (chemical+physical)
- ▪ 828/T403, T=65C (chemical+physical)
- ✕ 828/T403, T=75C (chemical+physical)
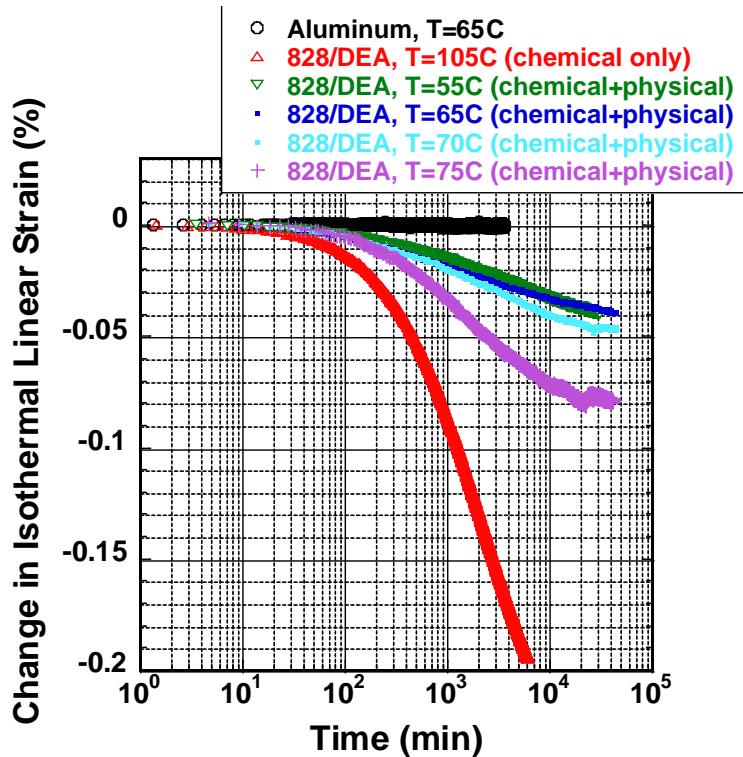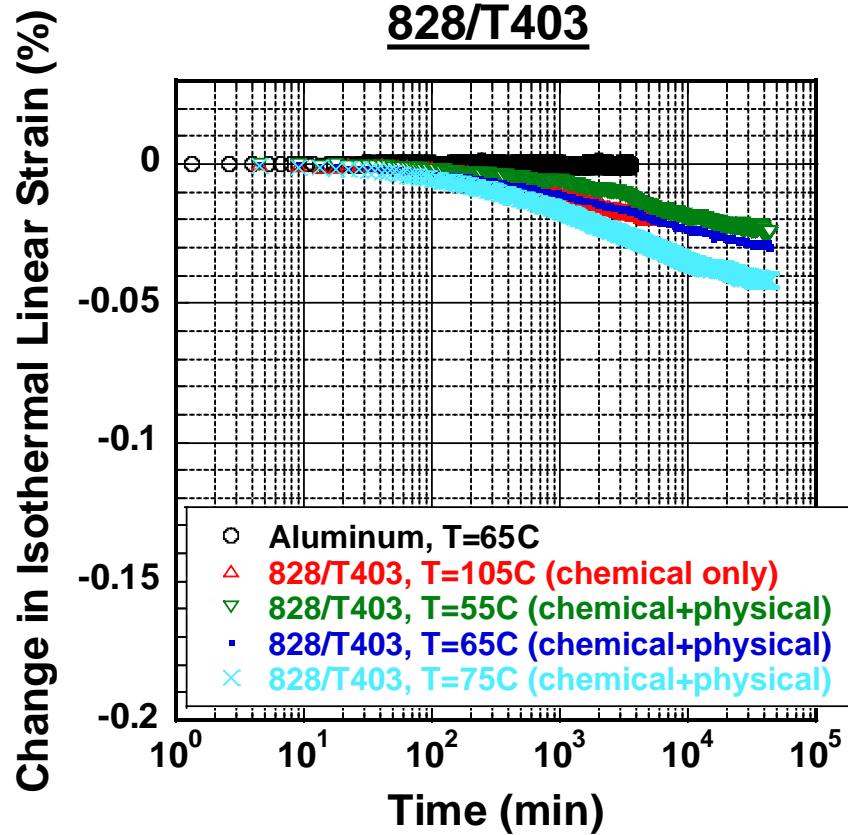
Note: Remaining reactive potential (excess epoxide groups in the case of 828/DEA) can play a significant role in total volume change

