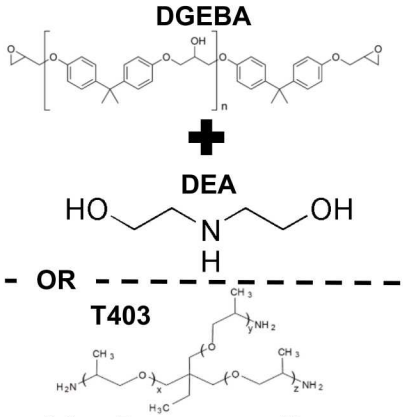
SAND2019-3566PE

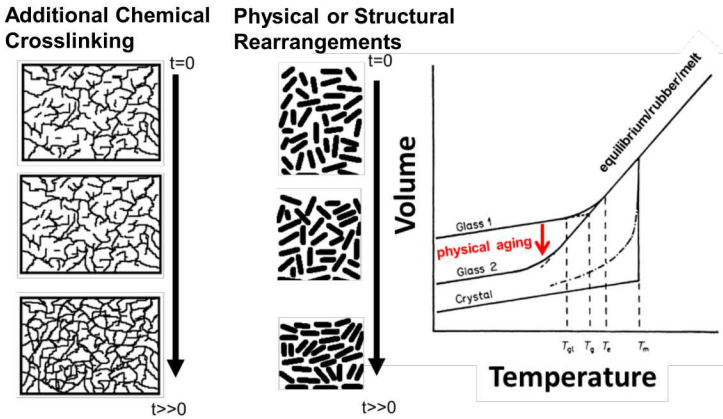
Exceptional service in the national interest

Sandia National Laboratories

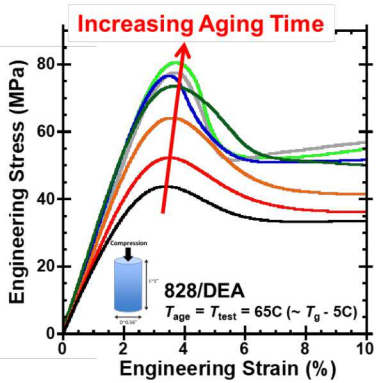
Materials

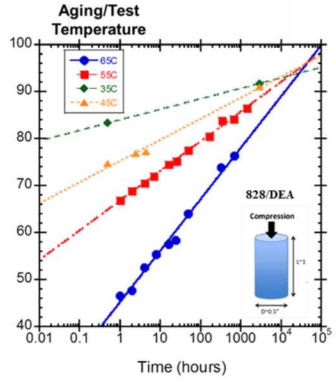


Chemical and Physical Aging



Thermal-Mechanical Response Changes





Understanding and Predicting the Evolution of Glassy Thermoset Polymers During Aging and the Impact of Aging on the Performance and Reliability of Engineering Devices

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

Northrop Grumman Seminar, Salt Lake City, April 1, 2019

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

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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

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

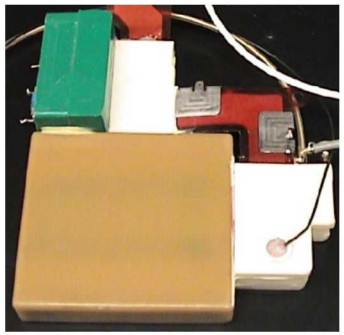
- Foams for:
  - energy dissipation
  - light constraints

- Plastic Parts for:
  - injection molded pieces

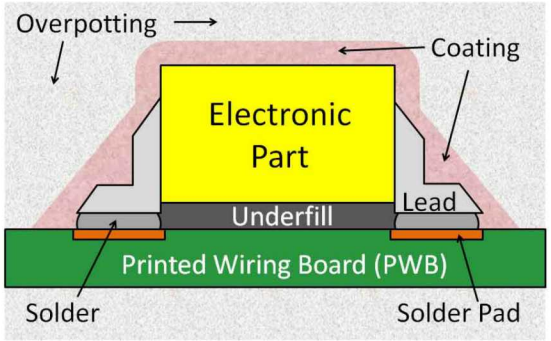
thermoplastics

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

elastomers

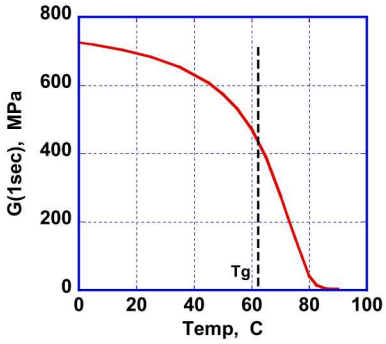


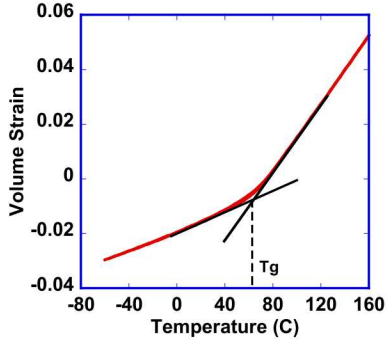
- Optimal use of polymers is not always obvious
- Poor choice of polymers can cause premature failures
- Modeling is important
- Must understand materials to represent them in models

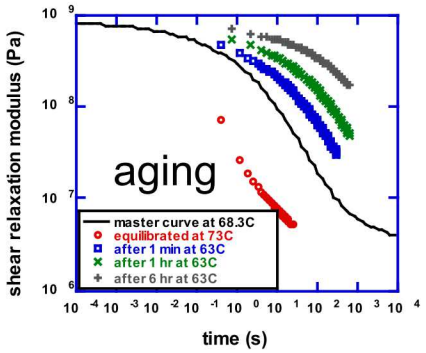


Polymers Are Complex Materials

They respond differently than metals and ceramics







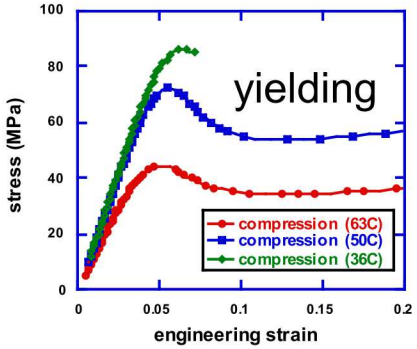


exhibit a glass transition:

- 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

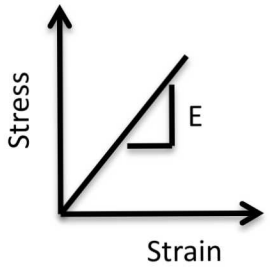
Performance predictions must be able to capture the full range of behavior for general thermo-mechanical loadings from manufacturing to failure.

- must be extensively validated
- computationally tractable

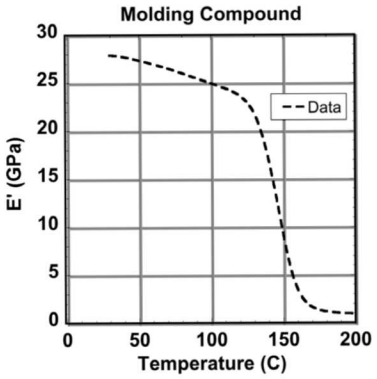
Capability Development: Evolution of Constitutive Representation of Polymers

Linear Elasticity → Linear Viscoelasticity → Nonlinear Viscoelasticity

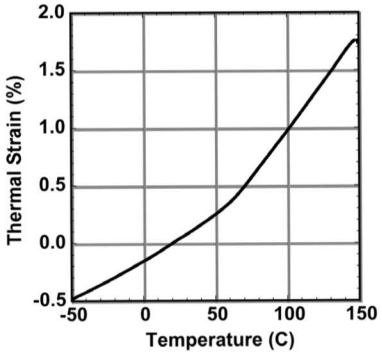
E, ν, α



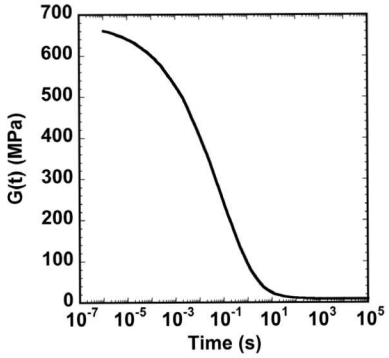
+ temperature dependencies



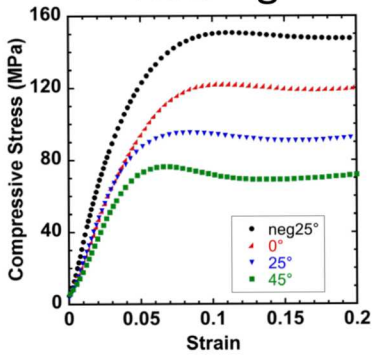
Glass Transition



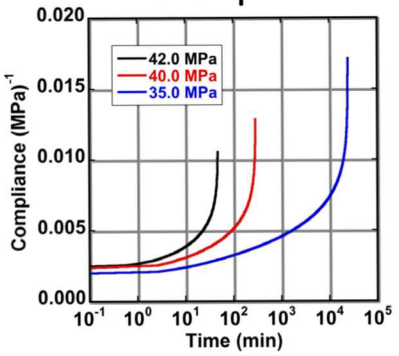
Stress Relaxation



Yielding



Creep



+ manufacturing
+ aging
+ failure metrics

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

Other Options not Possible

Bare Bones Approach

Measure:

1. calorimetric Tg
2. filler volume fraction

Model Parameterization:
Estimate NLVE response based on universal properties and rule of mixtures approach

Limitations/Potential Errors:

- Must be rigid fillers (e.g., alumina, silica, mica…)
- Breadth of relaxation spectra
- Nonlinear material clock

Material Evaluations

Quick and Dirty Approach

Measure:

1. filler volume fraction
2. thermal strain versus temperature
3. elastic shear modulus versus temperature

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.

Limitations/Potential Errors:
Lack definition of clock for nonlinear relaxations

Critical Encapsulants/Adhesives

The Whole Shebang

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:
Populate material specific SPEC NLVE model

Advantage:
Model can now predict yielding AND (physical) aging with more confidence

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

research
Physics
Chemistry

→ **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, Evolution of Mechanical Properties during Structural Relaxation of 828/DEA *MS Thesis*, 2017.
K. Wilson, Physical Aging in a Polyether-amine Cured DGEBA Epoxy *MS Thesis*, 2018.

manufacturing
cure chemistry

How do we make it?
(Cure Chemistry)

→ **thermal cycling**

Current talk

mechanical loading / aging

J.M. Kropka et al., SAND2018-10582
J.M. Kropka et al., *Int. J. Adhn. & Adhs*, 2015, 63, 14
J.M. Kropka et al., SAND2013-8681

→ **high rate**

Adhesive
failure

What can go wrong?
(Failure Metrics)

How does it perform?
(Constitutive Eqns)

J.D. McCoy et al., *Polymer*, 2016, 105, 243
J.M. Kropka et al., SAND2017-13680
J.M. Kropka et al., SAND2016-5543
J.M. Kropka et al., SAND2013-8681
J.D. McCoy et al., *Thermochimica Acta*, 2019, 671, 149
G. K. Arechederra et al., *Thermochimica Acta*, 2017, 656, 144

Current Focus Areas

What Happens to Polymers with Age?

News reports and scholarly articles alike tell us about the accumulation of plastics in landfills and oceans—will they ever go away?

China's Recycling Efforts

https://www.washingtonpost.com/news/energy-environment/wp/2018/06/20/a-giant-wave-of-plastic-garbage-could-flood-the-u-s-in-10-years-a-study-says/?noredirect=on&utm_term=.419f1f949e74

R. Geyer et al., *Science Advances*, 2017, 3 e1700782

A. Brooks et al., *Science Advances*, 2018, 4 eaat0131

"Great Pacific Garbage Patch"

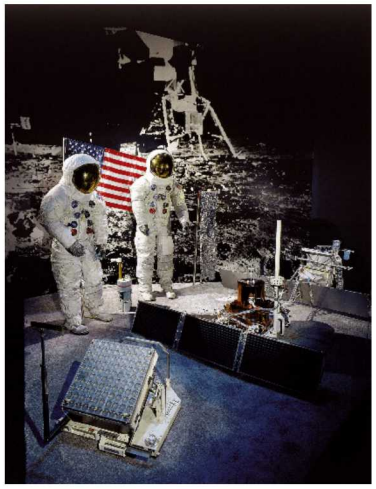
https://phys.org/news/2018-03-pacific-plastic-dump-larger.html

L. Lebreton et al., *Scientific Reports*, 2018, 8 4666

But we also hear about plastics "falling apart" in places that they are meant to last forever

Neil Armstrong's Spacesuit

at the Smithsonian's National Air and Space Museum in Washington, D.C.

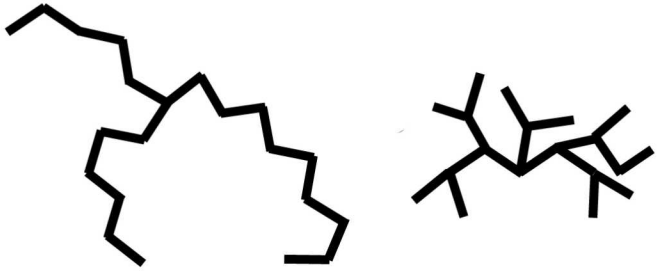


https://www.nytimes.com/2018/08/28/science/plastics-preservation-getty.html

So, What is Occurring in our Munitions Stockpile?

The Munitions Stockpile Depends on Hundreds of "Plastics"--Why Epoxies? And Why Now?

Doesn't the high cross-link density keep epoxies from "falling apart"?



Chain-growth Step-growth

Likely true for step-growth polymerizations, such as in typical epoxy-amine materials, but not necessarily for chain growth polymerizations (e.g., 828/DEA, anhydride-cured epoxies). Plus, the material may not need to "fall apart" to cause ND failure.

Can small strains associated with physical aging even cause failure?

(Glassy Modulus) x (Aging Strain)

O(10 GPa) x O(0.01)

O(100 MPa) > Yield Stress

A very definite MAYBE!

