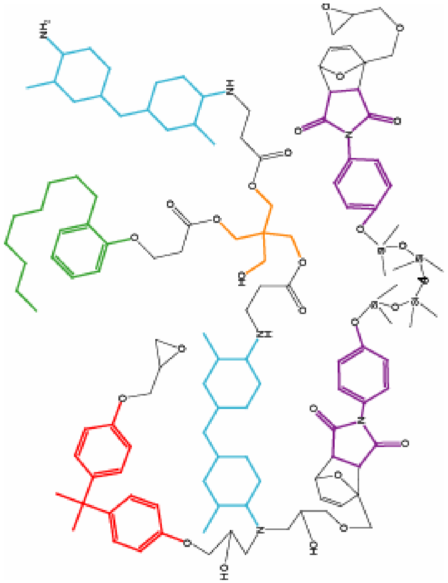
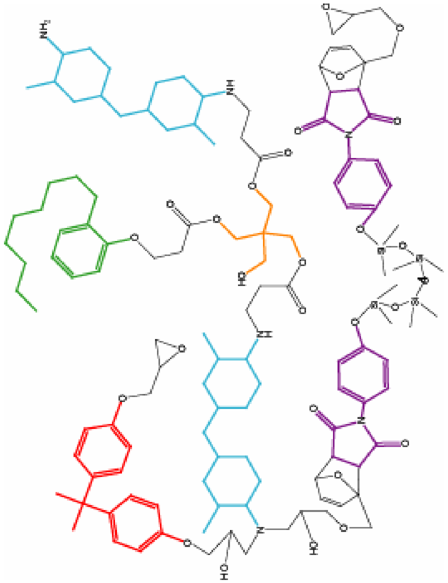
Modeling Epoxy Foams Exposed to Fire-Like Heat Fluxes

The 19th Annual ACERC & ICES Technical Conference





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Michael L. Hobbs
Thermal & Reactive Processes
Engineering Sciences Center
Sandia National Laboratories

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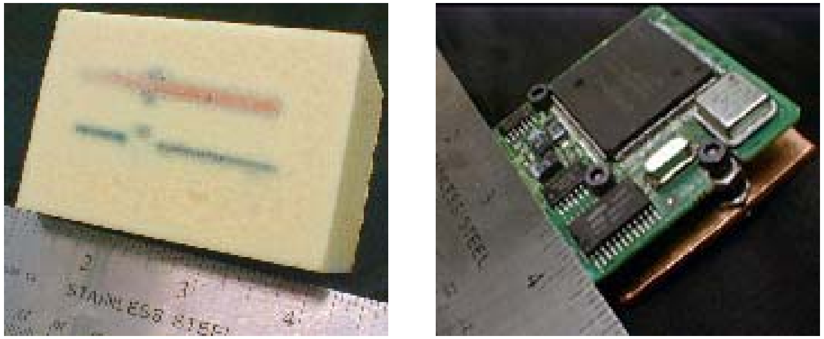
In 1987, Dr. Smoot set up a 1 hour/week tutorial with Drs. Grant and Pugmire to teach me lattice statistics. Smoot's goal was to predict/publish phenomenology to be confirmed later with experimental discovery. This work exemplifies Smoot's goal.

Introduction

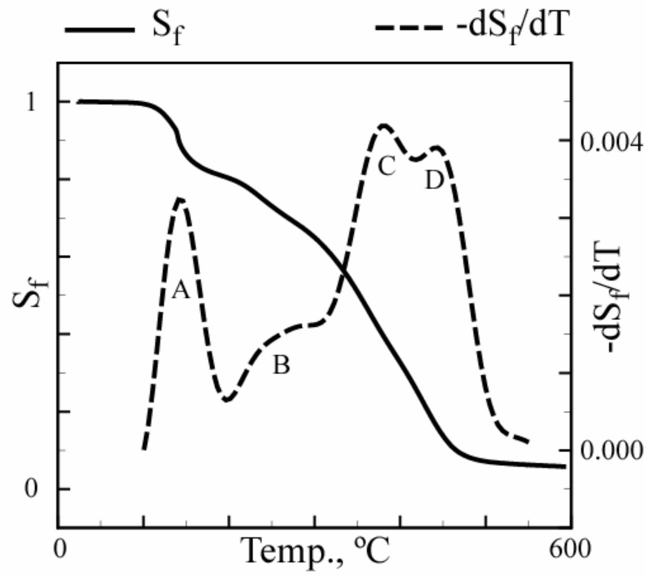
Why Study Removable Epoxy Foam (REF)?

Design Environment



Circuit board encapsulated in REF before (left) and after (right) removal with n-butanol at 90°C

Abnormal Environment

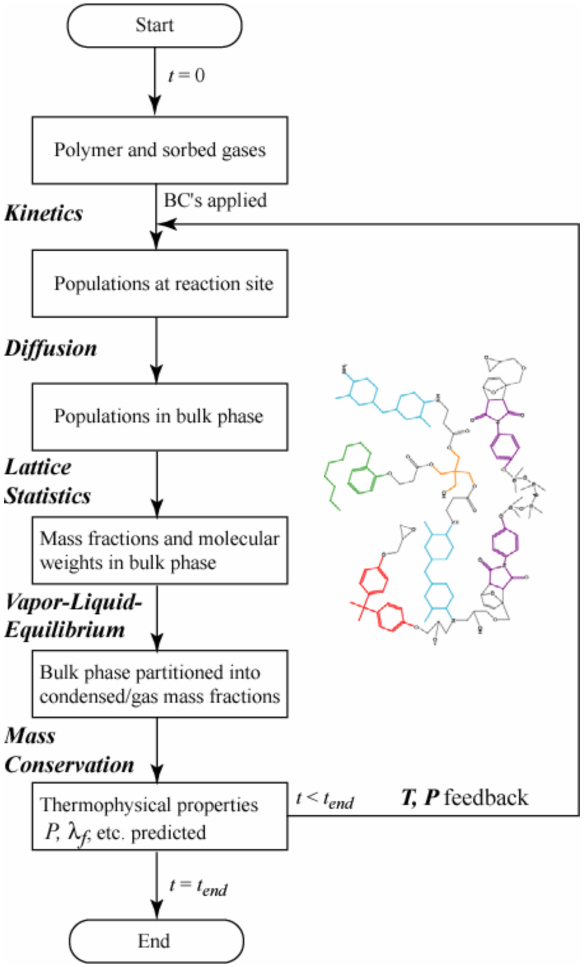


A Blowing agent/surfactant (BAS)
B Octamethylcyclotetrasiloxane (OS)
C Mixed products (MP)
D Bisphenol A (BPA)

