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Experiments to characterize particle flotation in a curing epoxy

Lisa Mondy, Amy Kaczmarowski, Rekha Rao, Anne Grillet, Haoran Deng, Christine Roberts , Melissa Soehnel, John Eric Bower, Carlton Brooks

Sandia National Laboratories, Albuquerque, NM 87185

Stephen Altobelli

ABQMR, 2301 Yale Blvd SE, Suite C-1
Albuquerque, NM 87106

Jeffrey Morris and Sidhant Pednekhar

Benjamin Levich Institute and Department of Chemical Engineering, City College of New York, New York, NY 10031

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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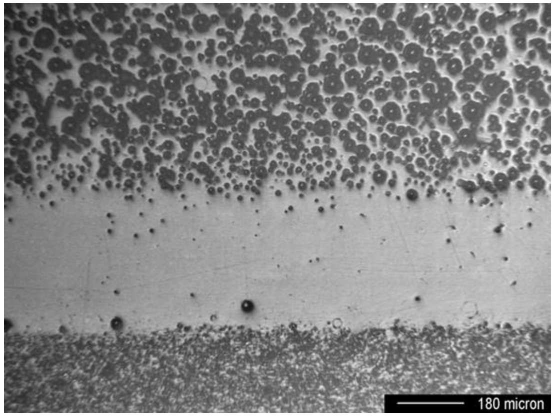
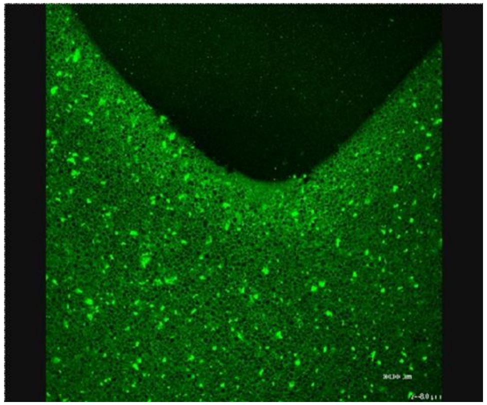
Introduction

- Epoxies are used to encapsulate electronic parts to give structural integrity and protect from vibration
- Filled with glass microballoons to reduce thermal stresses
- End process, so high value
  - Encapsulation defects, e.g. voids, fracture, delamination and property inhomogeneities, can lead to component failure
- Complex materials: polymerizing, high fraction of solids of various sizes
- Non-isothermal: exothermal reactions and oven cure
- Rheological depend on temperature, extent of reaction, particle concentration, surface interactions, shear rate, shear history, time
- Particle concentration can change locally due to buoyancy or shear
- Predict distribution of filler particles as a result of processing time and temperature changes



An optical micrograph of a final product shows a clear layer next to a surface.

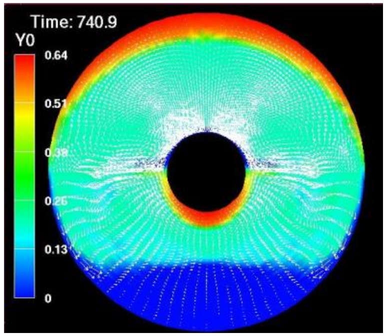


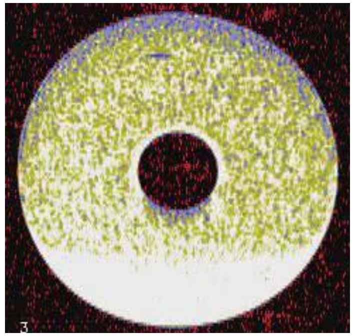
Confocal microscopy during wicking in an underfill of an integrated circuit shows small particles congregate near the advancing interface.

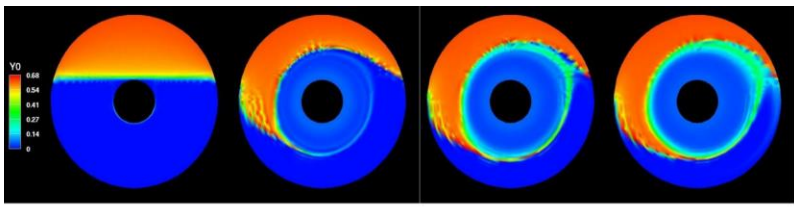
Outline

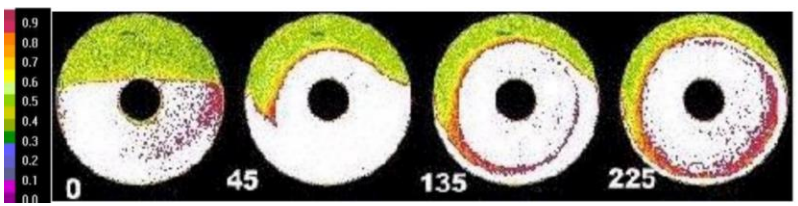
- Description of current engineering model of particle migration
- Particle Characterization and hindered settling
- Epoxy kinetics
- Rheology
- Example model results
- Needed extensions to the model and next steps

Diffusive Flux Model for Buoyant Particles in Curing Polymer









$$\rho\frac{\partial v}{\partial t}+\rho\boldsymbol{v}\bullet\nabla\boldsymbol{v}+\nabla p-\nabla\bullet\left(\eta\left(\nabla\boldsymbol{v}+\nabla\boldsymbol{v}^T\right)\right)-\left(\rho_f-\rho_s\right)\varphi g=0$$

$$\rho=\left(1-\varphi\right)\rho_f+\varphi\rho_s$$

$$\frac{\partial\xi}{\partial t}=\left(k_1+k_2\xi^m\right)\left(1-\xi\right)^n$$

$$\eta=\eta\left(\varphi,\xi,T\right)=\eta_0\left(T_g\right)\left(1-\frac{\varphi}{\varphi_{\max}}\right)^n\left(1-\left(\frac{\xi}{\xi_c}\right)^m\right)^{-p}10^{-\frac{c_1\left(T-T_g\right)}{c_2+T-T_g}}$$

$$\frac{\partial\varphi}{\partial t}+\nabla\bullet\left(\varphi\boldsymbol{v}\right)=\frac{\nabla\bullet J_s}{\rho_s}$$

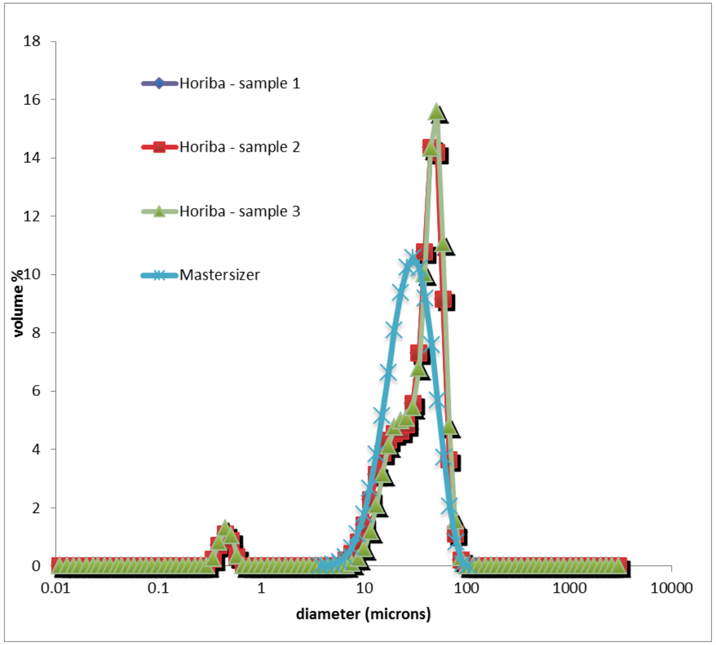
$$\frac{J_s}{\rho_s}=-\left(\varphi K_c\nabla\left(\dot{\gamma}\varphi\right)+\varphi^2\dot{\gamma}K_\eta\nabla\left(\ln\eta\right)\right)+f_{hindered}v_{stokes}\varphi$$

