This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

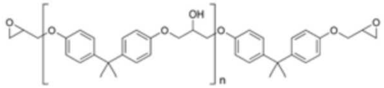
SAND2018-6496C

Exceptional service in the national interest

Sandia National Laboratories

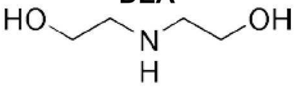
Materials

DGEBA



✚

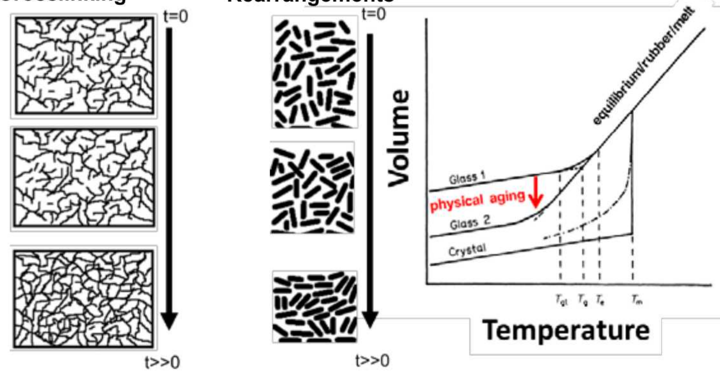
DEA



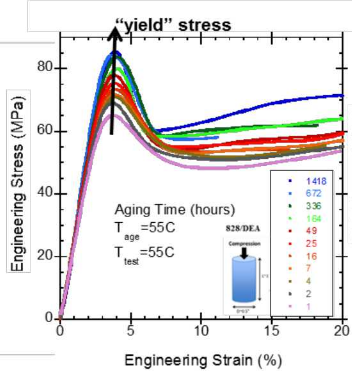
Chemical and Physical Aging

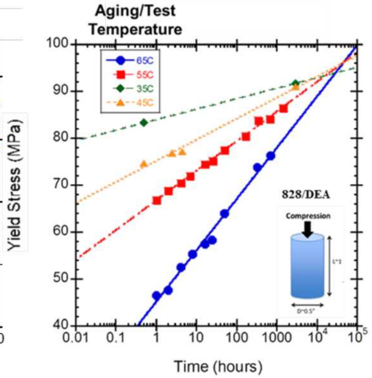
Additional Chemical Crosslinking

Physical or Structural Rearrangements



Thermal-Mechanical Response Changes





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

Jamie Kropka[1], Gabriel Arechederra[1] and John McCoy[2]
Sandia National Laboratories, Albuquerque, NM
New Mexico Institute of Mining and Technology, Socorro, NM

44th PolyMAC, Albuquerque, NM June 2018

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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

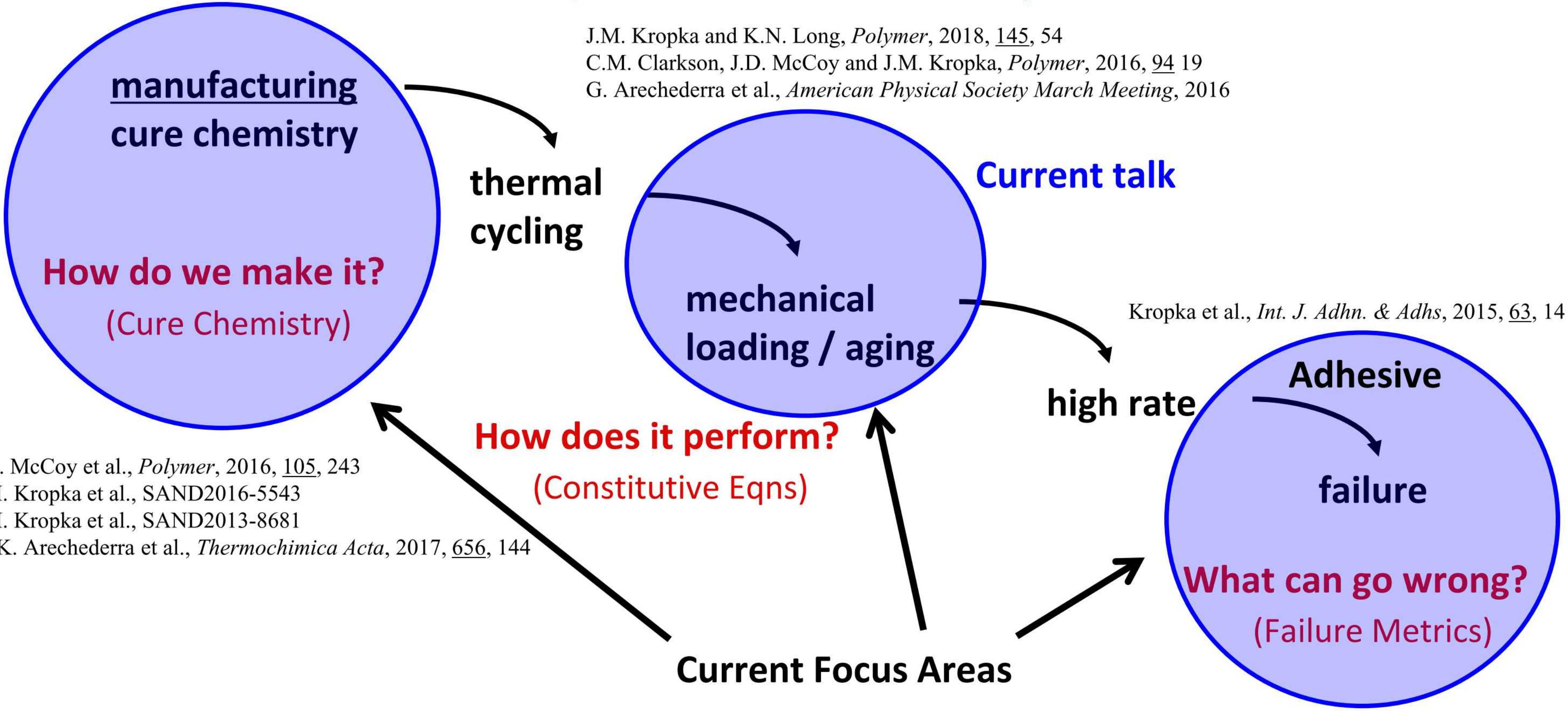
Polymer Nonlinear Viscoelastic (NLVE) Model

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 physics → **development** tools → **analysis** predictions

Predict Stress/Strain and Understand Impact on Performance

J.M. Kropka and K.N. Long, *Polymer*, 2018, 145, 54
C.M. Clarkson, J.D. McCoy and J.M. Kropka, *Polymer*, 2016, 94 19
G. Arechederra et al., *American Physical Society March Meeting*, 2016



