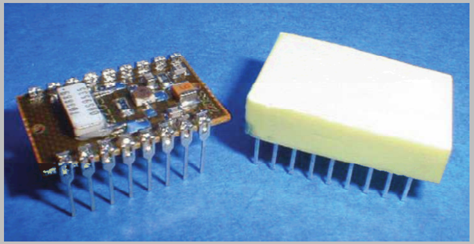
SAND2012-2756P

Exceptional service in the national interest

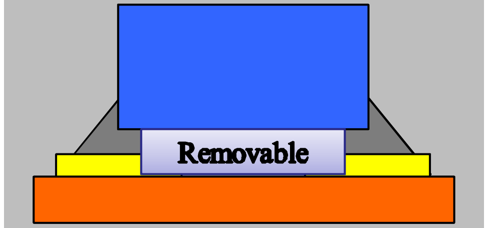
Sandia National Laboratories

Removable Encapsulation

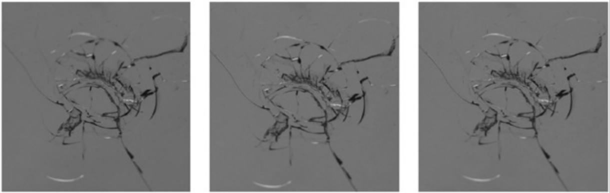


Mcelhanon, Russick, Aubert, *Science Matters* SAND 2010

Underfill Scenario



An Epoxy "Healing"



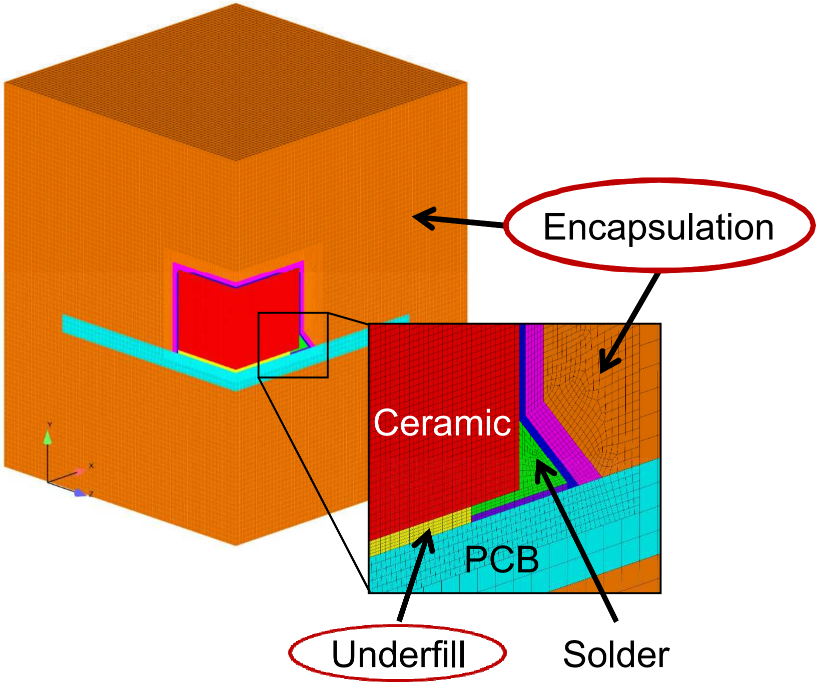
Tian, *et. al.*, J. Mat. Chem. 2009

The Mechanics of Removable Network Polymers

Kevin Long, Solid Mechanics Department, Engineering Sciences Center

The Need for Removable Encapsulation

- Encapsulation of Printed Circuit Boards (PCB) provides *mechanical integrity, voltage isolation,* and *isolation from moisture, dust, …*
- Traditional encapsulation cannot be removed without damaging PCBs
  - Reworking/upgrading components is not cost effective
  - In-service evaluation of components for lifetime assessment is not feasible
- *A removable encapsulation material is needed*

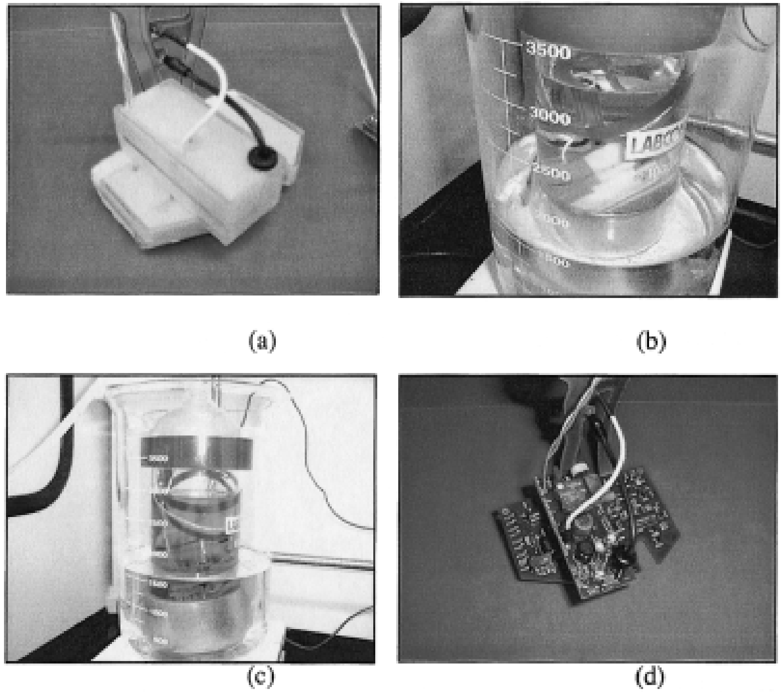


*Finite Element Mesh of a quarter symmetry capacitor showing the underfil and cover coat

*Adolf D., *et al.* SAND2011-4751

Removable Encapsulation Is Used at Sandia to Support Stockpile Stewardship

- Basic characterization and simple experimental demonstrations exist at Sandia and in the literature.
- Design/use is driven by experiment
- The effects of removability on the mechanical behavior of such materials during their service lifetimes have not been evaluated.