- 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
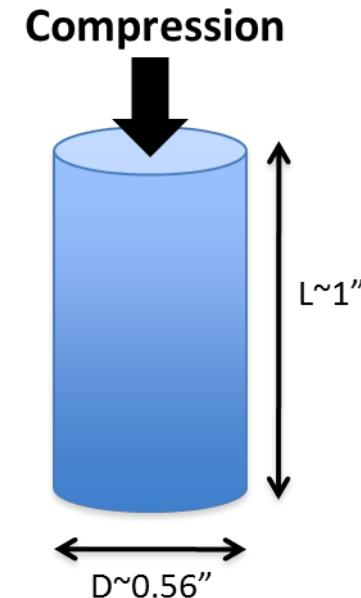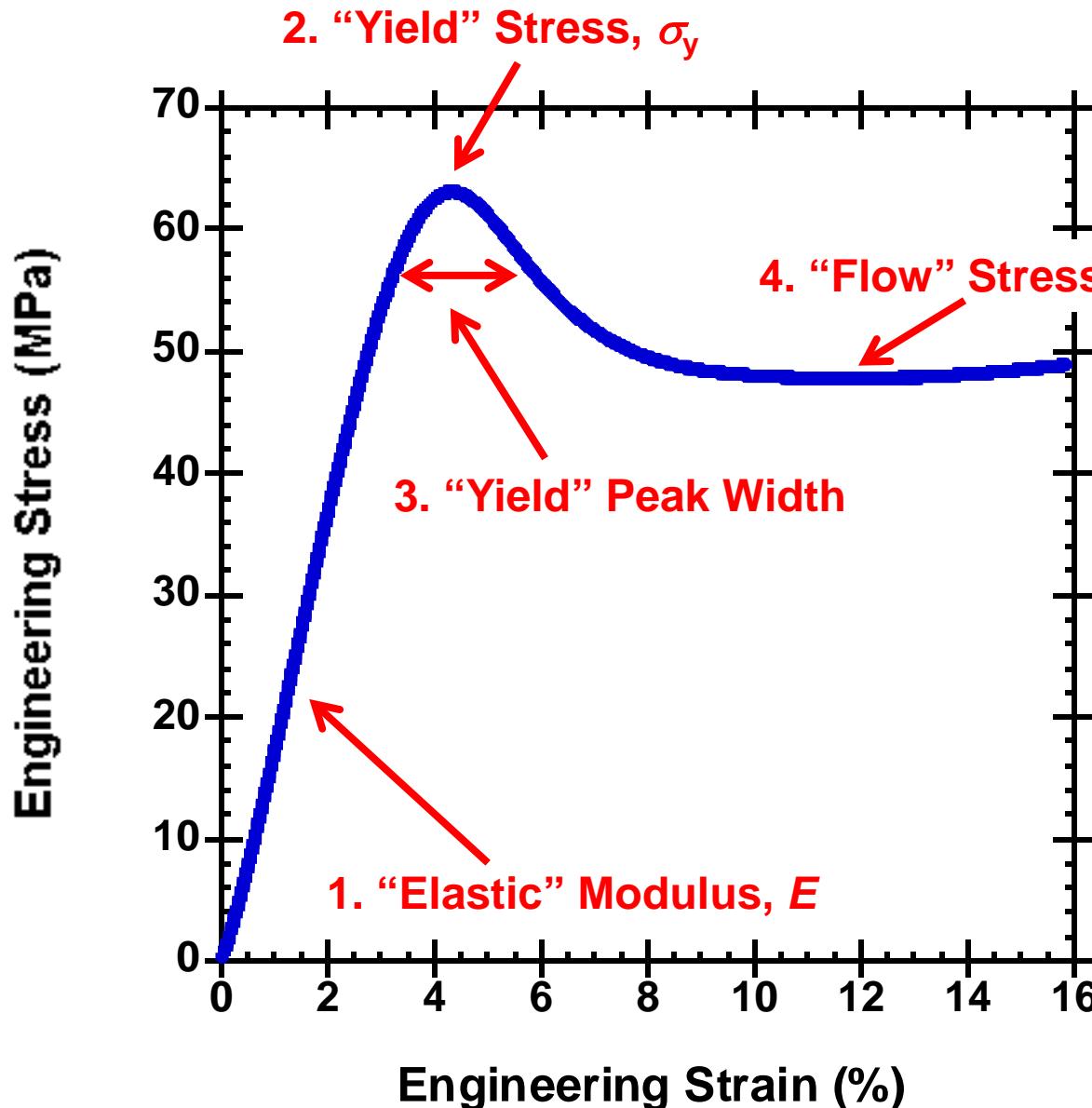
Changes in Compressive Stress-Strain Response Associated with Thermal Aging
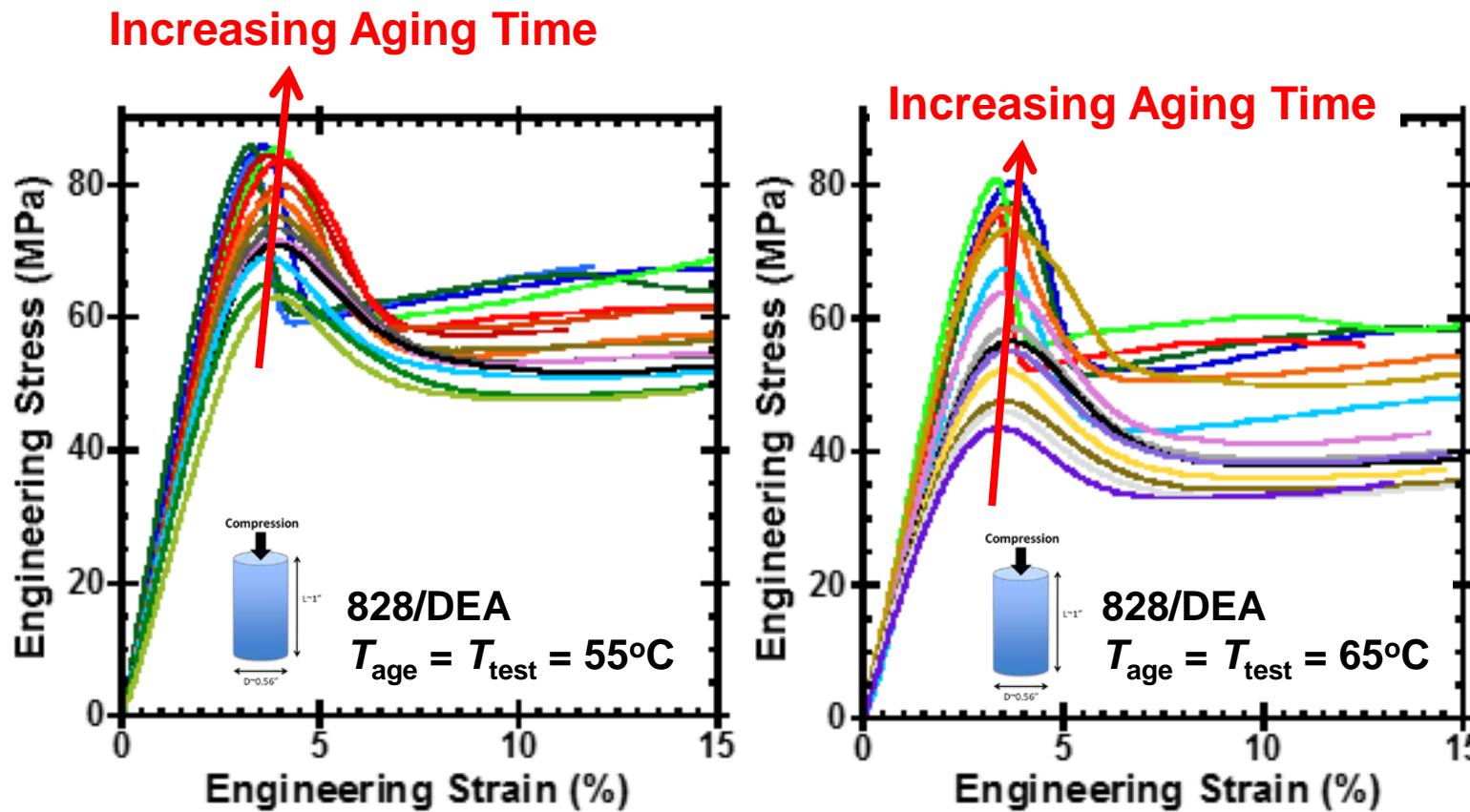
4 Distinguishable Changes in Compressive Stress-Strain Response Include:
- Increase in "elastic" compressive modulus
- **Increase in "yield" stress**
- Narrowing of "yield" peak
- Increase in "flow" stress

Evolution of Yield Stress during Thermal Aging

initial increase proportional to logarithm of aging time

T=55°C

Yield Stress (MPa)