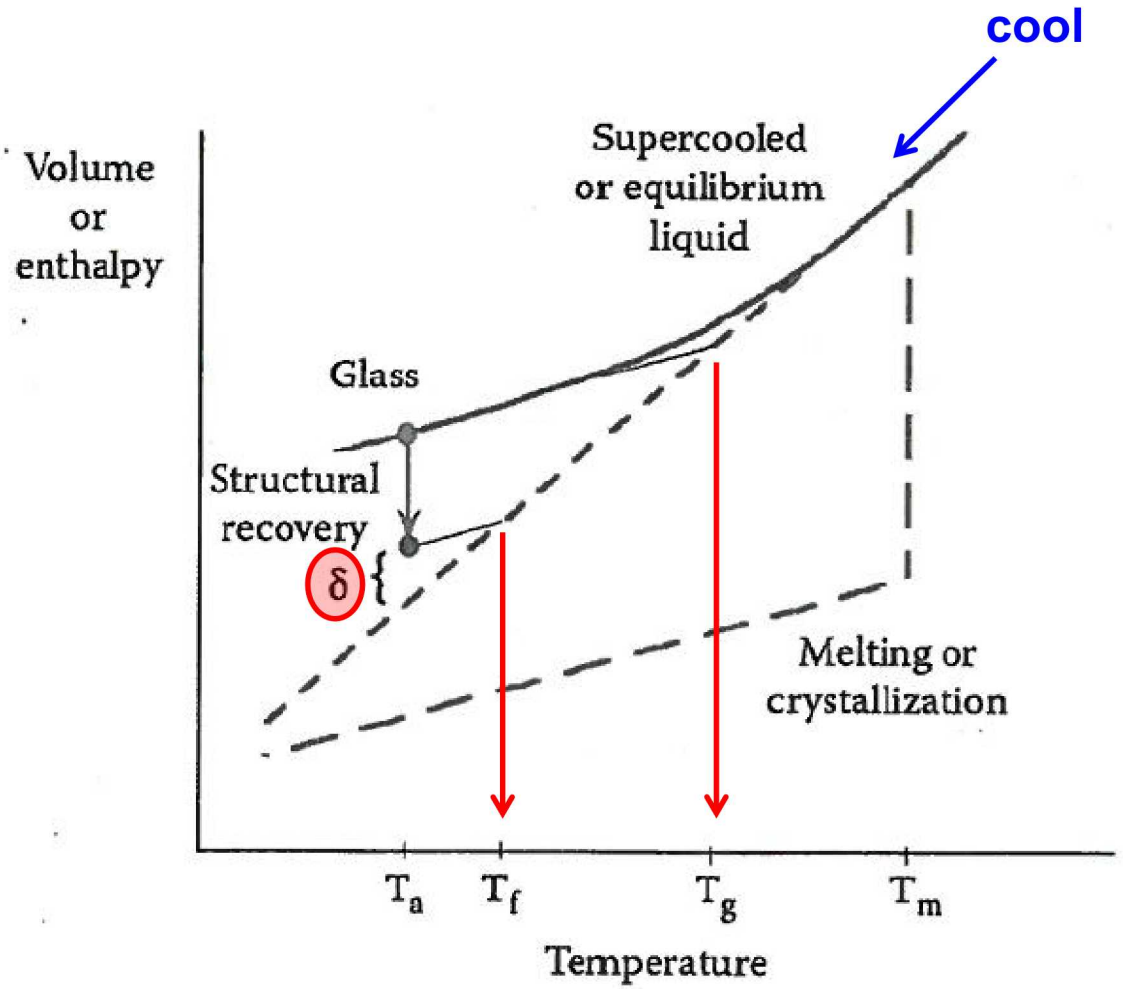
The wide use of epoxy thermosets in the ND stockpile, often in regions of high consequence should the epoxy fail, makes it important to distinguish the consequences of aging processes within these materials

SNL has a unique predictive capability to help assess consequences of aging in glasses

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?
- Highlights of Current Work
  - Materials
  - Volume and mechanical response changes associated with aging
  - Role of chemical oxidation on mechanical response
  - 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

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

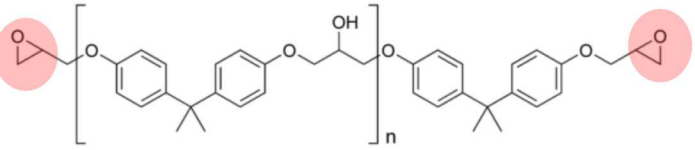
- Currently testing Sandia's non-linear viscoelastic modeling capabilities against aging data

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

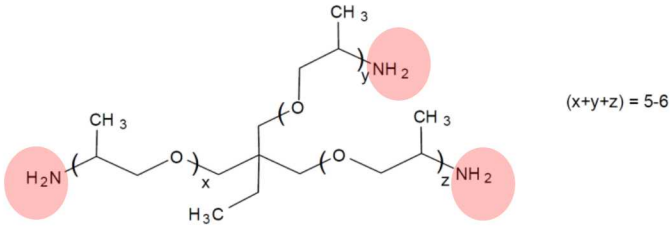
Materials

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

EPON® Resin 828
Diglycidylether of Bisphenol-A



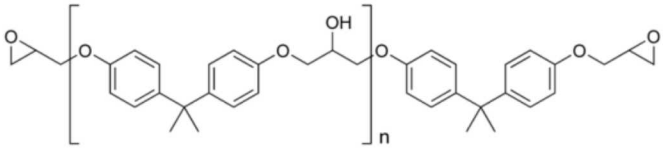
Jeffamine® T-403 Polyetheramine



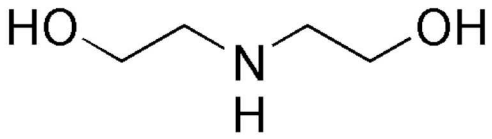
(x+y+z) = 5-6

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

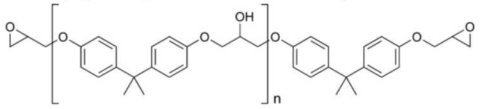
T_g ~ 90C
(when mixed stoichiometrically epoxy-amine)

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

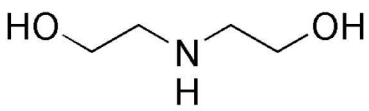
828/DEA[1]

EPON® Resin 828
Diglycidylether of Bisphenol-A



100 pbw

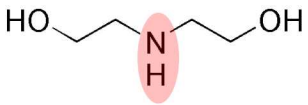
Diethanolamine



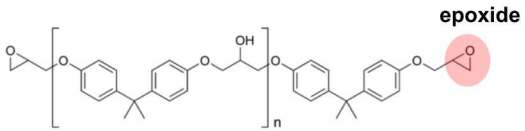
12 pbw

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

Adduct-Forming Reaction



secondary amine



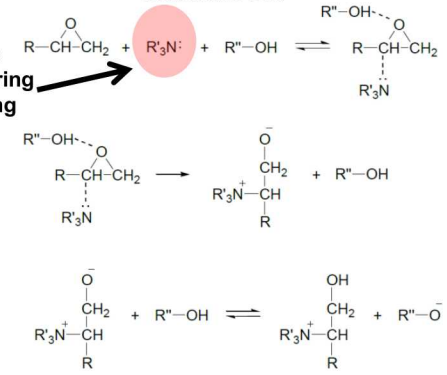
epoxide

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

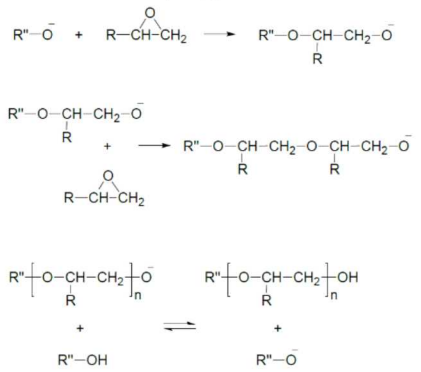
Proposed Gelation Reaction

Initiation

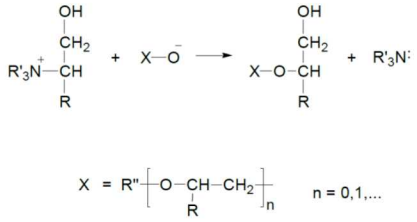
tertiary amine generated during adduct-forming reaction



Propagation



Termination



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

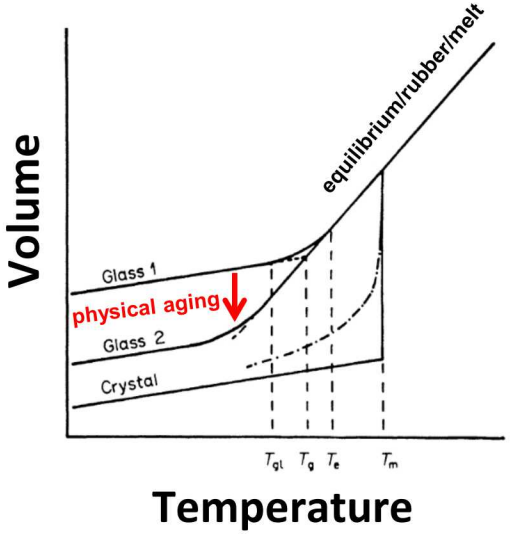
T_g ~ 70°C

J.D. McCoy et al., *Polymer*, 2016, 105, 243
J.D. McCoy et al., *Thermochimica Acta*, 2019, 671, 149

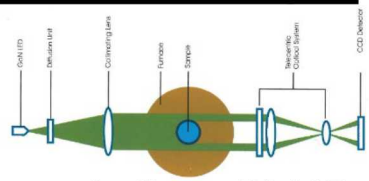
[when mixed 100:12 (pbw) 828:DEA and cured 24 hours at T=70°C]

