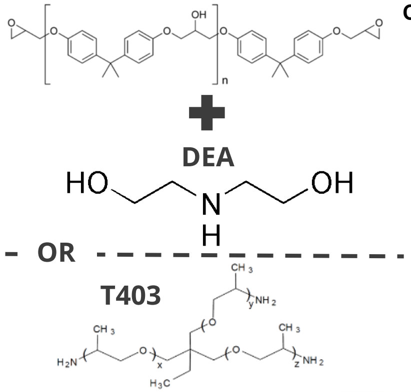
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2022-13373C

Sandia National Laboratories

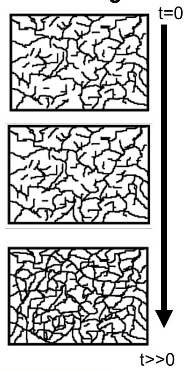
Chemical and Physical Aging in Epoxies

Materials

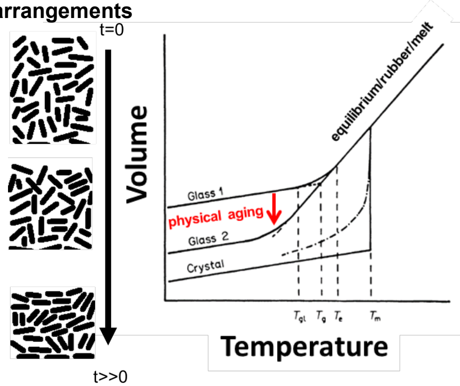


Chemical and Physical Aging

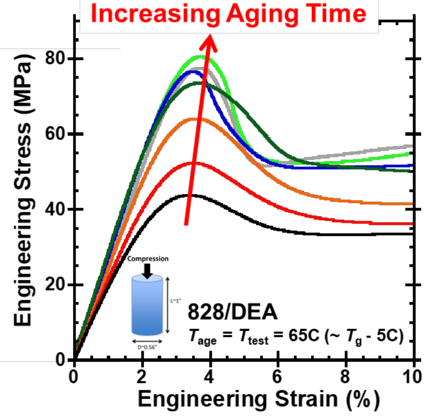
Additional Chemical Crosslinking



Physical or Structural Rearrangements



Thermal-Mechanical Response



Jamie M. Kropka, Gabriel K. Arechederra, Kelsey M. Wilson, Giovanni Gabaldon, John D. McCoy, Kevin N. Long, and Kenneth N. Cundiff

3rd International Conference on Polymer Science and Composite Materials
Rome, Italy October 2022

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

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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

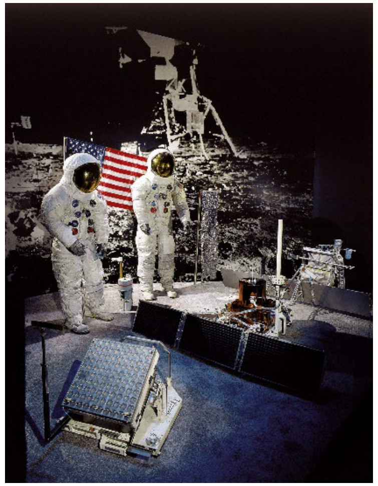
https://www.washingtonpost.com/news/energy-environment/wp/2018/06/20/a-giant-wave-of-plastic-garbage-could-flood-the-u-s-in-10-years-a-study-says/?noredirect=on&utm_term=.419f1f949e74
R. Geyer et al., *Science Advances*, 2017, 3 e1700782
A. Brooks et al., *Science Advances*, 2018, 4 eaat0131

"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

The Devil-is-in-the-Details Regarding the Situation at Hand

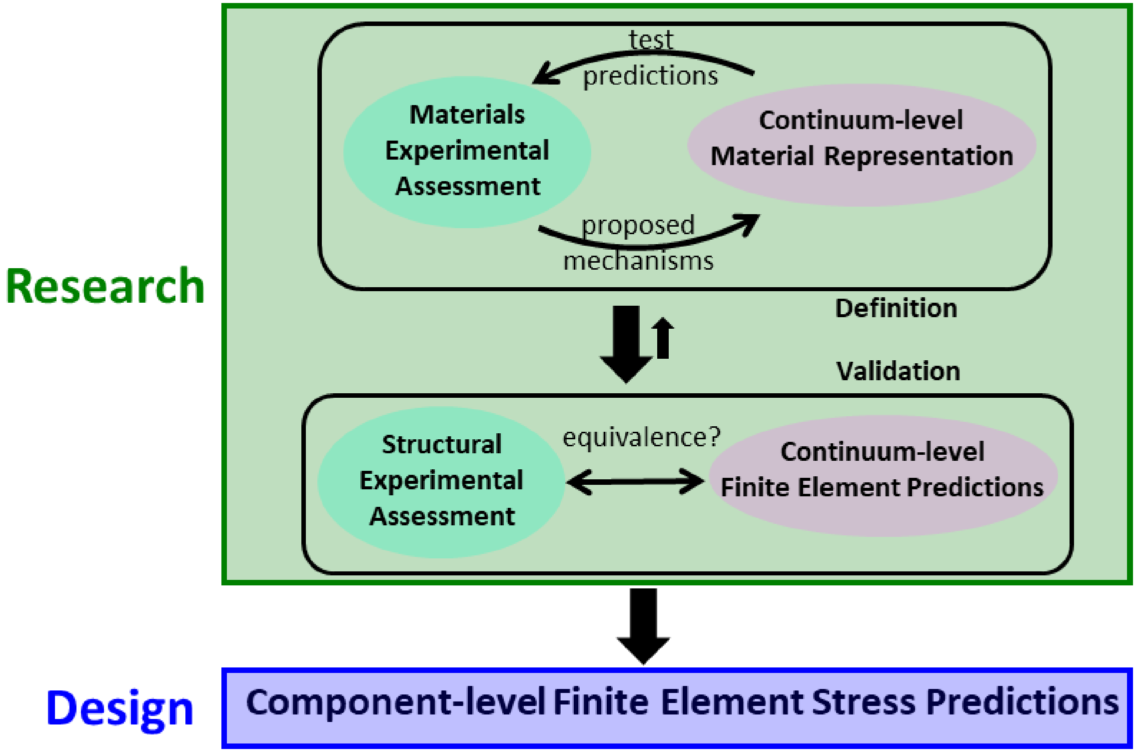
Who Cares if Polymers Age?

The US-DOE mission requires **guaranteeing the functional operation** of specialized devices over **lifetimes** that are **decades** long.

Polymers change via multiple mechanisms over this time sale

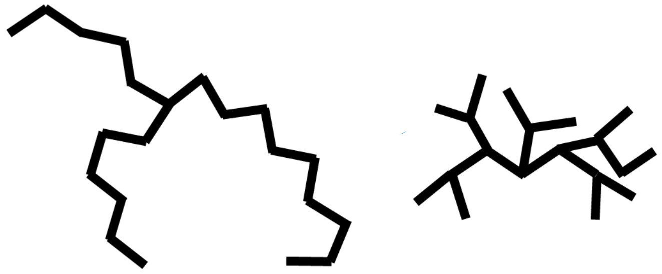
Contributing Mechanisms: physical aging, chemical oxidation, outgassing, reactive interactions, etc.
Resulting Effects: material embrittlement, evolving residual stress, cohesive/interfacial cracking, etc.

Need: predictive computational model to assess the broad range of geometries and conditions over lifetimes (the wide design space and long lifetimes are intractable experimentally)



There are 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 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!

"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

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

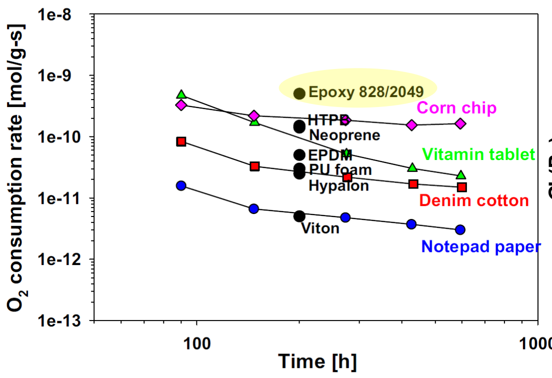
D.G. Legrand, *J. Appl. Pol. Sci.*, 1969, 13 2129

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

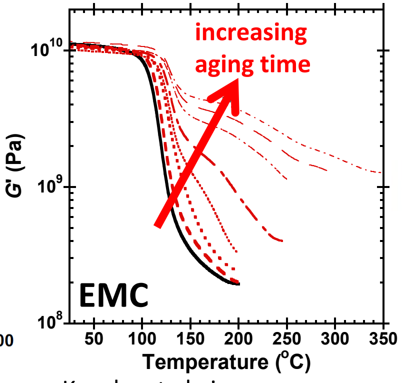
Sandia National Laboratories has a unique predictive capability to help assess consequences of aging in glasses

