Additive Manufacturing (AM) of Energetic Materials

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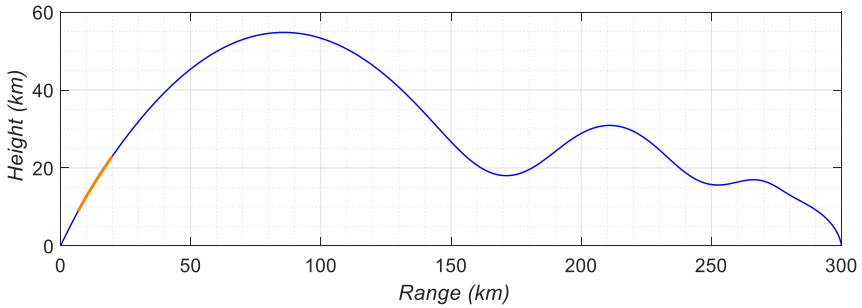
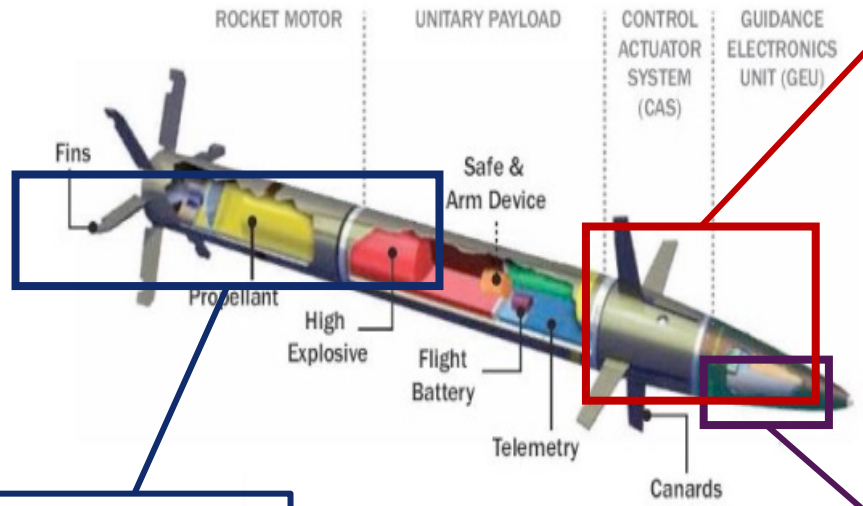
25 YEARS OF ESTCP
2019 | Enhancing DoD's Mission Effectiveness

Long Range Precision Fires (LRPF)

Weapon/gun propulsion: M109 self-propelled howitzer test bed, 58-caliber Extended Range Cannon Artillery armament, XM654 propellant supercharge



Raytheon Systems Company



Hybrid AM

- High-G Electronics Integration for:
  - *Fuzing*
  - *Guidance, Navigation and Control (GNC)*
  - *Communication*

Design Science

- *Integrated antenna design*
- *Efficient electronics package to volume*
- *Materials driven design for function and survivability*

Energetics AM

- Novel printable propellants or explosives
  - *Higher energy density*
  - *Control performance profile via structure*

Design Science

- *Tailored propellant thrust profile*
- *High G-survivable grain*

Metals AM

- Printed Frag Plates
  - *Ultra-High strength steels*
  - *Custom alloys for high ductility*

Design Science

- Tailored frag pattern
  - *Selectable*
  - *Efficient*

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ARL Energetic AM Focus Areas

Goals of Energetics AM

- Gun and Rocket Propellant – tailored burn profile
- Explosives – directionally focused detonation

Challenges

- Formulation – High energy formulation, high solids loading, energetic binders
- Manufacturing – Printing of high viscous pastes with resolution < 100 µm
- Performance – mech. properties to withstand high g-forces, enhanced combustion

Feedstock Development

- **Binders – energetic, better mech. properties (MPs), tailored for energetic solid**
- **Particle surface science – better processing and MPs**

AM Technique

- **Enables multiple binder chemistries**
- **Improved resolution – vibration assist and particle surface mod.**

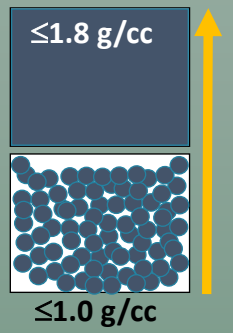
Modeling

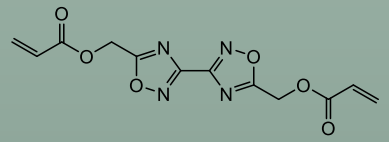
- **Interior Ballistics**
- **Topology Optimization**

Payoff: 20% increase in muzzle velocity

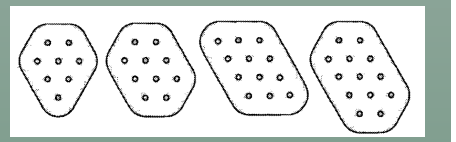
Supports NGCV and LRPF Priorities

Loading Density

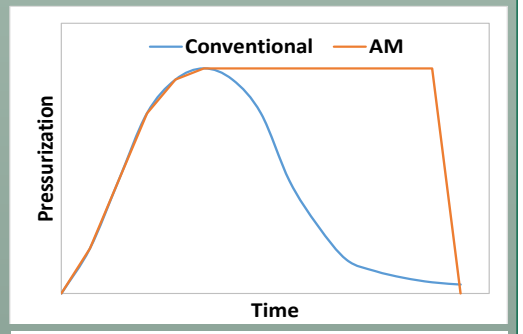


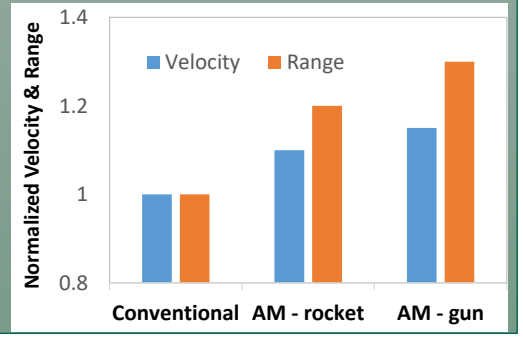


More Energy in Materials



Novel Geometries





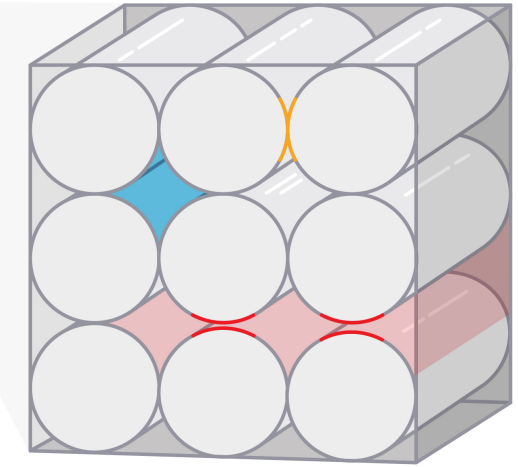
SERDP Program WP19-1338

Environmental Aspects Addressed:

- Removal or Reduction of Solvent/Waste Streams
  - From the 2016 EPA Toxic Release Inventory, Radford Army Ammunition Plant released over 38M pounds of waste in liquid and vapor form
  - AM of gun propellant eliminates the use of solvent, thereby minimizing waste streams
  - Nitrocellulose variability in starting products leads to out-of-spec batches that add to waste streams
- Reduction of hazardous materials
  - AM of gun propellant will utilize binder/oxidizer, which contain isocyanates in the binder
  - Exploring alternative binder chemistries for removal of isocyanates
- Reduction in HMX composition – through energy contribution of binder
- Personnel safety
  - Fewer processing steps
  - Room temperature AM – eliminates mixing energetics at high temperatures

Polymers Available for AM

- **Thermoplastics** – polylactic acid (PLA), acrylonitrile-butadiene-styrene (ABS), polyethylene terephthalate (PET), Nylon, thermoplastic polyurethane (TPU), polycarbonate (PC)
  - Reaction chemistry complete – select COTS product based on properties
  - Benefit: You can melt, dissolve polymer and return to original form Drawback: No covalent bonding = poor mechanical properties
    - Poor layer-to-layer adhesion
    - No control of reactivity with second phase filler

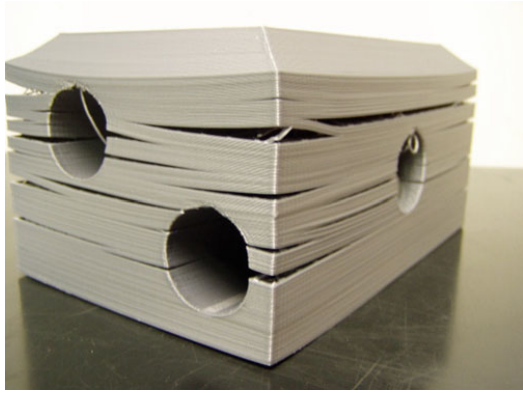


Fused Deposition Modeling

Void

Inter-Fiber Bonding Region

Void where layers didn't fully adhere



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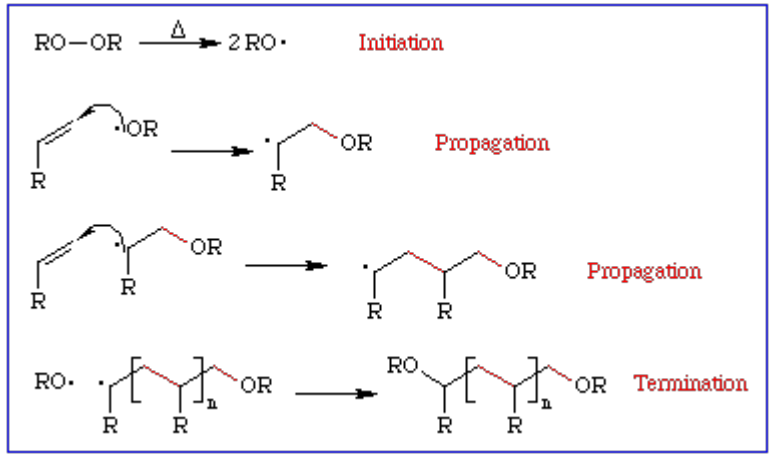
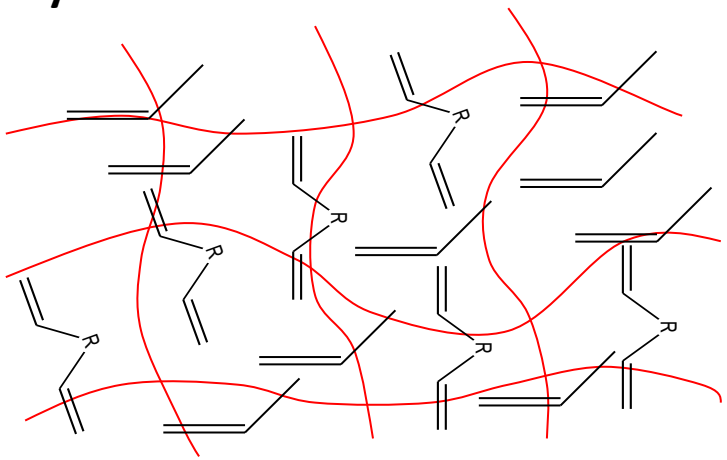
- **Thermosets** – epoxies, acrylates, polyureas, polyurethanes, etc.
  - Start with monomers – initiate polymerization for final product
  - Multiple variables for tuning polymer properties, cure kinetics, composite interfacial behavior, AM layer-to-layer reactivity, improved void space

