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Controlled Conversion Approaches to Selective Laser Sintering (SLS) Printing of High T_g Thermosets

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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

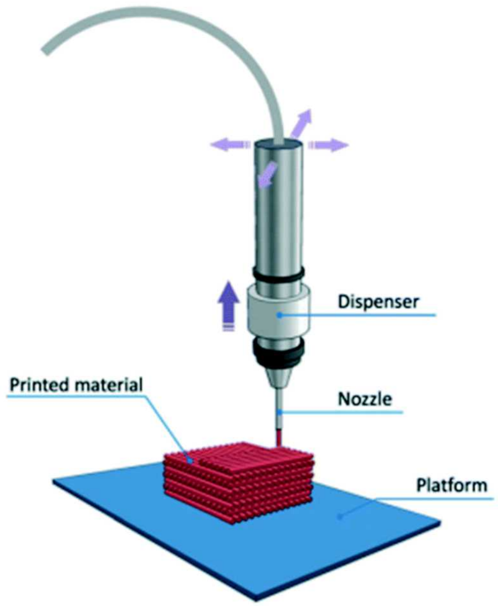
Summary

Acknowledgements

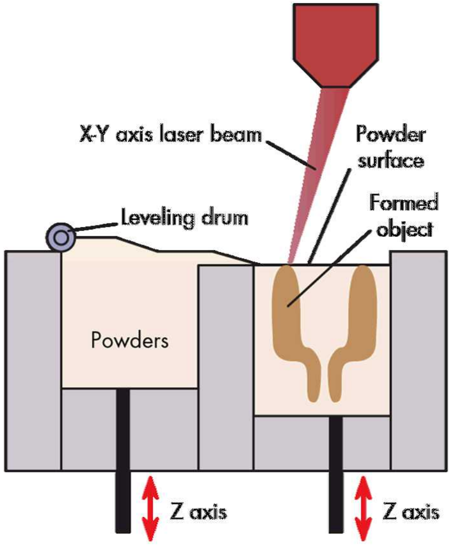
SLS Printing Background

- **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)**



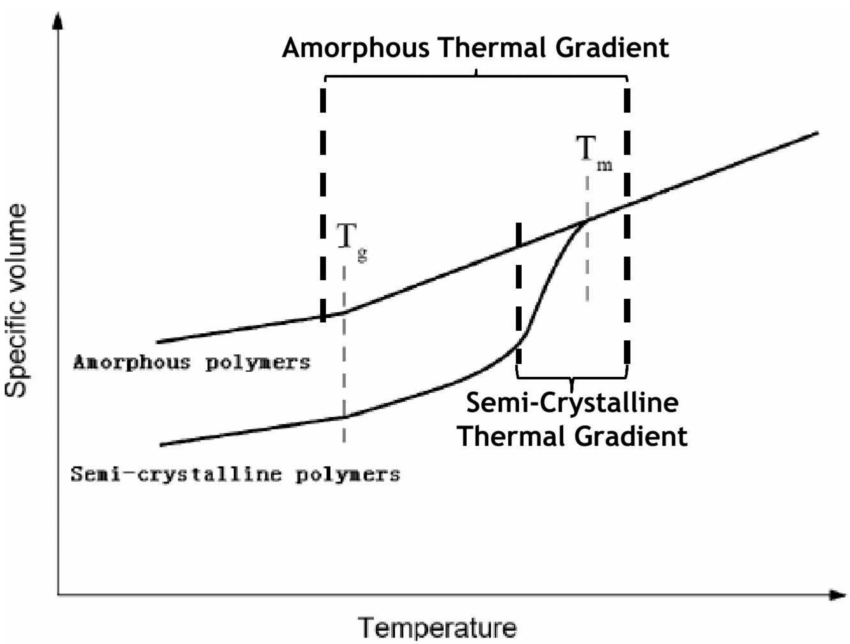
  - Polymer powder bed selectively sintered via laser heating
  - Scan speeds are much faster (less moving parts)
  - Support structures not needed to print overhangs
  - Highly filled (<30 wt% filler) thermoset materials reported
  - Requires large amount of material for R&D (>300g)

