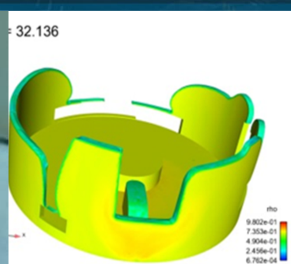
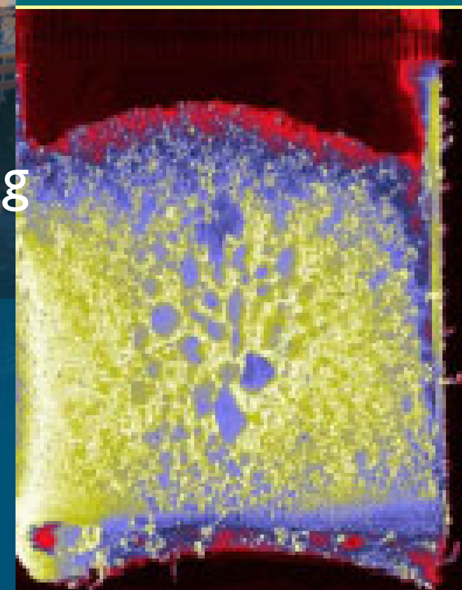
SAND2021-2167C

Sandia National Laboratories

Multiphysics Modeling of Coupled Chemical-Thermal-Mechanical Phenomena in Chemically Blown Polyurethane Foams during Manufacturing & Aging

PRESENTED BY

Kevin Long

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Sandia National Laboratories

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About the Presenter: Dr. Kevin Long, Sandia National Labs (SNL)

Kevin Long is a Principal Member of Technical Staff at SNL

Education

- **B.S. in Mechanical Engineering and Materials Science Engineering,** Double Major
- **M.S., 2008, Ph.D. Mechanical Engineering**, 2010, University of Colorado, Boulder. Dissertation Topic: *Photomechanics of Light Activated Network Polymers*

Dr. Long has authored/coauthored over 50 peer-reviewed journal articles, proceedings, and reports. His research interests include:

- Manufacturing to component lifetime material engineering
- Polymer and foam mechanics
- Constitutive modeling
- Multi-scale materials mechanics

Kevin Long with son Felix on a hike
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Introduction to Polyurethane Foams

- Polyurethane foams are widely used in manufacturing due to ease of production and varied material properties

We are developing models that can predict foam mold filling, void location, and final properties including density and modulus for structural foams and thermal conductivity for insulating material.

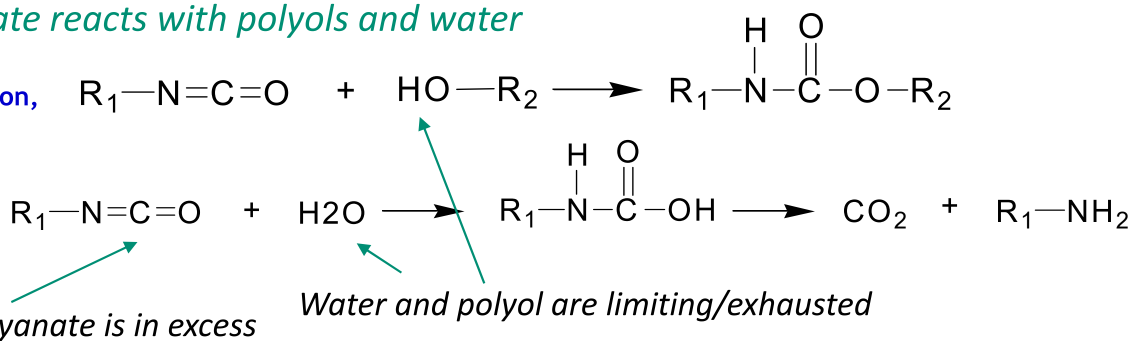
PMDI Foams Are Not Dimensionally Stable

What are PMDI Foams? *Polyurethane foams are used as an **encapsulant** and a **structural** material to provide voltage isolation and mitigate against shock and vibration*

How are they made? *Chemically blown manufacturing process with Two key reactions: Isocyanate reacts with polyols and water*

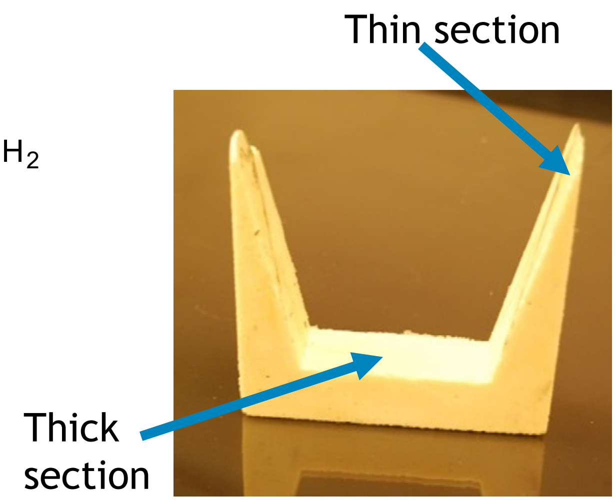
Urethane formation, crosslinking

Foaming reaction yields CO_2 and amine



Shape stability over weeks, months, years is problematic

- Tight tolerances (microns) lead to low part yields
- Expensive molds currently designed based on average shrinkage amounts, institutional knowledge, trial-and-error
- Dimensional changes are often not spatially uniform
- Many mechanisms for shrinkage identified



Small dimensional changes in foam translate to significant displacements in parts depending on geometries

Foam Part Life Cycle Process

Overarching Goal: **Life cycle models for foaming, vitrification, cure, aging for Structural Foam Parts**
Focus on moderate density PMDI foams

Injection, foaming and initial curing at lower T

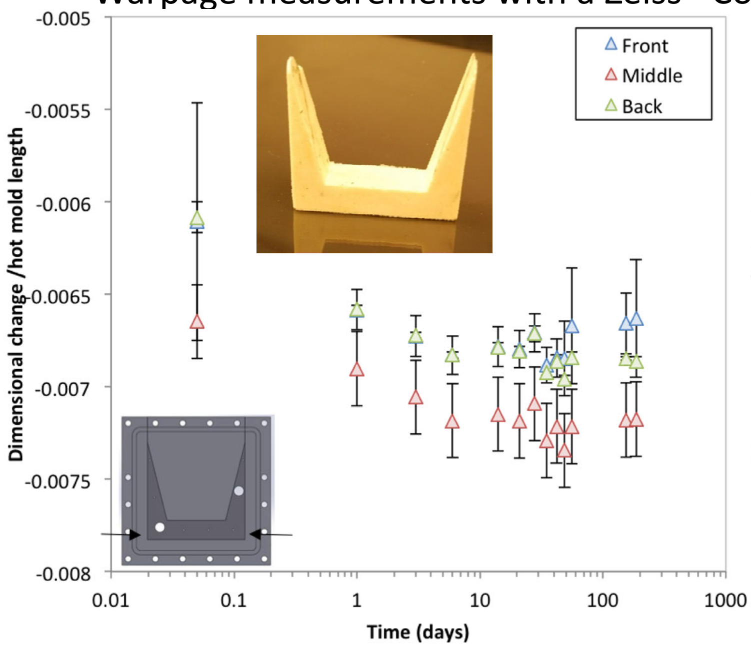
Oven time at higher T to make sure it is fully cured

