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Polymer Modeling for Electronic Packaging

Robert S. Chambers
Matthew A. Neidigk
Sandia National Laboratories
Albuquerque, NM

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Picatinny Arsenal Presentation

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Outline for the Talk

- What are polymers?
- How are polymers used in components?
- Polymer viscoelasticity
- Modeling Approaches & Sandia Vision
- NonLinear ViscoElasticity (NLVE)
  - PEC & SPEC models
  - Fillers
  - Universal SPEC
  - Curing
  - Adhesion
- NLVE Modeling Tips

Polymers: What are they?

Long chain-like molecules (macromolecules)

Synthesized from smaller molecules (monomers) during polymerization reaction

May be Linear (long threads), branched or crosslinked

May be amorphous, crystalline or some of each

"Thermoplastics": not crosslinked (e.g., polycarbonate)

"Thermosets": crosslinked systems (e.g., epoxies)

How are Polymers Used in Components?

- Encapsulants for:
  - structural integrity
    - impact
    - vibration
  - high voltage isolation
- Adhesives or Underfills for:
  - bonding materials
  - mounting surface components
- Printed Circuit Boards:
  - orthotropic composites

thermosets

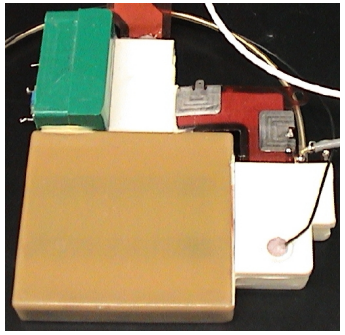
- Foams for:
  - energy dissipation
  - light constraints

- Plastic Parts for:
  - injection molded pieces

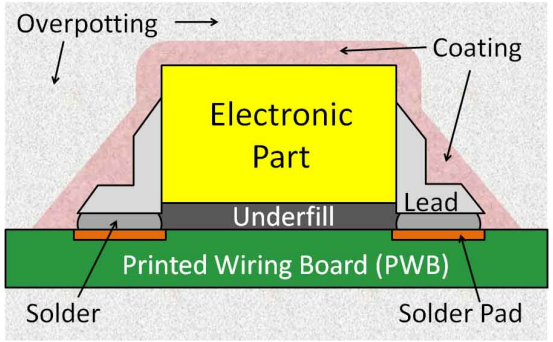
thermoplastics

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

elastomers

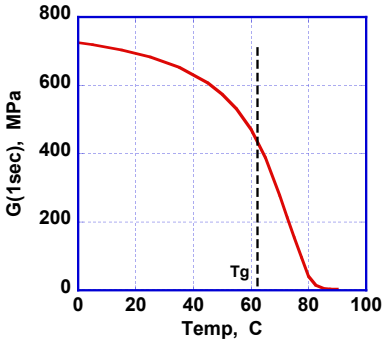


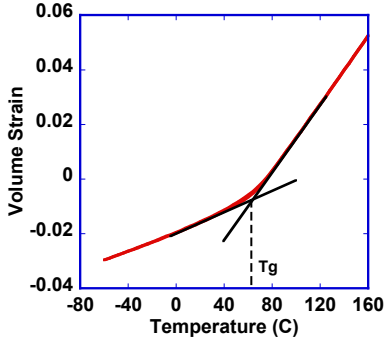
- Optimal use of polymers is not always obvious
- Poor choice of polymers can cause premature failures
- Modeling is important

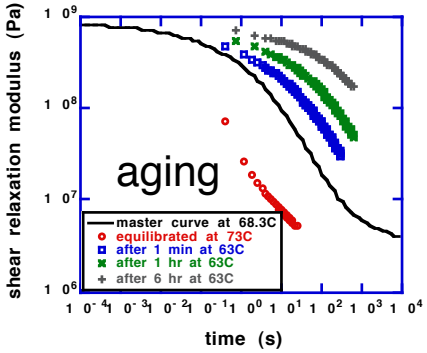


Polymers Are Complex Materials

They respond differently than metals and ceramics







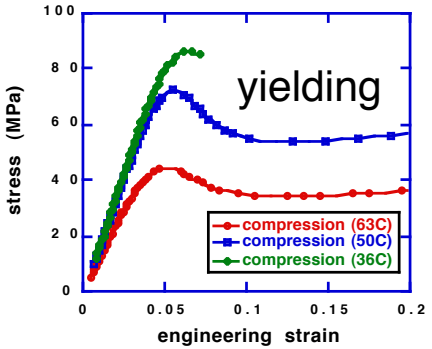


exhibit a glass transition:

- shear modulus can change by factor of 100
- 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

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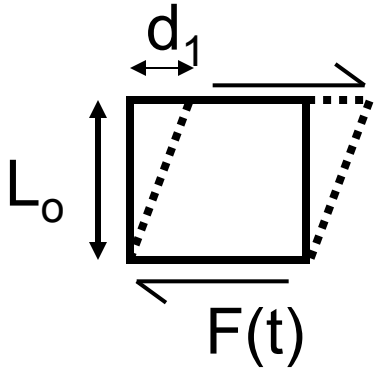
Polymers Are Viscoelastic

Impose a small step shear strain, $\Delta\gamma_1$

Measure decaying force, F(t)

Compute shear relaxation modulus, G(t)



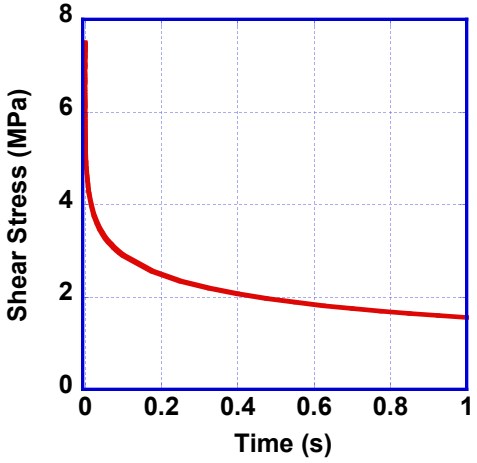
$$\Delta\gamma_1 = \frac{d_1}{L_o} \qquad \sigma_{xy} = \frac{F(t)}{A_o}$$

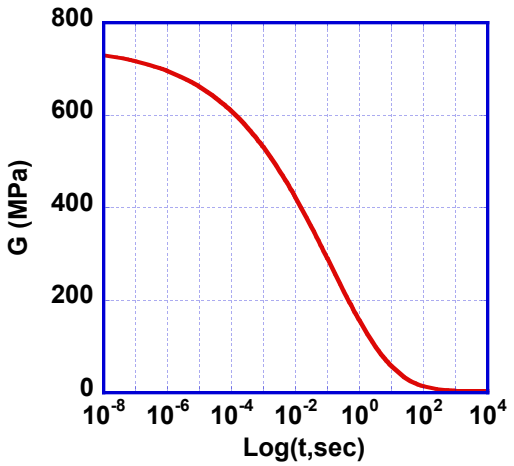
$$G(t) = \frac{\sigma_{xy}(t)}{\Delta\gamma_1} = \frac{F(t)\cdot L_o}{A\cdot d_1}$$

The polymer stress relaxes with the relaxation modulus

$$\sigma_{xy}(t) = G(t)\cdot\Delta\gamma_1$$

stress decays over time





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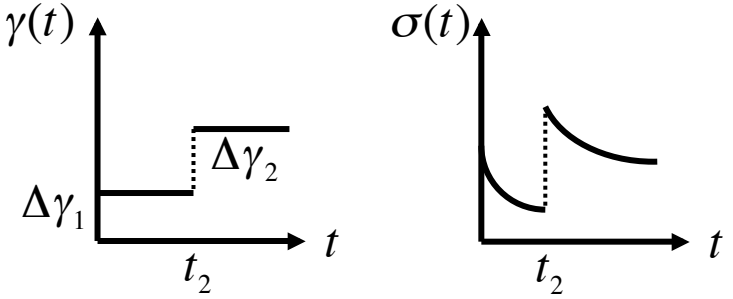
Linear Viscoelastic Constitutive Equations Are Integrals

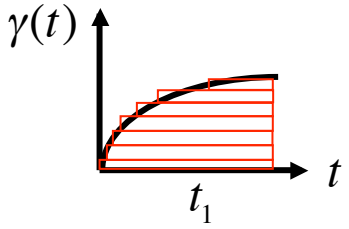
Now impose a 2nd step strain and compute the stress:



$$\sigma_{xy}(t) = G(t)\cdot\Delta\gamma_1 + H(t-t_2)G(t-t_2)\cdot\Delta\gamma_2$$

In general, for a series of "N" step strains:

$$\sigma_{xy}(t) = \sum_{i=1}^{N} H(t-t_i)G(t-t_i)\cdot\Delta\gamma_i$$



Since any strain field can be written as a linear combination of step strain increments:

$$\sigma_{xy}(t) = \int_0^t G(t-s)\cdot d\gamma = \int_0^t G(t-s)\cdot\frac{d\gamma}{ds}ds$$

Boltzmann's Superposition Principle

Current stress depends on prior strain history

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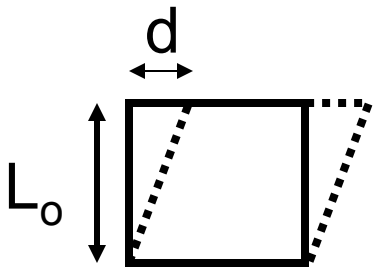
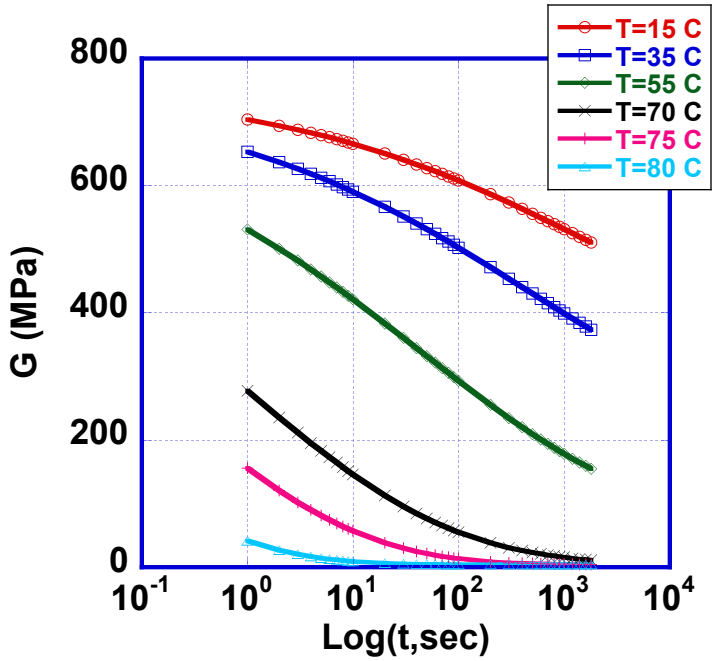
What If We Change Temperature?



