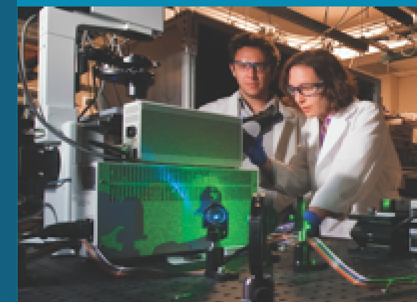
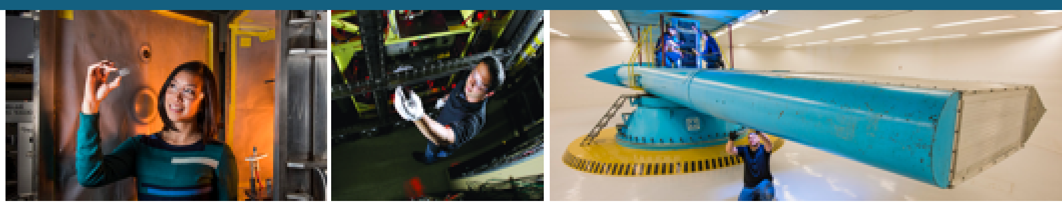
SAND2021-4349C

Sandia National Laboratories

Printing of High Tg Thermosets by Selective Laser Sintering (SLS) via Controlled Conversion

ACS Spring Virtual Meeting, April 2021





C. Garrett Campbell, Dominik Astorga, Rachel Collino, Mat Celina

Sandia National Laboratory, Department 1853

Los Alamos National Laboratory, MST-7

Overview

SLS Printing Background

- Overview of Printing Technique
- SLS printing of thermoplastics
- SLS printing of thermosets

Timing Approach to Cure State Control

- Correlation Between Cure State, T_g, and Gelation
- Reactive Resin Printing
- Curing Printed Objects

Stoichiometry Approach to Cure State Control

- Flory-Stockmayer Equation
- Production of Off-Stoichiometry Materials

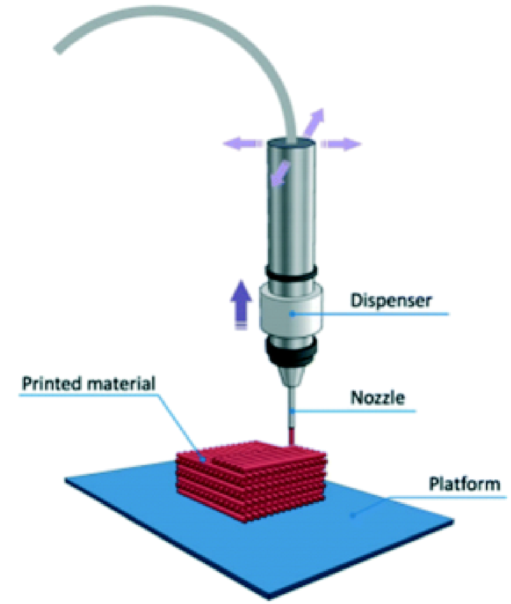
Summary

Acknowledgements

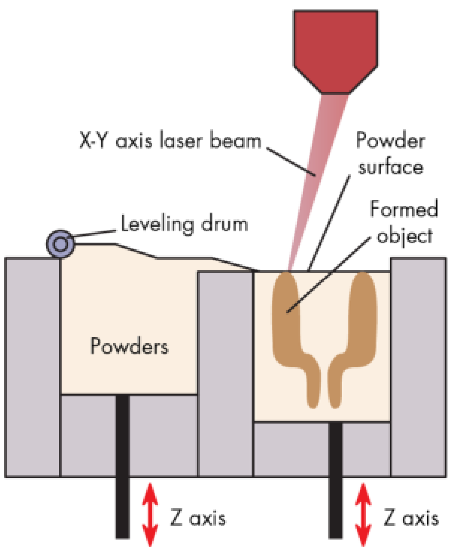
SLS Printing Background

- **Fused Deposition Modeling (FDM, FFD)/Direct Ink Write (DIW)**

  - Polymer Extruded through an orifice
  - Printing is mechanically driven-Limited speed
  - Support structures needed to print overhangs
  - Soft thermosets (silicones) and dual-cure resins