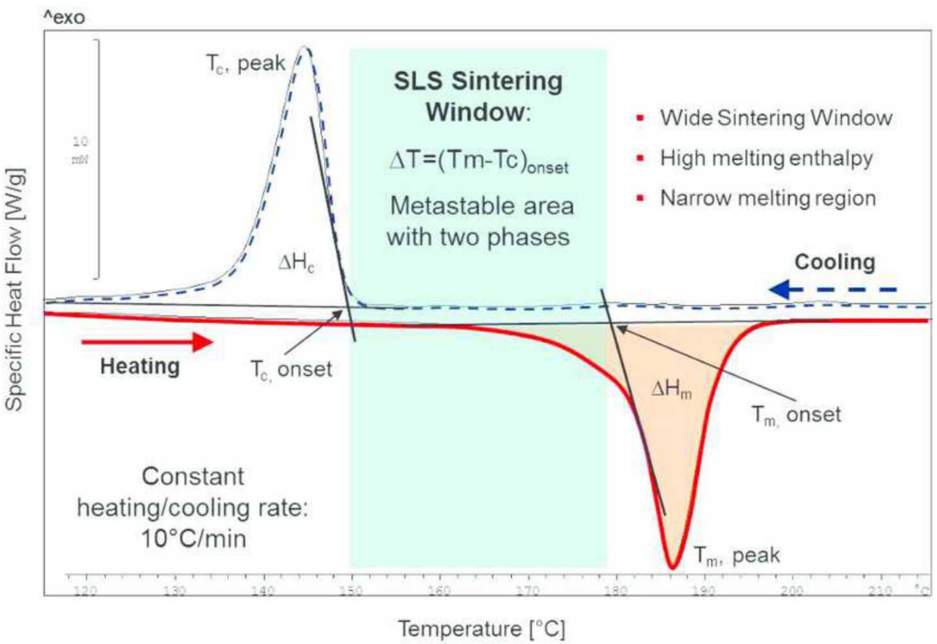
The Crystallinity Feature/Bug

- **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

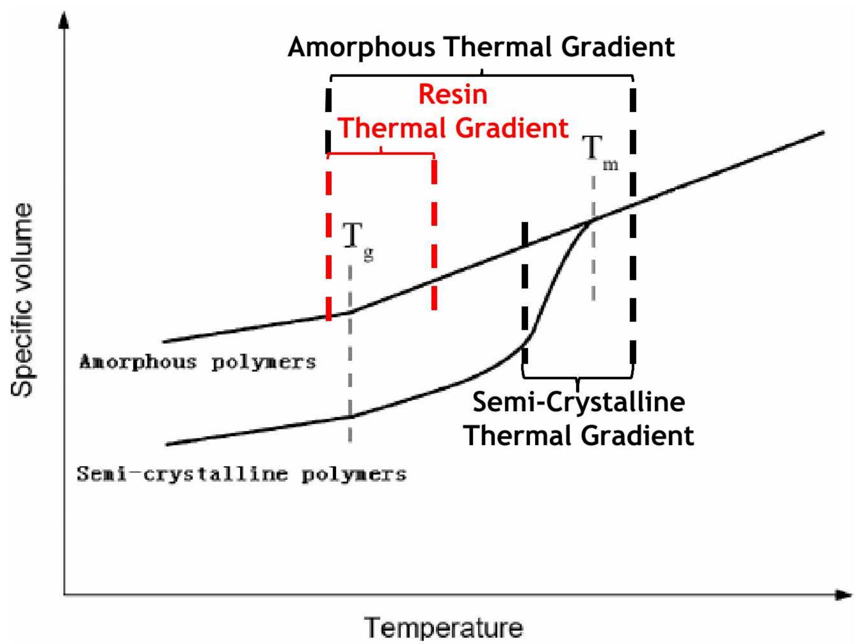
- **Thermosetting Resins:**
- Non-gelled resins tend to have low melt viscosity
- Mechanical properties are not achieved in the "green" part