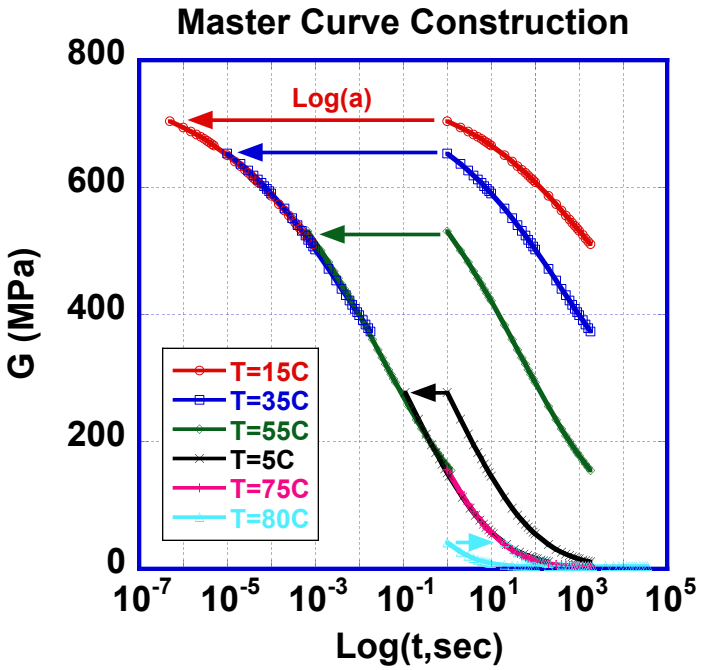
$$G(t) = \frac{\sigma_{xy}(t)}{\gamma_o} = \frac{F(t) \cdot L_o}{A \cdot d}$$

Conduct shear relaxation tests at different temperatures

- The polymer stress relaxes
- Stress relaxes faster at higher temperatures



Thermorheological Simplicity



Time-Temperature Superposition

- time-temperature equivalence
- relaxation curve shape does not change
- temperature shifts curve in Log(time)

Define a material time, t*, from the shift in Log(t) with temperature

$$Log(t^*) = Log(t) - Log(a)$$

"a" is shift factor in a material clock

$$t^*(t,T) = \frac{t}{a(T)}$$

Knowing G(t) at Tref, G(t) can be computed at any T

$$G(t)\Big|_{T} = G\left(\frac{t}{a(T)}\right)\Big|_{T_{ref}} = G(t^*)\Big|_{T_{ref}}$$

$$\sigma_{xy}(t) = \int_0^t G(t^* - s^*) \cdot \frac{d\gamma}{ds} ds$$

$$t^* - s^* \equiv t^*(t,T(t)) - s^*(s,T(s)) = \int_s^t \frac{du}{a(T(u))}$$

Current stress depends on prior thermal history

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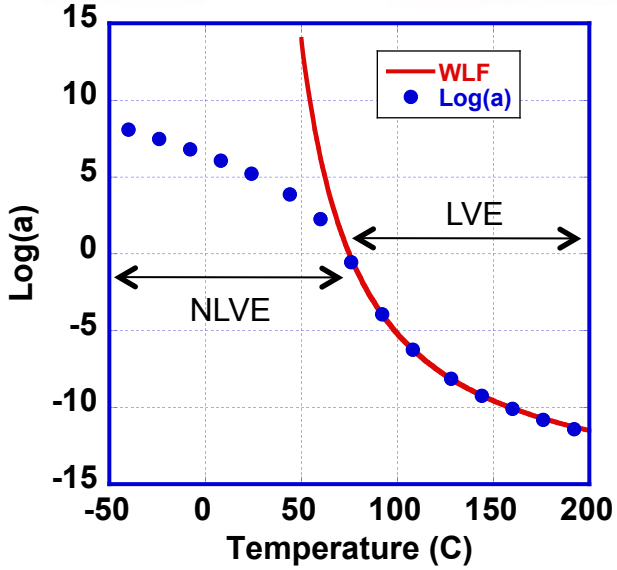
The Shift Factor in Material Clock

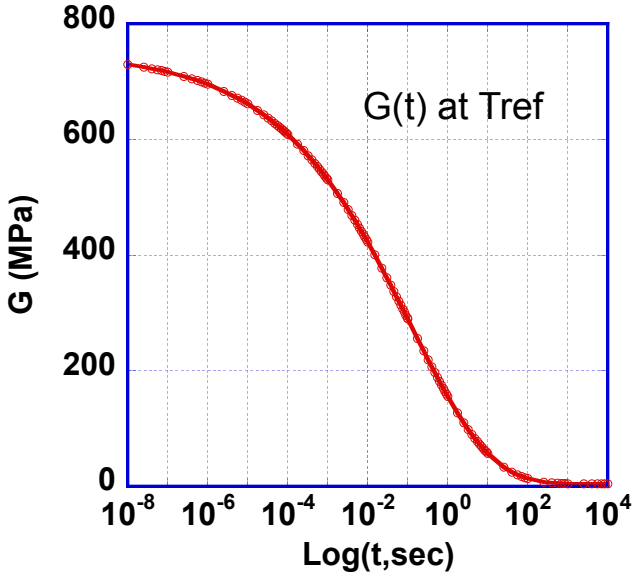


For equilibrated materials near Tg and above, WLF eqn fits data well

$$\log(a) = -\frac{C_1(T - Tref)}{C_2 + (T - Tref)}$$

where

$$t^* \equiv \int_s^t \frac{du}{a(T(u))} \qquad G(t)\Big|_T = G\left(t^*\right)\Big|_{T_{ref}}$$



The shear relaxation function can be defined by a Prony series:

$$G(t) = G_\infty + \sum_{i=1}^{N} \Delta G_i \, e^{-(t/\tau_i)}$$

If T=constant, then

$$t^* = \frac{t}{a(T)} \qquad G(t^*) = G_\infty + \sum_{i=1}^{N} \Delta G_i \, e^{-\frac{t}{a\tau_i}}$$

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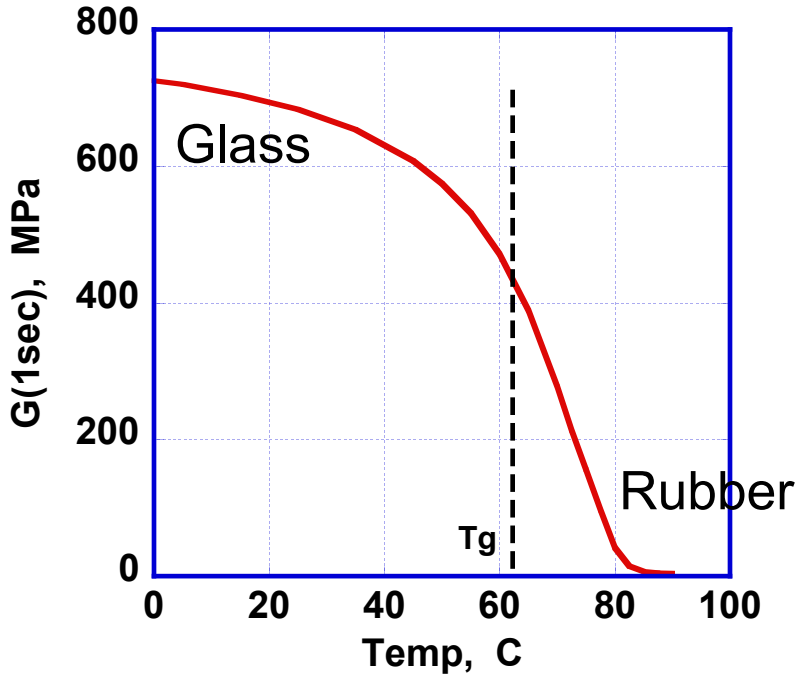
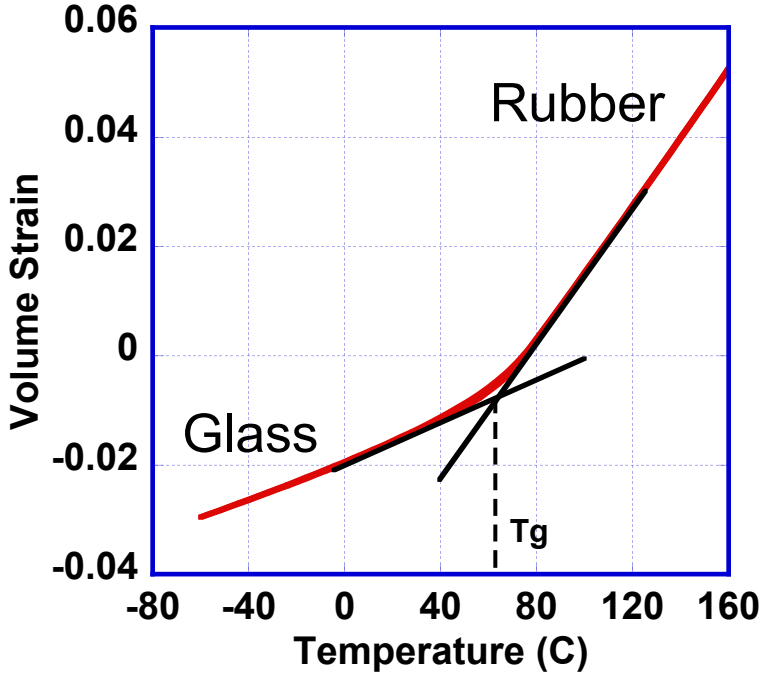
What Is Glass Transition, Tg?