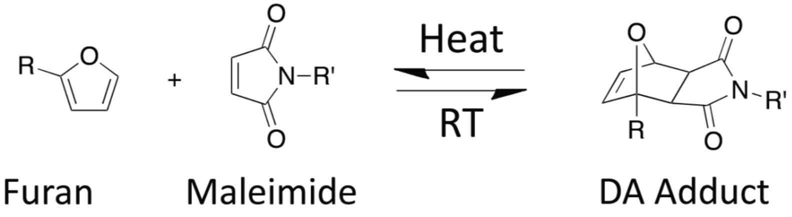


Mcelhanon, *et al.* App. Polymer Sci., 2002

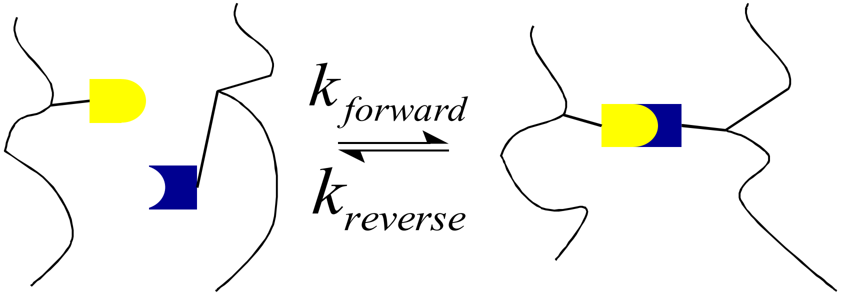
A foam fully encapsulating a PCB is non-destructively removed in the presence of a solvent at 40 Celcius.

Removable Network Polymer Basics

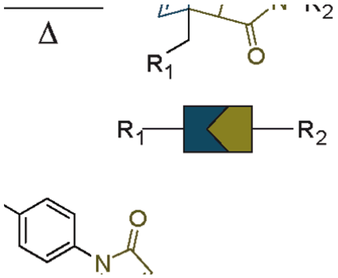
Diels-Alder Thermal Chemistry*



Network Scission/Reformation Mechanism



Network Architecture**



"Removability" arises from the cleavage and reformation of function groups along the polymer chain.

At Sandia, the thermally-activated Diels-Alder (DA) reaction is used to break and reform cross-links or chains.

When a sufficient number of cross-links break, the material behaves as a liquid (and can be removed)

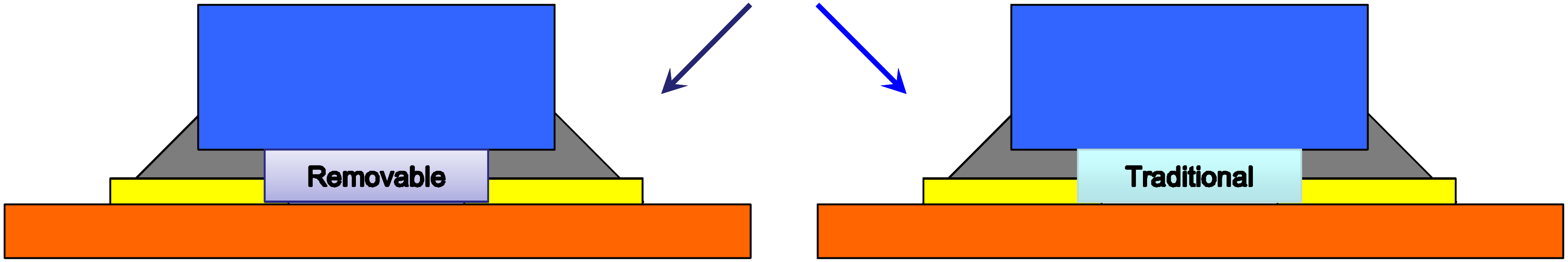
As cross-links break and reform, the network relaxes → the permanent shape of the material changes in time…

*Mcelhanon, Russick, Aubert, *Science Matters* SAND 2010
**Kloxin, *et al.* Macromolecules, 2010 d

Current Technology Gaps

- No theoretical/computational description of the effects of reversible chemistry on the performance of removable encapsulation *in service*

Pros vs. Cons



- Reversible chemistry effects on cure shrinkage stresses during encapsulation cure have not been studied
- No capability to predict behavior during removal

Our Approach And Goals

Develop a capability to predict the thermal-chemical-mechanical behavior of removable encapsulation to support Sandia’s NW mission

Phase I: Multi-Physics Model Development

- Diels-Alder Thermal Chemistry
- Thermodynamics consistent constitutive equation

Phase II: Investigate the Effects of Network Evolution in Encapsulation Scenarios

- Compare the behaviors of removable vs. standard thermosets in weapon applications
- Improve the technology
    - Optimize the current design to take advantage of the removable chemistry
    - Provide input/direction for future designs

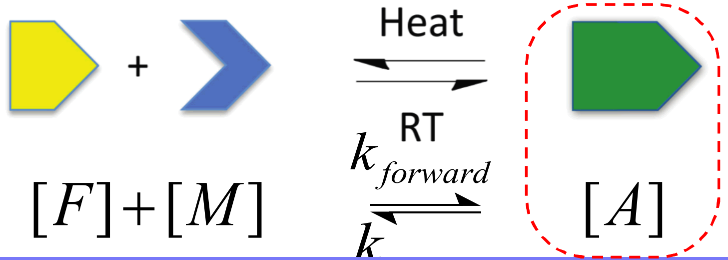
Diels Alder Thermal-Chemistry: Equilibrium