Thermoset Chemistries

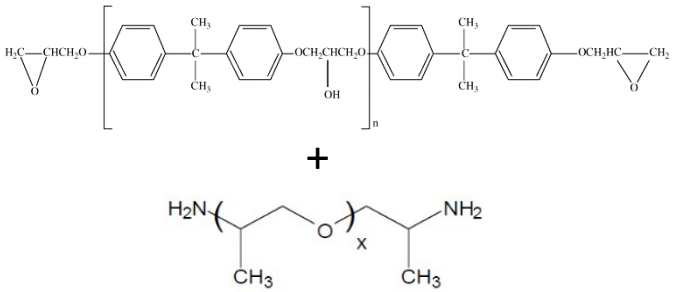
Free Radical Polymerization

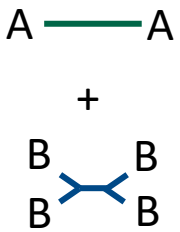


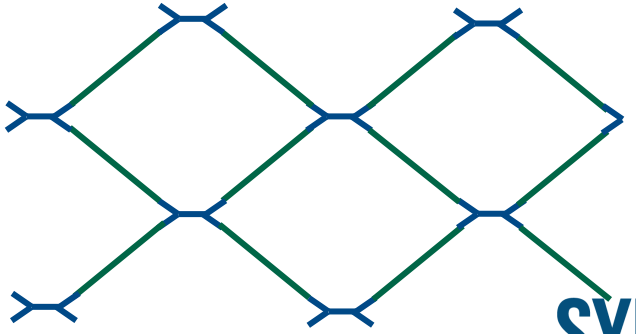


Co-polymerization rate and conversion of double bonds is critical

Step Growth Polymerization (such as epoxy-amine)







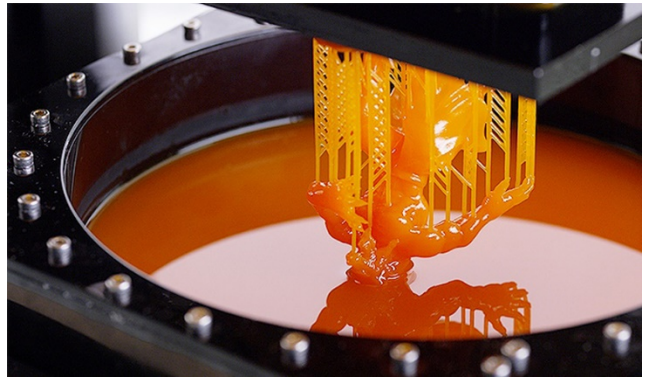
Stoichiometry, Monomer Mw, functionality are important

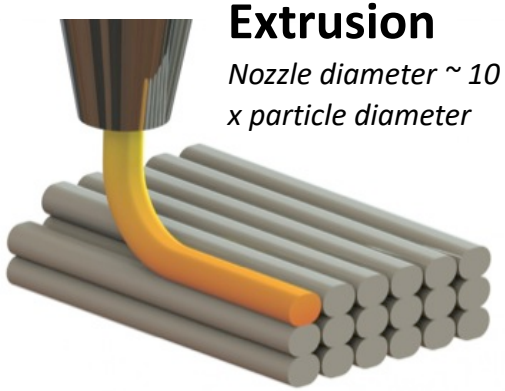
AM Techniques for Energetics

	SLA or DLP	FDM	Paste Extrusion	ARE
Environmental Impact	VOCs	High T Multi-step	Low	Low
Reactive chemistry	Yes – free radical	No	Yes – free radical	Yes –step-growth
Available chemistries	Photo	NA	Photo	Urea/urethane, Amine-acrylate, Photo, Epoxy
Resolution (micron)*	150 (unfilled)	200 (unfilled)	2,000	800
Multi-material	No	Yes	Yes	Yes
Max Solids loading (wt%)	50 %	80-85%	80-85%	80-85%
Production Rate	Low	100 lb/hr	45 lb/hr	45 lb/hr

SLA – Stereolithography
DLP – digital light projection
FDM – fused deposition modeling
ARE – ambient reactive extrusion

Vat polymerization (SLA OR DLP)



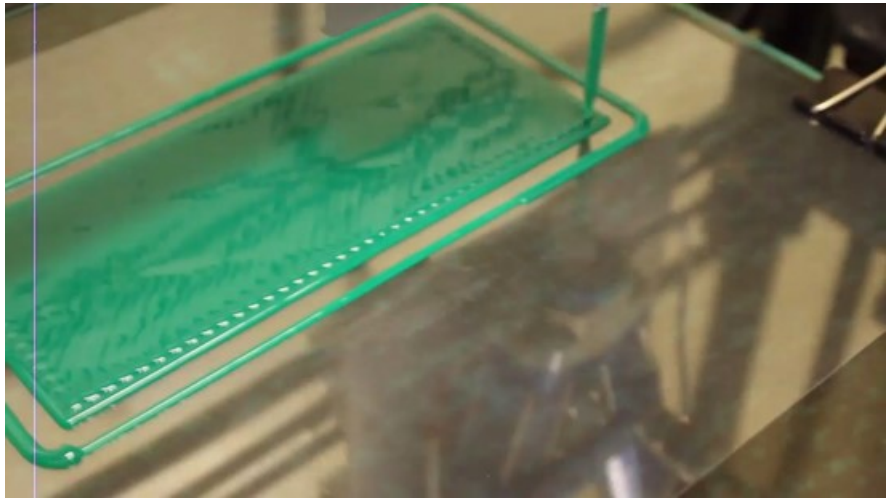


Extrusion

Nozzle diameter ~ 10 x particle diameter

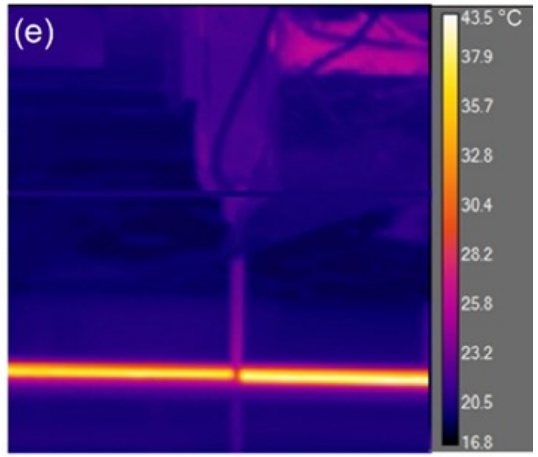
Ambient Reactive extrusion (ARE)

- Enables several new binder chemistries (polyurea, Michael Addition, etc.)
- Challenge: Improve resolution
  - Vibration assist technology
  - Design particle surface chemistry to reduce viscosity of feedstock

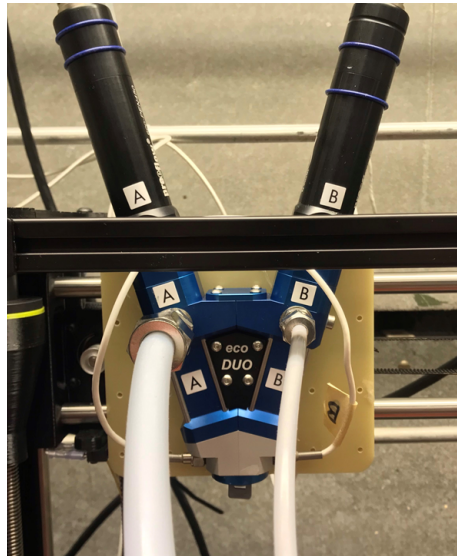


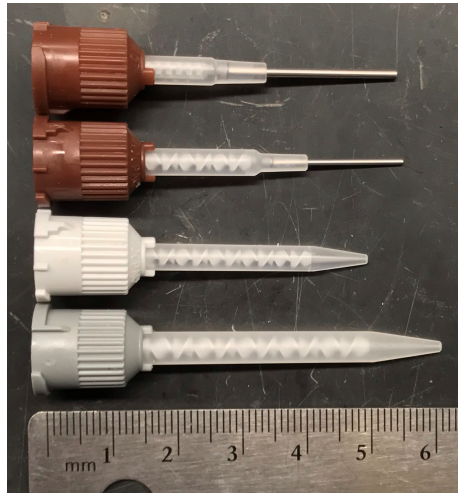
2x speed

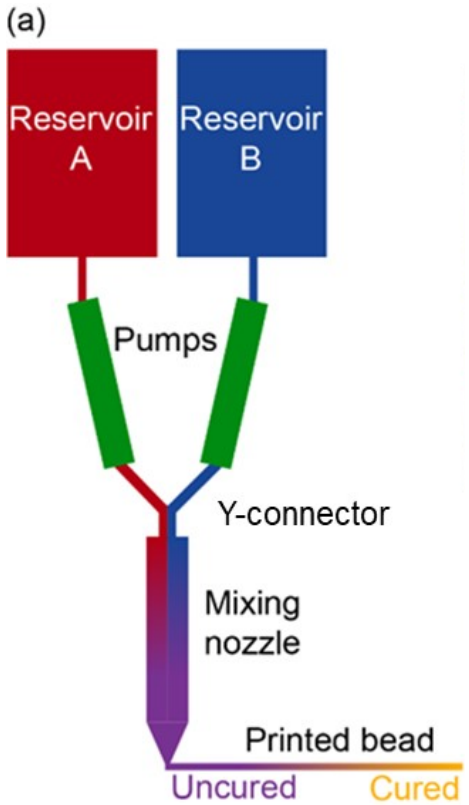
Low temperature



Scalable







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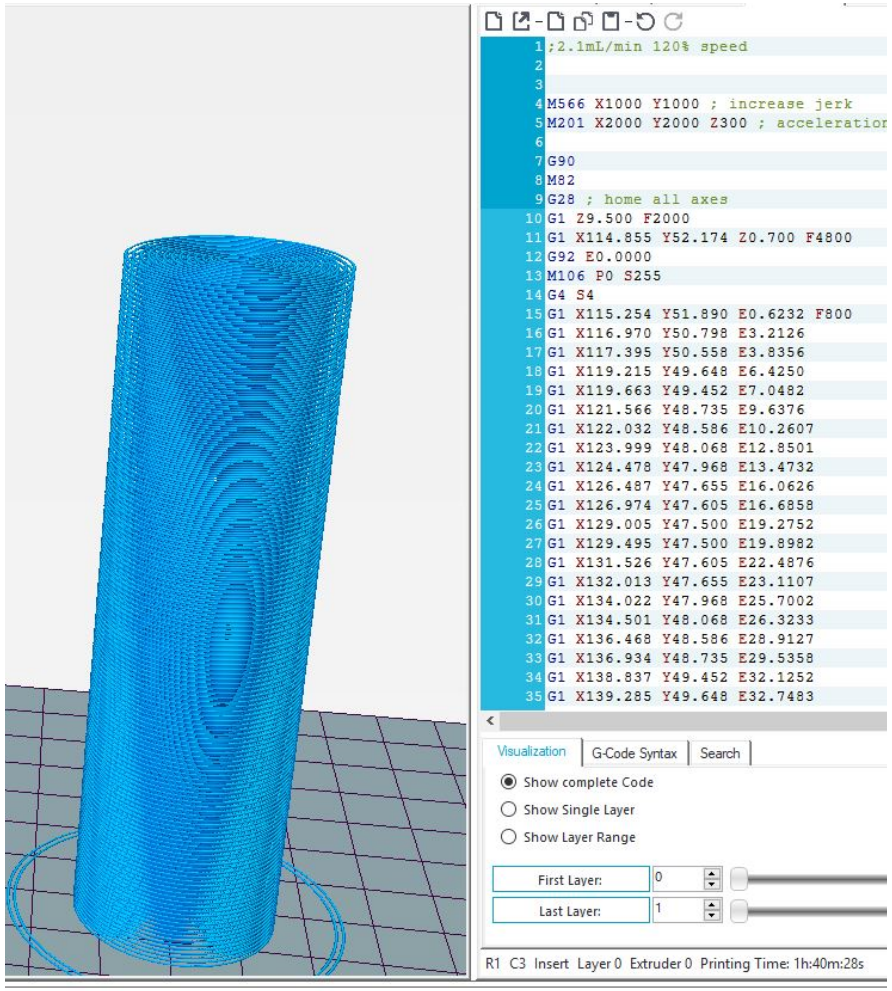
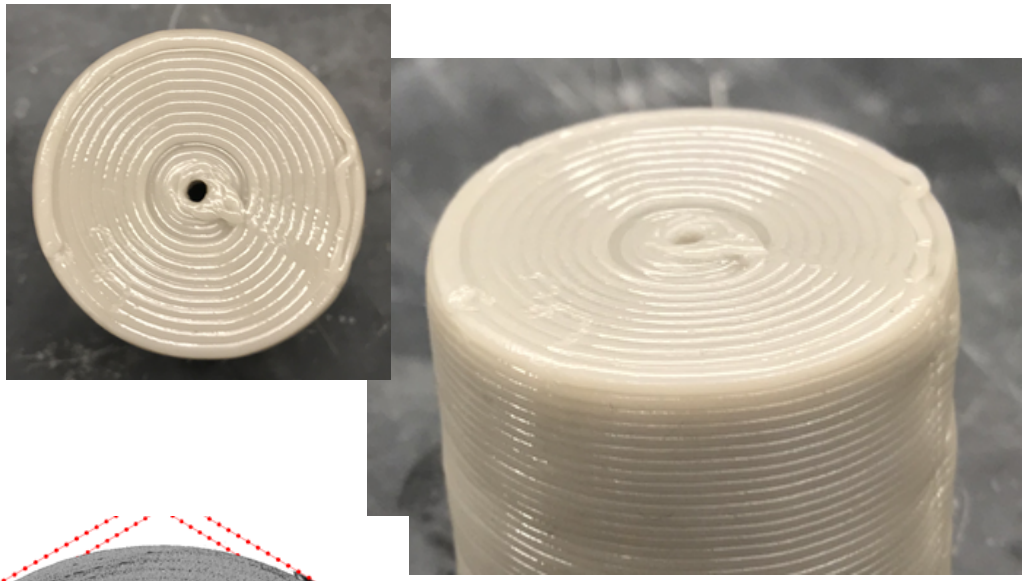
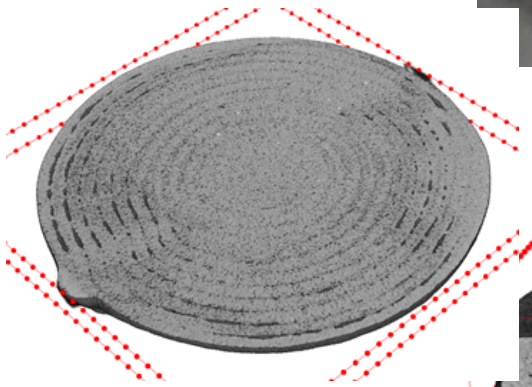
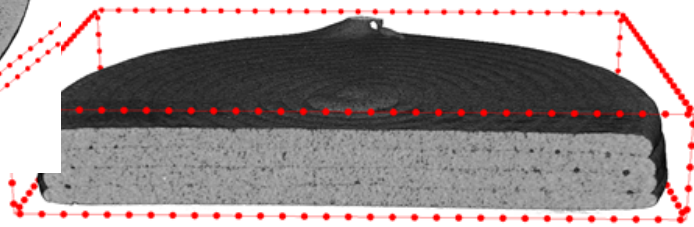
Printing strategies and G-code editing