Polymers Transition (Rubber to Glass) with Temperature

- Glassy State: lower CTE and higher shear modulus
- Rubbery State: higher CTE and lower shear modulus

Service/Operating Temperature Matters!

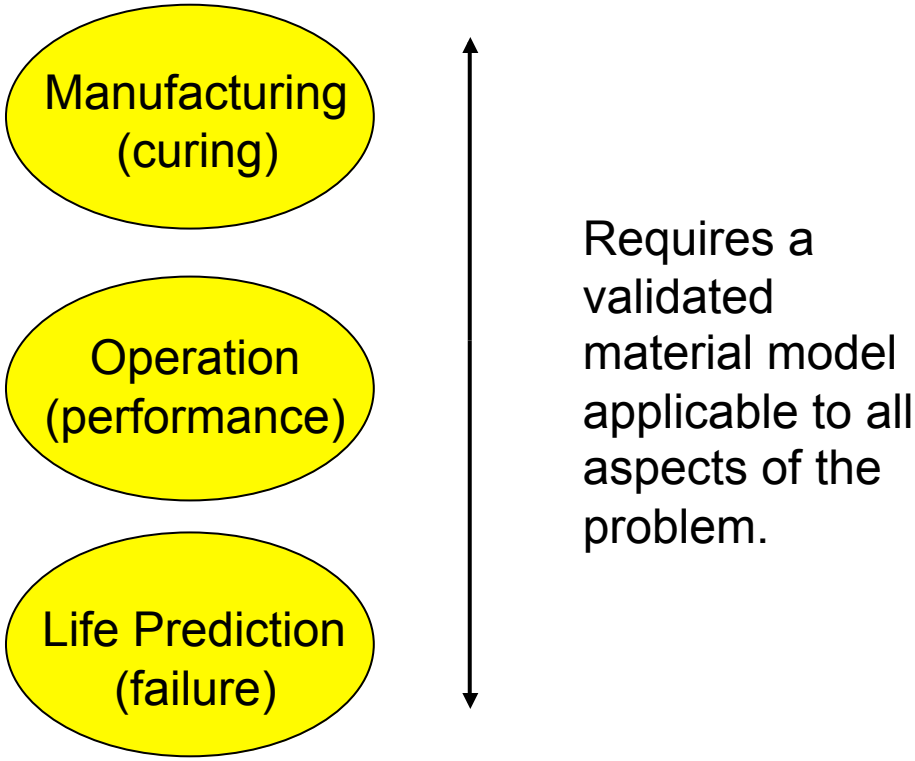
How Do Others Model Polymers?

Model	Shortcomings
Elasticity →	Stress-Free Temp, No history dependence,
Elastic + temp depend →	relaxation, Tg or yield
Plasticity →	No relaxation, Tg
Linear Viscoelasticity →	No yield or nonlinearity
Nonlinear viscoelasticity	
free volume →	No compression yield
strain	Data? Thermodynamically consistent???

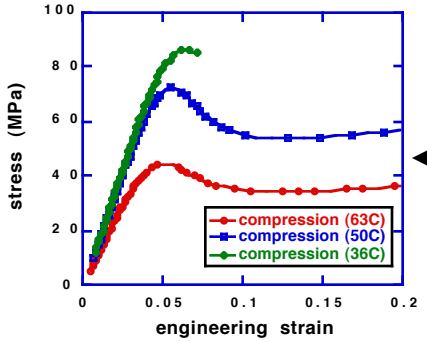
(Note: These are typical representations for cured materials)

Our Ultimate Goal:

Develop Comprehensive Suite of 3-D Modeling Tools for Quantitative Analyses of Thermoset Encapsulants

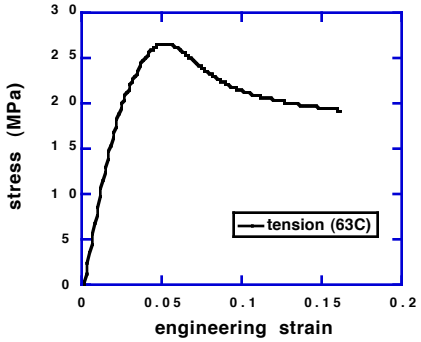


First Step: Quantitatively Predict Full Range of Polymer Behavior

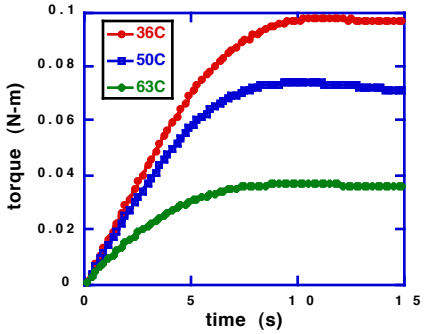


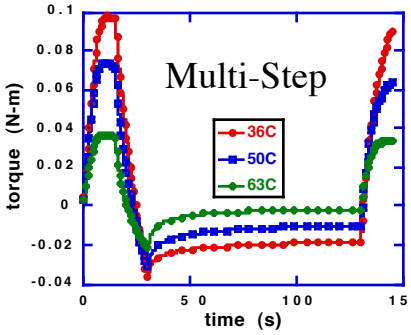
Tension →

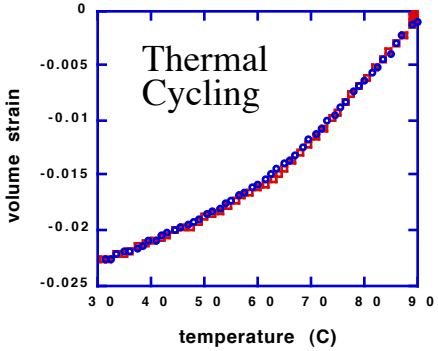
← Compression

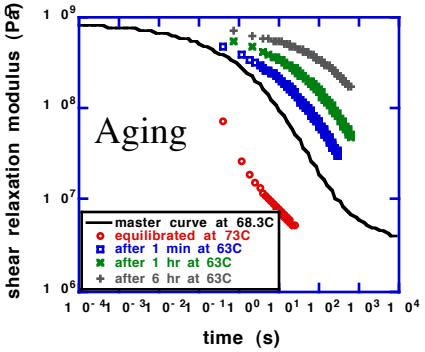


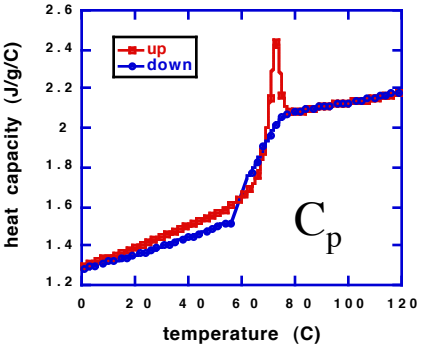
Torsion











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Our Approach: Be Physically Based

Material Behavior

intrinsic time dependence from underlying relaxation mechanism

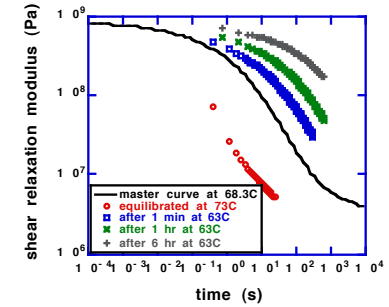
time-temperature superposition at infinitesimal deformations

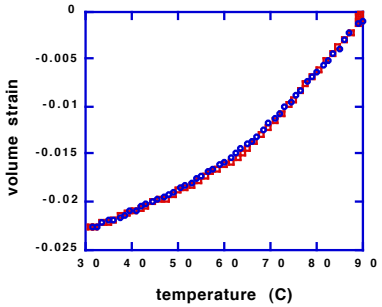
glass transition

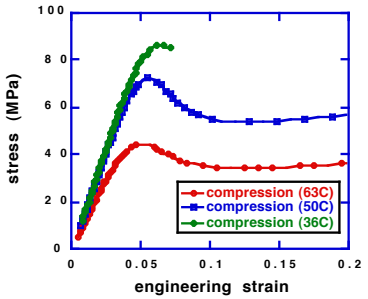
"yield-like" behavior under elevated stress levels

rapid relaxation under high strains

dissipative, reactive, sensitive to temperature







Model Requirements

viscoelasticity not plasticity

material clock
rheologically simple
limiting to WLF behavior

nonlinear formalism

finite strains

thermodynamically consistent

A Potential Energy Clock Model (PEC) for Glassy Thermosets

Sandia's high fidelity, nonlinear viscoelastic (NLVE) constitutive equation
(Caruthers, J. M.; Adolf, D. B.; Chambers, R. S.; Shrikhande, P. *Polymer* 2004; **45**: 4577-4597)