T=65°C

linear fits no longer accurate at long time

T=76°C

unique behavior associated with aging/testing temperature initially above T_g

828/DEA

Aging Time (hours)
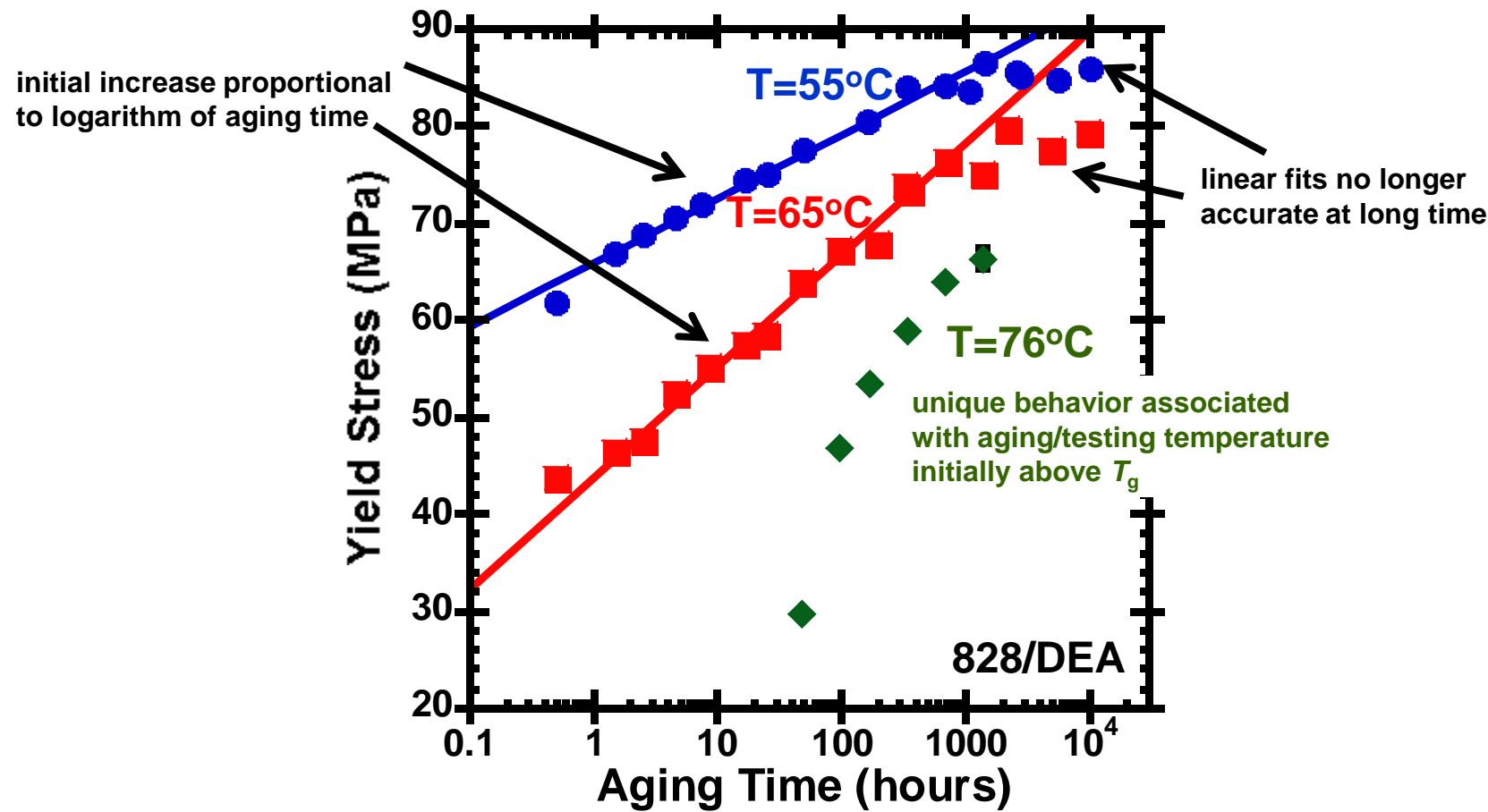
Focusing on *T* = 55°C and 65°C datasets for now:
- **Changes in yield stress are substantial—as high as 82%**
- **The evolution of yield stress with time changes (or possibly stops) after ~30 days**

What is the mechanism(s) driving this change?

Mechanisms Driving Evolution of Yield Stress during Thermal Aging

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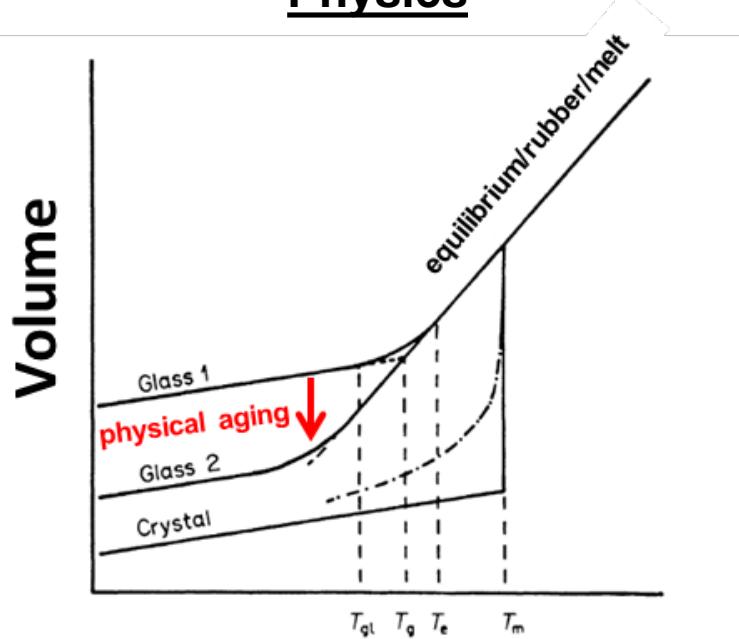
Volume relaxation (densification) of the material slows molecular motions in the polymer chain and this contributes to an increase in the observed yield stress in the compressive stress-strain response

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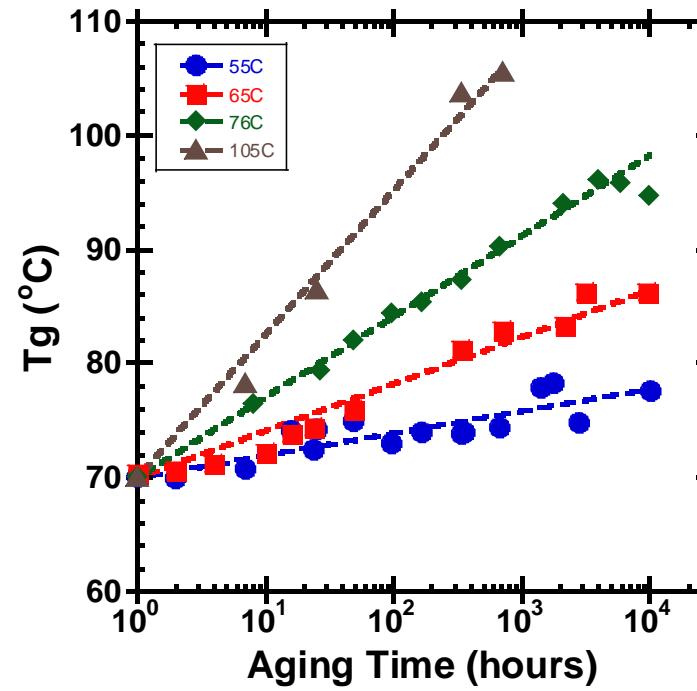
Continued chemical crosslinking increases the glass transition temperature of the material. This also slows molecular motions in the polymer chain (at a given temperature below T_g) and contributes to an increase in the observed yield stress in the compressive stress-strain response

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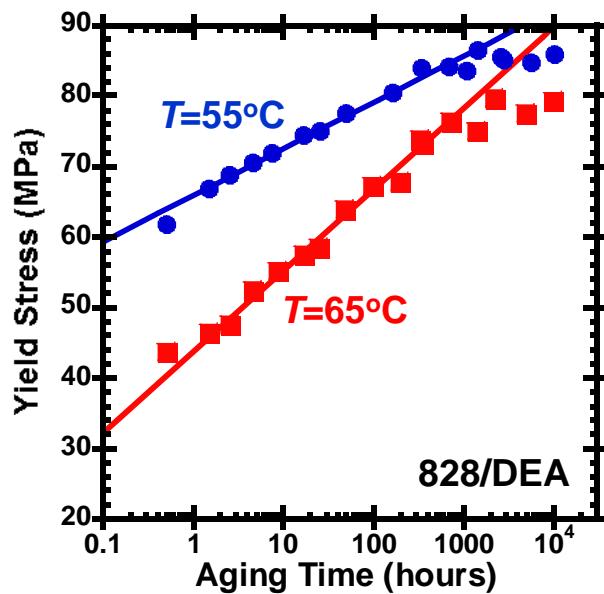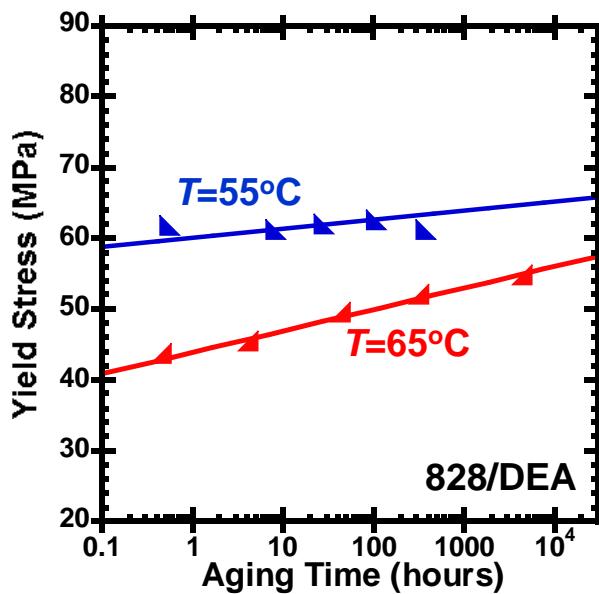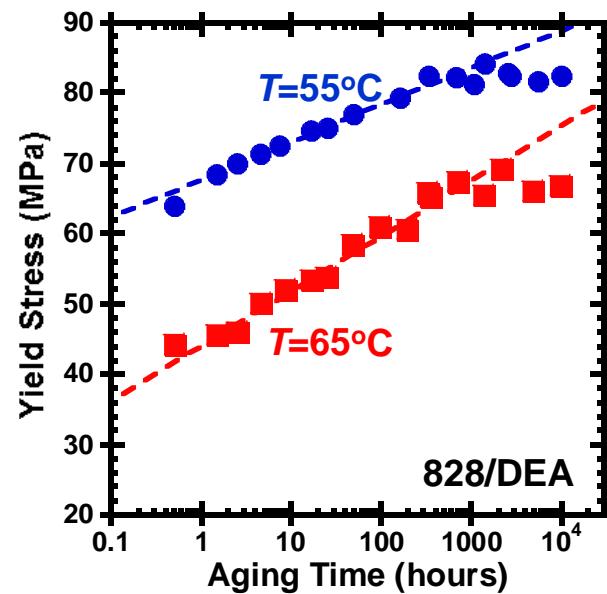
By thermally annealing the samples above the glass transition temperature (after aging), the physical history of the sample is erased and the chemical-only contributions to the evolution of the yield stress are resolved. Physical-only contributions are calculated by subtracting the chemical-only contributions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