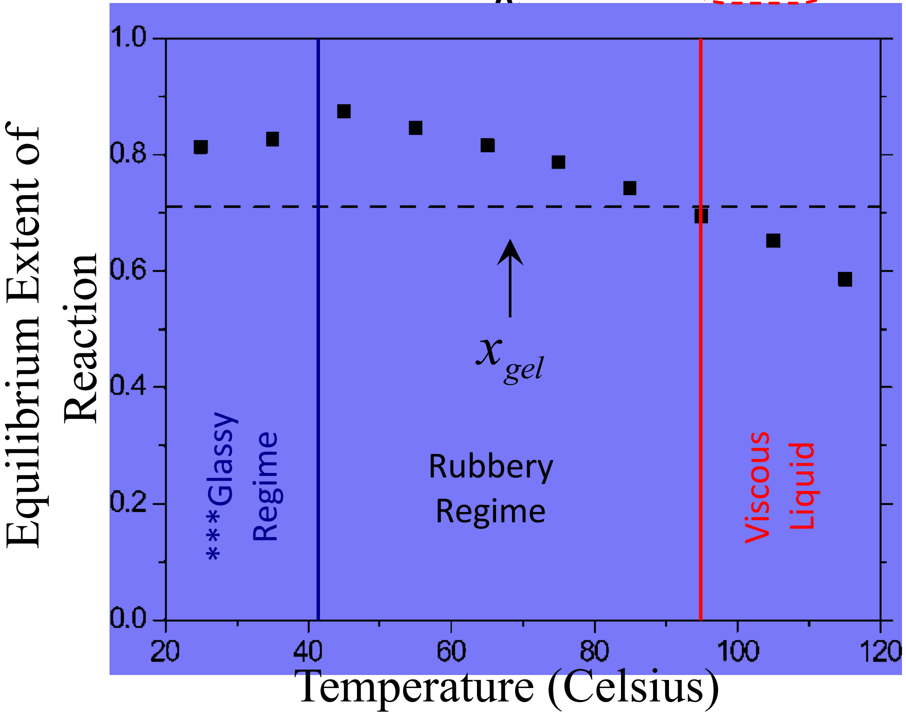
The cross-link density is set by the Extent of Reaction ([A]/[A]$_{max}$)

- The DA equilibrium reaction constant is temperature dependent and is set by the associated Gibbs free energy

- The transition solid to liquid polymer behavior is set by [F], [M], and [F]/[M]

Diels-Alder Thermal Chemistry*





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*Mcelhanon, Russick, Aubert, *Science Matters* SAND 2010

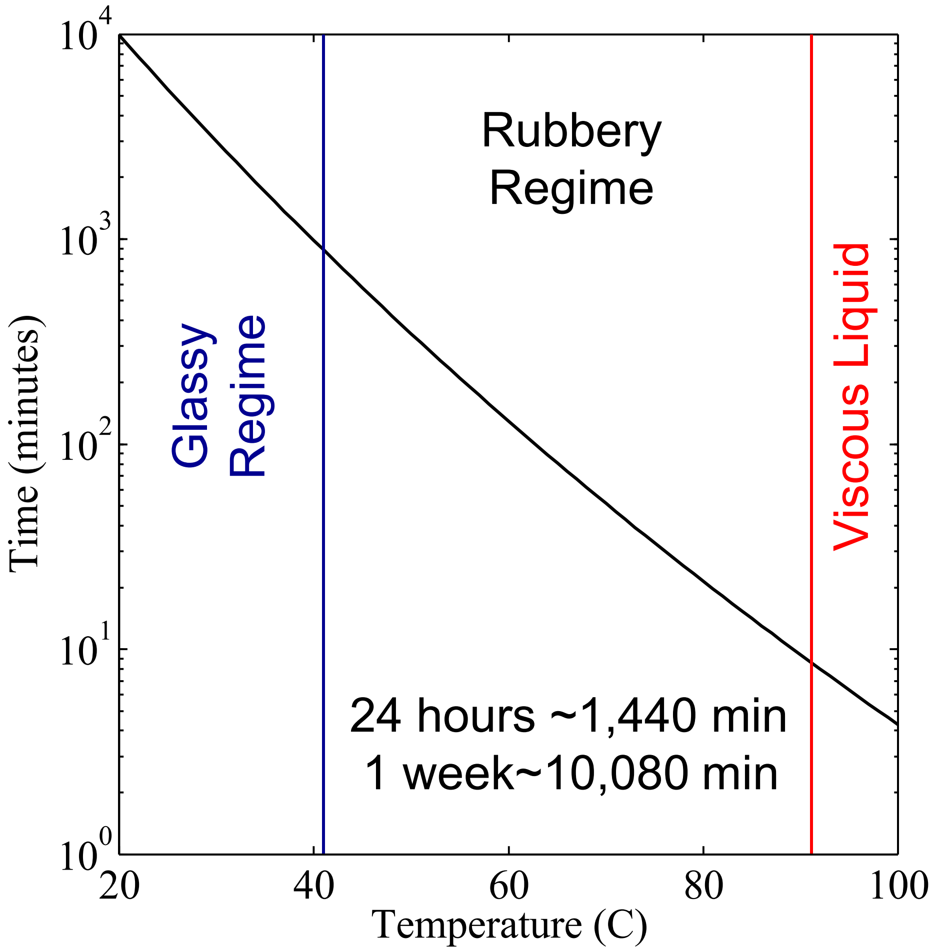
**Adzima, *et al.* Macromolecules, 2008

***Vitrification prevents reaching eq. extent of reaction

Diels Alder Thermal-Chemistry: Kinetics

The DA chemistry cannot be arrested even at lower T → material always evolves

Characteristic Half-Life of a Cross-link



DA Kinetics Model Summary

- Assume second order thermal chemical kinetics
- Conservation statement of chemical species
- Thermally activated forward and reverse reaction rates

