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Measuring The Cure Shrinkage Epon® 828/T403 Epoxy Through Bi-Material Beam Analysis

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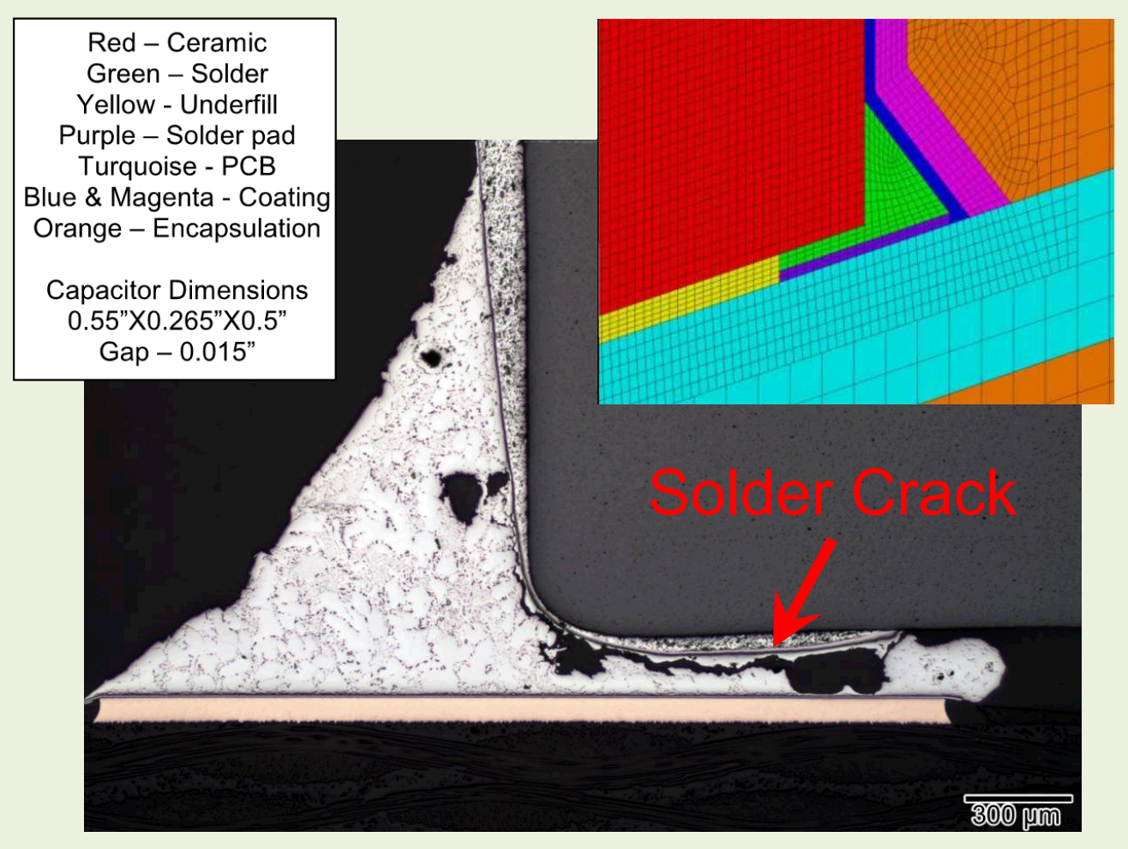
The Need for Residual Stress Modeling

Stress in encapsulation may cause failure in adjacent materials and components. For example, the right image shows the fatigue-failure of a solder-joint due to thermal cycling of the capacitor assembly and the associated large mismatch strains between the different materials[1]. Often, such assemblies are in states of large residual stress due to manufacturing before in-service thermal-cycling begins. The residual stress state is a combination of both cure shrinkage in the thermosetting foams, filled, or unfilled polymers and thermal stress due to cool down from curing temperatures, and while experimental efforts can be effective in guiding the minimization of residual stress in specific geometries[2], validated, high fidelity constitutive models are needed to reduce residual stresses in arbitrary encapsulation scenarios. A key parameter of such models is the cure shrinkage (volume change) associated with cross-linking the network. This parameter is difficult to measure, and many different approaches have been taken with varying degrees of success including: density measurements[3], confined force measurements[3] (and associated inverse modeling), embedded optical fibers[4], sophisticated Kovar or Pop-Off Tube tests (and associated inverse modeling)[2,5], and likely more. Generally these tests are complicated or require high fidelity inverse modeling for example via Finite Element Analysis (FEA).

Failure in Printed Circuit Boards From Stress in Surrounding Encapsulation[1]