Remove from mold – predict cure and thermal stresses

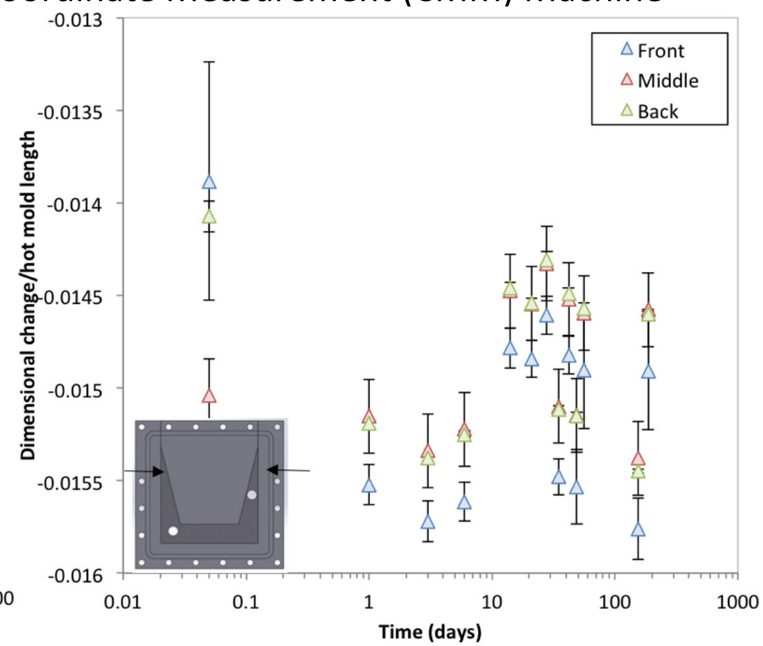
Predict shape and size over years

Motivation: Warpage and Aging Demonstration on Staple

- PMDI 10 S packed to 12.5 PCF
- Cure Schedule: 30 C for 10 minutes, 4 hours at 120 C
- Warpage measurements with a Zeiss® Coordinate Measurement (CMM) Machine



Monotonic and Consistent Warpage Trend in Thick Regions



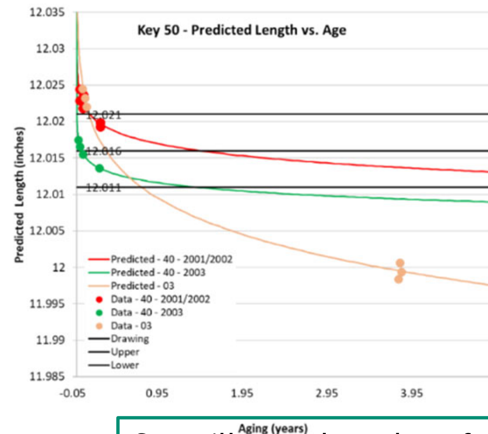
Non-Monotonic and Complex Warpage Trend On Thin Staple Arms

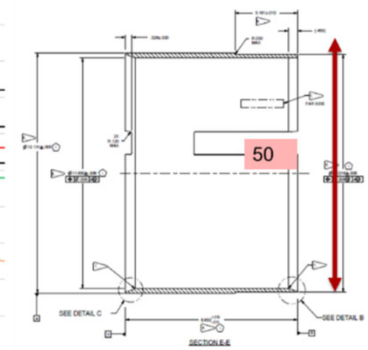
What are the key factors that make complex warpage behavior at the ”staple arms”?

Foam Structural Support Shrinkage Models

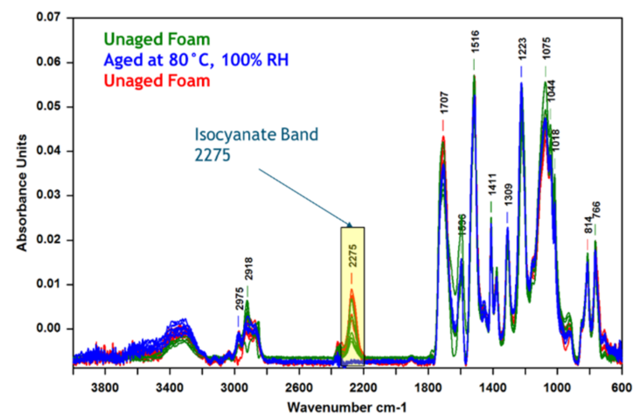
Mechanism	Time-scale	Approximate Strain
	Occurs over	Strain (%)
Thermal contraction/Manufacturing stress	Hours	~0.1% from 120 C to RT depending on density
CO_2 loss, bubble depressurization	Days/Weeks	~0.02% depending on density
Post-cure Isocyanate reaction	Months? Years? Depends on humidity	~0.05% depending on density
Viscoelastic relaxation (Physical aging)	Decades	Very small

- Manufacturing stresses and CO_2 loss cannot explain all of the experimentally observed deformation in PMDI support parts.
- Previous work shows water can react with isocyanate in PMDI foams to form CO_2 even below the T_g of the material. This causes shrinkage because new crosslinks are formed and the reaction off gases carbon dioxide.