Constitutive Model: Free Energy

- Focus on rubbery (elastomeric) state:

$$\boxed{T_{glass} < T < T_{gel}}$$

- Equilibrium Helmholtz free energy associated with elastic deformation

$$\boxed{\Psi\left(\mathbf{H}, T, x, \xi\right)}$$

Thermodynamic Variables	
Logarithmic Strain	$\mathbf{H}$
Absolute Temperature	T
Stress-Free Strain	ξ
Extent of Reaction	x

- Shear modulus dependence on T and x

$$\boxed{\mu = \mu_0\left(x - x_{gel}\right)k_{Boltzmann}T}$$

- Equilibrium bulk modulus assumed constant

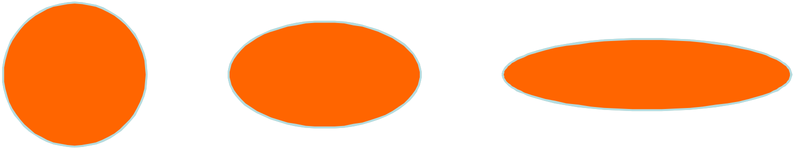
Shear modulus/free energy depend linearly on the cross-link density

Constitutive Model: Internal State Variable Evolution Rules

- Evolution of the stress-free shape:

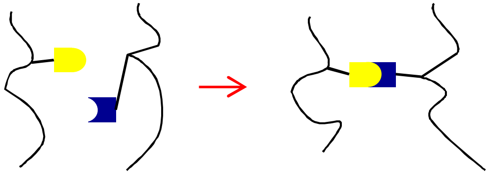
Adding/removing cross-links changes the permanent shape

$$\dot{\xi} = \frac{\dot{\mu}_+}{\mu}\left(\mathbf{H}_{dev} - \xi_{dev}\right)$$



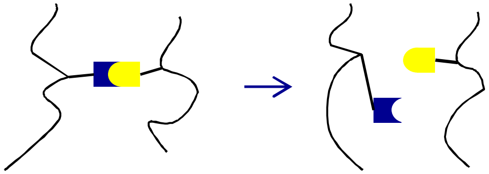
- Forward reaction increases the shear modulus:

$$\dot{\mu}_+ = \frac{\mu_0 K k_r}{2}[A_{\max}](1-x)^2 \qquad if \;\; x > x_{gel}$$



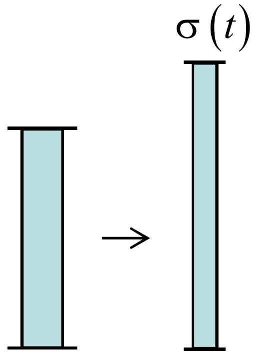
- Reverse reaction decreases the shear modulus:

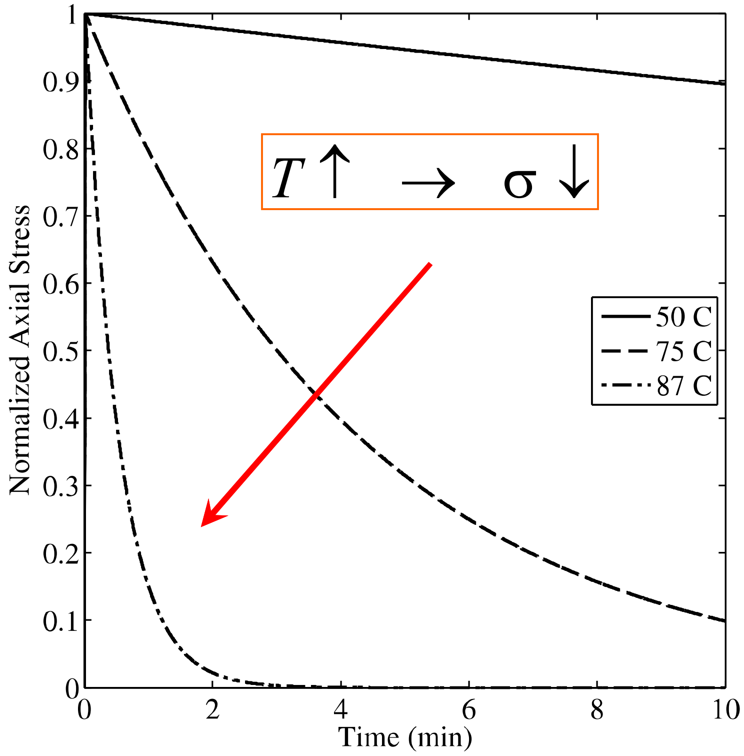
$$\dot{\mu}_- = \mu_0 k_r x \qquad if \;\; x > x_{gel}$$



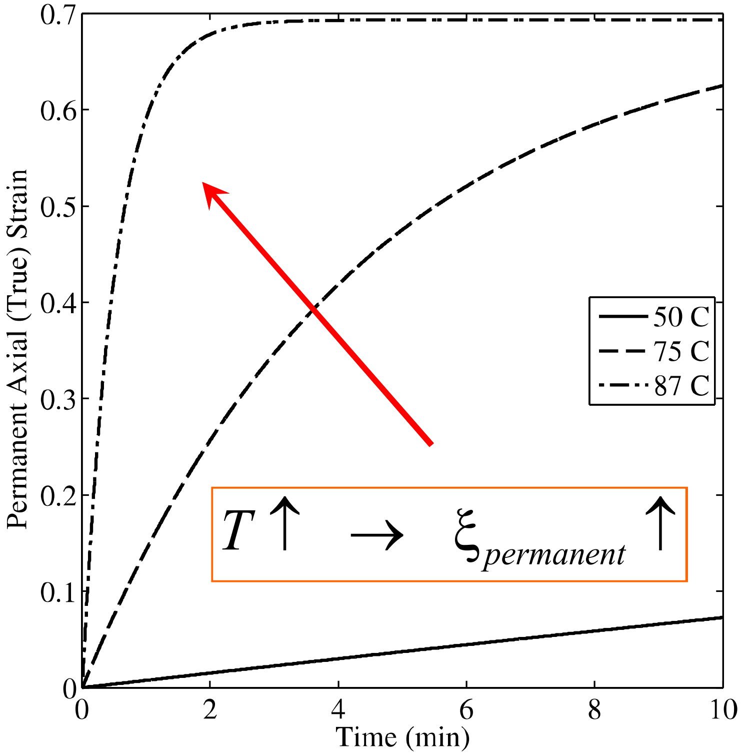
Current Results: Demonstration of Isothermal Stress Relaxation