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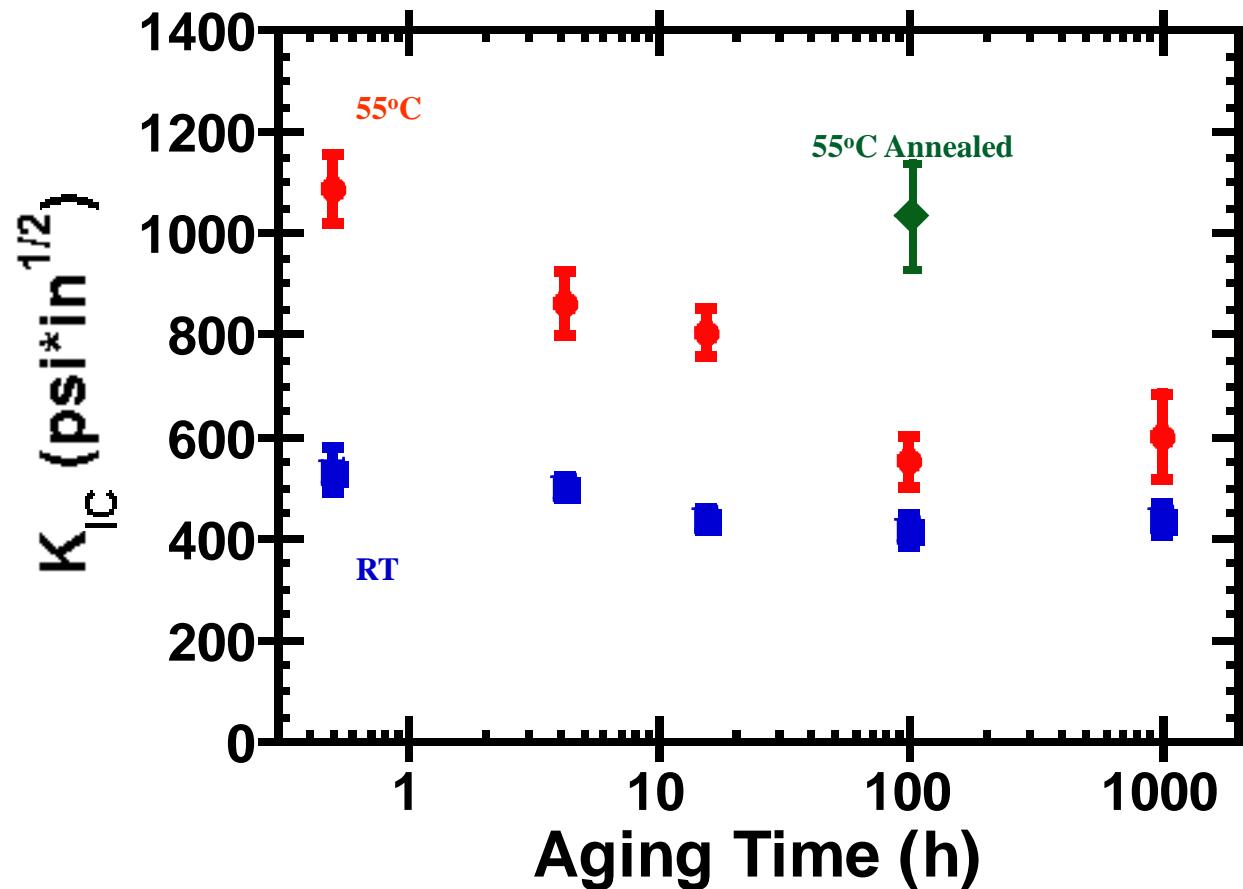
Fracture Toughness Changes Occur Over the Same Timescale and are Associated with Structural Relaxation

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°C, T_g-20°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

Adhesion Failure Tests

Napkin Ring

Saucer Design

test geometries to measure initiation of adhesive failure

3-D Finite Element Models
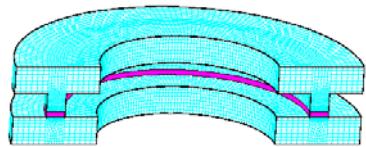
- **Shear loading only (torsion)**

- **air interface is ill-defined**
- **induce initiation at an embedded surface**
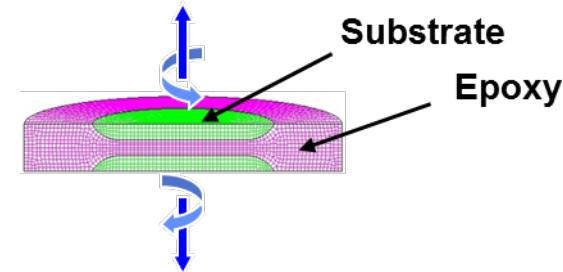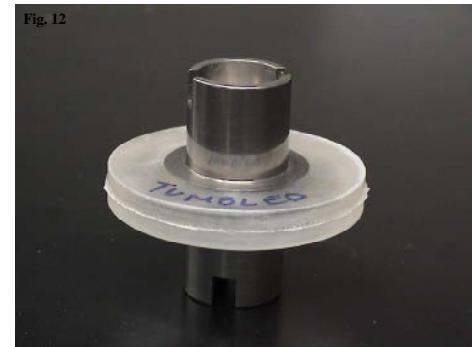
- **Shear**
- **Tension/Compression**
- **Combined**