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

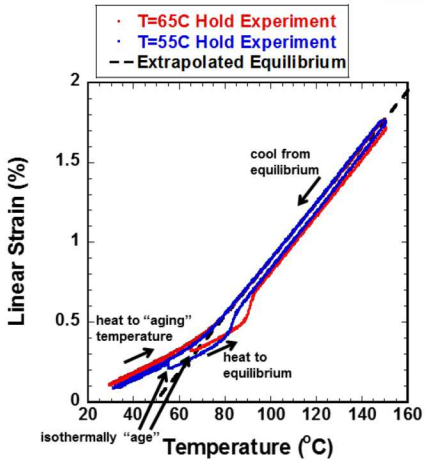
Polymer Glass Aging



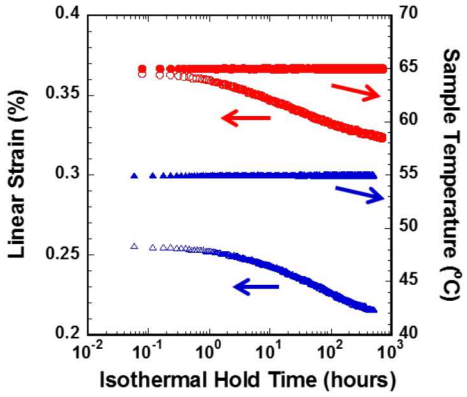
Material Volume Changes



optical resolution

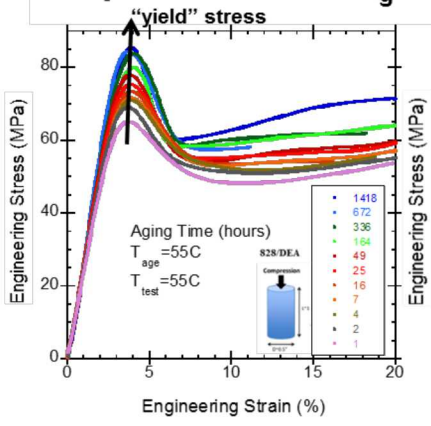


Isothermal Hold Response

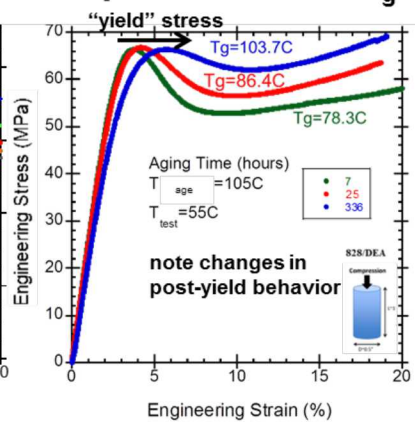


Material Mechanical Response Changes

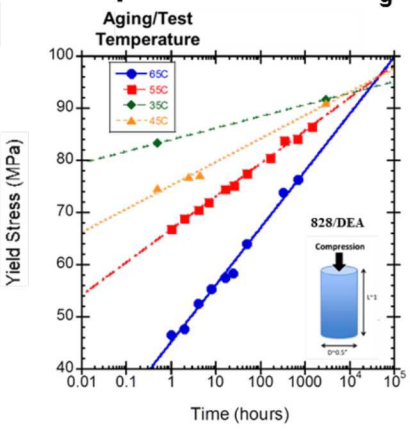
Exposure Below T_g



Exposure Above T_g



Exposure Below T_g

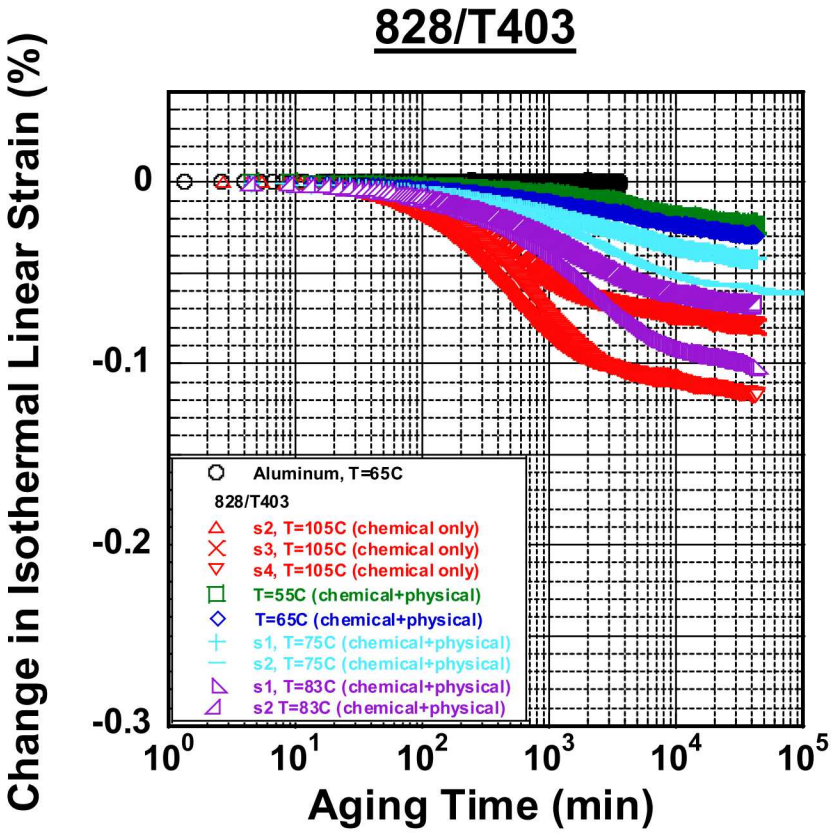


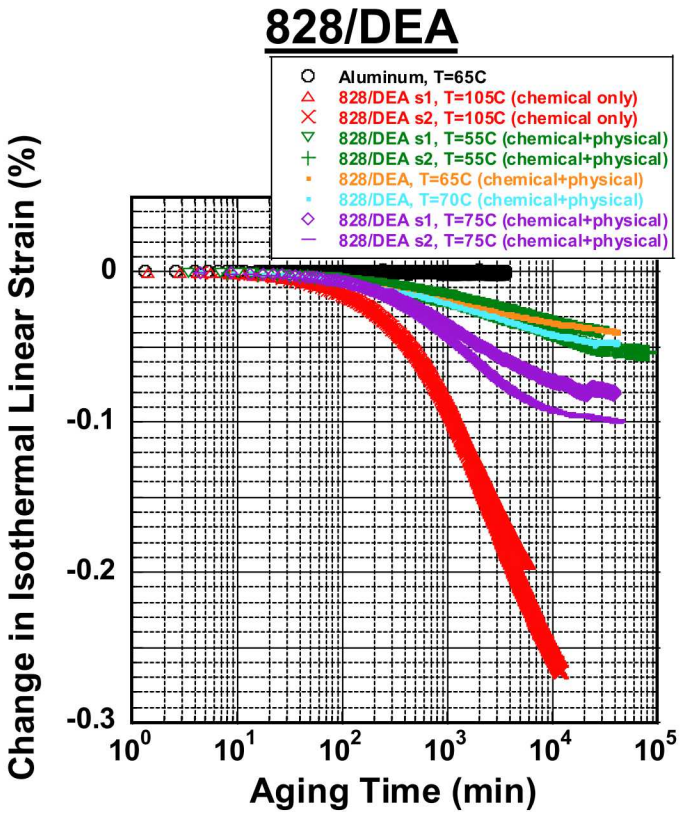
Kropka and Long, *Polymer*, 2018, 145, 54
Clarkson, McCoy and Kropka, *Polymer*, 2016, 94 19
G. Arechederra, *MS Thesis*, 2017.
K. Wilson, *MS Thesis*, 2018.

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

Volume

Isothermal Volume Response for 2 Common Epoxy Thermosets



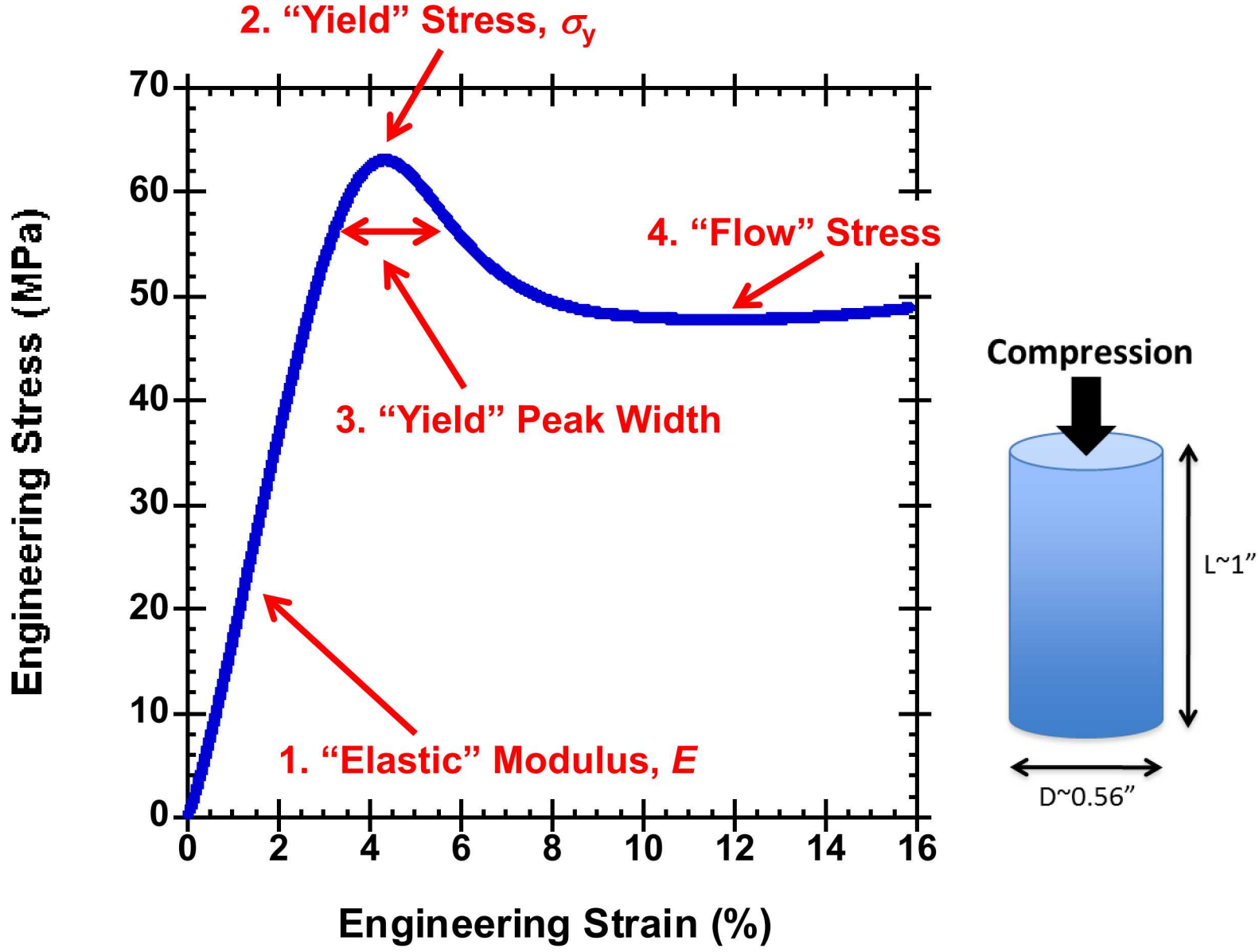


Note: Remaining reactive potential (excess epoxide groups in the case of 828/DEA) can play a significant role in total volume change

- 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

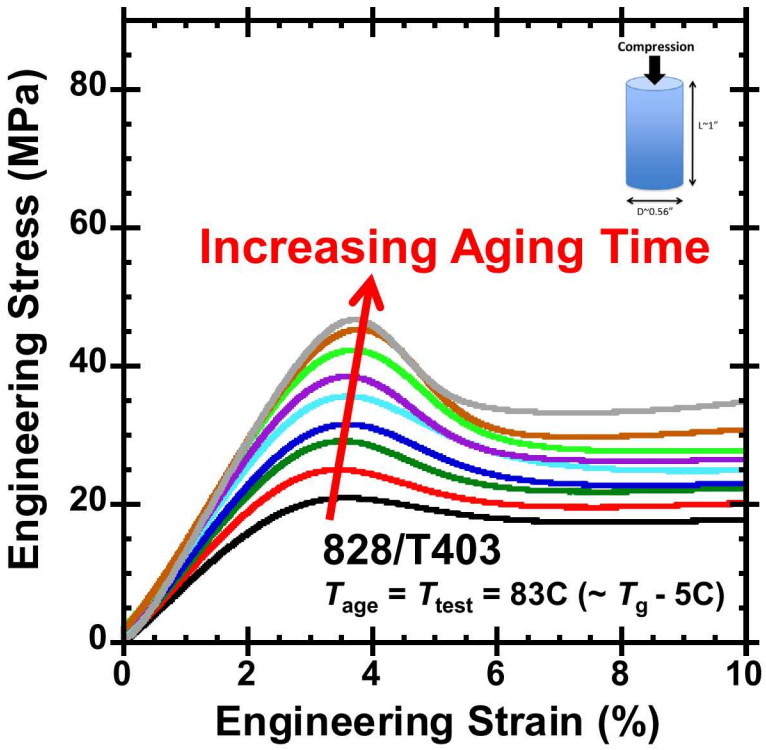
Mechanical

Anatomy of Compressive Stress-Strain Response of Glassy Polymers

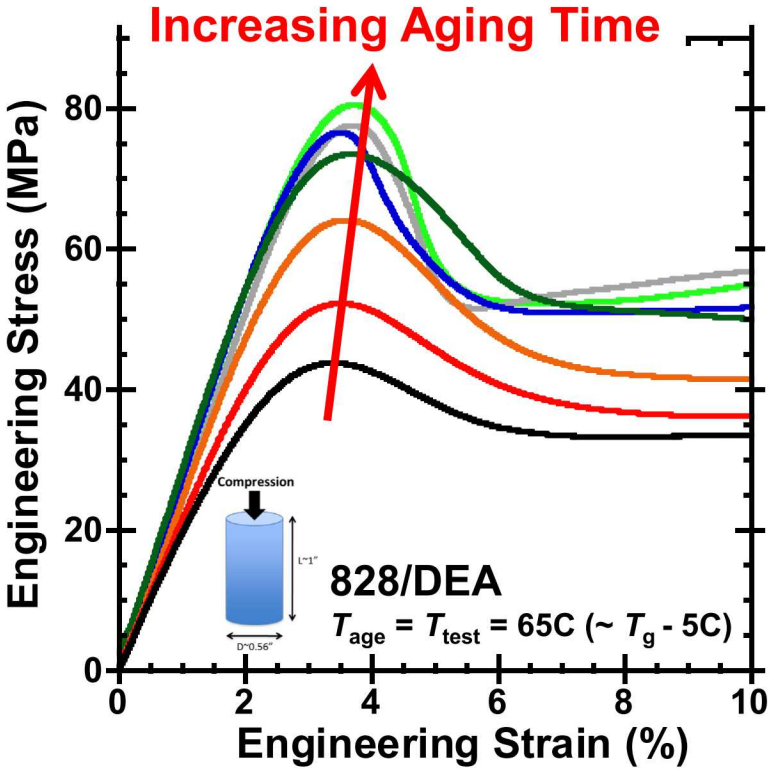


Changes in Compressive Stress-Strain Response Associated with Thermal Aging

Physical Aging Only?



Chemical + Physical Aging Mechanisms?

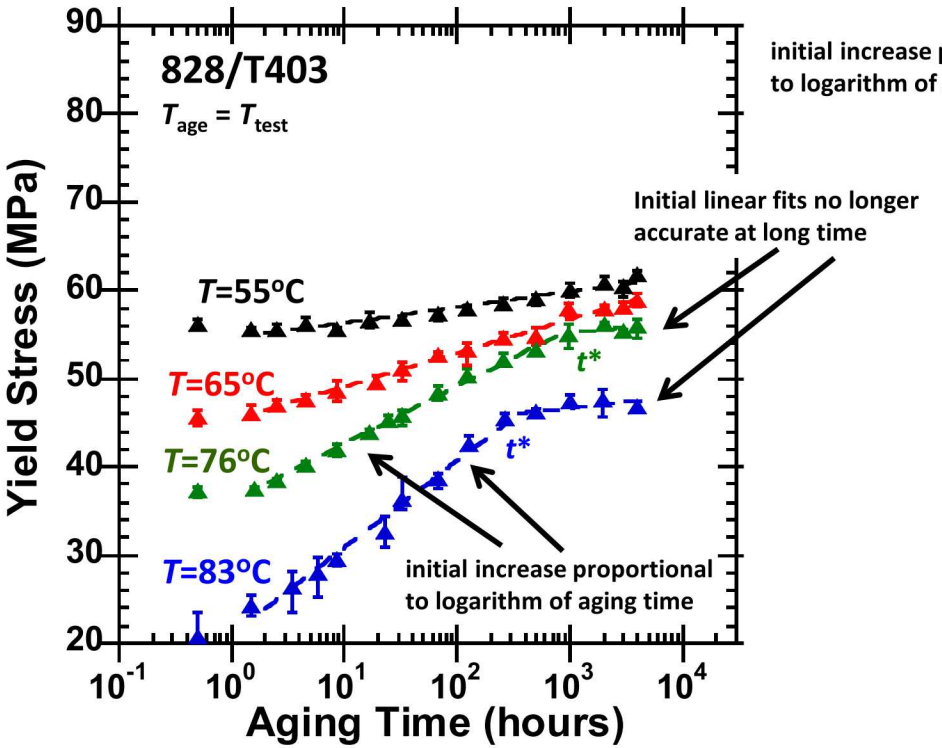


4 Distinguishable Changes in Compressive Stress-Strain Response Include:

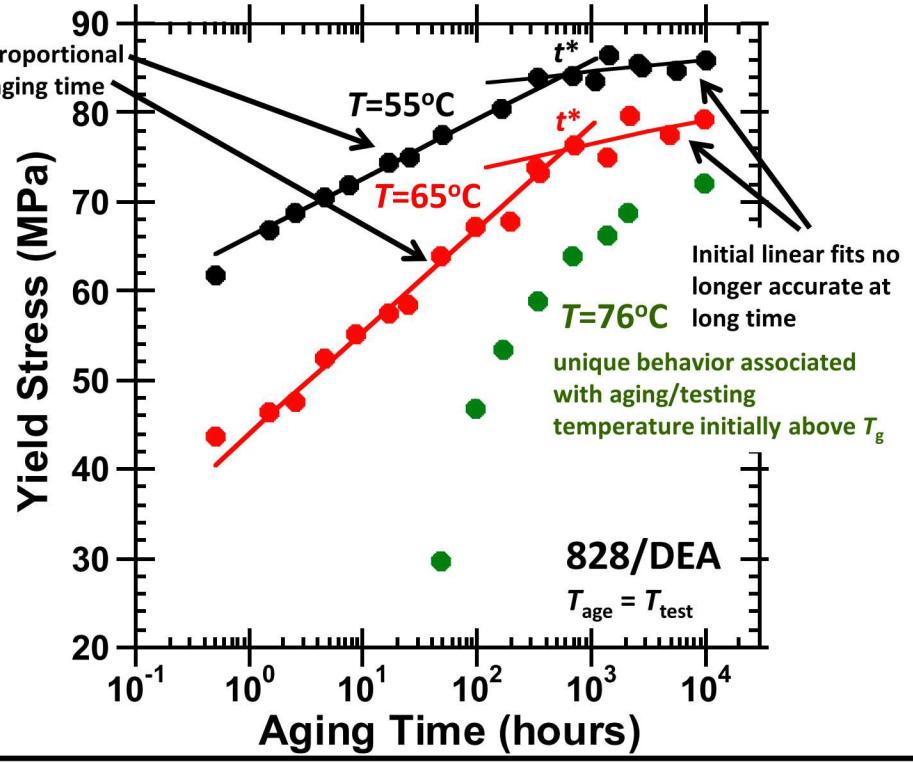
- Increase in "elastic" compressive modulus
- Increase in "yield" stress
- Narrowing of "yield" peak
- Increase in "flow" stress

Evolution of Yield Stress during Thermal Aging

Physical Aging Only?