Adding/removing cross-links changes the permanent shape





Normalized Axial Stress



Permanent Axial Deformation

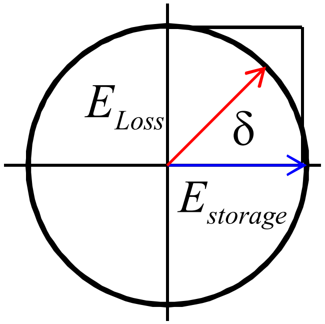
Current Results: Validation Against Dynamic Mechanical Analysis Data

No Fitting Parameters in the Model

- Examine the dissipation behavior of cyclically loaded specimens

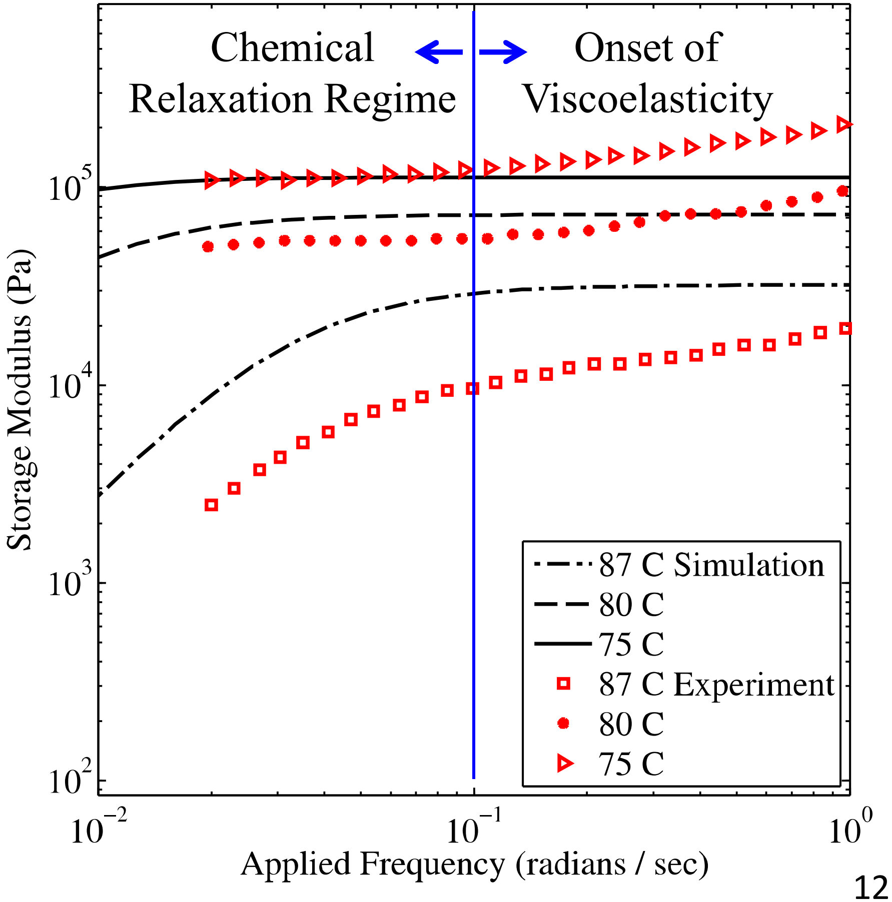
$$\varepsilon(t) = \varepsilon_0 \sin(\omega t)$$