Describe REF behavior in fires

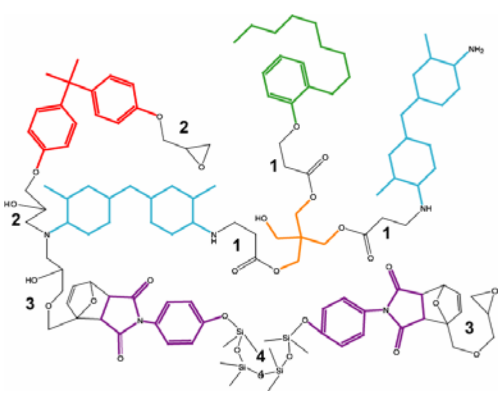
Outline

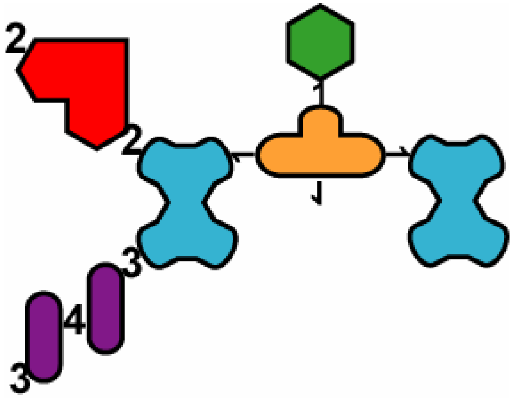
- **Chemical Structure**
- **Lattice Statistics**
- **Kinetic Mechanism**
- **Mass Transport Resistance**
- **Vapor Liquid Equilibrium**
- **Thermal Conductivity**
- **Data Comparison**



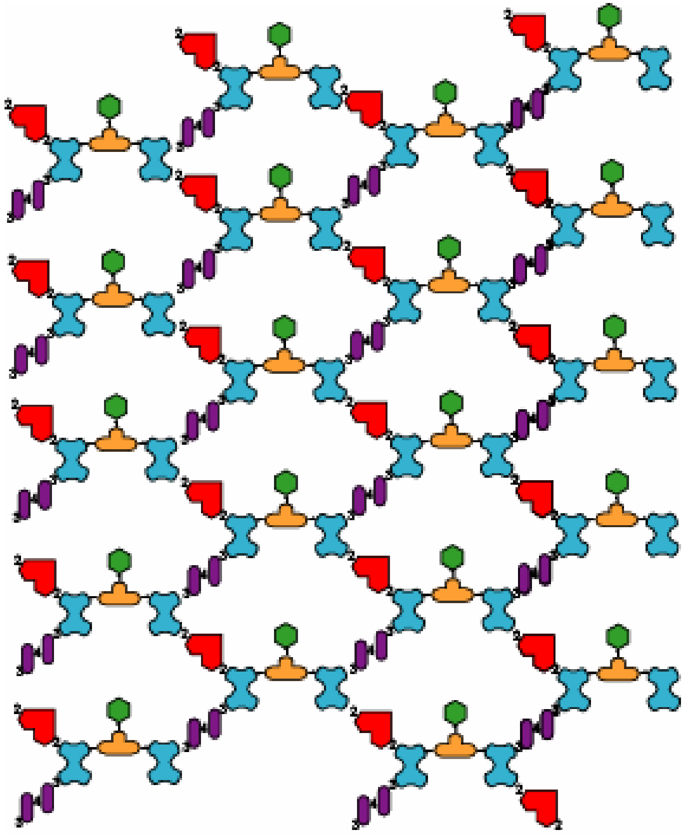
Polymer Structure for REF

Repeating Unit (RU)

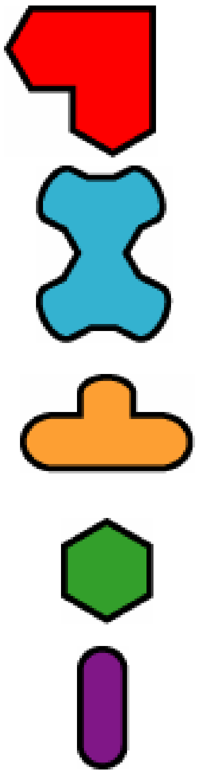




Model Structure



Graphic



Diglycidyl Ether of Bisphenol A

Dimethyldicyane (Ancamine 2049)