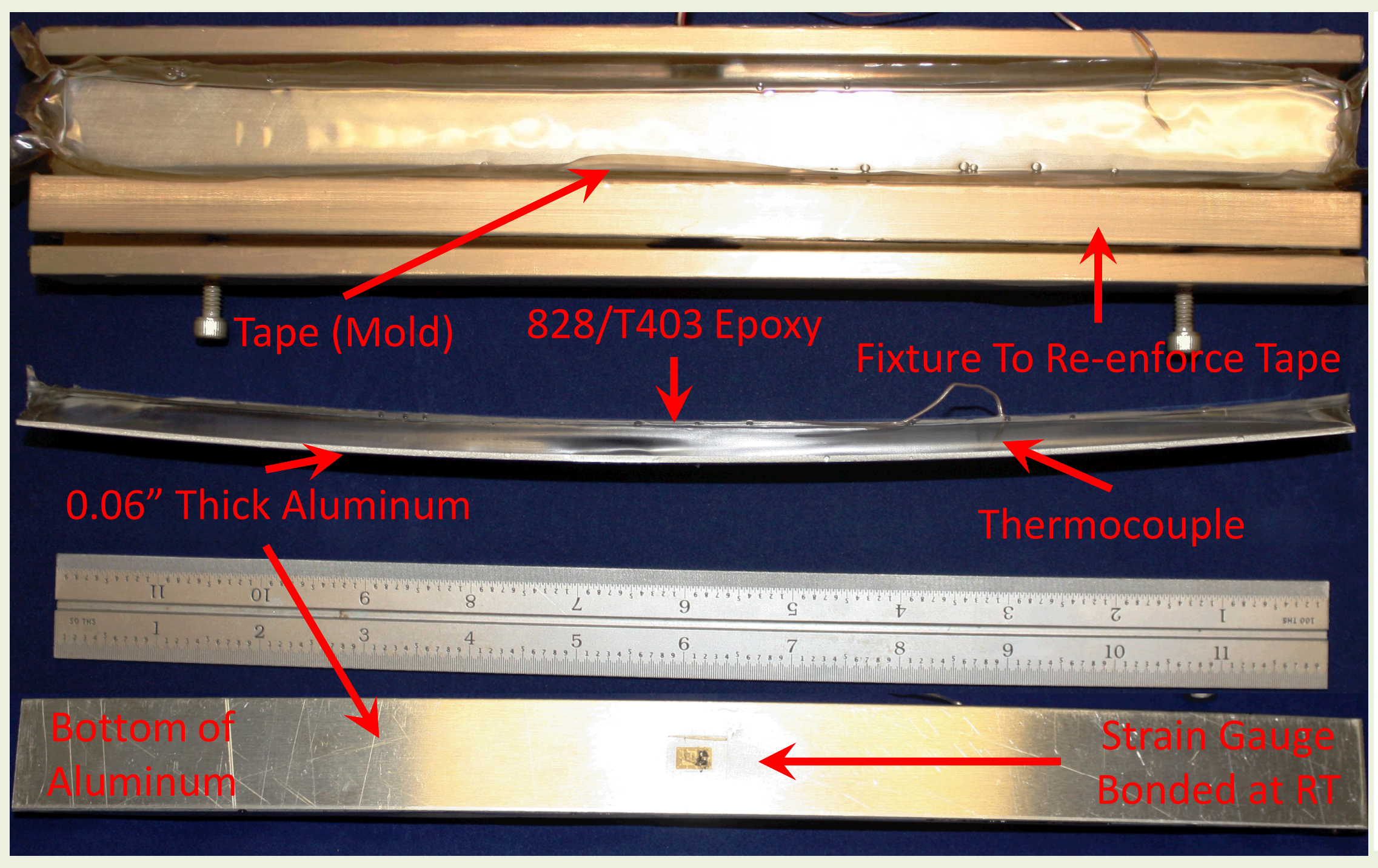


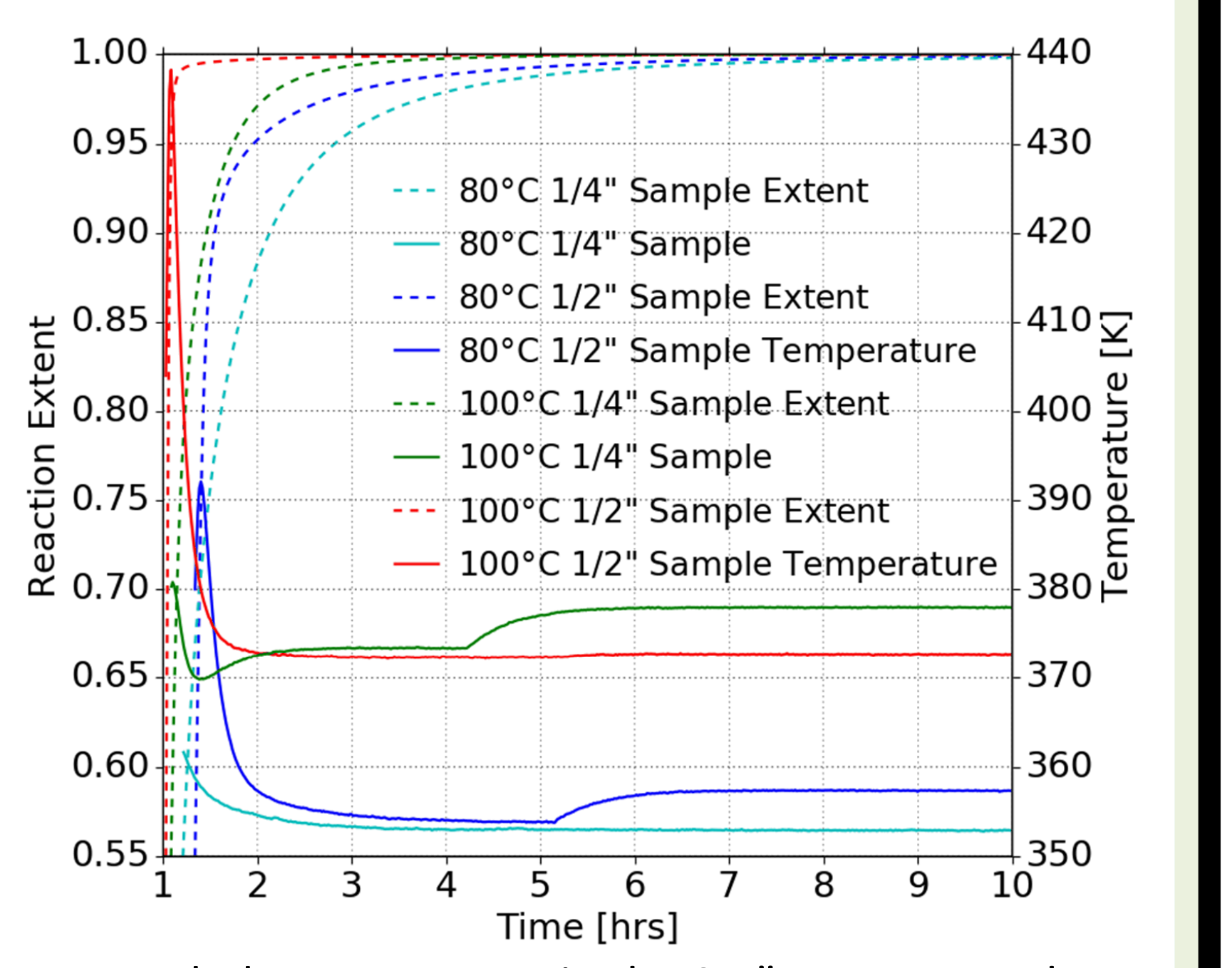
1 Adolf et al., *SAND2011-4751*
2 Kropka et al., *SAND2016-5453*
3 Kropka et al., *SAND2013-8681*
4 Leng et al., *Smart Mat. And Struct.* **2002**
5 Adolf et al., *J Rheology* 51 **2007**
6 Timoshenko, *J Opt Soc Am & Rev Sci Inst.* ***1925***

Here, we explore a comparatively simple, alternative approach to measuring residual stress during cure based on the bi-layer beam geometry inspired by Timoshenko[6]. Simple inverse modeling is required that does not require sophisticated codes, and we will show good agreement with other techniques.

