SAND2013-9810C

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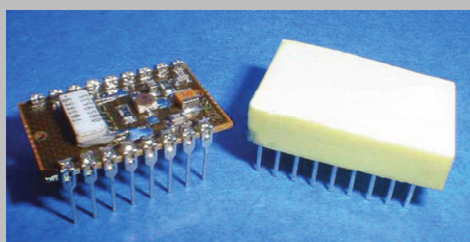
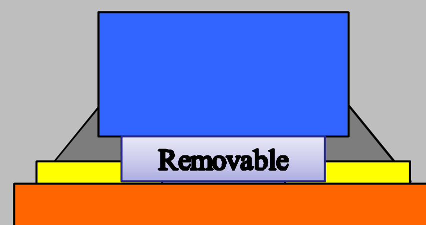
Removable Encapsulation

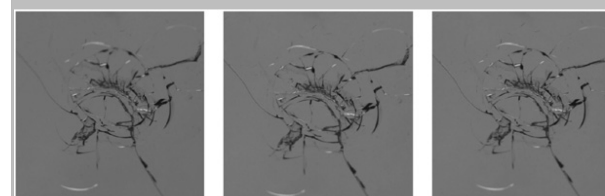


Mcelhanon, Russick, Aubert, *Science Matters* SAND 2010

Underfill Scenario



An Epoxy “Healing”



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

Thermal-Mechanics of Network Polymers with Diels-Alder Linkages

Kevin Long, Solid Mechanics Department, Sandia National Laboratories

ASME IMECE 2013, San Diego CA

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

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Acknowledgements

Funding—Early Career LDRD Program, Sandia National Lab.

Experimental Data

B. J. Adzima, H. A. Aguirre, C. J. Kloxin, T. F. Scott, C. N. Bowman, Rheological and Chemical Analysis of Reverse Gelation in a Covalently Cross-Linked Diels-Alder Polymer Network, Macromolecules 41 (23) (2008) 9112–9117.

Theory of Curing Polymer Mechanics

D. B. Adolf, R. S. Chambers, A thermodynamically consistent, nonlinear viscoelastic approach for modeling thermosets during cure, Journal of Rheology 51 (1) (2007) 23–50

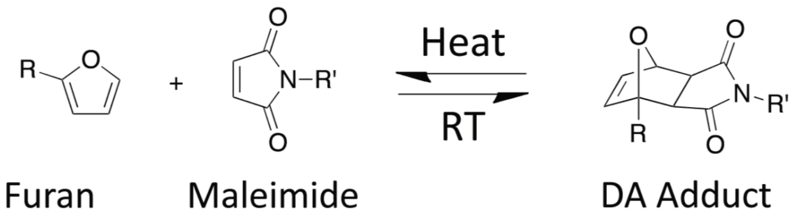
Discussions and Guidance

David R. Wheeler, Robert S. Chambers, William M. Scherzinger , Benjamin Reedlun

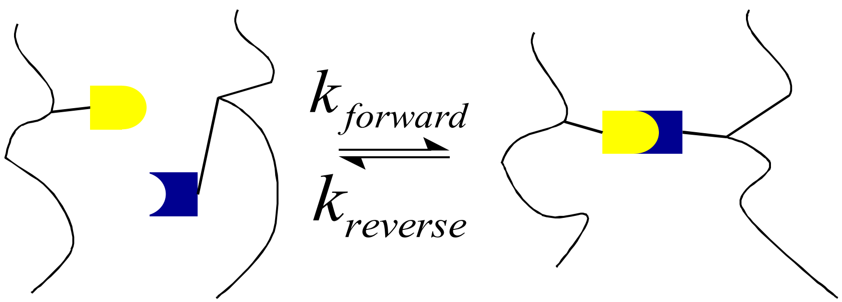
Sandia National Laboratories, New Mexico

Removable Network Polymer Basics

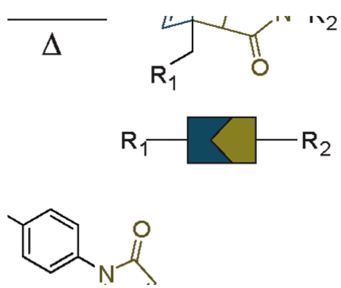
Diels-Alder Thermal Chemistry*



Network Scission/Reformation Mechanism



Network Architecture**



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

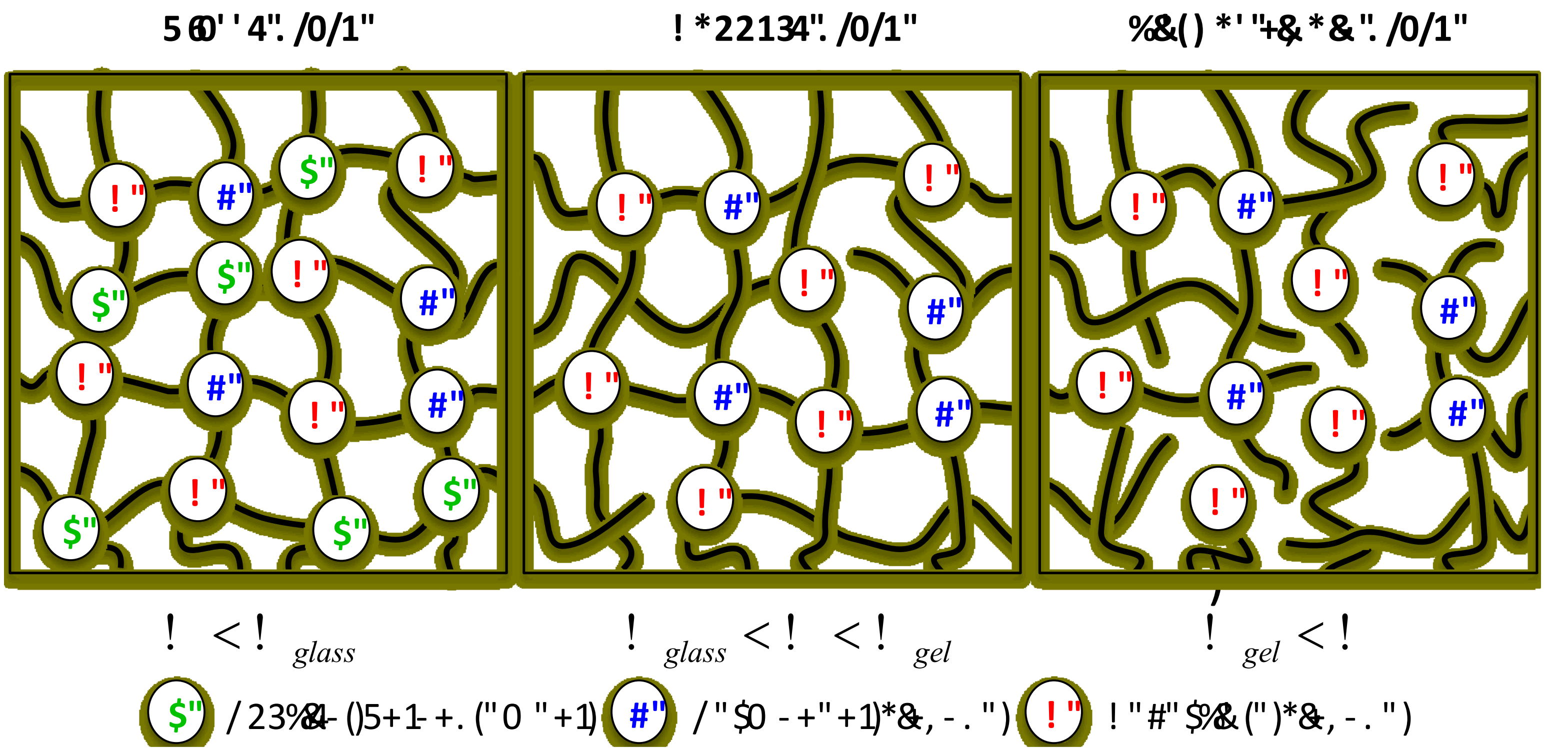
Here, we examine functionalities that undergo the thermally reversible Diels-Alder reaction.