Pentaerythritol Triacrylate

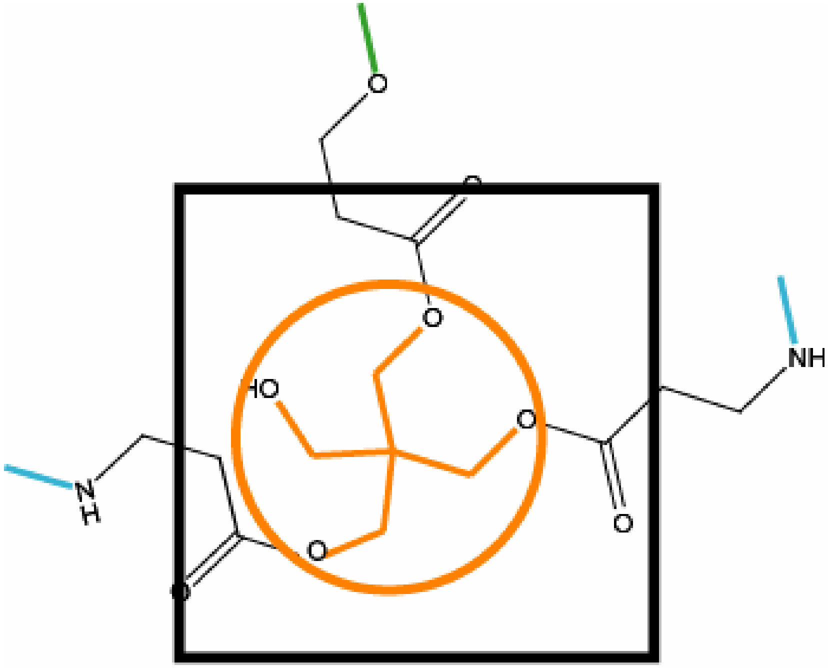
Nonyl Phenol

Part of RER

Real lattice approximated with Bethe lattice

Lattice Sites

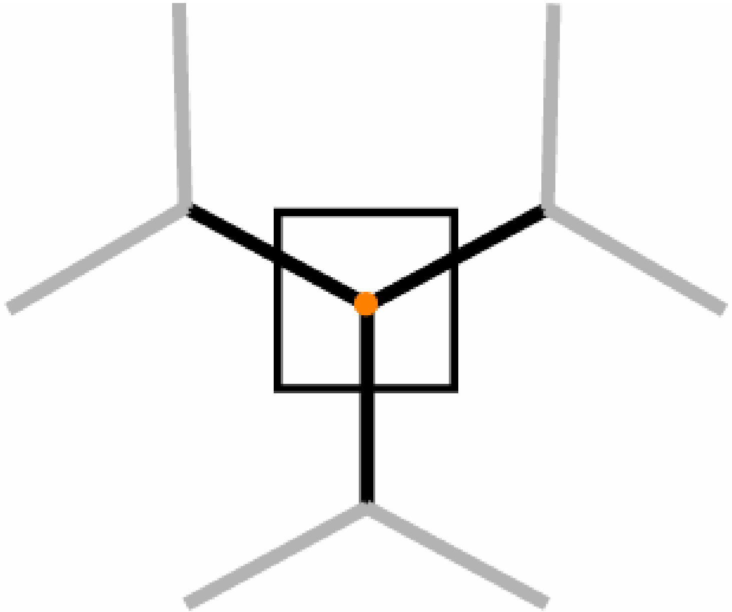
Traditional Site



site - does not include bridge mass

"extended **site**" - includes half the bridge mass from neighboring sites

Simplified Site



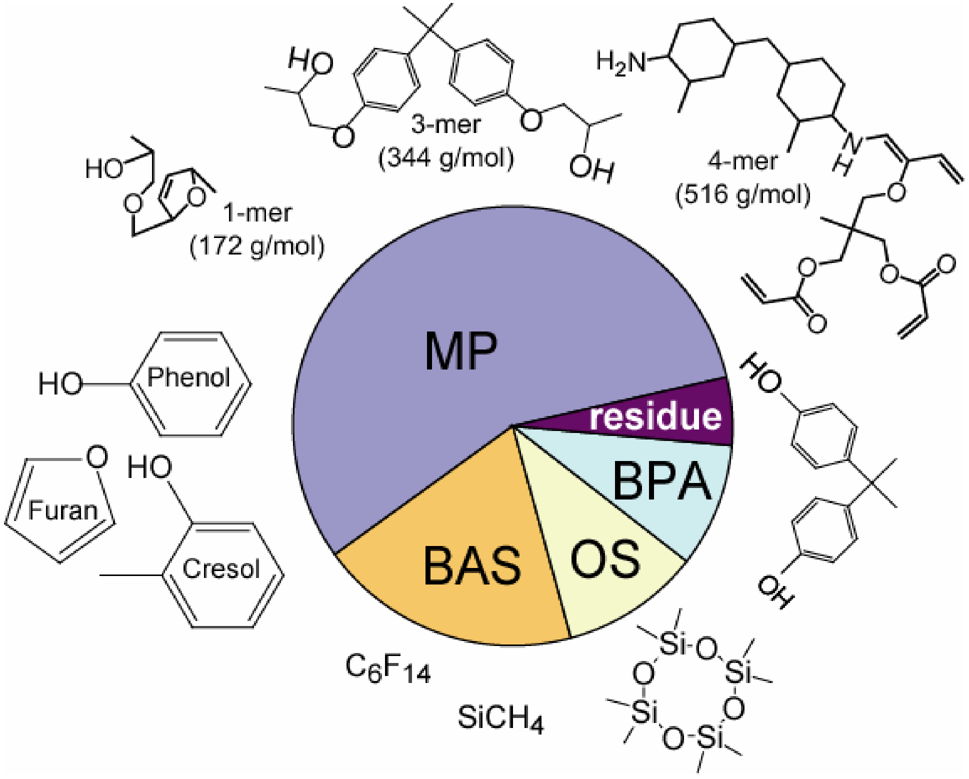
site - does not have any mass

"extended **site**" - includes half the bridge mass from neighboring sites ($Mw_{site} = 1.5 \times Mw_{bridge}$)

Bridge M_w has same composition as polymer

Species in SREF Model

Decomposition Products



VLE Species (7)

- **BAS (Blowing Agent and Surfactant)**
- **OS (OctamethylcyclotetraSiloxane)**
- **MP (Mixed Products)**
- **BPA (BisPhenol A)**
- **2-mer, 3-mer, and 4-mer**

Nonvolatile Species (3)

- **Nonvolatile residue**
- **L-mers (5-mer through n_{max}-mer)**
- **XL-mers (n_{max}-mer to ∞-mer)**