- thermodynamically consistent
  - starts from Helmholtz free energy
  - Rational Mechanics approach

"nlve_polymer" model in Sierra Codes

$$\Psi = \Psi_{decaying} + \Psi_{equilibrium}$$

$$= \frac{1}{2}\Psi_1 \int_0^t \int_0^t ds\, du\, f_1(t^*-s^*, t^*-u^*) \frac{dI_X}{ds}(s) \frac{dI_X}{du}(u) + \Psi_2 \int_0^t \int_0^t ds\, du\, f_2(t^*-s^*, t^*-u^*) \frac{d\underline{\underline{X}}}{ds}(s) : \frac{d\underline{\underline{X}}}{du}(u)$$

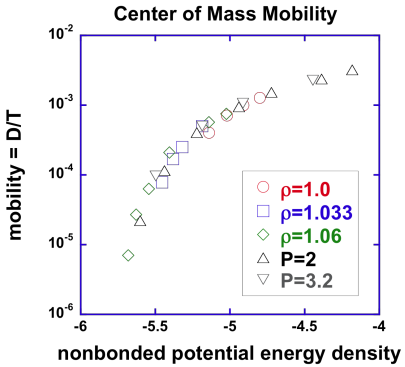
$$+ \Psi_3 \int_0^t \int_0^t ds\, du\, f_3(t^*-s^*, t^*-u^*) \frac{dI_X}{ds}(s) \frac{dT}{du}(u) + \frac{1}{2}\Psi_4 \int_0^t \int_0^t ds\, du\, f_4(t^*-s^*, t^*-u^*) \frac{dT}{ds}(s) \frac{dT}{du}(u)$$

$$+ \Psi_\infty(\rho_{ref}, T_{ref}) + \left(\psi_I I_X + \psi_T \Delta T\right) + \left(\frac{1}{2}\psi_{II} I_X^2 + \psi_{XX} II_X + \psi_{IT} I_X \Delta T + \frac{1}{2}\psi_{TT}\Delta T^2\right)$$

$$+ \left(\frac{1}{2}\psi_{IIT} I_X^2 \Delta T + \frac{1}{2}\psi_{ITT} I_X \Delta T^2 + \frac{1}{6}\psi_{TTT}\Delta T^3 + \ldots.\right) + \left(\frac{1}{24}\psi_{TTTT}\Delta T^4 + \ldots.\right) + \ldots.$$

- potential energy accelerates polymer relaxations through a material clock
  - enabling physics identified by Sandia
  - proven by MD simulations

(Budzien, J.; McCoy, J. D.; Adolf, D. B. *J. Chem. Phys.* 2004; **121**: 10291-10298)



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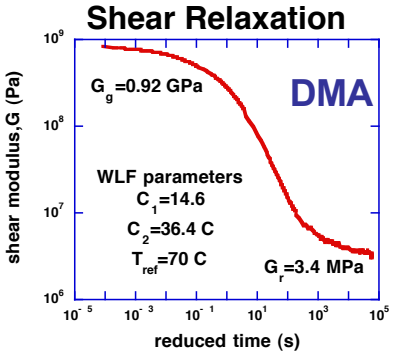
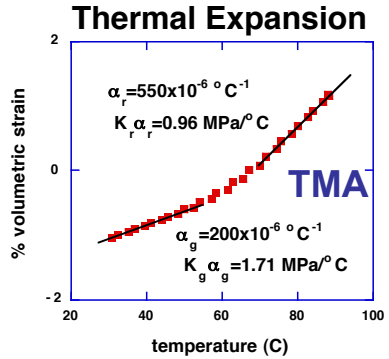
PEC Material Characterization

How do we define material properties for the model?

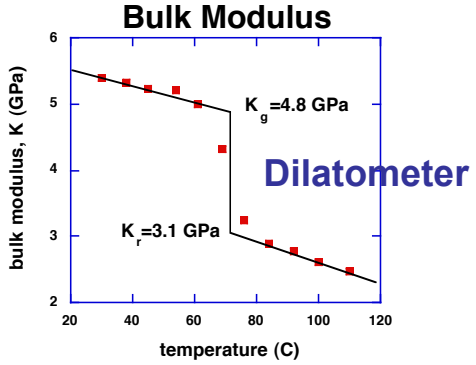


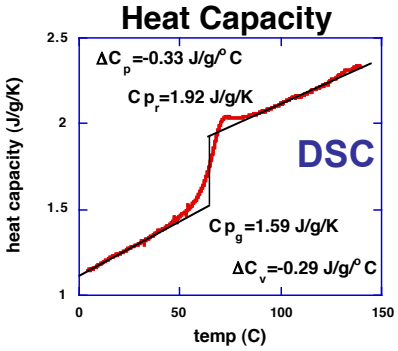


- Measure select properties including temperature and volume dependencies
- Deduce remaining coefficients and spectra by analyzing DSC and TMA experiments

Note this is a zero parameter nonlinear theory

- There are no free fitting parameters
- All model inputs come from linear viscoelastic tests





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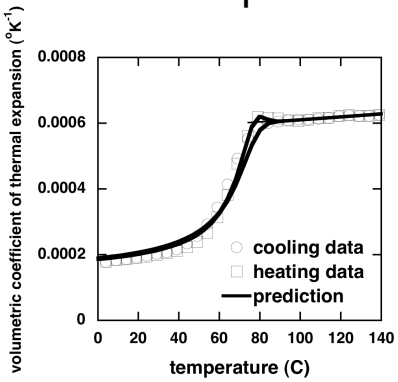
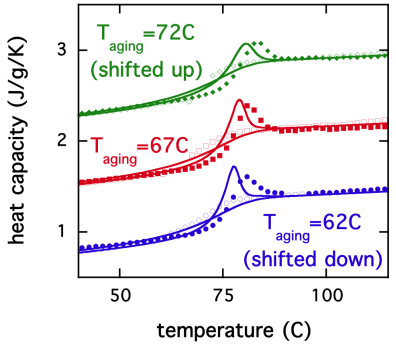
PEC Model Extensively Validated

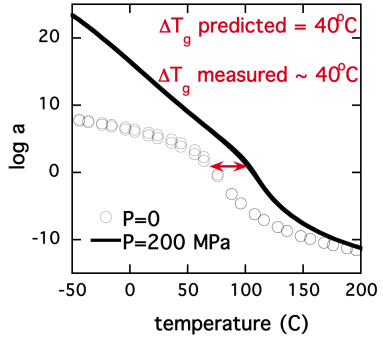
thermal expansion



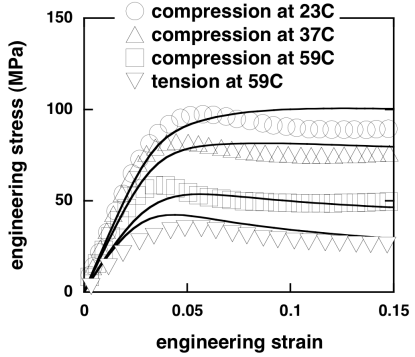
enthalpy relaxation



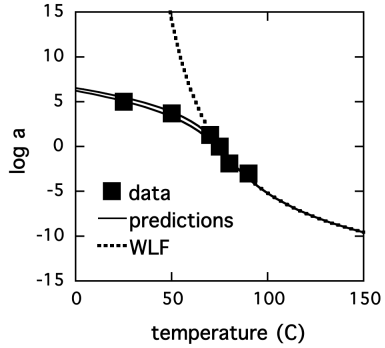
pressure dependence of the glass transition temperature



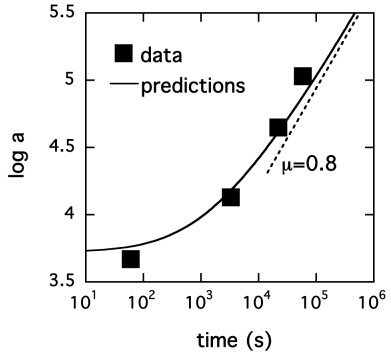
"yield" in compression and tension at three temperatures



temperature dependence of the viscoelastic shift factor



physical aging of the viscoelastic shift factor



Adolf, D. B.; Chambers, R. S.; Caruthers, J. M. *Polymer*; 2004; **45**: 4599-4621

Validated but not so easy to parameterize & compute

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Simplified Potential Energy Clock (SPEC)

- Engineering model reduces complexity of equations
  - ➢ eliminates less important T, V dependencies
  - ➢ simplifies the strain measure
  - ➢ reduces number of spectra from 4 to 2
  - ➢ makes clock more phenomenological

$$\underline{\underline{\sigma}} = \left[\Delta K \int_0^t ds\, \mathrm{f}_v(t^*-s^*)\frac{d\mathrm{I}_\varepsilon}{ds}(s) - \Delta(\mathrm{K}\alpha)\int_0^t ds\, \mathrm{f}_v(t^*-s^*)\frac{dT}{ds}(s)\right]\underline{\underline{\mathrm{I}}} + 2\Delta\mathrm{G}\int_0^t ds\, \mathrm{f}_s(t^*-s^*)\frac{\mathrm{d}\underline{\underline{\varepsilon}}_{dev}}{ds}(s)$$

$$+\left[K_\infty I_\varepsilon - K_\infty\alpha_\infty\Delta T\right]\underline{\underline{I}} + 2G_\infty\underline{\underline{\varepsilon}}_{dev} \qquad where \quad \log a = -\hat{C}_1 N/(\hat{C}_2+N)$$

$$N = \left\{\left[T(t)-T_{ref}\right] - \int_0^t ds\, \mathrm{f}_1(t^*-s^*)\frac{dT}{ds}(s)\right\} + C_3\left\{I_1(t)_{ref} - \int_0^t ds\, \mathrm{f}_1(t^*-s^*)\frac{d\mathrm{I}_1}{ds}(s)\right\}$$

$$+ C_4\left\{\int_0^t\int_0^t ds\,du\, f(t^*-s^*,t^*-u^*)\frac{d\underline{\underline{\varepsilon}}_{dev}(s)}{ds} : \frac{d\underline{\underline{\varepsilon}}_{dev}(u)}{du}\right\}$$