Why "Saucer" Adhesion Test Geometry

1. Max stresses do not reside at an air interface (failure at "embedded interface")

Tensile Load

maximum normal traction located at center of adherend

normalized distance

Torsion Load

maximum shear traction located at initiation of adherend curvature

normalized distance
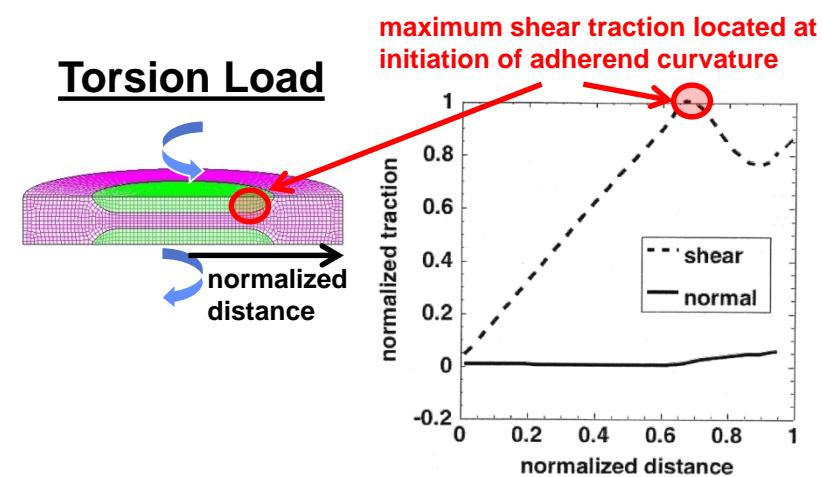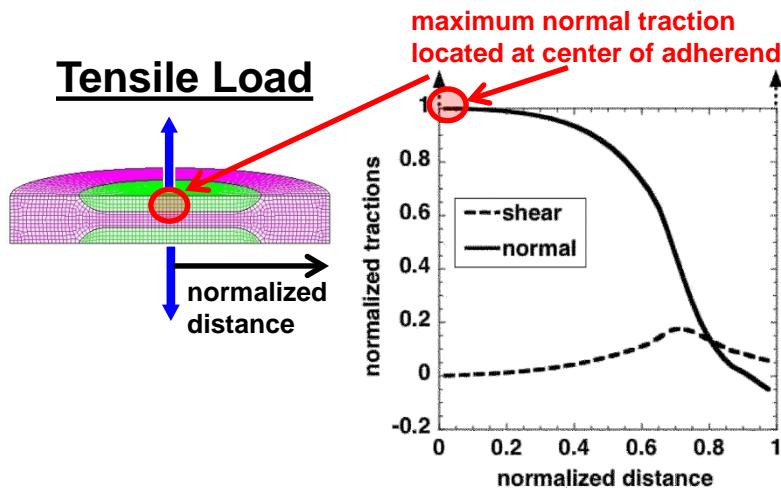
Combined Load (0.6% tensile strain + 1% shear strain)

normalized distance

maximum traction locations unchanged
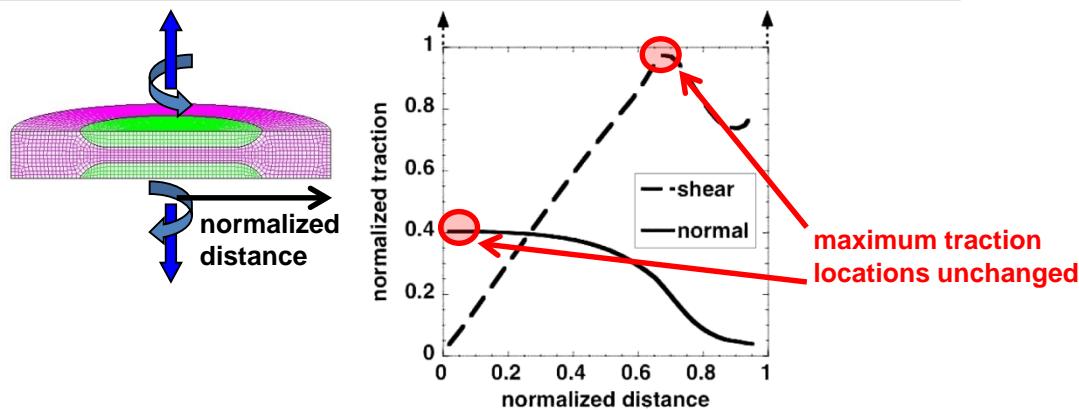
2. Max stresses are smooth functions, not "spiked"
3. Sample allows for mixed loading modes: tension, compression, shear, etc.

Aging Test

Saucer Test Geometry

Fig. 12

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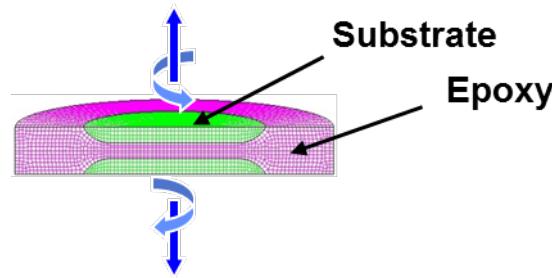
**Initial focus on tensile loading only
(it may be the most sensitive to aging)**

Aging Conditions

Volume or enthalpy

Test Conditions
•Smaller total change in material
•Material changes occur in a reasonable (~40 days) timeframe

Application Conditions
•Larger total change in material
•Material changes take ???