- **Selective Laser Sintering (SLS)**



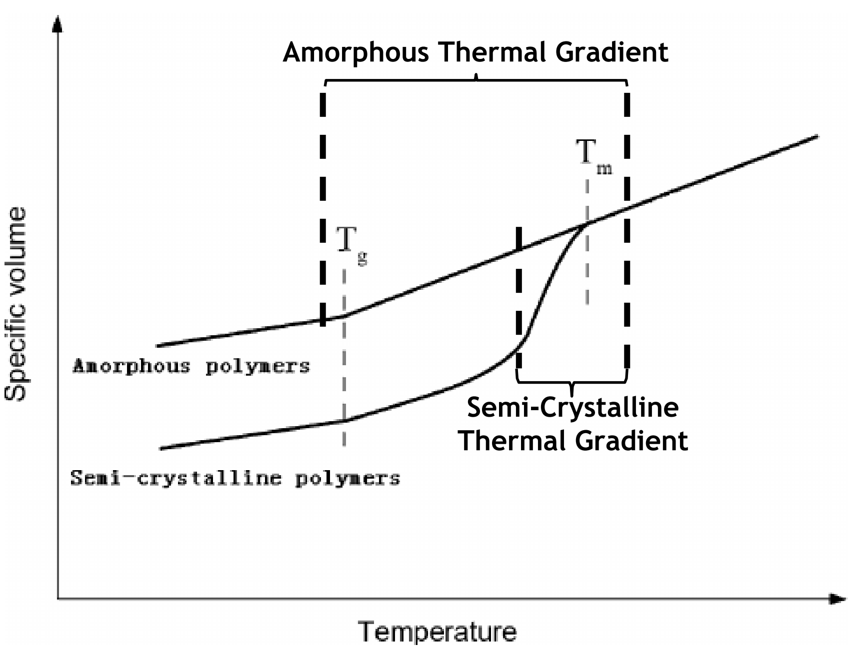
  - Polymer powder bed selectively sintered via laser heating
  - Scan speeds are much faster (less moving parts)
  - Support structures not needed to print overhangs
  - Highly filled (<30 wt% filler) thermoset materials reported
  - Requires large amount of material for R&D (>300g)

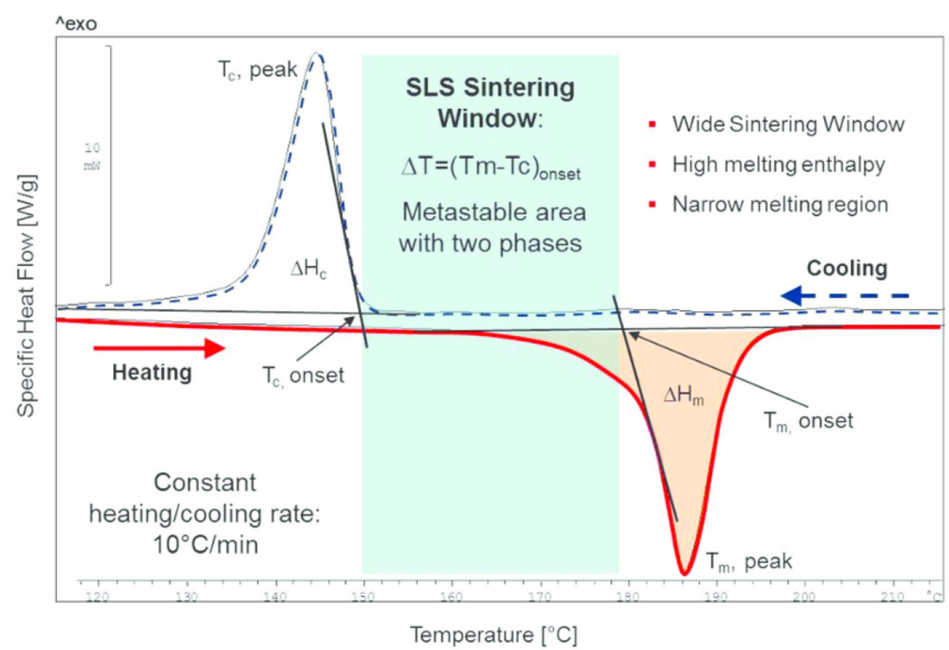
The Crystallinity Feature/Bug

- **Problem:** SLS printable materials require a crystallinity, but thermosetting resins are amorphous.