Chemical + Physical Aging Mechanisms?



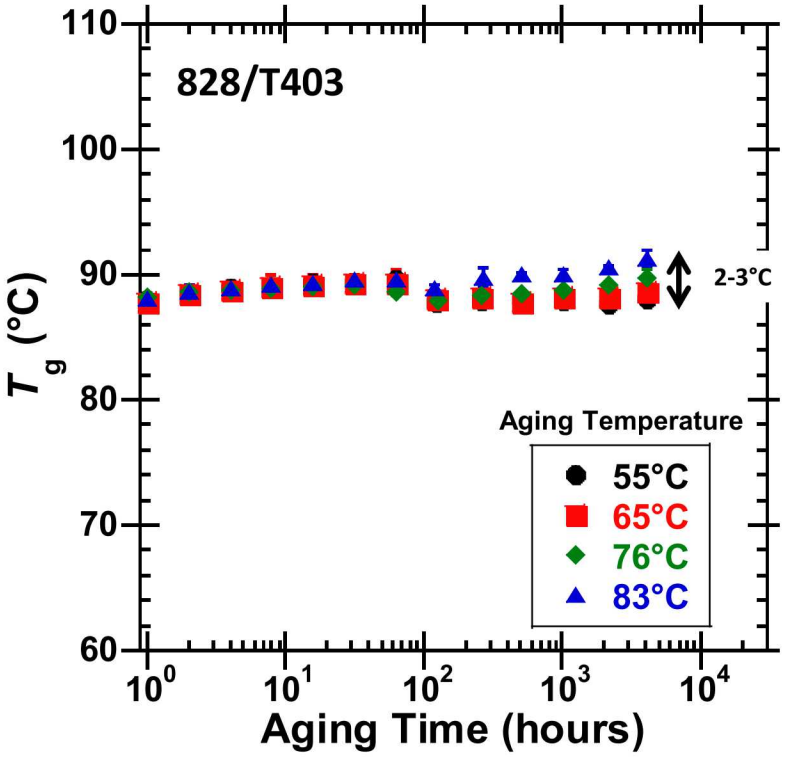
Findings:

- At a given T-T_g, 828/DEA exhibits a higher yield stress than 828/T403 (at all aging times). Thus, yield stress is not a universal function of T-T_g for all polymers and molecular structure plays a role in defining the stress-strain response.
- While changes in yield stress during isothermal aging are substantial for both materials, at approximately equivalent distances from T_g 828/DEA exhibits more marked narrowing of the "yield" peak (previous slide).
- When aged close to T_g, the evolution of yield stress with time changes (and possibly stops) at long times for both materials. For 828/T403, the increase in the time at which the change in evolution behavior occurs (t^*) is apparent as the aging temperature is decreased further below T_g. For 828/DEA, such a trend is more difficult to resolve.

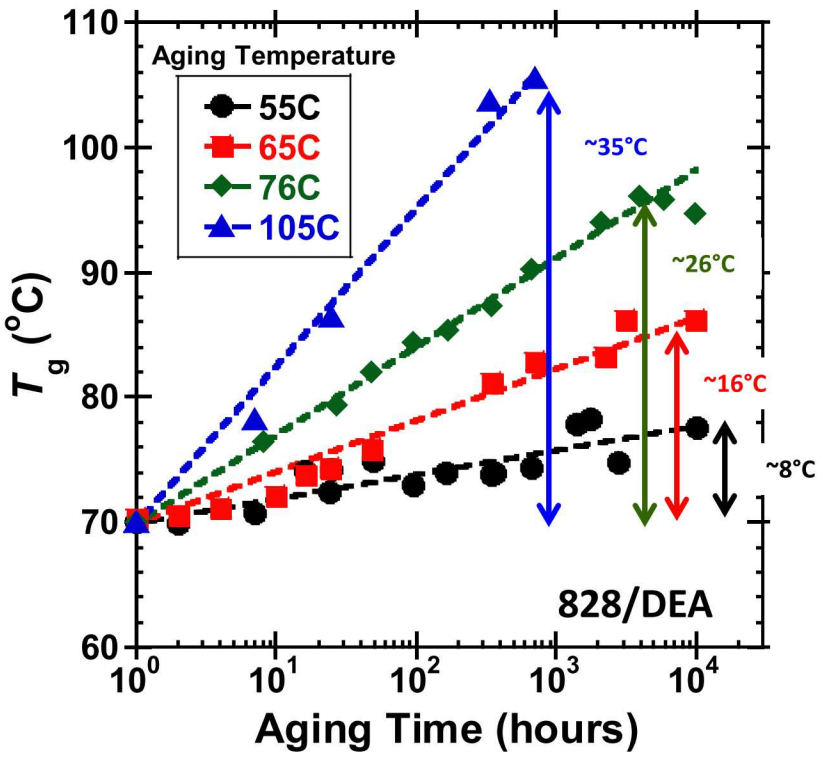
What is the mechanism(s) driving this change?

Signature of Chemistry Progression during Thermal Aging

Physical Aging Only!



Chemical + Physical Aging Mechanisms

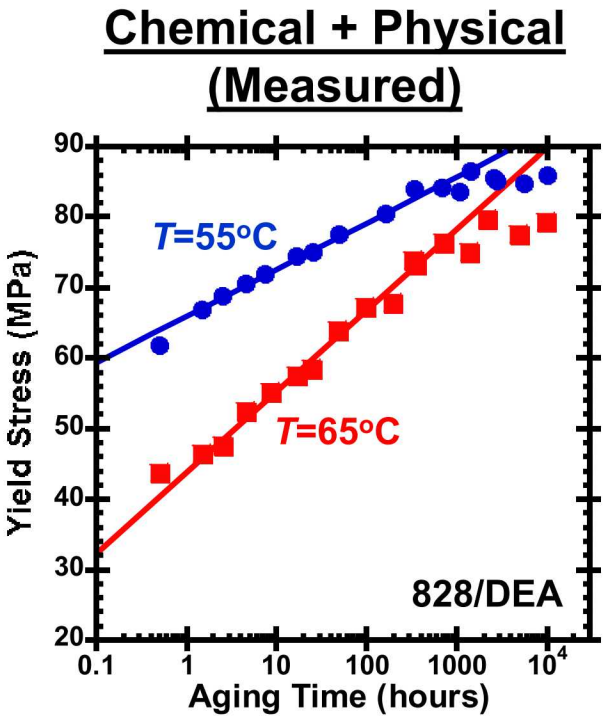


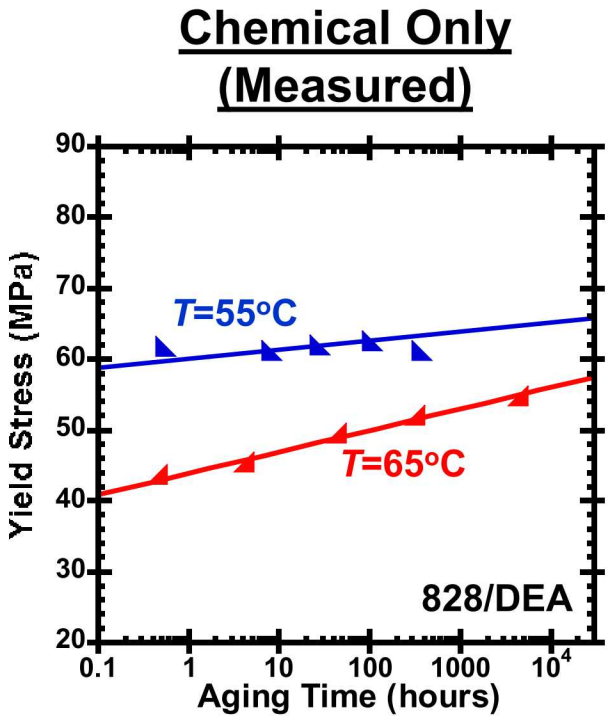
Findings:

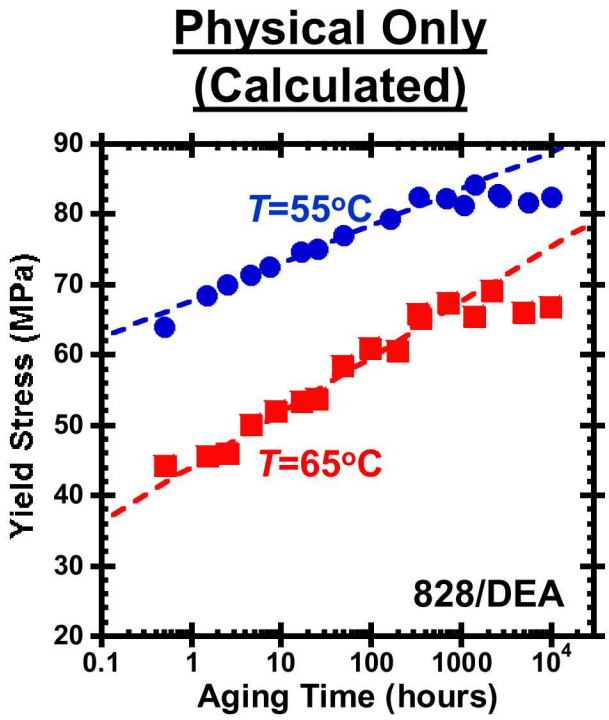
- The 2-3°C change in T_g for 828/T403 during aging is very small. This variation is typical of batch-to-batch variance.[1]
- The much larger changes in T_g for 828/DEA are associated with additional crosslink formation and are consistent with observations in previous work.[2]

1. C.M. Clarkson, J.D. McCoy and J.M. Kropka, *Polymer*, 2016, 94 19
2. C.V Lundberg, *Ind. Eng. Chem. Prod. Res. Dev.*, 1980, 19 319

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

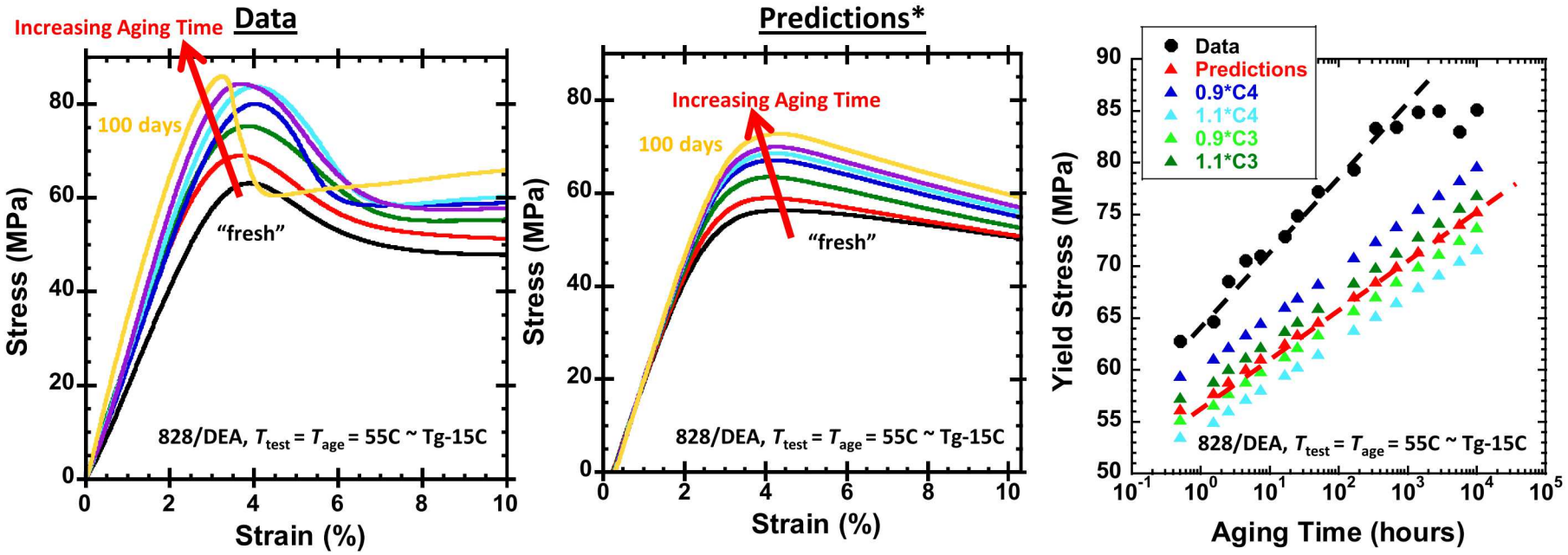






By thermally annealing the samples above the glass transition temperature (after aging), the physical history of the sample is erased and the chemical-only contributions to the evolution of the yield stress are resolved. Physical-only contributions are calculated by subtracting the chemical-only contributions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

Can We Predict Changes in Compressive Stress-Strain Response Associated with Thermal Aging?