- Enhances computational efficiency
- Simplifies experimental characterization
- Universal_Polymer Model (UPM) in Sierra Codes ← SPEC Model

Adolf, D. B.; Chambers, R. S.; Neidigk, M. A. *Polymer* 2009; **50**: 4257-4269

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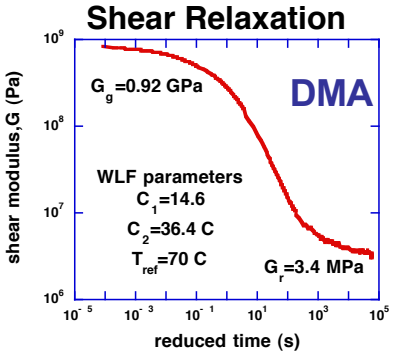
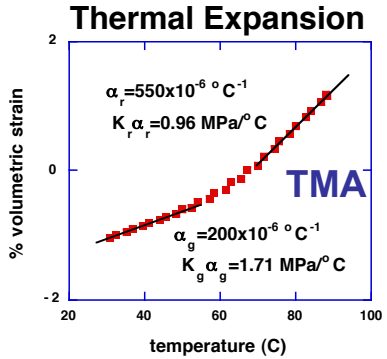
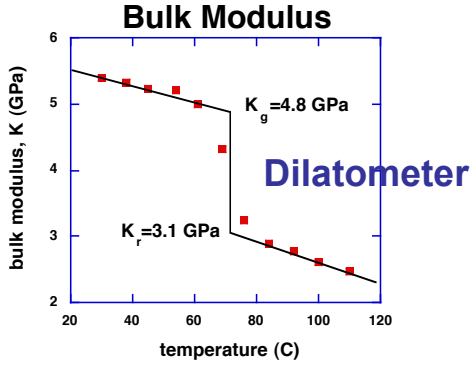
SPEC Material Characterization

How do we define material properties for these equations?

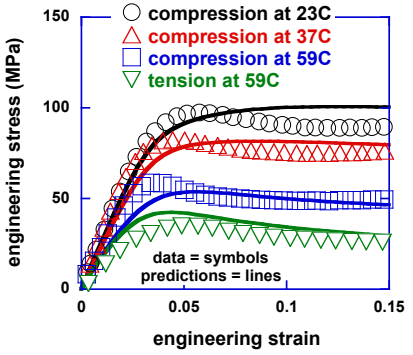




- Measure select properties
  - shear master curve
  - glassy/rubbery moduli
  - glassy/rubbery CTEs
  - bulk moduli
- Deduce clock parameters and thermal relaxation function
  - model thermal strain test
  - analyze several stress-strain tests at various temperatures
  - choose the two undefined material clock parameters to best fit data



Stress-Strain



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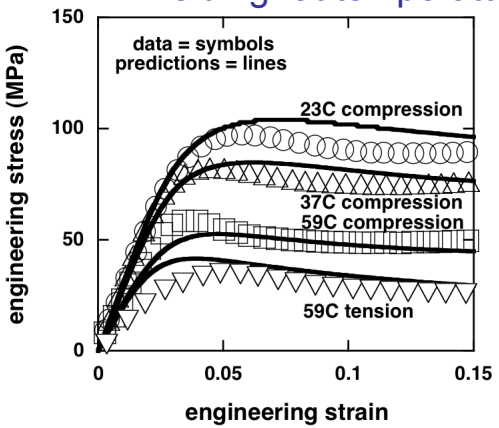
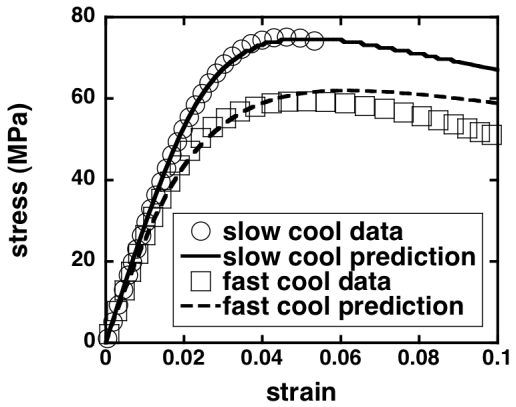
Extensively Validated SPEC Model

"Yielding" at temperature

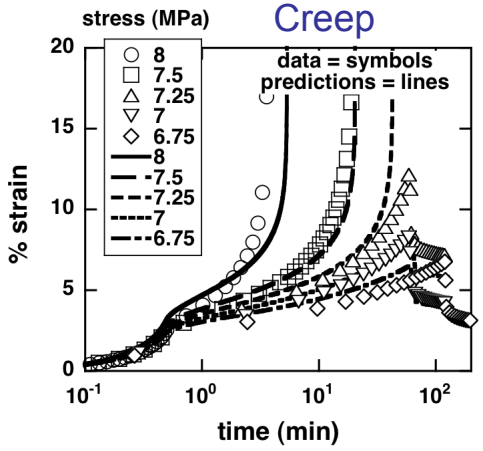


Unfilled Thermoset
Epon 828/DEA

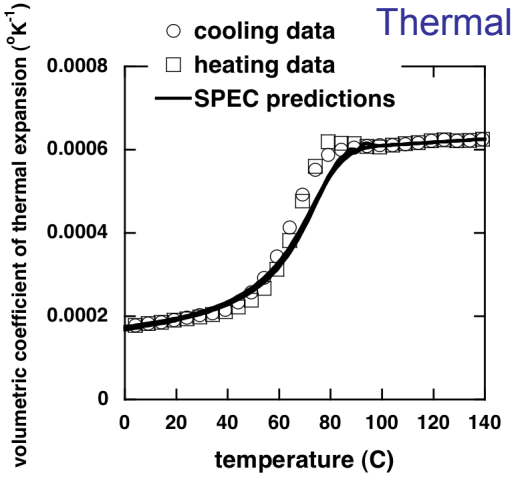
"Yield" vary VE History



Creep



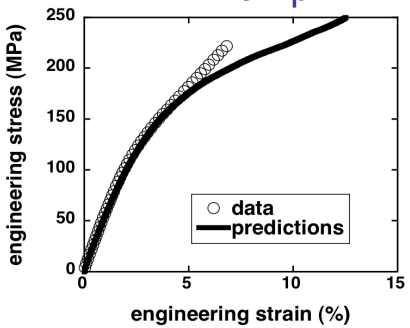
Thermal Expansion



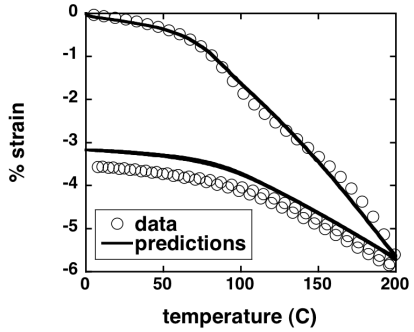
SPEC Monofilament Nylon Predictions

- nylon is a semi-crystalline thermoplastic
- process-induced anisotropy: preload above Tg, cool to 0 C, unload
  - ➢ Isoforce tests: thermal cycle under constant force
  - ➢ Isostrain tests: thermal cycle under constant strain