Apply an oscillating strain



Record the complex modulus

Storage Modulus



Experimental data from Adzima, *et al.* Macromolecules, 2008

Current Results: Effects of Permanent Shape Evolution During a Thermal Cycle

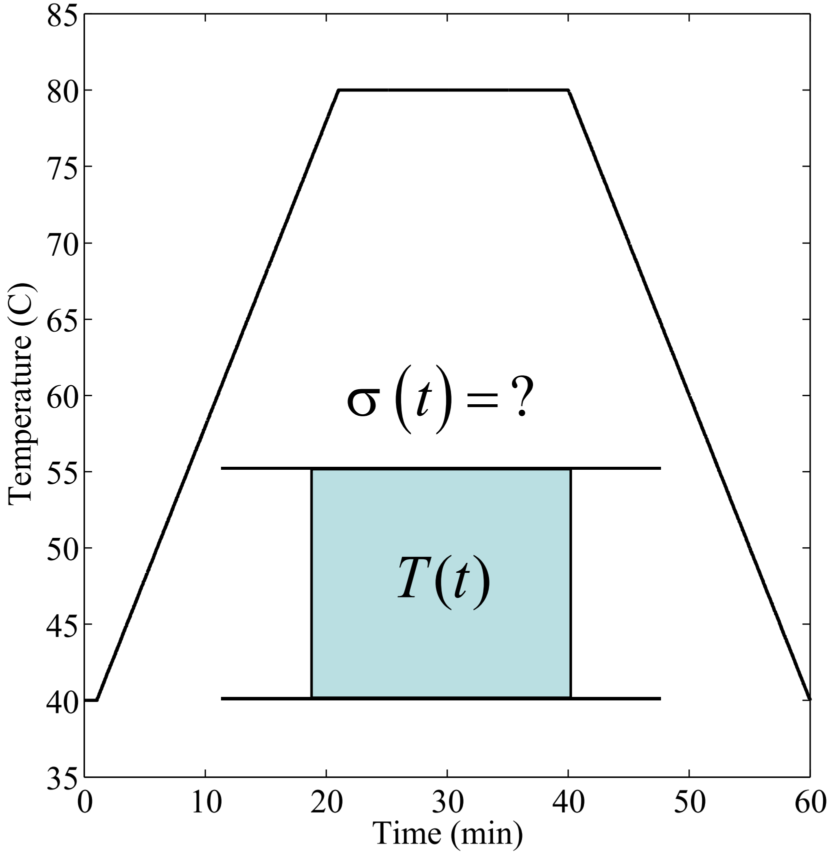
Thermal-Mechanical Cycle

- Specify temperature history
- Fix deformation in 1 direction

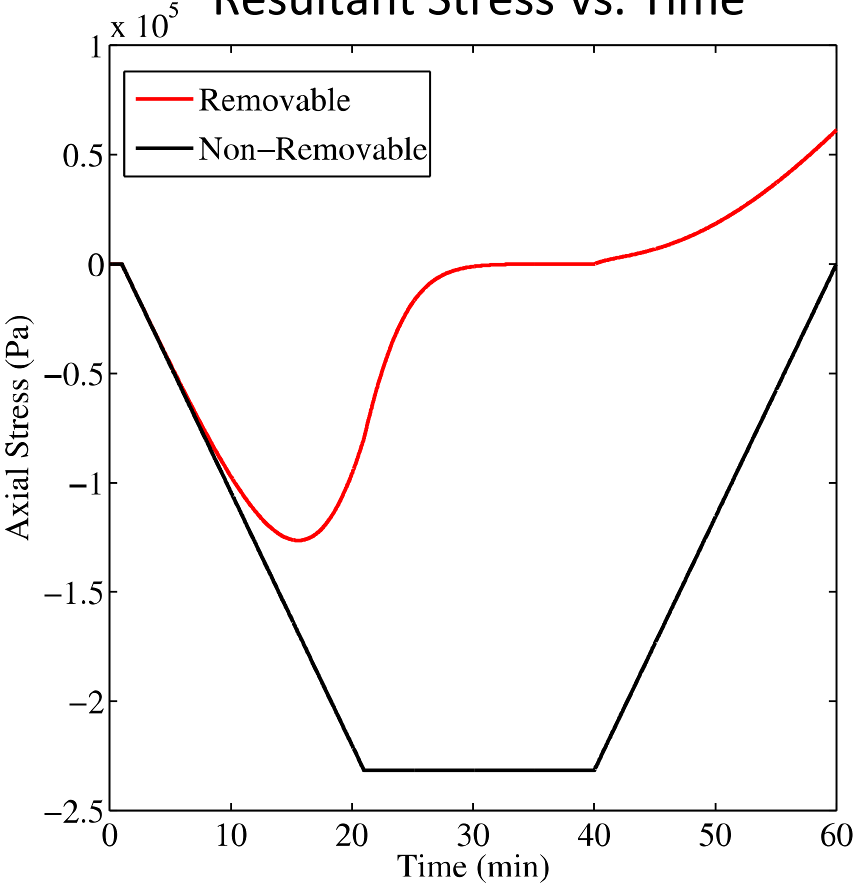
"To Flow, or Not to Flow…?"

Reversible Chemistry Reduces Peak Stresses

Applied Temperature vs. Time



Resultant Stress vs. Time



Future Work

Phase I: Multi-Physics Model Development

- Currently adding Sandia’s non-linear viscoelastic model for amorphous thermosets to capture the glassy behavior
- Currently augmenting the permanent deformation tensor evolution to account for the *Loss of Cross-links*

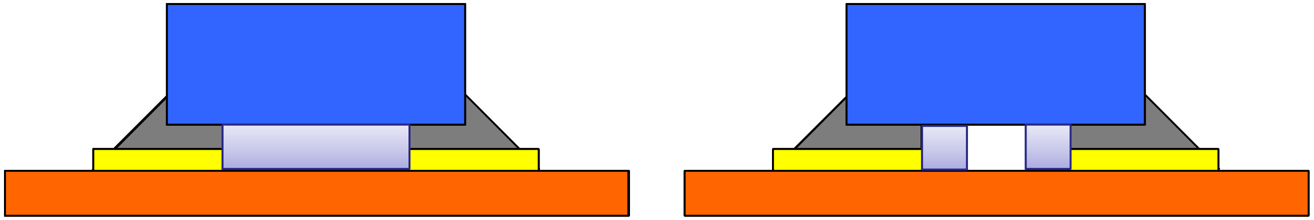
$$\boxed{\dot{\xi} = \frac{\dot{\mu}_+}{\mu}\left(\mathbf{H}_{dev} - \xi_{dev}\right) \rightarrow fun\left(\dot{\mu}_+, \dot{\mu}_-, \mu, \mathbf{H}_{dev}, \xi_{dev}\right)}$$