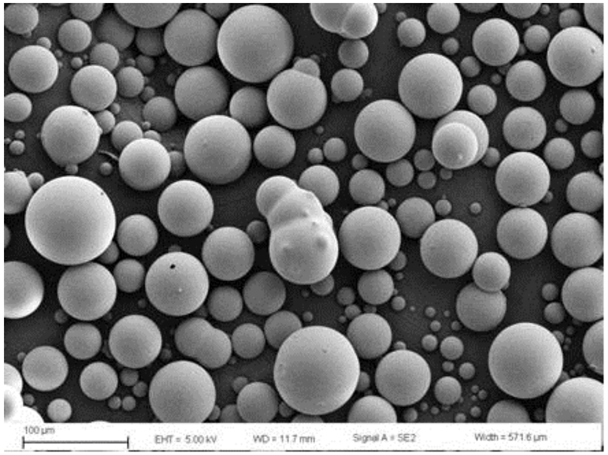
$$\nabla\bullet\boldsymbol{v}=\frac{\left(\rho_f-\rho_s\right)}{\rho_s\rho_f}\nabla\bullet J_s$$

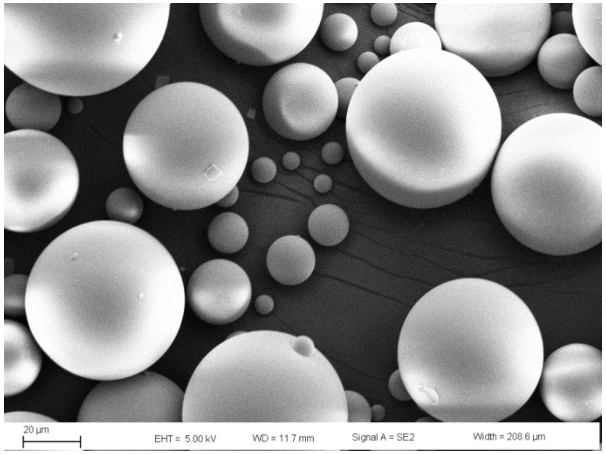
$$\rho C_p\frac{dT}{dt}=-\boldsymbol{v}\cdot\nabla\left(\rho C_pT\right)-\nabla\cdot\boldsymbol{q}+H\left(\xi\right)$$

- Diffusive flux model included in open source finite element code GOMA. (Phillips et al., Phys. Fluids A 1992; Rao et al, Int. J Numer. Meth. Fluids 2006; Mondy et al. J. Appl. Poly. Sci. 2011; GOMA Research &Development 100 Award 2014)
- Model parameters that must be collected to model flow and track particles for each new encapsulant are circled in red.

3M™ Glass Bubbles (GMB) Characterization: Size







- Two instruments using laser diffraction method (intensity converted to volume distribution based on glass properties)
  - Horiba Laser Scattering Particle Size Distribution Analyzer LA-950
  - Malvern Mastersizer 3000 laser diffraction particle size analyzer
- Laser diffraction on hollow spheres?

3M™ Glass Bubbles (GMB) Characterization: Density

Particle	Type of measure	Density g/cm³
D32 unseived	Manufacturer	0.32
D32 unsieved	Weigh known volume and estimate max packing (0.68 - 0.80)	0.260 – 0.22
D32-Sieved-65µm-45µm	Pycnometer	0.234 s.d.=0.00027
D32-Sieved-25µm	Pycnometer	0.162 s.d.=0.00046

Hindered settling

$$u_d / u_{Stokes} = f$$

Richardson – Zaki:

$$f = (1-\phi)^n$$

Acrivos:

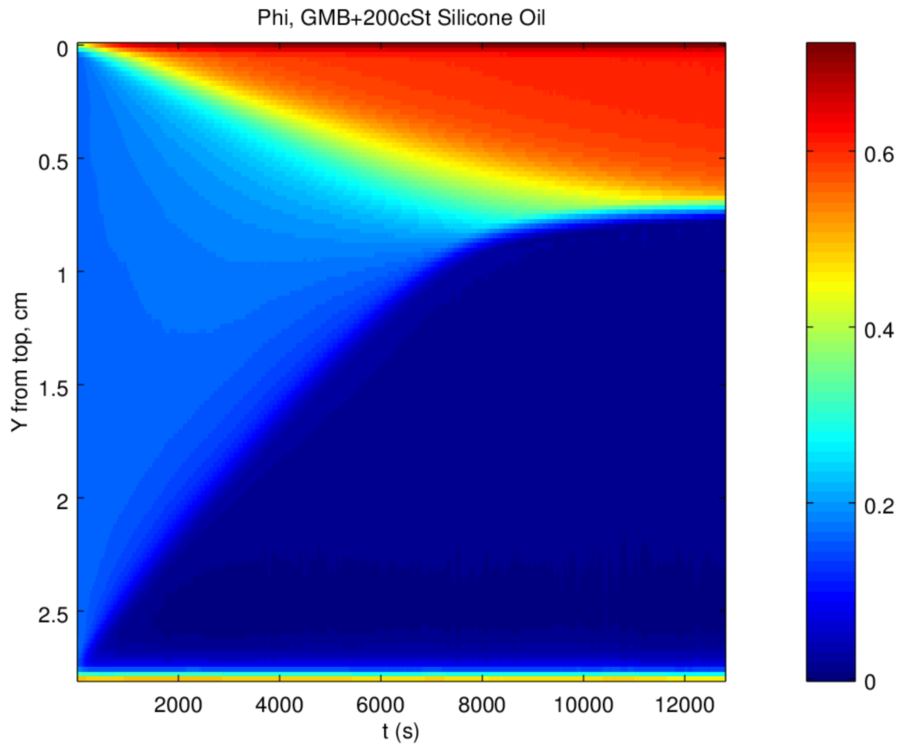
$$f = \frac{(1-\phi)}{\mu_{rel}}, \mu_{rel} = (1-\frac{\phi}{\phi_{\max}})^m$$

When a suspension settles (or floats), a particle goes slower than the Stokes' velocity of an isolated particle.

A broad distribution of particle sizes leads to diffuse interface between particles and clear zone and a "well-mixed" zone that has changing average particle size

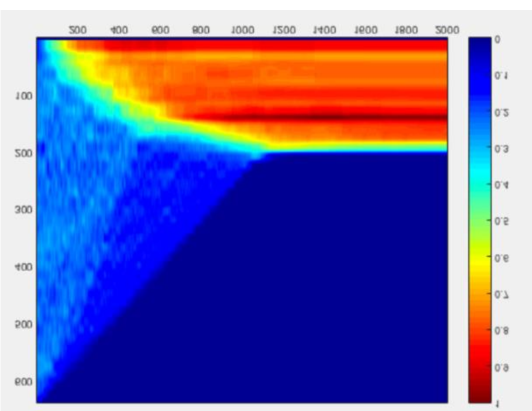
- Suspension of uniform particles will form 3 distinct zones when floating . A sharp front forms between the two extremes and the suspension in the middle remains close to the initial concentration.
- Most studies track the interface velocity to get the hindrance function *f*.
- NMR allows calculation of discrete phase average velocity (Altobelli & Mondy, 2002)
  - ✓ Do not have to track a clearing front velocity, especially if the front is not sharp because of a broad distribution of particle sizes
  - ✓ Can get same hindered settling function in one experiment, instead of having to test a range of particle concentration

NMR Imaging to Determine Hindrance Function



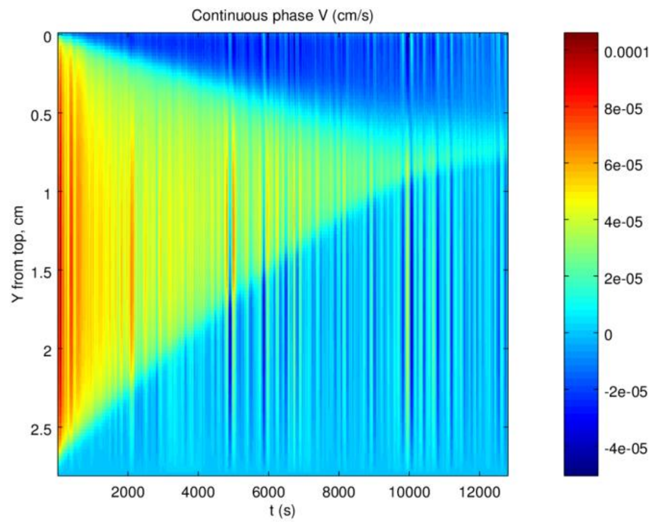
- Fluid fraction p_c is proportional to NMR signal strength
- 1-D NMR imaging can map the particle concentration with height Y and time t
- For each discrete value of t (Δt on order of 1 minute), we get a measure of p_c at each location y (ΔY=0.05 cm)