Foam degrades as either gas or polymer fragment

SREF Mechanism

$S \rightarrow p_{BAS}$ **(Blowing Agent and Surfactant, Mw_{BAS} = 120 g/mol)**

$L1 \rightarrow p_{OS}$ **(Octamethylcyclotetrasiloxane, Mw_{OS} = 296 g/mol)**

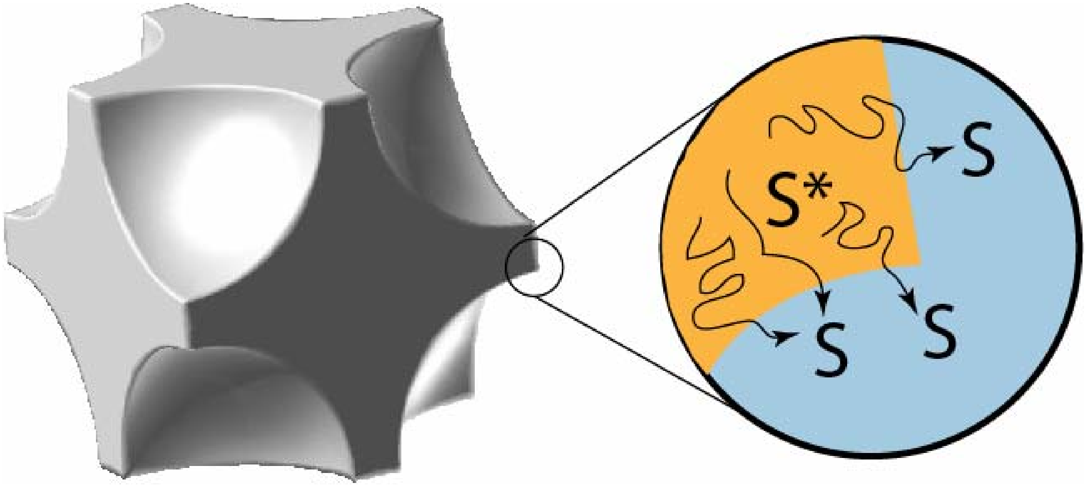
$L2 \rightarrow p_{MP}$ **(Mixed Products , Mw_{MP} = 140 g/mol)**

$L3 \rightarrow p_{BPA}$ **(Bisphenol A , Mw_{BPA} = 228 g/mol)**

Bridge population is the tie back to lattice statistics:

$$p = (L_1+L_2+L_3)/ (L_{1,o}+L_{2,o}+L_{3,o})$$

Mass Transport Resistance



$$\boxed{\begin{gathered} r = k_m(s - s^*) \\ r = k_c(s^*) \end{gathered}} \longrightarrow \boxed{r = \frac{1}{\frac{1}{k_c} + \frac{1}{k_m}}(s)}$$

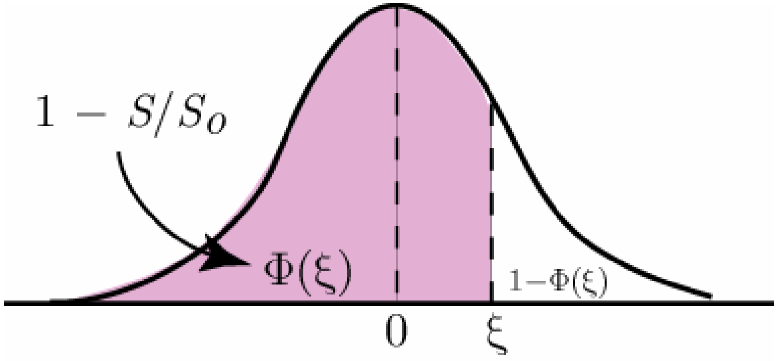
$$k_c = A\exp[(-E \pm \xi\sigma_E)/RT]$$

$$k_m = 2D/S_f d^* \approx \frac{2\theta D_{m,o}\left(\frac{T}{298.15}\right)^{1.67} P^{-1}}{S_f d^*}$$

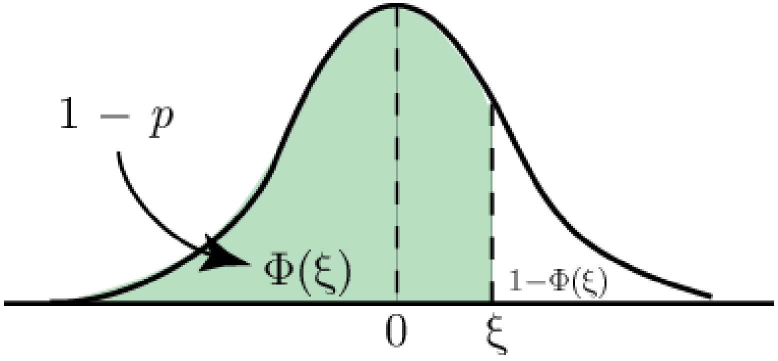
Effective rate constant like parallel resistance

Distributed Activation Energy Model

“Sorbed Species”