- Ensure updated model consistency with the Second Law of Thermodynamics

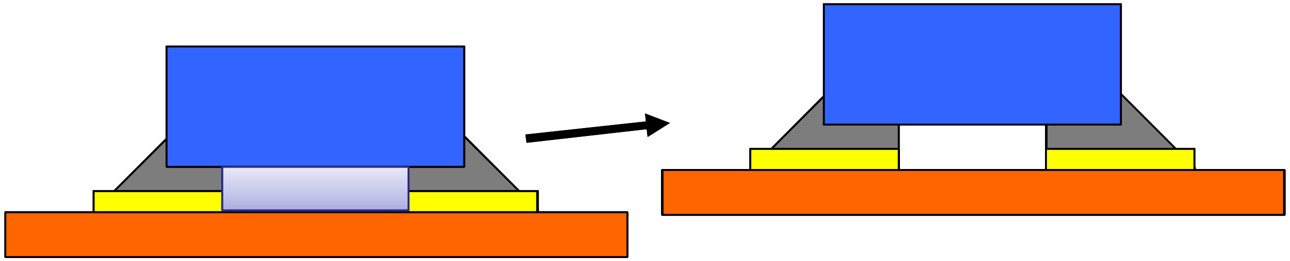
Future Work

Phase II

- Examine/optimize the effects of cross-link evolution and the role of confinement, voids, free surfaces in real encapsulation scenarios



- Simulate the process of removing the polymer and the effects of surface tension via coupling with in house fluids codes



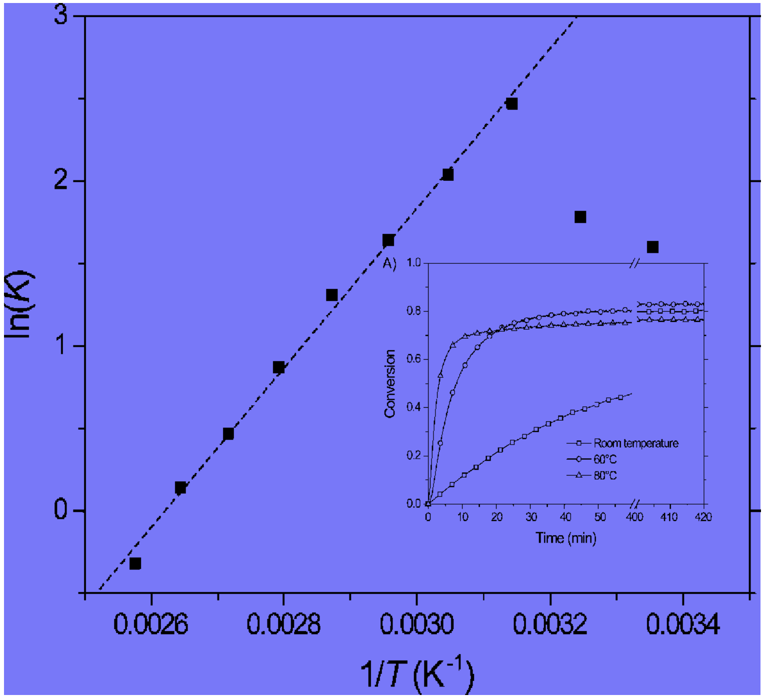
Summary

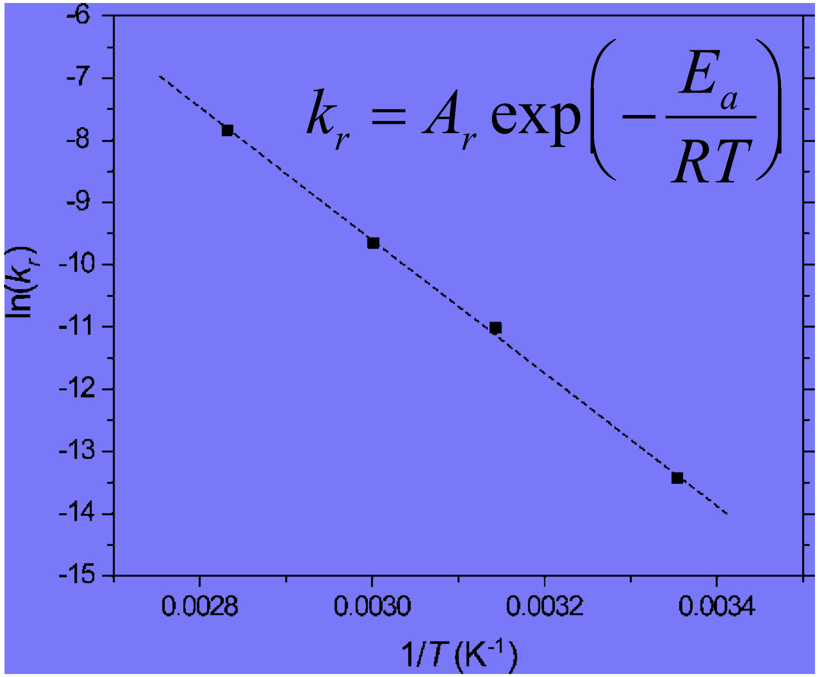
- A **multi-physics constitutive framework** was developed to represent removable encapsulation
  - Adding/removing cross-links relaxes the state of stress and causes permanent shape change
  - The kinetics of adding/removing cross-links can be slowed, but it cannot be shutoff
- Model implemented in the **Sierra Mechanics Code Suite**
- The effects of **reversible chemistry** may beneficially **mitigate stresses** developed during thermal cycling of encapsulation materials.