Examples of Polymer Aging Effects and Relevant Applications

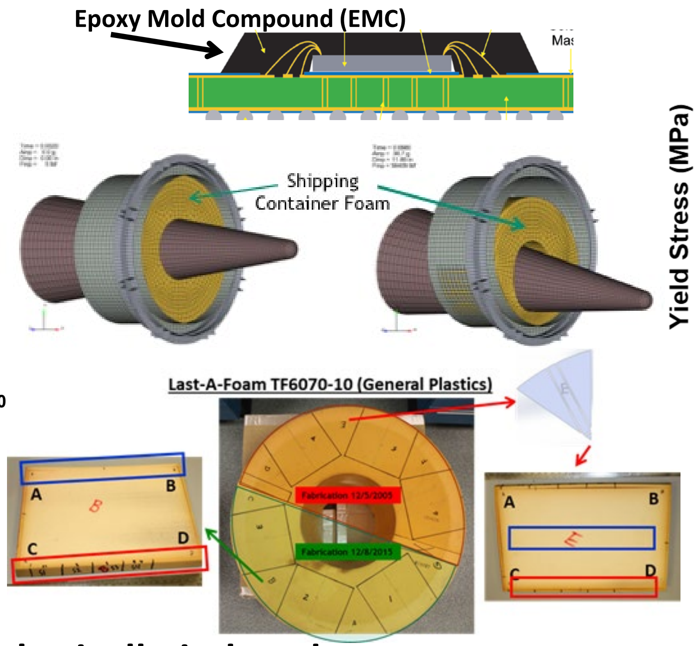
Chemical Oxidation



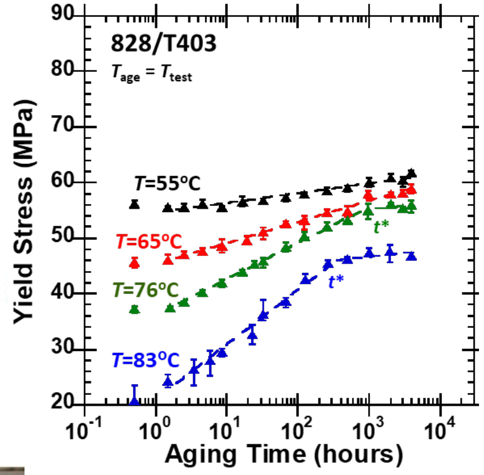
Celina et al., *Polymer* 54 (2013) 3290



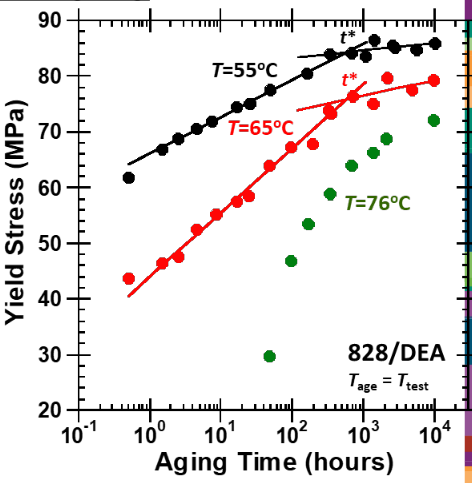
Kropka et al., in prep



Physical Aging



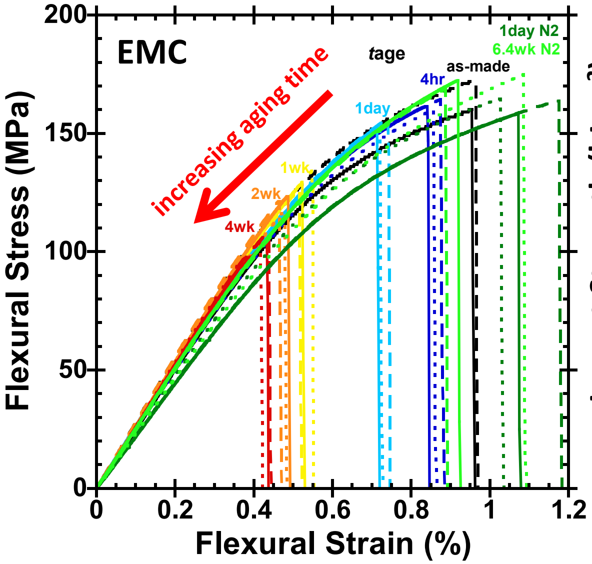
K. Wilson, *MS Thesis*, 2018



Arechederra et al., *Polymer* 185 (2019) 121937

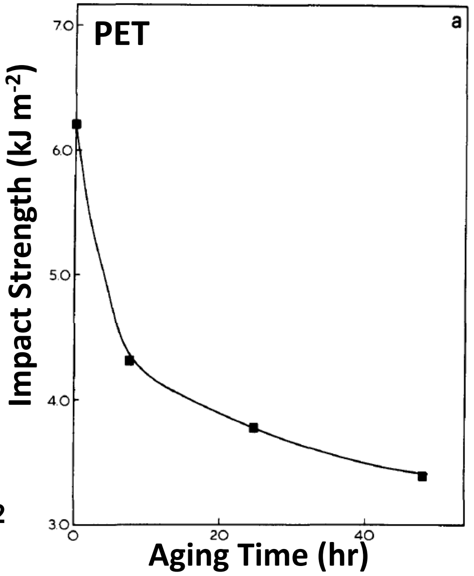
Embrittlement

oxidation-induced

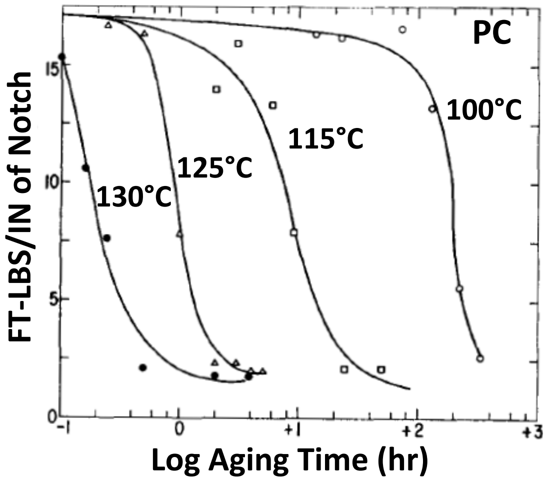


Kropka et al., in prep

physically-induced



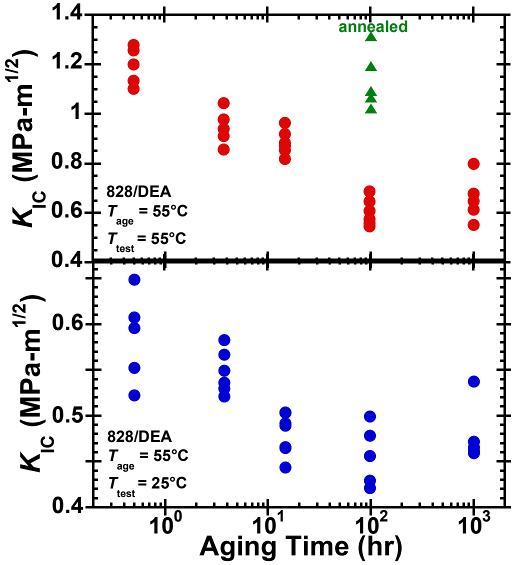
Haward et al., *Polymer* 24 (1983) 1245



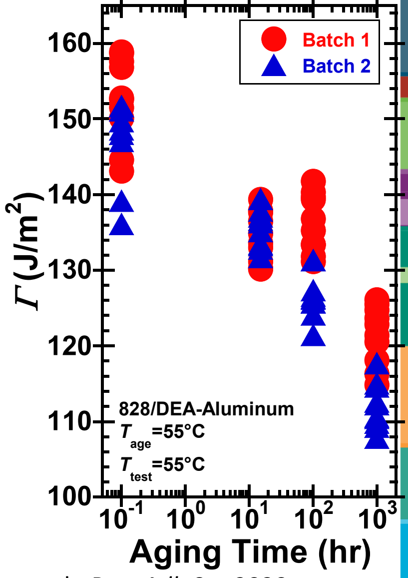
Legrand, *J Appl Pol Sci* 13 (1969) 2129

Crack Initiation/Propagation

cohesive



interfacial

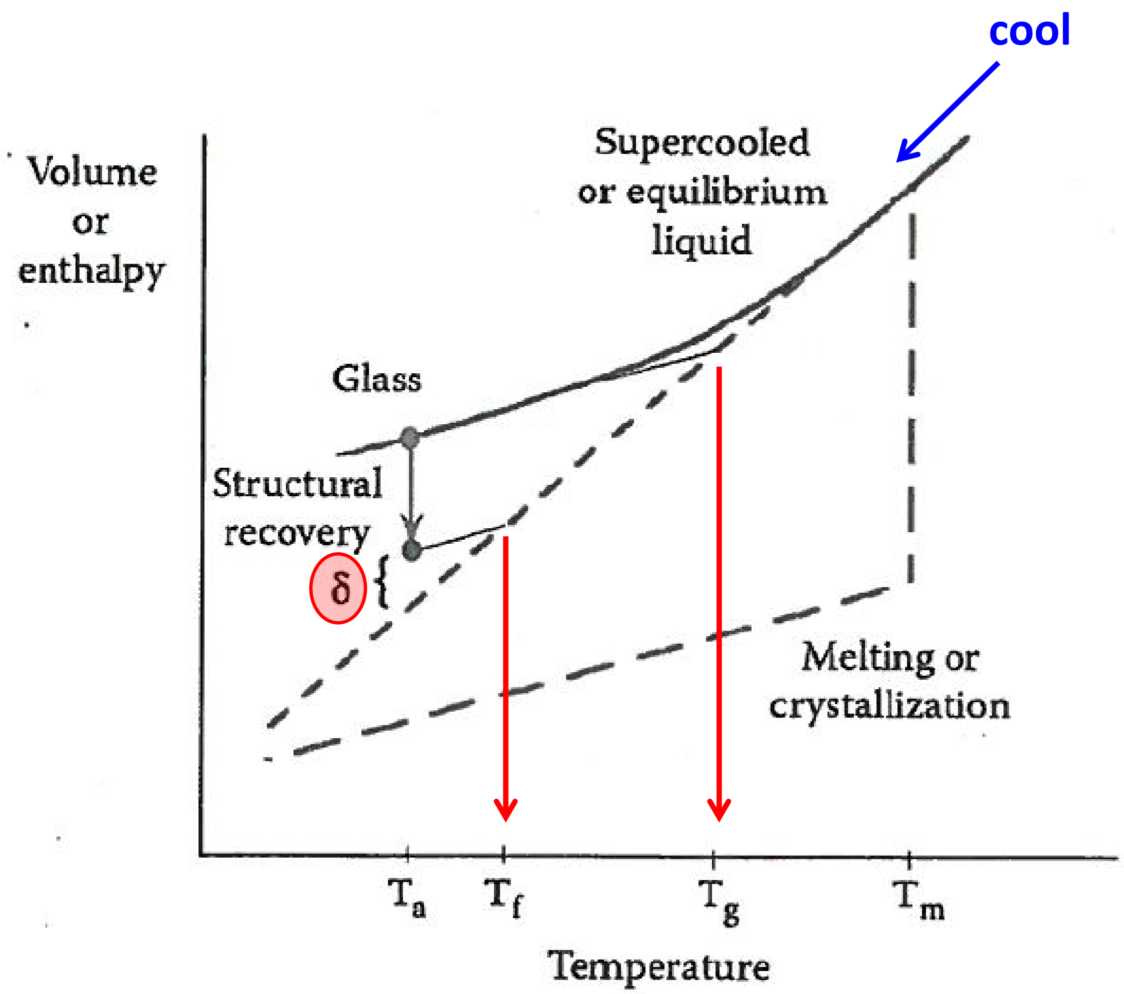


Kropka et al., *Proc Adh Soc* 2020

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 changes
  - Linear viscoelastic (LVE) dynamics evolution
  - Nonlinear response evolution
  - Role of chemical oxidation on mechanical response
  - Prediction of material evolution
  - Simple structural response tests to validate predictive tools
  - Assessment of impact of aging on stress and failure in application relevant geometries