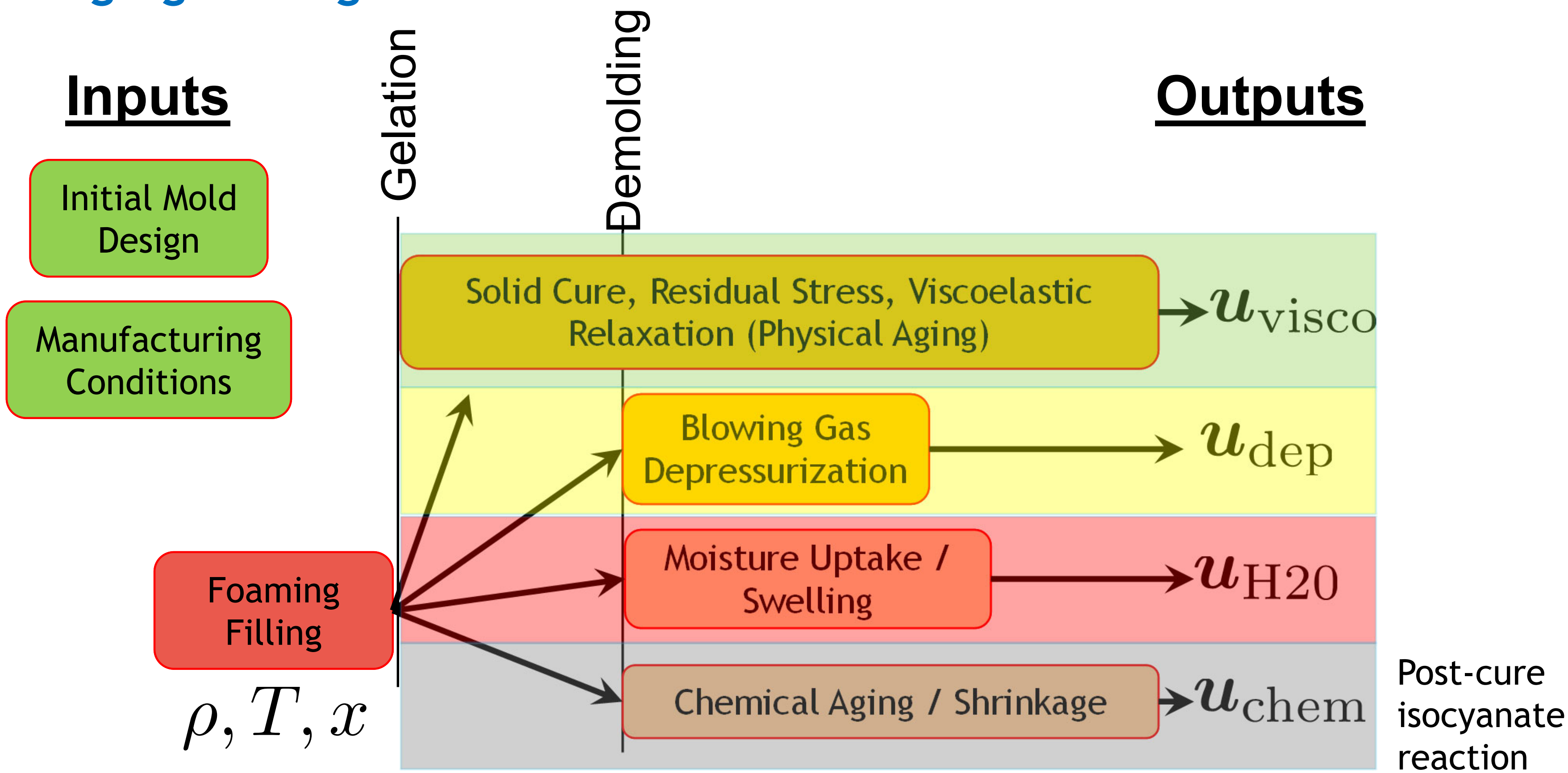


Surveillance data show foam structural parts change shape over time in storage



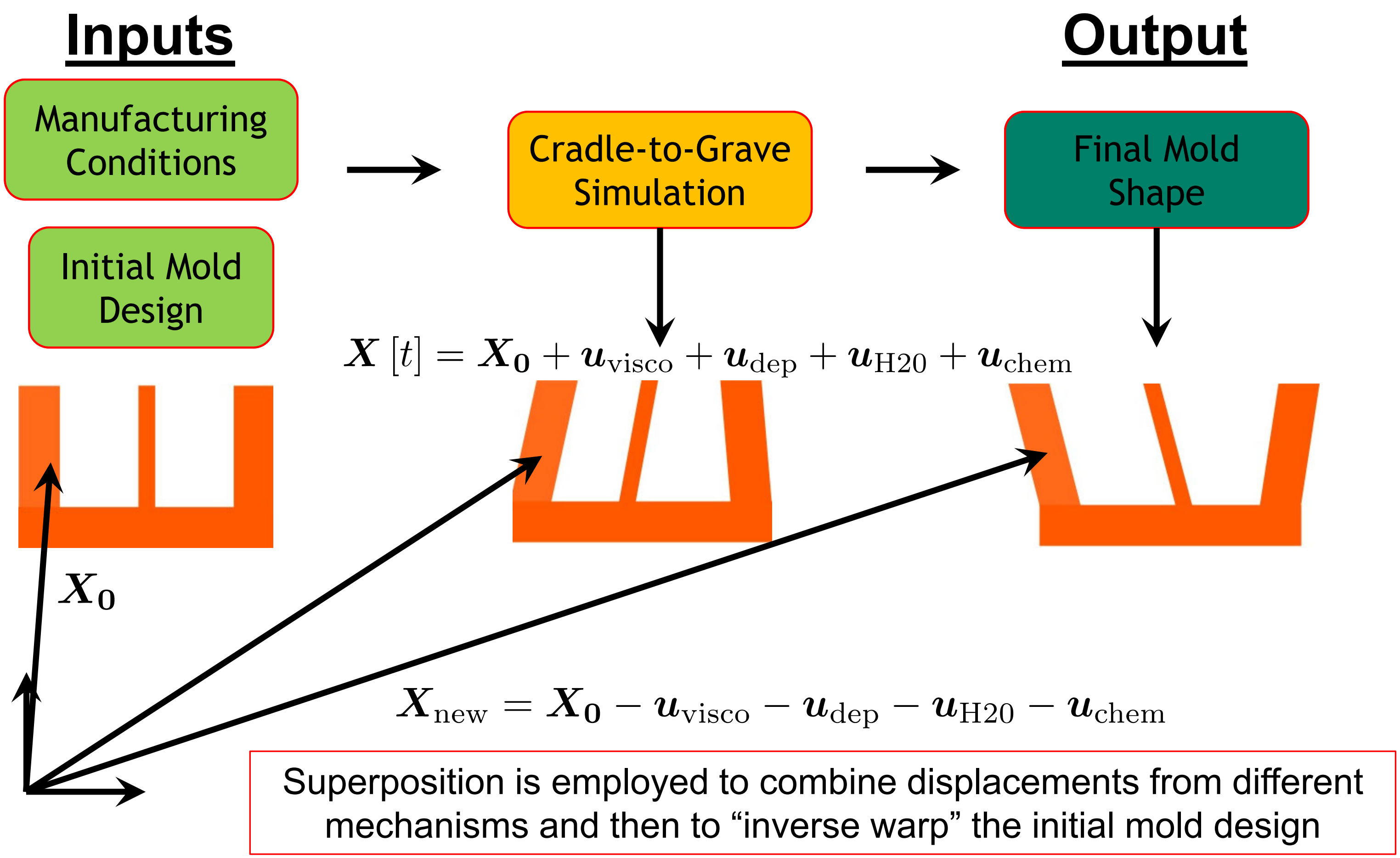
FTIR data show that the residual isocyanate exists post-manufacture and will be consumed in humid environments

Engineering-scale model framework for manufacturing and in-service aging for Rigid PMDI Foams



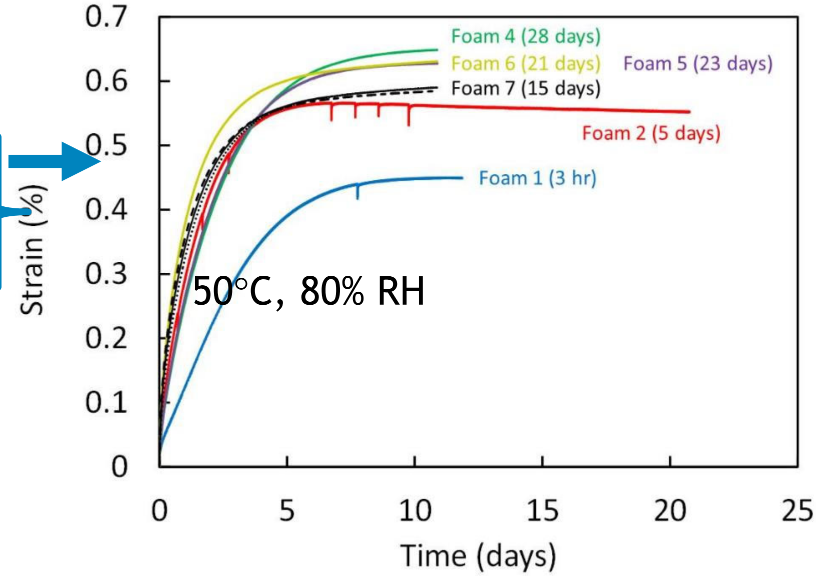
$$\boldsymbol{u} = \boldsymbol{u}_{\text{visco}} + \boldsymbol{u}_{\text{dep}} + \boldsymbol{u}_{\text{H20}} + \boldsymbol{u}_{\text{chem}}$$

A Key Model Target: Inverse mold design for manufacturing/age aware shrinkage mitigation



Review of the Theory

- We consider that water concentration infiltrates and diffuses into foam components post manufacture
  - Water infiltration is associated with Swelling and Tg depression
- Water reacts with residual isocyanate to shrink the foam and elevate the glass transition (anti-plasticization)
- The stress response considers:
  - Primary cross-linking (degree of cure, x)
  - Secondary cross-linking, NCO consumption (degree of cure, y)
  - Moisture Uptake via a water concentration, (C_{H20})
  - Thermal Expansion
  - Shear and Bulk Responses



FBG-derived strain profiles during equilibration of PMDI foam cylinders at 50 °C, 80% RH. The duration for which each foam cylinder was initially equilibrated at 50 °C, 0% RH is indicated in parentheses.