When a sufficient number of chains break, the material behaves as a liquid

As chains 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

Three States and Two Competing Time Scales



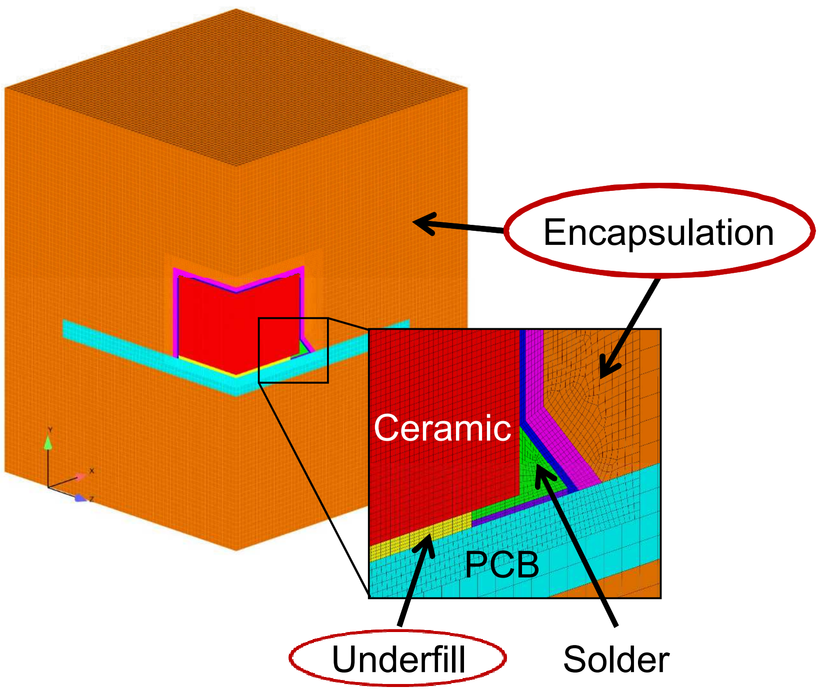
Dynamic bond rearrangement competes against the characteristic relaxation time scale of the network

At low temperature, reversible linkages cannot alter network topology --> typical glassy thermoset behavior expected

The Need for Removable Thermosets In Electronics 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 for components that must survive long lifetimes and potentially be serviced

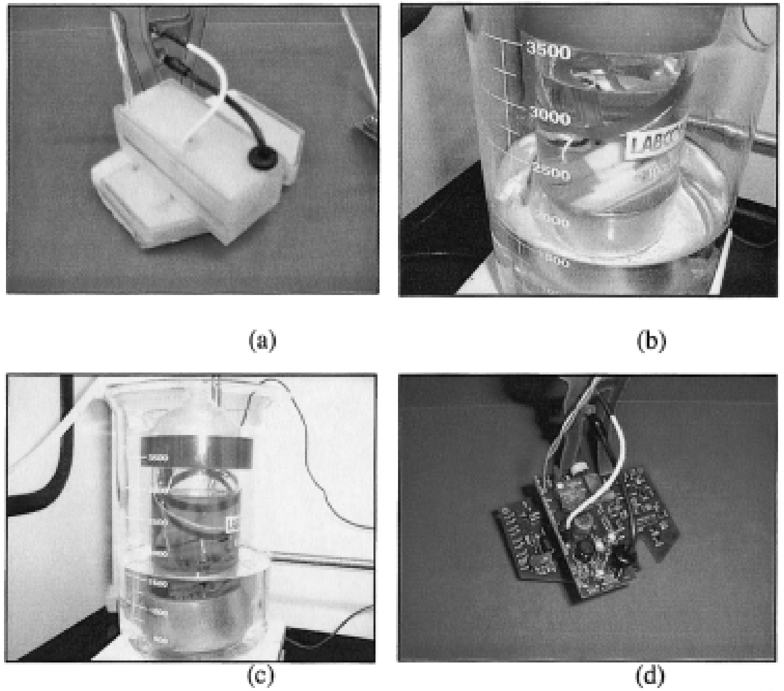


*Finite Element Mesh of a quarter symmetry capacitor showing the underfill and cover coat

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

Removable Encapsulation Used at Sandia to Support Stockpile Stewardship

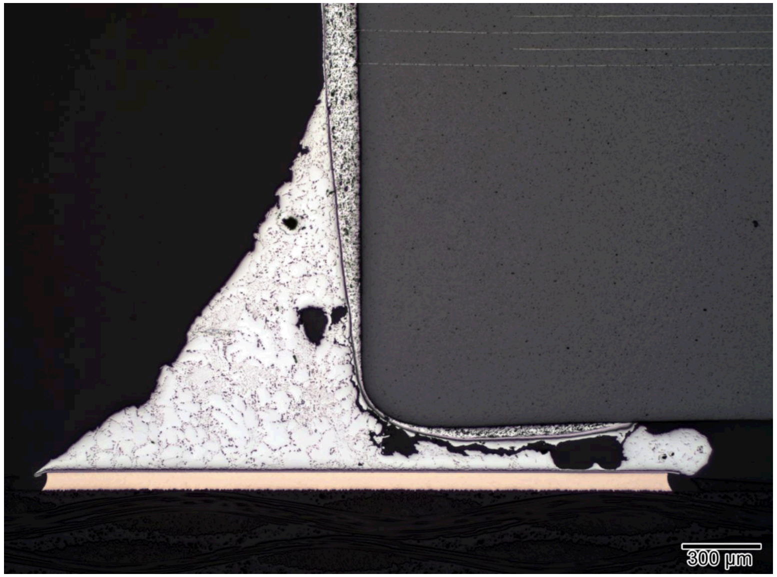
Use: Non-Contact Removal



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.

A Concern: Adverse Consequences on Other Components



Adolf et al., SAND2011_4751_Fig3_1

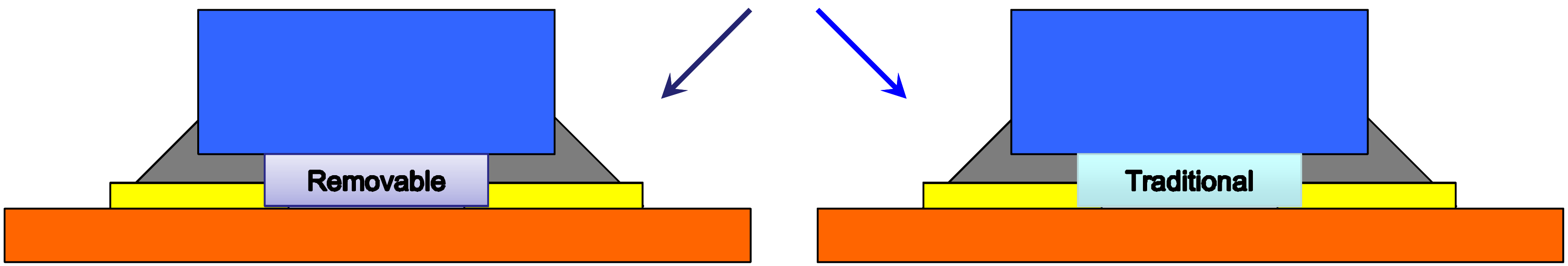
Thermal cycling of underfills may crack solder joints and deactivate electronics

Are RNP's better than traditional thermosets for this application?