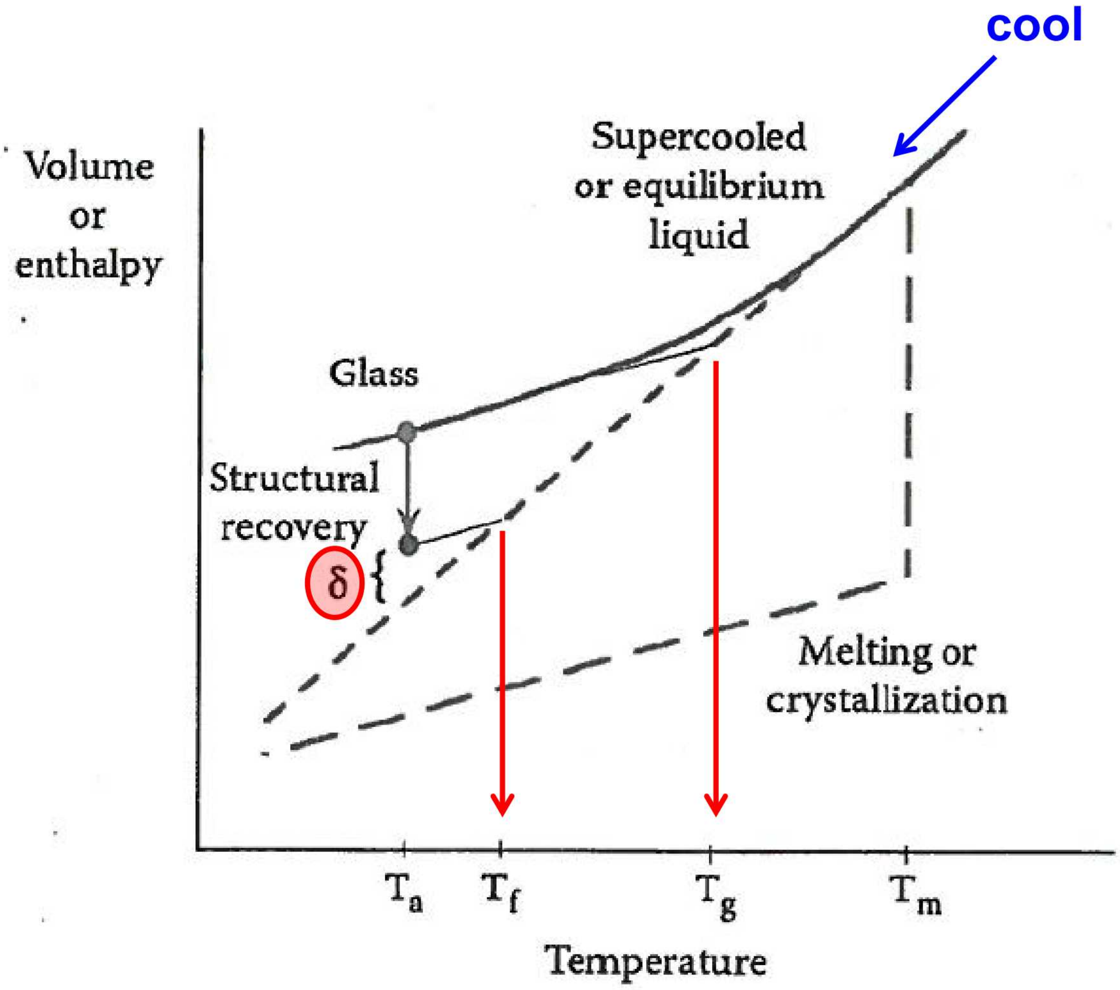
Kropka et al., *Int. J. Adhn. & Adhs*, 2015, 63, 14

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
  - Simple structural response tests validate predictive tools

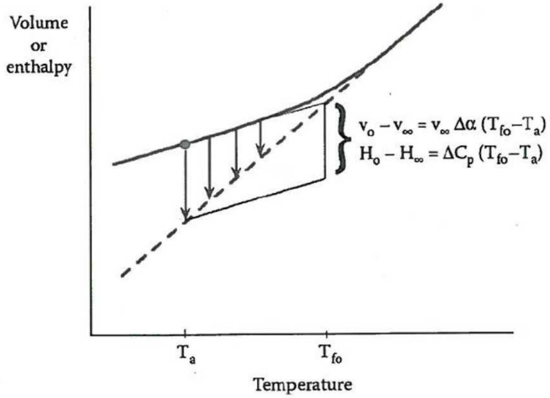
Glass Formation and Structural Recovery/Relaxation

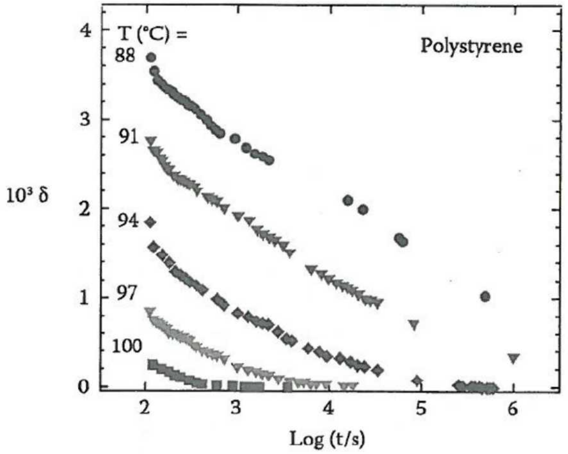


Simon and McKenna, Structural recovery and physical aging of polymeric glasses, in **Polymer Glasses**, 2017

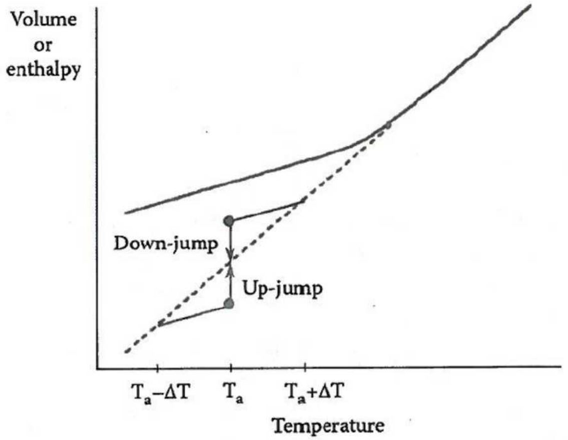
Signatures of Structural Recovery/Relaxation

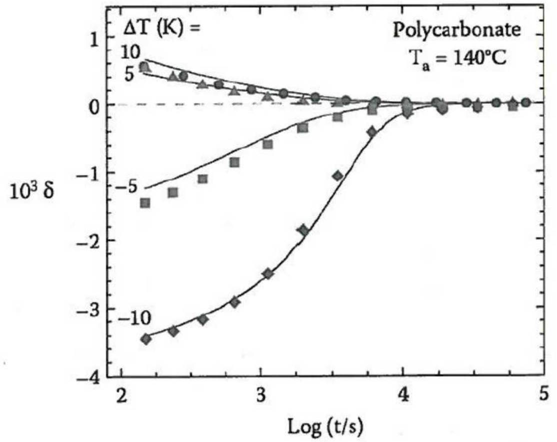
Intrinsic Isotherms





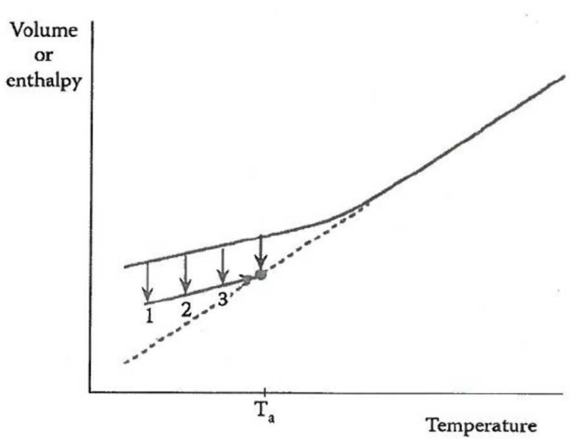
Asymmetry of Approach

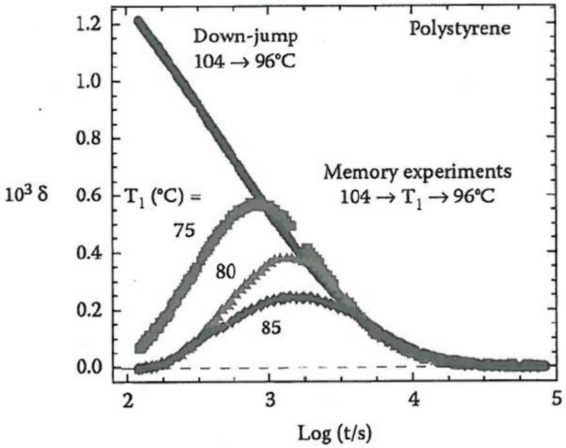




Relaxation Depends on Structure

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

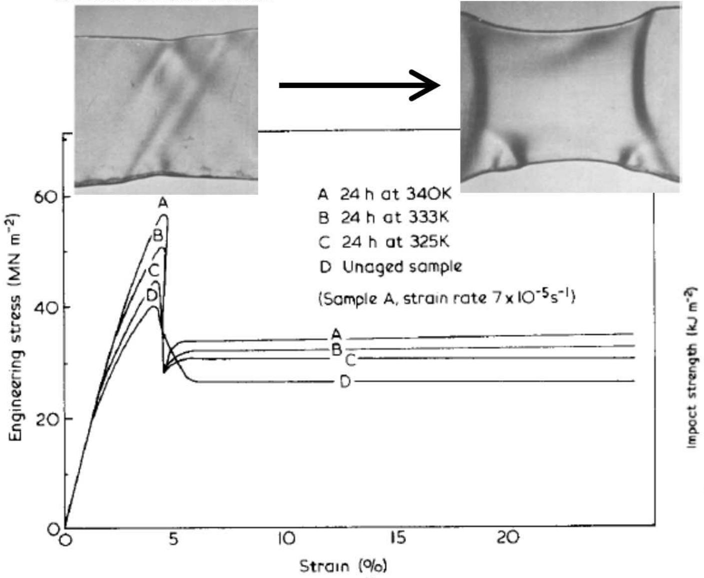
Impact of Structural Recovery and Physical Aging