- **Thermoplastic Materials:**
- Sintering window is narrow in semi-crystalline polymers
- SLS printing amorphous polymers tends to result in brittle porous parts
  - "Good" mechanical properties → high molecular weight → high viscosity → poor sintering

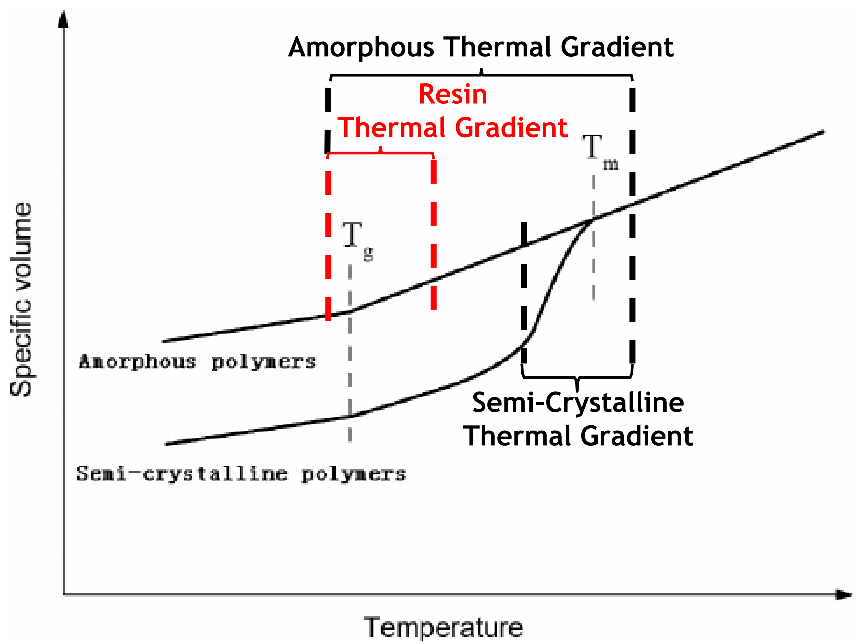
- **Thermosetting Resins:**
- Non-gelled resins tend to have low melt viscosity
- Mechanical properties are not achieved in the "green" part