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
- No understanding of the interplay between the glass transition and the network topology evolution

Diels Alder Thermal-Chemistry: Equilibrium

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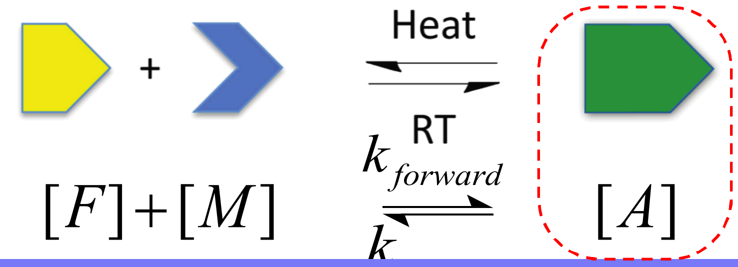
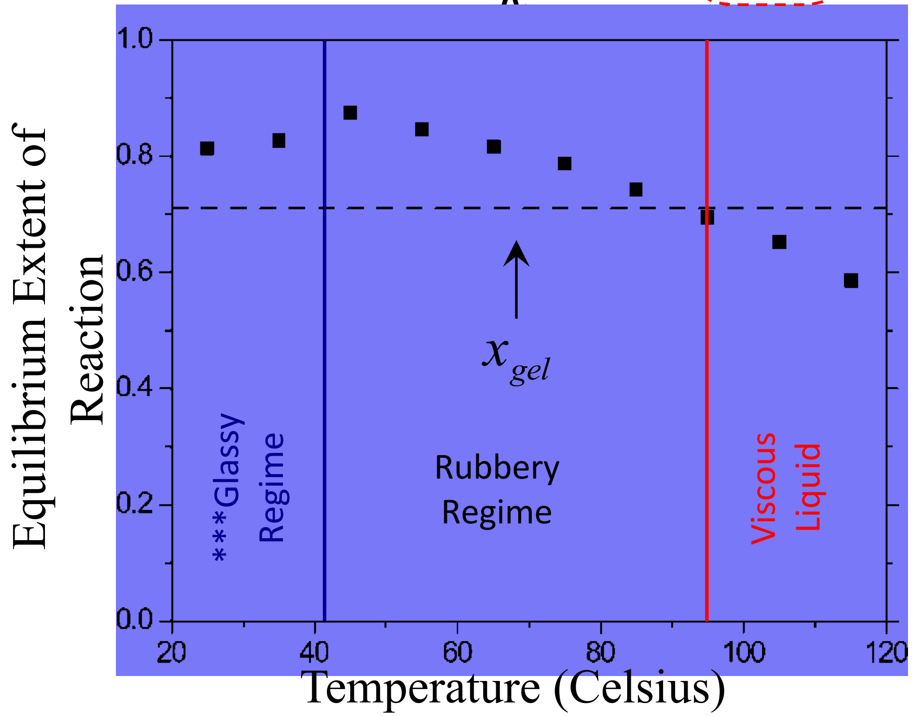
The number density of chains is set by the extent of Reaction ($[A]/[A]_{max}$)

Diels-Alder Thermal Chemistry*



- 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]

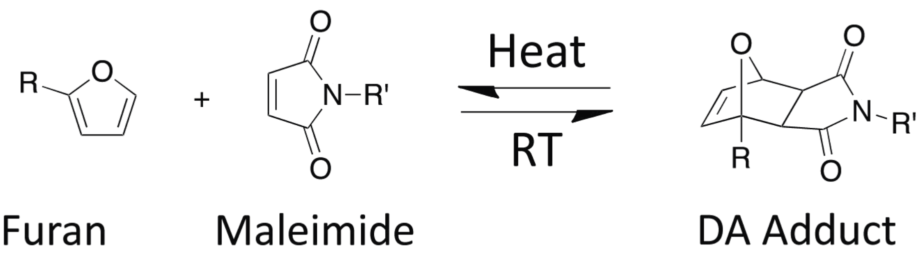


*Mcelhanon, Russick, Aubert, *Science Matters* SAND 2010

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

***Vitrification prevents reaching eq. extent of reaction

Diels Alder Thermal-Chemistry: Equilibrium



Total Species Density NOT CONSERVED

$$N = N^A + N^F + N^M$$

Total Possible Bond Density CONSERVED

$$\phi = N^A + \frac{1}{2}\left(N^F + N^M\right)$$

<u>Extent of Reaction</u>

$$N^A = \phi x,$$

$$N^F = N^M = \phi(1-x), \qquad N = \phi(2-x).$$

<u>Equilibrium Constant</u>

$$K^{\infty}[\Theta] = \frac{N^A_{\infty}/\phi}{(N^F_{\infty}/\phi)(N^M_{\infty}/\phi)} = \frac{x}{(1-x)^2},$$

Diels Alder Thermal-Chemistry: Kinetics

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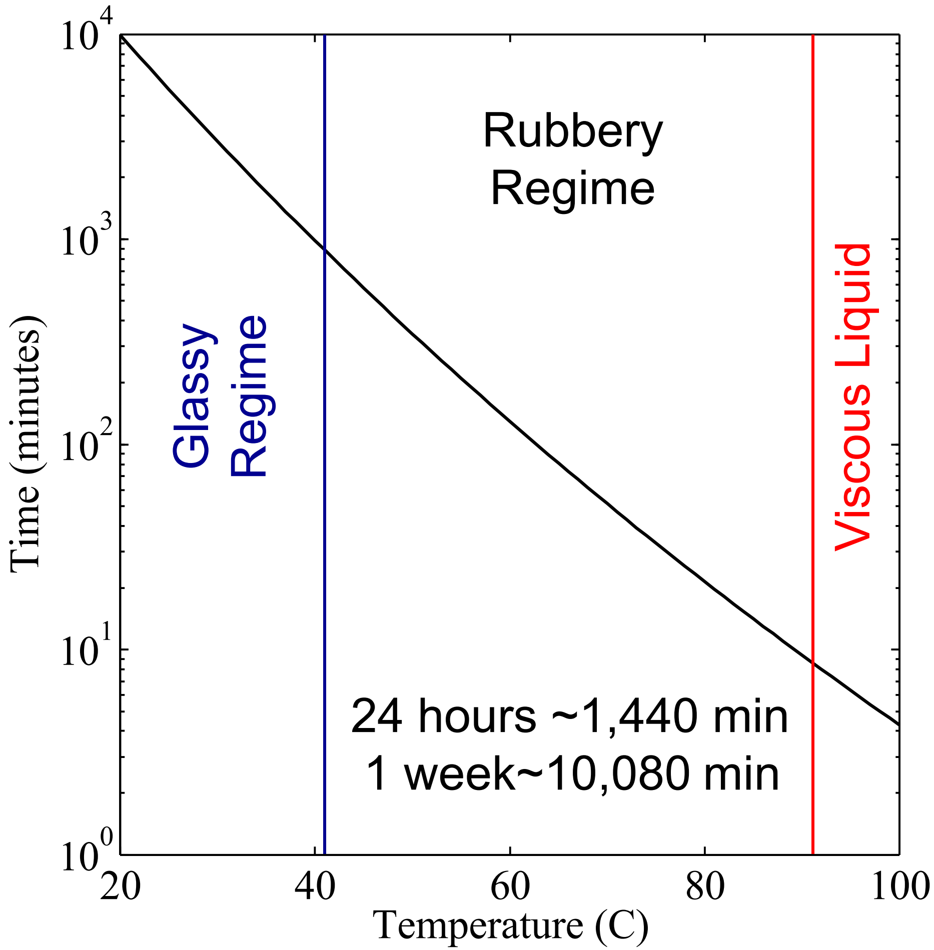
The DA chemistry cannot be arrested even at lower T
→ material always evolves

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

Diels Alder Thermal-Chemistry: Kinetics

Law of Mass Action Kinetics
(single step reaction)

$$\dot{N}^F = \dot{N}^M = -k^f N^F N^M + k^r N^A,$$

$$\dot{N}^A = k^f N^F N^M - k^r N^A$$

From Equilibrium

$$\frac{k^f}{k^r} = \frac{K^\infty[\Theta]}{\phi}.$$

Thermally-Activated Coefficients

$$k^r = k^0 \exp\left[\frac{-E_{act}}{RT}\right]$$

$$k^r = k^{visco} k^0 \exp\left[\frac{-E_{act}}{RT}\right] = \frac{k^0}{a_{mat}} \exp\left[\frac{-E_{act}}{RT}\right]$$

Constitutive Model

- Focus on rubbery (elastomeric) state:

$$\Theta_{glass} < \Theta < \Theta_{gel}$$

- Equilibrium Helmholtz free energy associated with thermal, elastic, and chemical changes

$$\Psi(\Upsilon, \Theta, x, \xi)$$

- Shear modulus dependence on Θ and x

$$G = G_0 \left(x - x_{gel} \right) \Theta$$

- Equilibrium bulk modulus assumed constant

<u>Thermodynamic Variables</u>

Logarithmic Strain Υ

Absolute Temperature Θ

Extent of Reaction (or Species Densities) x

<u>Internal State Variables</u>

Stress-Free Strain Tensor ξ

Shear modulus depends linearly on the number density of chains

Constitutive Model: Helmholtz Free Energy Density:

- Additive Split: Equilibrium + Non-Equilibrium Responses

$$\Psi\left(\Upsilon_{ij},\Theta,N^{\alpha},\xi_{ij}\right)=\Psi^{\infty}+\Psi^{visco}$$