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

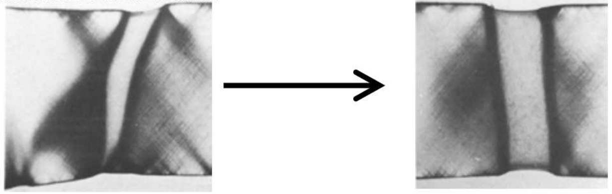
S.L. Simon and G.B. McKenna, in *Polymer Glasses*, 2017, pg. 46

Tensile and impact tests of PET during isothermal “aging”

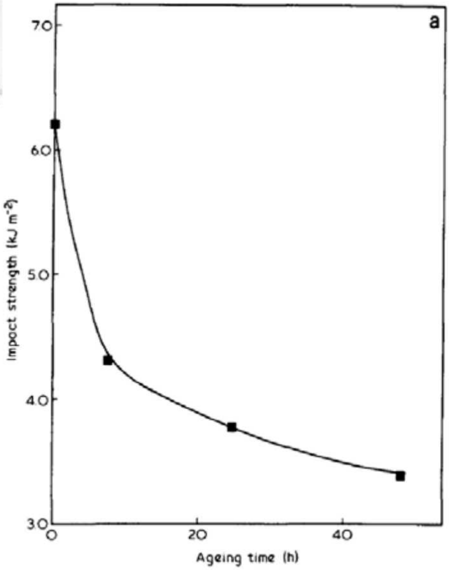
initial shear band **unaged** **neck propagation**



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



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



Izod impact studies of PC during isothermal “aging”

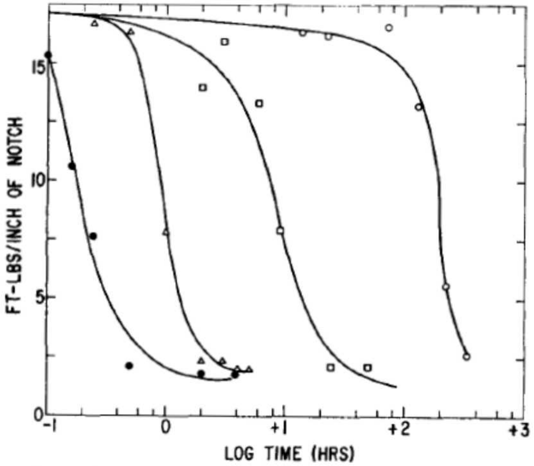


Fig. 3. Effect of annealing temperature on Izod impact data. ○) 100; □) 115; △) 125; ●) 130; $[\eta i] = 0.58$.

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

Approach to Understanding/Predicting Epoxy Aging

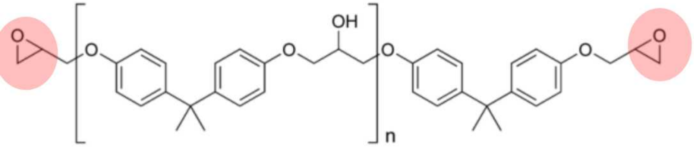
- Identify material aging mechanisms and their impact on material physical behavior (**current efforts and results**)
- Develop/augment science-based modeling tools to predict material aging behavior with high fidelity
- Demonstrate impact of aging on stress in application relevant geometries (**scoping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

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

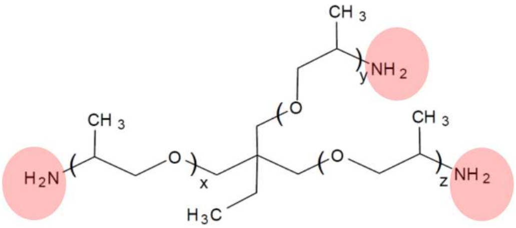
Materials

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

EPON® Resin 828
Diglycidylether of Bisphenol-A



Jeffamine® T-403 Polyetheramine

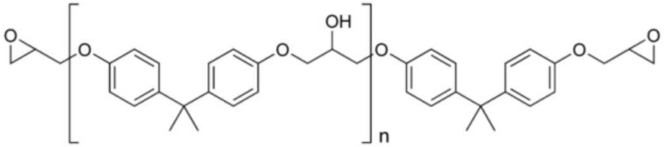


(x+y+z) = 5-6

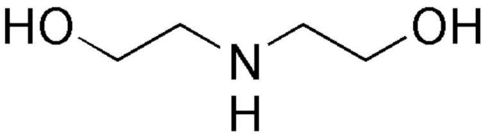
T_g ~ 90C
(when mixed stoichiometrically epoxy-amine)

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

3M D32 glass microballoons

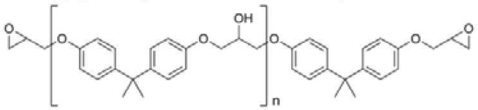
[1] Mix ratio, cure schedule, and more can be found in SAND2013-8681

[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

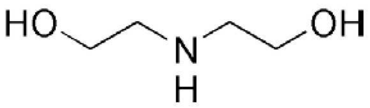
828/DEA[1]

EPON® Resin 828
Diglycidylether of Bisphenol-A



100 pbw

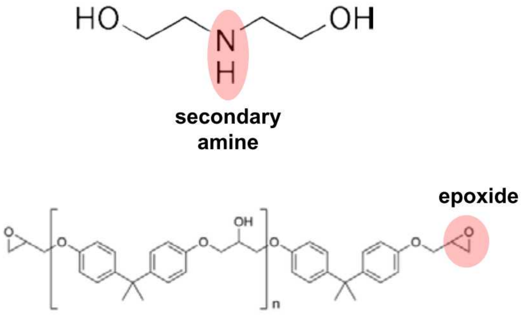
Diethanolamine



12 pbw

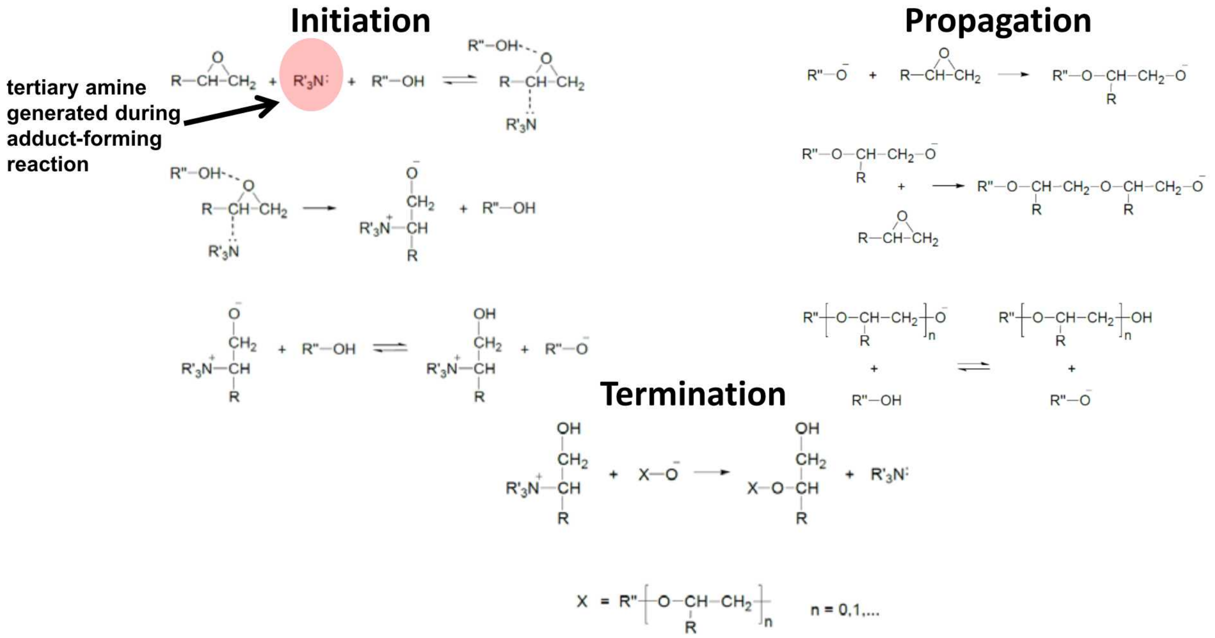
Polymerization at T = 70°C (the cure process before aging)