Glass Formation and Structural Recovery/Relaxation



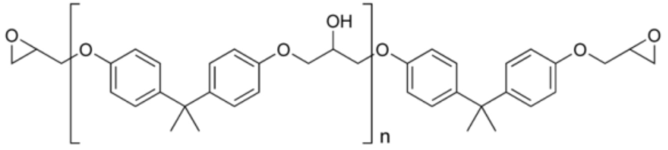
This aging leads to (1) increased residual stress in and (2) embrittlement of the polymer glass

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

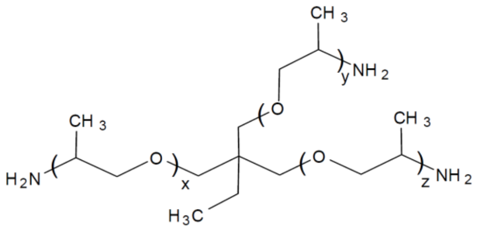
Materials

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

EPON® Resin 828
Diglycidylether of Bisphenol-A



Jeffamine® T-403 Polyetheramine



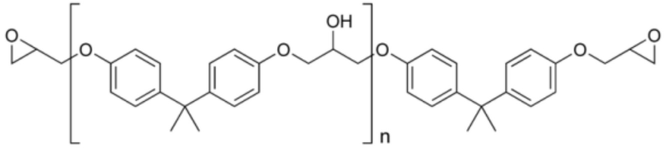
(x+y+z) = 5-6

Clarkson et al., *Polymer*, **2016**, 94 19
Wilson, MS Thesis, **2018**, NMTech

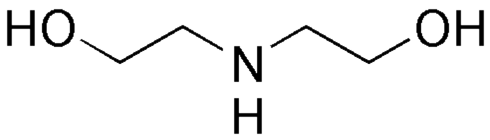
T_g ~ 90C
(when mixed stoichiometrically epoxy-amine)

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

EPON® Resin 828
Diglycidylether of Bisphenol-A



Diethanolamine



McCoy et al. *Polymer* **2016,** 105, 243-254
Arechederra et al., *Polymer*, **2019**, 185 121937

T_g ~ 70C

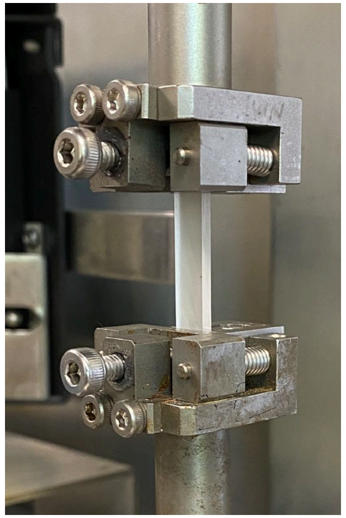
3M D32 glass microballoons

[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

Direct Assessment of the Evolution of the LVE Shear Dynamic Shift Factor During Isothermal Aging

Shear Dynamic Shift Factor Evolution: Technique Definition

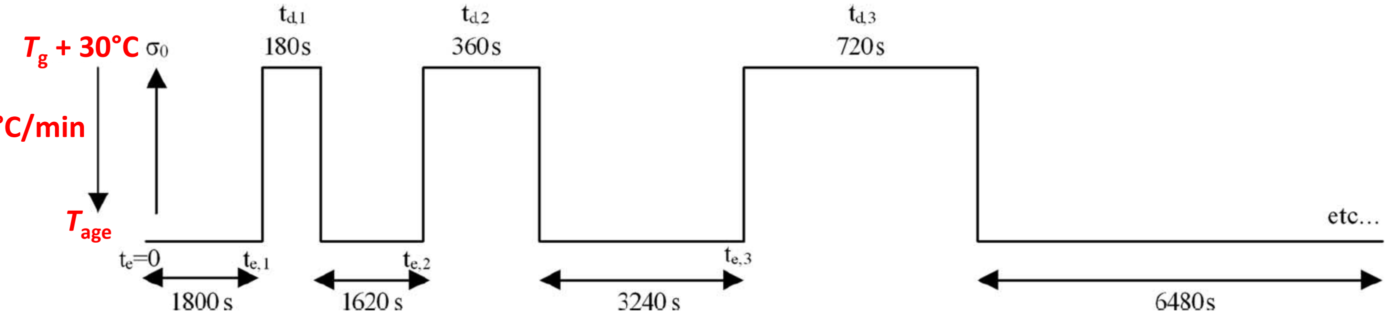
Test Set-up



Conditions

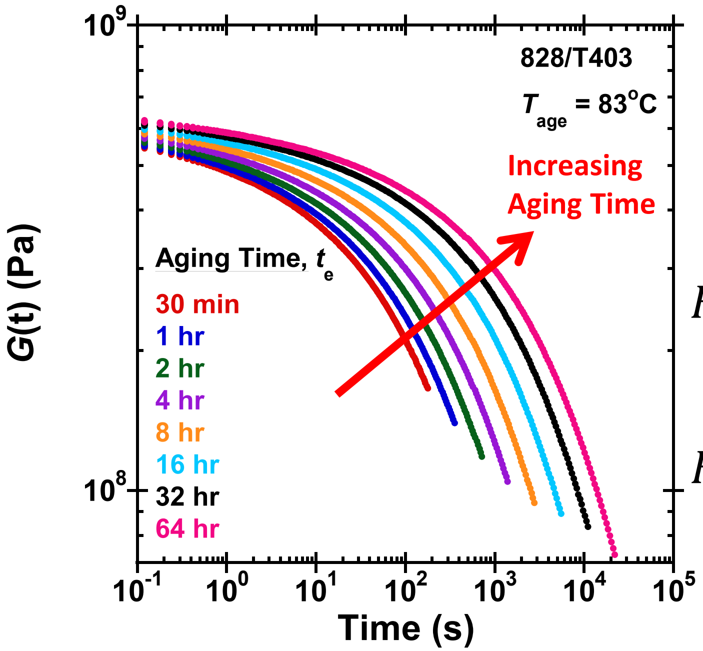
- temperature stability: +/-0.1°C
- sample geometry: torsion rectangular
- Strain in linear response regime (~0.1%)
- either N_2 or air convection

Struik Loading Protocol



Struik, *Physical Aging in Amorphous Polymers and Other Materials*, 1978
Zhao and McKenna, *J. Chem. Phys.* 136 154901 (2012)

Example Stress Relaxation Results



$$G(t) = \sigma(t)/\gamma$$

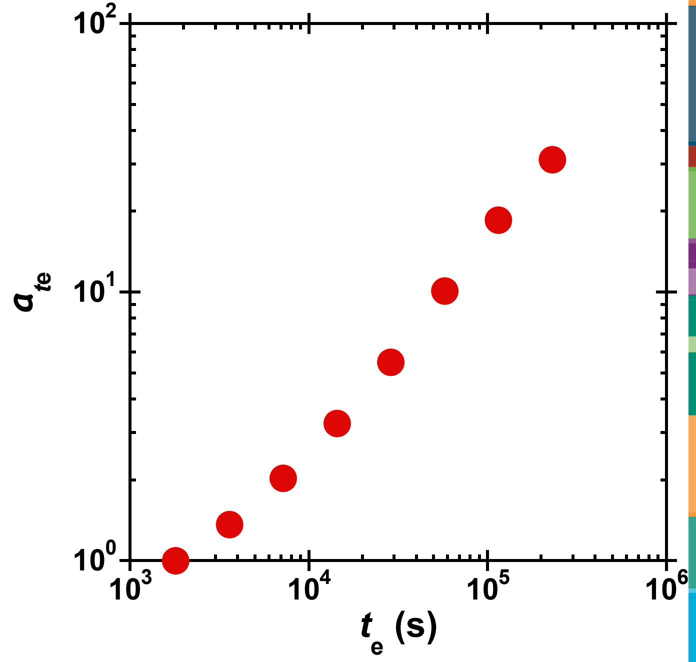
$$\gamma = K_\gamma \theta$$

$$\sigma = K_\sigma M$$

$$K_\gamma = \frac{T}{L}\left\{1 - \left[0.378\left(\frac{T}{W}\right)^2\right]\right\}$$

$$K_\sigma = 1000\left\{\frac{3 + \left[1.8\left(\frac{T}{W}\right)\right]}{WT^2}\right\} G_c$$

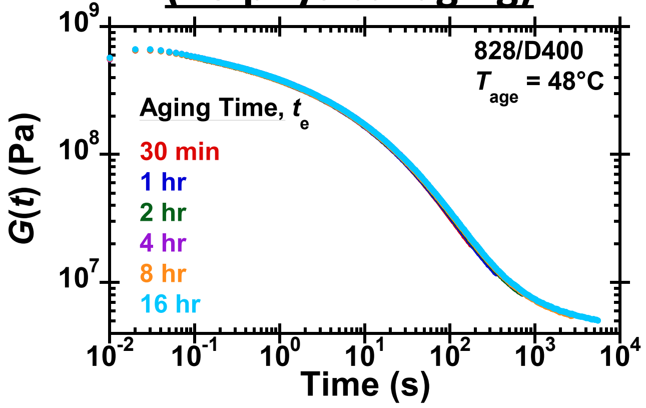
$$a_{t_e} = \frac{\tau(t_e)}{\tau(t_{e,ref})}$$



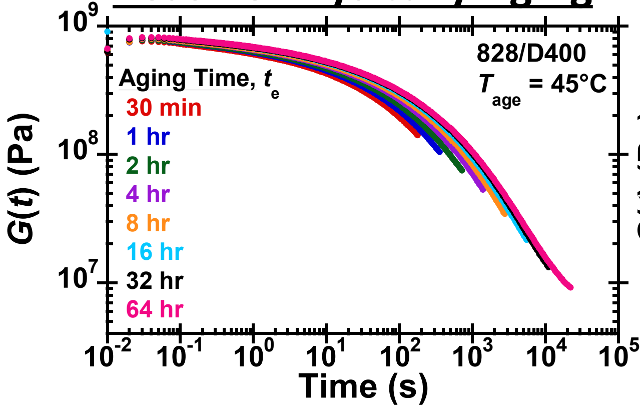
Shear Dynamic Shift Factor Evolution: Technique Demonstration

(after a material "pretreatment" to extinguish small amounts of remaining chemical reaction potential)

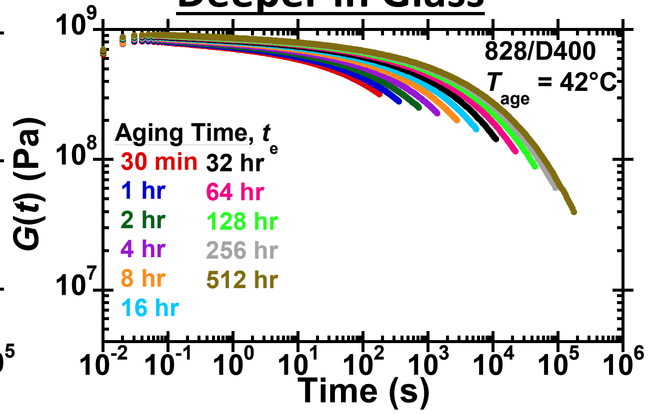
Essentially Stable (no physical aging)