- Thermodynamic Fluxes

$$S^{\Gamma}_{ij}=S^{\Gamma\infty}_{ij}+S^{\Gamma visco}_{ij},\qquad \eta_0=\eta_0^{\infty}+\eta_0^{visco},\qquad \mu^{\alpha}=\mu^{\alpha visco}+\mu^{\alpha visco}$$

- Equilibrium Helmholtz Free Energy Density

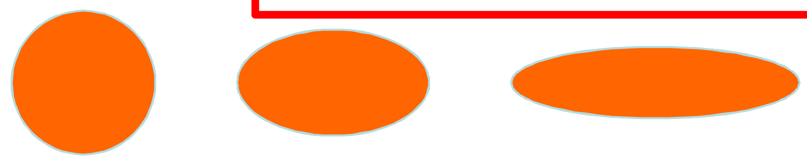
$$\begin{aligned}
\Psi^{\infty}\left(\Upsilon_{ij},\Theta,N^{\alpha},\xi_{ij}\right)&=\Psi^{\infty}_{elastic}+\Psi^{\infty}_{thermal}+\Psi^{\infty}_{chemical}+\Psi^{\infty}_{mixed}+\Psi_{ref},\\
\Psi^{\infty}_{elastic}&=P_{ref}I_1[\Upsilon]+\frac{K^{\infty}_{bulk}}{2}(I_1[\Upsilon])^2+G\left[x,\Theta\right]I_2\left[\Upsilon^{dev}_{ij}-\xi^{dev}_{ij}\right],\\
\Psi^{\infty}_{thermal}&=\frac{C_{F0}}{\rho_{ref}}\left(\Theta-\Theta_{ref}-\Theta\log\left(\frac{\Theta}{\Theta_{ref}}\right)\right)-\frac{C_{F1}}{2\rho_{ref}\Theta_{ref}}(\Theta-\Theta_{ref})^2,\\
\Psi^{\infty}_{chemical}&=\sum_{\alpha}\left(\mu^{\alpha}N^{\alpha}\right),\\
\Psi^{\infty}_{mixed}&=-K_{bulk}\beta_{vol}(x-x_{ref})I_1[\Upsilon]-K_{bulk}\alpha_{vol}(\Theta-\Theta_{ref})I_1[\Upsilon].
\end{aligned}$$

Constitutive Model: Internal State Variable and Property Evolution Rules

- Adding/removing chains changes the permanent shape
- Material time scale arrests this process

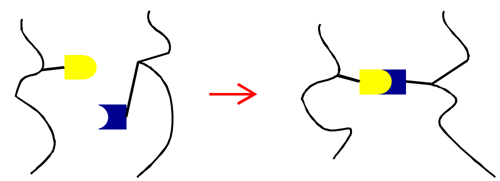
- Evolution of the stress-free shape:

$$\dot{\xi} = \frac{\dot{G}_+}{G}\left(\Upsilon_{dev} - \xi_{dev}\right) \propto \frac{1}{1+a}$$



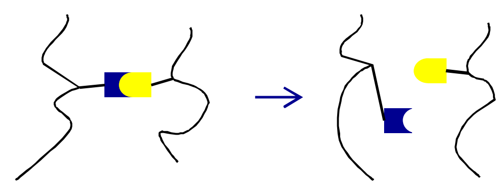
- Forward reaction increases the shear modulus:

$$\dot{G}_+ = \frac{G_0 K_\infty k_r}{2}[A_{\max}](1-x)^2 \qquad if \;\; x > x_{gel}$$



- Reverse reaction decreases the shear modulus:

$$\dot{G}_- = G_0 k_r x \qquad if \;\; x > x_{gel}$$



Constitutive Model:
Non-Equilibrium Constitutive Behavior

- <u>Non-Equilibrium Helmholtz Free Energy Density:</u> Functional Taylor Expansion of the free energy about the equilibrium state keeping only second order terms:

$$\Psi^{visco} = \frac{1}{2}(K^G - K^\infty)\int_0^t ds\int_0^t du f^1(t'-s',t'-u')\frac{dI_{1\Upsilon}}{ds}\frac{dI_{1\Upsilon}}{du}$$ Volumetric Energy

$$+(G^G - G^\infty)\int_0^t ds\int_0^t du f^2(t'-s',t'-u')\frac{d(\Upsilon_{ij}^{dev}-\xi_{ij}^{dev})}{ds}\frac{d(\Upsilon_{ij}^{dev}-\xi_{ij}^{dev})}{du}$$ Shear Energy

$$-\frac{\rho_0(\overline{C}_{FG}-\overline{C}_{F1\infty})}{2\Theta_{ref}}\int_0^t ds\int_0^t du f^5(t'-s',t'-u')\frac{d\Theta}{ds}\frac{d\Theta}{du}$$

$$-(K^G\alpha^G - K^\infty\alpha^\infty)\int_0^t ds\int_0^t du f^3(t'-s',t'-u')\frac{dI_{1\Upsilon}}{ds}\frac{d\Theta}{du}$$ Volumetric Thermal Coupling

$$-(K^G\beta^G - K^\infty\beta^\infty)\int_0^t ds\int_0^t du f^4(t'-s',t'-u')\frac{dI_{1\Upsilon}}{ds}\frac{dx}{du}$$ Volumetric Chemical Coupling

$$+(\Delta\eta_{rxnG} - \Delta\eta_{rxn}^\circ)\int_0^t ds\int_0^t du f^6(t'-s',t'-u')\frac{d\Theta}{ds}\frac{dx}{du}$$

Constitutive Model: Rheological Simplicity

- Minimal Network Evolution near and below the glass transition

  → Assumption of Rheological Simplicity is reasonable

- Proney-Series Representation of Characteristic Relaxation Functions

$$f^k\left(t'-s',t'-u'\right)=\sum_{j=1}^{m_k}A^{j(k)}\exp\left(\frac{-\left(t'-s'\right)}{\tau_j}\right)\exp\left(\frac{-\left(t'-u'\right)}{\tau_j}\right)$$

- Horizontal (Time-Temperature) Shift Factor:

$$G^*(\omega,\Theta)=G^*(a_\Theta\omega,\Theta_{ref}) \qquad \log a=\frac{-C_1N}{C_2+N}$$

- Material Relaxation Time Scale

$$N=\left(\Theta-\Theta_{glass}-\int_0^t ds\, f^v\left(t'-s',0\right)\frac{d\Theta}{ds}\right)\ldots$$

Thermal History →

Volumetric History →

$$+C_3\left(I_{1\Upsilon}-\int_0^t ds\, f^v\left(t'-s',0\right)\frac{dI_{1\Upsilon}}{ds}\right)\ldots$$

Shear History →

$$+C_4\int_0^t ds\int_0^t du\, f^s\left(t'-s',t'-u'\right)\frac{d(\Upsilon_{ij}^{dev}-\xi_{ij}^{dev})}{ds}\frac{d(\Upsilon_{ij}^{dev}-\xi_{ij}^{dev})}{du}.$$

Equations of Motion Summary

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NOTE: (Most) Quantities Are Defined on a Time Invariant Reference Configuration

- Mass Continuity

$$\frac{\rho_{current}}{\rho_0} = J = \det\left(F_{ij}\right), \qquad F_{ij} = \frac{\partial x_i}{\partial X_j}$$

- Species Density Continuity

$$\dot{N}^\alpha = -\frac{\partial H_i^\alpha}{\partial X_i} + H^\alpha$$

- Linear, Angular Momenta Balances

$$\frac{\partial P_{ij}}{\partial X_i} + Jb_j = 0_j, \qquad F_{ik}P_{jk} = P_{ik}F_{jk}$$

- Energy Balance

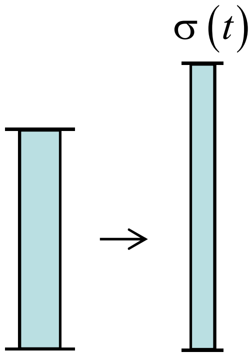
$$C_F\dot{\Theta} = Q - \frac{Q_i}{X_i} + \sum_\alpha \left(\Theta \frac{\partial^2 \Psi}{\partial \Theta \partial N^\alpha} \dot{N}^\alpha - H_i^\alpha \frac{\partial \mu^\alpha}{\partial X_i} \right)$$

$$\ldots + \Theta \frac{\partial^2 \Psi}{\partial \Theta \partial \Gamma_{ij}} \dot{\Gamma}_{ij} + \sum_\beta \left(\Theta \frac{\partial^2 \Psi}{\partial \Theta \partial Z^\beta} - \frac{\partial \Psi}{\partial Z^\beta} \right) \dot{Z}^\beta$$