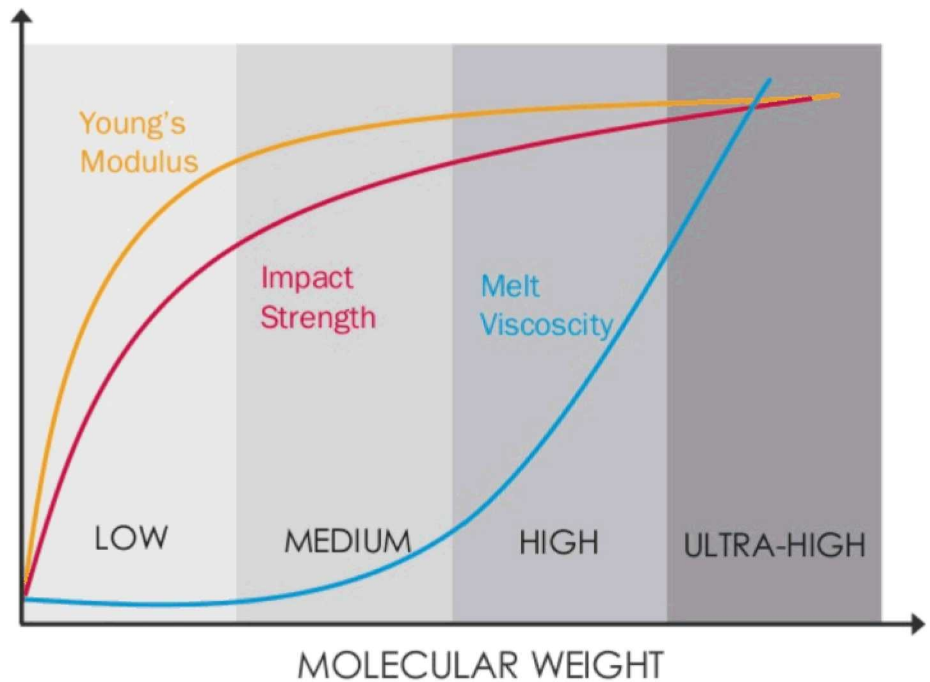




Rheological Advantage of Reactive Resins

- 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>

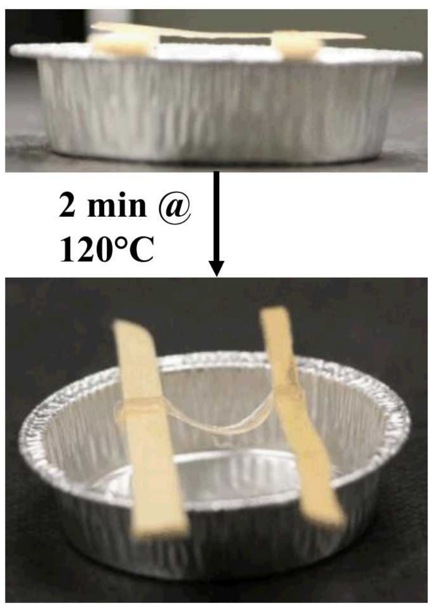
Post-Printing Hurdle: Thermal Cure = Deformation

- **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)