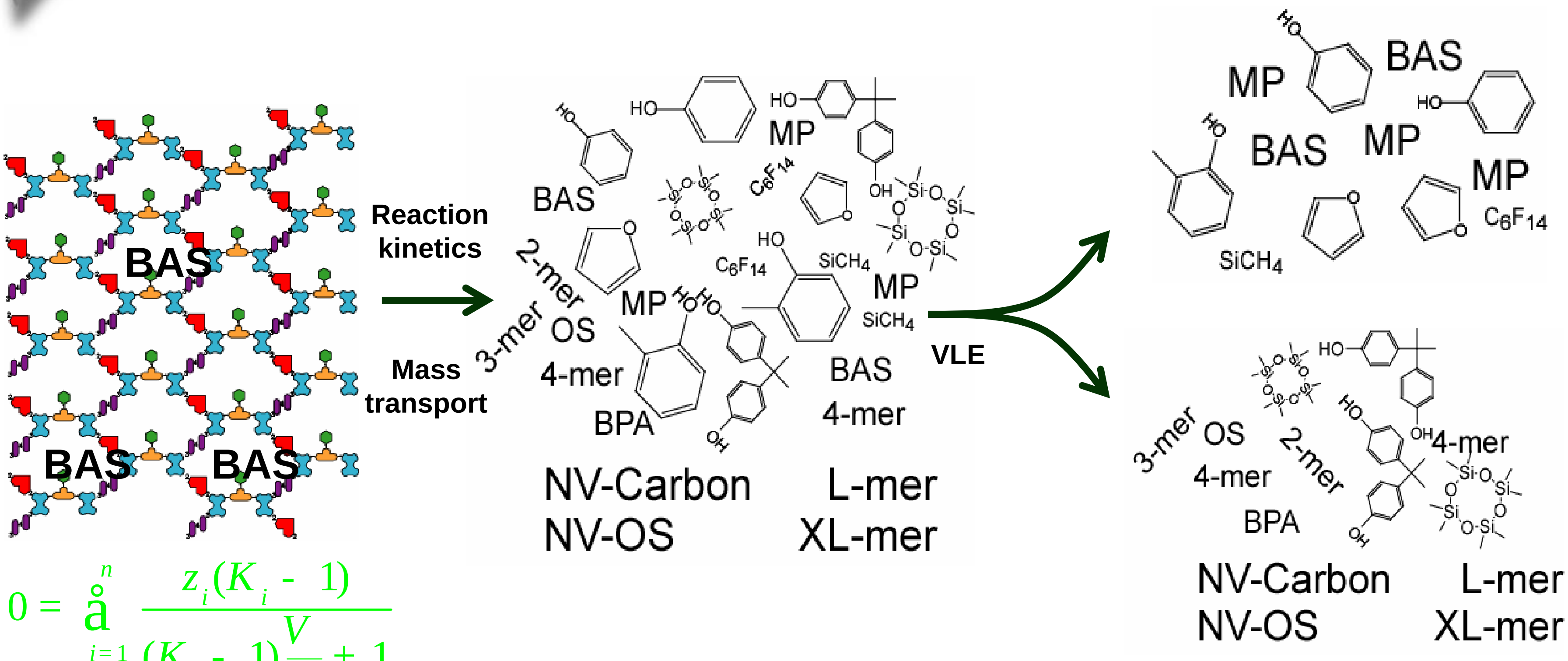
Polymer Reactions



$$k_i = A_i \exp[(-E_i \pm \xi \sigma_{E_i})/RT]$$

Mimics thermal damage caused by reaction

Vapor Liquid Equilibrium



$$0 = \sum_{i=1}^{n} \frac{z_i(K_i - 1)}{(K_i - 1)\frac{V}{F} + 1}$$

$$\frac{V}{L} = f\left(K_{value,i}, P_i^*, P, \gamma_i\right)$$

$$\gamma_i = \begin{cases} \gamma_{i,o} & \text{if } P \le P_{c,i} \\ \gamma_{i,o} P / P_{c,i} & \text{if } P > P_{c,i} \end{cases}$$

$$K_{value,i} = \frac{\gamma_i P_i^*}{P}$$

VLE defines the vapor/liquid split

Thermal Conductivity

$$\lambda = \phi\lambda_g + \tfrac{2}{3}(1-\phi)\lambda_c + \frac{16\sigma T^3}{3[\omega a_g + (1-\omega)a_c]}$$

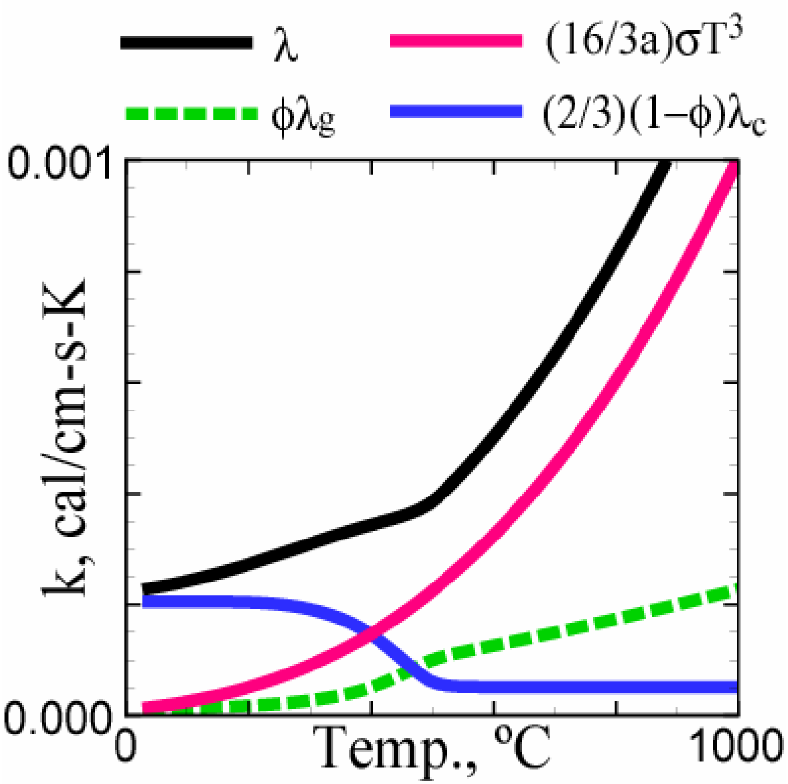
$$\phi = 1 - S_f\left(\frac{\rho_f^o}{\rho_p}\right)$$

$$\omega_g = \frac{\phi\rho_g}{(1-\phi)\rho_c + \phi\rho_g}$$

$$\rho_g = m_g / V_g$$

$$\rho_f = \phi\rho_g + (1-\phi)\rho_c$$

$$P = \frac{\rho_g RT}{Mw}$$



Properties depend on extent of reaction

More Equations and Parameters

Energy

$$\rho C \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) + \sum_{i=1}^{4} q_i r_i$$