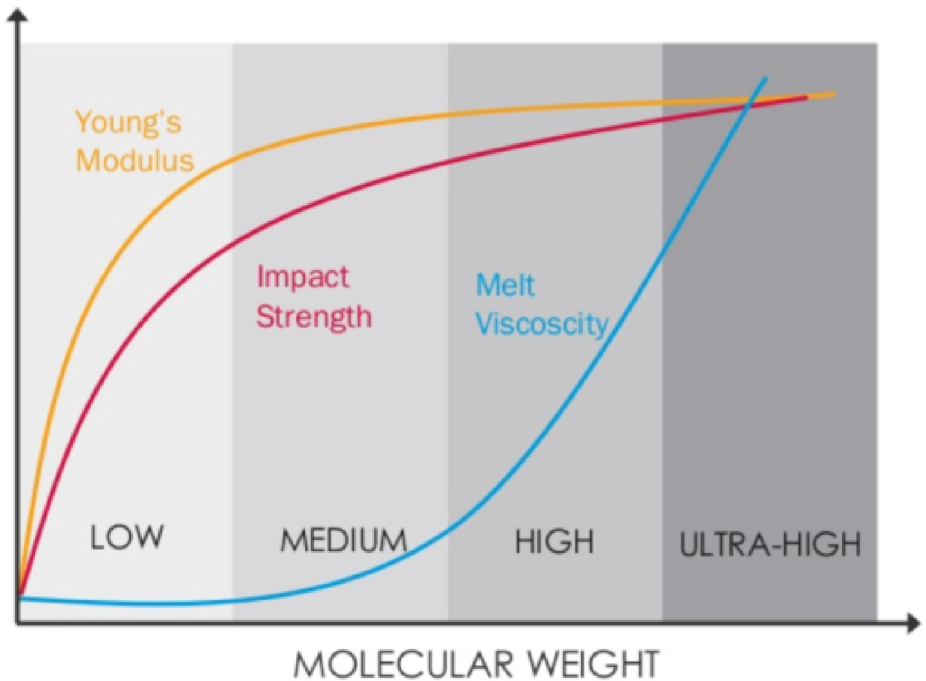




Rheological Advantage of Reactive Resins

- Traditionally, only semi-crystalline polymers are printed with SLS – **Sintering Window**
- For non-reactive polymers, high M_w is needed to achieve acceptable mechanical properties
- However, viscosity at any temperature above T_g increases with M_w
- Glassy resins can be printed with low M_w (low viscosity) and achieve maximal mechanical properties through post-print cure (gelation)





Glassy reactive resins are intrinsically more "printable" than amorphous thermoplastics due to low molecular weight.

<u>However, they must be cured after print!</u>

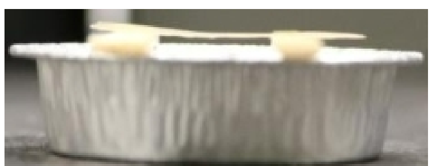
Post-Printing Hurdle: Thermal Cure = Deformation

- **Problem:** Thermoplastics are ready-to-use immediately after printing. Thermosets require a thermal cure step to achieve maximal properties.
- **Semi-Crystalline Thermoplastics:**
- "Physical cross-linking" happens during cooling (recrystallization)

- **Thermosetting Resins:**
- As-printed parts are brittle
- Post-cure above T_g results in deformation (sagging)

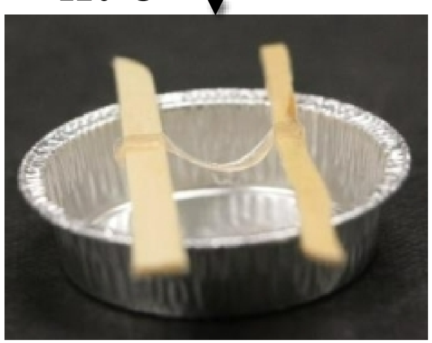
Example from Sandia National Labs

As Sintered (200°C Oven)



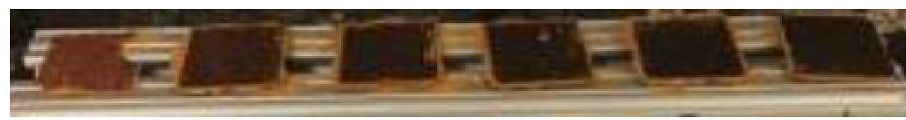
2 min @ 120°C

High-Temp Exposure



Example from NASA Glenn Research Center

As Printed



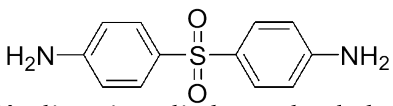
Heat 200 °C

Heat 250 °C

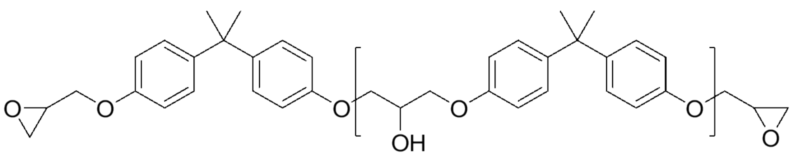
*K.C. Chuang, T.J. Gornet, K. Schneidau, H. Koerner, Laser Sintering of Thermoset Polyimide Composites, The Composites and Advanced Materials Expo, Anaheim, CA, 2019, p. 10p