Objective: Demonstrate the effectiveness of Bi-material tests to determine thermoset cure shrinkage

Experimental Methods and Results





Test Procedure

1. At RT, mix resin (Epon® 828) and cross-linker (Jeffamine® T403). Pour onto the tape-molded Al beam to a target thickness.
2. Place bi-material beam in the oven with a controlled temperature.
3. Cure for 24 hours. Remove from oven and let cool to RT.

- Recorded temperatures in the 0.5" epoxy runs show large exotherms of up to 70 C above the oven temperature (100 C case). Much smaller exotherms are observed for the 0.25" epoxy runs.
- Large exotherms cure the epoxies quickly (within 2 hours from mixing) compared with more than 5 hours for the cooler runs

Model for *Rubbery* Thermosets During Cure[5]

(Isotropic) Stress Response

$$\boldsymbol{\sigma} = K_\infty[T]\Big(\underbrace{\boxed{I_1}}_{\text{Volume Strain}} - \underbrace{\boxed{\alpha_\infty(T - T_{\mathrm{gel}})}}_{\text{Thermal Strain}} - \underbrace{\boxed{\beta_\infty(x - x_{\mathrm{gel}})}}_{\text{Cure Strain}}\Big)\mathbf{1} + \underbrace{\boxed{2\int_{s=0}^{s=t} G_\infty(s)\frac{d\boldsymbol{\epsilon}_{\mathrm{dev}}}{ds}ds}}_{\text{Shear Strain and Evolving Stress-Free Shape}}$$

Material Constants for Epon 828/T403 Epoxy from Reference [3]

k_0 (s^{-1})	2.17E5
b	0.17
M	0.33
N	1.37
E_a $(\mathrm{cal\ mol}^{-1})$	13.8E3
K_∞ (MPa)	920
G_∞ (MPa)	8.2
$\frac{dG_\infty}{dT}$ MPa / K	32E-3
T_{ref} (C)	90
α_∞ (K^{-1})	0.0005
x_{gel}	0.55
x_{ref}	1.0

Kamal (Condensation Chemistry) Cure Kinetics

$$\frac{dx}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right)\left(b + x^M\right)(1-x)^N$$

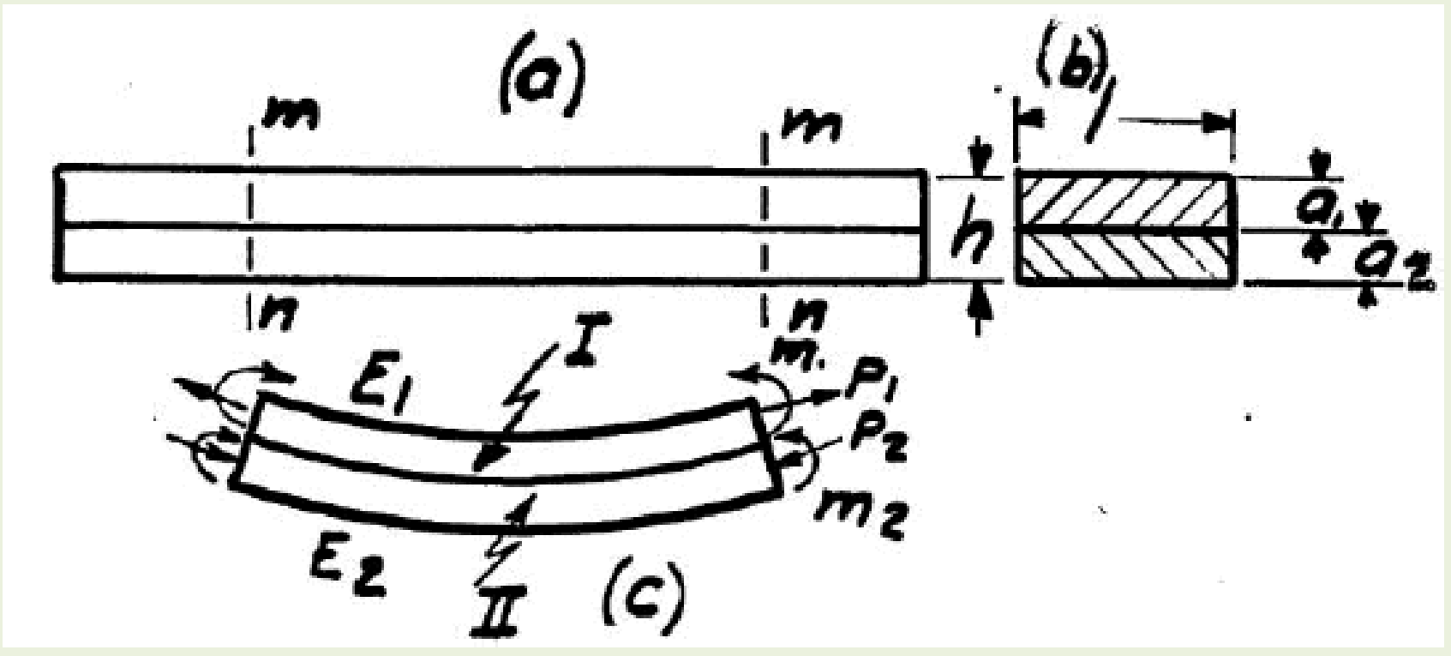
Shear Modulus Evolution During Cure

$$G_\infty[T,x] = \left(G_{\infty\,\mathrm{ref}} + \frac{dG_\infty}{dT}(T - T_{\mathrm{gel}})\right)\left(\frac{x^2 - x_{\mathrm{gel}}^2}{x_{ref}^2 - x_{\mathrm{gel}}^2}\right)^{8/3}$$