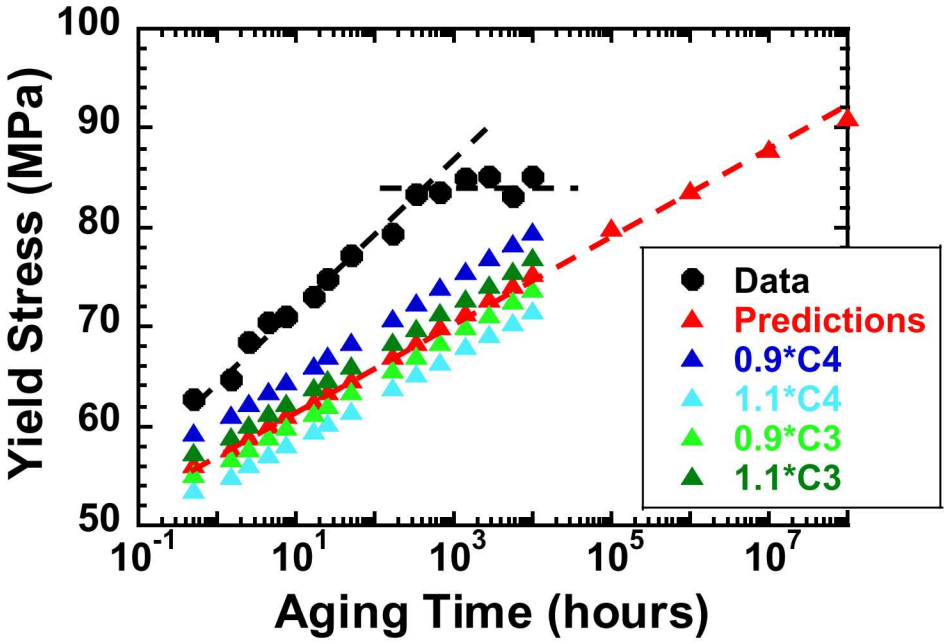
Findings:

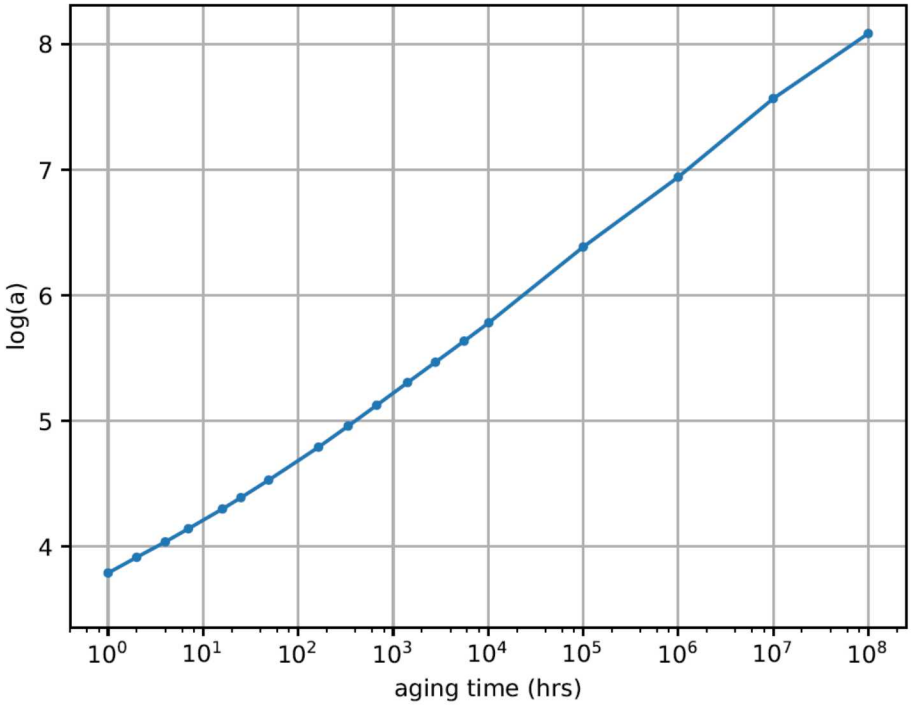
- The Simplified Potential Energy Clock (SPEC) model under predicts "yield" stress and yield stress evolution with aging time at temperatures close to T_g
- The SPEC model does not predict the slowdown in yield stress evolution with log(aging time) at the same time as observed in measurements

It is anticipated that model parameters can be tuned to better represent long-time aging behaviors

*1-element simulations will not predict post-yield behavior

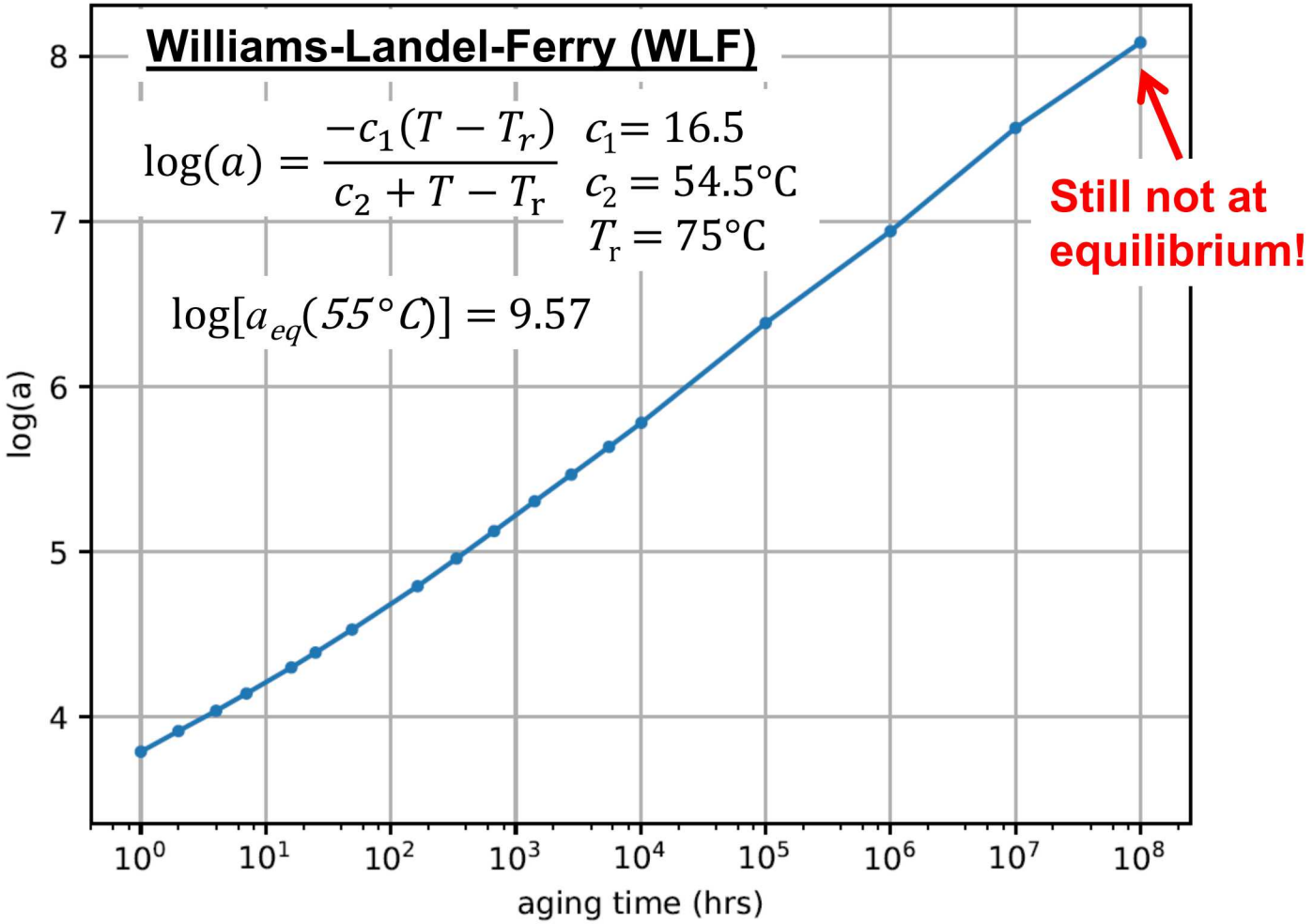
Why Doesn't SPEC Model Predict Change in Yield Stress Evolution?





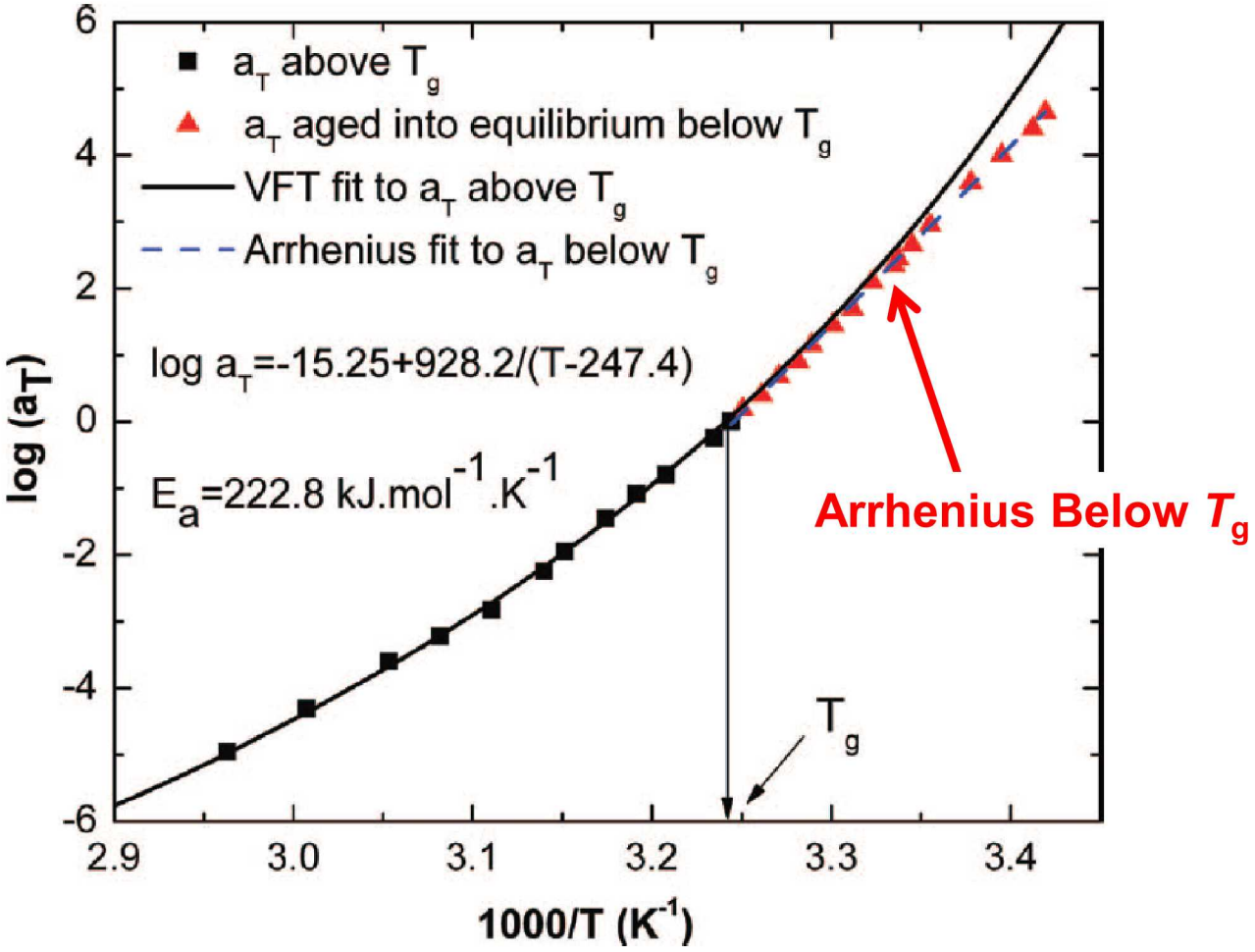
SPEC does not reach equilibrium to 10^8 hours, 5 orders of magnitude longer than experiments

What is Equilibrium in SPEC Model?