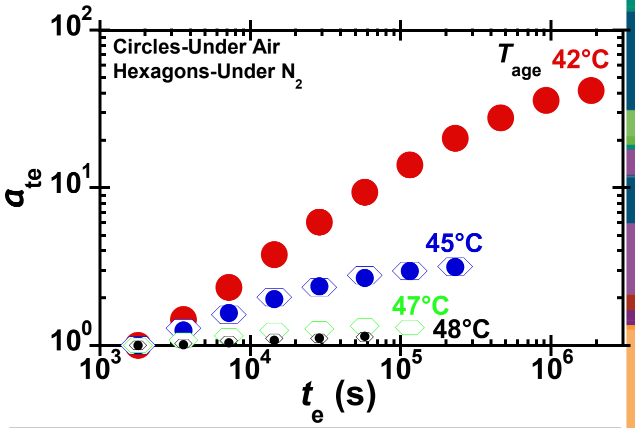


Sufficiently in Glass to Resolve Physically Aging

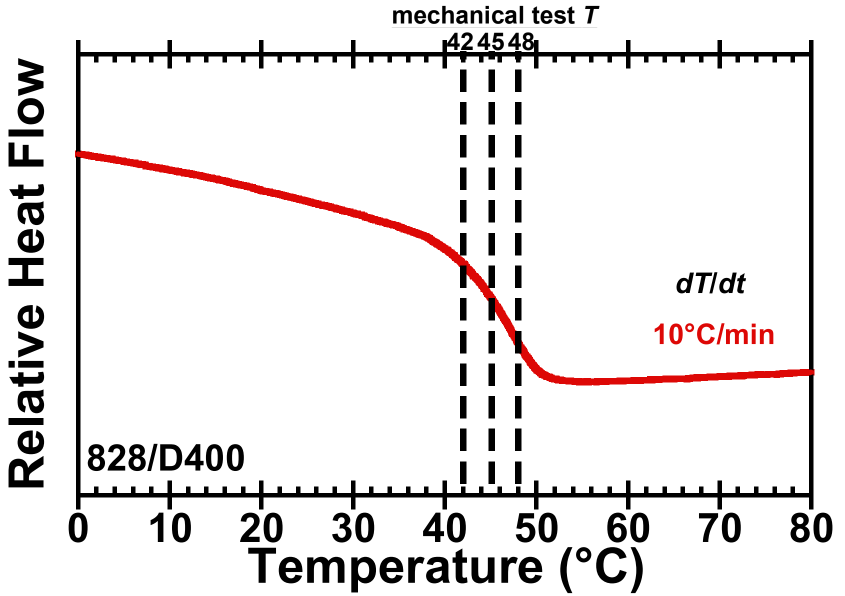


Larger Dynamic Evolution Deeper in Glass





Equivalence between Air and N_2

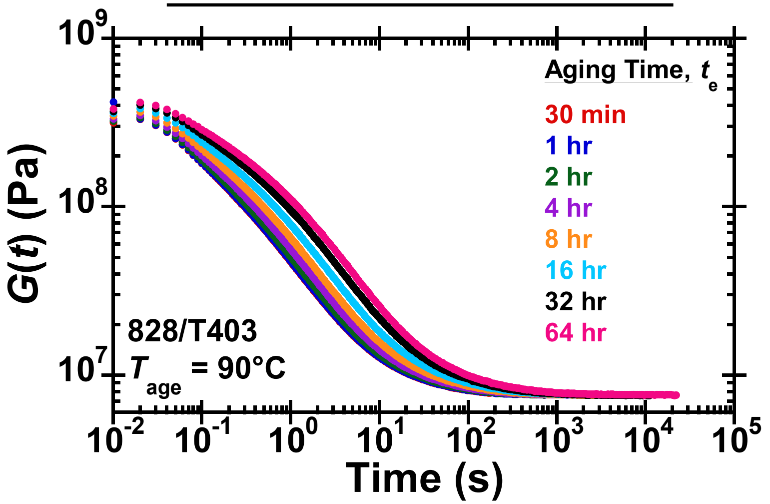


Note position of test temperatures relative to calorimetric T_g (upon cooling)

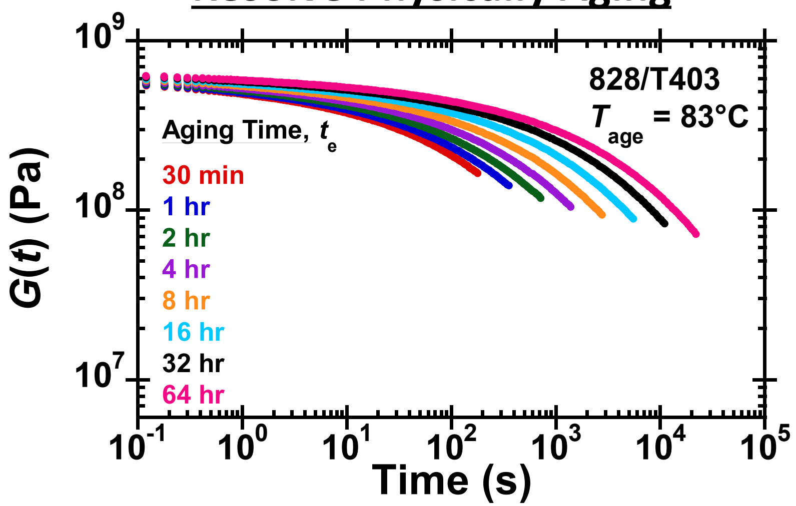
The above effects are "pure" physical aging, reversible upon annealing above T_g

Shear Dynamic Shift Factor Evolution: 828/T403

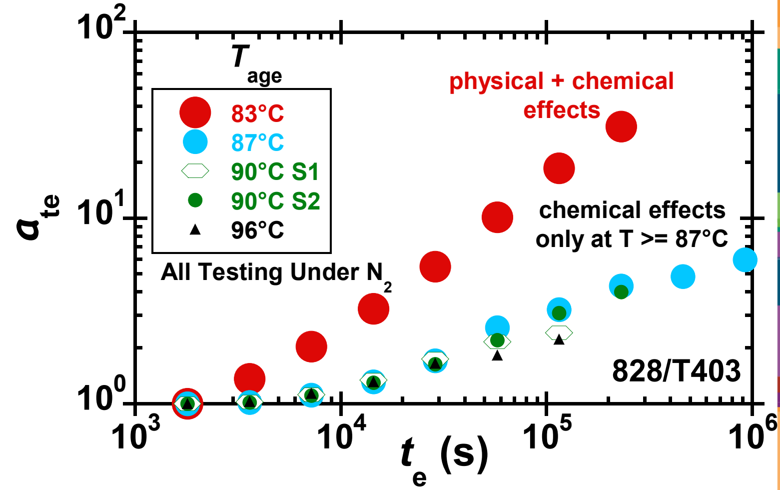
No Stable State Observed



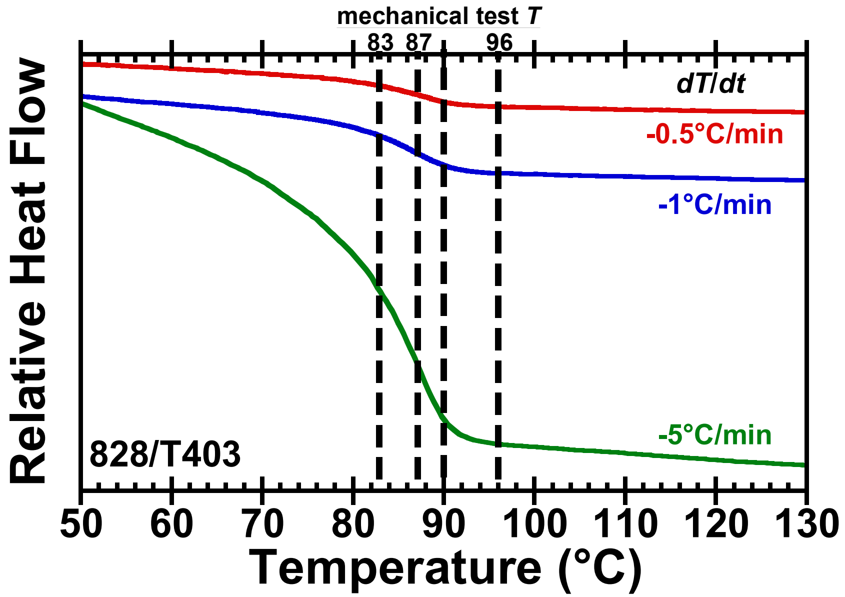
Sufficiently in Glass to Resolve Physically Aging