- **Challenges**
  - Slumping/creep
  - Layer and contour size
  - Part height and weight of material
  - Overhang angle
  - Layer time vs cure chemistry
- **Key Parameters**
  - Flow rate
  - Extruder speed
  - Layer height
  - Bead width

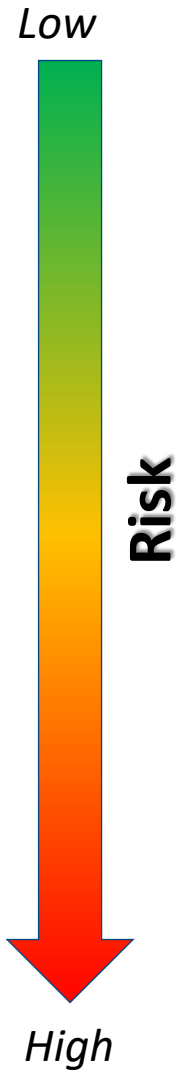




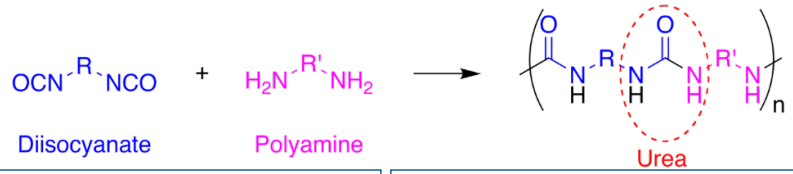


Binder Development Strategy

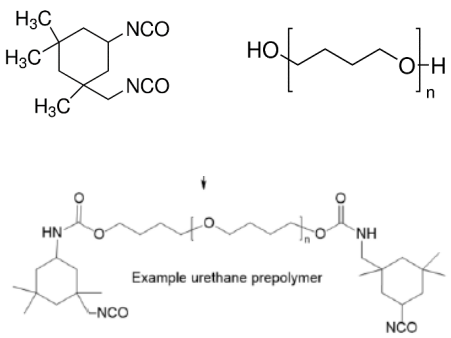
- **Photo-curable Binder Development**
  - Supports SLA, paste extrusion
  - Printed elastic in-house formulation via SLA (Tg ~ - 50 deg C, > 100% elongation)
- **ARE polyurea (PU) – established chemistry**
  - Elastic formulation (Tg ~ -70ºC) – anticipated to be better than HTPB
  - Goal of HMX-loading to 75+ wt. %
  - Current status: Increasing inert solids loading in PU
- **Aza Michael Addition (MA) – amine + acrylate chemistry**
  - Eliminates use of isocyanate in formulation
  - Formulate MA binders that fall within the ARE processing window
  - Adapt MA formulations to yield low Tg polymer with good mechanical properties
  - Current status: Developed a printable chemistry with good MPs and fast gel time
- **Energetic binder development (PU, MA, and photo-curable)**
  - Formulated several energetic photo-curables
  - Beginning to formulate energetic moieties into PU and MA binders



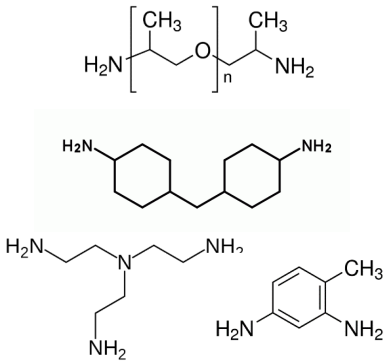
ARE Chemistries



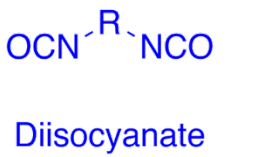
Diisocyanate



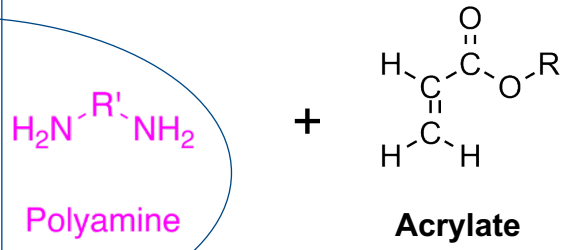
Amine

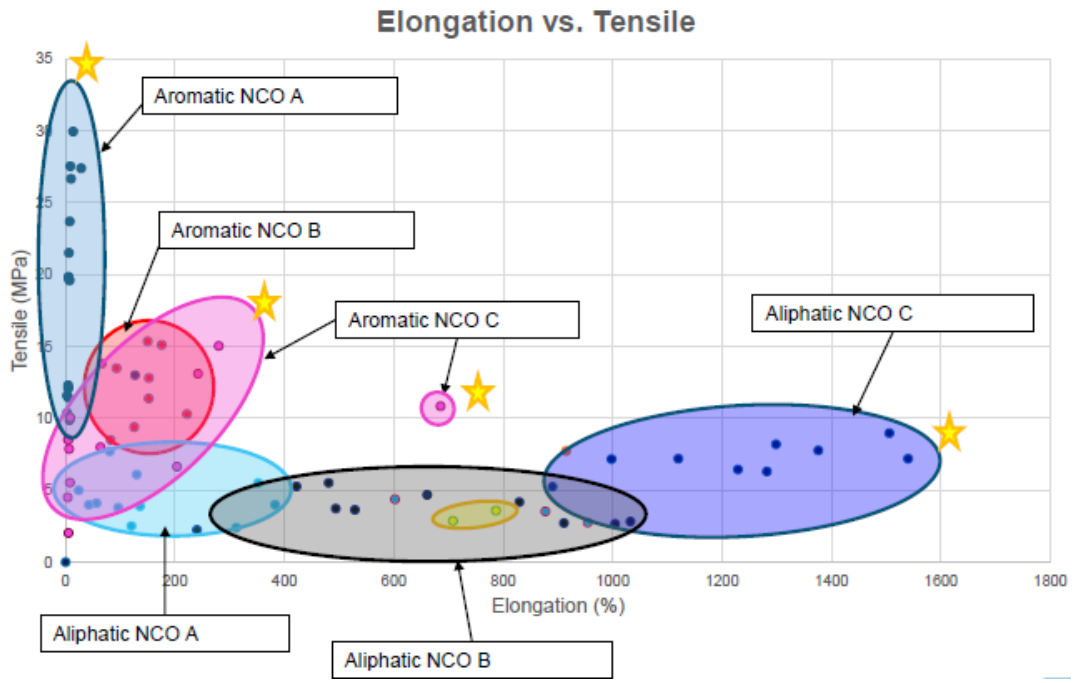


ARE Polyurea



ARE Michael Addition





Polyurea Formulation

- Change diisocyanate component
- Monomer molecular weight
- Monomer functionality
- Backbone chemistry

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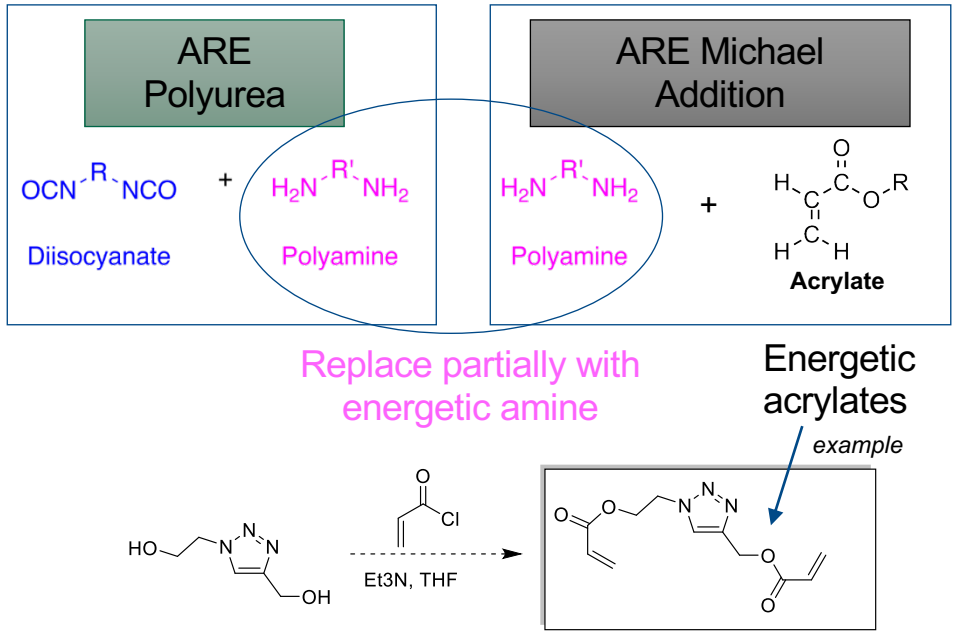
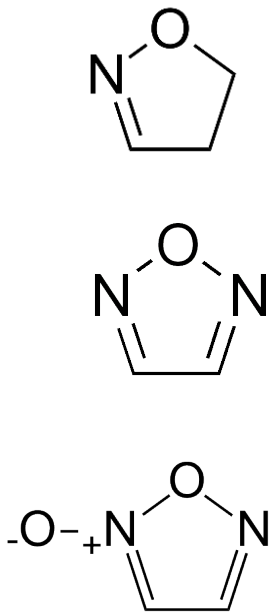
Energetic binder development

Blend energetic monomers into working ARE chemistries without reduction in processing ability or mechanical properties