Controlled Conversion via Timed Cure

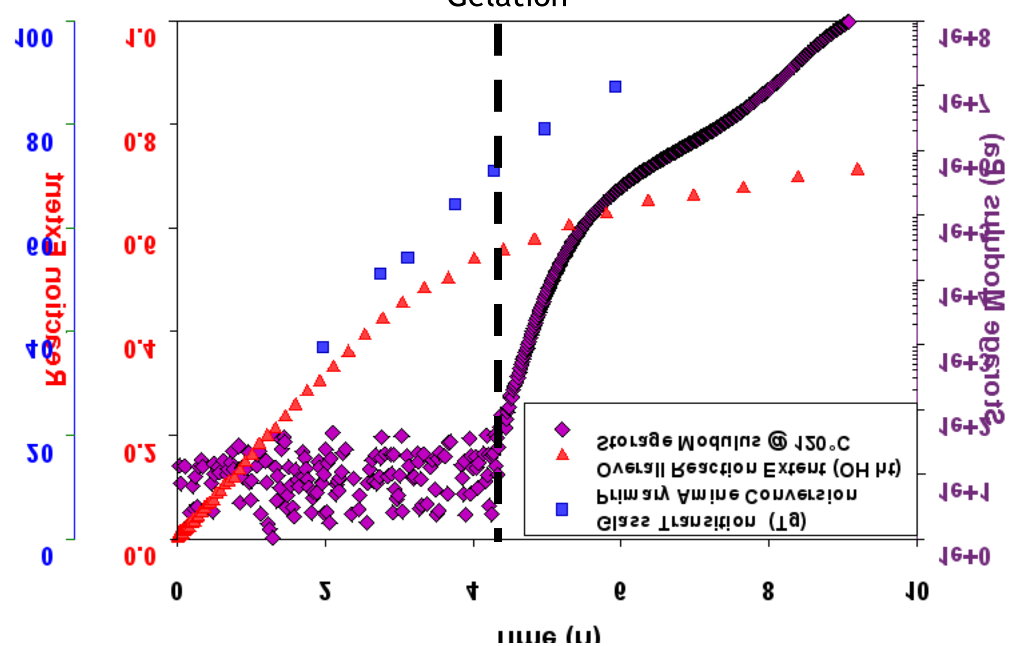
- **Goal: Produce reactive resin that requires little extra chemistry to achieve gelation**
  - 828/4,4'-DDS formulation chosen due to slow controlled kinetics and high final T_g
  - Correlation between reaction extent, initial T_g, and viscosity increase (gelation)
  - Determine "ideal" cure state and drive reaction there



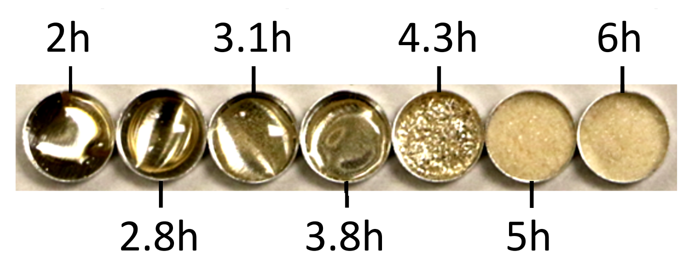
4,4'-diaminodiphenylsulphone (DDS)



Epon 828



Melting behavior at indicated cure times



Initial SLS Print Attempt: Lessons Learned

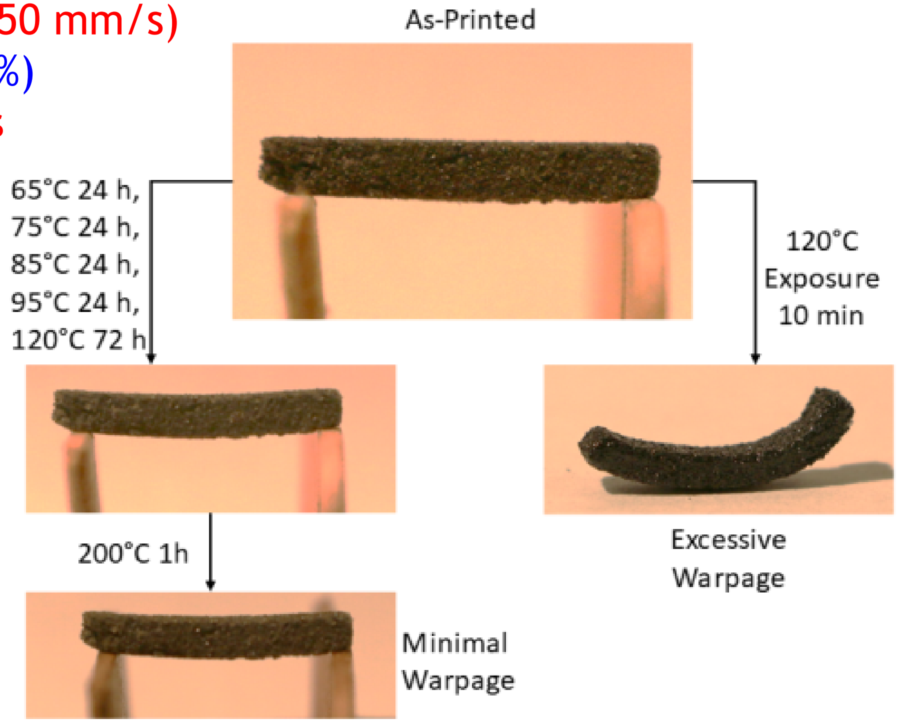
Resin Formulation: 828/4,4-DDS, 1:1 stoichiometry, Cured @ 120°C for 4.5 h, Onset $T_g \approx 71°C$