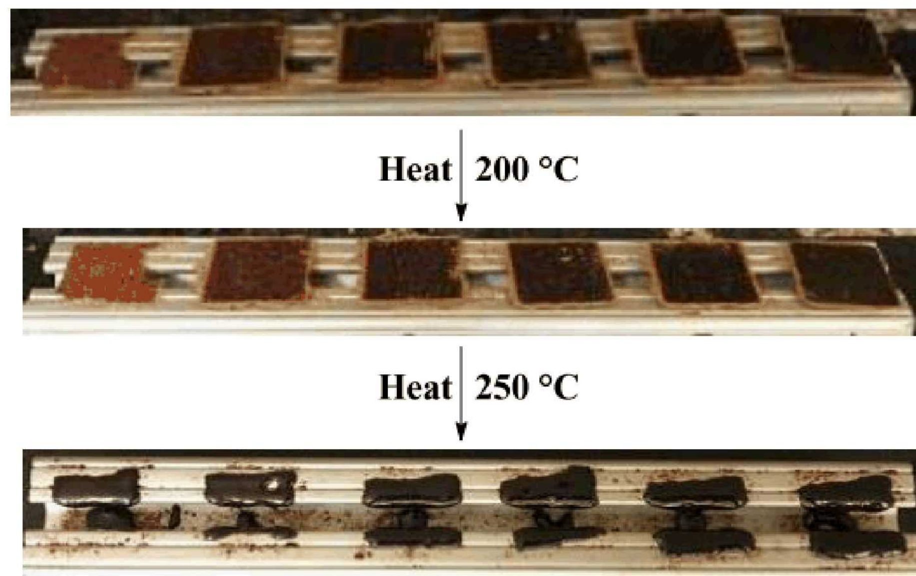


2 min @ 120°C

High-Temp Exposure

Example from NASA Glenn Research Center

As Printed



Heat 200 °C

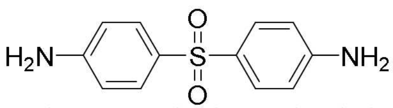
Heat 250 °C

*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

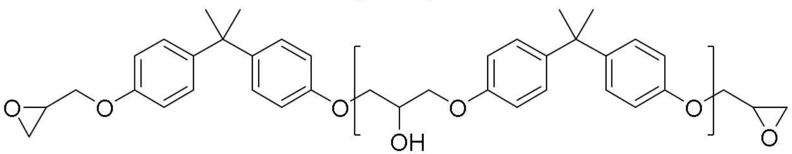
Controlled Conversion via Timed Cure

- **Goal: Produce reactive resin that requires little extra chemistry to achieve gelation**

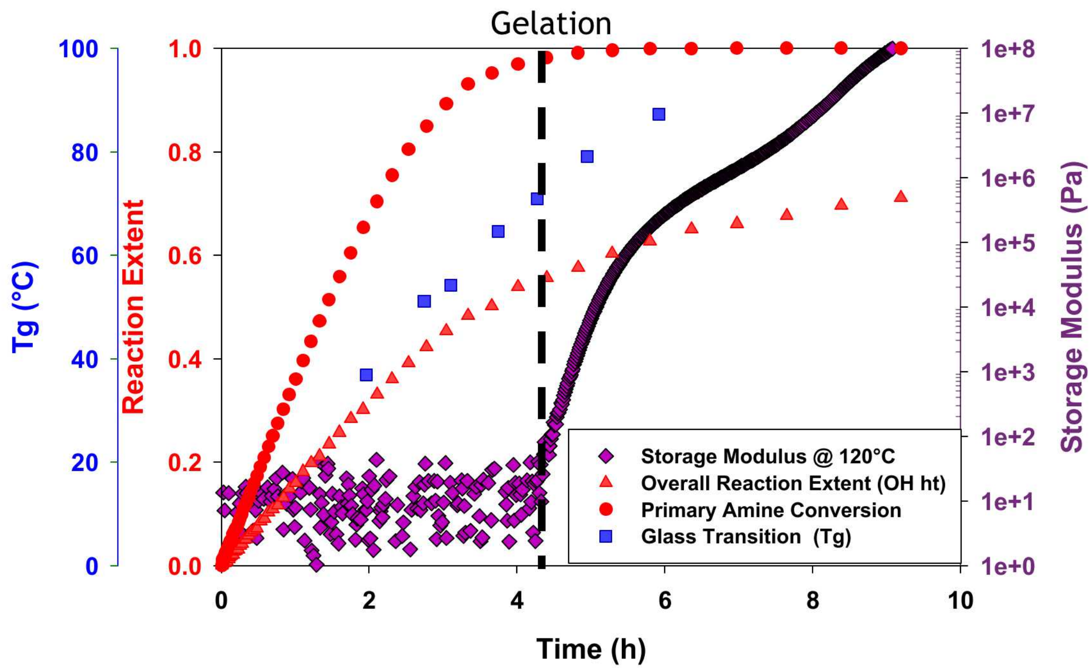
  - 828/4,4'-DDS formulation chosen due to slow controlled kinetics and high final T_g
  - Correlation between reaction extent, initial T_g, and viscosity increase (gelation)
  - Determine "ideal" cure state and drive reaction there