Adduct-Forming Reaction



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 ~ 70°C

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

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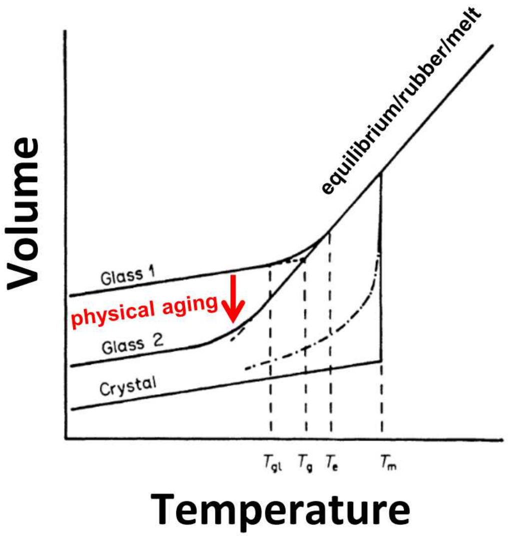
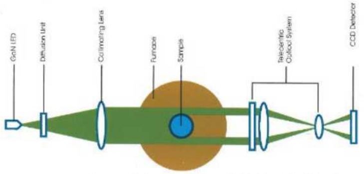
[1] Mix ratio, cure and typical properties can be found at: http://www.sandia.gov/polymer-properties/828_DEA.html

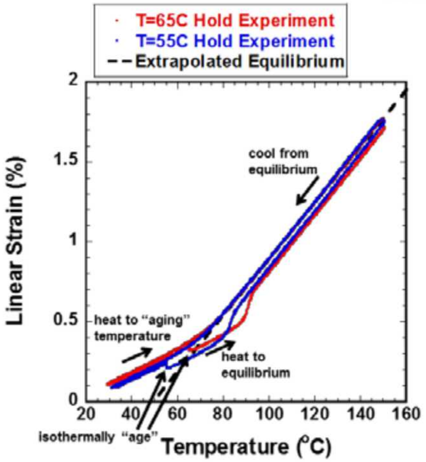
Polymer Glass Aging



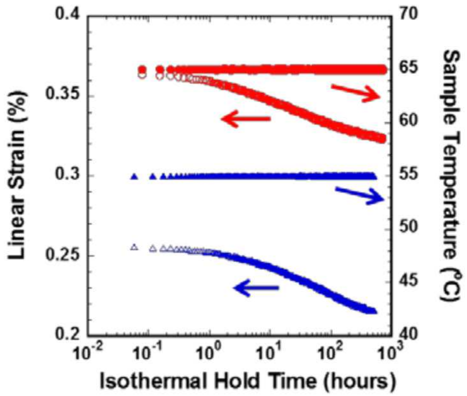
Material Volume Changes

optical resolution



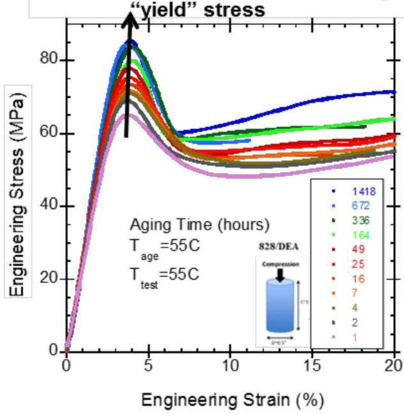


Isothermal Hold Response

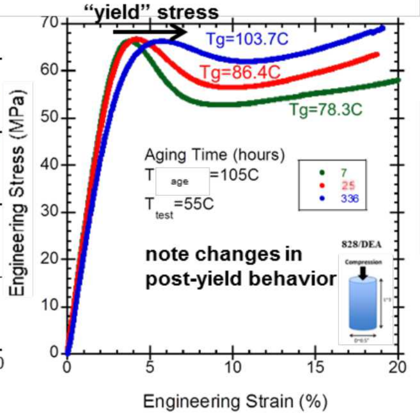


Material Mechanical Response Changes

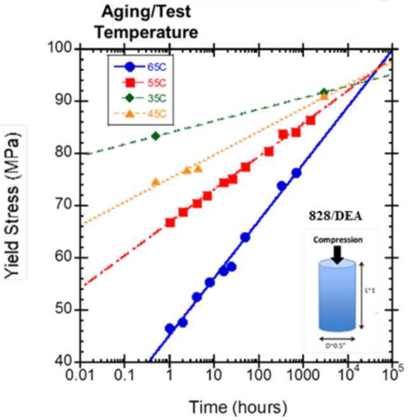
Exposure Below T_g



Exposure Above T_g



Exposure Below T_g



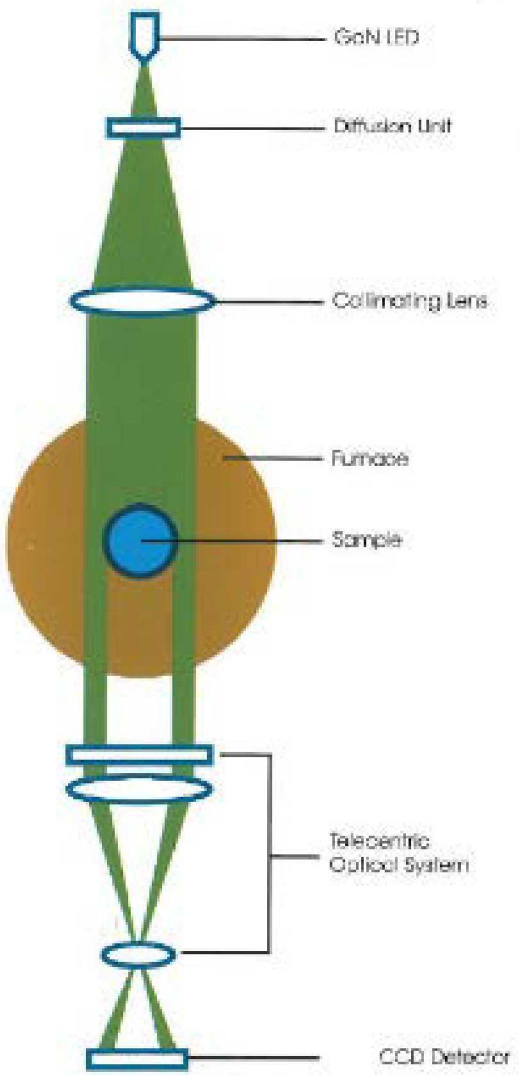
SNL NLVE polymer models (e.g., SPEC) have the framework to predict the aging behavior and should be tested against measurements

Kropka and Long, *Polymer*, 145 (2018) 54, Clarkson, McCoy and Kropka, *Polymer*, 94 (2016) 19, Arechederra et al., APS 2016