Equations of motion and Constitutive Models for the Solid Foam

Displacement as a function of water concentration, and secondary cure

Equations of Motion

- Species balance
- Mass
- Momentum
- Energy

Constitutive Law for the Cauchy Stress

$$\boldsymbol{S}_{\varepsilon} = \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}} = \boldsymbol{S}_{\varepsilon}{}^{\text{mech}} - \delta^{\infty} K^{\infty} \left(C_{H_2O} - C^{\text{ref}}_{H_2O} \right) \mathbf{1}$$

$$\boldsymbol{S}_{E} = \frac{1}{2} \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}} : \frac{\partial \boldsymbol{\varepsilon}}{\partial \boldsymbol{C}}$$

$$\boldsymbol{\sigma} = J^{-1} \boldsymbol{F} \boldsymbol{S}_{\boldsymbol{E}} \boldsymbol{F}^{T}$$

Lagrangian Species Balances for Isocyanate, Water, and dissolved Carbon Dioxide in the Foam

$$\frac{dC_{NCO}}{dt} = -k_{NCO} C^{2}_{NCO} C^{2}_{H_2O}$$

$$\frac{dC_{H_2O}}{dt} = -k_{NCO} C^{2}_{NCO} C^{2}_{H_2O}$$

$$\frac{dC_{CO_2}}{dt} = +k_{NCO} C^{2}_{NCO} C^{2}_{H_2O}$$

Rubbery Response

$$\begin{aligned} S^{\varepsilon\infty}_{ij} = \frac{\partial \Psi^{\infty}}{\partial \varepsilon_{ij}} = {} & 2G^{\infty}(\varepsilon^{dev}_{ij} - \xi^{dev}_{ij}) \\ & + (P_{ref} - K^{\infty}\alpha^{\infty}(\Theta - \Theta_{ref}) - K^{\infty} I_{1\varepsilon})\, \delta_{ij} \\ & - (K^{\infty}\beta^{\infty}(x - x_{ref}) - K^{\infty}\gamma^{\infty}(y - y_{ref}))\, \delta_{ij} \\ & - K^{\infty}\delta^{\infty} \left(C_{H_2O} - C^{\text{ref}}_{H_2O} \right) \delta_{ij} \end{aligned}$$

Combined (Glassy + Rubbery) Response

$$\begin{aligned} S^{\varepsilon}_{ij} = \frac{\partial \Psi}{\partial \varepsilon_{ij}} = {} & S^{\varepsilon\infty}_{ij} + (K^{G} - K^{\infty}) \int_0^t ds\, f^{v}(t' - s', 0) \frac{dI_{1\varepsilon}}{ds} \delta_{ij} \\ & + 2(G^{G} - G^{\infty}) \int_0^t ds\, f^{s}(t' - s', 0) \frac{d(\varepsilon^{dev}_{ij} - \xi^{dev}_{ij})}{ds} \\ & - (K^{G}\alpha^{G} - K^{\infty}\alpha^{\infty}) \int_0^t ds\, f^{v}(t' - s', 0) \frac{d\Theta}{ds} \delta_{ij} \\ & - (K^{G}\beta^{G} - K^{\infty}\beta^{\infty}) \int_0^t ds\, f^{v}(t' - s', 0) \frac{dx}{ds} \delta_{ij} \\ & - (K^{G}\gamma^{G} - K^{\infty}\gamma^{\infty}) \int_0^t ds\, f^{v}(t' - s', 0) \frac{dy}{ds} \delta_{ij} \\ & - (K^{G}\delta^{G} - K^{\infty}\delta^{\infty}) \int_0^t ds\, f^{v}(t' - s', 0) \frac{dC_{H_2O}}{ds} \delta_{ij} \end{aligned}$$

Evolving foam chemistry terms

Constitutive Models for the Solid Foam

Prony Series (Viscoelastic Relaxation Functions)

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

Relation between material and laboratory time

$$t'-s' = \int_s^t \frac{dz}{a(z)} dz. \qquad \log a = \frac{-C_1 N}{C_2 + N}$$

Determination of time-history superposition

$$\begin{aligned} N = & \left(\Theta - \Theta_{glass} - \int_0^t ds f^v(t'-s',0)\frac{d\Theta}{ds}\right) \\ & + C_3\left(I_{1\varepsilon} - \int_0^t ds f^v(t'-s',0)\frac{dI_{1\varepsilon}}{ds}\right) \\ & + C_4 \int_0^t ds \int_0^t du f^s(t'-s', t'-u') \frac{d(\varepsilon_{ij}^{dev} - \xi_{ij}^{dev})}{ds}\frac{d(\varepsilon_{ij}^{dev} - \xi_{ij}^{dev})}{du} \\ & + C_5\left(x - x_{ref} - \int_0^t ds f^v(t'-s',0)\frac{dx}{ds}\right) \\ & + C_6\left(y - y_{ref} - \int_0^t ds f^v(t'-s',0)\frac{dy}{ds}\right). \\ & + C_7\left(C_{H_2O} - C_{H_2O}^{\text{ref}} - \int_0^t ds f^v(t'-s',0)\frac{dC_{H_2O}}{ds}\right). \end{aligned}$$

Evolving foam chemistry terms

Change in the glass transition from curing and swelling

$$\Theta_{ref}(x,y) = -\frac{(C_3\beta_\infty + C_5)(x - x_{ref}) + (C_3\gamma_\infty + C_6)(y - y_{ref}) + (C_3\delta_\infty + C_7)\left(C_{H_2O} - C_{H_2O}^{ref}\right)}{1 + C_3\alpha_\infty}$$

Total Helmholtz FE per unit undeformed volume

Chemical Potential of Water Uptake

$$\mu = \frac{\partial \psi}{\partial C_{H_2O}} = A\left(C_{H_2O} - C_{H_2O}^{\text{ref}}\right) - \delta^\infty K^\infty \text{tr}\boldsymbol{\varepsilon} - \mu_{\text{ref}}.$$

Assumption of Water Transport Kinetics

$$\boldsymbol{j} = -m\nabla\mu = -m\left(A\nabla C_{H_2O} - \delta^\infty K^\infty \nabla(\text{tr}\boldsymbol{\varepsilon})\right)$$

Near-Fickian diffusion of water into foam

Flux of H_2O concentration is proportional to the spatial gradient of the chemical potential

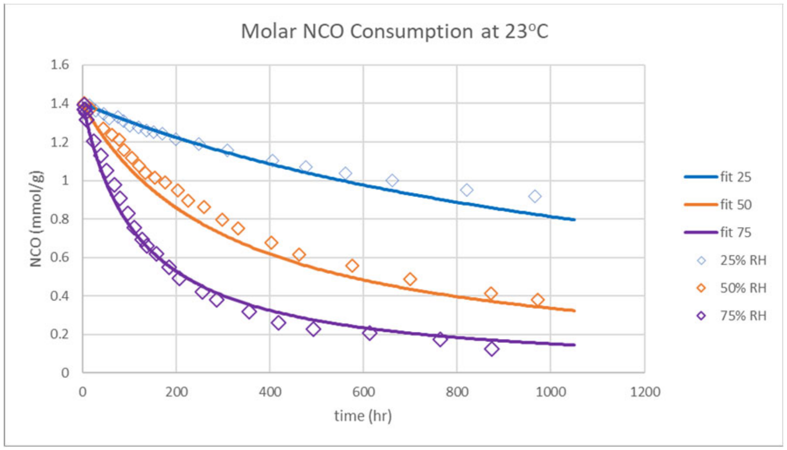
Ultimately, we simplified transport kinetics:

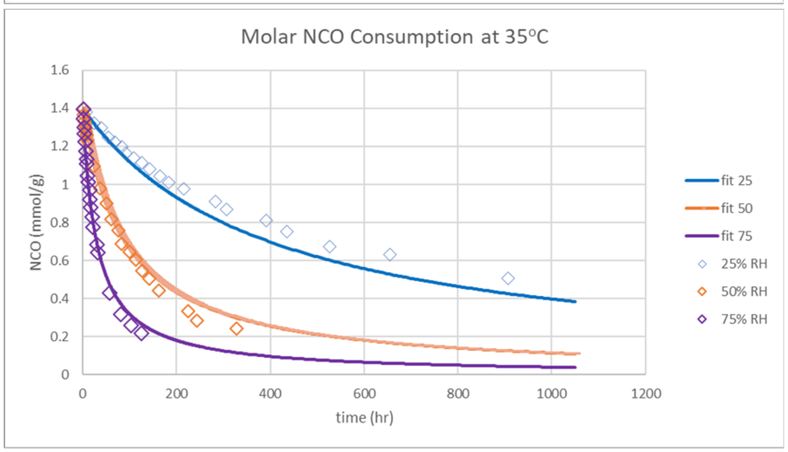
$$D_{H_2O}^{eff} = D_{H_2O} e^{-E_{H_2O}/RT}$$

$$D_{CO_2}^{eff} = D_{CO_2} e^{-E_{CO_2}/RT}$$

Effective diffusivity of water and CO_2 into foam

NCO Kinetics as a Function of Temperature and Humidity





$k=k_o\exp(-E_a/RT)*\exp(-a*C/RT)$

$$k_{NCO} = k_o \exp(-E_{NCO}/RT)$$

$$E_{NCO} = E_a + a(T)C_{H_2O}$$

$$\frac{dC_{NCO}}{dt} = -k_{NCO}C_{NCO}^2 C_{H_2O}^2$$

$$\frac{dC_{H_2O}}{dt} = -k_{NCO}C_{NCO}^2 C_{H_2O}^2$$

$$\frac{dC_{CO_2}}{dt} = +k_{NCO}C_{NCO}^2 C_{H_2O}^2$$

Temperature (K)	296.15	308.15	323.15
a(T)	-800	-2400	-4100

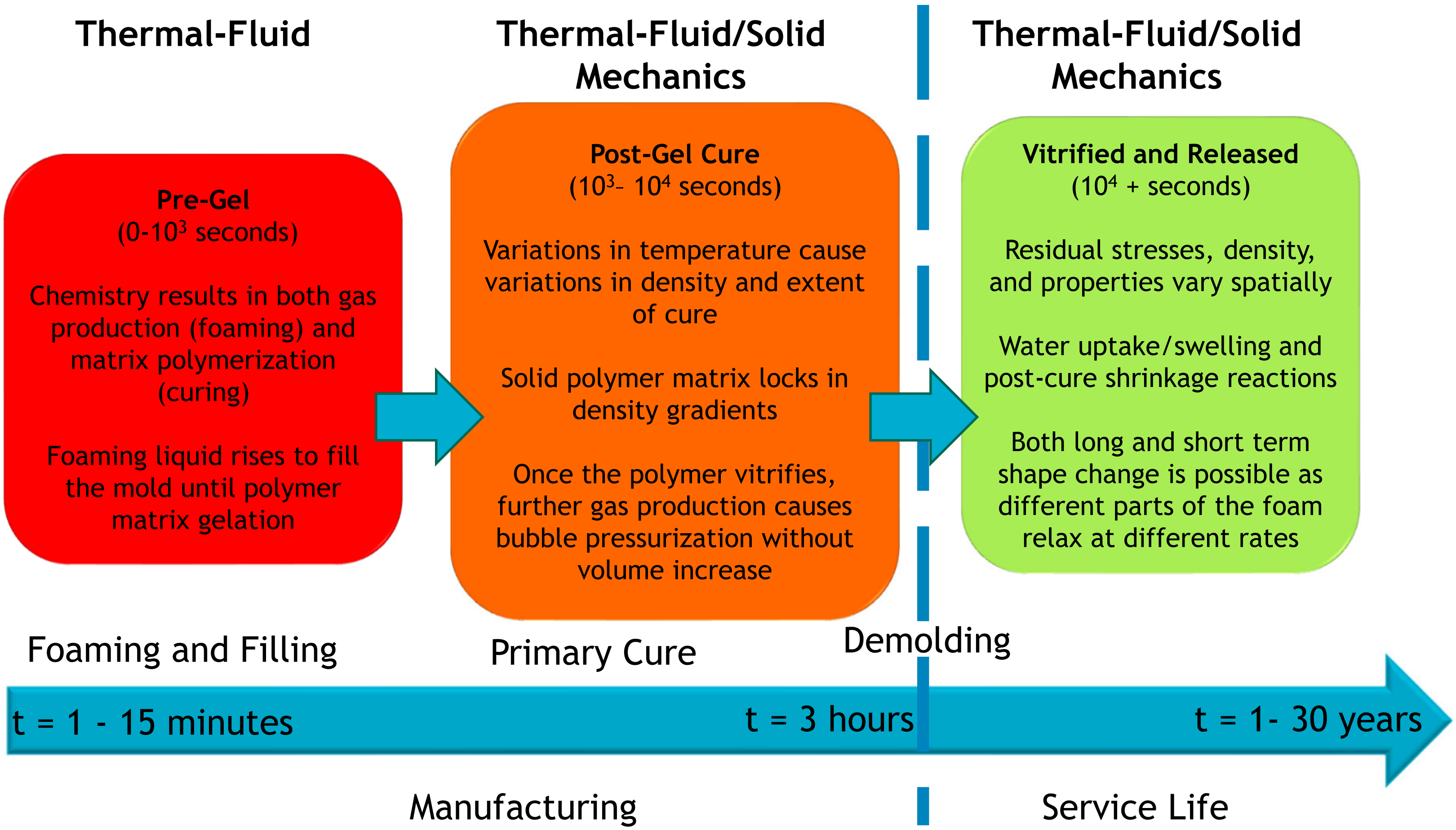
Parameter	Value
Ea (J/mol)	39500
k0(ml³/hr mmol³	1.05E+04

- New model with water concentration accelerating the reactions and modifying the activation energy of NCO post-cure reactions
  - Arrhenius relationship for k_{NCO} with activation energy dependent on temperature and water concentration

Cradle-to-Grave Modeling of Foam Parts

Sierra Mechanics FEA Code Suite

Kinetics and species balances for CH20 and YRCT were developed and coupled to the solid mechanics FE code through an ALE formulation in the thermal-fluid FE code



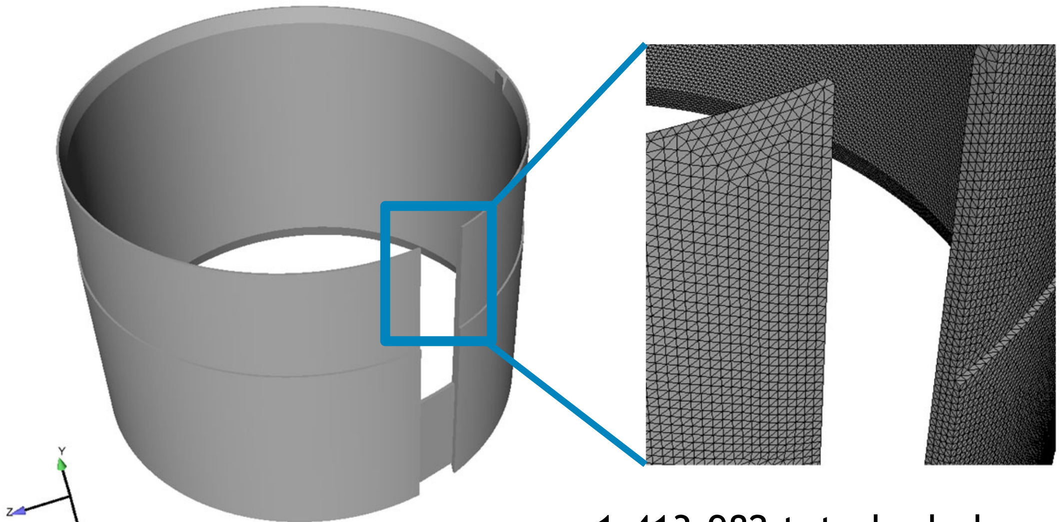
Example: Structural Foam Cylinder

- Thin-walled cylinder with notch cut-out to test behavior of thin sections and tight dimensional tolerances