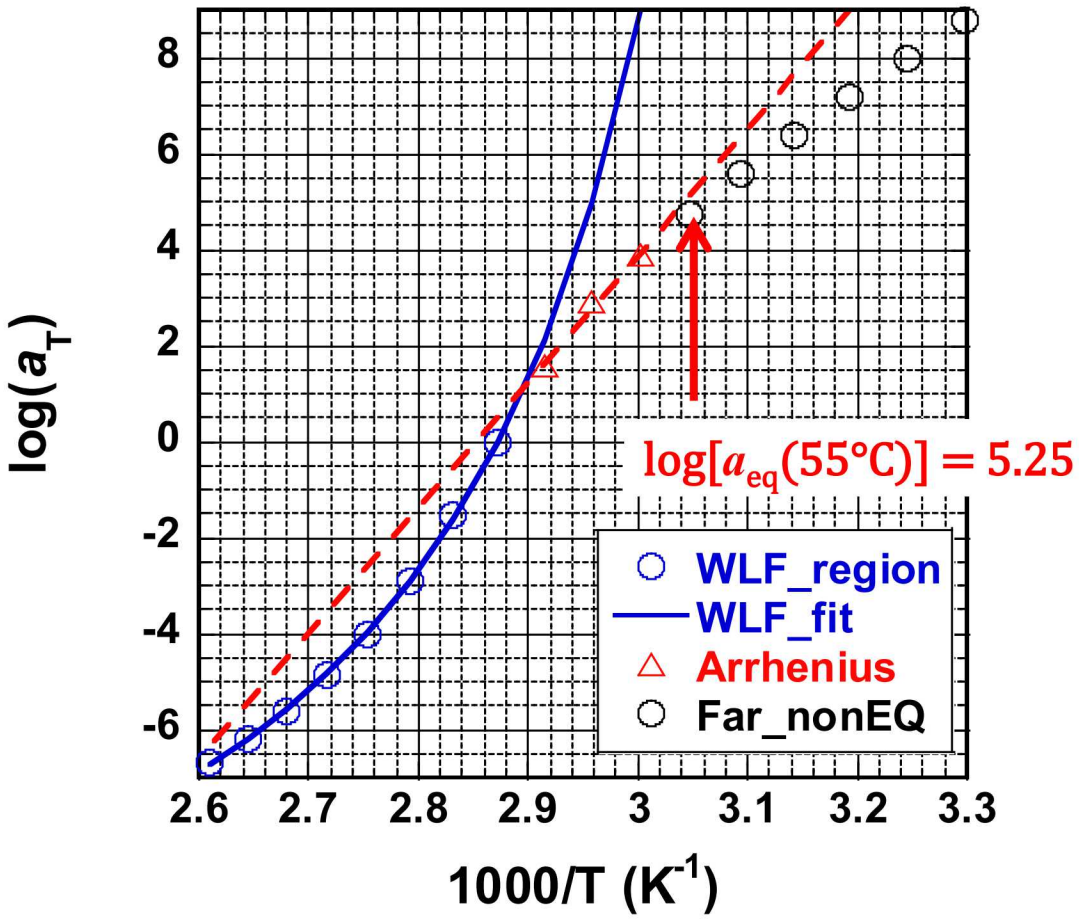
Is WLF valid below Tg?—note divergence when $T = T_r - c_2 = 20.5°C$

Proposal for sub-T_g Equilibration



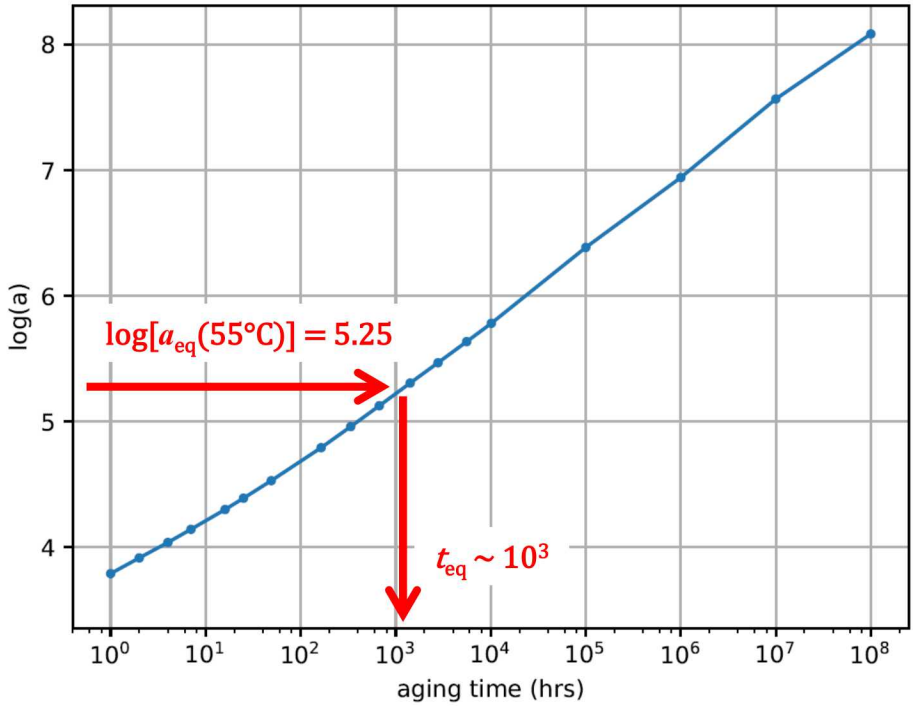
J. Zhao and G.B. McKenna, *J. Chem. Phys.*, 2012, 136, 154901

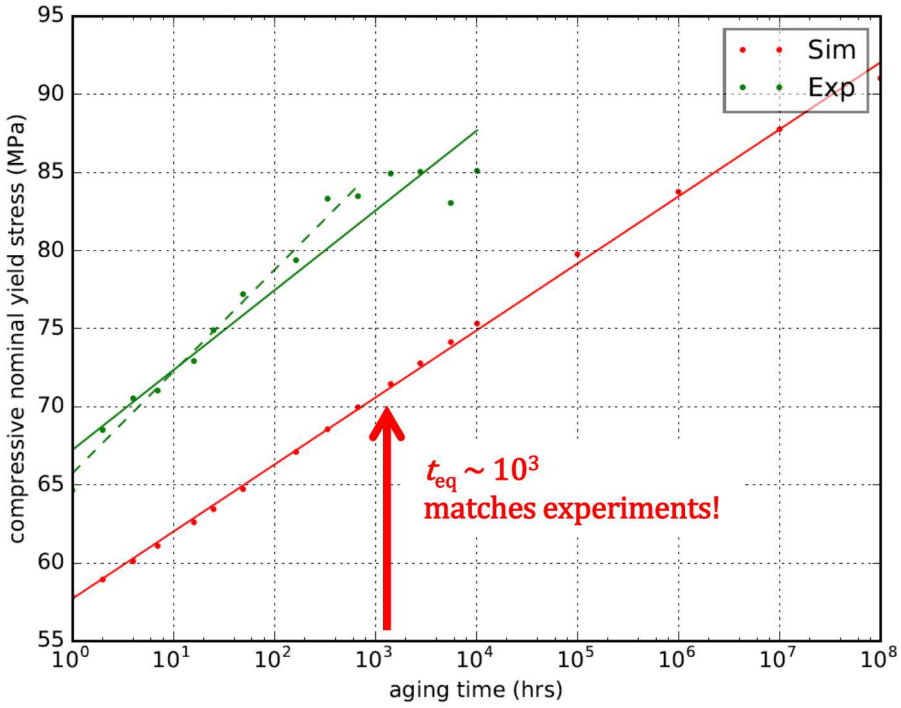
Apply Arrhenius sub-T_g Equilibration to 828/DEA



What would this imply to SPEC yield stress evolution prediction?

How Does Arrhenius sub-T_g Equilibration Reduce Experiment-SPEC Model Discrepancy





Quite Promising!

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 115%) of the 828/DEA and 828/T403 materials 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 and fracture toughness during isothermal aging
- Distinguished the importance of molecular structure on yield stress and yield stress evolution with aging (e.g., limitations to material equivalence at same T-T_g)
- Identified a “model”, physical aging only, epoxy material
- Demonstrated the ability of NLVE model to predict yield stress evolution associated with physical aging

Other Areas of Progress to Learn About Soon

- **Tuning of SPEC model parameters to better represent long-time aging and identification of the impact to predictions of other material behaviors**
- **Aging of epoxy composites versus neat epoxies**
- **Aging under mechanical AND thermal environments**
- **Effects of chemical oxidation on epoxy failure**

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

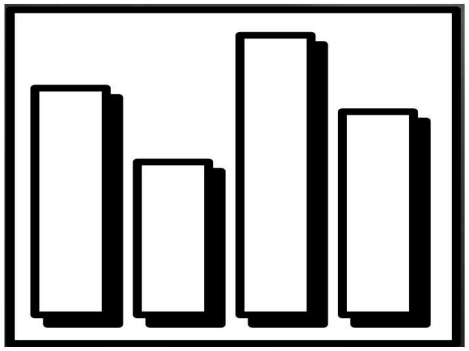
Extras…if time allows

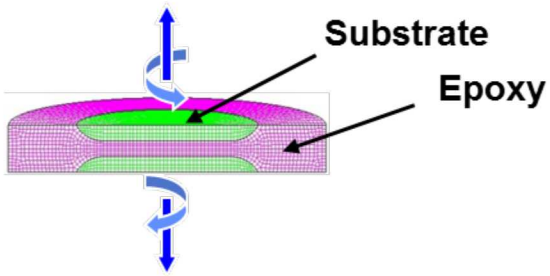
Impact of Aging on Bond Strength

Adhesive Strength Tests

Initiation of Failure

Saucer Test Geometry

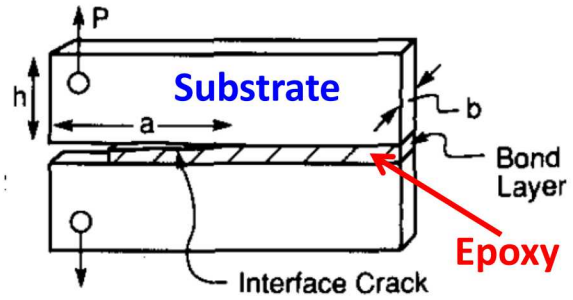




Initial focus on tensile loading only
(it may be the most sensitive to aging)

Interfacial Fracture

Asymmetric Dual Cantilever Beam (ADCB)



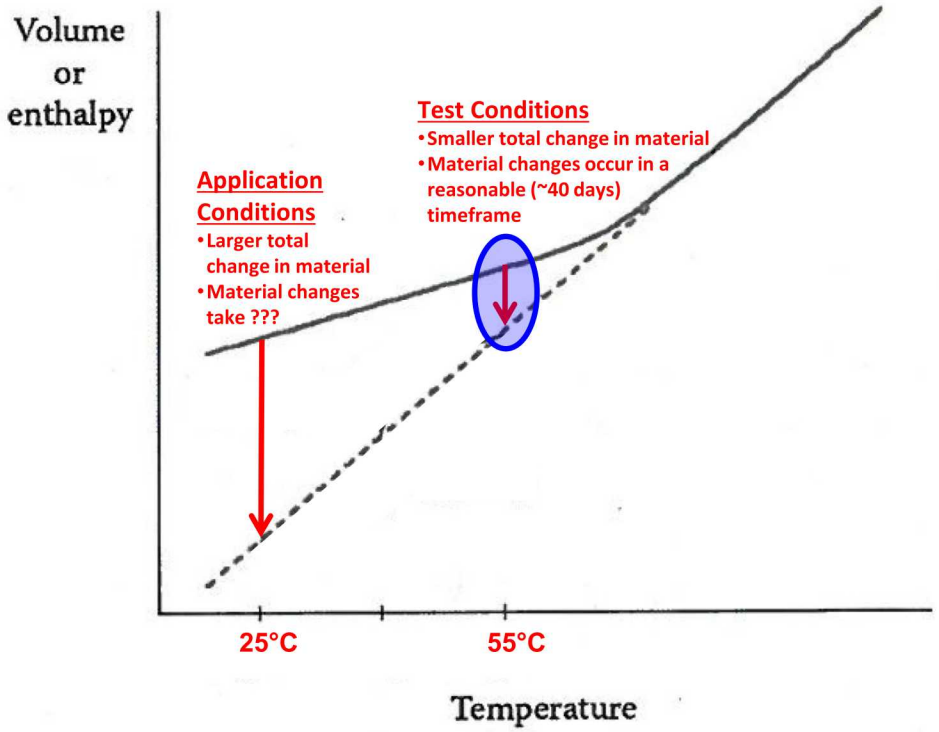
Adhesive (828/DEA) K_{Ic} changes, what about interfacial fracture?

D.B. Adolf et al., *J. Adh.*, 2006, 82 63

A.G. Evans et al., *Mater. Sci. Eng. A*, 1990, A126 53

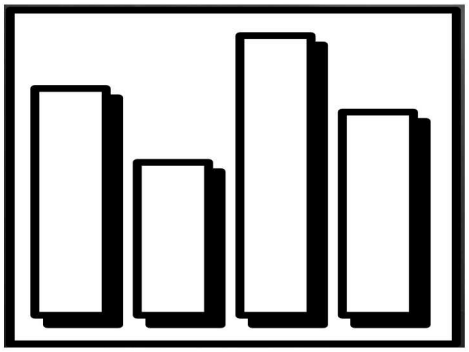
Adhesive Strength Tests: Dependence on Aging

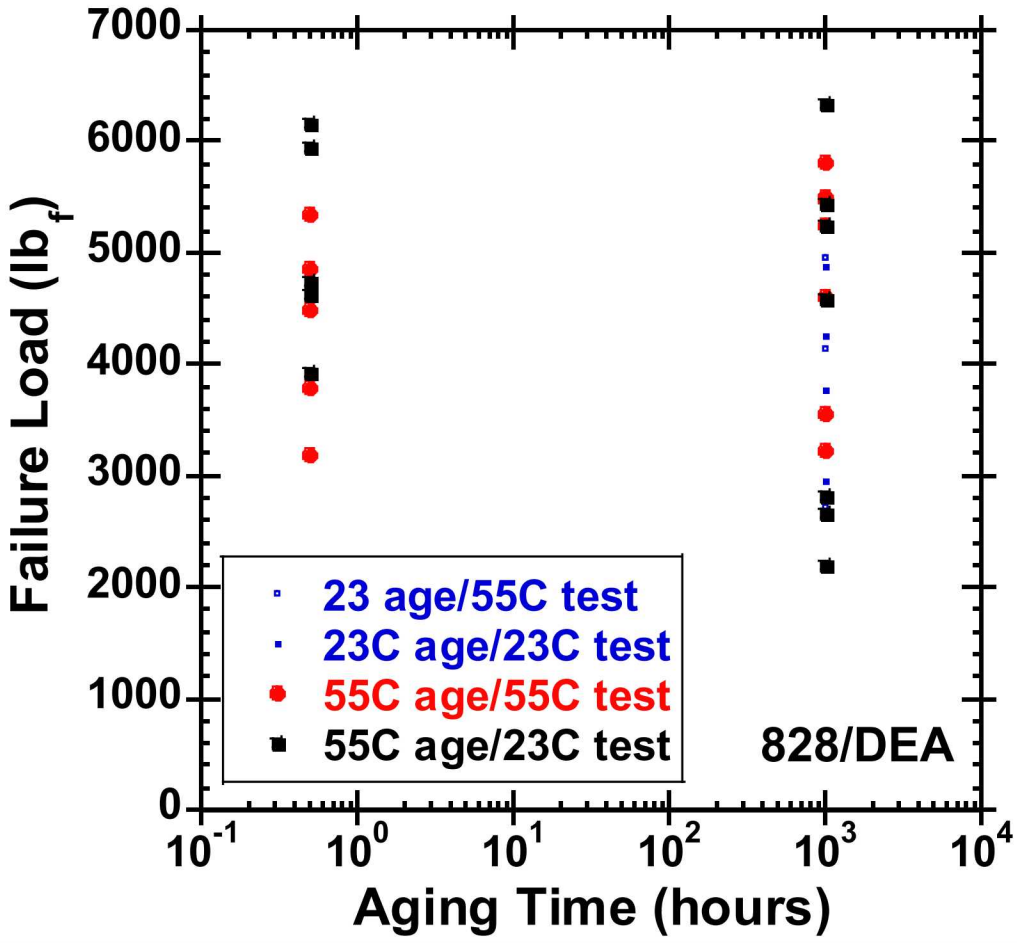
Aging Conditions



If changes in bond strength are observed during aging at 55C, then need to assess the timescale over which changes would be anticipated at T=25C