Evolving Reference (Stress-Free) Strain Offset

$$\boldsymbol{\epsilon}_{\mathrm{ref}} = \frac{1}{G_\infty[t]}\int_{s=0}^{s=t} G_\infty[s]\frac{d\boldsymbol{\epsilon}_{\mathrm{dev}}}{ds}ds - \boldsymbol{\epsilon}_{\mathrm{dev}}$$

Modified Timoshenko Bi-Material Beam Analysis[6]



Schematic of the uniformly heated bi-layer beam from Timoshenko (reference [6])

Assumptions

- Uniform temperature and geometry
- No variation along the length or width
- Perfectly bonded interface between the epoxy (1) and metal (2) layers
- Small deformations and Euler Beam Bending
- Stress-Free in the thickness direction
- In-plane strains are equal
- Uniform temperature throughout the epoxy and metal layers at all times
- Linear-Elastic metal and isotropic, thermal/curing epoxy models

Approach

- Balance axial/width forces and moments
- Enforcing displacement compatibility at the bond line

Beam Curvature Due to Mismatch Strain

$$\frac{1}{\rho} = \frac{6\epsilon_\Delta}{h\left(3 + \left(1 + mn^3\right)\left(1 + \frac{1}{mn}\right)/\left(1+n\right)^2\right)}$$

Total Mismatch Strain

$$\epsilon_\Delta(T,x) = \frac{\beta_\infty}{3}(x - x_{\mathrm{gel}}) + \alpha_2(T - T_{\mathrm{start}}) - \left(\alpha_\infty(T - T_{\mathrm{gel}}) - \epsilon_{pp}^{SF}\right)$$

Assumed Total Strain in the Epoxy Layer

$$\varepsilon = \begin{bmatrix} \varepsilon_{pp} & 0 & 0 \\ 0 & \varepsilon_{pp} & 0 \\ 0 & 0 & \varepsilon_{tt} \end{bmatrix}$$

Out-of-Plane Strain (Enforces Traction Free)

$$\epsilon_{tt} = -\frac{2\epsilon_{pp,\,m}\Lambda}{2G_\infty + \Lambda} + \alpha_\infty(T - T_{\mathrm{gel}}) - \epsilon_{\mathrm{ref,tt}} - \frac{\beta_\infty}{3}(x - x_{\mathrm{gel}})$$

$$\Lambda = K_\infty - \frac{2G_\infty}{3}$$

Mechanical and Total In-Plane Strains

$$\epsilon_{pp,\,m} = \frac{h}{6\rho}\left[\frac{mn^3 + 1}{mn(1+n)^2}\right] + \frac{a_1}{2\rho}$$

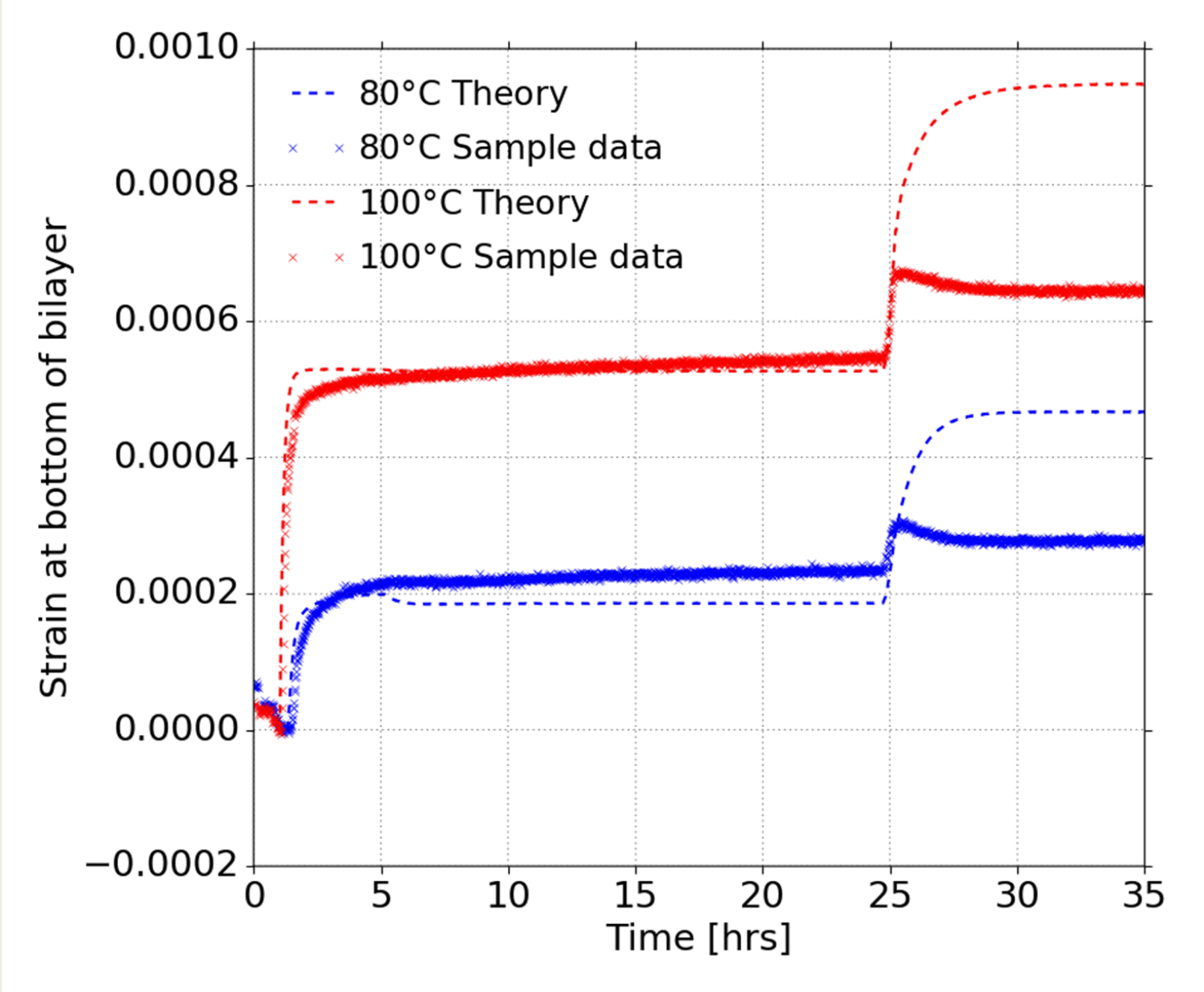
$$\epsilon_{pp} = \alpha_\infty(T - T_{\mathrm{gel}}) - \epsilon_{\mathrm{ref,\,pp}} - \frac{\beta_\infty}{3}(x - x_{\mathrm{gel}}) + \epsilon_{pp,\,m}$$