***The Early Career Laboratory Directed Research and Development Program supports this work and has connected me with materials science colleagues well outside of the Engineering Sciences Center

SUPPLEMENTARY MATERIAL

Equilibrium And Chemical Kinetics





$$k_r = A_r \exp\left(-\frac{E_a}{RT}\right)$$

Assuming equal concentrations of [F],[M]

$$K = \frac{[A]}{[M][F]} = \frac{x}{c_0(1-x)^2}$$

At the reaction equilibrium:

$$0 = \frac{d[F]}{dt} = -k_f[F][M] + k_r[A] \rightarrow K = \frac{k_f}{k_r}$$

Adzima, *et al.* Macromolecules, 2008

Equilibrium Helmholtz Free Energy Per Unit Mass

- Focus on Tglass < T < Tgel
- Equilibrium Helmholtz Free Energy expanded via a functional Taylor series about a reference state:
- <u>Thermodynamic Variables</u>

$$\boxed{\Psi\left(\mathbf{H},T,x,\xi\right)}$$

Hencky Strain	$\mathbf{H}$	Extent of Reaction	x
Temperature	T	Stress-Free Strain	ξ

$$\Psi\left(\mathbf{H},T,x,\xi\right)=\Psi_{ref}+\Psi_{I}I_{1H}+\Psi_{T}\left(T-T_{ref}\right)+\Psi_{x}\left(x-x_{ref}\right)+\dots$$

0th and 1rst Order

$$\dots\frac{1}{2}K_{BULK}I_{1H}^{2}+\frac{1}{2}\Psi_{TT}\left(T-T_{ref}\right)^{2}+\frac{1}{2}\Psi_{xx}\left(x-x_{ref}\right)^{2}+\dots$$

2nd Order

$$\dots K_{BULK}\alpha_{vol}I_{1H}\left(T-T_{ref}\right)+\Psi_{xT}\left(x-x_{ref}\right)\left(T-T_{ref}\right)+\dots$$

$$\dots\mu\left(\mathbf{H}_{dev}-\xi\right):\left(\mathbf{H}_{dev}-\xi\right)+\Psi_{xH}\left(x-x_{ref}\right)I_{1H}+HOTs$$

Cross-Terms

Thermodynamic Considerations

Principal Inequality of Rational Mechanics (PIRM) on combining:

- Energy Balance
- Helmholtz Free Energy Sensitivity
- Second Law (Total Entropy Production Clausius-Duhem)

$$-\left(\frac{\partial\Psi}{\partial\mathbf{E}}-\frac{1}{\rho_{ref}}\mathbf{S}\right):\frac{d\mathbf{E}}{dt}-\left(\frac{\partial\Psi}{\partial T}-\eta\right):\frac{dT}{dt}\dots$$

$$\dots-\left(\frac{\partial\Psi}{\partial\nabla T}\bullet\frac{d\nabla T}{dt}+\frac{\partial\Psi}{\partial x}\frac{dx}{dt}+\frac{\partial\Psi}{\partial\xi}:\frac{d\xi}{dt}+\frac{1}{\rho T}\mathbf{q}\bullet\nabla\mathbf{T}\right)\geq 0$$

Coleman and Gurtin, J. Chem. Phys., 1967

Thermodynamic Considerations

PIRM Constrains Time Evolution of Internal State Variables and Identifies Work Conjugate Variable Pairs

$$\mathbf{S} = \rho_{ref}\left(\frac{\partial\Psi}{\partial\mathbf{E}}\right)_{T,x,\xi} = \rho_{ref}\left(\frac{\partial\Psi}{\partial\mathbf{H}}\right)_{T,x,\xi} : \frac{d\mathbf{H}}{d\mathbf{E}} = \mathbf{S}_{\mathbf{H}} : \frac{d\mathbf{H}}{d\mathbf{E}},$$

Second PK Stress

$$\eta = -\left(\frac{\partial\Psi}{\partial\mathbf{T}}\right)_{\mathbf{E},\mathbf{x},\xi} .$$

Entropy

$$\left(\frac{\partial\Psi}{\partial x}\frac{dx}{dt} + \frac{\partial\Psi}{\partial\xi} : \frac{d\xi}{dt}\right) \leq 0$$

Internal State Variables

$$\frac{1}{\rho T}\mathbf{q} \bullet \nabla\mathbf{T} \leq \mathbf{0}$$

Heat Flux

Separate Considerations of Different Thermodynamic State Variables

Coleman and Noll, Arch. Rat. Mech., 1964

Hencky Stress and Simplifications

The work conjugate Hencky Stress:

$$\mathbf{S}_H\left(\mathbf{H},T,x,\xi\right)=\rho_{ref}\left(\frac{\partial\Psi}{\partial\mathbf{H}}\right)_{T,x,\xi}=2\mu\left(\mathbf{H}_{dev}-\xi\right)+\ldots$$

$$\ldots\mathbf{1}\left(\Psi_I+K_{BULK}I_{1H}+K_{BULK}\alpha_{vol}\left(T-T_{ref}\right)+\Psi_{xH}\left(x-x_{ref}\right)\right)+HOTs$$

Assume that: $\Psi_I=\Psi_{xH}=HOTs=0$

$$\boxed{\mathbf{S}_H\left(\mathbf{H},T,x,\xi\right)=2\mu\left(\mathbf{H}_{dev}-\xi\right)+\mathbf{1}\left(K_{BULK}I_{1H}+K_{BULK}\alpha_{vol}\left(T-T_{ref}\right)\right)}$$

Equilibrium Model Inputs

Material Properties

μ_0	Reference Equilibrium Shear Modulus
x_{gel}	Gel Point Adduct Extent of Reaction
c_0	Net [F],[M],[A] concentrations normalized to [Amax]
$K(T)$	Equilibrium constant vs. Temperature for [F],[M], and [A]
A_r	rDA reaction pre-factor
E_a	rDA reaction activation energy

K_{bulk}	Equilibrium Bulk Modulus
ΔH^{Θ}	Standard Enthalpy of the DA Reaction
ΔS^{Θ}	Standard entropy of the DA Reaction

Model Inputs and Calibration

Initial Conditions

T_0 Reference State Temperature

x_0 Reference State Adduct reaction extent

ξ_0 Reference State Stress Free Configuration

- Reference state chosen at T_0=75C
  - E_{young} ~ 0.1 Mpa
  - Assume:

$$K_{bulk} / \mu_0 \sim 10^4$$

- All thermal-chemical constants extracted directly from Adzima *et al.* 2008

Dynamic Mechanical Analysis: Load Cases