Experiments: Manufacture + Aging

Manufacturing Parameters	Test Number					
Serial Numbers	X112	X117	X120	2001	2002	2003
Mold Pre-Heat (˚F)	95 ± 5			95 ± 5		
Pour Wt. (g)	810.3	810.0	809.7	830.0		
Cure Temp (˚F)	250			250		
Cure Time (hrs)	4			4		
Mold Strip Temp (˚F)	<200			<200		
Inspection Timing (days)	42 / 1399	35 / 1392	26 / 1386	7,14,28,90+		
Inspection	CMM Zeiss/ Weight			CMM Zeiss/ Weight		

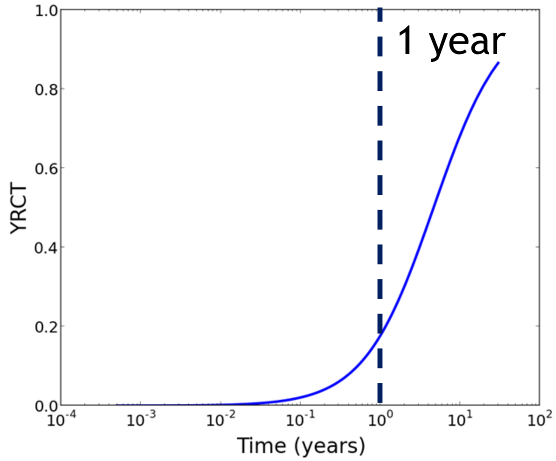
3-D Finite Element Model



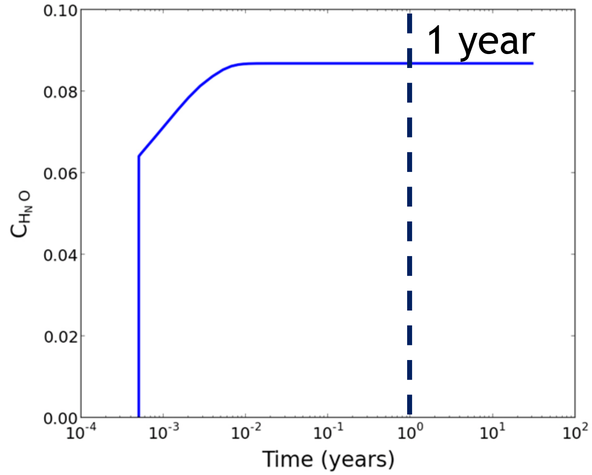
1,413,982 tetrahedral elements

Chemistry Evolution Over 30-Year Lifespan

Secondary Cure Reaction Progress



Water Concentration



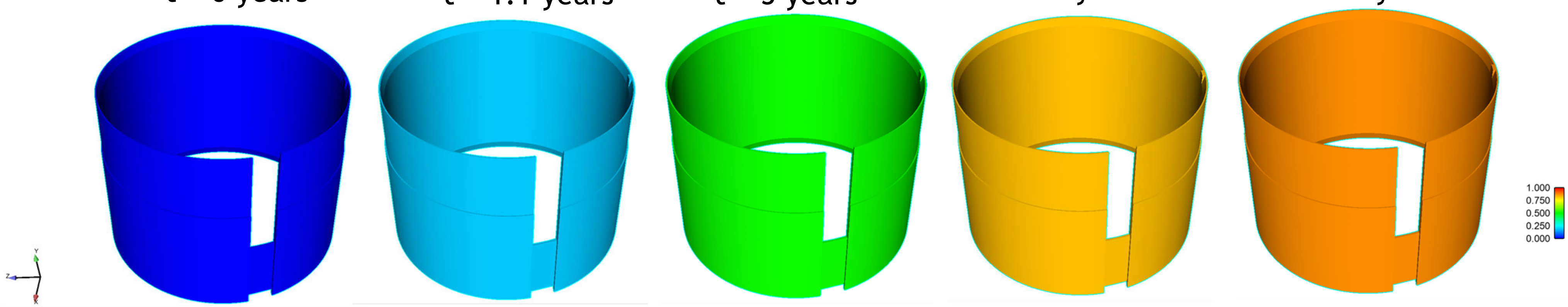
t = 0 years