Strain At the Bottom of the Aluminum Beam

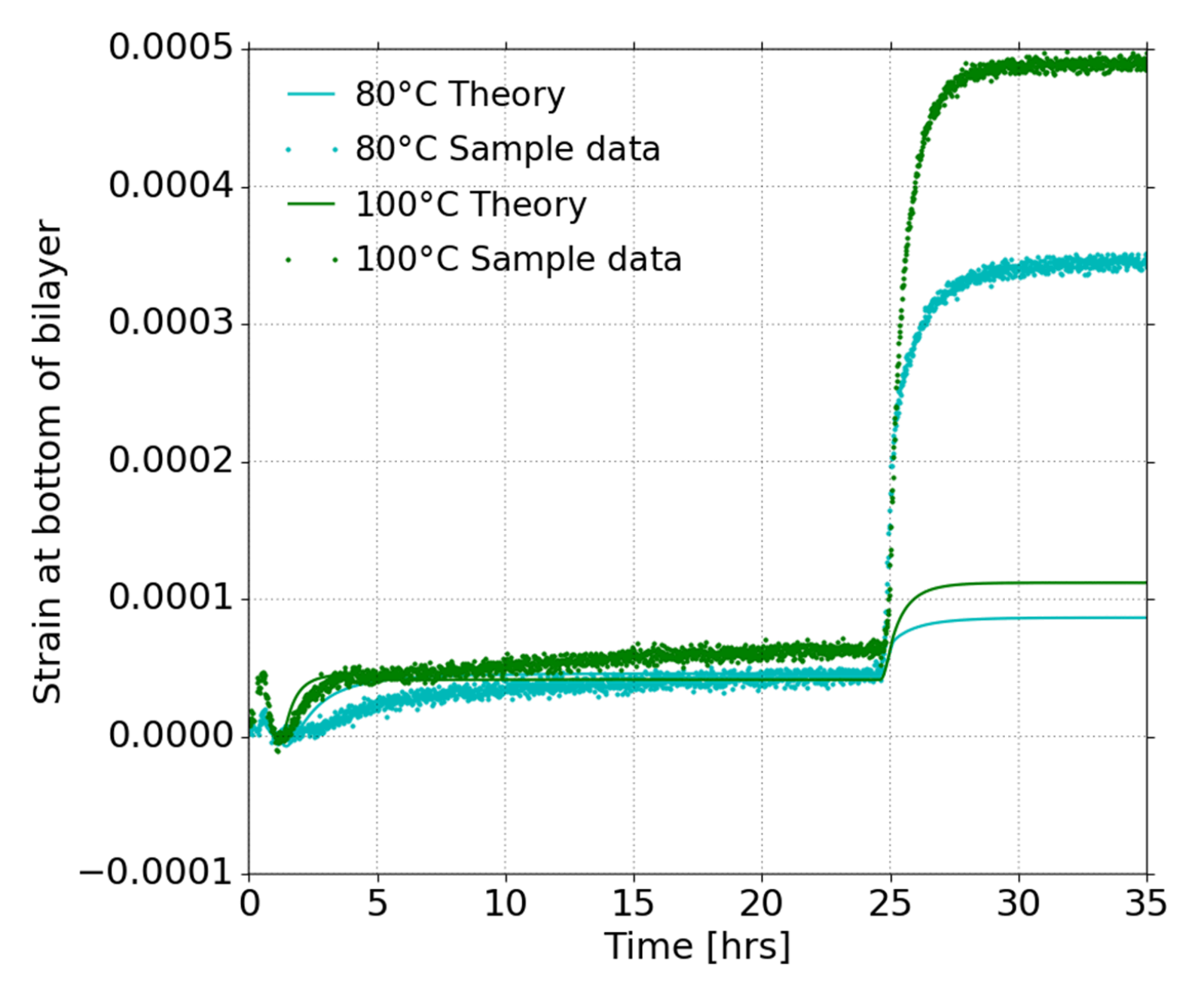
$$\boxed{\varepsilon_{bottom} = \alpha_2\Delta T + \frac{a_2}{\rho}\left[\frac{mn^3 + 3n + 4}{6(n+1)}\right]}$$