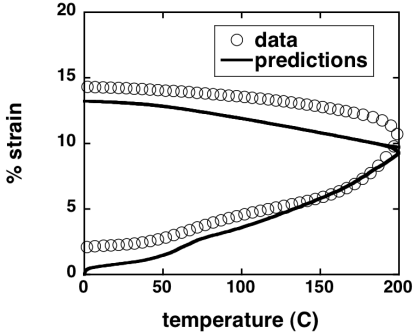
RT Ramp



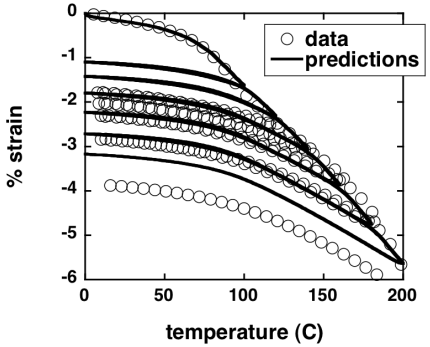
0 N Isoforce



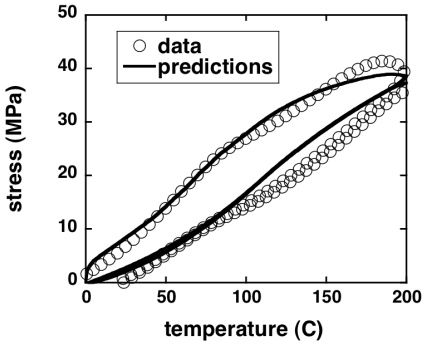
8 N Isoforce



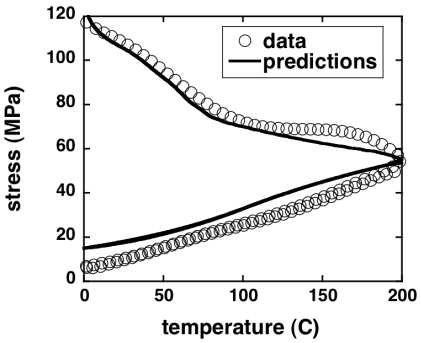
Ratcheted 0 N Isoforce



0% Isostrain

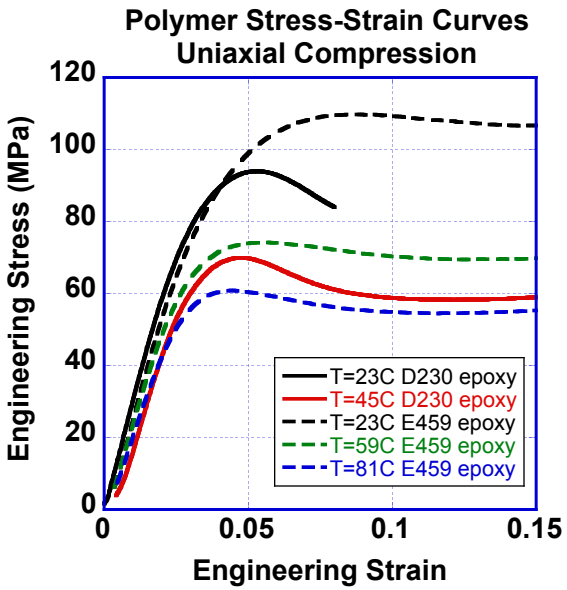


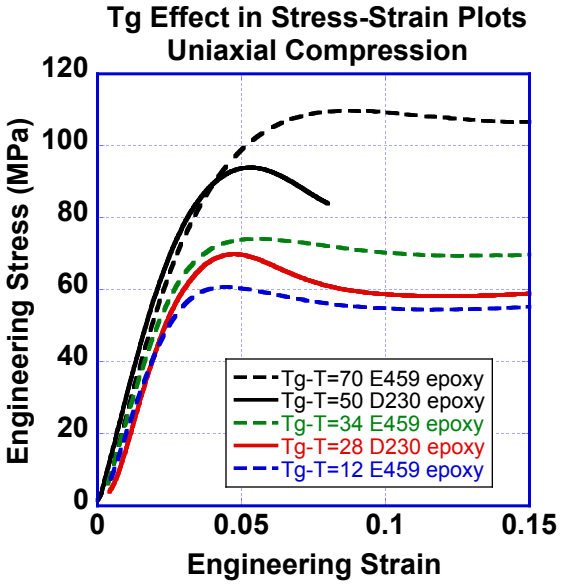
3% Isostrain

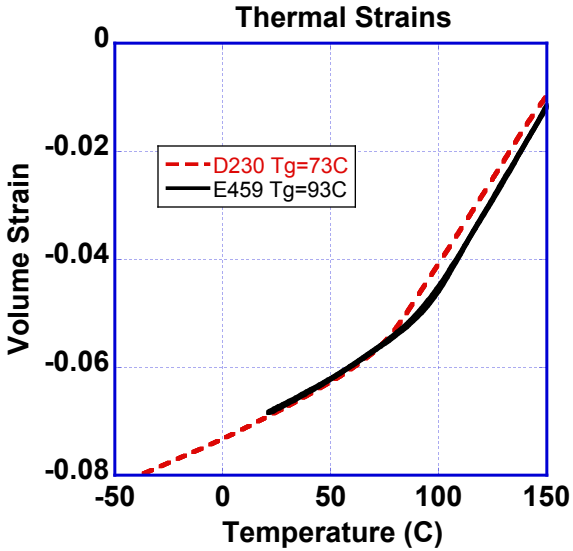


Adolf, D. B.; Chambers, R. S.; Hammerand, D. S.; Tang, M.-Y.; Westgate, K.; Gillick, J.; Skrypnyk, I., *Polymer* 2010; **51**: 1530-1539

Similarity & Order in Polymers







- Perform compression tests on unfilled polymers at different temperatures
  - plot stress-strain curves for each material at each temperature
  - curves all look quit different
- Replot data ordering it (Tg-T), i.e., by temperature difference from Tg
  - data orders systematically
  - polymer properties are very similar when normalized to Tg
  - But Tg matters!

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What about Filled-Epoxies?

- The CTE of an unfilled epoxy is a lot different from metals and ceramics (65 ppm/C versus 7 ppm/C)
- Fillers are added to epoxies to change properties
  - Glass Micro-Balloons (GMB)
    - reduce CTE and bulk moduli
    - little effect of shear moduli
  - Hard Fillers (silica, alumina, titania)
    - reduce the CTE
    - substantially increase the moduli

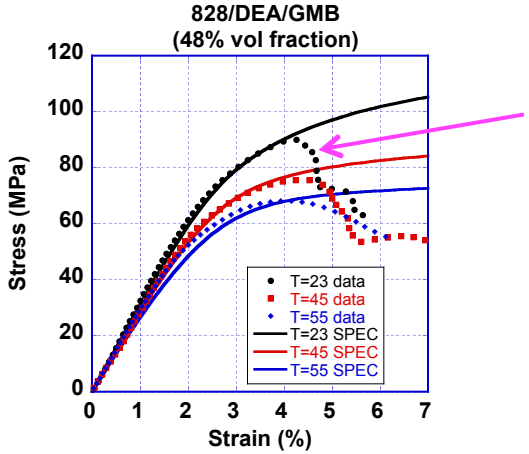
variable	828/DEA (unfilled)	828/DEA/GMB (48% FVF)	828/D230/Alox (20% FVF)
glassy CTE (ppm/C)	65	35	49
G (GPa)	0.95	1.1	2.3
K (GPa)	6	3.4	6.3
E (GPa)	2.7	3	6.2
Eα (kPa/C)	176	105	304
Kα (kPa/C)	390	120	309

Wise use of fillers can help tailor stress state

Fitting Filled-Epoxies to SPEC Model

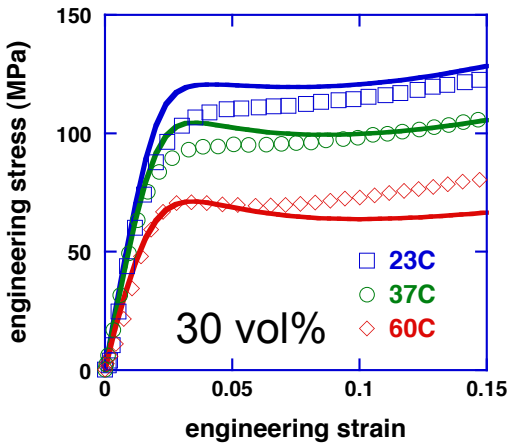
Filled epoxies can be fit to SPEC model as homogenized materials

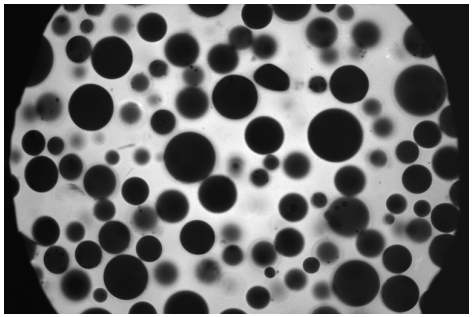
48% filler volume fraction of Glass Microballons (GMB



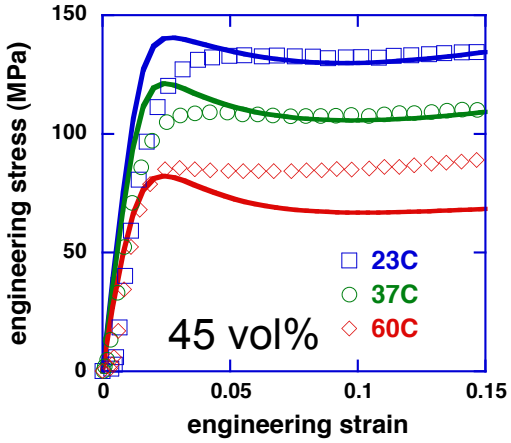
breaking of Glass Micro-Balloons

Fairly round, monodisperse silica spheres in 828/DEA





SPEC Model fits filled epoxies well



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Universal SPEC for Filled Epoxies

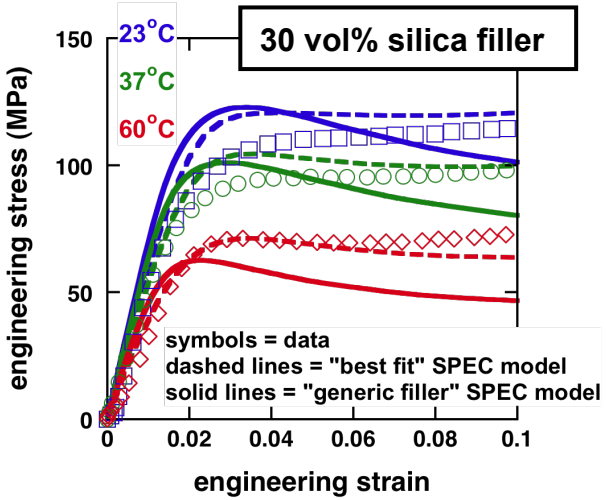
- Reasonable estimates for properties of hard-filled polymers are attainable:
  - Moduli and CTE can be approximated by the rule of mixtures:

$$\psi = \psi_p \left(1 - \phi_f\right)^x$$

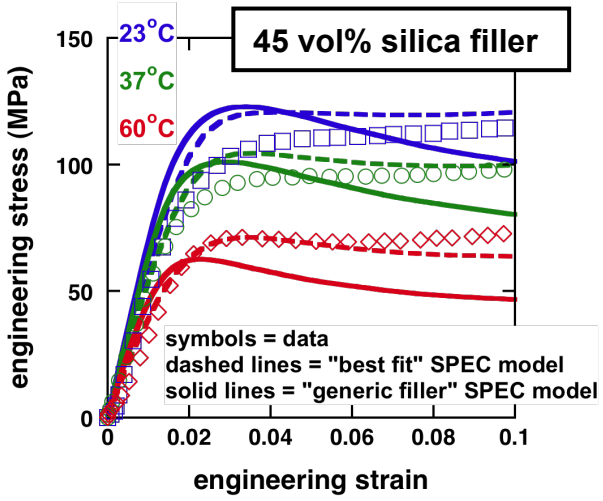
ψ is the filled material property
ψ_p is the unfilled material property
Φ_f is the filler volume fraction
x is a constant determined by fit to data