25°C   55°C

Temperature
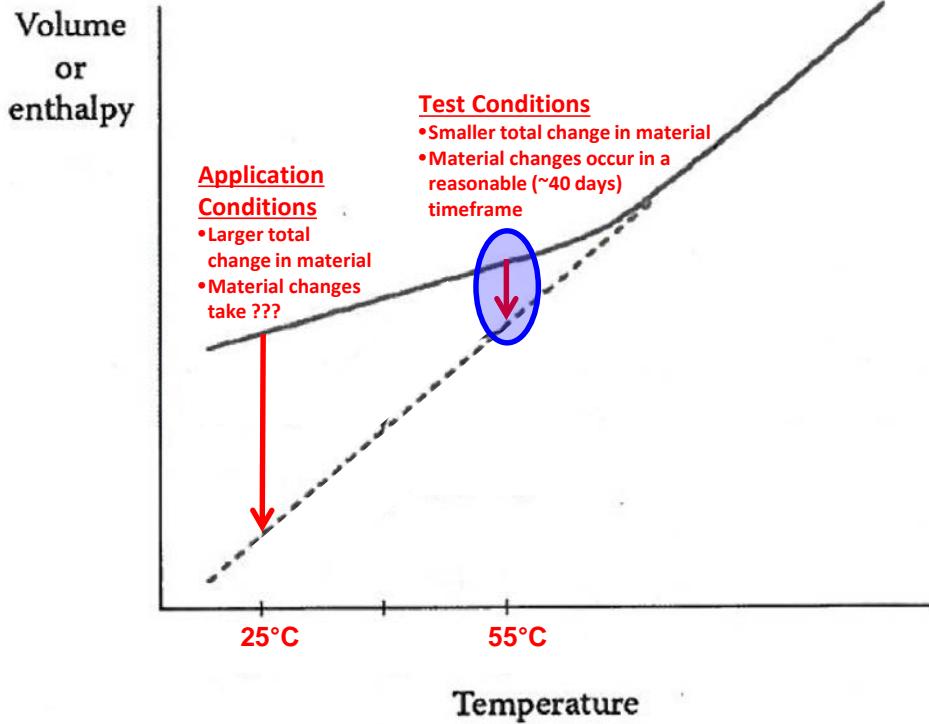
Results Coming Soon

Simple Structural Response Test for Validation

Confined Aging Experiment
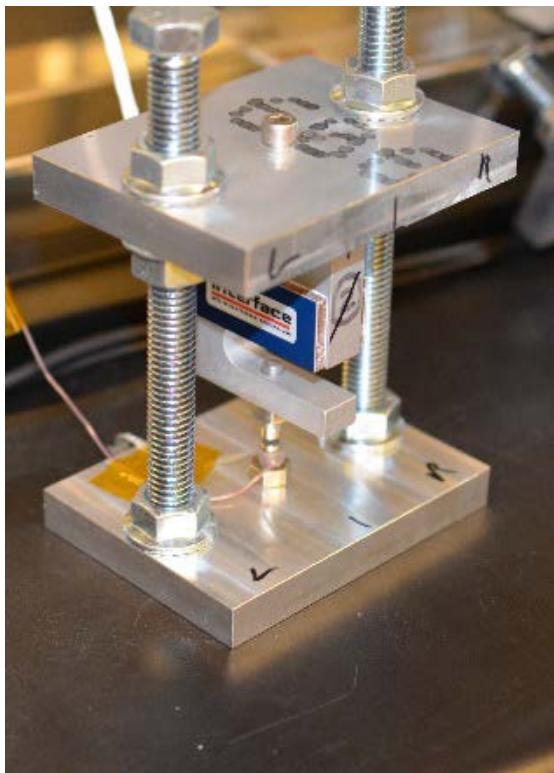

**Stiff Structure
With
Load Cell**
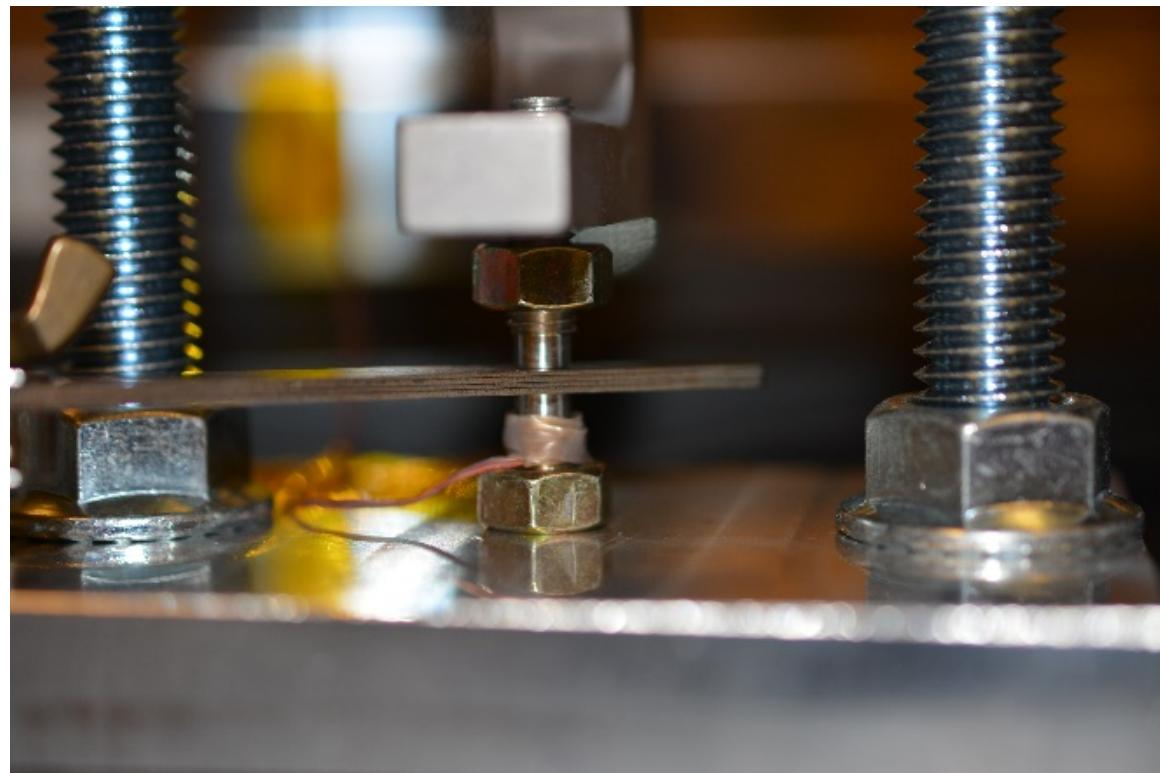
Defined Gap for Adhesive

Aging Under Tension
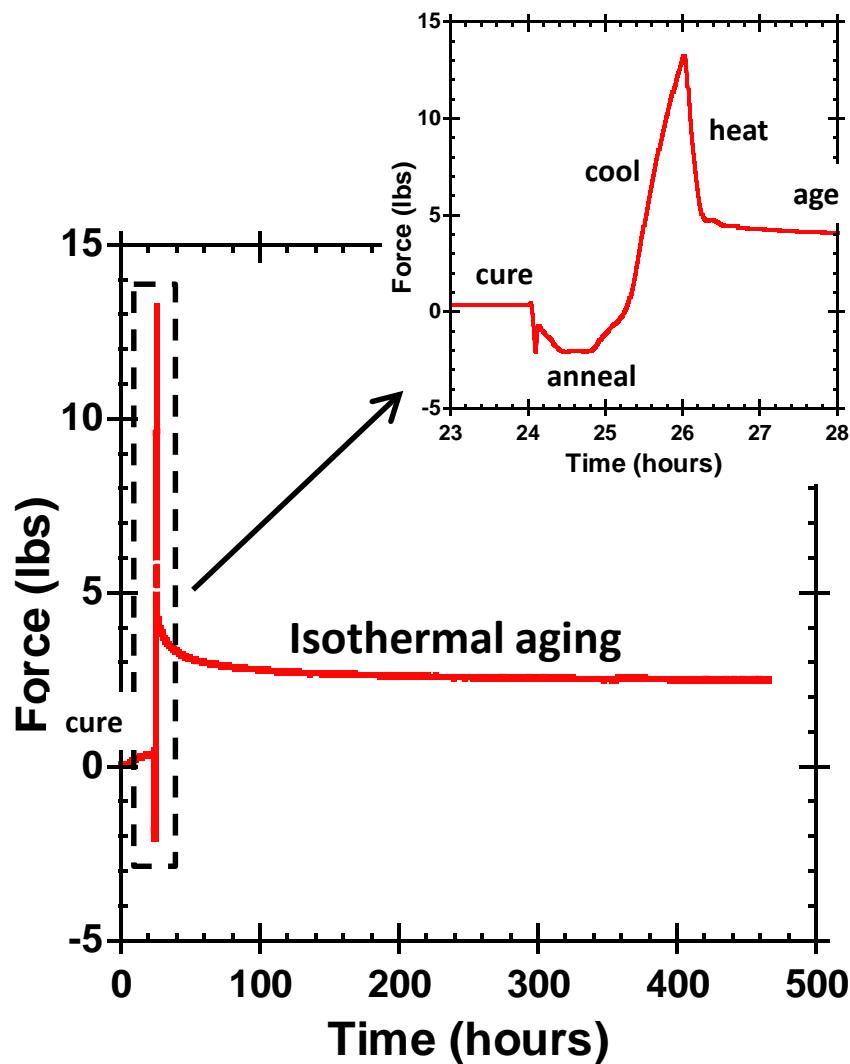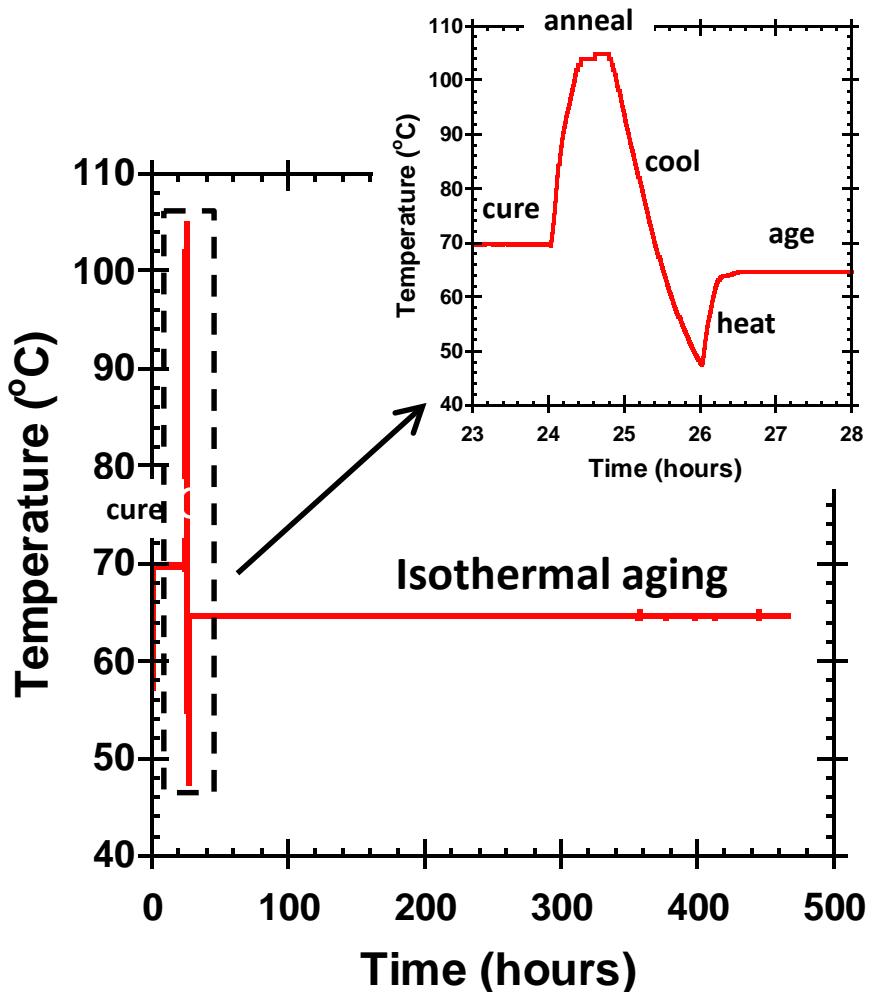
- Full thermal/force history captured from cure to aging
- Force decreases during isothermal aging, indicating stress relaxation dominates over physical aging under these test conditions