Bi-Material Analysis

Cure Shrinkage *Calibration*: 0.5" 828/T403 to 0.06" Aluminum Tests

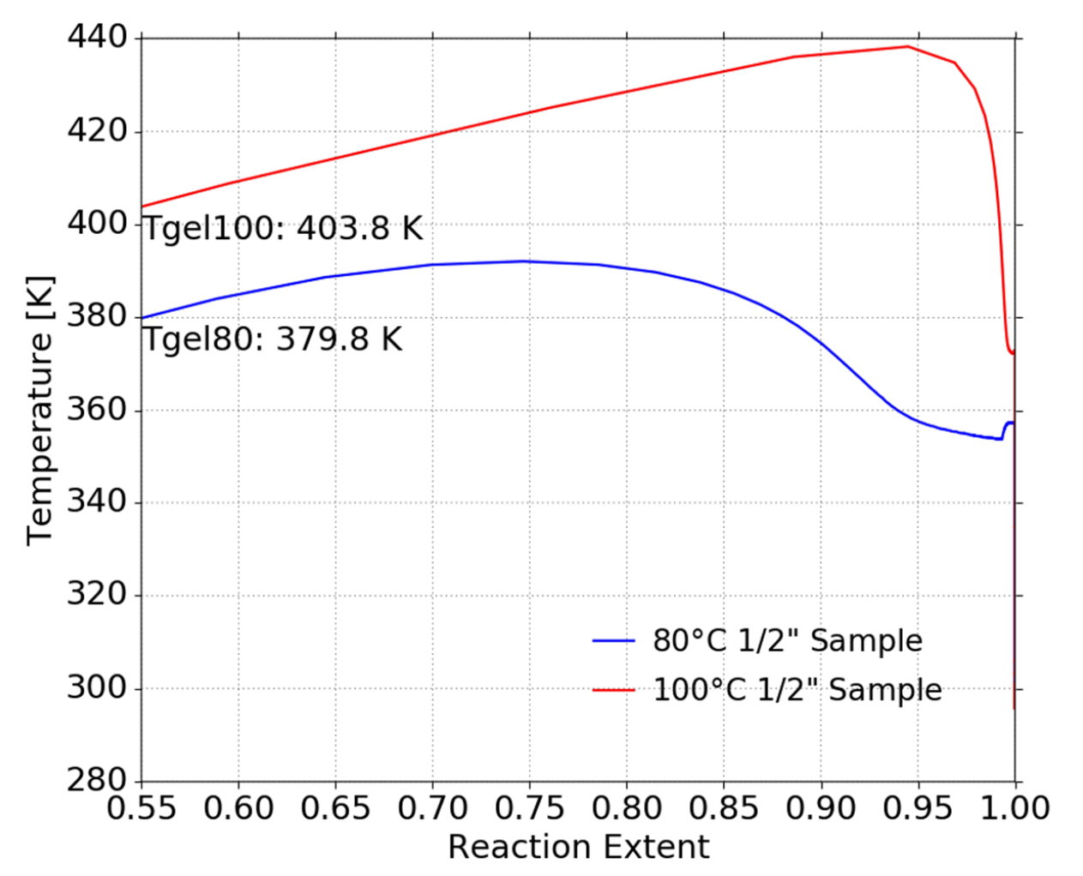


Cure Shrinkage *Predictions*: 0.25" 828/T403 to 0.06" Aluminum Tests

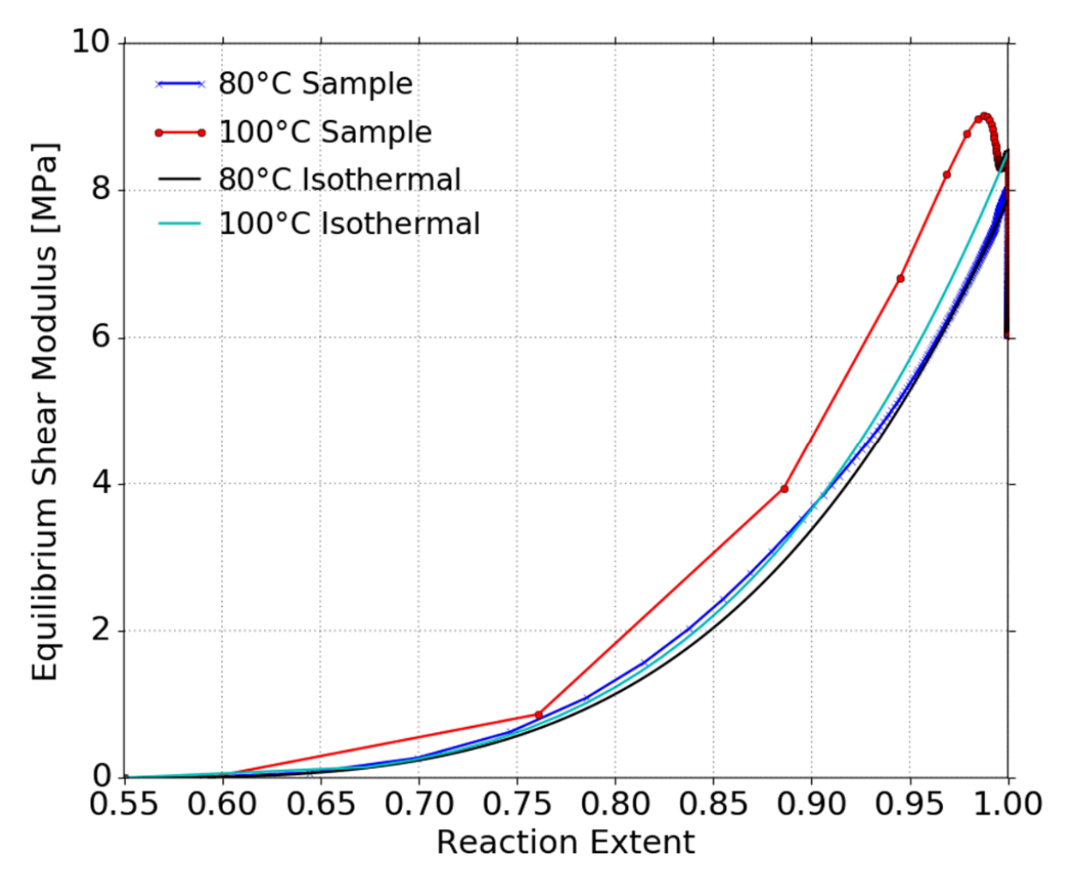


Model Details in the 0.5" Epoxy Tests

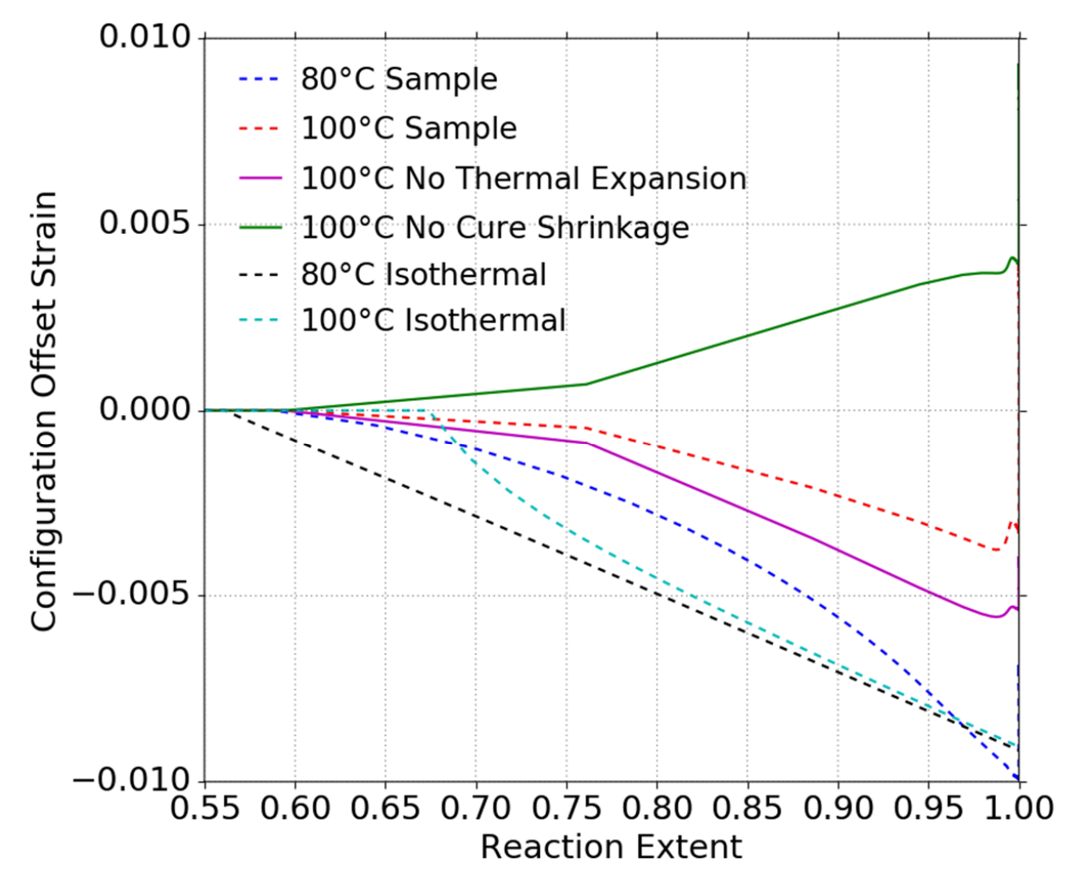
Temperature As a Function of Cure



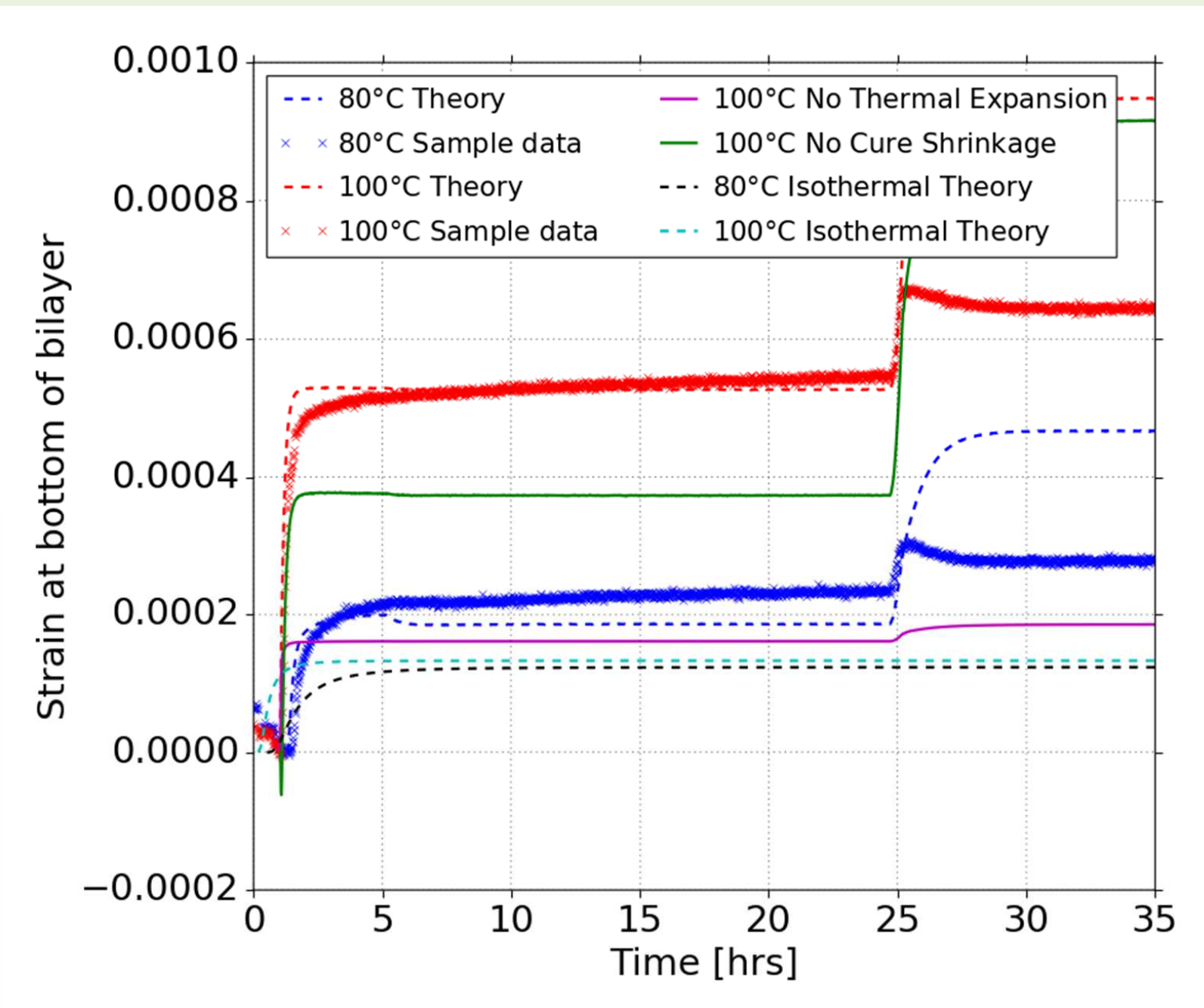
Shear Modulus Evolution



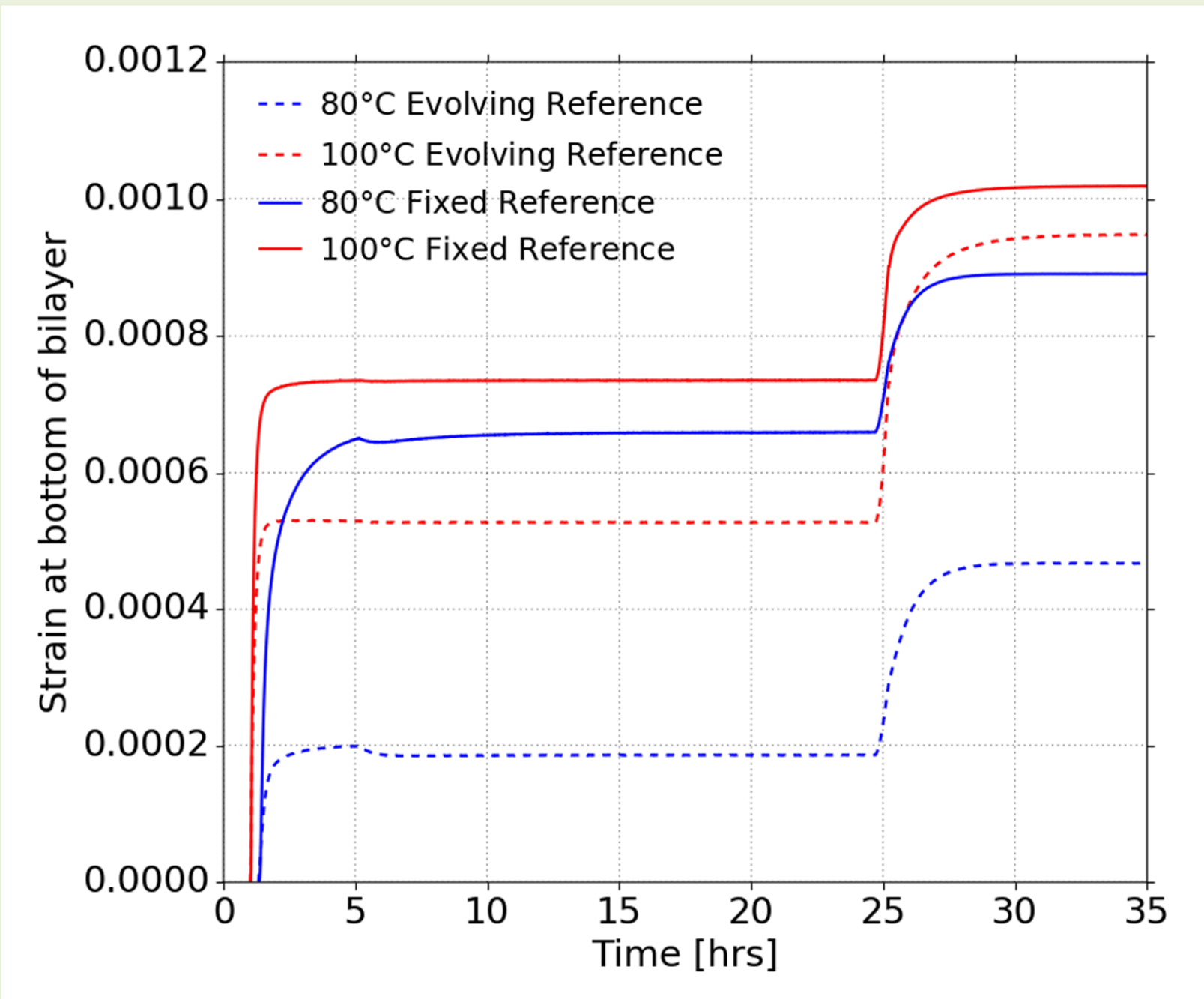
Evolving Reference Strains



Limiting Cases: Isothermal vs. No Cure Shrinkage



Analysis Without An Evolving Stress-Free Shape



Conclusions

- Bi-material beam analysis is effective in determining the rubbery cure shrinkage of Epon® 828/T403 Epoxy at different temperatures and beam thicknesses compared with previous measurements from [3]
- Simple inverse modeling based on reference [6] is required, but the overall approach is robust to large exotherms and associated temperature change.
- The experiments show continued cure well after the cross-linking reaction is complete according to the reaction kinetics from [3]. This physics could be considered in future work
- The model does not include viscoelasticity and could be extended to include vitrification during cure, which we are currently pursuing with Epon® 828/DEA
- Some anomalous behavior in the difference between 0.25 and 0.5 inch epoxy tests are still under investigation.

Comparison of Cure Shrinkage Parameters

$\beta_\infty^{\mathrm{high}}$	from [3]	0.082
$\beta_\infty^{\mathrm{OPT}}$	from 0.5" tests	0.0804
$\beta_\infty^{\mathrm{low}}$	from [3]	0.060

- Cure shrinkage was optimized over 0<x<0.9999 cure simultaneously for 0.5" tests
- Agreement is good compared with different experimental measurements

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