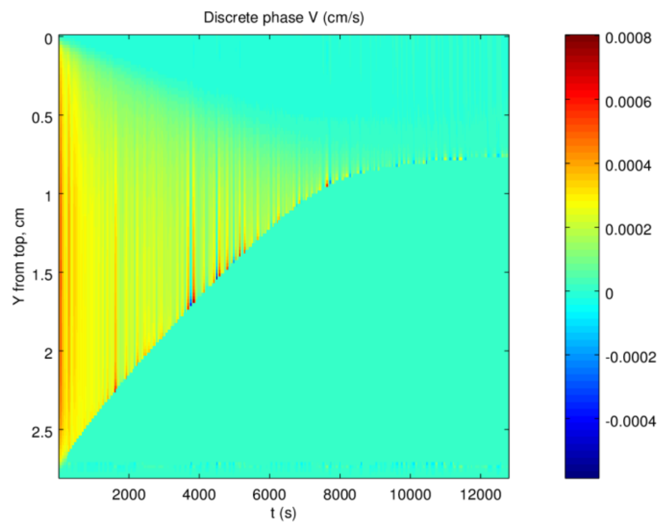
$$\phi = (1 - p_c)$$



Bimodal results 2:1 size ratio from discrete-particle simulation (2000 particles) by the lattice-Boltzmann technique (Ladd 1994; Aidun, Lu & Ding 1998)

NMR Imaging to Determine Hindrance Function





- Continuity of liquid phase:

$$\nabla \cdot p_c u_c = -\frac{\partial p_c}{\partial t}$$

- Assume 1-D flow

$$\frac{\partial u_c}{\partial Y} = \frac{-\left(\partial p_c / \partial t \right) - u_c \left(\partial p_c / \partial Y \right)}{p_c}$$

  - Calculate partials from NMR data
  - At each time step, evaluate $\partial u_c / \partial Y$ (RHS) for each Y and integrate starting at $Y=0$, $u_c=0$ to give u_c at next time step
- Discrete phase velocity is related (upward flux of one phase must equal downward of the other):

$$u_d = -\frac{u_c(1-\phi)}{\phi}$$

NMR Imaging to Determine Hindrance Function

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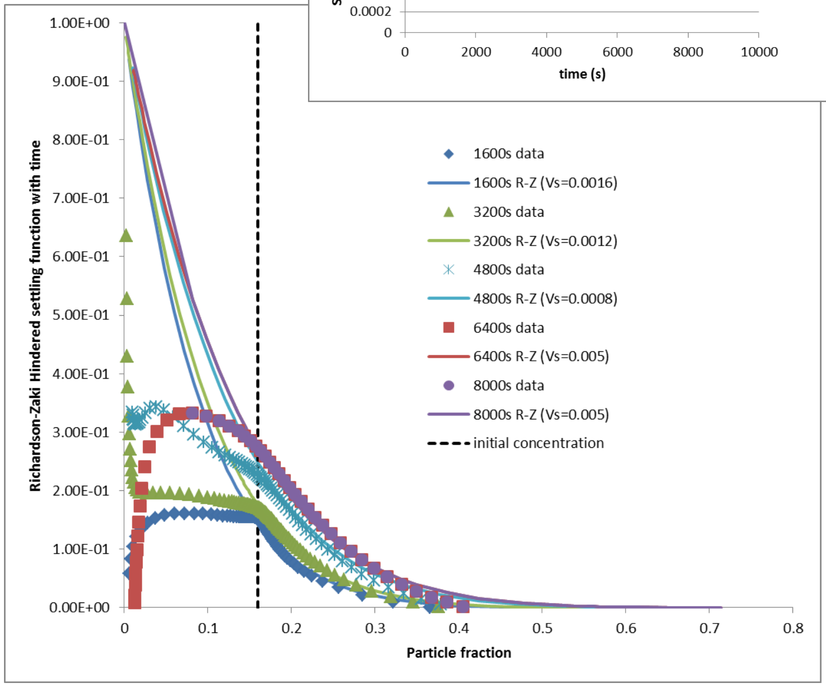
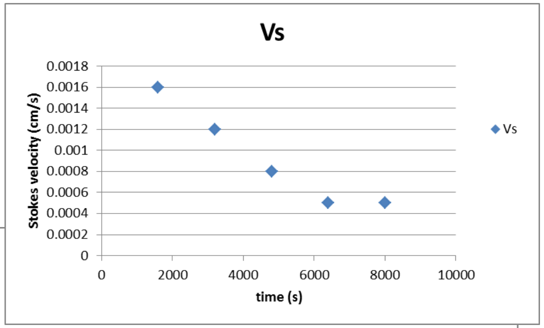
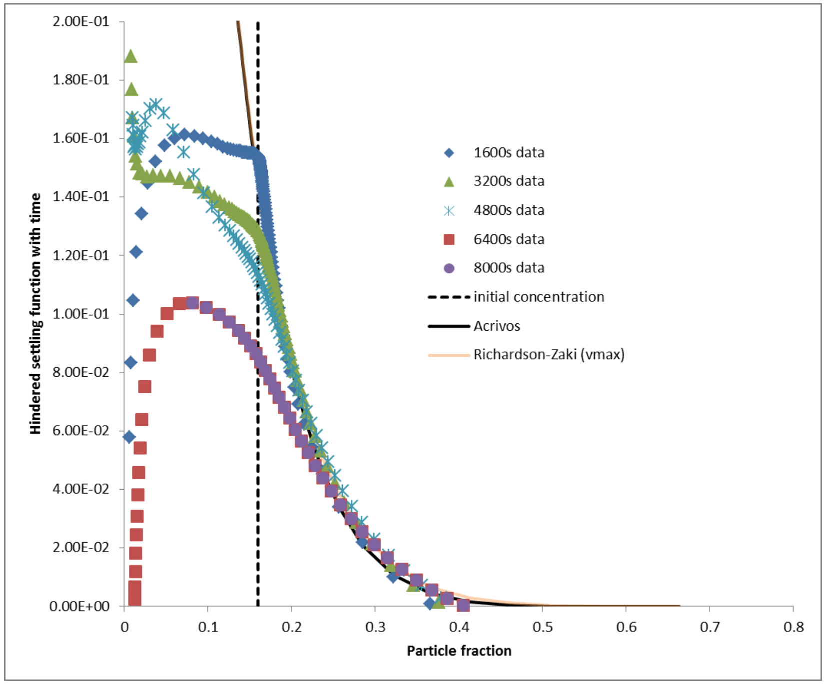
- Well-behaved data above the initial concentration
- Can either :
  - allow the fit to change as the particles size segregate (left) or
  - fit to largest particles and miss the later time behavior (right)