Scoping Tests: Dependence of Initiation of Failure on Aging



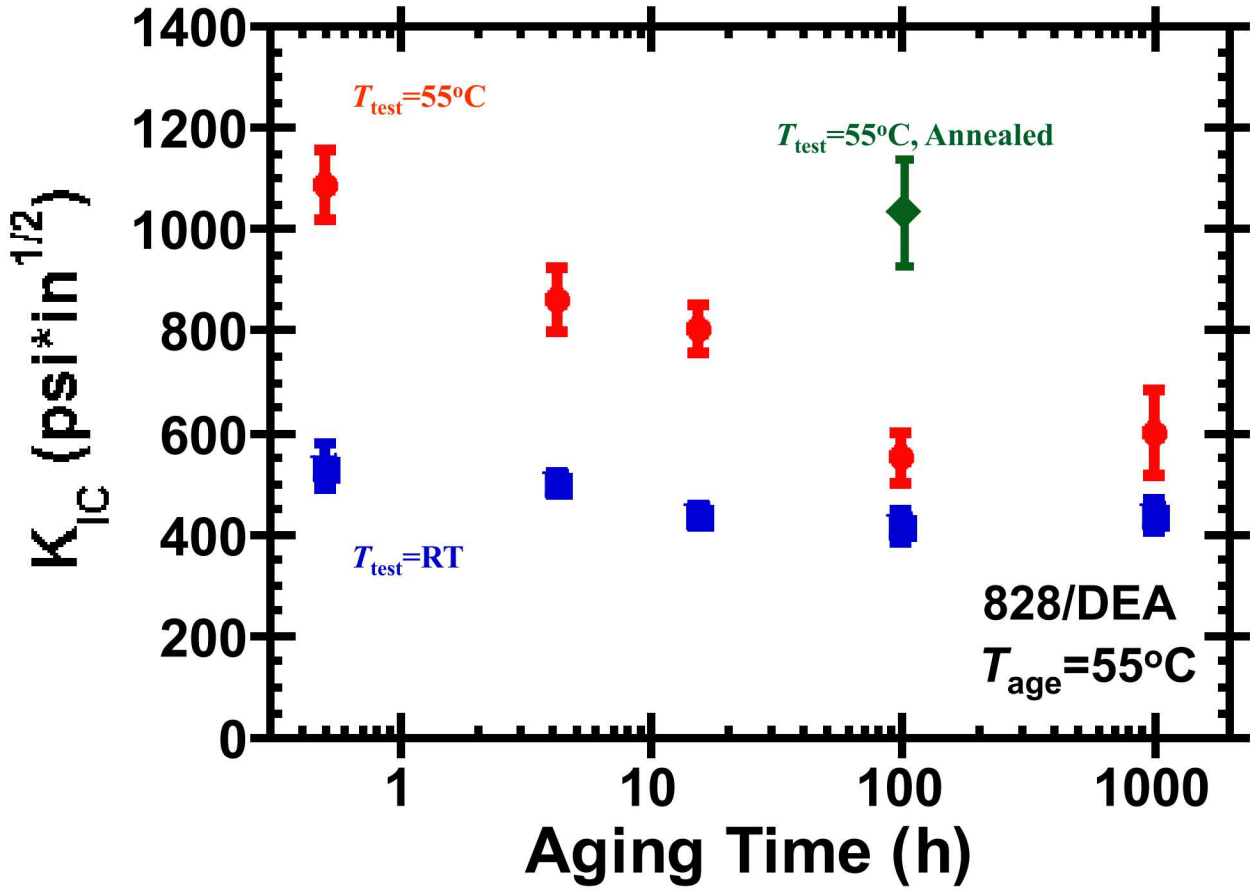


Findings:

- Considerable scatter in the data
- No significant change can be resolved within experimental uncertainty

Find a test that gives a narrower distribution of the strength measure

Adhesive Fracture Toughness: Dependence on Aging



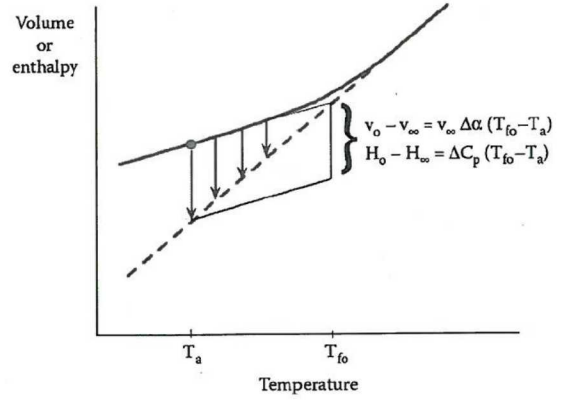
Fracture Toughness Changes Occur Over the Same Timescale as Yield Stress Changes and are Associated with Structural Relaxation

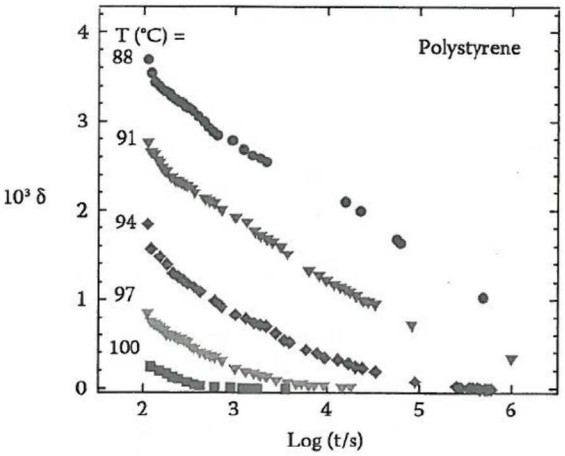
Interfacial Fracture Toughness: Dependence on Aging

Results Coming Soon!

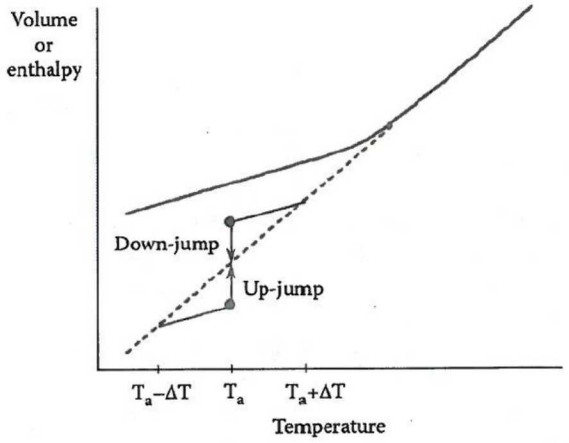
Signatures of Structural Recovery/Relaxation

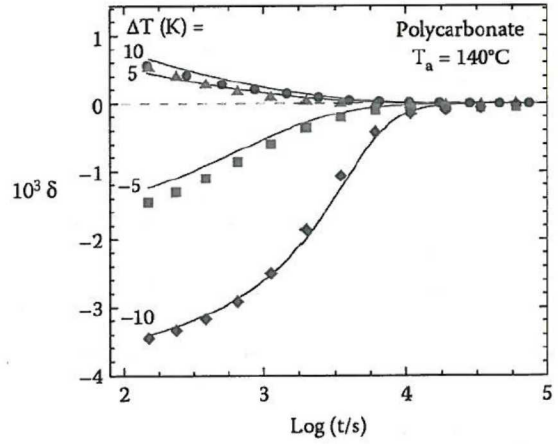
Intrinsic Isotherms



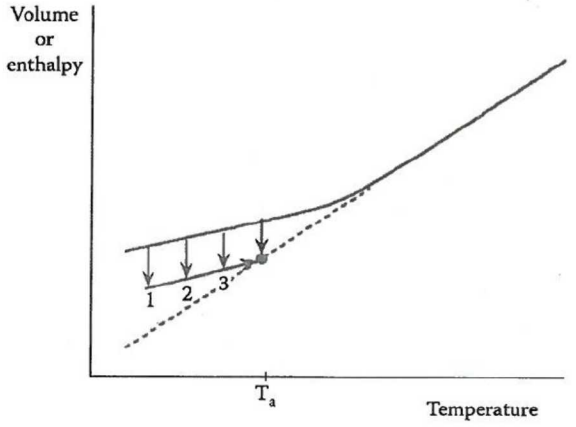


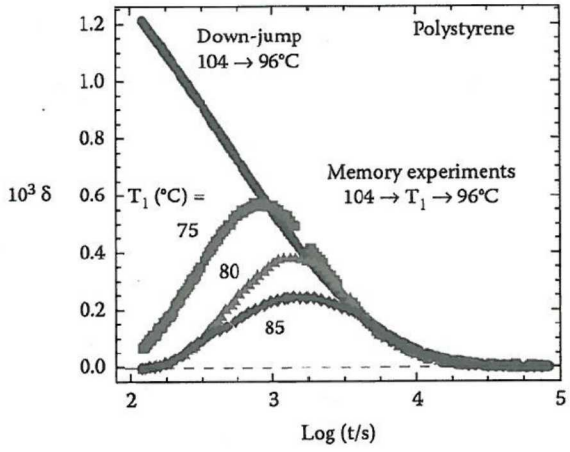
Asymmetry of Approach





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

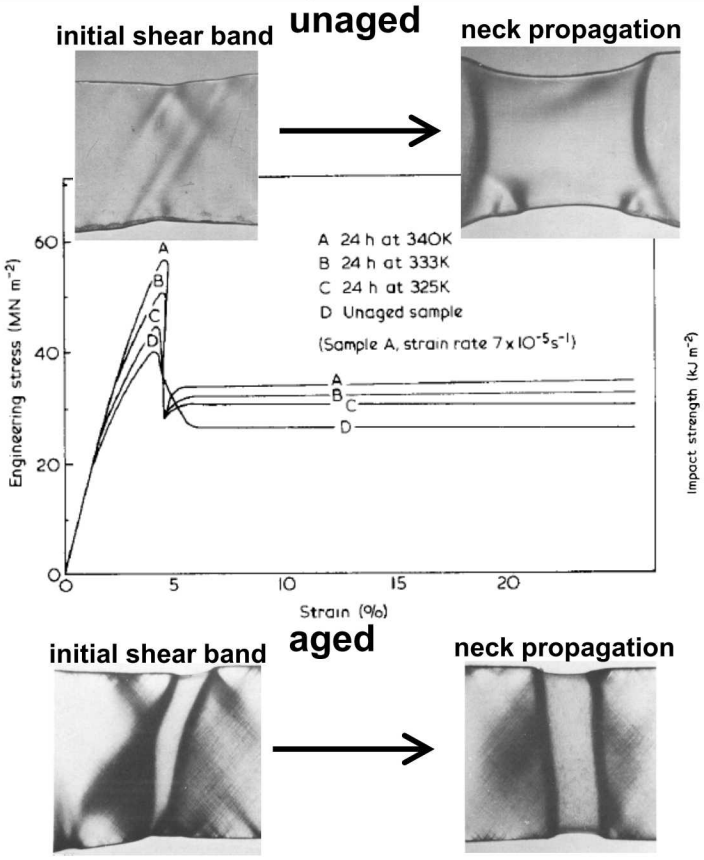
Simon and McKenna, Structural recovery and physical aging of polymeric glasses, in **Polymer Glasses**, 2017

Impact of Structural Recovery and Physical Aging

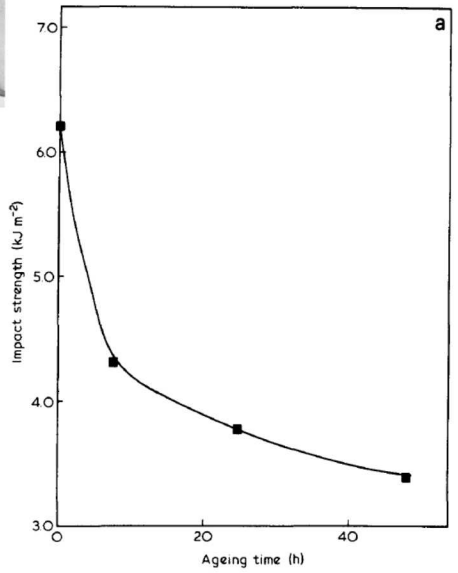
"Failure modes of polymers can change from ductile to brittle failure with aging"

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"