"Optimal" Printing Parameters of Blackened Powder:

- Bed Temp.: 65°C
- Laser Power: 2.3 watts (Very low power)
- Layer Thickness: 150 μm
- Hatch Distance: 200 μm
- Laser Speed: 650 mm/s

Problems and Solutions:

- Laser power insufficient to melt neat powder (@ 50 mm/s)
- Carbon black was dry-mixed with powder (0.7 wt%)
- Low adhesion with "optimal" printing parameters
- Slower laser speed resulted in "curling" of layers due to thermal gradient
- Print bed temperature raised (on 2nd attempt)



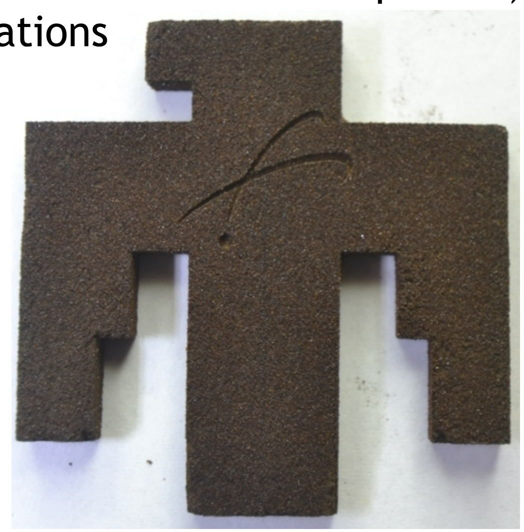
Proofs of Concept:

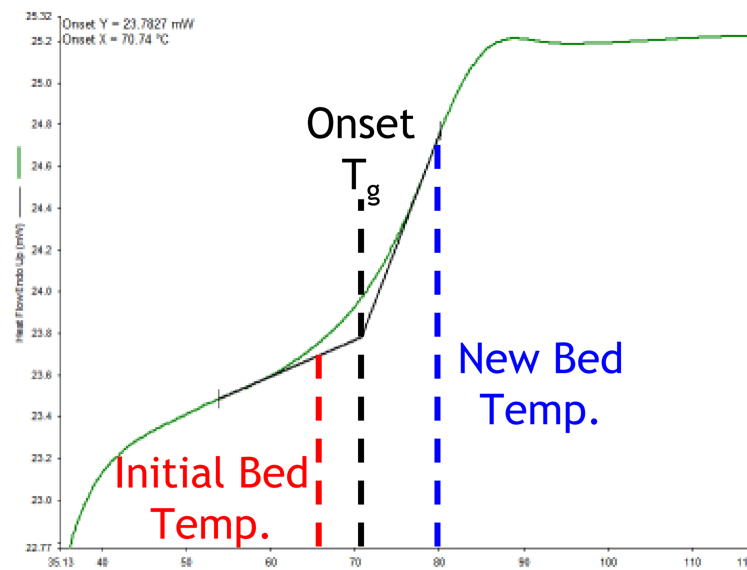
- SLS printing of minimally filled thermosets is possible (although not perfect)
- Curing of printed parts can be achieved with minimal warpage using a slow ramped cure

Second Printing Attempt: Getting Better

- Bed temperature increased to 80°C
    - 80°C was decided based on 30 minute temperature exposures. Particle sintering at this temperature was minimal.
- Laser speed reduced to 500 mm/s.