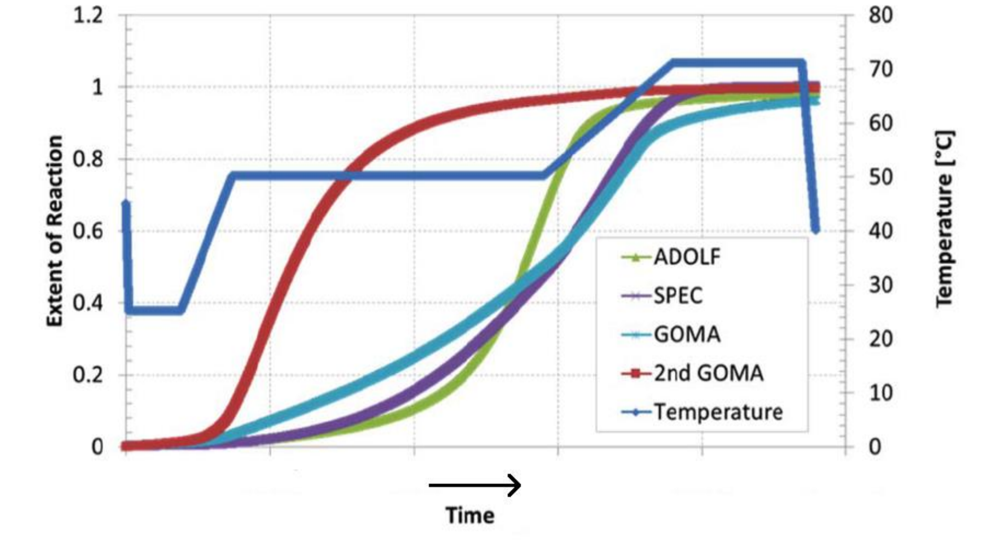


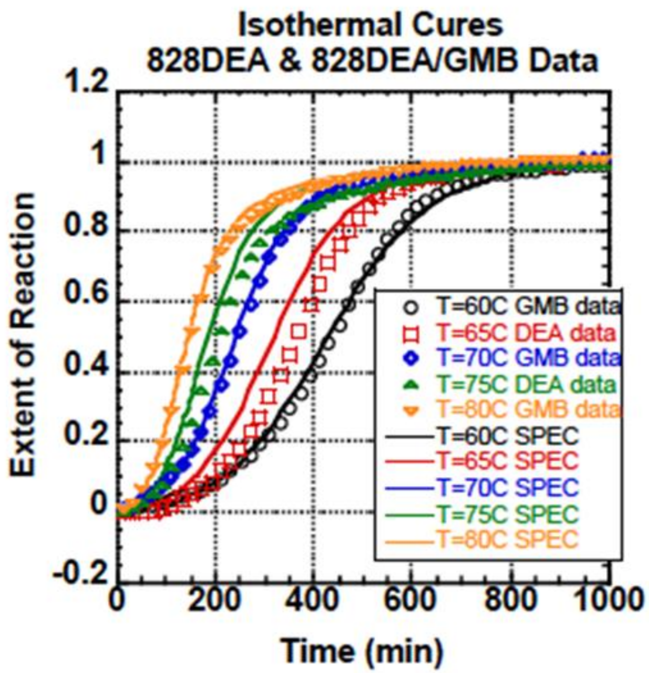




Polymerization Kinetics

- Differential Scanning Calorimetry used to determine heat of reaction and extent of reaction in isothermal cures (by integrating heat flow, extent of reaction at any time could be estimated)
- Model forms yield very different extent of reaction with time
- Various kinetic models fit to data (Epon 828 cured with DEA): SPEC model best fit with and without added GMB





SPEC:

$$\frac{dx}{dt} = \frac{k_o \exp\left(-E_a/RT\right)}{\left(1+wa_{shift}\right)^{\beta}}\left(b+x^m\right)\left(1-x\right)^n$$

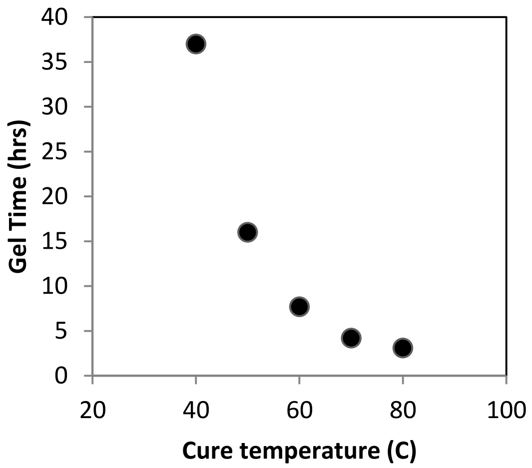
$$n = n_1 + n_2 \tanh\left(n_3\left\{T-n_4\right\}\right)$$

We assume w=0 for now and no vitrification is seen in the liquid phase

Bob Chambers, Doug Adolf

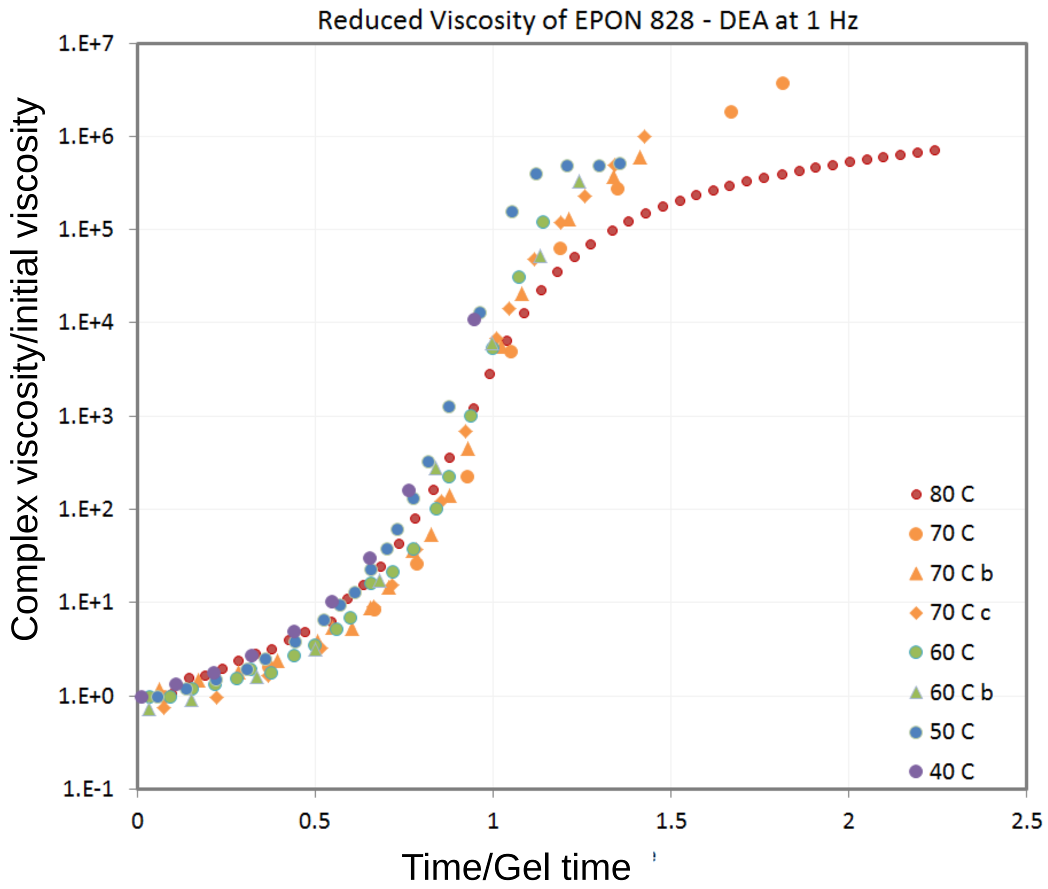
Erin Karasz

Rheology of Continuous Phase: EPON 828 + DEA During Curing



Measured with ARES rheometer using disposable parallel plates (25mm). Isothermal experiment

Challenging due to length of time for experiments, sudden high stresses at cure



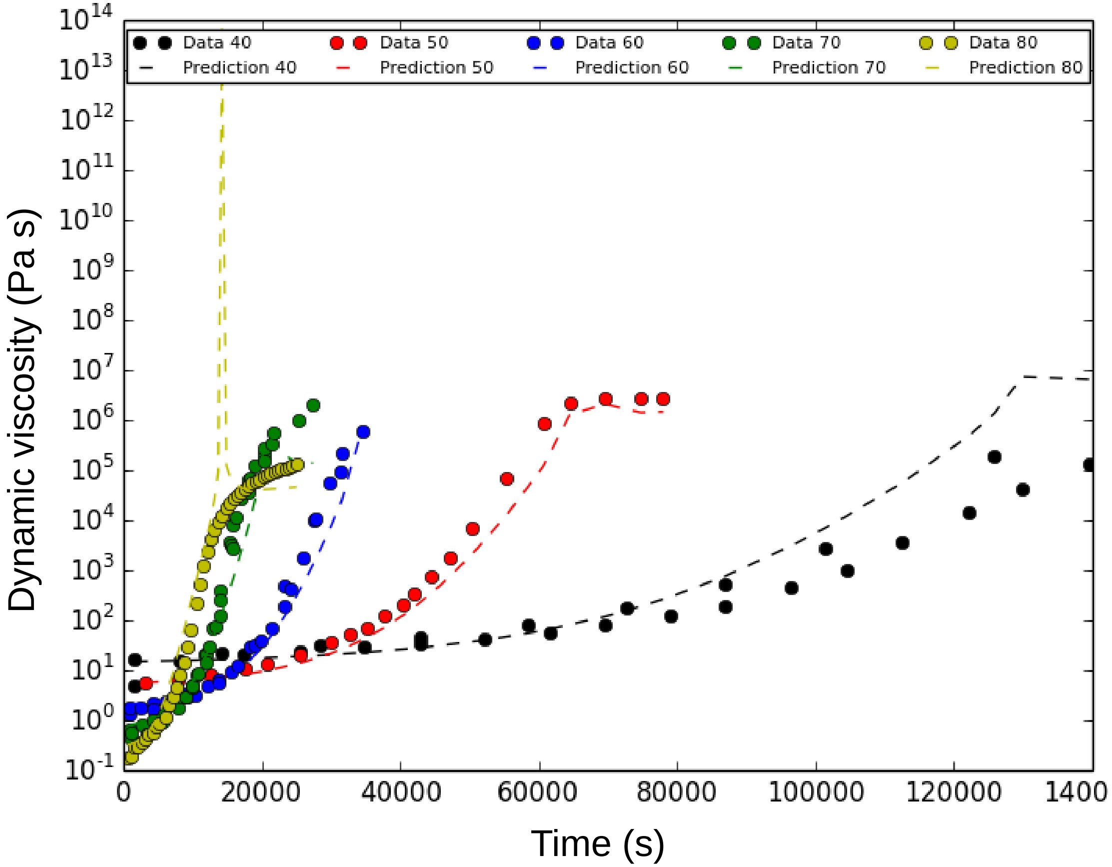
- Modulus vs. frequency collected at each time point throughout cure
- Initial viscosity and final shear modulus are both dependent on cure temperature
- Collapse of data when scaled by gel time and initial viscosity at that temperature.