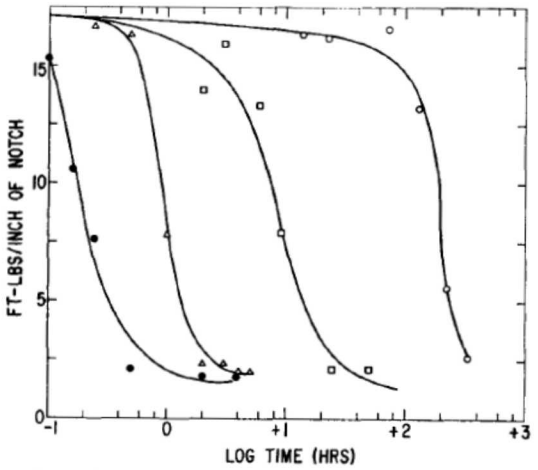


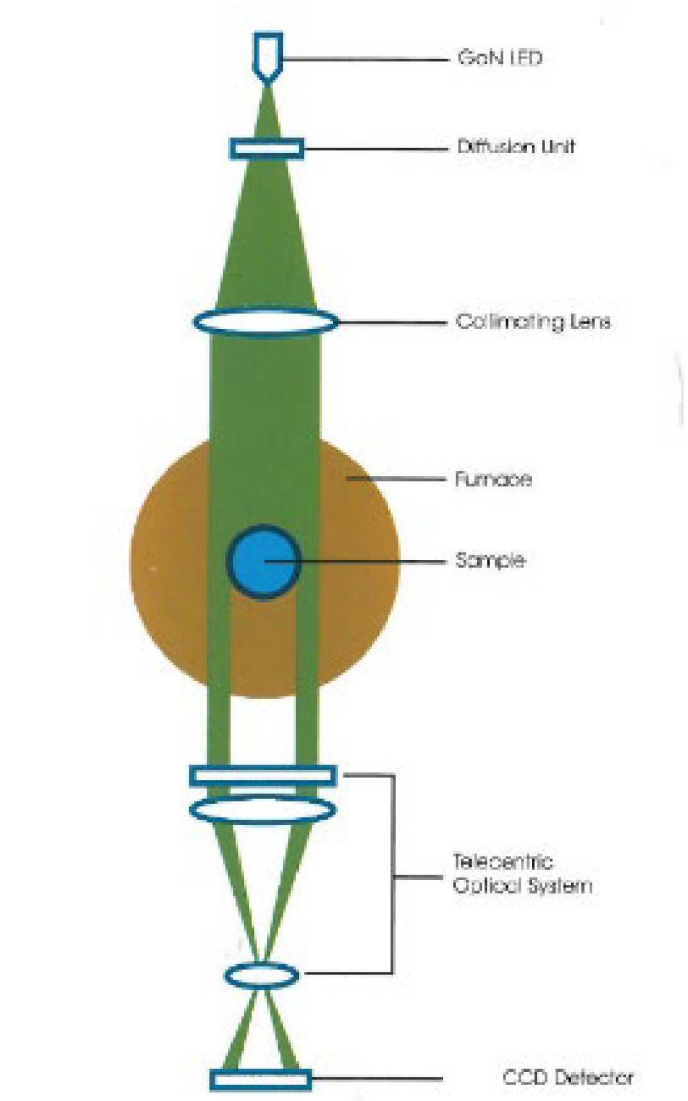
Fig. 3. Effect of annealing temperature on Izod impact data. ○) 100; □) 115; △) 125; ●) 130; [η] = 0.58.

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

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

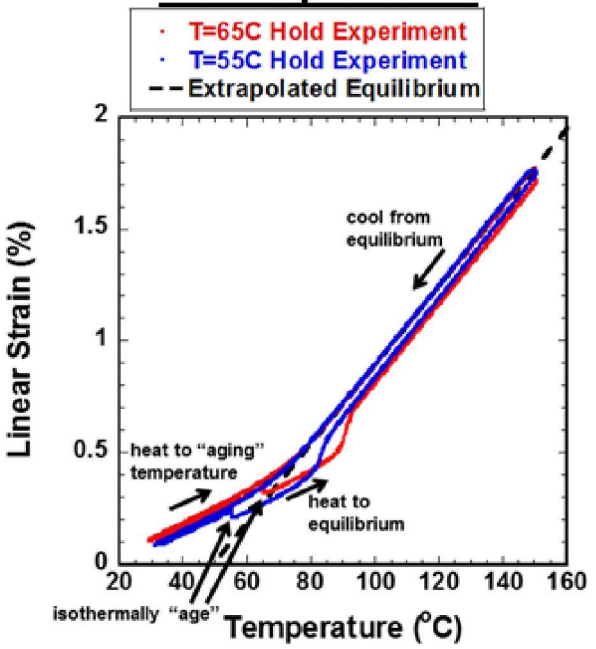
Measuring Volume Response Associated with Aging

Optical Resolution of Length*

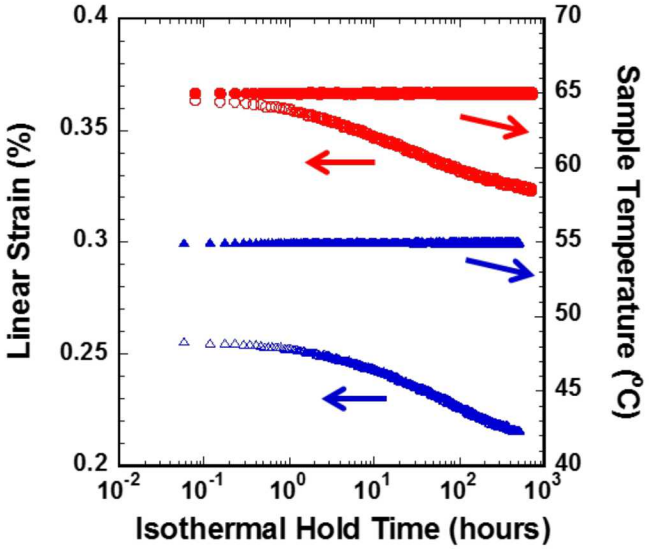


*for isotropic materials $\Delta V = 3\Delta L$

Full Experiment

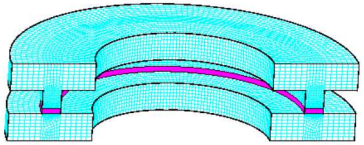


Isothermal Hold Response



Adhesion Failure Tests

Napkin Ring



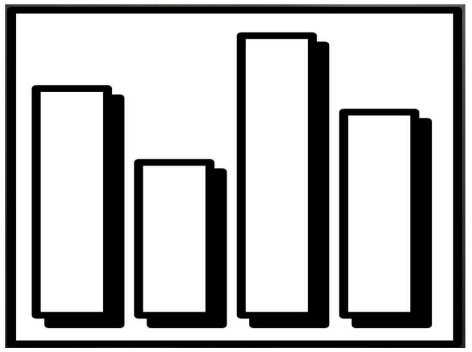
- Shear loading only (torsion)

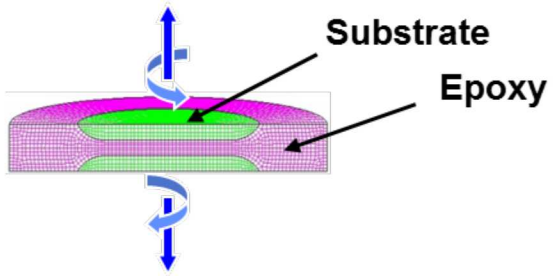
test geometries to measure initiation of adhesive failure

3-D Finite Element Models

- air interface is ill-defined
- induce initiation at an embedded surface

Saucer Design

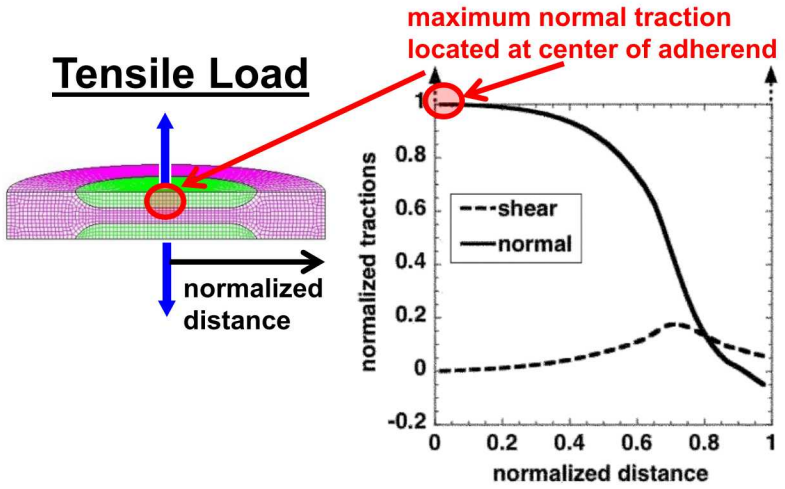


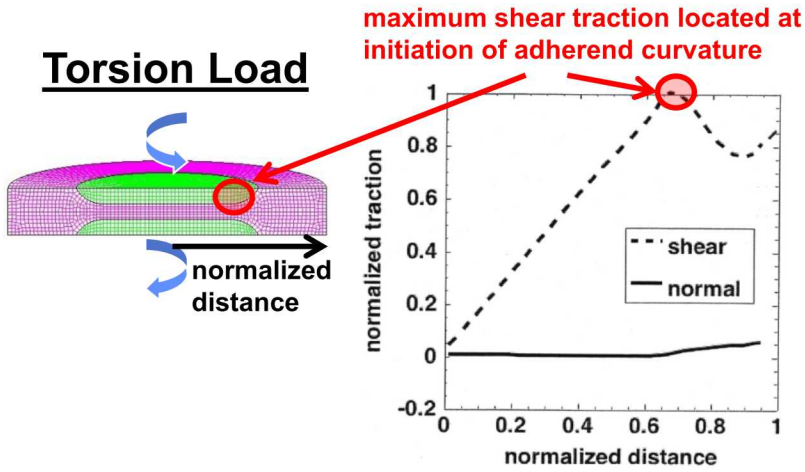


- Shear
- Tension/Compression
- Combined

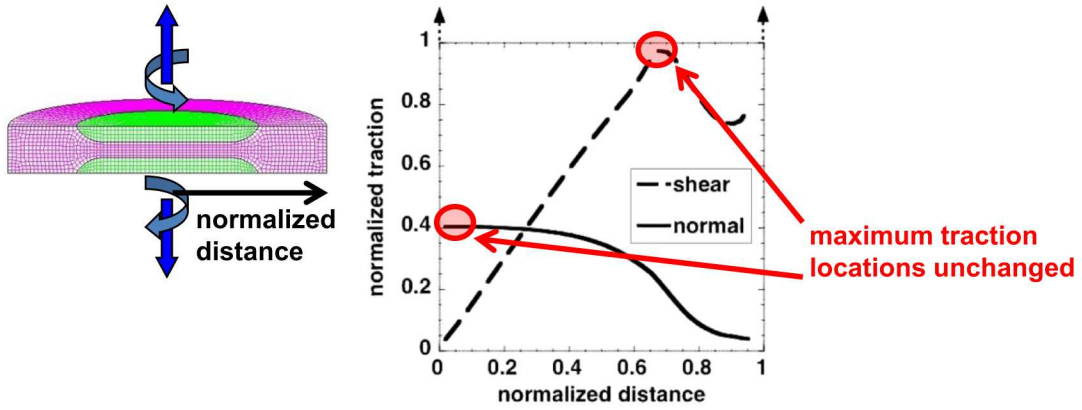
Why “Saucer” Adhesion Test Geometry

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



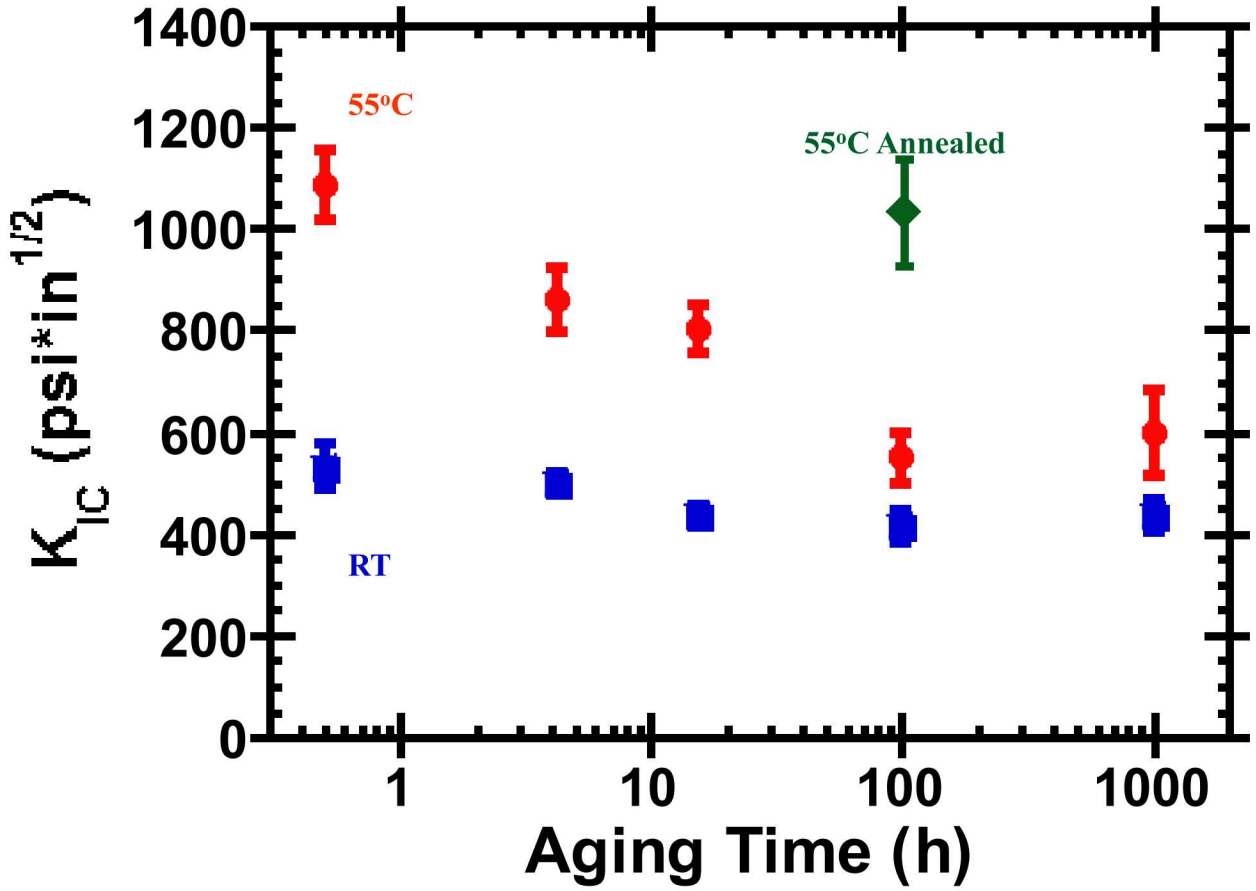


Combined Load (0.6% tensile strain + 1% shear strain)



2. Max stresses are smooth functions, not “spiked”
3. Sample allows for mixed loading modes: tension, compression, shear, etc.

Fracture Toughness Changes with Aging Too



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