- **Results:**
- Minimal layer curling; bed temperature higher than T_g
- Better part density and mechanical properties (better sintering)
- Still high porosity (room for improvement)
- **Next Steps for This Formulation:**
- Finer powder and lower layer height (100 μm)
- Multi-scanning layers (not possible with current printer)
- Stoichiometry-driven formulations





First SLS Printing of "Unfilled" Thermoset Material
Critically Important for DOE Cross-Lab AM Effort – Multi-Lab Collaboration

Theory-Based Solution: Targeted Pre-Reaction via Off-Stoichiometry

- **Problem:** Timing approach requires high precision ovens, repeatable low batch thickness, and constant temperature monitoring to prevent premature gelation.

Theory-Based Solution: Targeted Pre-Reaction via Off-Stoichiometry

- **Problem:** Timing approach requires high precision ovens, repeatable low batch thickness, and constant temperature monitoring to prevent premature gelation.

Theory-Based Solution: Targeted Pre-Reaction via Off-Stoichiometry

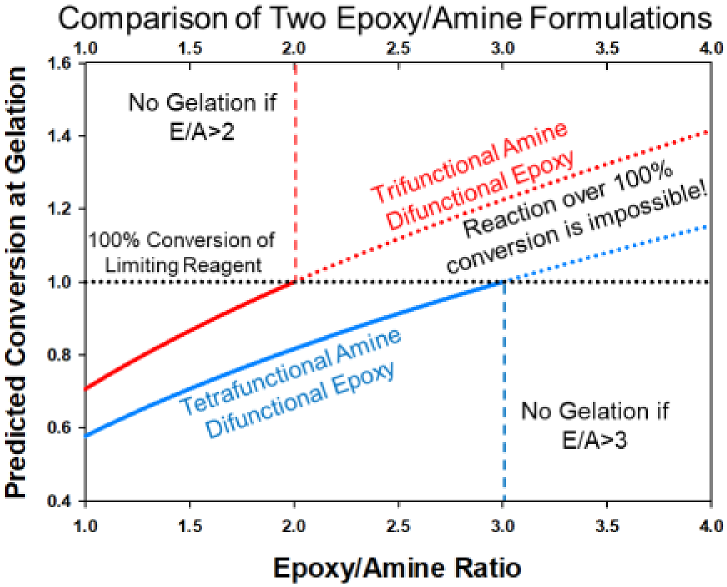
- **Problem:** Timing approach requires high precision ovens, repeatable low batch thickness, and constant temperature monitoring to prevent premature gelation.
- **Solution:** Stoichiometry based approaches would not require timing

- **Flory-Stockmayer Equation**

f_a,f_e= amine, epoxy functionality
A_{gel}= critical gelation conversion
B=Epoxy/Amine Ratio

$$A_{a\_gel} = \sqrt{\frac{B}{(f_a-1)*(f_e-1)}}$$ when epoxies are in excess (B>1)

$$A_{e\_gel} = \sqrt{\frac{1}{B*(f_a-1)*(f_e-1)}}$$ when amines are in excess (B<1)

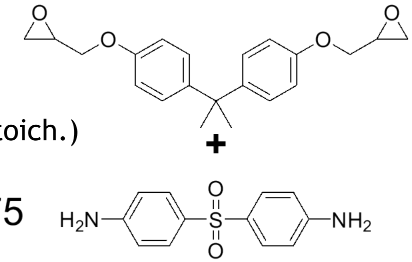


- Alter stoichiometry to a point where >100% conversion is required to reach gelation
- "Cure" until limited reagent is completely consumed. No gelation occurs!
- Pair amine-rich formulation with an epoxy-rich formulation or a commercial glassy epoxy

Eliminates precision timing and temperature control, but…
Extruding materials which are near their gel point could prove troublesome

Off-Stoichiometry Formulation and Extrusion

1



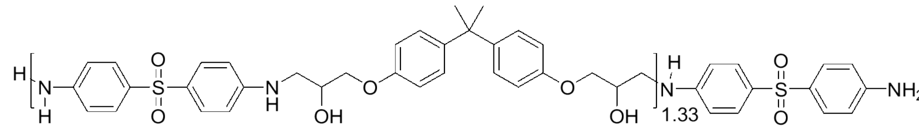
(3.5:1 stoich.)