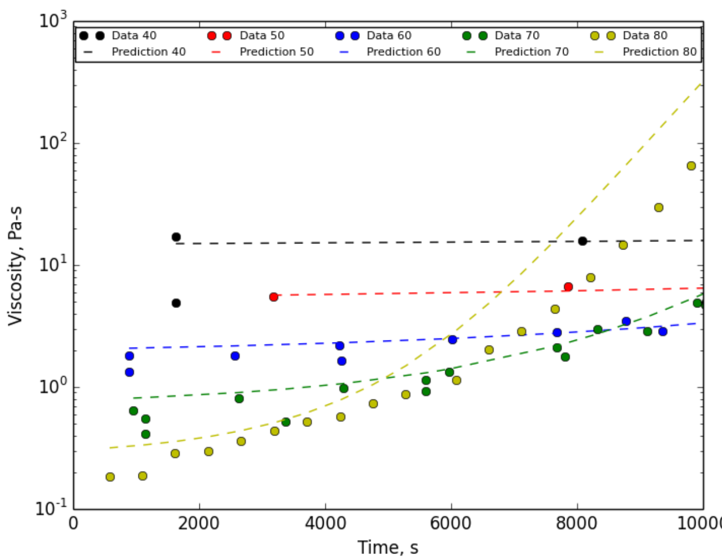
Fit to New Curing Rheology Data (Epoxy Only)

$$\eta = \eta(\xi, T) = \eta_0(T_g)\left(1-\left(\frac{\xi}{\xi_c}\right)^m\right)^{-p} 10^{-\frac{c_1(T-T_g)}{c_2+T-T_g}} \qquad T_g = \frac{T_{g0}}{1-A\xi}$$

η_0 = 2.016e-01 Pa-s
C_1 = 40.13
C_2 = 999.3
A = 0.2336
ξ_g = 0.8137
T_{g0} = 357.6 K

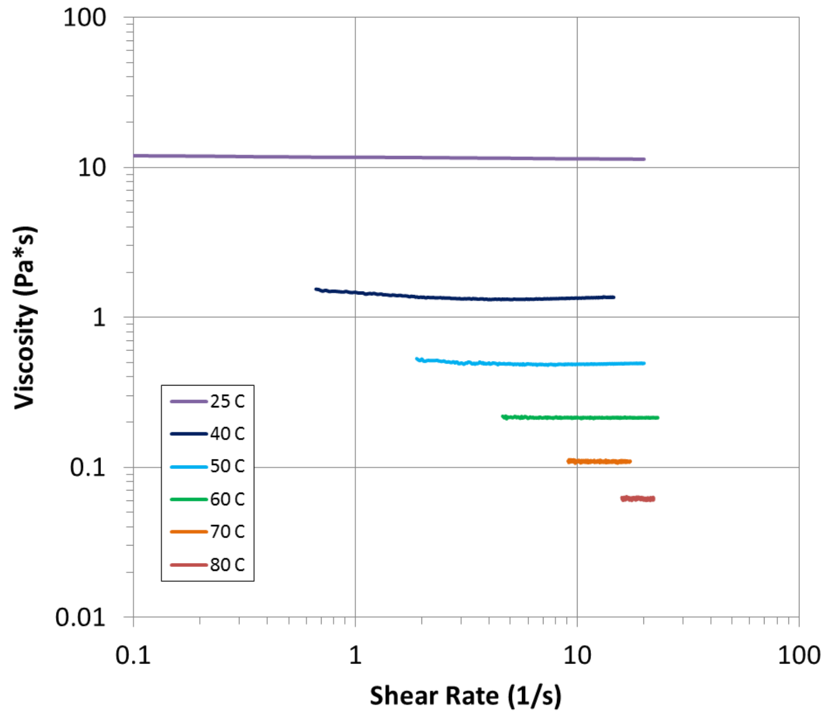
m=2
p=4/3

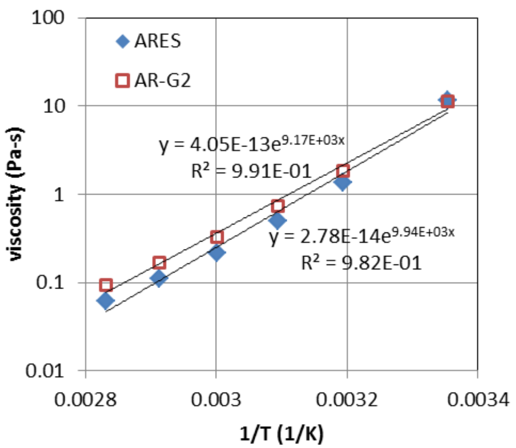




Rheology of Filled (Non-Curing) Systems: Neat Epoxy

- Measured neat Epon, then filled Epon at several temperatures
- Neat Epon: Viscosity was measured using two different rheometers using two different geometries. (parallel plates expected to be less accurate, but has to be used for curing system)
- ARES = 25 mm parallel plates
- AR-G2 = Couette



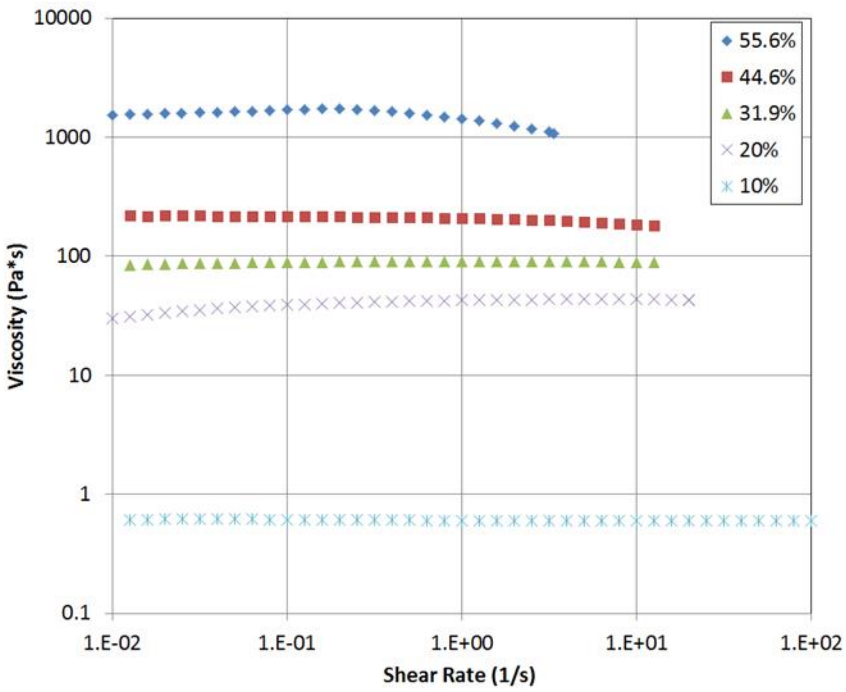


Viscosity follows Arrhenius type behavior with temperature, as expected.