Aging Under Compression
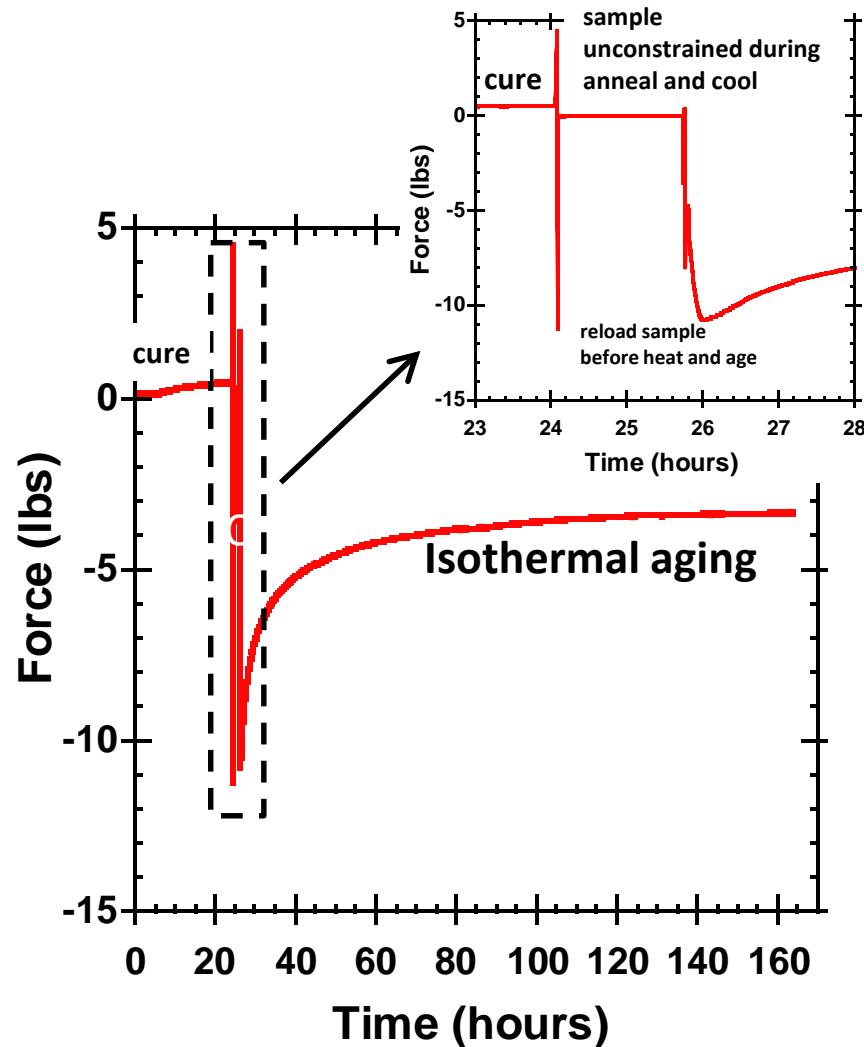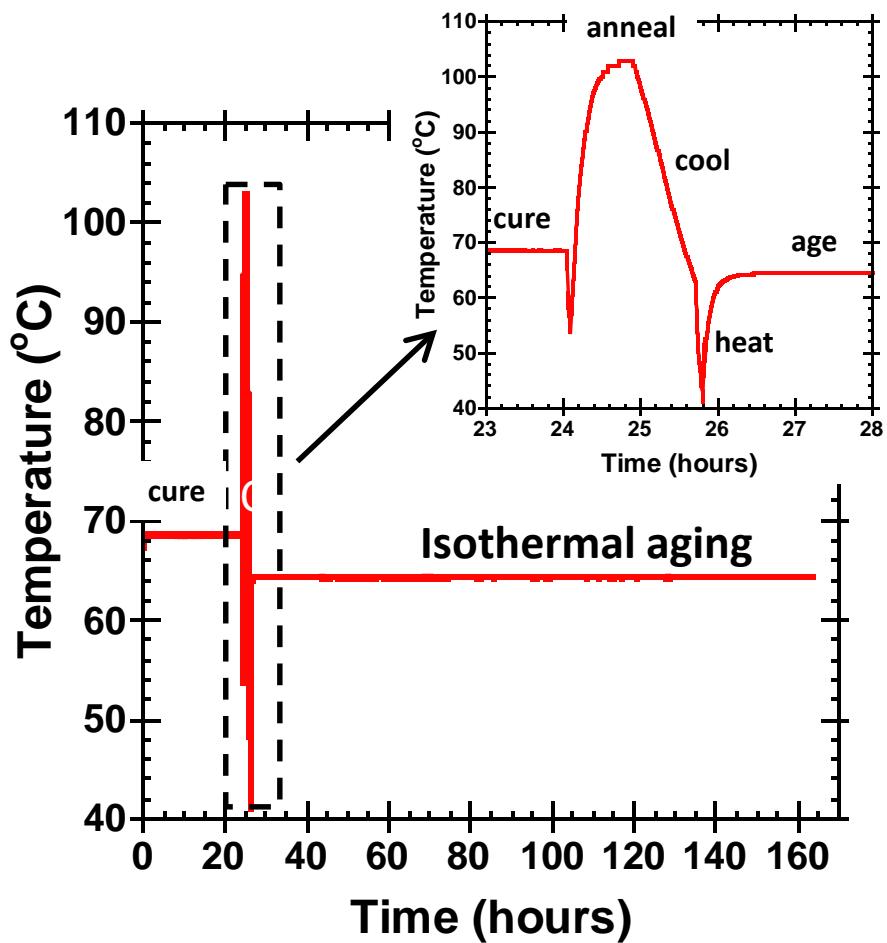
- Cure, compressive loading during heating and aging history captured
- Magnitude of force decreases during isothermal aging. Both stress relaxation and physical aging tend to decrease the magnitude of force during isothermal aging under these conditions.