- Second Law of Thermodynamics Constraint

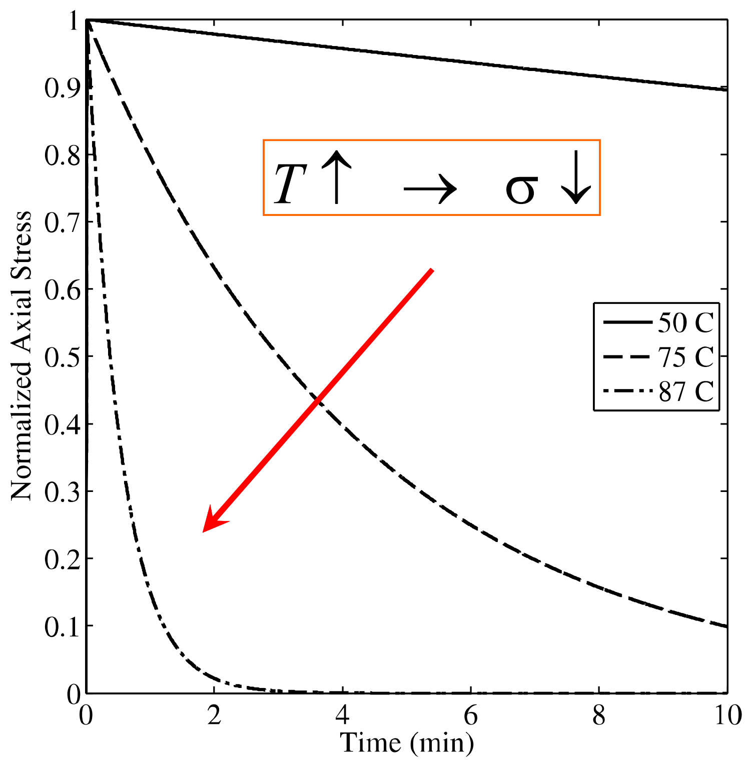
$$\dot{\Psi} + \eta_0 \dot{\Theta}_0 - S_{ij}^\Gamma \dot{\Gamma}_{ij} + \frac{Q_k}{\Theta} \frac{\partial \Theta}{\partial X_k} - \sum_\alpha \left(\mu^\alpha \dot{N}^\alpha - H_i^\alpha \frac{\partial \mu^\alpha}{\partial X_i} \right) \leq 0.$$

Results: Demonstration of Isothermal Stress Relaxation

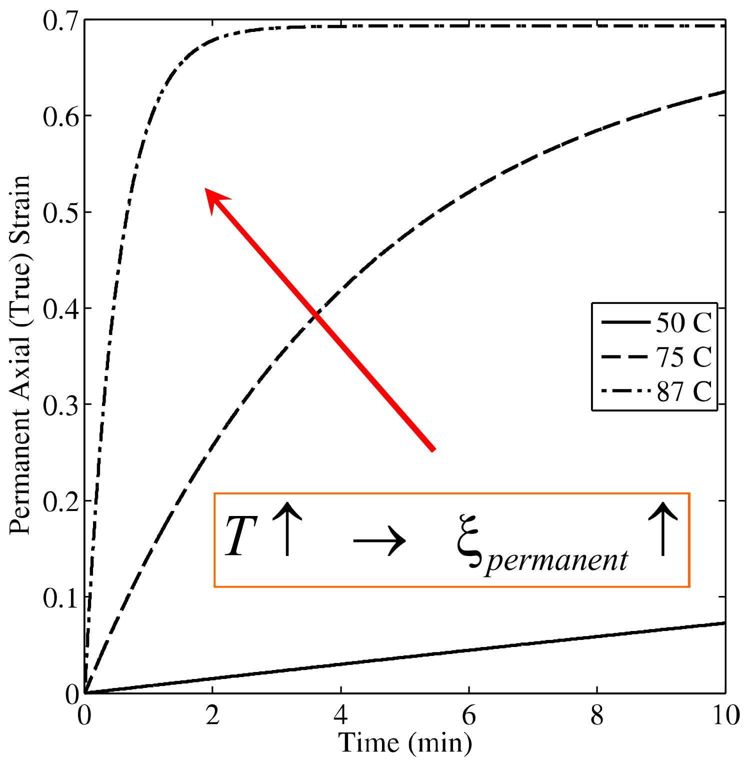


Adding/removing cross-links changes the permanent shape

Normalized Axial Stress



Permanent Axial Deformation

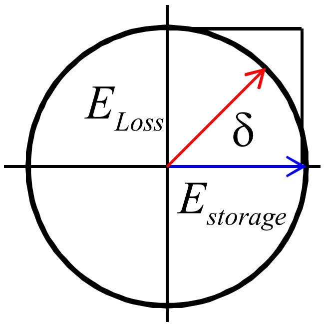


Results: Validation Against Dynamic Mechanical Analysis Data

- Examine the dissipation behavior of cyclically loaded specimens

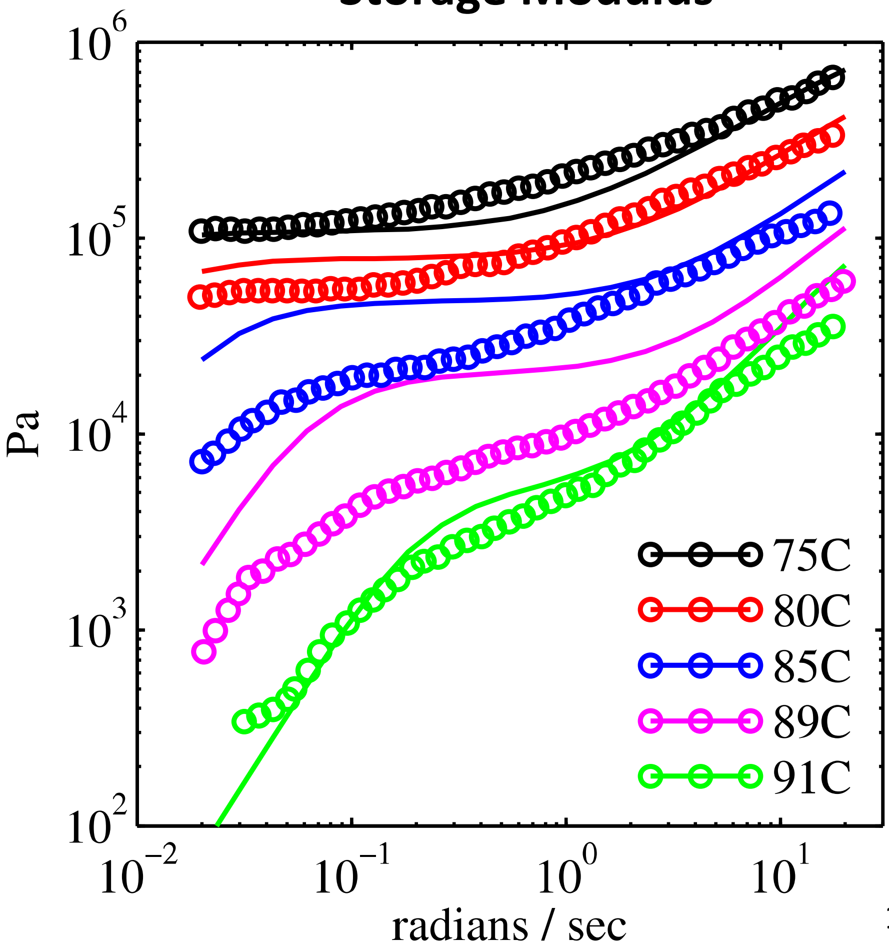
$$\varepsilon(t) = \varepsilon_0 \sin(\omega t)$$