Chemically Evolving Material Throughout Test



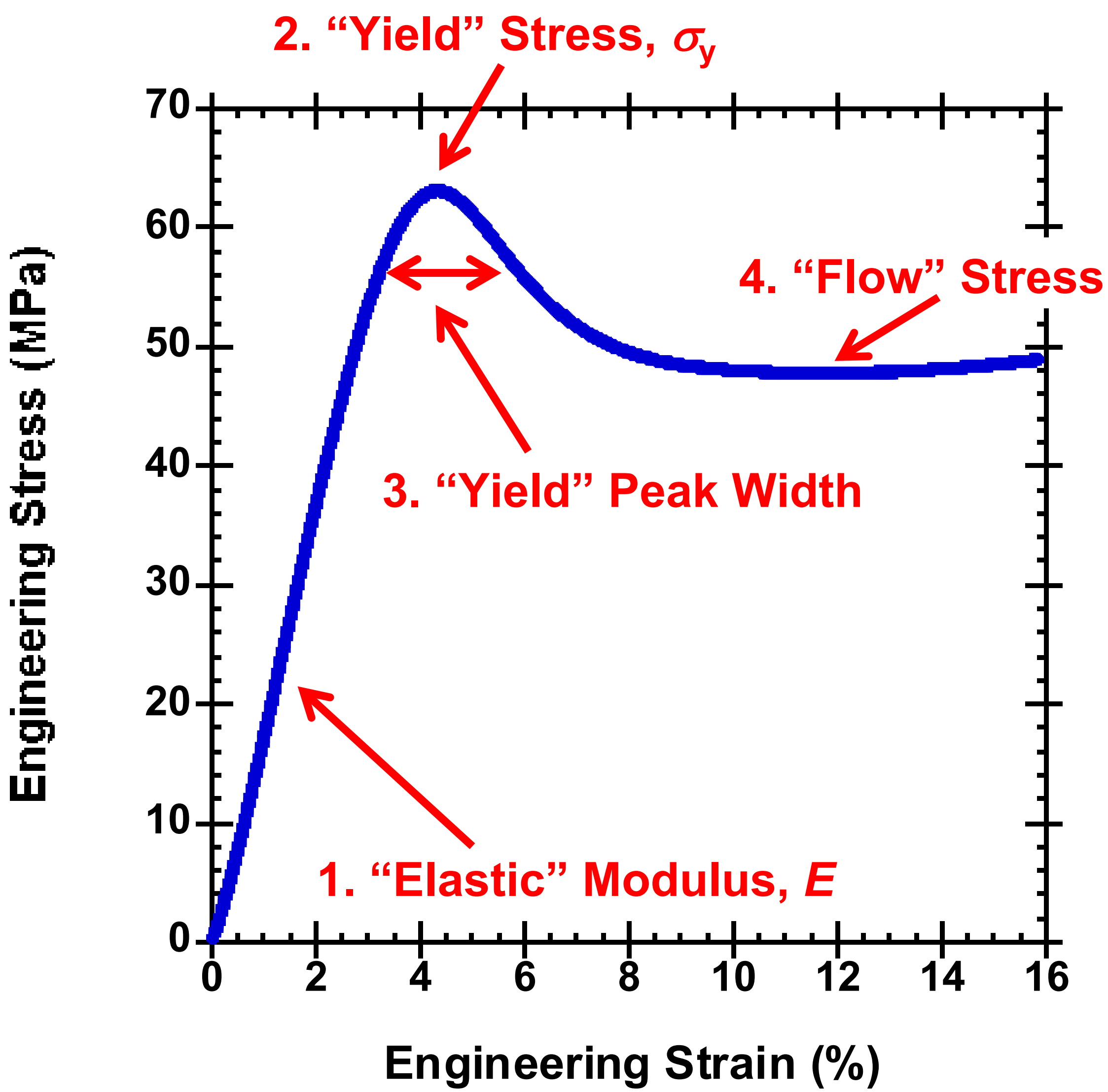
Note position of test temperatures relative to calorimetric T_g (upon cooling)

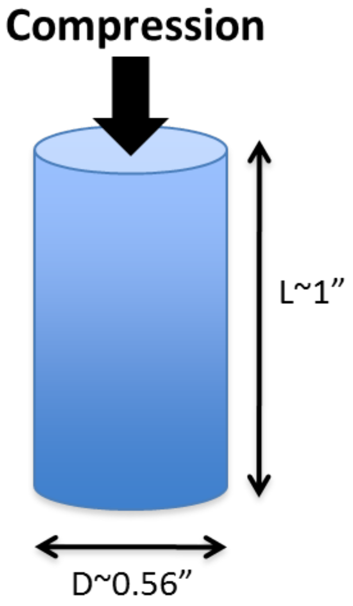


Chemical contributions (DLO) to the changes in dynamics must be discriminated from physical contributions

Evolution of the Nonlinear Viscoelastic Response During Isothermal Aging

Anatomy of Compressive Stress-Strain Response of Glassy Polymers

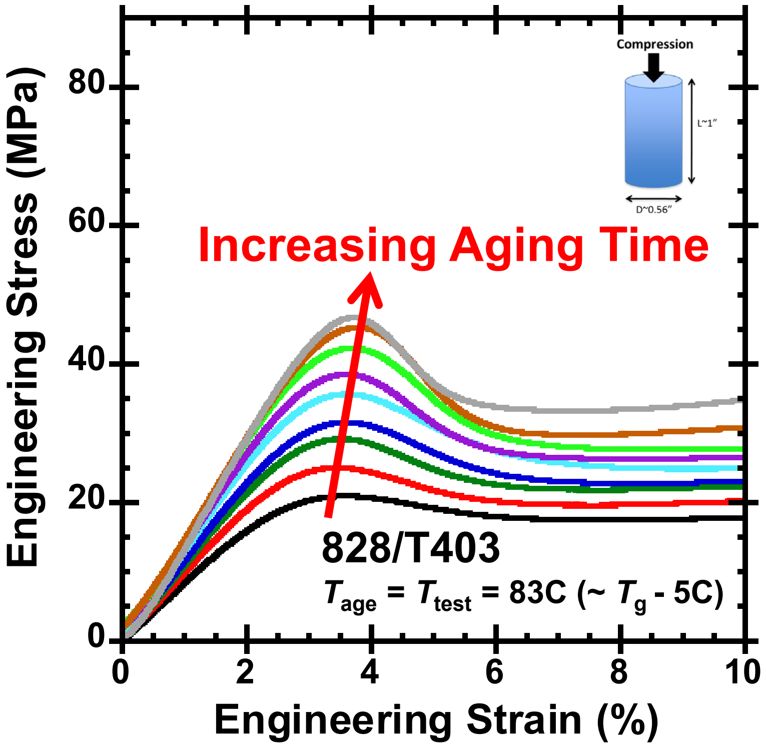




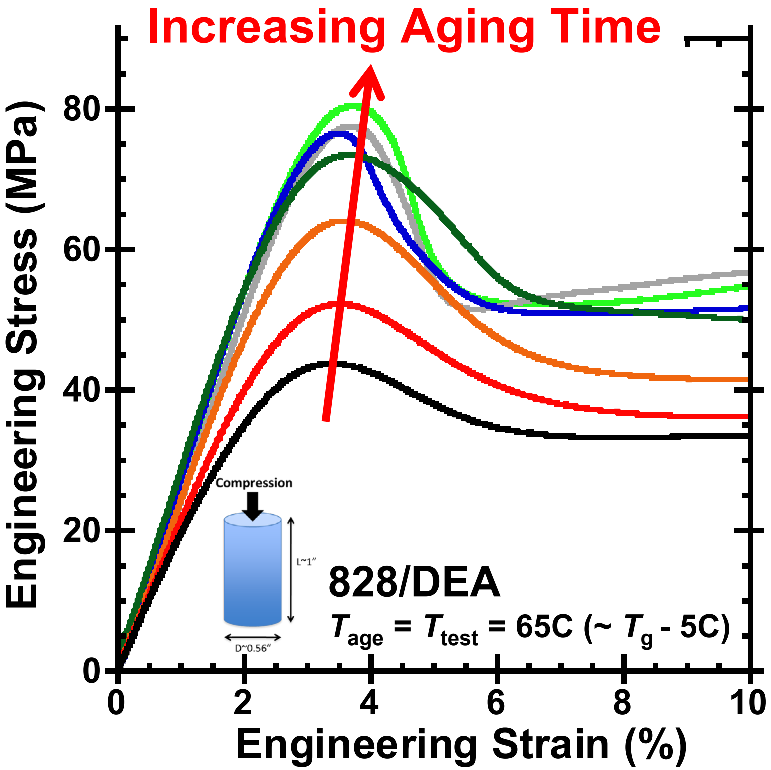
Arechederra et al., *Polymer*, **2019**, 185 121937

Compressive Stress-Strain Response: Thermal Aging Effects

Physical Aging Only?



Chemical + Physical Aging Mechanisms



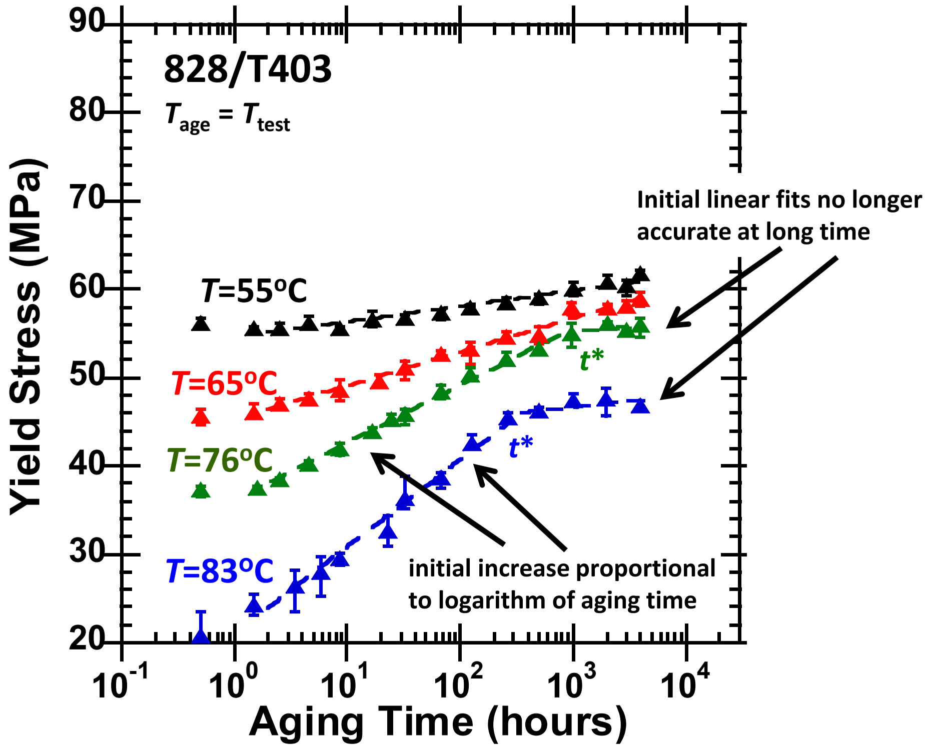
4 Distinguishable Changes in Compressive Stress-Strain Response Include:

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

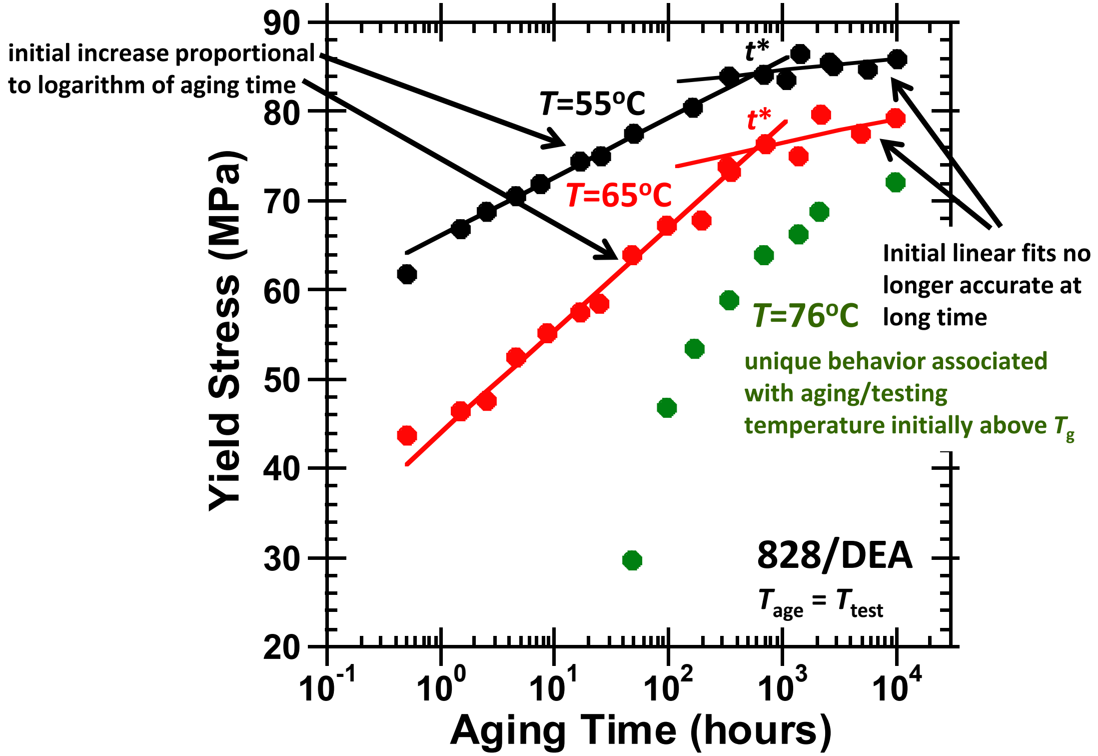
Arechederra et al., *Polymer*, **2019**, 185 121937
Wilson, MS Thesis, **2018**, NMTech

Evolution of Yield Stress during Thermal Aging

Physical Aging Only?



Chemical + Physical Aging Mechanisms

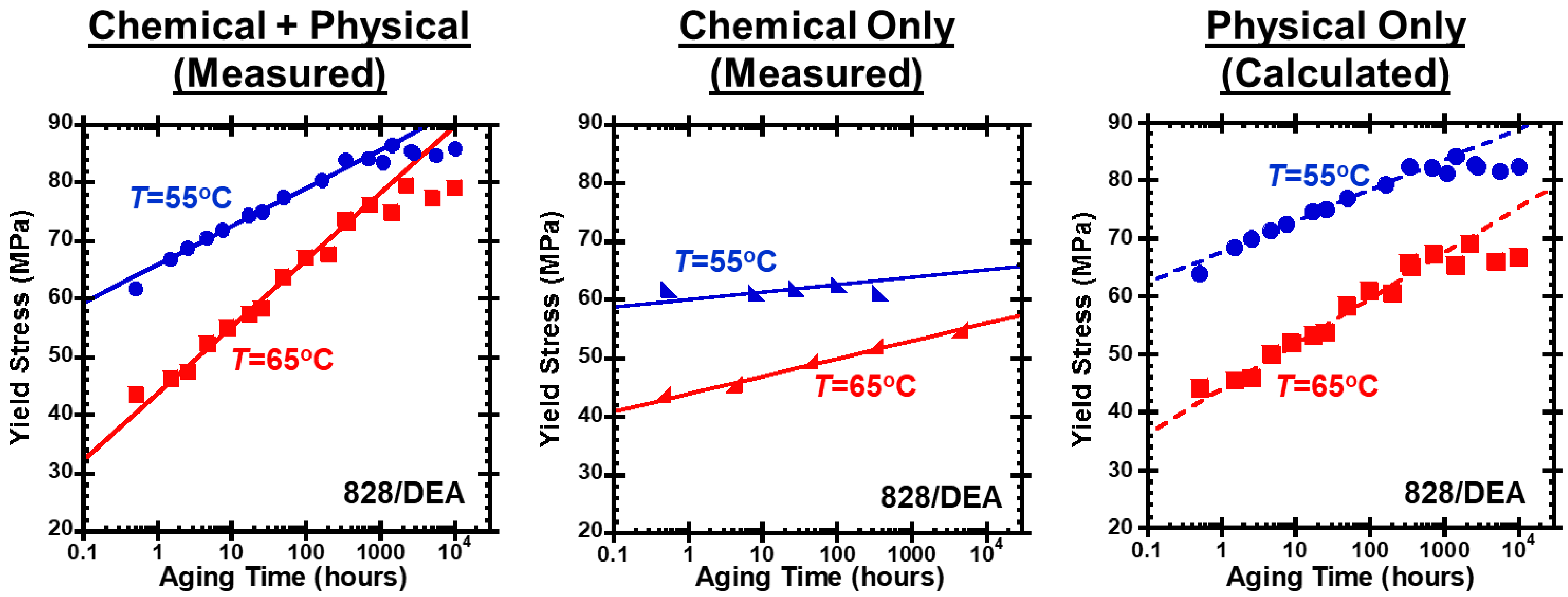


Findings:

- At a given T-T_g, 828/DEA exhibits a higher yield stress than 828/T403 (at all aging times). Molecular details influence the stress-strain response.
- At approximately equivalent distances from T_g, 828/DEA exhibits more marked narrowing of the "yield" peak (previous slide) with aging
- 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 less distinct.

Arechederra et al., *Polymer*, **2019**, 185 121937
Wilson, MS Thesis, **2018**, NMTech

Chemical and Physical Contributions to the Evolution of Yield Stress



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.

Arechederra et al., *Polymer*, **2019**, 185 121937

Prediction of Material Evolution: SPEC(tacular) Model

Helmholtz Free Energy

Volume Strain Contributions; Shear Strain Contributions

$$\Psi(t) = \Psi_\infty(\boldsymbol{H},\theta) + \frac{1}{2}K_D(\theta)\int_0^t\int_0^t f_1(t^*-s^*,t^*-u^*)\frac{dI_1}{ds}\frac{dI_1}{du}\,dsdu + G_D(\theta)\int_0^t\int_0^t f_2(t^*-s^*,t^*-u^*)\frac{d\boldsymbol{H}^{dev}}{ds}:\frac{d\boldsymbol{H}^{dev}}{du}\,dsdu$$

$$-L_D(\theta)\int_0^t\int_0^t f_3(t^*-s^*,t^*-u^*)\frac{d\theta}{ds}\frac{dI_1}{du}\,dsdu - \frac{C_D(\theta)}{2\theta_{ref}}\int_0^t\int_0^t f_4(t^*-s^*,t^*-u^*)\frac{d\theta}{ds}\frac{d\theta}{du}\,dsdu$$

Thermal-Strain Contributions; Thermal Contributions

Coleman-Noll →

$$\frac{\partial\Psi}{\partial\boldsymbol{H}} = \boldsymbol{\sigma}(t)$$

$$\frac{\partial\Psi}{\partial\theta} = \eta(t)$$

All relaxation functions monotonically decrease from 1 to 0

Stress

$$\boldsymbol{\sigma}(t) = K_D\mathbf{1}\int_0^t f_1(t^*-s^*)\frac{dI_1}{ds}ds - L_D\mathbf{1}\int_0^t f_3(t^*-s^*)\frac{d\theta}{ds}ds + 2G_D\int_0^t f_2(t^*-s^*)\frac{d\boldsymbol{H}^{dev}}{ds}ds + [K_\infty I_1 - L_\infty(\theta-\theta_{sf})]\mathbf{1} + 2G_\infty\boldsymbol{H}^{dev}$$

History Dependent Shift Factor

Material time difference

$$t^* - s^* = \int_s^t \frac{dx}{a(x)}$$

Laboratory time difference (t-s)

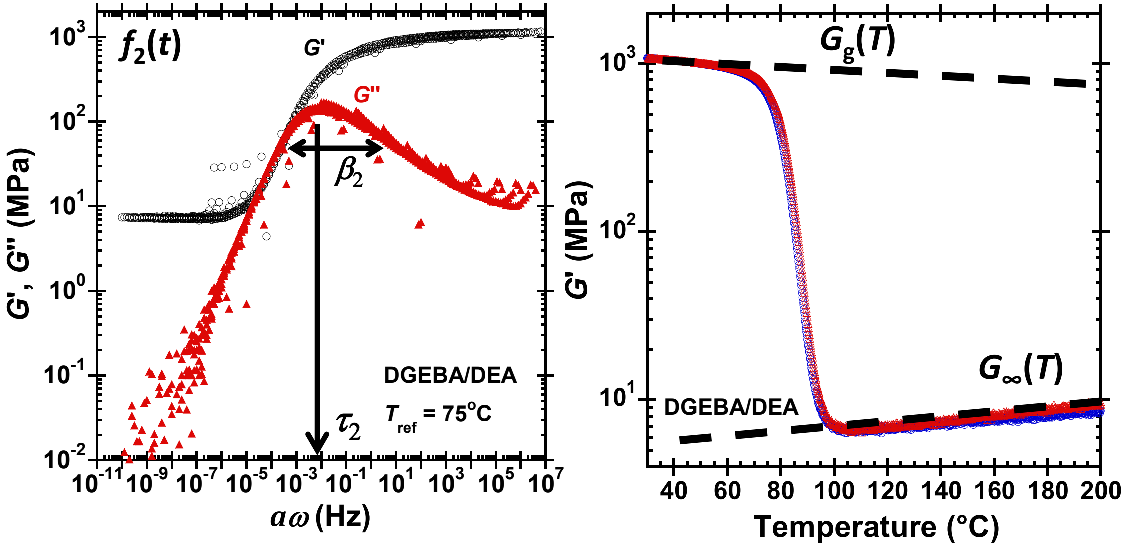
$$\log a = -\frac{C_1 N}{C_2'' + N} \quad \text{where}$$

$$N = \left[\{T - T_{ref}\} - \int_0^t ds f_3(t^*-s^*)\frac{dT}{ds}\right] + C_3\left[I_1 - \int_0^t ds f_1(t^*-s^*)\frac{dI_1}{ds}\right] + C_4\int_0^t\int_0^t ds\,du f_2(t^*-s^*,t^*-u^*)\underline{\underline{d}}_{dev}(s):\underline{\underline{d}}_{dev}(u)$$

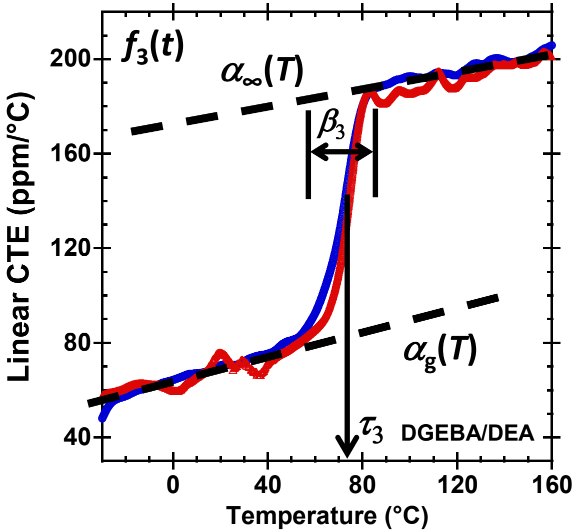
D.B. Adolf, et al., *Polymer*, **2004**, 45, 4599
D.B. Adolf, et al., *Polymer*, **2009**, 50, 4257