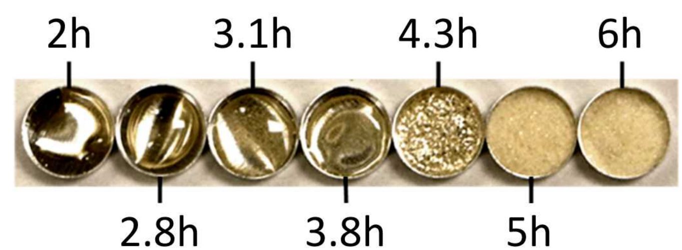
4,4'-diaminodiphenylsulphone (DDS)



Epon 828



Melting behavior at indicated cure times



Initial SLS Print Attempt: Lessons Learned

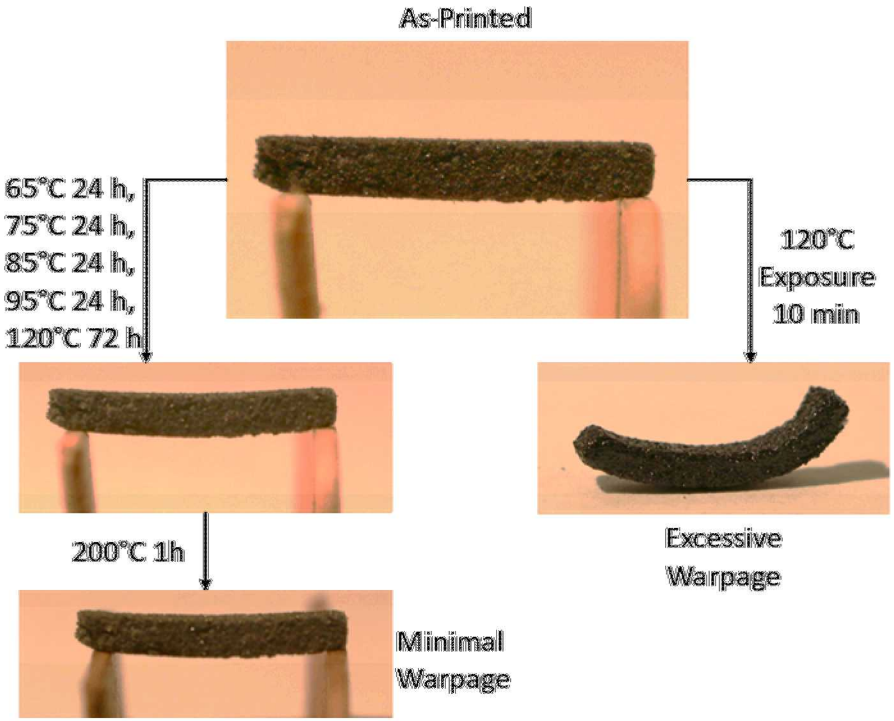
Resin Formulation: 828/4,4-DDS, 1:1 stoichiometry, Cured @ 120°C for 4.5 h, Onset T_g≈71°C

"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 (@
- Carbon black was dry-mixed with powder (0.7 wt
- Low adhesion with "optimal" printing parameter
- Slower laser speed resulted in "curling" of layers due to thermal gradient
- Print bed temperature raised (on 2nd attempt)



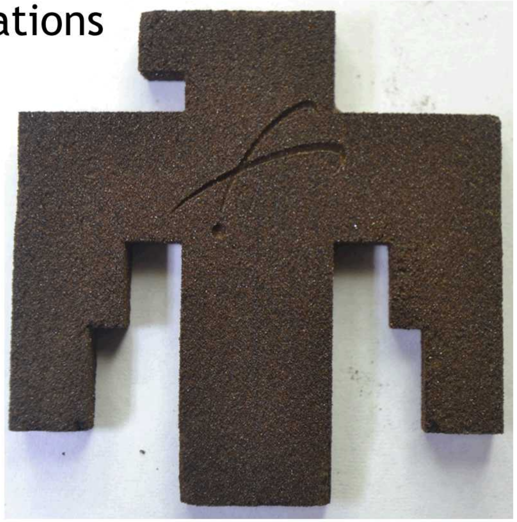
Proofs of Concept:

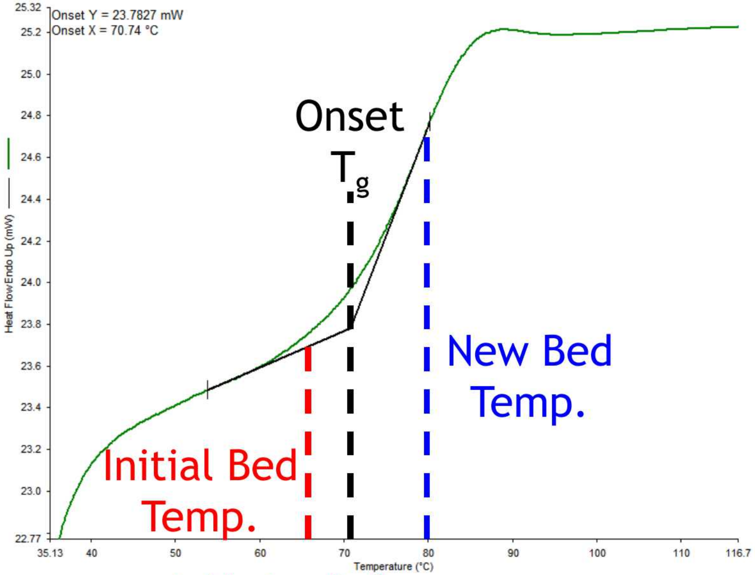
- SLS printing of minimally filled thermosets is possible (although not perfect)
- Curing of printed parts can be achieved with minimal warpage using a slow ramped cure

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.

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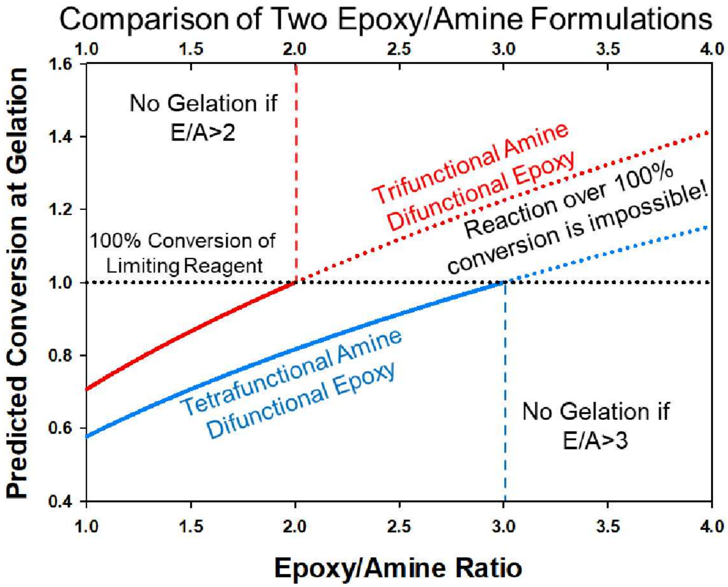
- **Problem:** Timing approach requires high precision ovens, repeatable low batch thickness, and constant temperature monitoring to prevent premature gelation.
- **Solution:** Stoichiometry based approaches would not require timing

- **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)

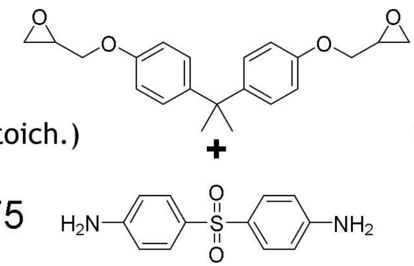


- Alter stoichiometry to a point where >100% conversion is required to reach gelation
- “Cure” until limited reagent is completely consumed. No gelation occurs!
- Pair amine-rich formulation with an epoxy-rich formulation or a commercial glassy epoxy

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

Off-Stoichiometry Formulation and Extrusion

1



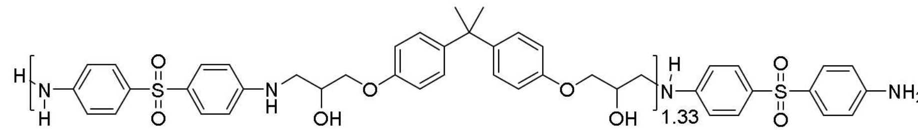
(3.5:1 stoich.)