Species

$$\frac{\partial L_i}{\partial t} = r_i$$

Kinetic Parameters

Symbol	Value	Units
A_1	1×10^{13}	s^{-1}
A_2	2×10^{15}	s^{-1}
A_3	2×10^{16}	s^{-1}
A_4	6×10^{12}	s^{-1}
E_1	28.7±1	Kcal/mol
E_2	46.4±1	Kcal/mol
E_3	58.1±1	Kcal/mol
E_4	43.5±1	Kcal/mol
σ_{E1}	0.76	Kcal/mol
σ_{E2}	2.8	Kcal/mol
σ_{E3}	6.6	Kcal/mol
σ_{E4}	0.79	Kcal/mol

Lattice Statistic Parameters

Symbol	Value	Units
$\sigma+1$	3	none
S_o	0.192	none
L_{1o}	0.104	none
L_{2o}	0.563	none
L_{3o}	0.091	none
Mw_{BAS}	120	g/mol
Mw_{OS}	296	g/mol
Mw_{MP}	140	g/mol
Mw_{BPA}	228	g/mol
$Mw_{NV\text{-}residue}$	1000	g/mol
$Mw_{XL\text{-}mer}$	4000	g/mol
max-mer	10	none

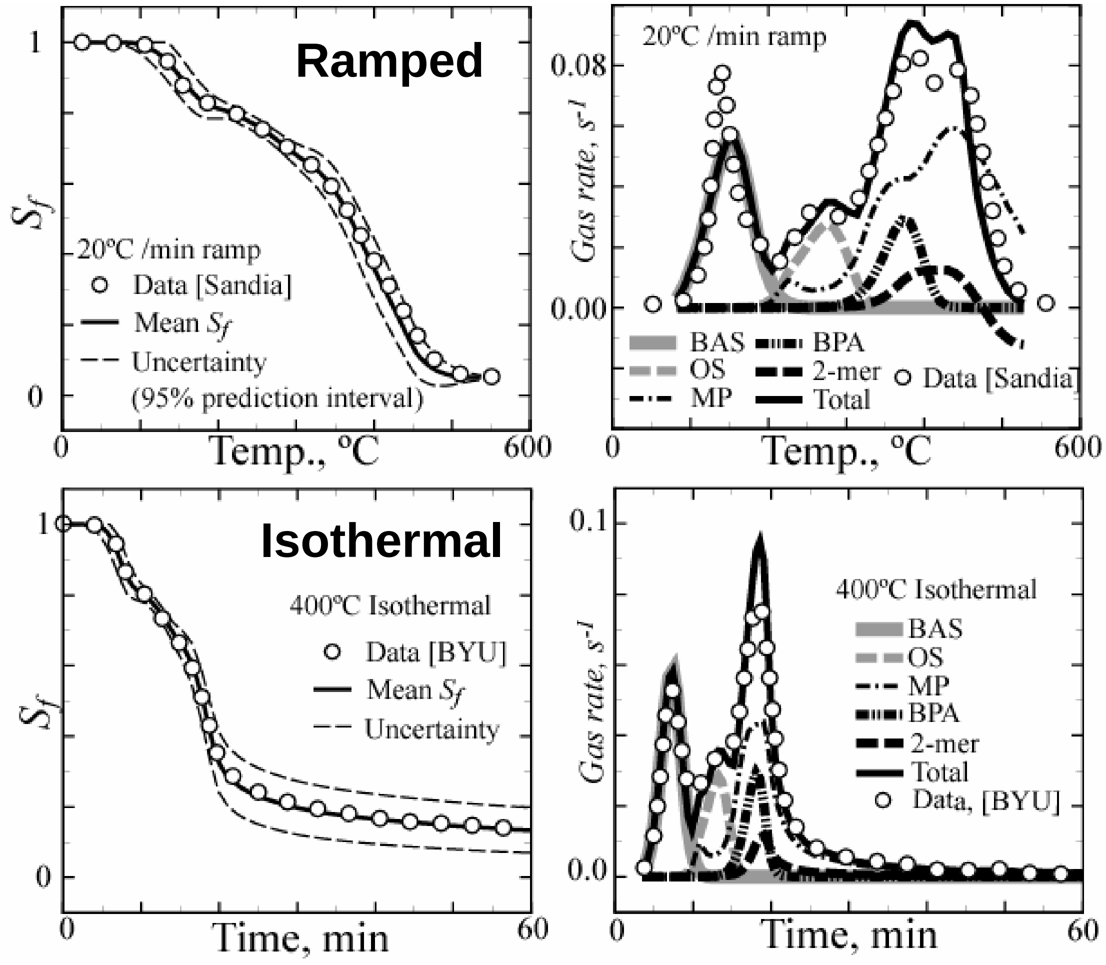
VLE/MT/Physical parameters

Symbol	Value	Units
$P_{c,BAS}$	5	atm
$P_{c,OS}$	13.1	atm
$P_{c,MP}$	52	atm
$P_{c,BPA}$	28.9	atm
$P_{c,n\text{-}mer}$	40	atm
d^*/θ	1	none
$\gamma_{i,o}$	1	none
P	1	atm
$\rho_{f,o}$	0.312	g/cc
ρ_p	1.09	g/cc
$V_{hot\ cell}$	0.638	cc