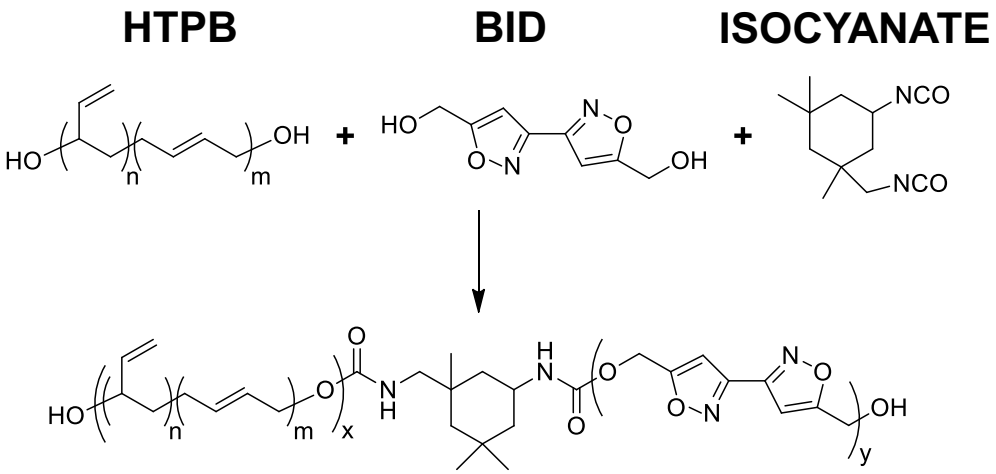
Backbone chemistry well established with diol functionality – synthesis of amine and acrylate functionalities underway

- **Strategy – formulate energetic ring structures into polymer backbone or as pendant groups**
  - **Isoxazole, furazan, furoxan, tetrazole**
  - **Thermally stable**
  - **Highly positive heat of formation**
  - **Higher density**
  - **Not thoroughly investigated as polymers**
- **Challenges:**
  - **Solubility – Most of these monomers are solids – need to formulate blends**
  - **Low Tg – ring structure and reactive diluents yield high Tg**
  - **Copolymerization - uniform network structure**
  - **Extent of cure**
  - **Maintain low viscosity**

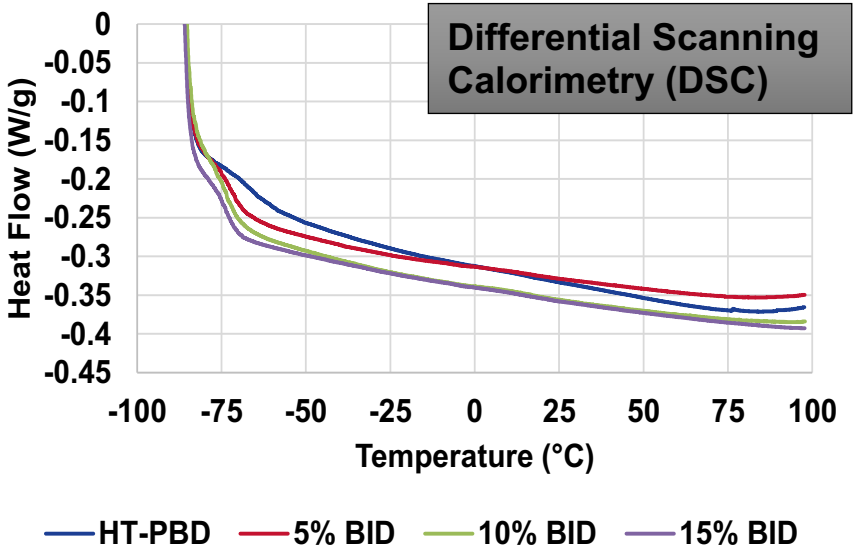


Hydroxyl terminated polybutadiene (HTPB) replacement

- Bis-isoxazoline diol (BID) incorporated as hard block chain extender
- Impact on processing properties, storage properties (T_g, fragility)
- Low miscibility with HT-PBD
- Sequential reaction to initially functionalize with IPDI
- Successfully replaced up to 17.5% of OH functionality in formulation with BID



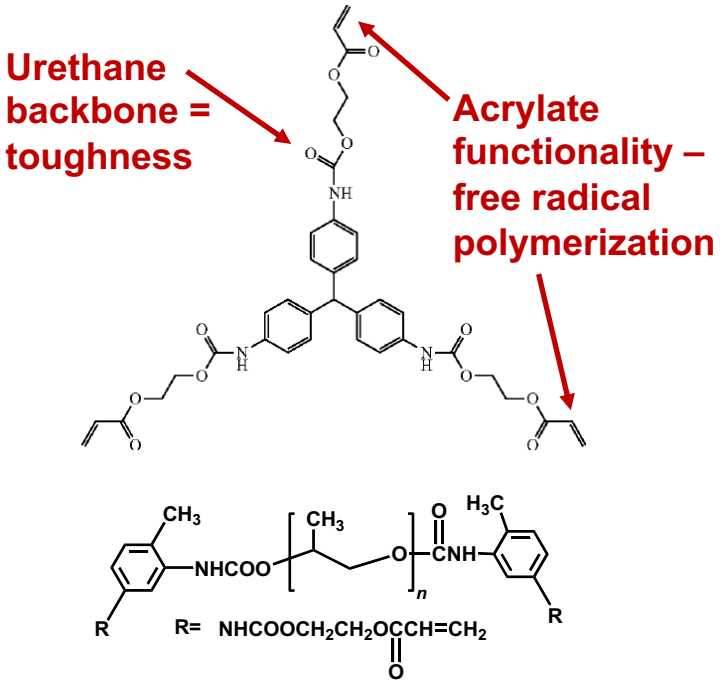
PRE-POLYMER



Sample	T_g
HT-PBD	-64.7
5% BID	-71.8
10% BID	-71.6
15% BID	-73.5

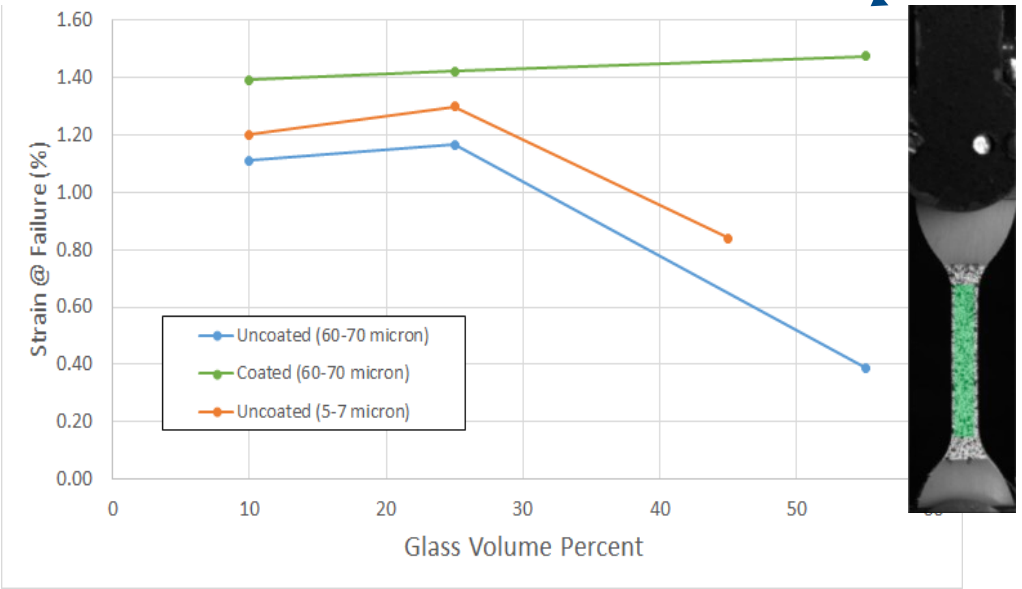
Photo-curable Chemistries

Inert AM binder formulation



Optimizing Particle Surface Chemistry

60 vol% solids loading

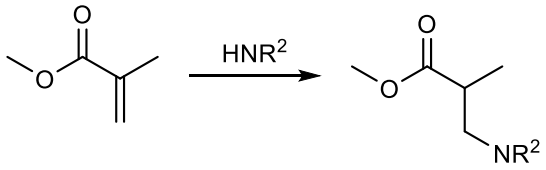


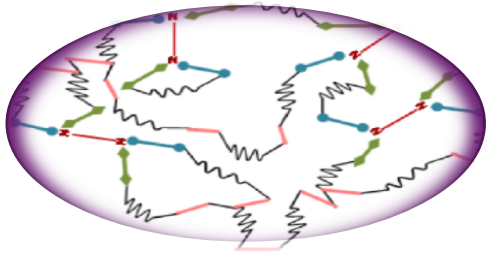
Energetic polymer

- Low Tg
- High extent of cure
- No smoke
- Low char

Aza-Michael Addition

Aza-Michael Addition

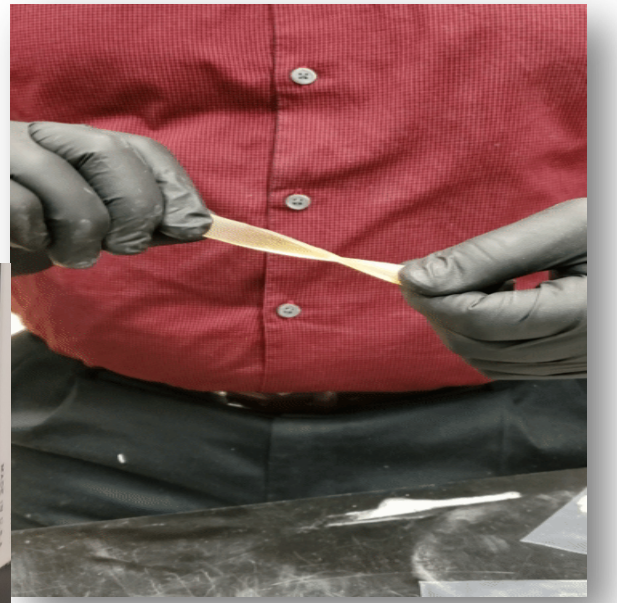




Crosslinked network

Rigid

Elastomeric



Processing conditions

- cured at 60 °C overnight
- postcured 120 °C for 5 hours

Can obtain T_gs ranging from - 40 °C to 46 °C depending on choice of monomers and stoichiometry.

Influence of Amine Structure

DPGDA cured with various amines

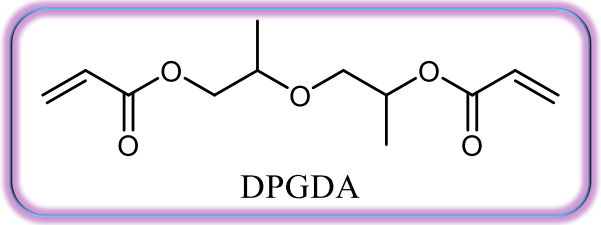
Amine	Tg (°C) [a]
PACM	-10.7
1,5-Diaminopentane	-18.3
diethylenetriamine	-22.0
Jeff Amine D-230	-32.3
Jeff Amine D-400	-40.9[b,c]