Apply an oscillating strain



Record the complex modulus

Fit a the 75 C Curve and Predict Remaining DMA Data



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

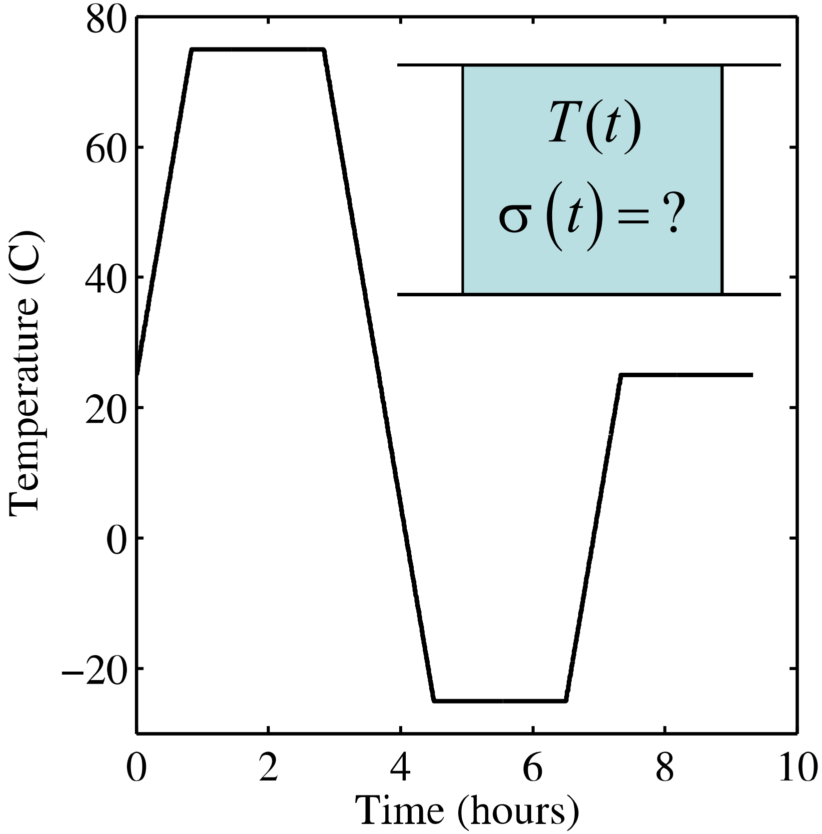
Results: Effects of Permanent Shape Evolution During a Thermal Cycle

Thermal-Mechanical Cycle

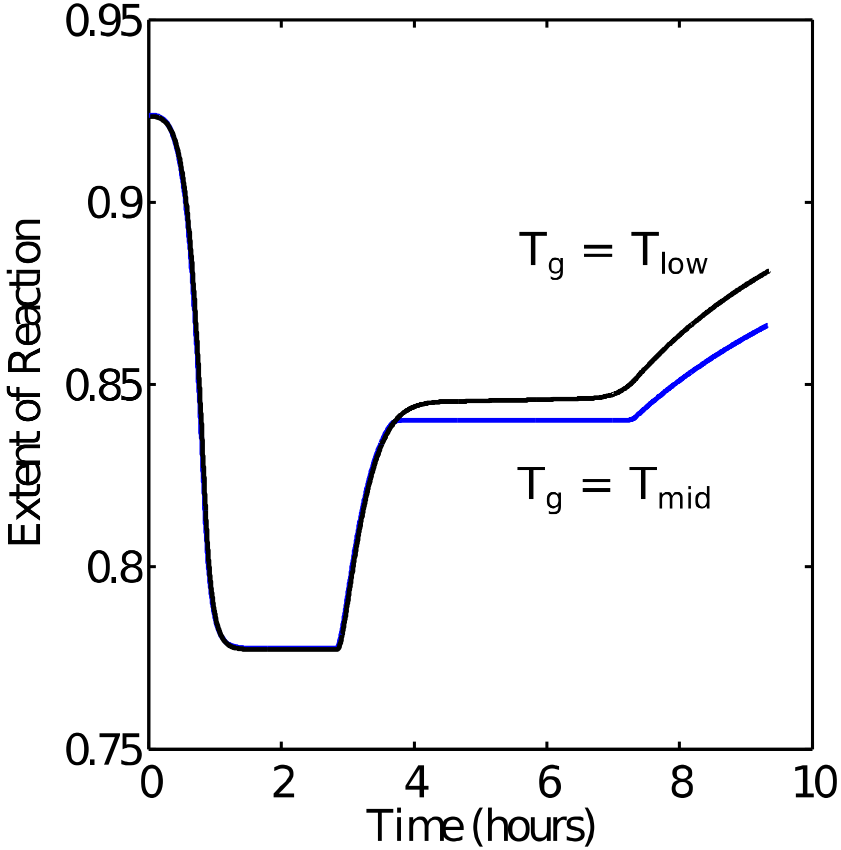
- Specify temperature history relevant to possible thermal cycles
- Fix deformation in 1 direction

"To Flow, or Not to Flow…?"

Applied Temperature vs. Time



Extent of Reaction vs. Time



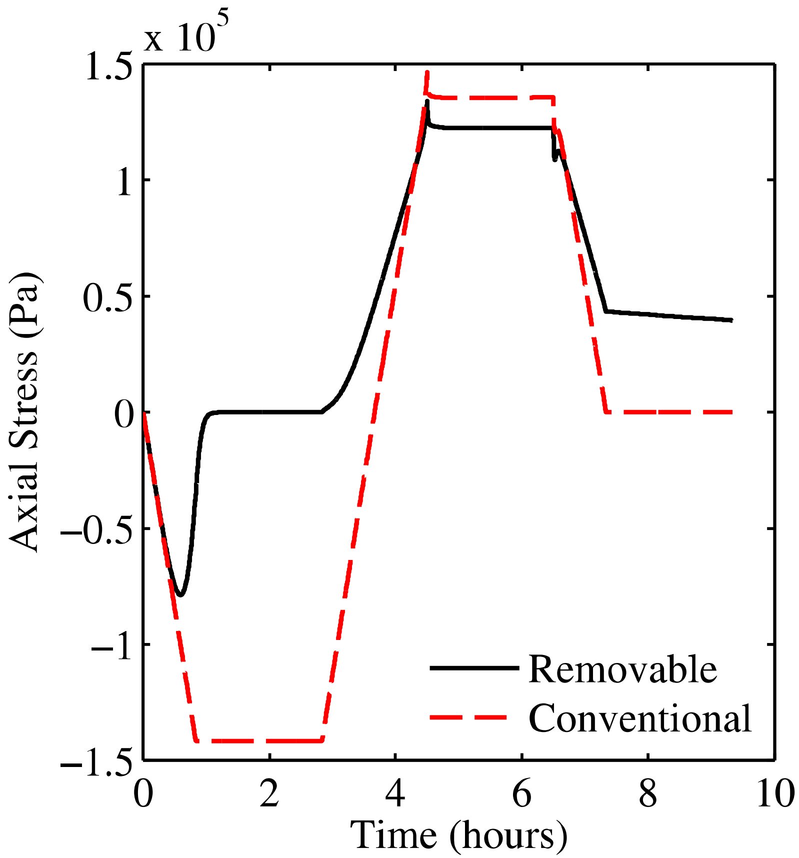
Results: Effects of Permanent Shape Evolution During a Thermal Cycle

Reversible Chemistry Changes The Stress History Compared with Conventional Thermosets