Prediction of Material Evolution: SPEC(tacular) Model Calibration

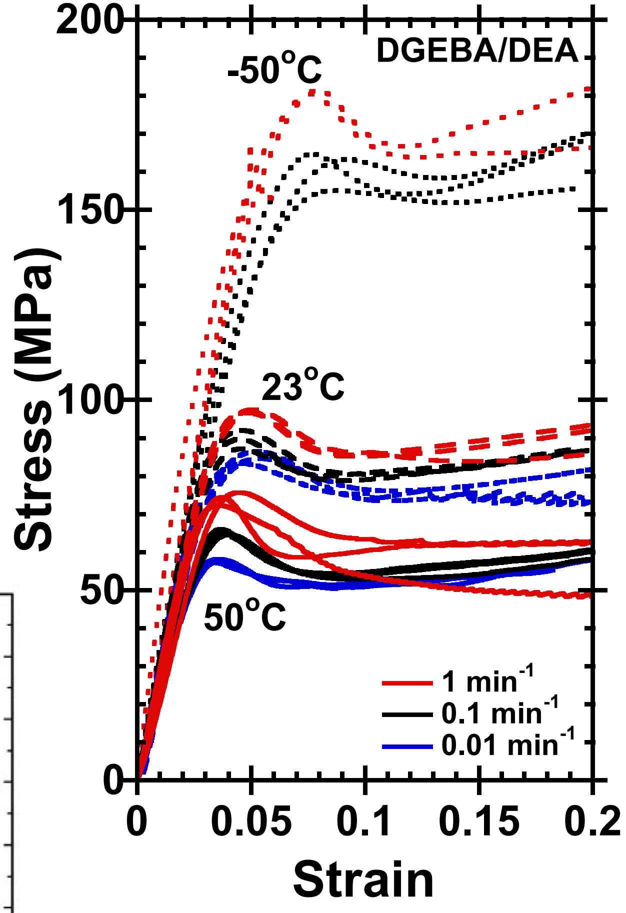
Shear Relation Spectrum and Moduli Temperature Dependencies



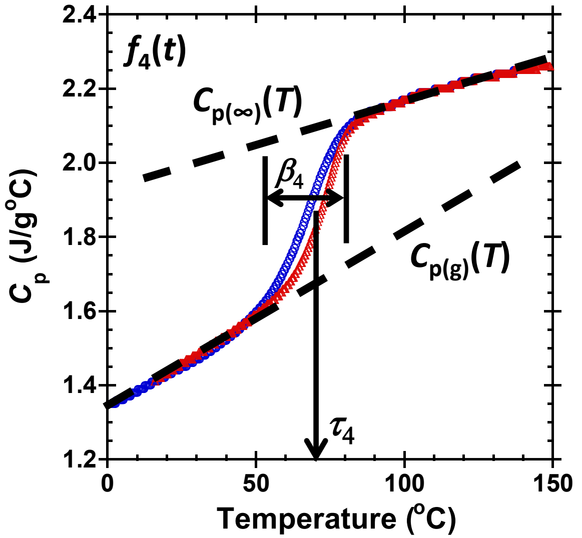
Thermal Expansion Relaxation Spectrum and Temperature Dependence



Non-linear Response: Yield as a Function of Temperature and Strain Rate

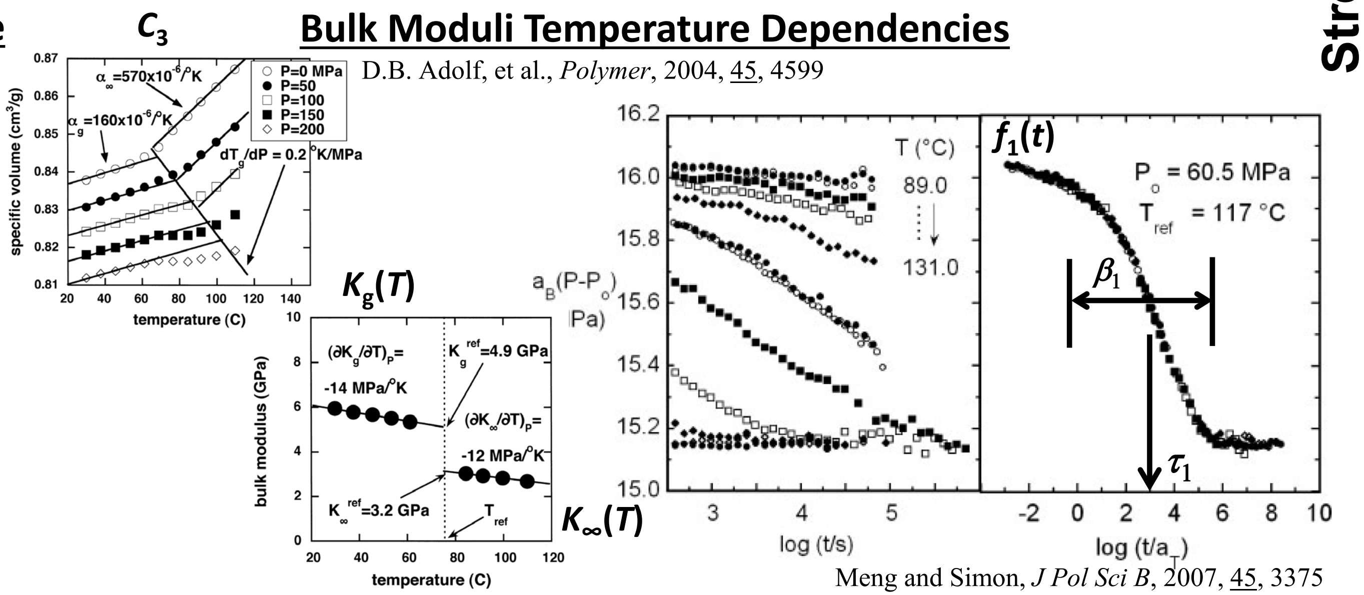


Heat Capacity Relaxation Spectrum and Temperature Dependence



Volume Relation Spectrum and Bulk Moduli Temperature Dependencies

D.B. Adolf, et al., *Polymer*, 2004, 45, 4599

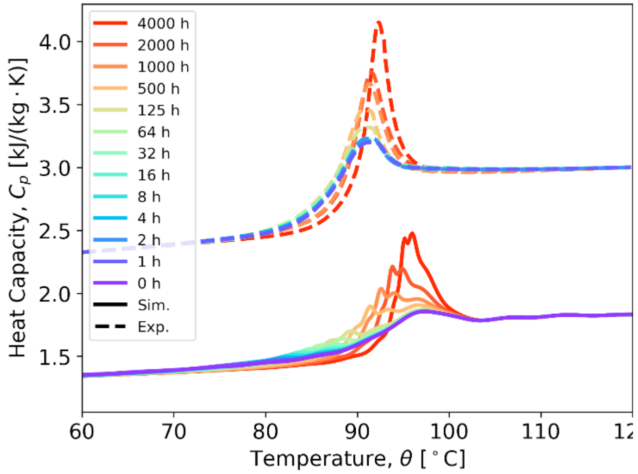


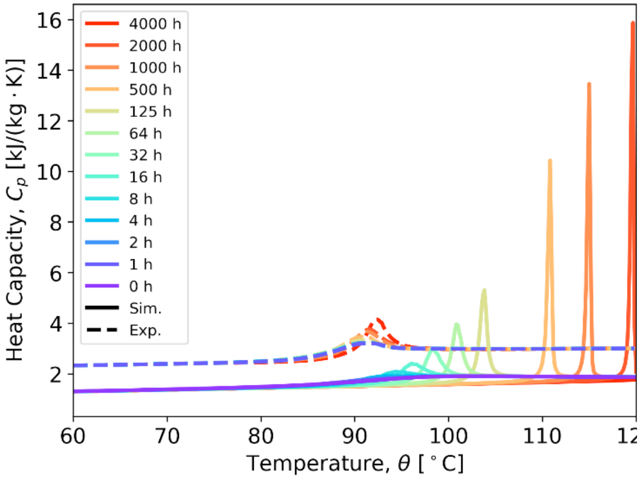
Meng and Simon, *J Pol Sci B*, 2007, 45, 3375

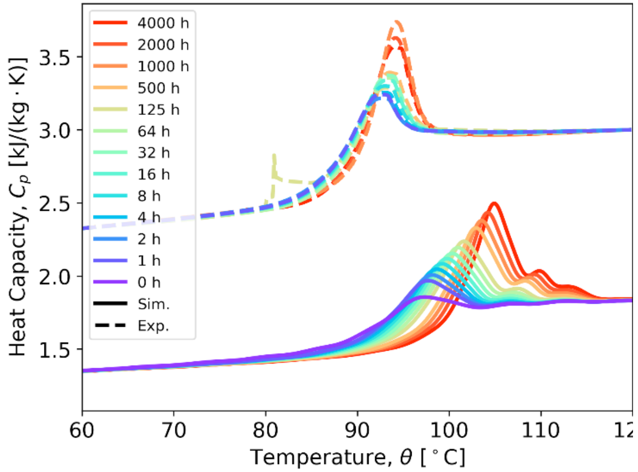
Prediction of Material Evolution: SPEC(tacular) Model Results for 828/T403