Decreasing Tg

Influence of rigidity

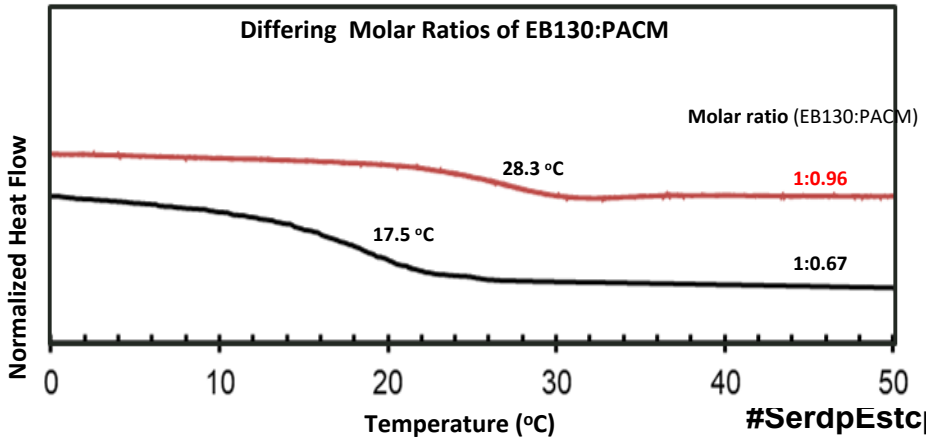
Influence of hetero-atom

Influence of chain length



Conditions

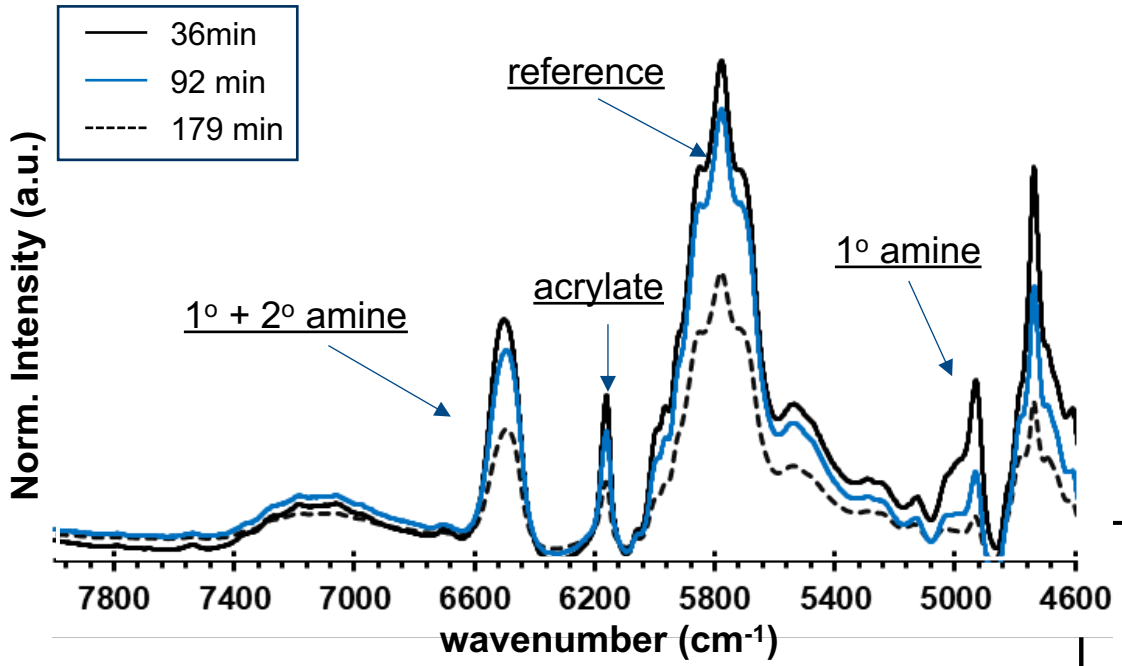
- Cured at 60 °C for 16 hours
- postcured at 120 °C for 5 hours. Ratio of acrylate to amine 1:0.67 (molar ratio)
- T_g measured by DSC



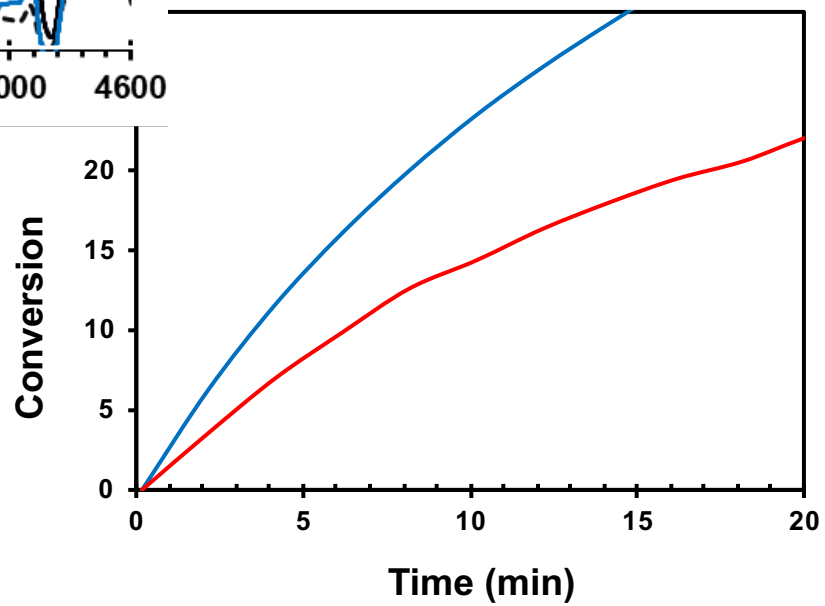
DETA and D-400 required alternate conditions:

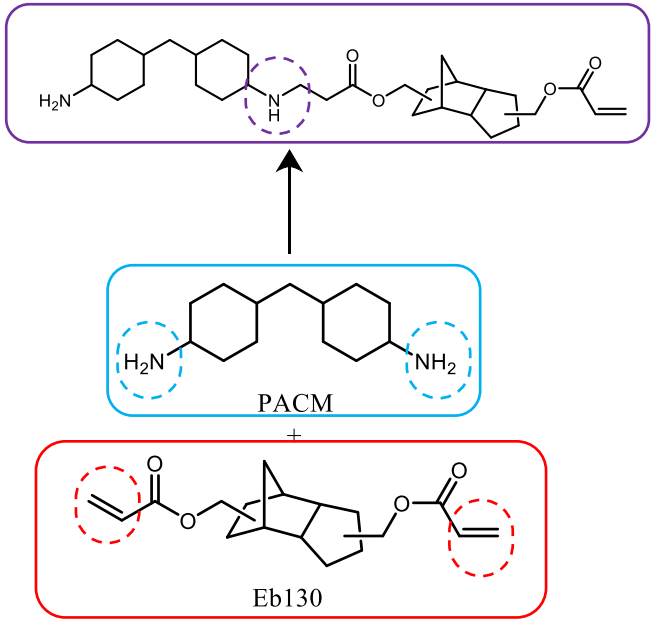
- DETA: acrylate amine ratio was 2:1
- D-400: acrylate amine ratio was 2:1, extended postcure of 10 h at 120 °C.

Reaction with Primary Amines is too Slow

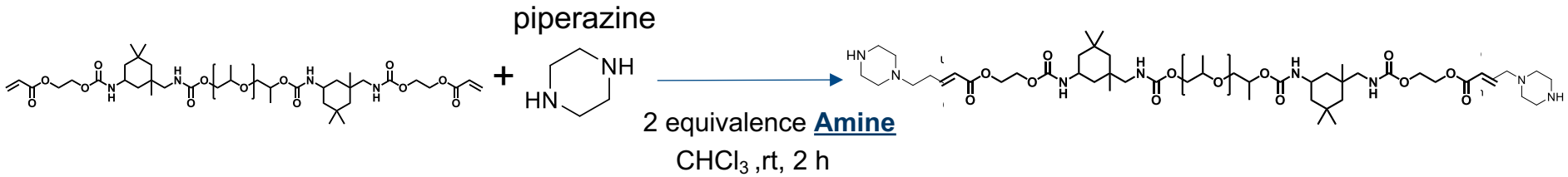


- Can use NIR to monitor reaction kinetics.
- At 25 °C 2° amine (formed) is unreactive.
- Thus change in [acrylate] is due to reaction with 1° amine.

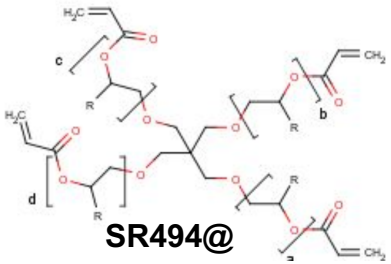




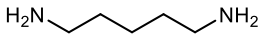
Piperizine Modification and Tetra-functional monomer to Reduce Gel Time



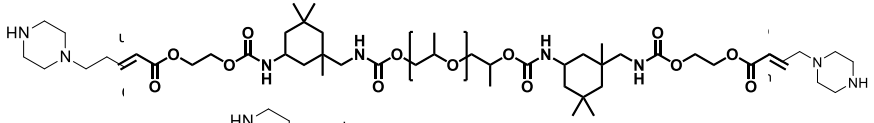
Acrylate

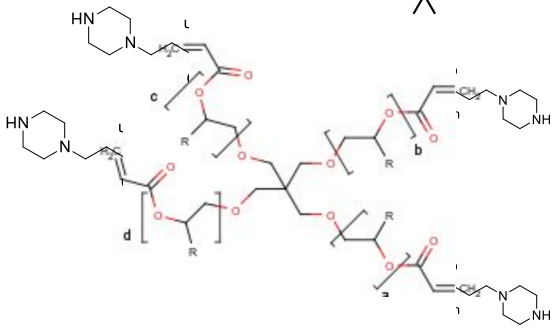


Amine



1,5-Diaminopentane

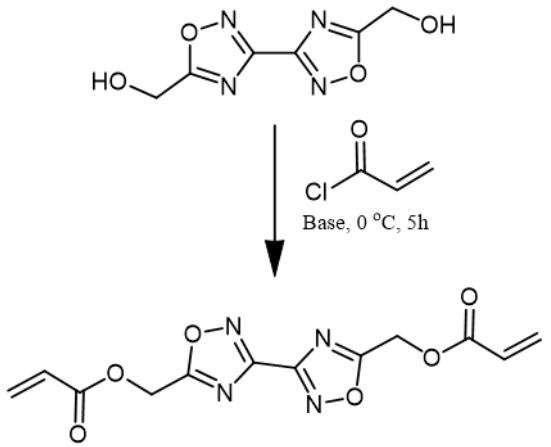




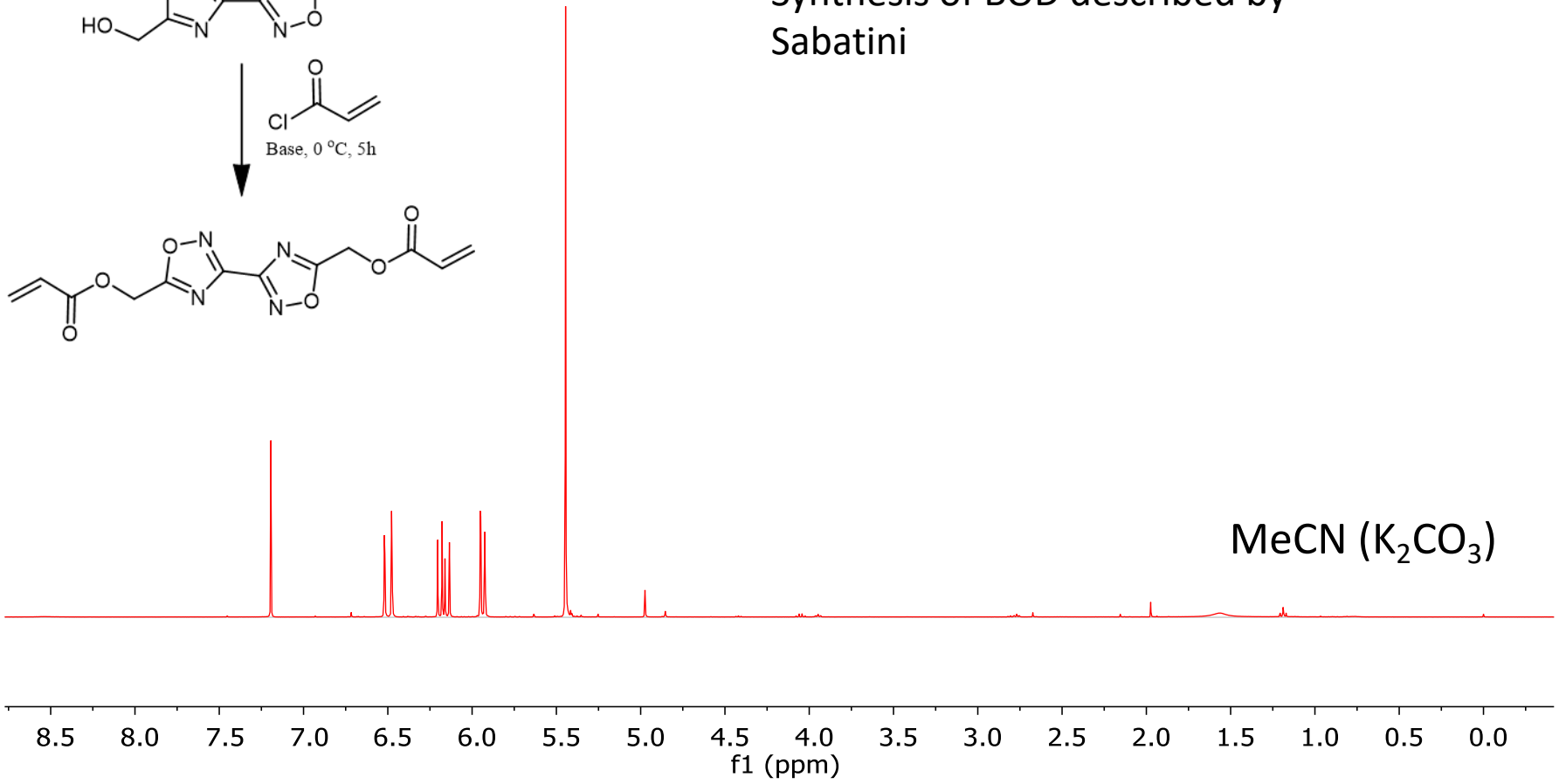
2:2:1 mixture

Gelled after ~2 minutes; (1.05:1) acrylate N-H equivalent amine functionality;
5% cabosil; 1.5% pTsOH-IPA (2:1)≤