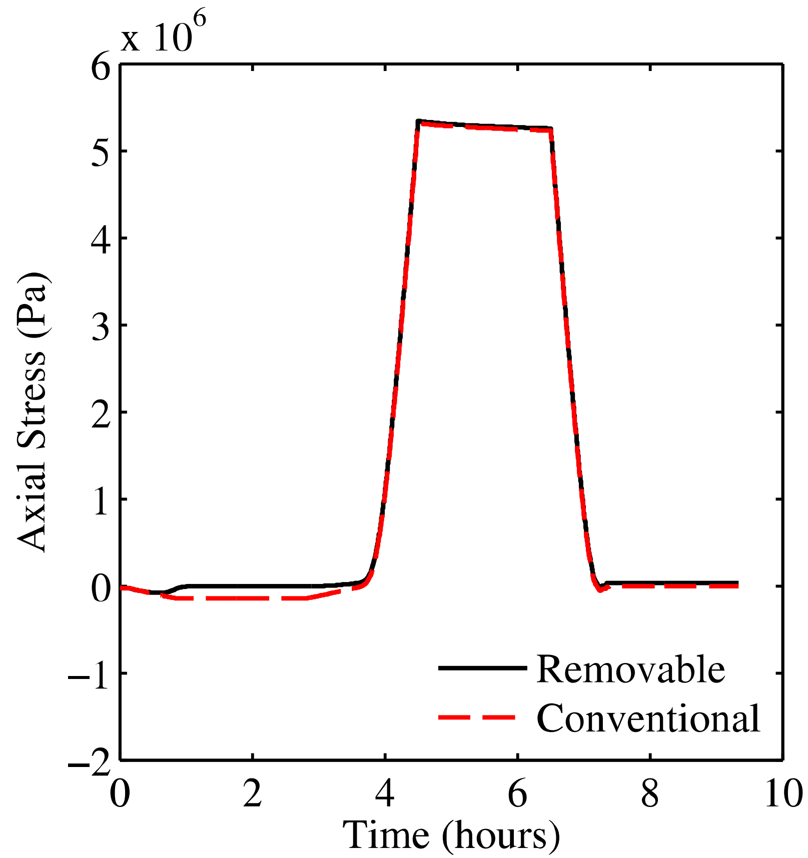
Thermal-Mechanical Cycle

- Specify temperature history relevant to possible thermal cycles
- Fix deformation in 1 direction

Stress vs. Time (Tg=Tlow)



Stress vs. Time (Tg=Tmid)

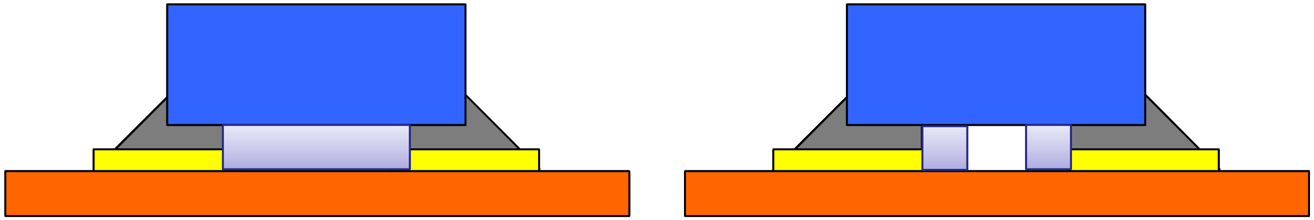


Future Work

- Augment the permanent deformation tensor evolution to account for the *Loss of Cross-links*

$$\dot{\xi} = \frac{\dot{G}_+}{G}\left(\Upsilon_{dev} - \xi_{dev}\right) \rightarrow fun\left(\dot{G}_+, \dot{G}_-, G, \Upsilon_{dev}, \xi_{dev}\right)$$

- Examining different shear modulus dependencies on the extent of reaction to account for short chain networks
- Examine/optimize the effects of cross-link evolution and the role of confinement, voids, free surfaces in real encapsulation scenarios



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

Energy Balance

- Referential Energy Density

$$\dot{E}_{total} = \dot{Q}_{total\ in} - \dot{W}_{by\ system} + \dot{E}_{species}$$

$$\overline{\int_{\omega_0} \epsilon_0 dV}^{\,\cdot} = -\int_{\partial\omega_0} Q_i N_i dA + \int_{\omega_0} Q dV$$

$$\ldots + \int_{\partial\omega_0} P_{ij} N_j v_i dA + \int_{\omega_0} J b_i v_i dV$$

$$\ldots + \sum_{\alpha} \left(-\int_{\partial\omega_0} \mu^{\alpha} H_i^{\alpha} N_i dA + \int_{\omega_0} \mu^{\alpha} H^{\alpha} dV \right) .$$

$$\dot{\epsilon}_0 = -\frac{\partial Q_k}{\partial X_k} + Q + S_{ij}^{\Gamma} \dot{\Gamma}_{ij} + \sum_{\alpha} \left(\mu^{\alpha} \dot{N}^{\alpha} - H_i^{\alpha} \frac{\partial \mu^{\alpha}}{\partial X_i} \right)$$

Entropy Production—Clausius Duhem 2nd Law of Thermodynamics

$$\int_{\omega_0} \dot{\eta}_0 dV + \int_{\partial\omega_0} \frac{Q_i N_i}{\Theta} dA - \int_{\omega_0} \frac{Q}{\Theta} dV \geq 0,$$

$$\dot{\eta}_0 - \frac{Q}{\Theta} + \frac{1}{\Theta}\frac{\partial Q_i}{\partial X_i} - \frac{Q_k}{\Theta^2}\frac{\partial \Theta}{\partial X_k} \geq 0$$

$$\Psi = \epsilon_0 - \Theta \eta_0,$$

Constitutive Assumptions and the Dissipation Inequality

$$\dot{\Psi} = \frac{\partial \Psi}{\partial \Gamma_{ij}} \dot{\Gamma}_{ij} + \frac{\partial \Psi}{\partial \Theta} \dot{\Theta} + \sum_{\alpha} \left(\frac{\partial \Psi}{\partial N^{\alpha}} \dot{N}^{\alpha} \right) + \sum_{\beta} \left(\frac{\partial \Psi}{\partial Z^{\beta}} \dot{Z}^{\beta} \right) .$$

- Combine Energy Balance, Helmholtz Free Energy Density Time Derivative, Legendre Transform, and the Clausius Duhem inequality

$$\dot{\Psi} + \eta_0 \dot{\Theta}_0 - S^{\Gamma}_{ij} \dot{\Gamma}_{ij} + \frac{Q_k}{\Theta} \frac{\partial \Theta}{\partial X_k} - \sum_{\alpha} \left(\mu^{\alpha} \dot{N}^{\alpha} - H^{\alpha}_i \frac{\partial \mu^{\alpha}}{\partial X_i} \right) \leq 0.$$

$$S^{\Gamma}_{ij} = \frac{\partial \Psi}{\partial \Gamma_{ij}}, \qquad \eta_0 = -\frac{\partial \Psi}{\partial \Theta}, \qquad \mu^{\alpha} = \frac{\partial \Psi}{\partial N^{\alpha}}.$$

$$\mathrm{d}^{diss} = \sum_{\beta} \left(\frac{\partial \Psi}{\partial Z_{\beta}} \dot{Z}_{\beta} \right) + \sum_{\alpha} \left(H^{\alpha}_i \frac{\partial \mu^{\alpha}}{\partial X_i} \right) + \frac{Q_k}{\Theta} \frac{\partial \Theta}{\partial X_k} \leq 0,$$

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

Temperature Equation of Motion

- From the energy balance, PIRM, and Helmholtz Free Energy Assumptions,

$$C_F = \left(\frac{\partial \epsilon_0}{\partial \Theta}\right)_{\Gamma_{ij}, N^\alpha, Z^\beta} = -\Theta \left(\frac{\partial^2 \Psi}{\partial \Theta \partial \Theta}\right)_{\Gamma_{ij}, N^\alpha, Z^\beta}$$

$$C_F \dot{\Theta} = Q - \frac{Q_i}{X_i} + \sum_\alpha \left(\Theta \frac{\partial^2 \Psi}{\partial \Theta \partial N^\alpha} \dot{N}^\alpha - H_i^\alpha \frac{\partial \mu^\alpha}{\partial X_i} \right)$$

$$\ldots + \Theta \frac{\partial^2 \Psi}{\partial \Theta \partial \Gamma_{ij}} \dot{\Gamma}_{ij} + \sum_\beta \left(\Theta \frac{\partial^2 \Psi}{\partial \Theta \partial Z^\beta} - \frac{\partial \Psi}{\partial Z^\beta} \right) \dot{Z}^\beta$$

Chemical Equilibrium and Potentials

Van't Hoff Relation

$$\log K^{\infty} = -\frac{\Delta g^{\circ}_{rxn}}{RT} = -\frac{-\Delta H^{\circ}_{rxn}}{R\Theta} + \frac{\Delta \eta^{\circ}_{rxn}}{R}$$