Parameter mean and standard deviation estimated

Comparison with TGA data

$S_f = m/m_o$ Gas Evolution Rates



Observations

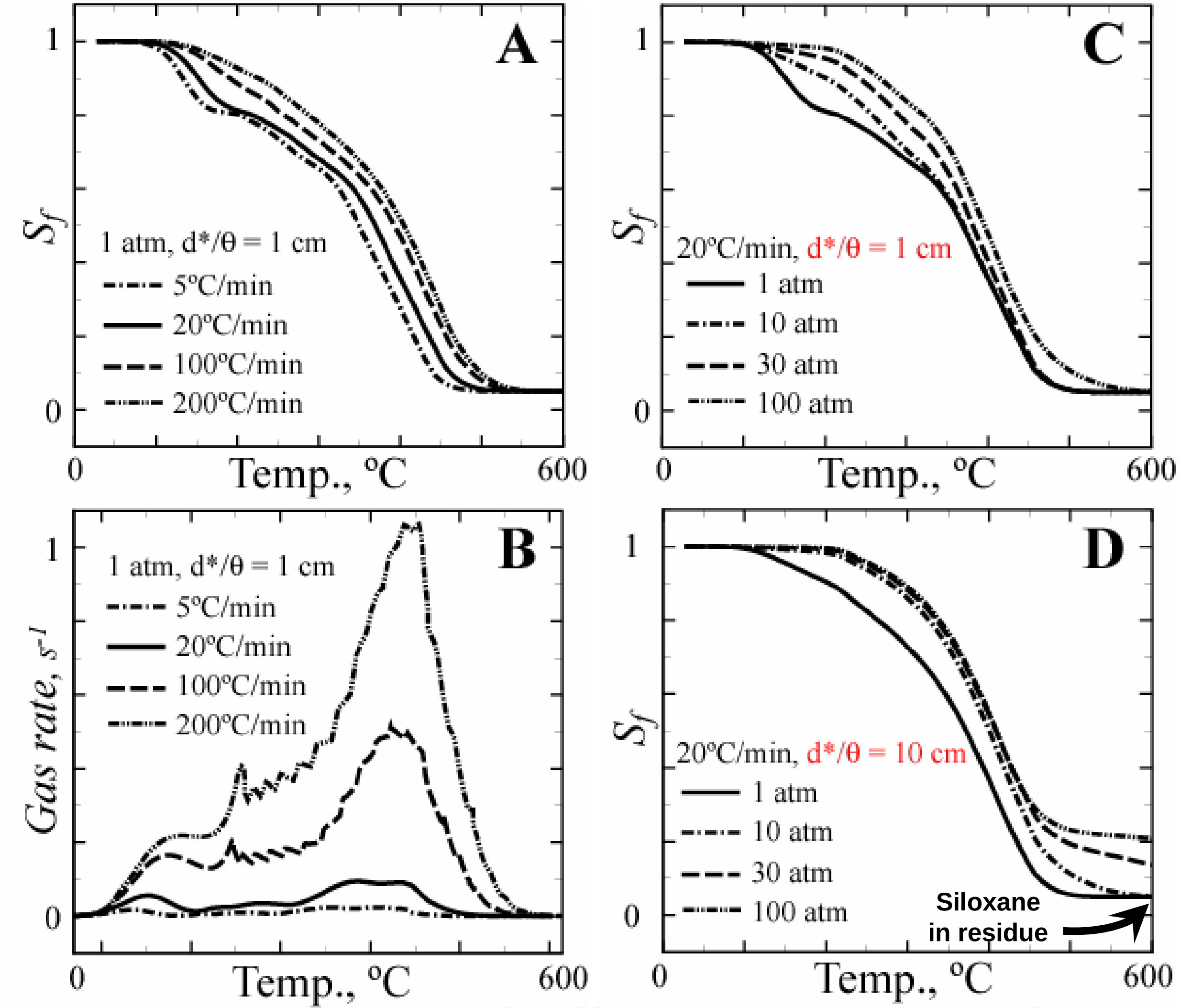
- **Sample temperature specified**
- **1.8% RMS error for Sandia TGA data**
- **1.0% RMS error for BYU TGA data**
- **Matches derivative data, *-dS_f/dT***
- **Gas evolution consistent with measurements**

Quantitative agreement with data from <u>two</u> labs

Predicted TGA Trends

Heating Rate

Static Pressure



Observations

Heating Rate

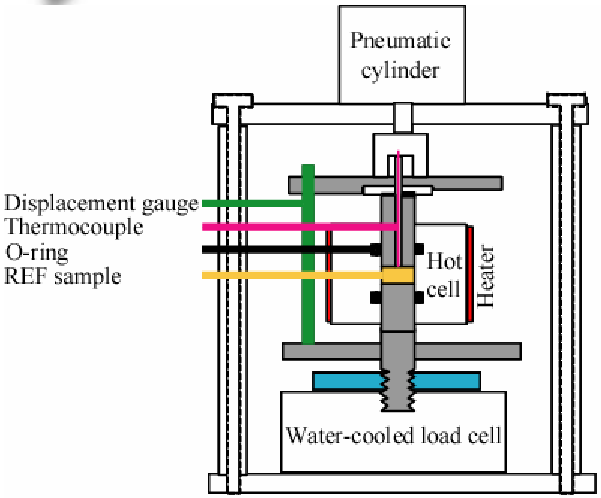
- **Profiles shift to higher T**
- **Magnitude related to kinetics**

Pressure

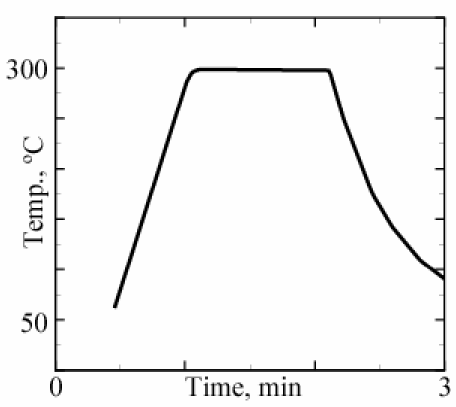
- **Profile shifts to higher T**
- **Magnitude related to VLE and diffusion model**
- **Increasing diffusion resistance is *similar* to confinement effect**
- **Confinement should be addressed using change in bulk gas composition due to influx and efflux.**