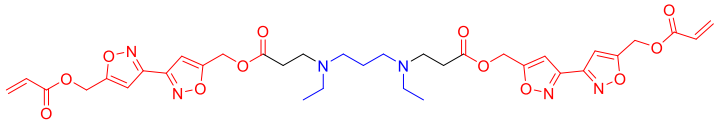
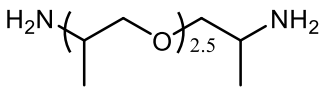
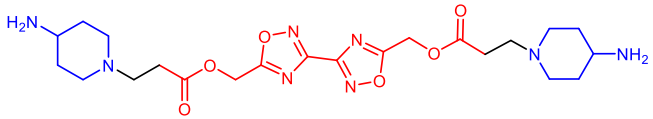
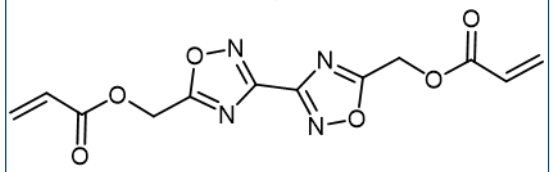
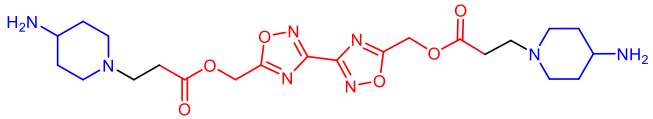
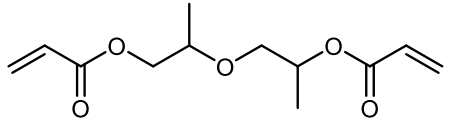
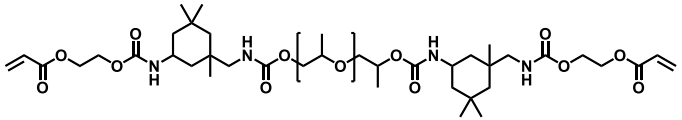
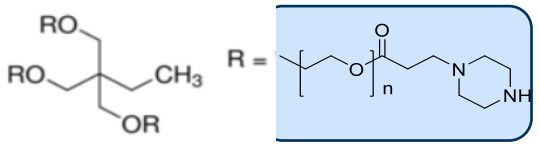
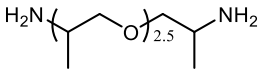
Synthesis of Clean-Burning Monomers



Synthesis of BOD described by Sabatini



Cured Energetic Elastomers

Energetic Monomer (EM)	Curative	Results
	 Jeff Amine D-230	Acrylate:Amine mass amounts 0.5g:0.1g Tg: -10.5 °C
		Acrylate:Amine mass amounts 1.25g :1g Tg: 19 °C
	 DPGDA	Acrylate:Amine mass amounts 1g:1.25g EM = 55 wt% Tg: -29 °C
 **Ebecryl 4848**	 (TMPETP) (Mn~1170)  Jeff Amine D-230	• Tg's determined from DSC. • All formulations featured (3:2) Acrylate:Amine molar ratio • -20 °C Tg • >400% elongation

DEVCOM ARMY RESEARCH LABORATORY

SERDP • ESTCP SYMPOSIUM #SerdpEstcp2019

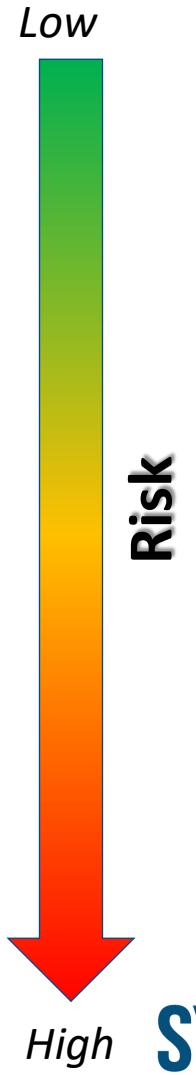
Binder development status

- **Photo-curable Binder Development**
  - Supports SLA, paste extrusion
  - **Printed elastic in-house formulation via SLA (Tg ~ - 50 deg C, > 100% elongation) and paste extrusion**

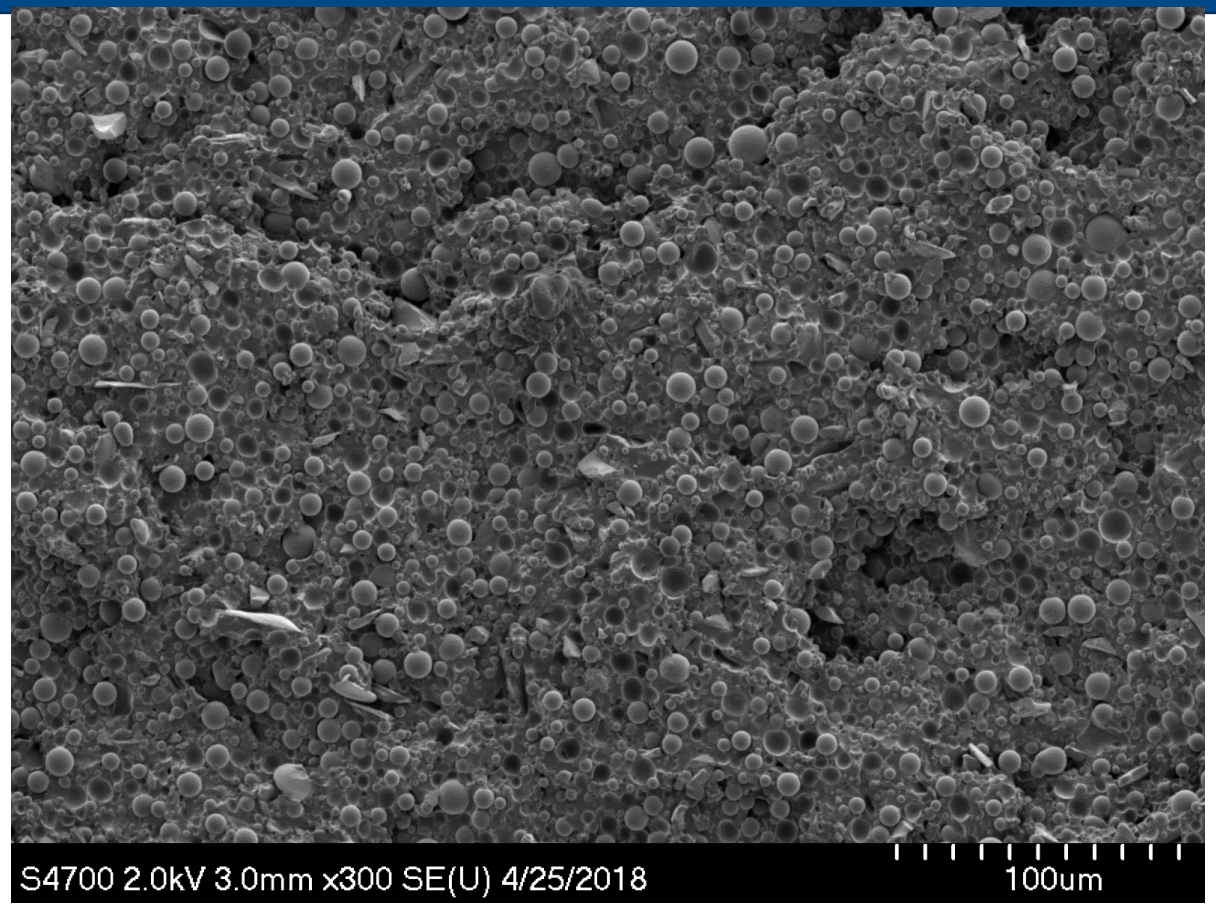
- **ARE polyurea (PU) – established chemistry**
  - Elastic formulation (Tg ~ -70ºC) – anticipated to be better than HTPB
  - Goal of HMX-loading to 75+ wt. %
  - **Increasing inert solids loading in PU from 60 vol. %**

- **Aza Michael Addition (MA) – amine + acrylate chemistry**
  - Eliminates use of isocyanate in formulation
  - Formulate MA binders that fall within the ARE processing window
  - Adapt MA formulations to yield low Tg polymer with good mechanical properties
  - **Developed a printable chemistry with good MPs and fast gel time**

- **Energetic binder development (PU, MA, and photo-curable)**
  - **Formulated several energetic photo-curables**
  - **Formulating energetic moieties into PU and MA binders**



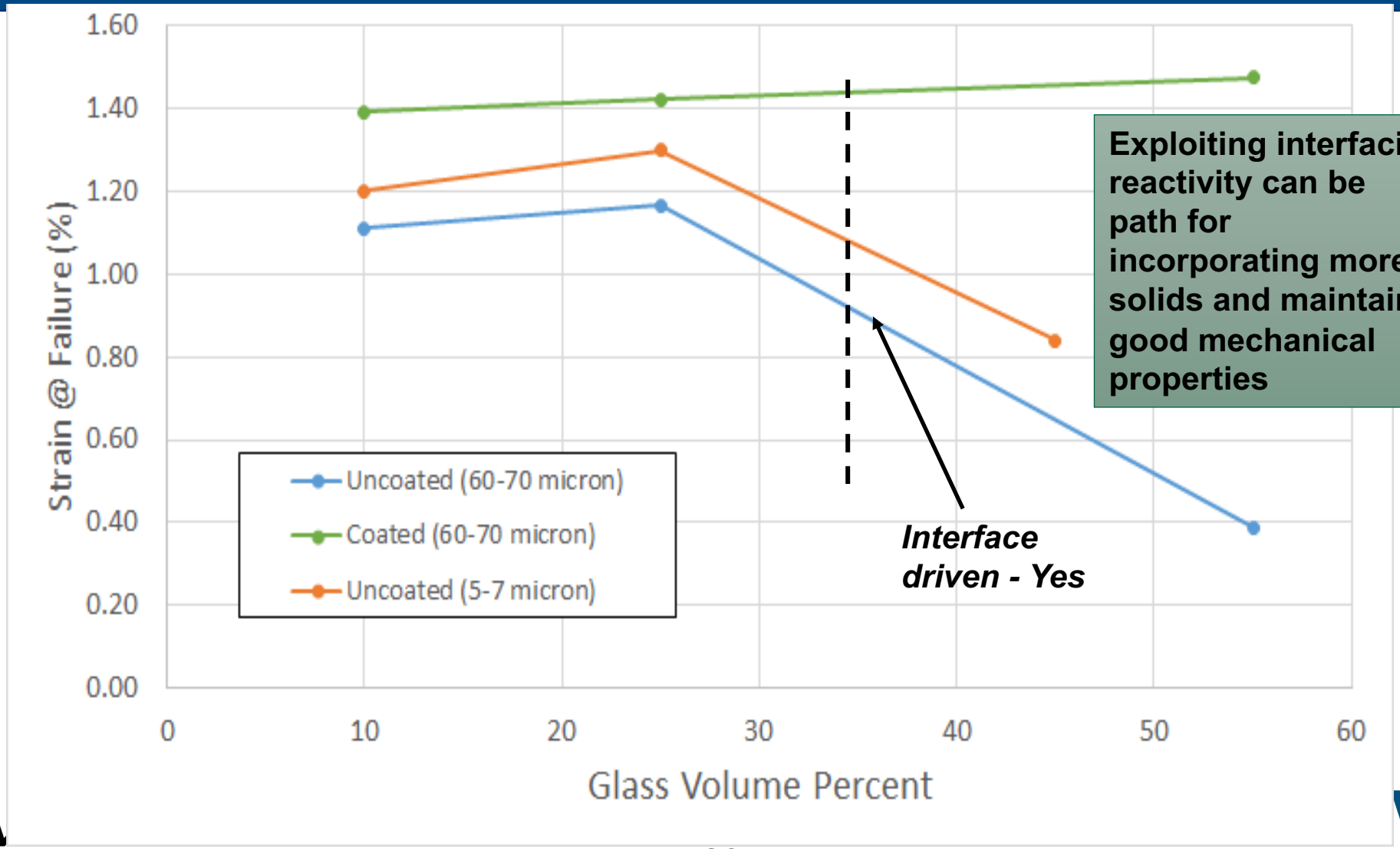
Tailor the Interface for the Binder



Highly solids-loaded elastomer – approaching maximum packing fraction (~55 vol%)