No dependence on shear rate.

Rheology of Filled (Non-Curing) Systems: Behavior as a Function of GMB Volume Fraction

- Measured vs. shear rate using AR-G2 rheometer, double gap cylinder geometry
  - Particle migration less of a concern
- Viscosity is approximately Newtonian

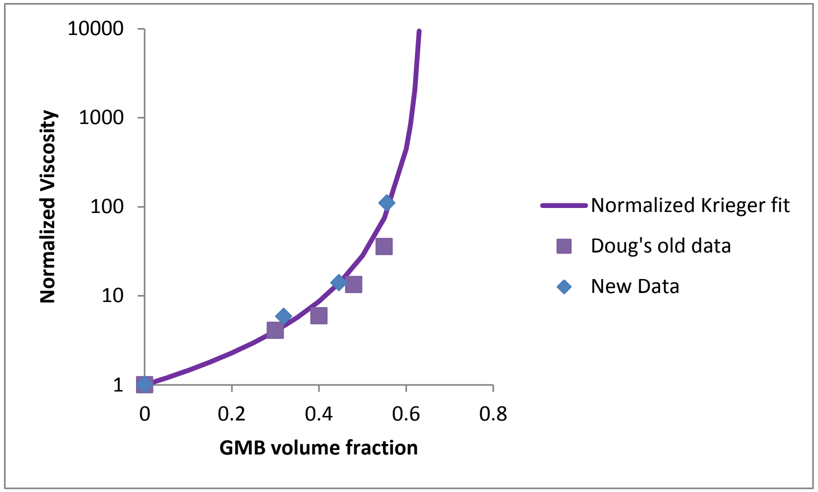


Epon + GMB

Parameters for New Krieger model
ϕ_{max}= 0.64
n= 2.2

$$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_{max}}\right)^{-n}$$

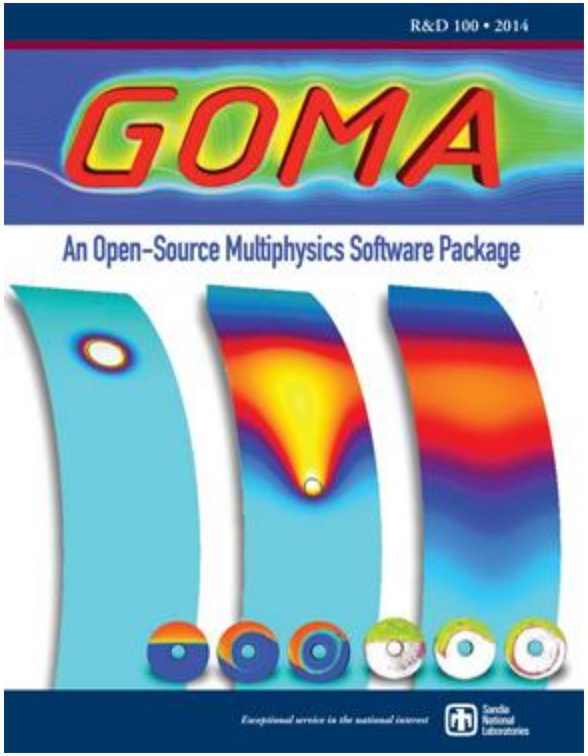
In model η_0 is taken to be the curing continuous phase viscosity



Doug Adolf

Numerical Method & Issues

- **Galerkin Finite element method used for spatial discretization with biquadratic velocities, bilinear pressure, shear-rate and concentration**
- **Finite difference method used for temporal discretization**
- **Taylor-Galerkin 2nd order method used for species equations time integration**
- **Fully coupled solution algorithm using Newton's method**
- **Pressure stabilization (GLS) is used to enable use of iterative solvers, which reduces solution times (Hughes et al., 1990)**
- **Parallel implementation based on MPI**
- **Boundary conditions are generally simple such as no slip or specified heat flux**
- **Shear-rate invariant must be interpolated as a variable**
- **Kinematic shocks form as suspension settles forming three phases: fluid phase, a particle phase at maximum packing and a suspension phase**
- **Fluid phase/suspension interface susceptible to oscillations that grow in time**



Example Numerical Results

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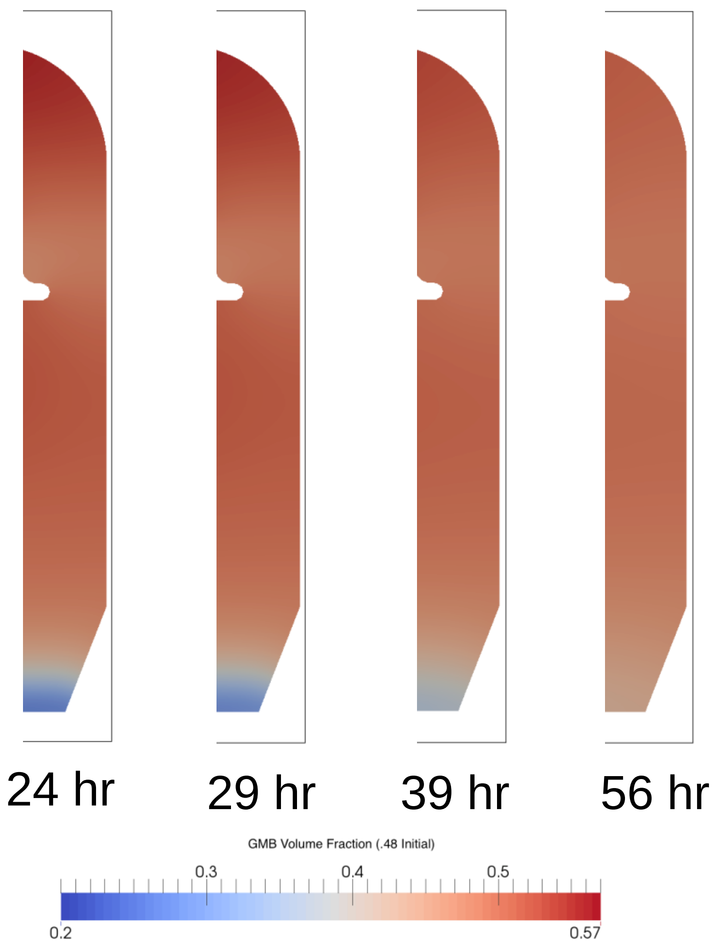
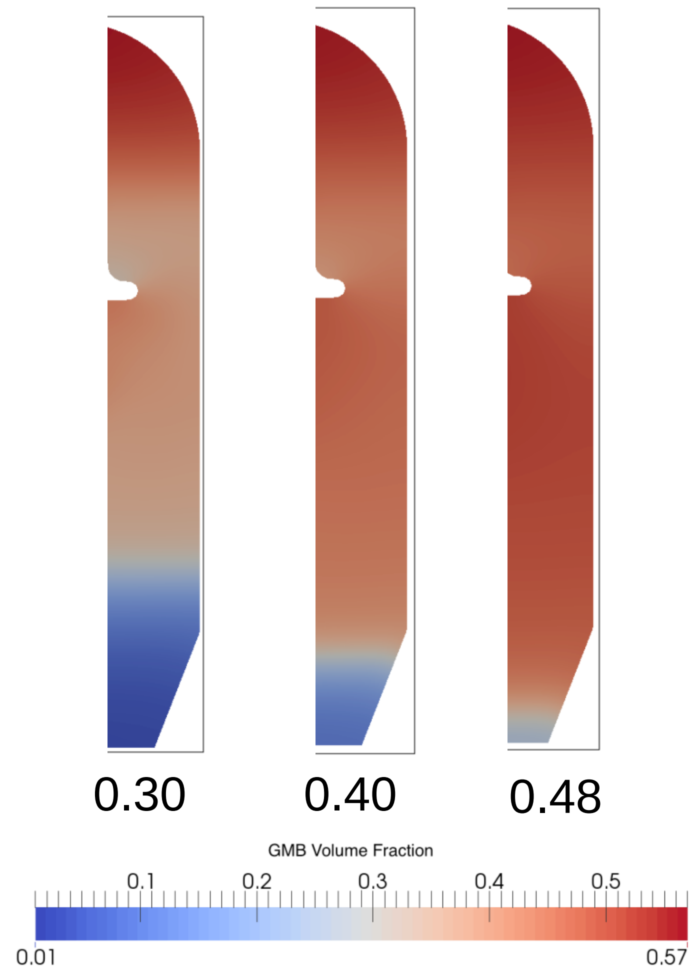
Process/geometry changes can be examined more rapidly with modeling