+

1.75

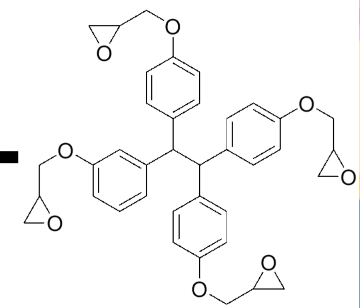
120-150°C

Full Epoxy Conversion

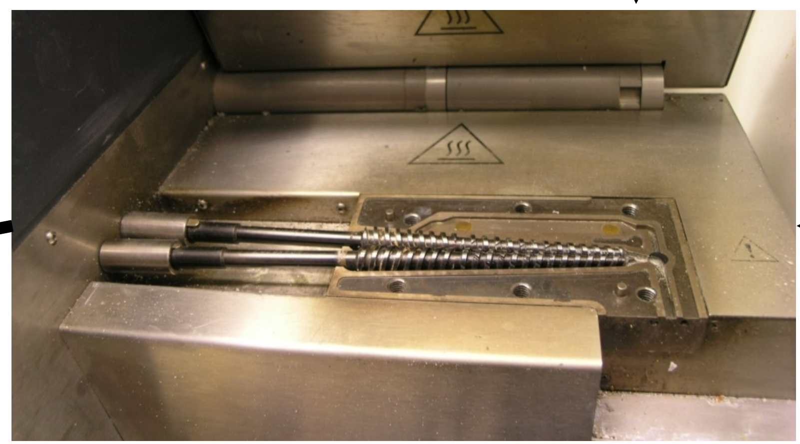


(Idealized Polyamine Structure)

Stoich. Balance with Polyamine



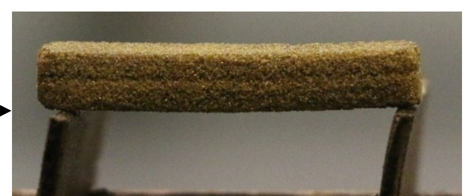
(Epon 1031)



Onset T_g=75°C uncured

Printing

Incremental Sub-T_g Cure



Final T_g >250°C

This approach addresses scale-up challenges, but not printing/curing issues

Could be part of broader molecular design strategy

Summary and Impact

- **SLS Printing of Thermosets - Current Status**
  - High T_g printable thermosets are produced via exact timing to control cure state
  - Printing of pre-reacted resins is possible but requires optimization of printing parameters
  - Curing of printed objects can be conducted below evolving T_g to achieve gelation
  - **First example of SLS printing and curing of minimally filled thermosets**
  - Potential processing issues and solutions to these have been identified
- **Future Activities**
  - Scaling material production
  - DMA characterization to optimize initial cure temperature
  - Optimization of print parameters to yield materials with lower inherent porosity
  - Dry-blend with GMB to produce controllable low-density thermosets
  - Investigate reactive polymeric additives to allow higher temperature post-print cure

Development of SLS printable thermosets can yield materials with enhanced physical properties (T_g>200°C) and minimal printer requirements
Why? - Because post-print cure is decoupled from lower T printing

Acknowledgements

- Dominik Astorga – Formulation mixing and cure kinetics
- Estevan Martinez and Nick Giron - Cure kinetics
- Rachel Collino (LANL MST-7) – 3D printer usage
- Leah Appelhans for SNL ACT management and reporting
- Enlightening discussions with other ‘ACT’ members
- Ongoing financial support by the NNSA ACT administrator, Jay Edgeworth

Sandia National Laboratories

Los Alamos NATIONAL LABORATORY EST.1943

NNSA National Nuclear Security Administration

DEPARTMENT OF ENERGY UNITED STATES OF AMERICA

*Not an Official Logo of Either Los Alamos National Laboratory or Sandia National Laboratories