t = 1.1 years

t = 5 years

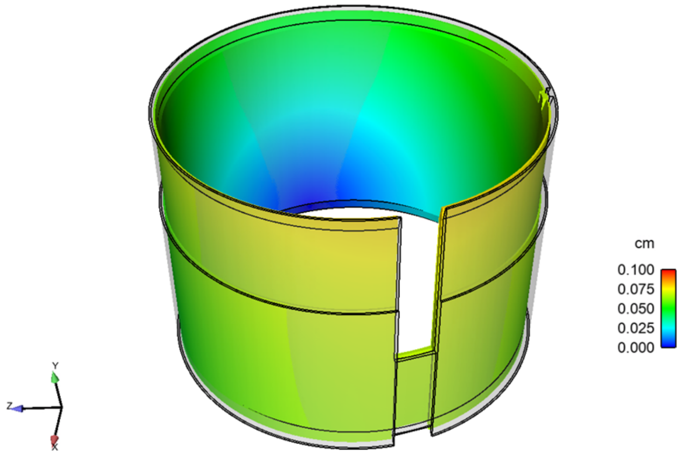
t = 20 years

t = 30 years

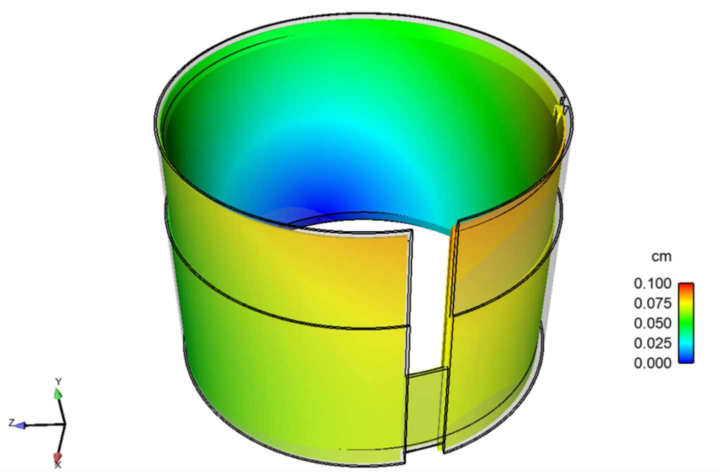


Model Predicts Part Shrinkage Over Time

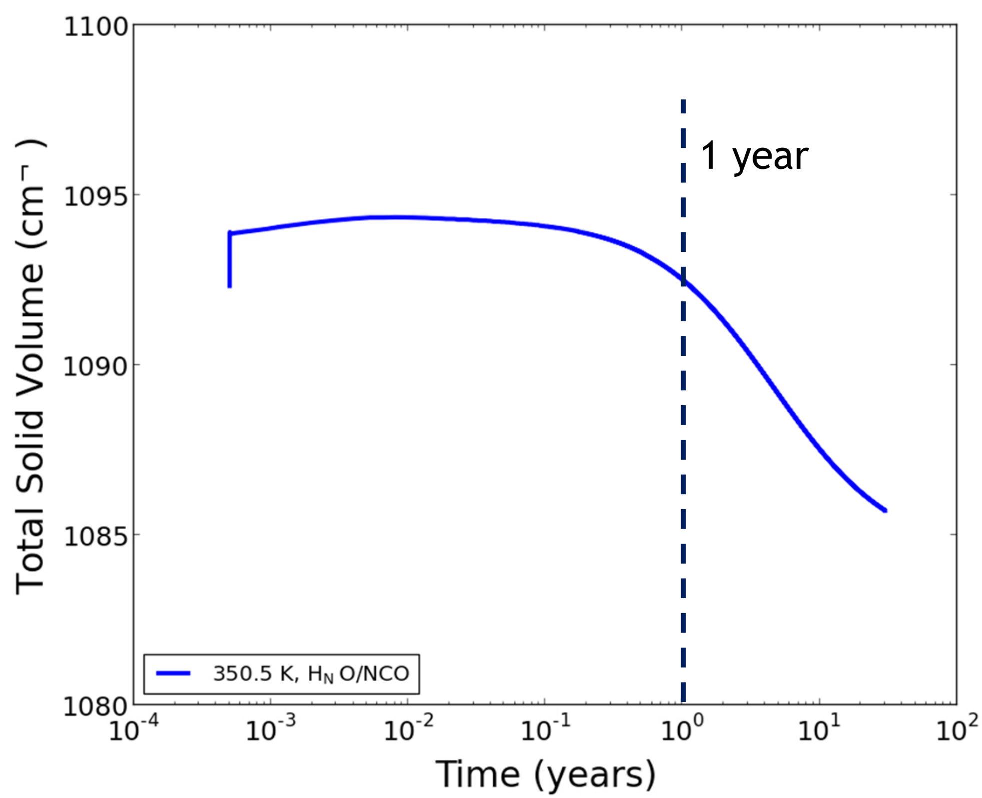
Manufacturing
+
Viscoelasticity



Moisture
Uptake +
Secondary
Cure

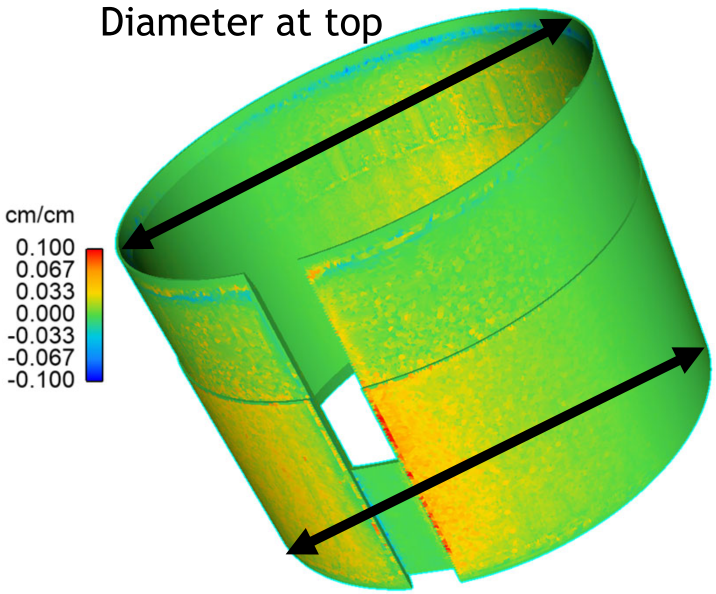


Volume Change from All Mechanisms Combined



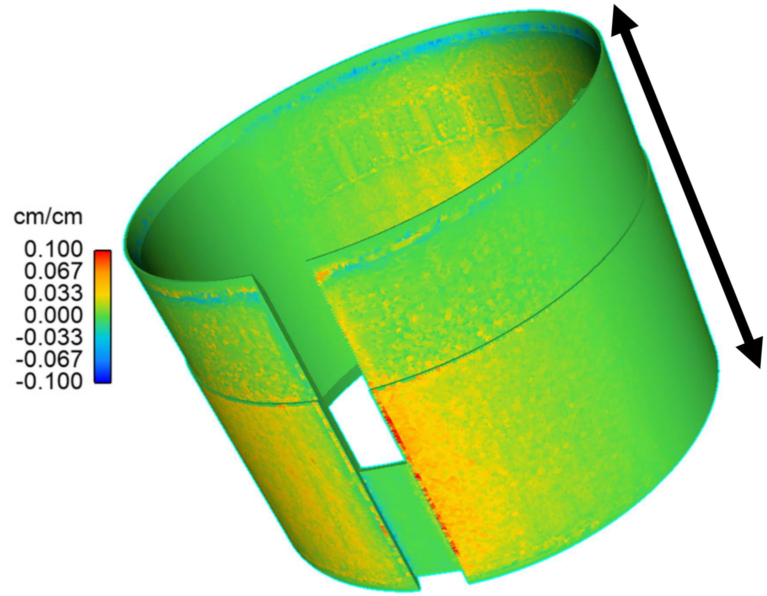
Comparison Metrics with Experimental Measurements

Key 50 = Outer Diameter at top



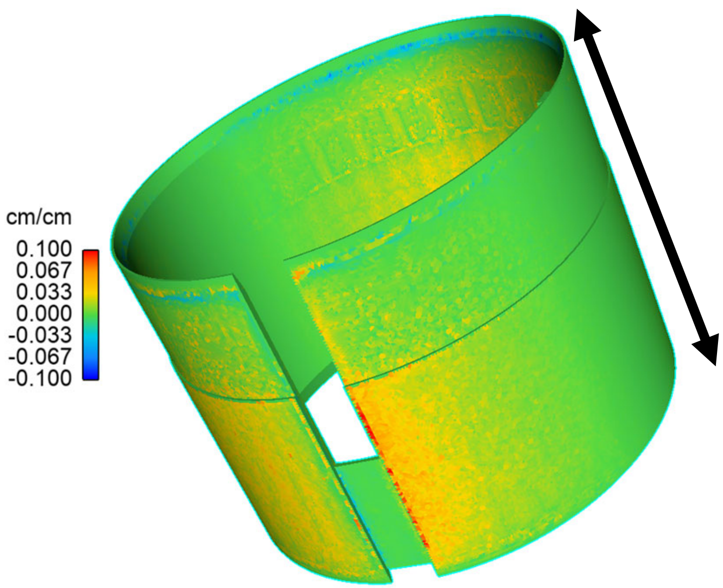
Key 10 = Outer Diameter at bottom

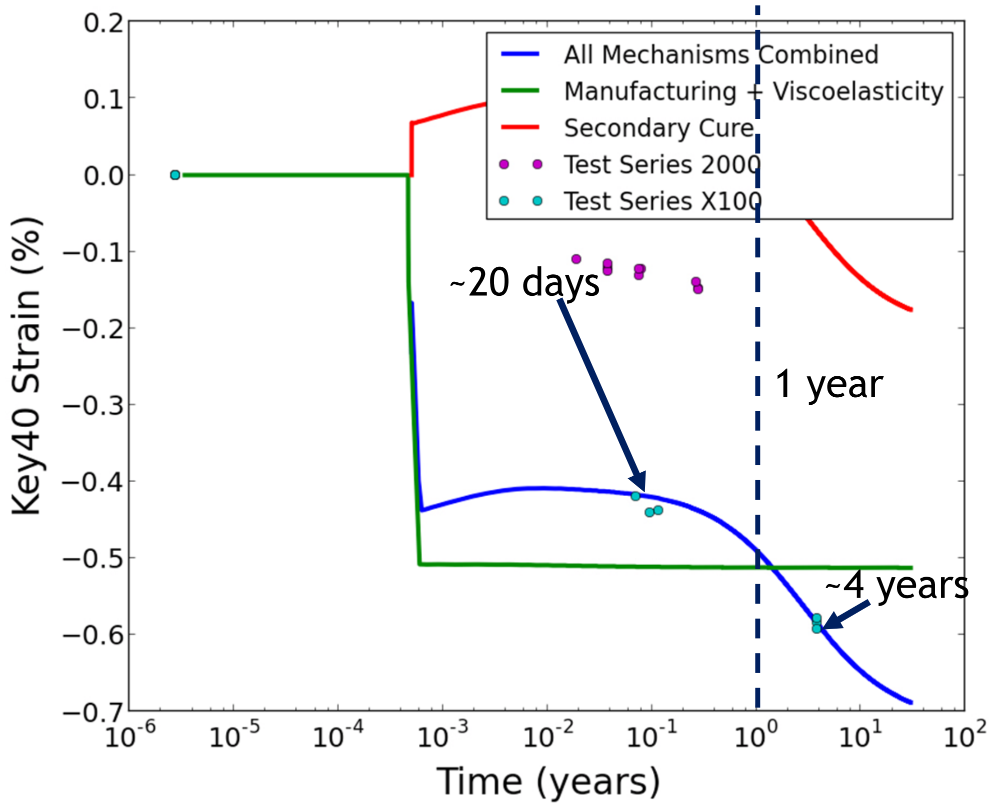
Key 40 = Height (distance between top surface and bottom surface)