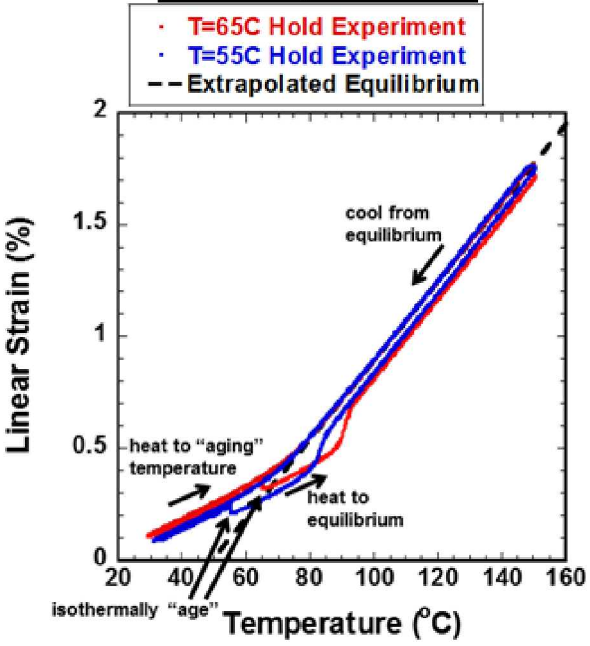
Volume

Measuring Volume Response Associated with Aging

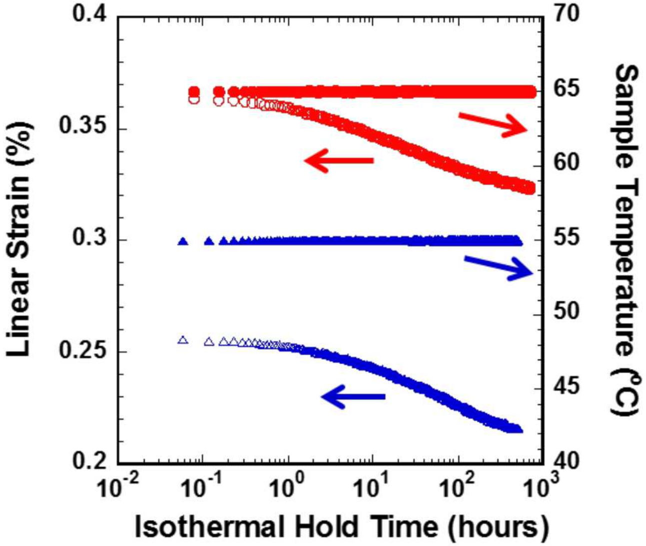
Optical Resolution of Length*



Full Experiment

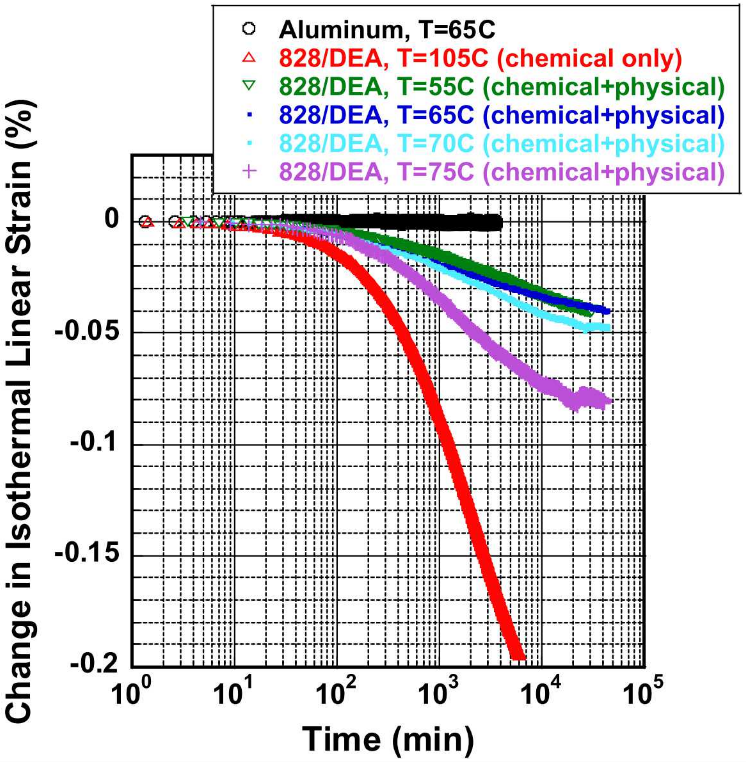


Isothermal Hold Response

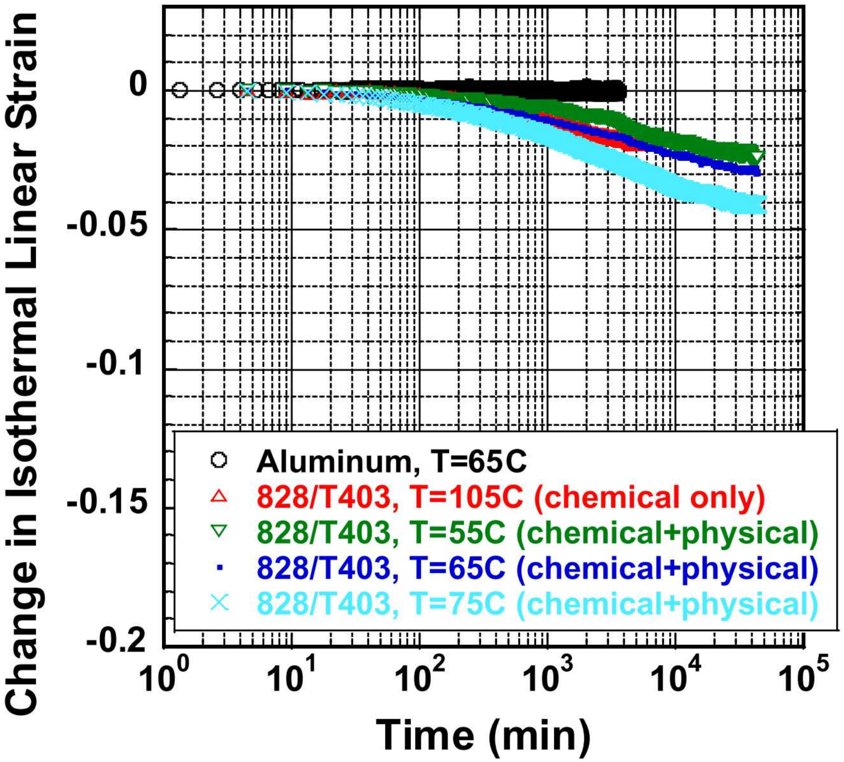


*for isotropic materials $\Delta V = 3\Delta L$

Isothermal Volume Response for 2 Common Epoxy Thermosets



828/DEA