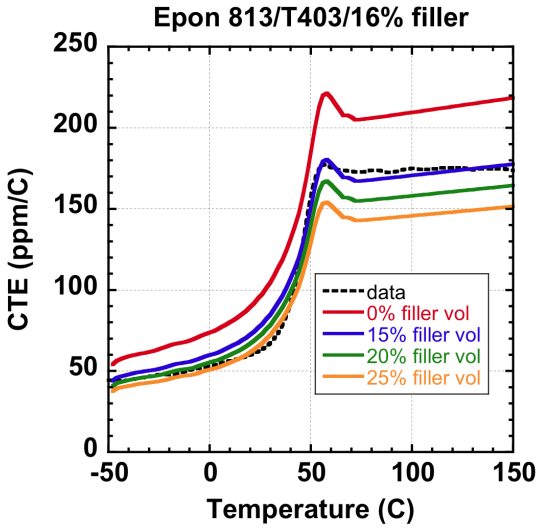
  - Similar process can be applied for GMB-filled epoxies
    - ✓ exponent is different
    - ✓ only CTE is scaled (moduli are not)
- Because all epoxies behave similarly relative to their own Tg, it is possible to construct an approximate "universal" or generic SPEC parameter set
  - User must input only two parameters: Tg and filler volume fraction
  - All other inputs are defined from defaults or approximated
- Powerful tool for performing design feasibility studies (optimize material)

Universal SPEC Comparisons

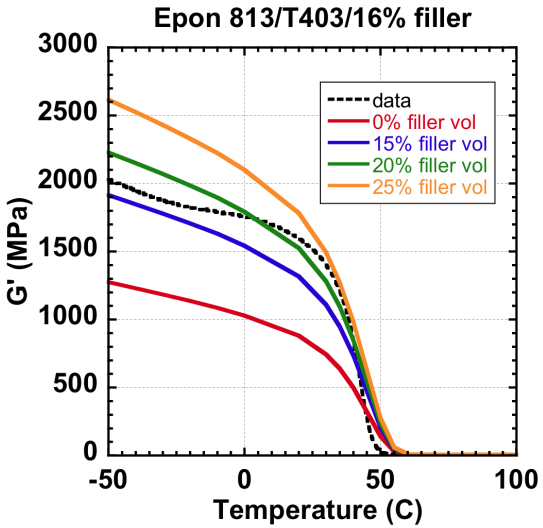


Compare data "fit" "generic"





Compare data to "generic"



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SPEC Model for Curing

Polymerization during manufacturing can generate stresses and strains

Adolf, D. B.; Chambers, R. S. *J. Rheol.* 2007; **51**: 23-50

- epoxy reactions can be exothermic generating temperature gradients
- cross-linking produces cure shrinkage
- Tg increases with extent of cure

Cure shrinkage effects can be captured by introducing a new independent variable, the extent of reaction (x), to the nonlinear viscoelastic equations

$$\underline{\underline{\sigma}} = \left[\Delta K \int_0^t ds\, f_v(t^* - s^*) \frac{d\mathrm{I}_\varepsilon}{ds}(s) - \Delta(\mathrm{K}\alpha) \int_0^t ds\, f_v(t^* - s^*) \frac{dT}{ds}(s) - \Delta(\mathrm{K}\beta) \int_0^t ds\, f_v(t^* - s^*) \frac{dx}{ds}(s) \right] \underline{\underline{\mathrm{I}}}$$

$$+ 2\Delta \mathrm{G} \int_0^t ds\, f_s(t^* - s^*) \frac{d\underline{\underline{\varepsilon}}_{dev}}{ds}(s) + \left[K_\infty I_\varepsilon - K_\infty \alpha_\infty \Delta T - K_\infty \beta_\infty \Delta x \right] \underline{\underline{I}} + 2 \int_0^t ds\, G_\infty(s) \frac{d\underline{\underline{\varepsilon}}_{dev}}{ds}(s)$$

cure shrinkage terms

permanent set term

Cure modeling enables:

- higher fidelity residual stress predictions (do not have to neglect manufacturing)
- model based optimization of manufacturing process (cure schedule design)

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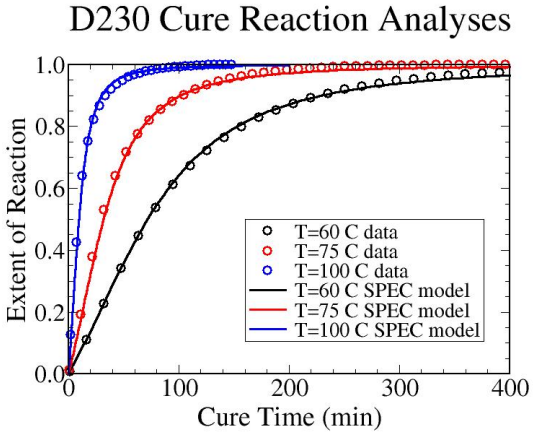
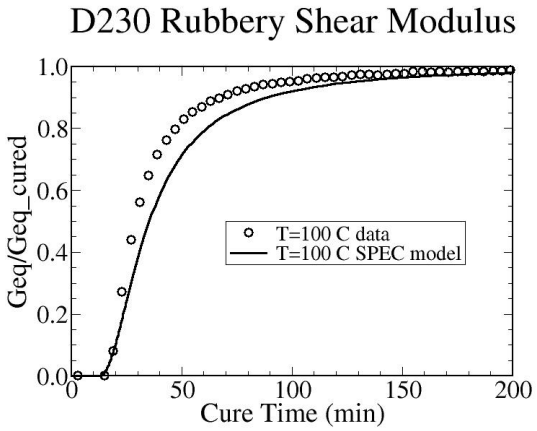
SPEC Curing Predictions

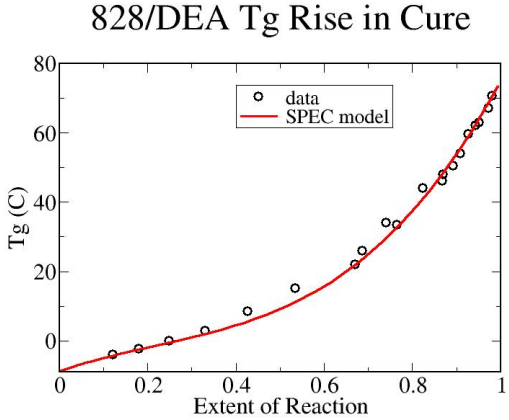


Reaction rate varies with reaction and temperature and quenches through material clock during vitrification

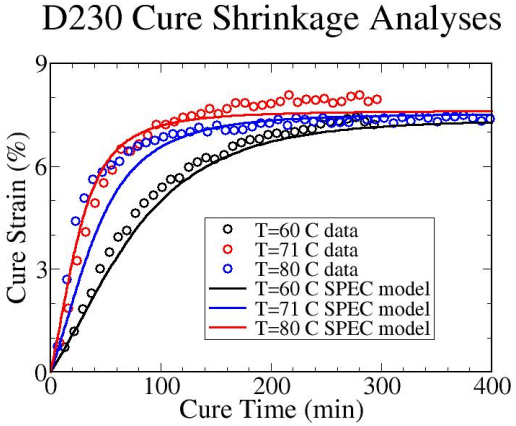
$$\frac{dx}{dt} = \hat{k}\left(b + x^m\right)(1-x)^n$$

$$\hat{k} \equiv \frac{k_o e^{-\frac{E_a}{RT}}}{\left(1 + w\,a\right)^{\beta}}$$





Model naturally predicts Tg rise and cure shrinkage during polymerization



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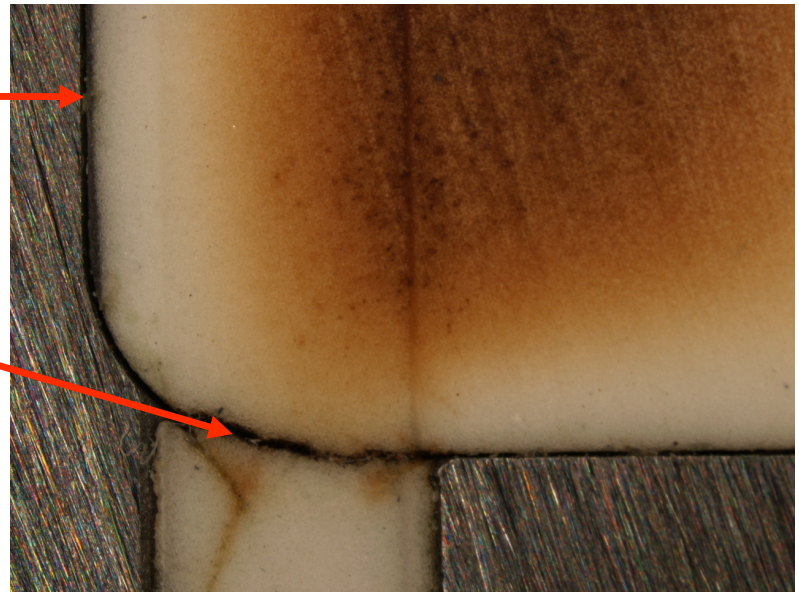
What About Epoxy Failures?