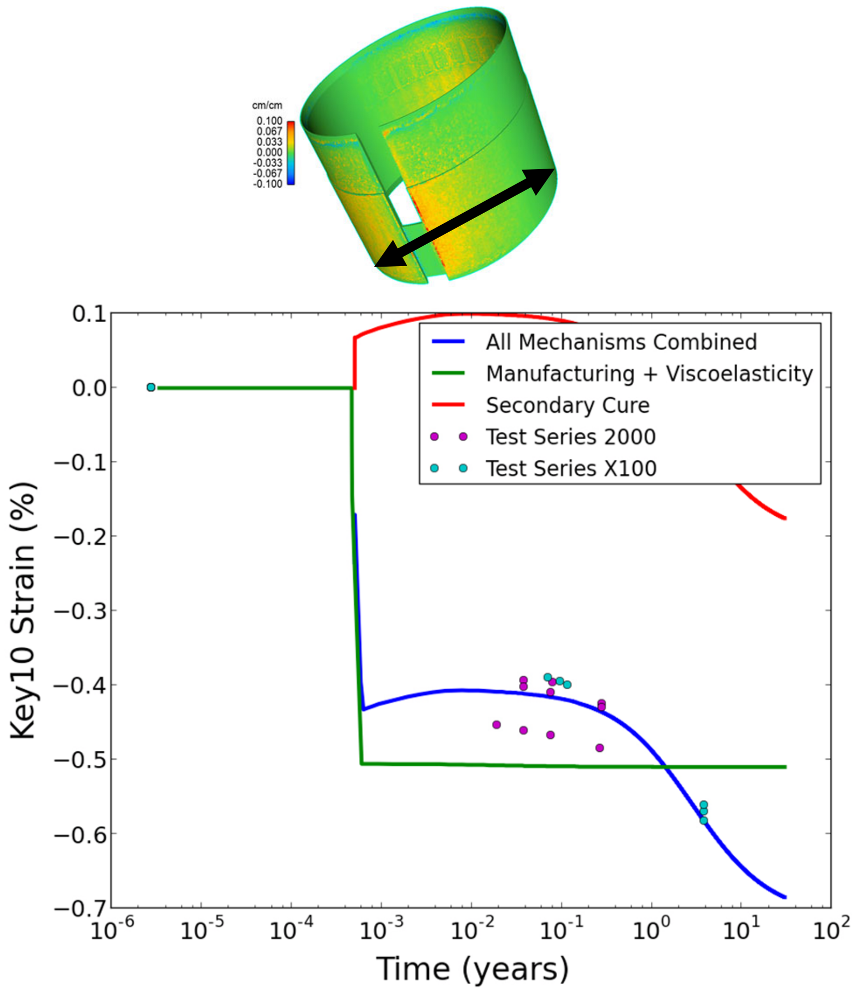
Structural Foam Part Predictions: Height

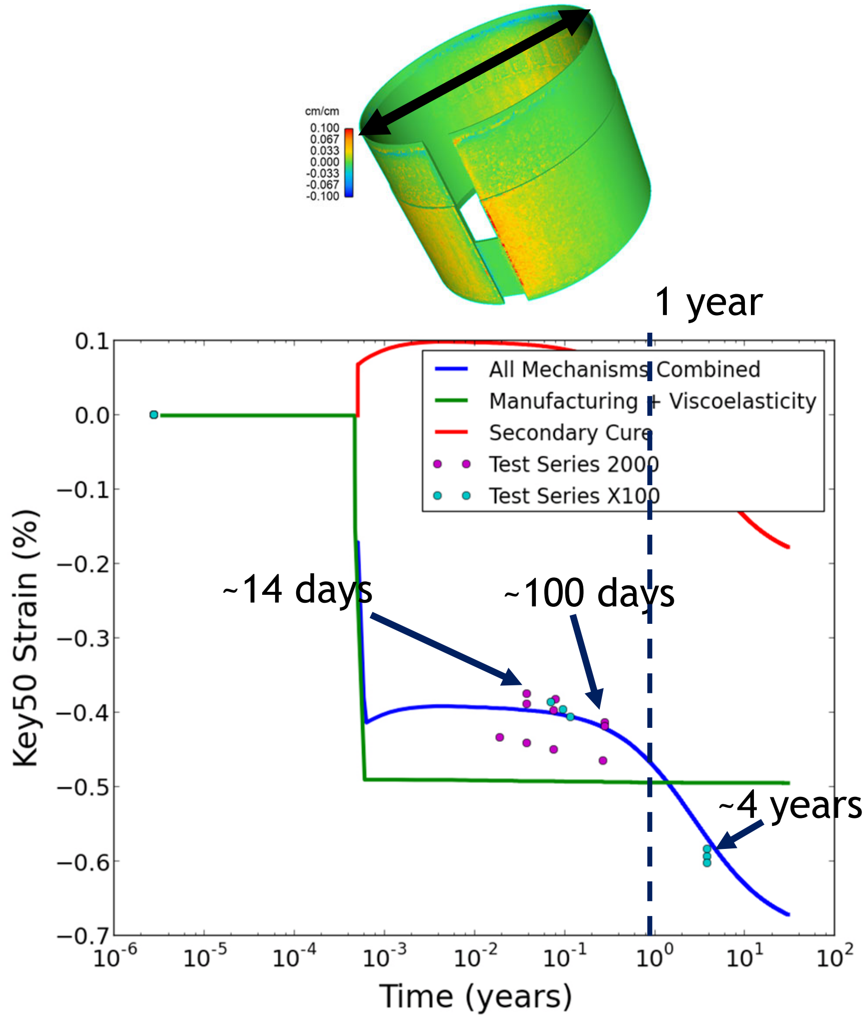
Key 40 = Height





Structural Foam Part Predictions: Bottom & Top Diameter





Conclusions

- Multiple sources contribute to shrinkage of PMDI foams
- Long-term (months) dimensional changes are due to isocyanate reacting with water.
- Pre-aging foamed parts with a humidity treatment could remove excess isocyanate and make them dimensionally stable against additional chemical shrinkage
- However, water swelling, though reversible, can be significant

Phenomenon	Time Scale	Strain (%)
Thermal contraction	Hours	~0.1% from 120 C to RT depending on density
Water Swelling	Hours	~2.1%
Depressurization	Days/Weeks	~0.02% depending on density
Isocyanate reaction	Weeks/years	~0.05% depending on density
Viscoelastic relaxation (Physical aging)	Decades	Very small

Conclusions & Next Steps

- A new kinetic model of post-cure reactions was developed (second order in NCO and water concentration with plasticization from water)
- The time scale for cure shrinkage is highly dependent on the water environment and temperature seen by the part.
- For our dry oven and 10% RH boundary conditions, we see shape change continuously for 30 years
- Extend model to other foams and geometries of interest
- Incorporate bubble-scale data from population balance modeling

Thank you for your attention!

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