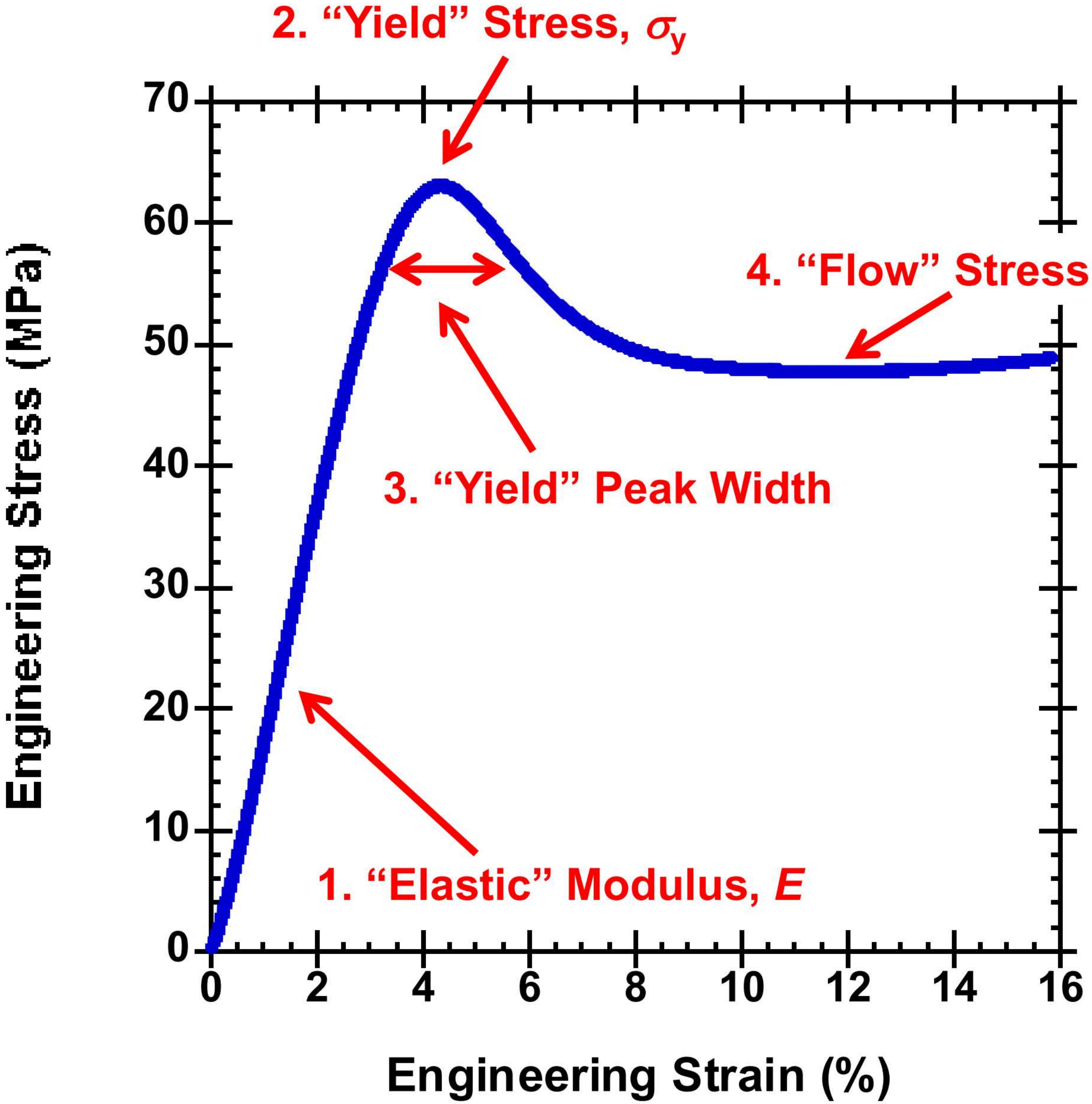
828/T403

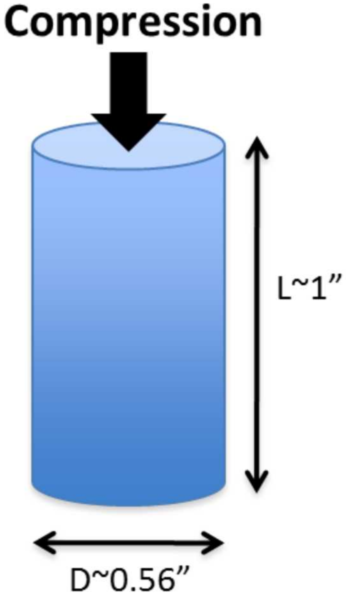
Note: Remaining reactive potential (excess epoxide groups in the case of 828/DEA) can play a significant role in total volume change

- 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

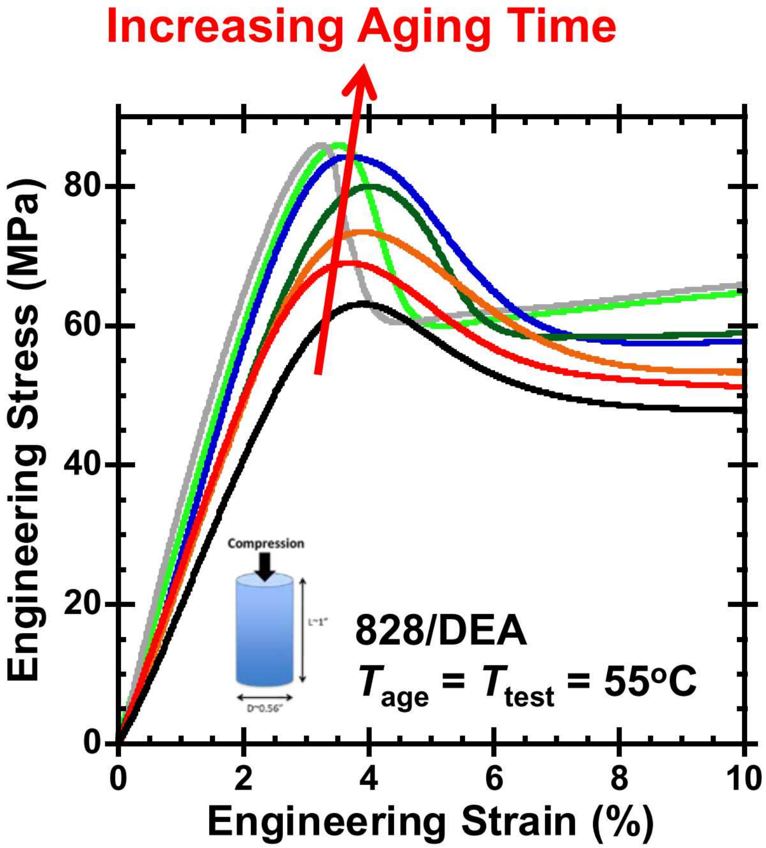
Mechanical

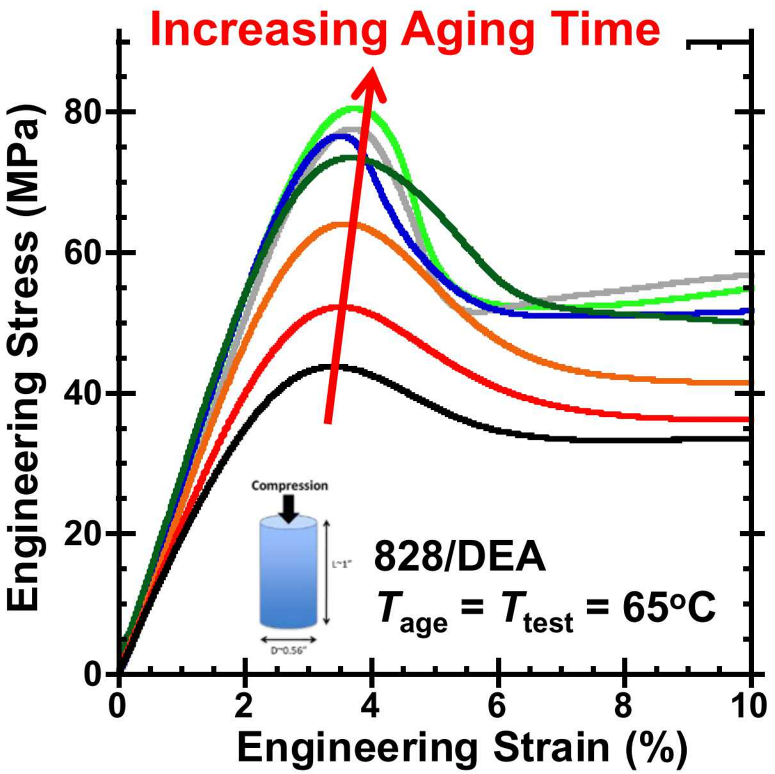
Anatomy of Compressive Stress-Strain Response of Glassy Polymers