Reproducibility During Cure
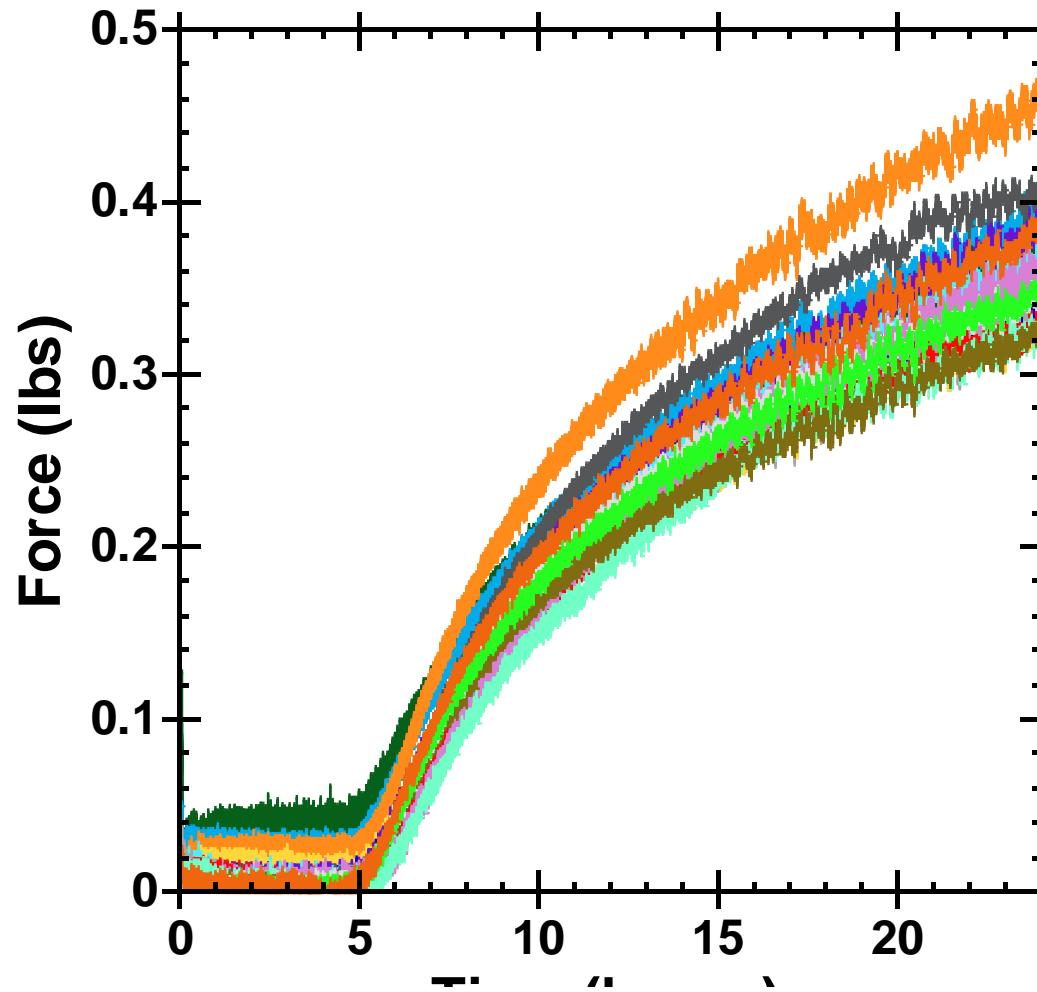
- All tests give consistent measurement of the force developed during cure
- This provides another geometry (in addition to the Bimaterial Beam and the Thin-Disk-On-Cylinder) to assess stress associated with cure

Aging Response

Under Tension
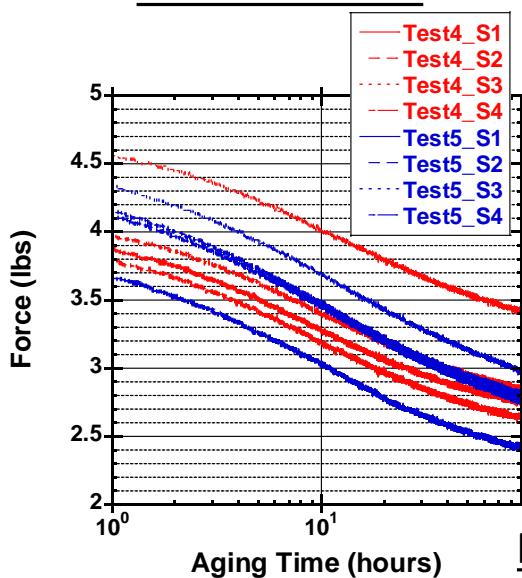
Under Compression

Change in force linear with log(time) for long periods
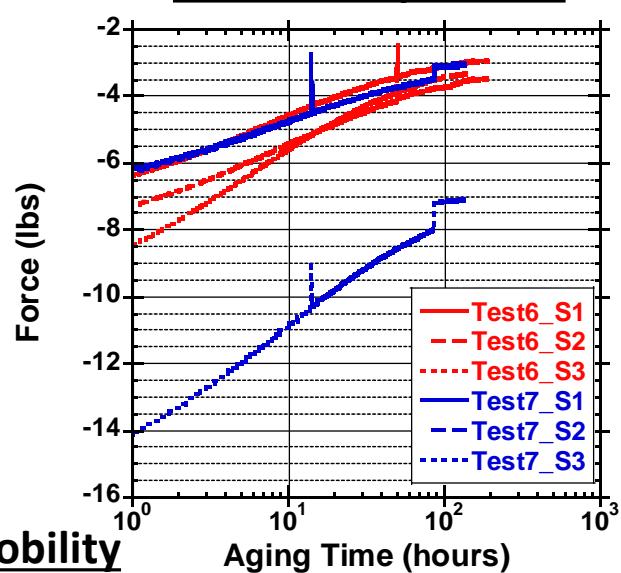
Resolution of Deformation Induced Mobility
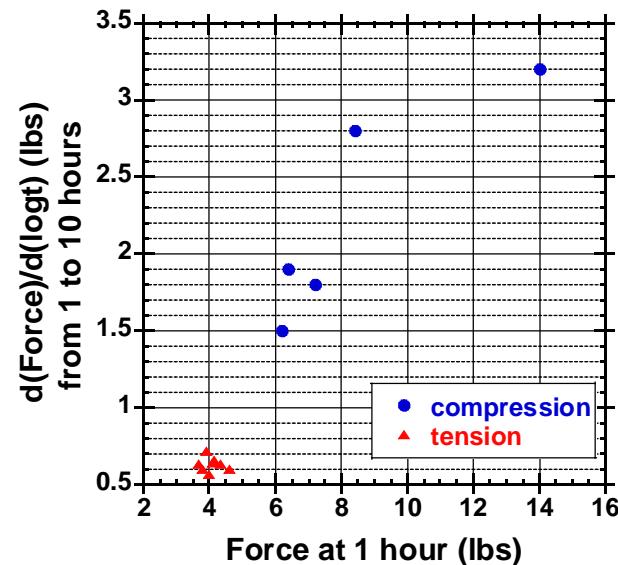
Change in force faster under higher loads

Final Remarks

o 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
o Based on what is learned from materials testing, we are designing structural tests to examine the impact of materials aging on application designs
o 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