Gibbs Equilibrium Condition

$$0 = dg|_{\Theta, P_{ij}} = F_{ij} dP_{ij} - \eta_0 d\Theta + \sum_{\alpha = A,F,M} (\mu^{\alpha} dN^{\alpha} + d\mu^{\alpha} N^{\alpha})$$

$$\ldots = \sum_{\alpha = A,F,M} (\mu^{\alpha} dN^{\alpha})$$

Via Gibbs-Duhem Equality

Chemical Potentials

$$\mu^{A} = \mu^{A\circ} + R\Theta \log(a_A), \qquad a_A = \frac{N^A}{N}$$

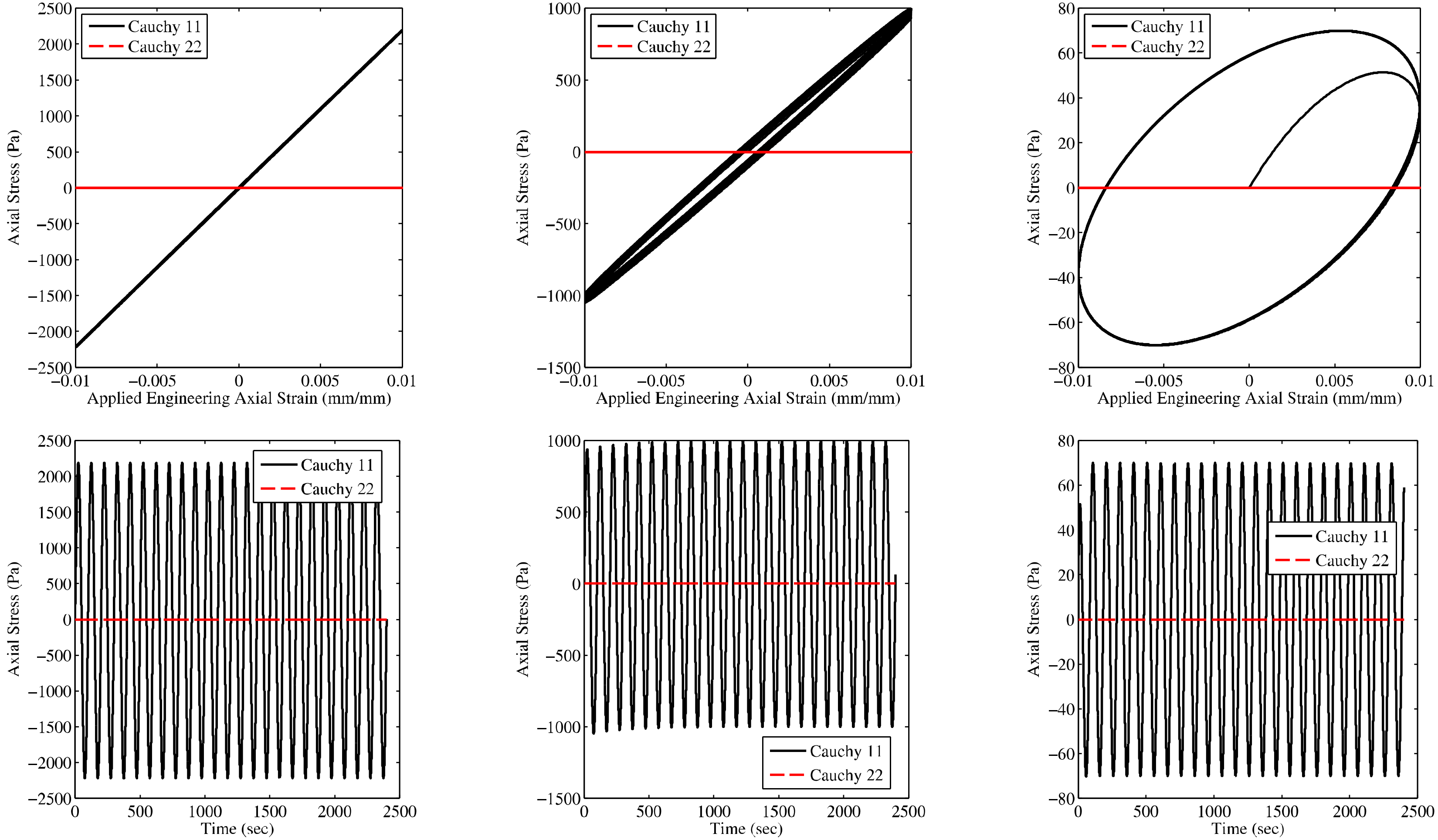
$$\mu^{F} = \mu^{F\circ} + R\Theta \log(a_F), \qquad a_F = \frac{N^F}{N}$$

$$\mu^{M} = \mu^{M\circ} + R\Theta \log(a_M), \qquad a_M = \frac{N^M}{N}$$

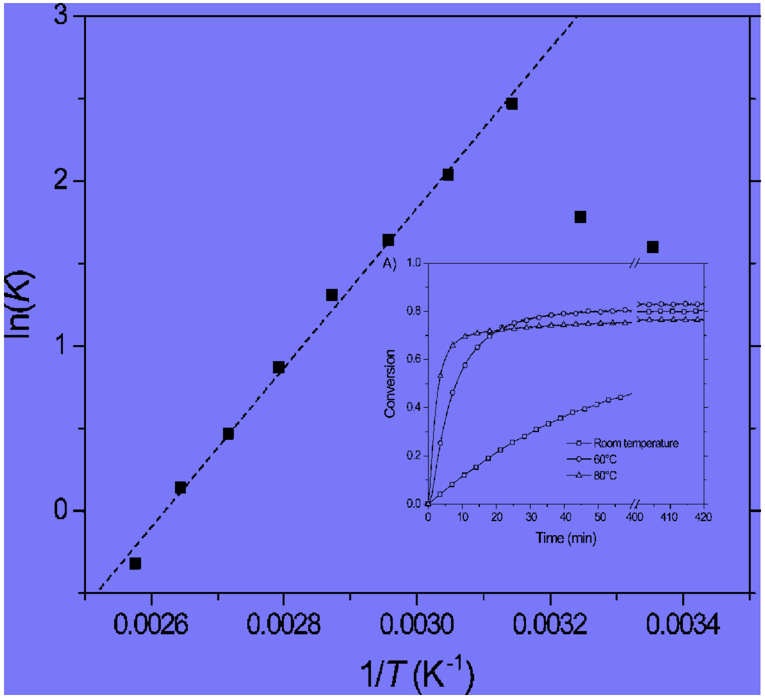
Statement of Equilibrium

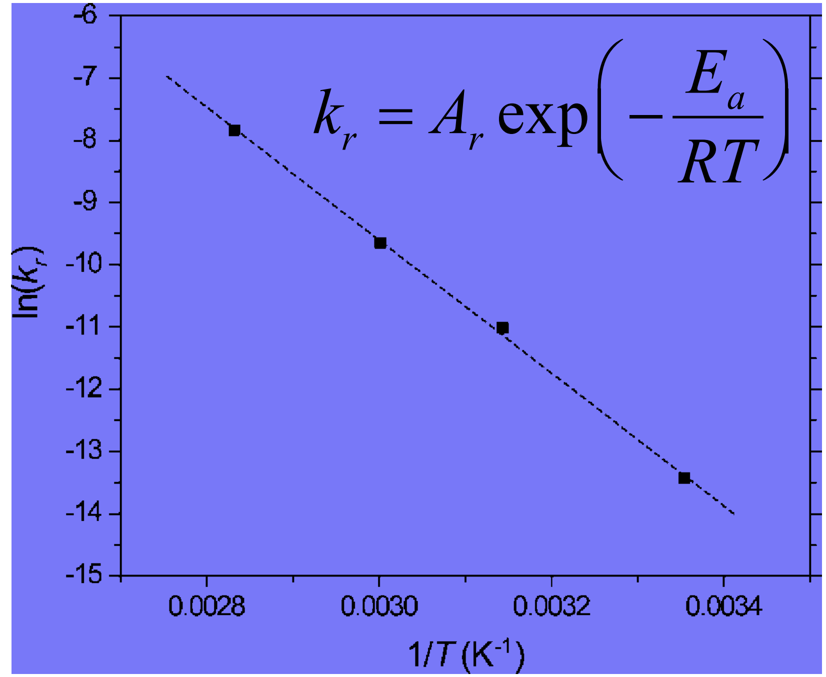
$$\mu^{A\circ} - \mu^{F\circ} - \mu^{M\circ} = \Delta g^{\circ}_{rxn}.$$

Dynamic Mechanical Analysis: Load Cases



EXPERIMENTAL BASIS: Equilibrium And Chemical Kinetics





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