Changes in Compressive Stress-Strain Response Associated with Thermal Aging

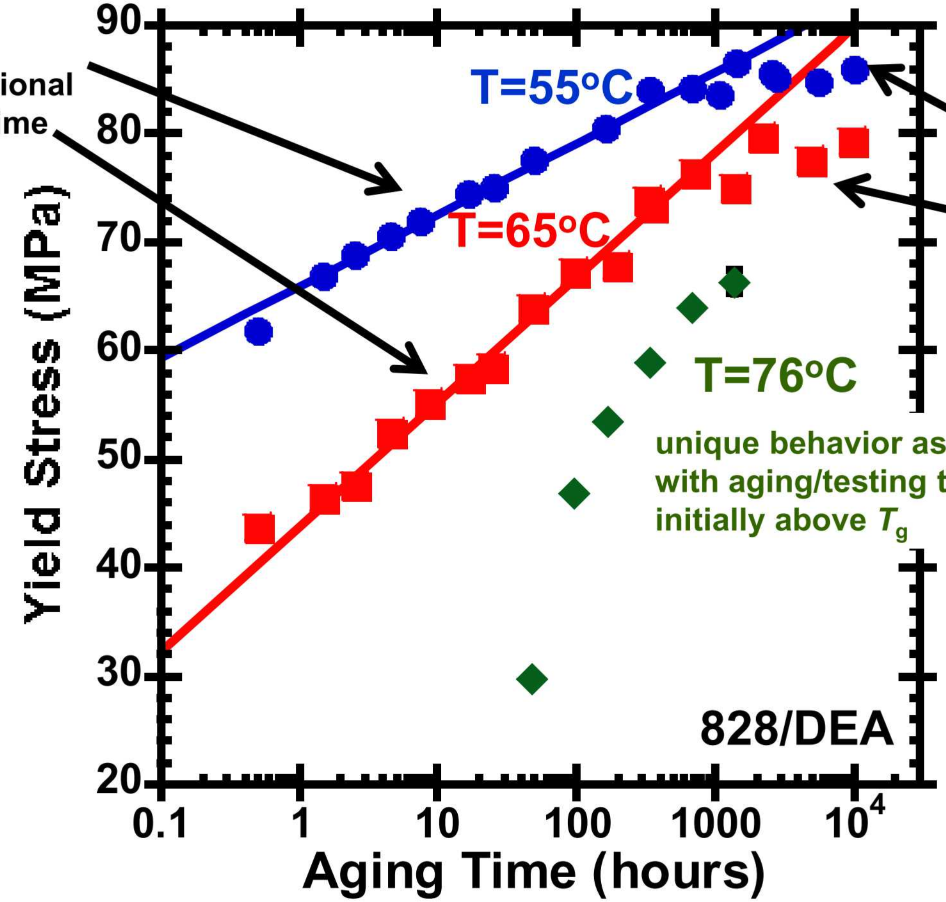




<u>4 Distinguishable Changes in Compressive Stress-Strain Response Include:</u>

- 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

linear fits no longer accurate at long time

unique behavior associated with aging/testing temperature initially above T_g

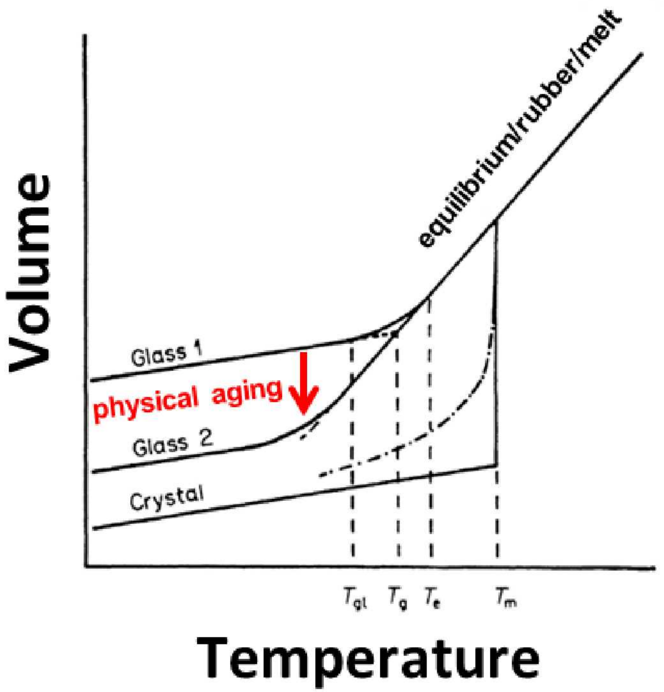
<u>**Focusing on *T* = 55^{o}C and 65^{o}C datasets for now:**</u>

- **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?

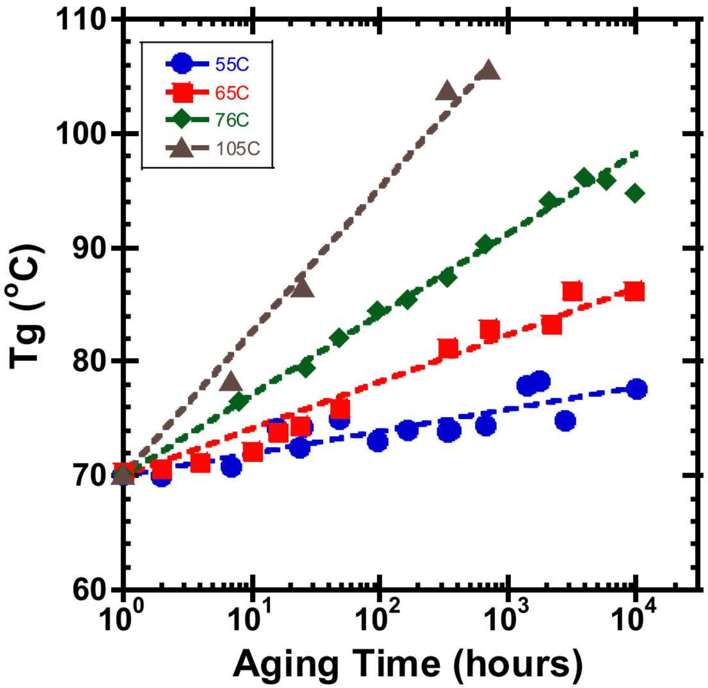
Mechanisms Driving Evolution of Yield Stress during Thermal Aging

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

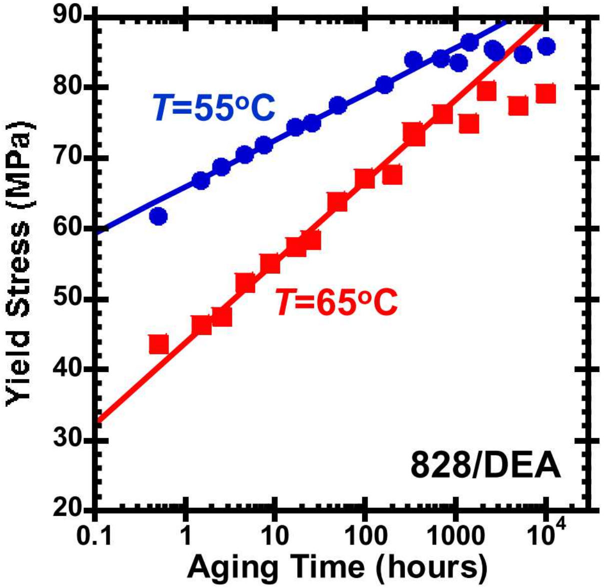


Continued chemical crosslinking increases the glass transition temperature of the material. This also slows molecular motions in the polymer chain (at a given temperature below T_g) and contributes to an increase in the observed yield stress in the compressive stress-strain response

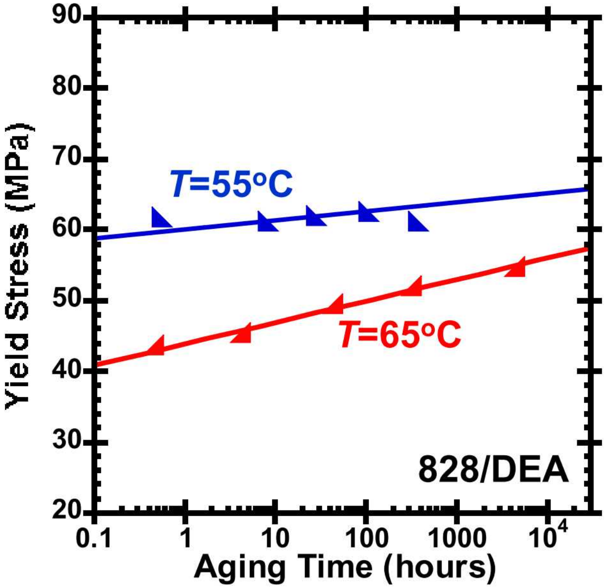
Can these contributions to the overall increase in yield stress be separated?