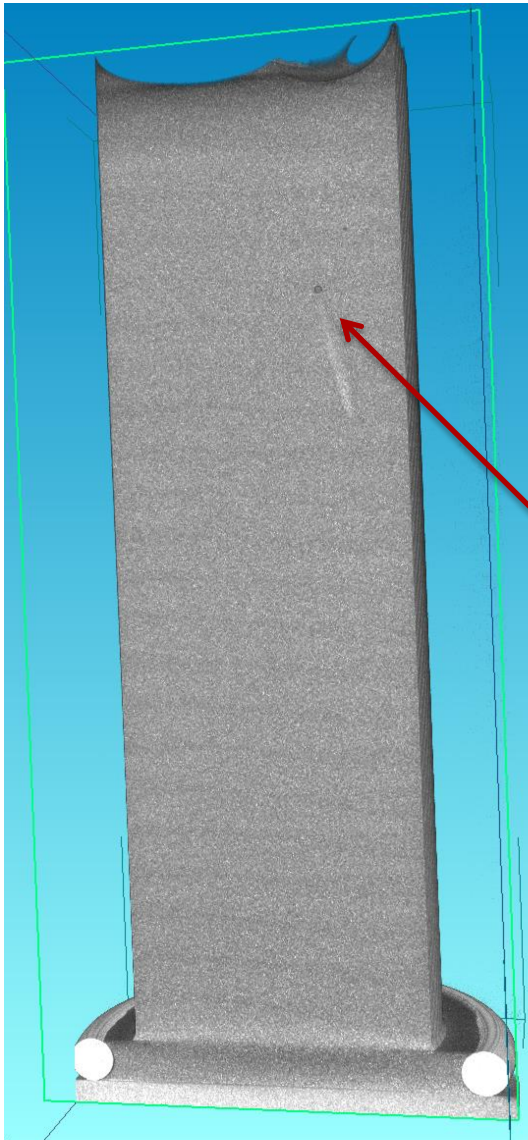
Particle migration minimized in 56 hour cure

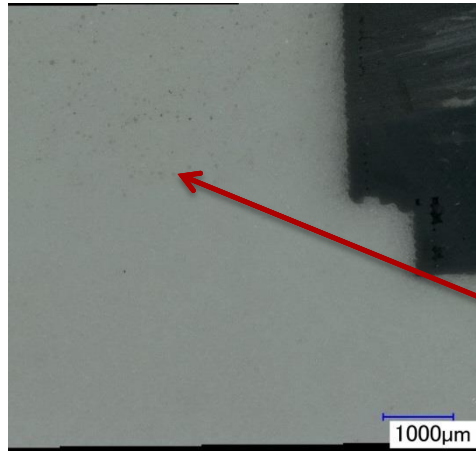


Varied volume fraction: 0.3 to 0.48
Used 27 hour cure profile



What’s Missing?





Particles size segregate during cure

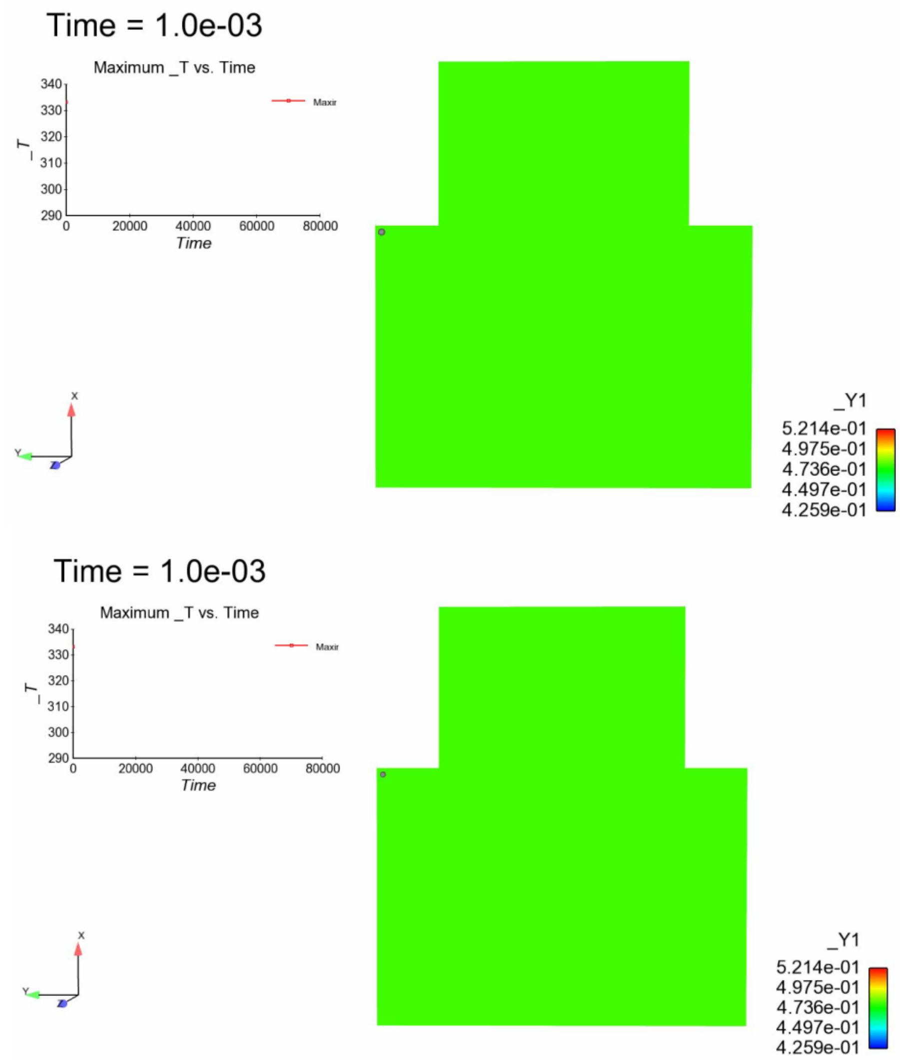
Larger particles can be seen at top

Large bubble formed when pouring into a cylindrical mold, rises during curing, leaving an epoxy-rich region in its wake.

bright => higher density => higher epoxy content
dark => higher particle content (or void)

Summary

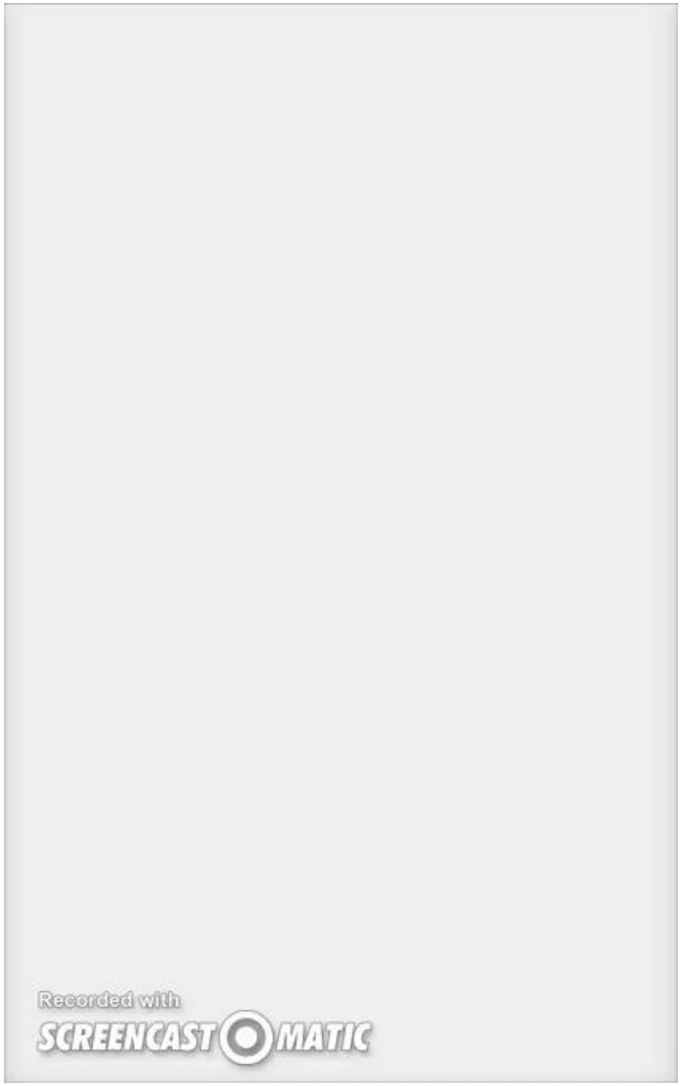
- Goal is to predict distribution of filler particles as a result of processing time and temperature changes
- Finite element model developed to help optimize processing conditions
- Experiments performed to determine model parameters. Improvements needed.
  - Particle characterization – sizes and densities
  - Hindered settling function
  - Polymer kinetics
  - Rheology – effects of particle fraction and extent of cure