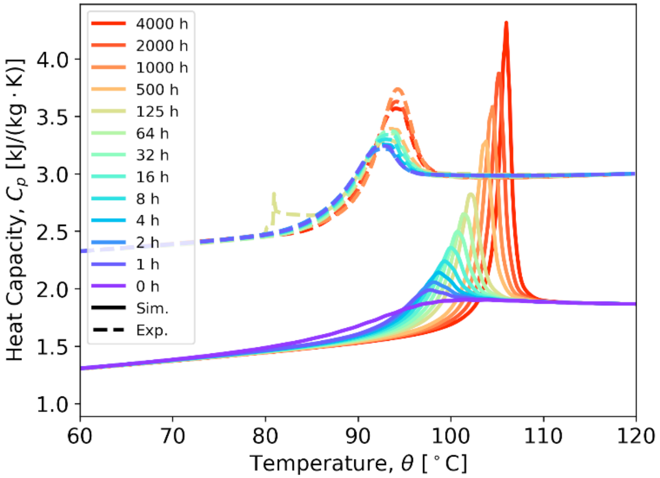
Enthalpy Recovery

Calibration 1 / Calibration 2



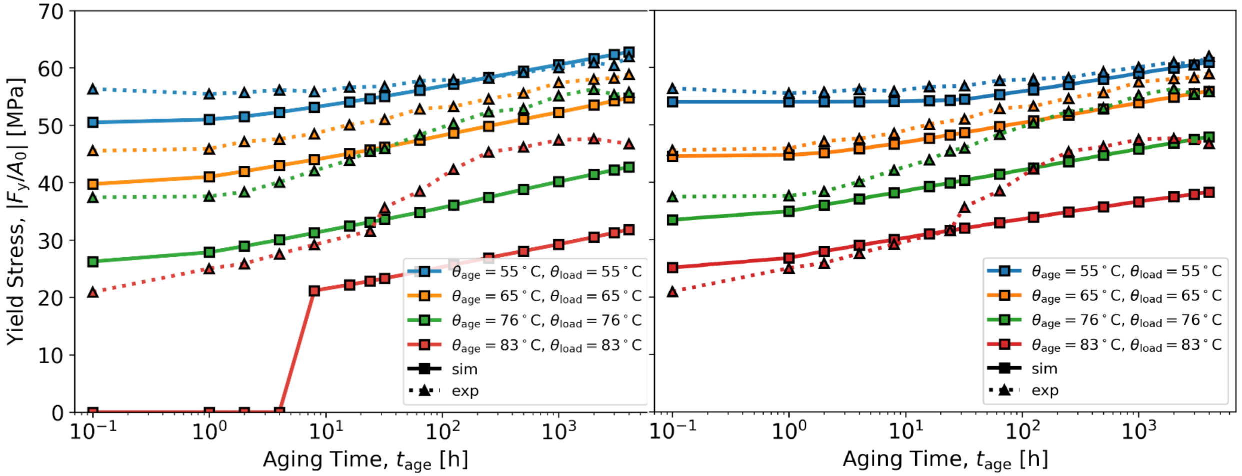


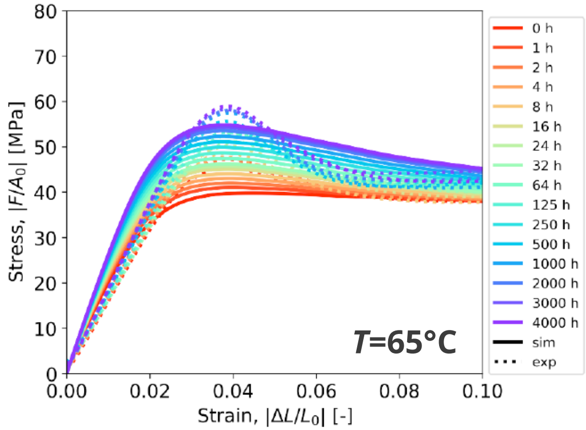


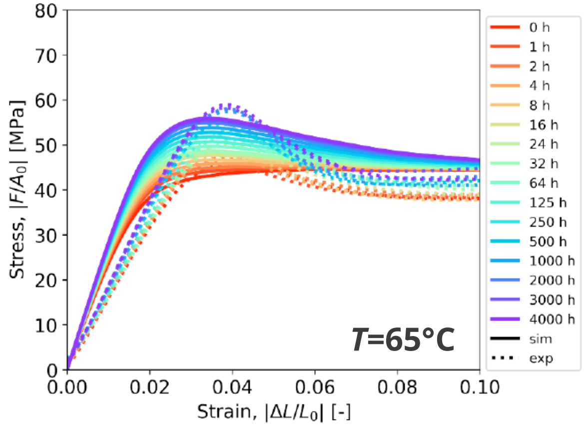


Compressive Yield Stress Evolution

Calibration 1 / Calibration 2







Findings:

- SPEC can qualitatively predict a wide variety of viscoelastic and physical aging phenonmena
- No single calibration protocol best captures ALL aging responses

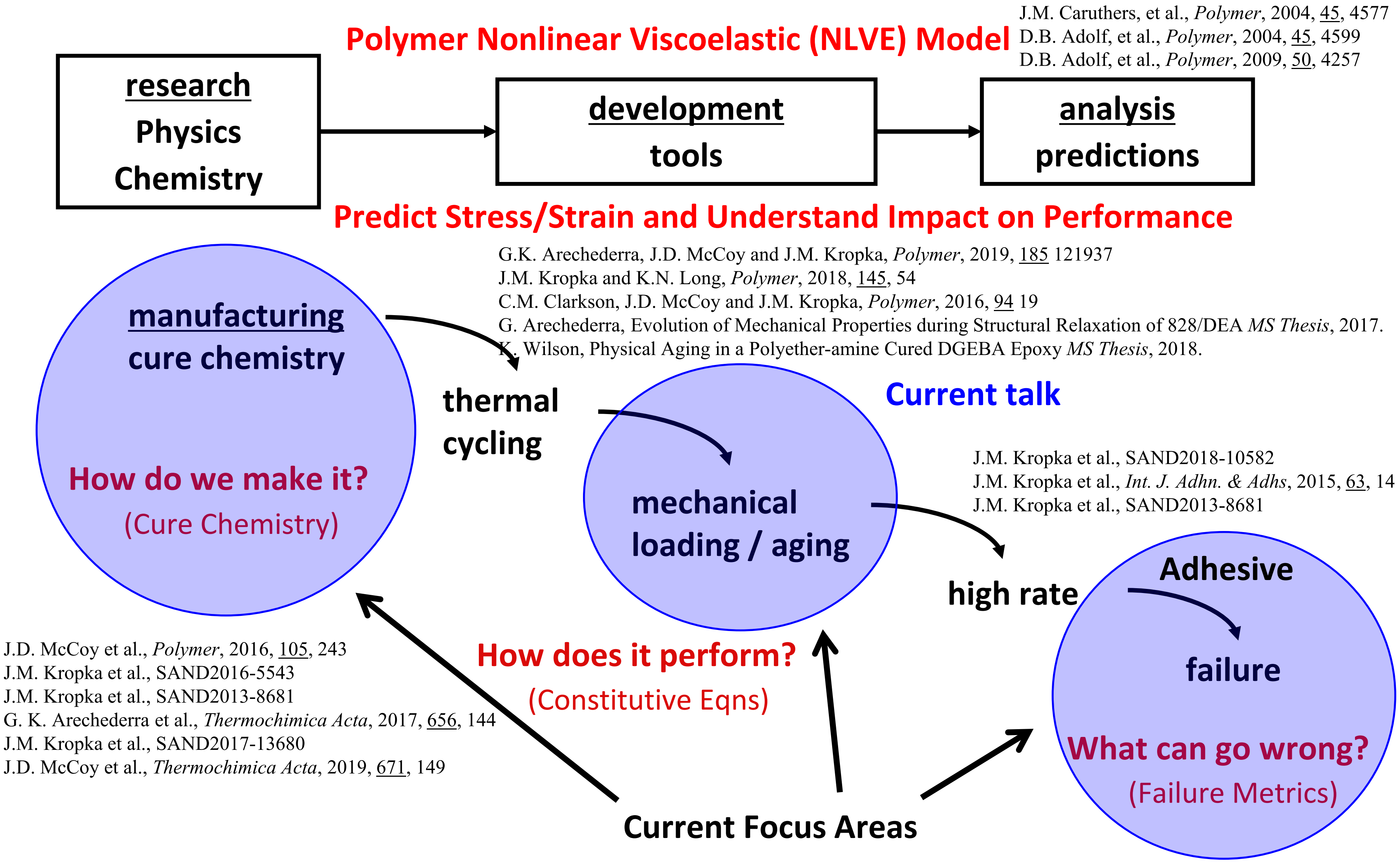
Cundiff et al., *SAND2021-11193*, **2021**

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)
- **Demonstrated ability to resolve the evolution of the LVE shear dynamic shift factor during isothermal aging with "pure" physical aging at low temperature, while at high temperature chemical contributions occur**
- **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°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**
- **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 qualitatively predict aspects of aging phenomena and sensitivities of the predictions to calibration protocol. Known "issues" with model under investigation:**
  - **Implementation of non-diverging equilibrium shift factor definition**
  - **Relaxation function evolution with age**

Back-up

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



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

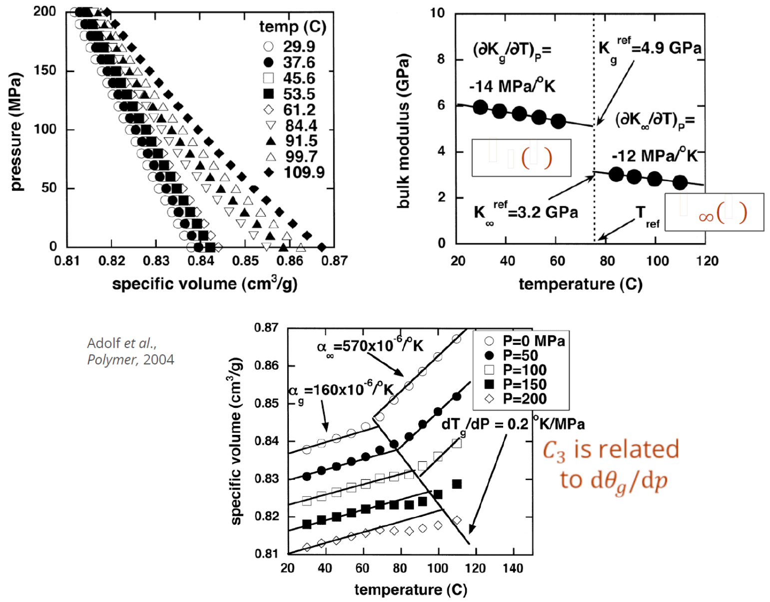
Is physical aging a concern in terms of stress evolution in application designs?

Prediction of Material Evolution: SPEC(tacular) Model Calibration

Start! Choose θ_{ref}

Experiment	Calibrated parameters
Dilatometry	$K_g(\theta), K_\infty(\theta)$
Shear Master Curve	$G_g(\theta), G_\infty(\theta), C_1, C_2, f_2$
Thermo-mechanical Analyzer (TMA)	$\alpha_g(\theta), \alpha_\infty(\theta), f_3 = f_1$
Differential Scanning Calorimetry (DSC)	$C_g(\theta), C_\infty(\theta), f_4$
Glassy Compression	4

Dilatometry



Adolf et al., Polymer, 2004

C_3 is related to $d\theta_g/dp$

Shear Mastercurve