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

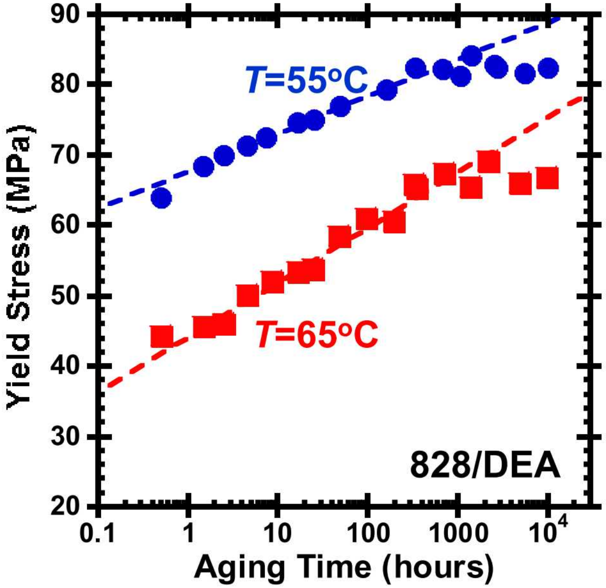
Chemical + Physical (Measured)



Chemical Only (Measured)

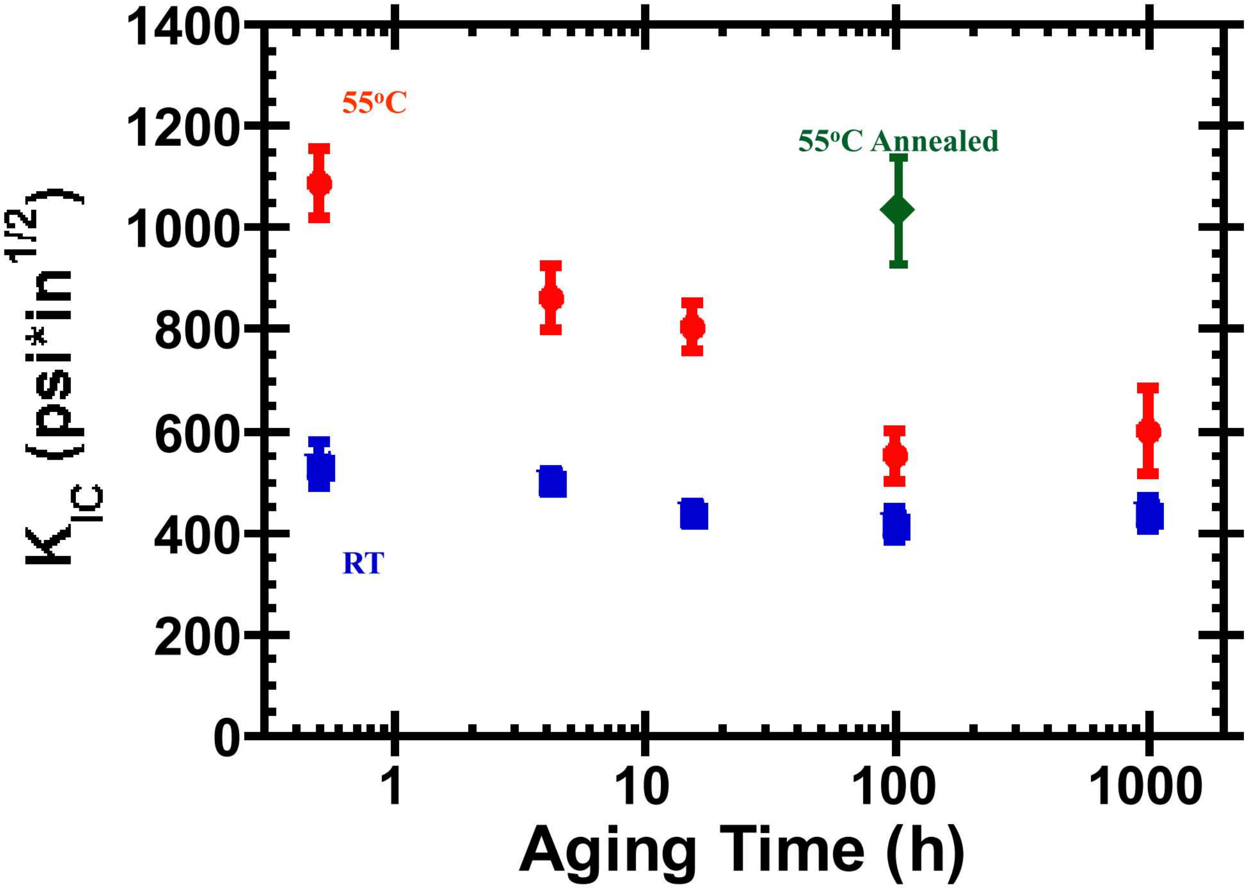


Physical Only (Calculated)



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.

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 and fracture toughness during isothermal aging**

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Lindsey Hughes

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Taylor Gabaldon

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Mark Stavig

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Jamie Kropka

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Modelers

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Main Contributors to Today's Topics

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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

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

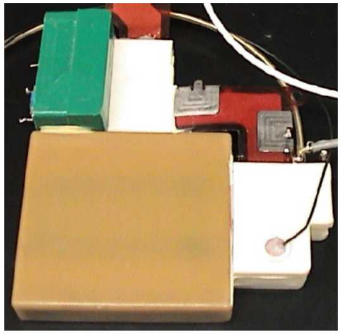
- Foams for:
  - energy dissipation
  - light constraints

- Plastic Parts for:
  - injection molded pieces

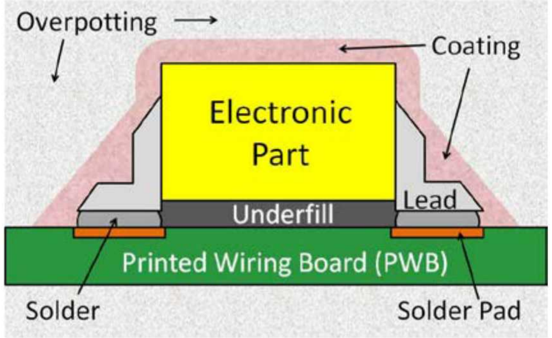
thermoplastics

- Gaskets and O-rings for:
  - sealing cavities
- Cushions, Pads, Coatings for:
  - stress relief
  - damping

elastomers

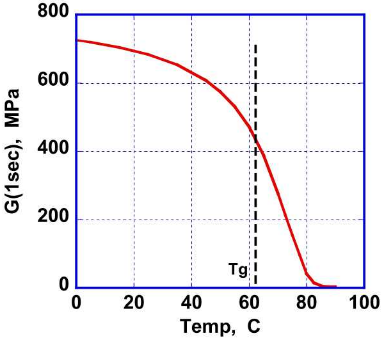


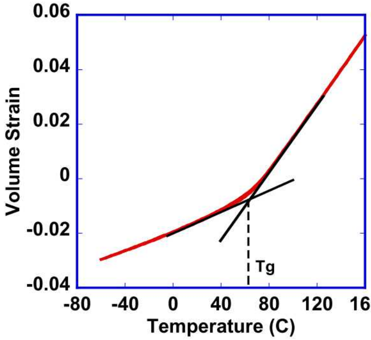
- Optimal use of polymers is not always obvious
- Poor choice of polymers can cause premature failures
- Modeling is important
- Must understand materials to represent them in models

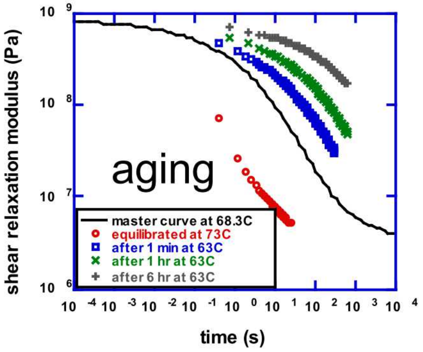


Polymers Are Complex Materials

They respond differently than metals and ceramics







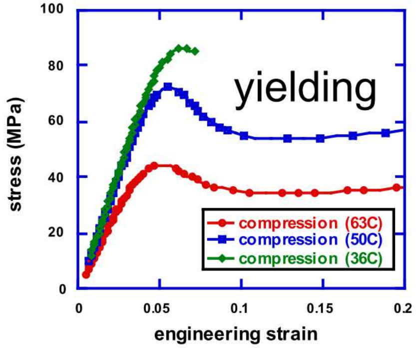


exhibit a glass transition:

- 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