Richardson-Zaki vs. Acrivos

Next Steps

- Improve hindered settling function description
  - Better particle characterization
  - Capture effects of size distribution: Can we capture size segregation?
  - Examine effects of possible surface interactions
- Improve curing and rheology dependence
  - Improve DEA-Epon curing model with new DSC and IR data
  - Extend rheology measurements to longer times
  - Capture change of curing mechanism at higher temperatures
  - Improve T_g model using Di Benedetto form: Vitrification is seen in rheology data!
  - Measure rheology of filled, curing systems – do we get expected behavior?
- Run 3D models
- Validate against concentration, temperatures in various geometries
- Enrich continuum model with particle migration behavior of multimodal size distributions
  - Sub-grid models to understand more complex behavior: e.g., discrete-particle simulation.
  - Does mold-filling create initial particle concentration/size gradients?



Discrete-particle simulation by the lattice-Boltzmann technique (Ladd 1994; Aidun, Lu & Ding 1998) -- Morris & Pednekhar

Thank you

Job Opening ID: 651319
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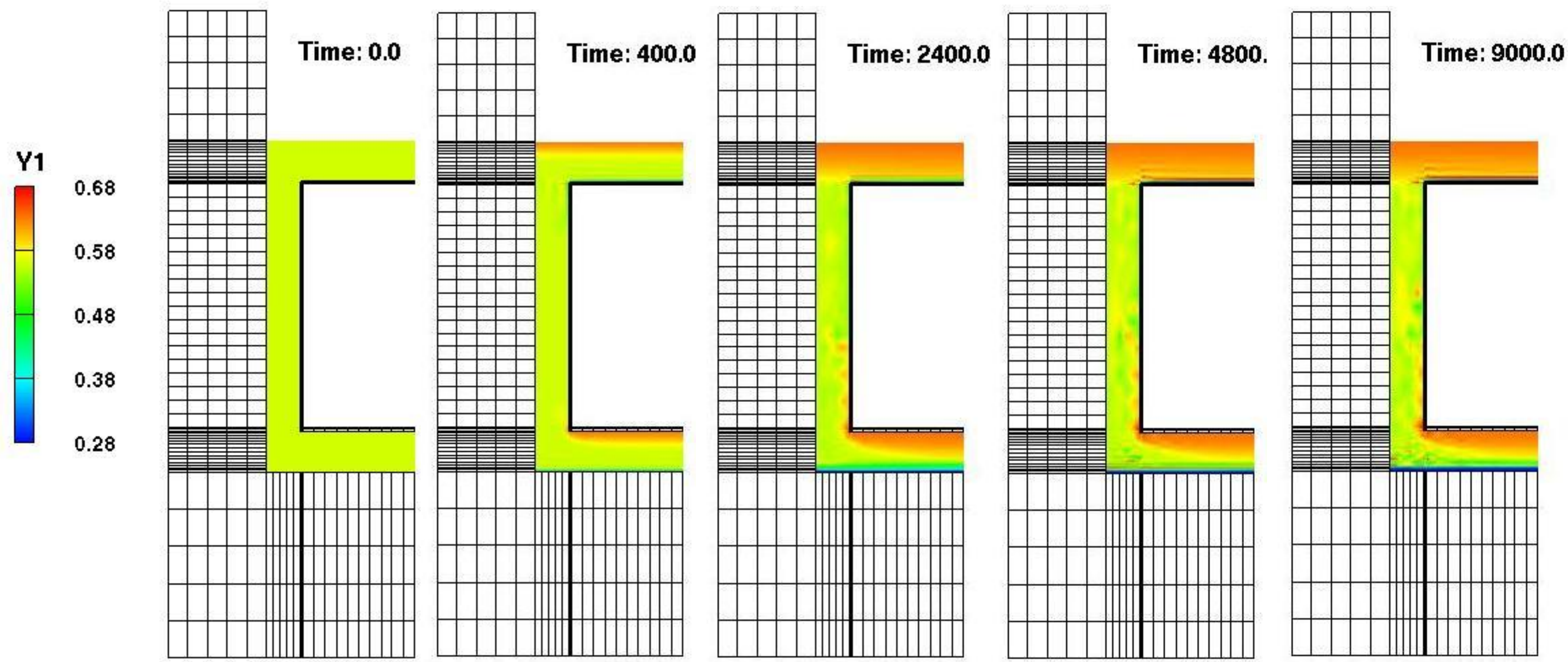
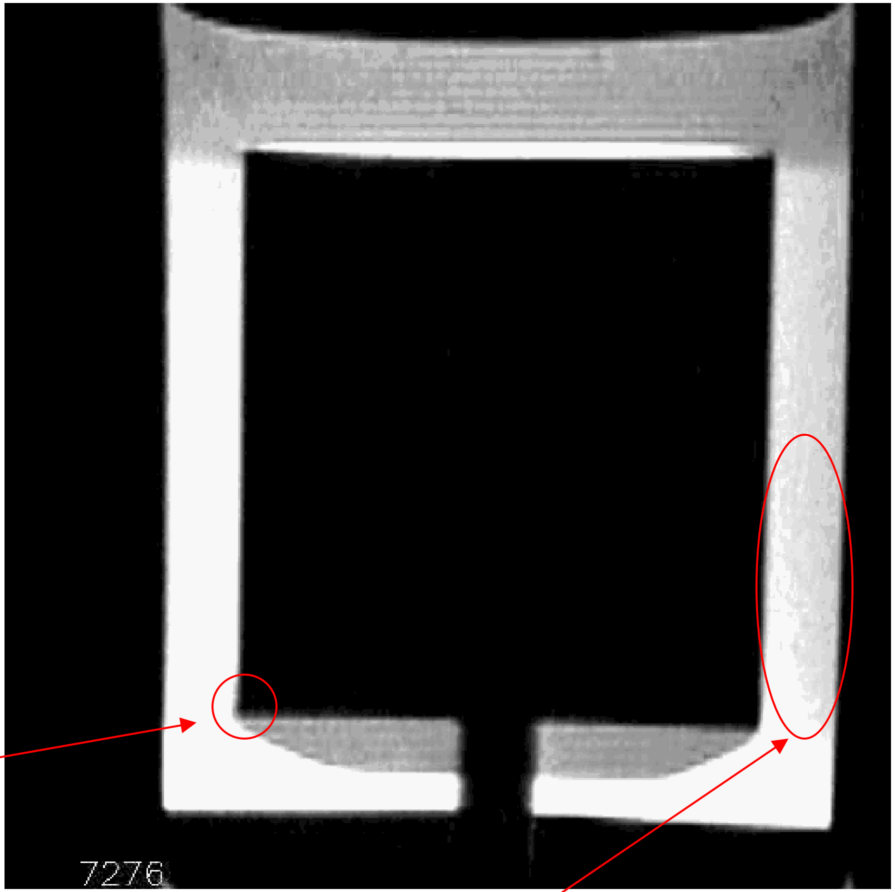
GMB Flotation as a Function of Time for Curing Epoxy



Model shows instabilities that lead to inhomogeneities in particle concentration

GMB Flotation as a Function of Time for Model System

NMR data does not give enough resolution to distinguish possible "blobs" from instabilities



High particle region curving around lip?

Mottled area real?