+

1.75

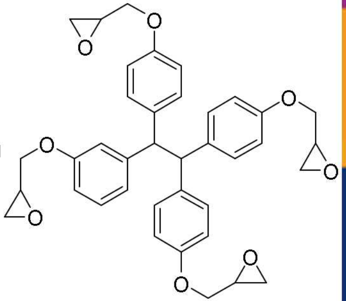
120-150°C

Full Epoxy Conversion

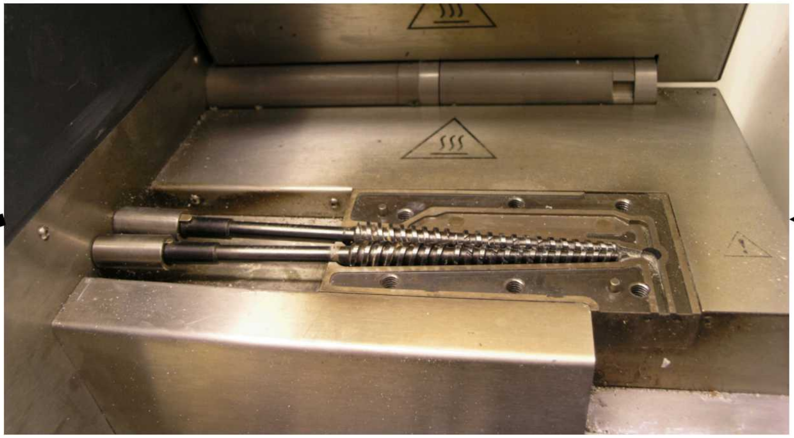


(Idealized Polyamine Structure)

Stoich. Balance with Polyamine



(Epon 1031)



140°C

Onset T_g=75°C uncured

T_g > 250°C when cured

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
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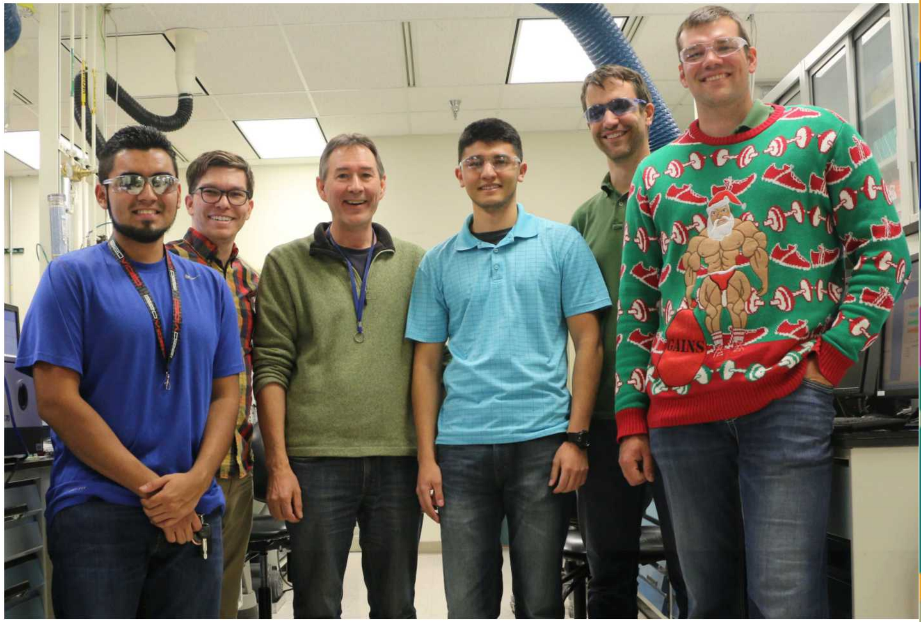

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