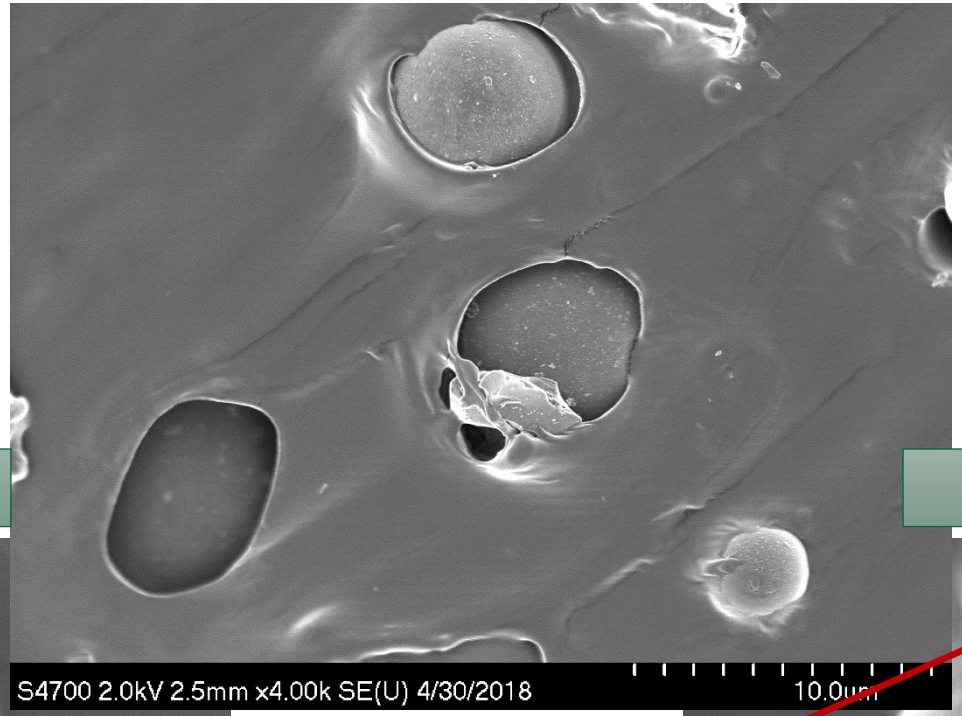
- Bonding agent: Molecule that reacts with both solid and binder
- Approach 1: Additive bonding agent that preferentially migrates to solid surface
- Approach 2: Modify solid surface prior to mixing

Glass-polymer interface drives mechanical performance

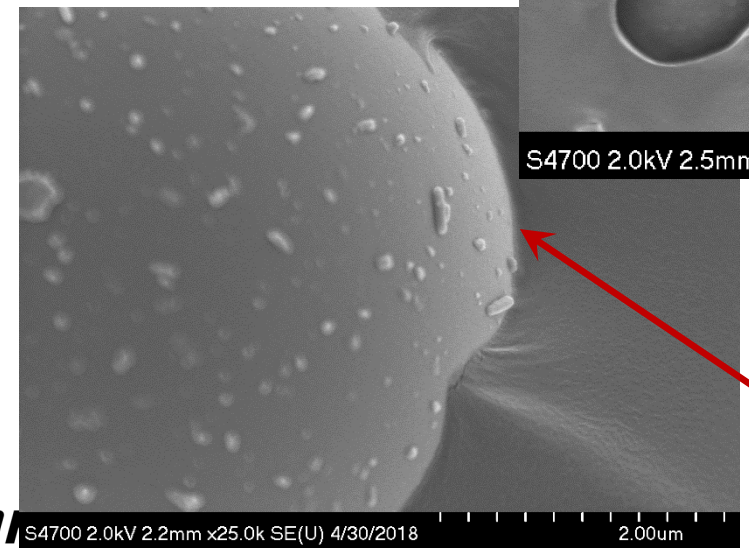


Exploiting interfacial reactivity can be path for incorporating more solids and maintain good mechanical properties

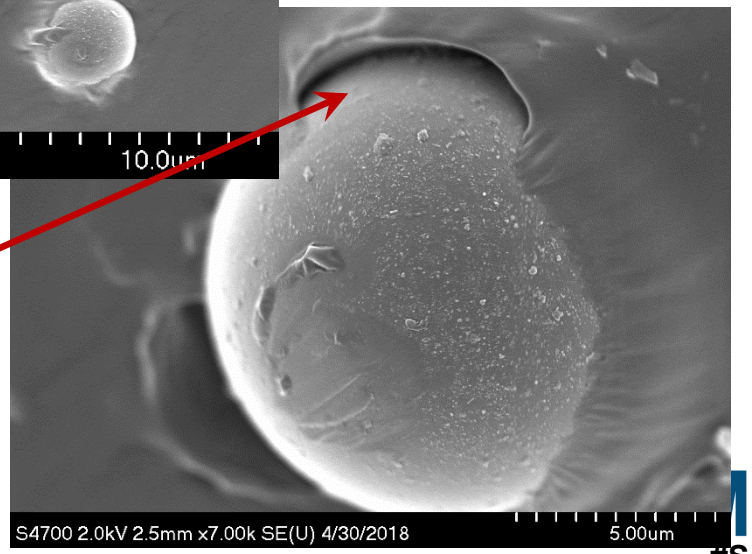
SEM of Failed Fracture Plane from Tensile Tests



Surface Coating



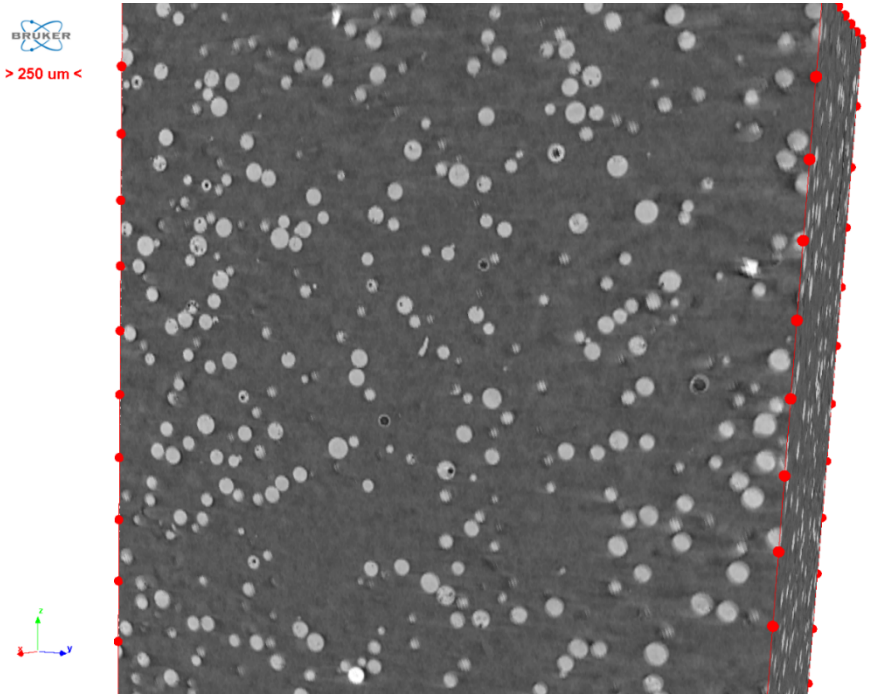
No Surface Coating



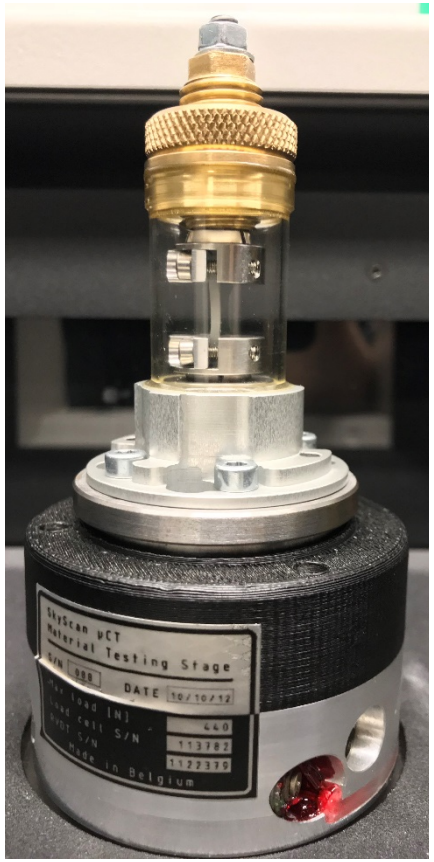
Onset of particle cavitation

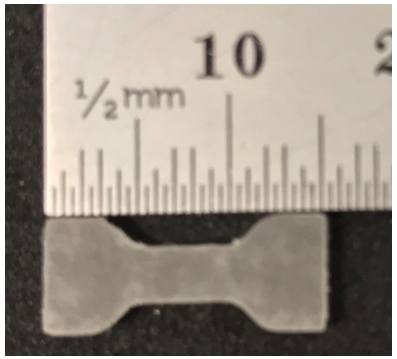
Good interfacial bonding – no cavitation

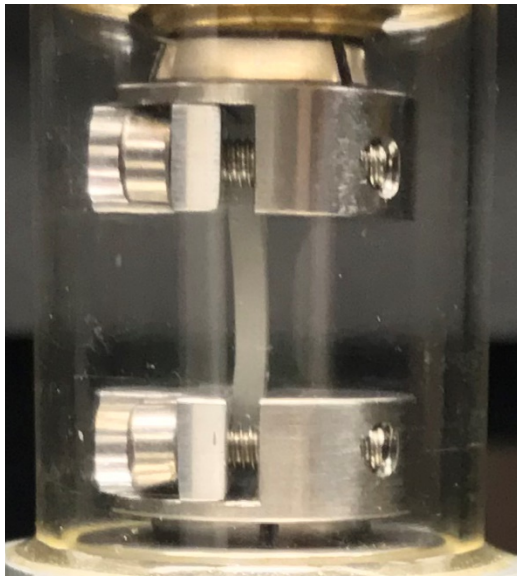
CT scans for use to investigate polymer-particle interactions prior to fracture