Similar to measured trends

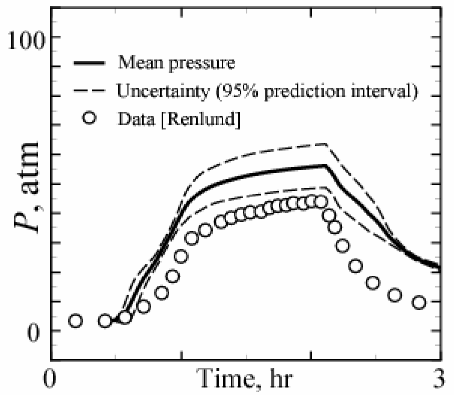
Constant Volume Hot Cell



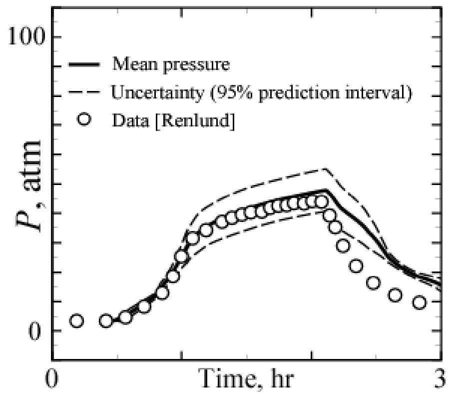
Sample Temperature



"Unconfined" ($d^*/\theta = 1$ cm)



"Confined" ($d^*/\theta = 10$ cm)



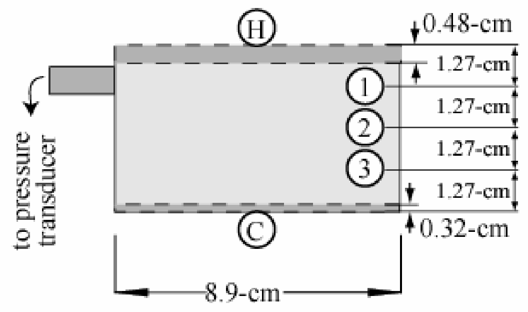
Observations

- **Preload displacement (~2 mm) occurred at glass transition temperature**
- **Sample T assumed to be same as thermocouple T, actual sample may have gradients**
- **+27% error at 2 h** ($d^*/\theta = 1$ cm)
- **+7% error at 2 h (**$d^*/\theta = 10$ cm)
- **Largest error in unloading region where reversible reactions may occur**
- **Confinement should be addressed using change in bulk gas composition due to influx and efflux.**

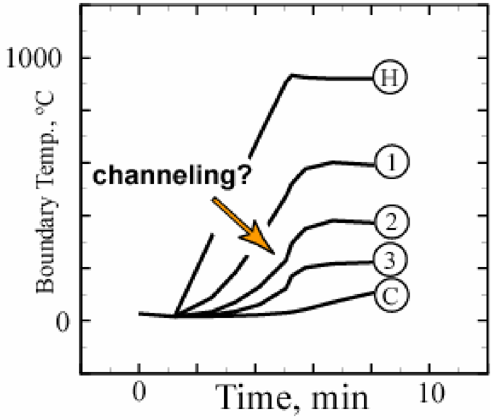
Sample size increased almost 2 orders of magnitude over TGA samples (0.005 g to 0.2 g)

Pressurization in a “TUNA” Can

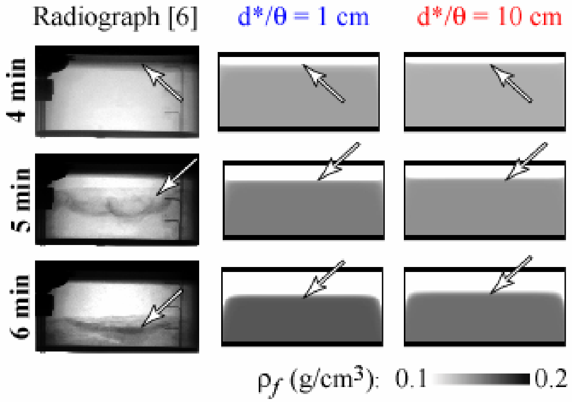
Schematic



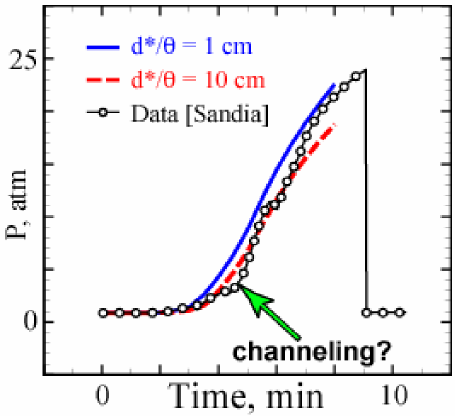
Temperature BC



Radiographs Comparison



Pressure Comparison



Observations

- Measured fronts were dark and irregular (liquid?)
- T jumps on container sides (orange arrow) implied channeling of hot products
- Significant deformation after 8 m
- +5% error at 8 m when $d^*/\theta = 1$ cm
- -10% error at 8 m when $d^*/\theta = 10$ cm
- Confinement affects are different at different scales (hot cell vs Tuna)
- Confinement should be addressed using change in bulk gas composition due to influx and efflux

Sample size increased almost 4 orders of magnitude over TGA samples (0.005 g to 34 g)

Summary and Conclusions

- Semi-empirical model based on chemical structure, lattice statistics, mass transport with chemical reactions, VLE with pressure dependent activity coefficients, and thermophysical properties that change with reaction
- Results were within experimental uncertainty for confined and unconfined samples ranging in size from 0.005 g to 34 g, a difference of nearly 4 orders of magnitude
- Despite success, model deficiencies should be addressed
    - Effect of confinement (influx and efflux of decomposition products)
    - Reactive elastic/viscoplastic constitutive stress/strain model
    - Thermal expansion and elastic/plastic response of the confinement
    - Better activity coefficient, diffusivity, and thermophysical property models
- Need detailed coupled-physics modeling approach (thermal, chemical, mechanical, flow, etc.) of both the gas and condensed phases to better understand polymeric foam response during exposure to fire