Epoxies can fail:

- cohesively – cracking
- adhesively – debonding at a material interface

In general, a polymer will de-bond prior to cracking if it can.

Adhesive de-bonds can propagate as a cohesive crack.

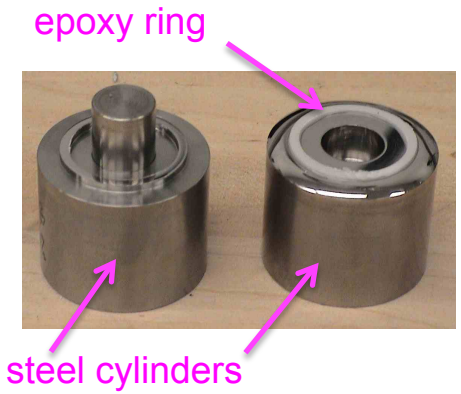


Debonding can:

- shear off PCB components
- damage solder joints
- generate high voltage breakdowns

Consequently, our focus has been on predicting the *initiation of debonding* at a polymer interface

Initiation of Adhesive Failure in Napkin Ring Test

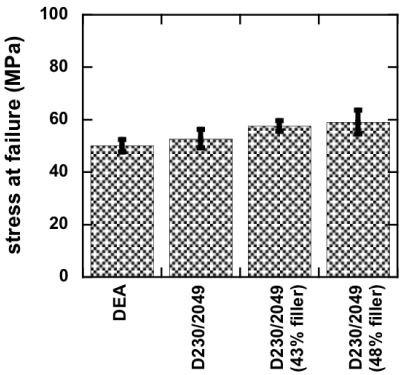


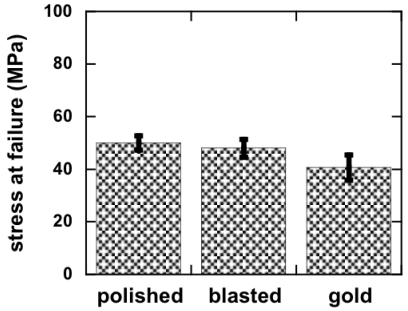
Napkin Ring Geometry

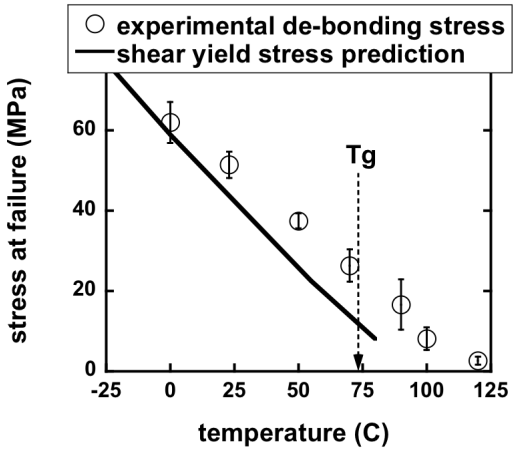
- measure torque at failure under monotonic loading
- analyze test with SPEC model for epoxy
- examine stresses/strains at failure seeking failure criterion

failure stress varying resin, filler, substrate & finish

Adolf, D. B.; Stavig, M. E.; Kawaguchi, S.; Chambers, R. S., *J. Adhesion* 2007; **83**: 85-104







- Initiation is not sensitive to resin, filler, substrate, finish
- Initiation event correlates with polymer yielding

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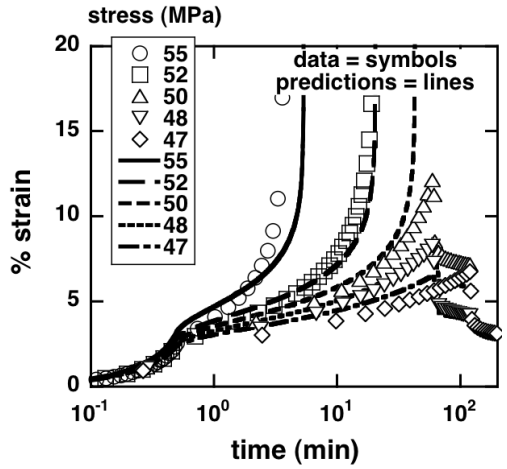
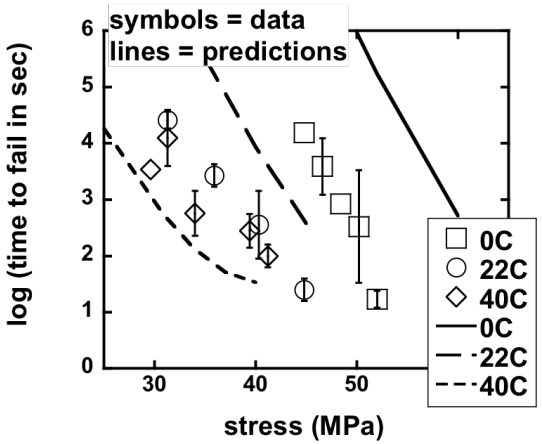
Failure Initiation Is Time Dependent

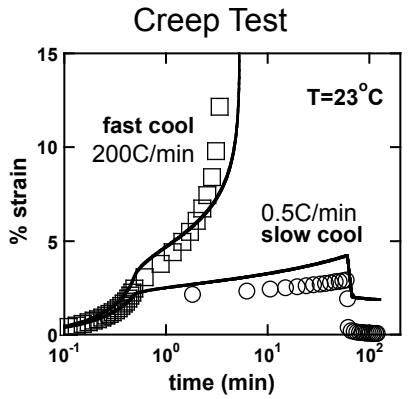


Perform Napkin Ring Creep Tests

- vary applied load and temperature
- compare data to FEA predictions using SPEC model
- note model "failures" as strains blow up
- run-away viscoelasticity appears to be a natural metric for initiation of debonding



- **SPEC model predict epoxy yielding and creep**
- **Predicts initiation of adhesive debonding through run-away viscoelasticity**
- **BUT – results are very sensitive to history**



Adolf, D. B.; Chambers, R. S.; Hance, B.; Elisberg, B. accepted for publication in *J. Adhesion* 2010

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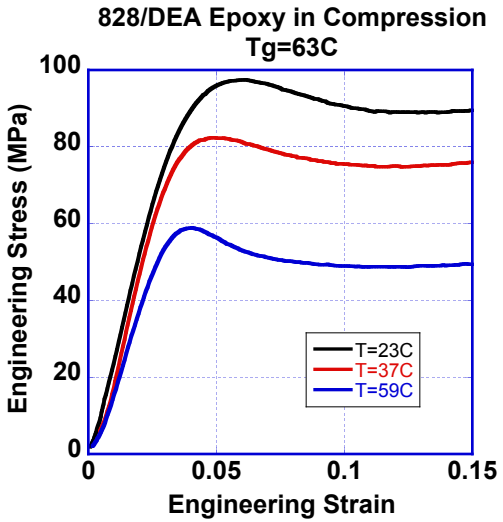
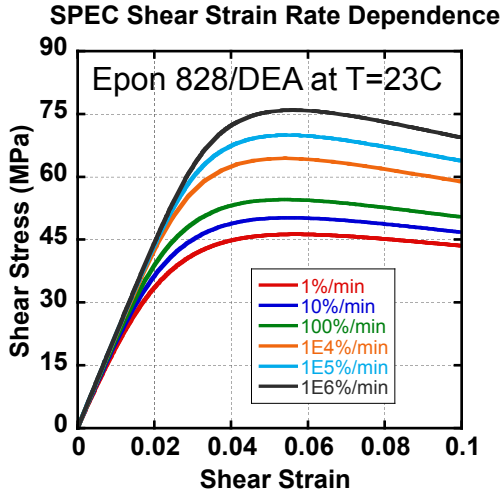
Things to Remember about SPEC NLVE Polymer Modeling

The higher fidelity SPEC model can make life for the analyst much easier:

- eliminates the need for many simplifying property assumptions
- physically based model naturally accounts for:
  - ✓ temperature dependence: Tg, changes in CTE and G modulus
  - ✓ loading rate sensitivities – including temperature dependence
  - ✓ time dependence: stress relaxation, creep, physical aging
  - ✓ material nonlinearities: "yielding"
  - ✓ a failure mechanism: run away nonlinear viscoelasticity





More Things to Remember about SPEC NLVE Polymer Modeling

To attain the higher fidelity results, analyses become more complicated:

- viscoelastic analyses are history dependent (fading memory)
  - ✓analysis cannot start at room temp if Tg is much higher (stress integrals would not be able to decay away that far below Tg)
  - ✓analysis must begin at a known stress-free state, e.g., cure temp
- a sequential material time-history including temperature and accompanying BCs must be specified
- solutions are tracked by stepping through the actual time history (time steps have meaning – they are not just load increments)
- viscoelastic stresses from manufacturing (e.g., cure) define residual stress state for subsequent thermal and/or dynamic environments

Even if you do not have a fully characterized material, the Universal SPEC model can make reasonable predictions based on knowing only Tg and filler volume fraction.