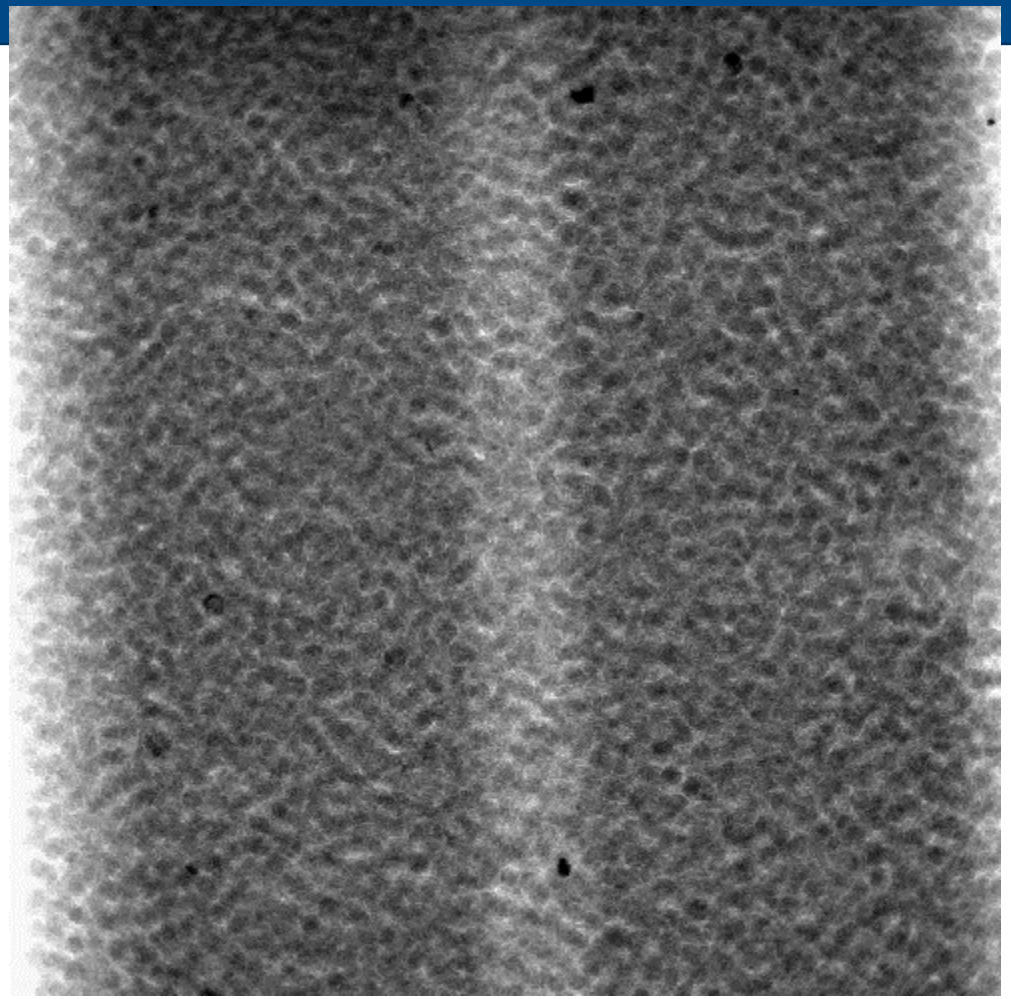
10 vol. % glass loading







Sample Failure



45 vol. % glass spheres

Video saved at 20 fps
4 second exposure time per frame
300 total frames

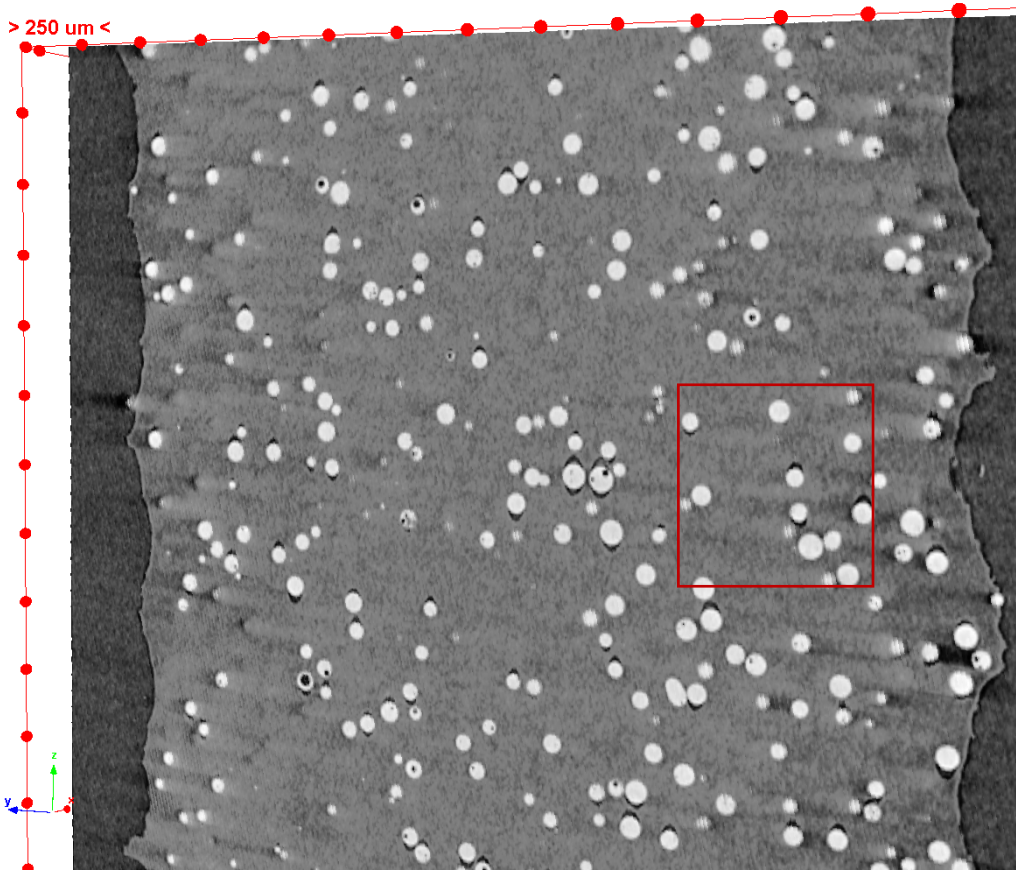
~15 second video shows failure over approximately 20 minutes

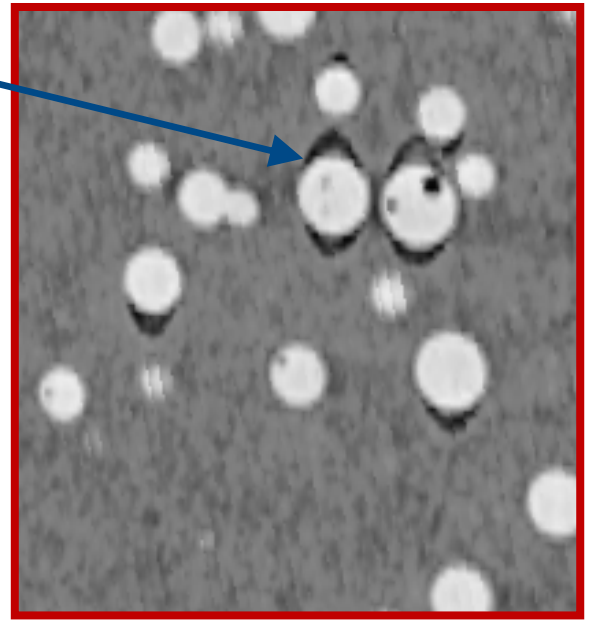
Coated Particles

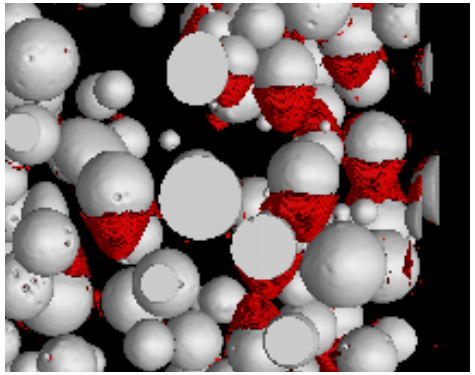
Uncoated Particles

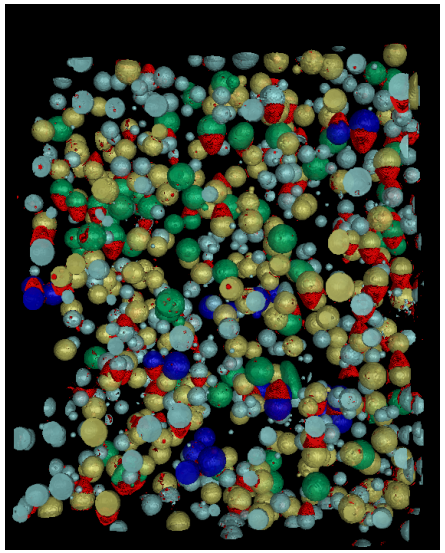
CT Scans under Strain

1. *Particle cavitation*
2. *Void dilation and growth*





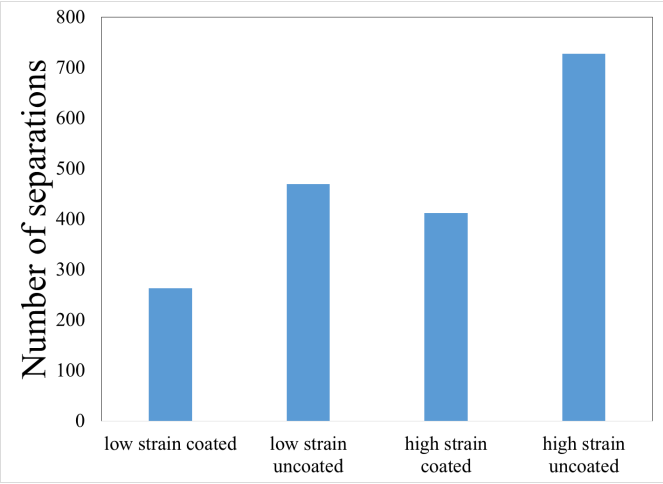


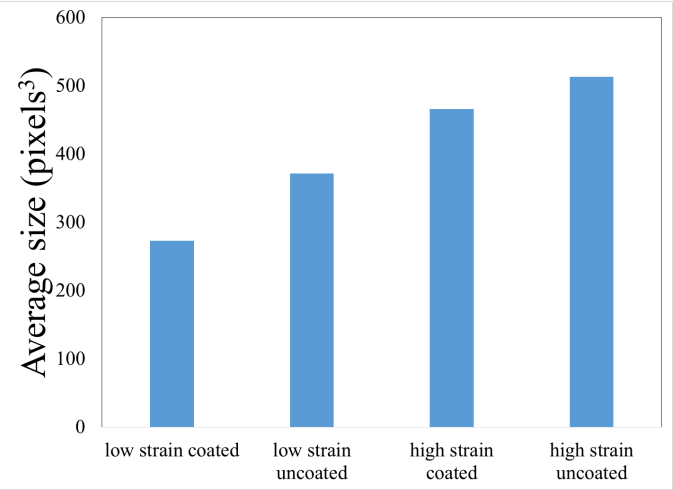


Strain direction

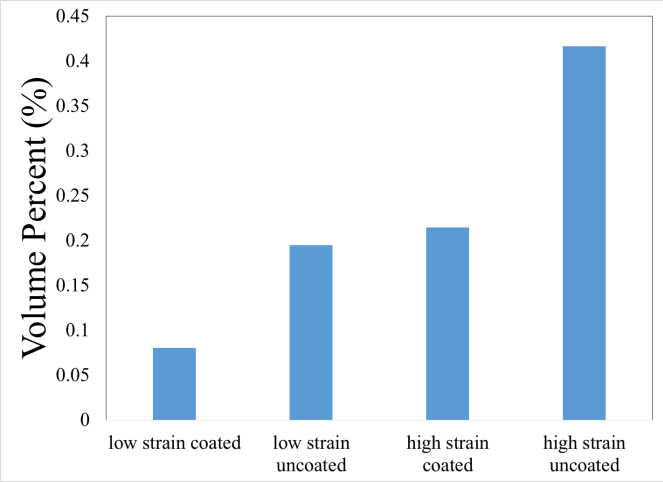
10 vol. % glass loading

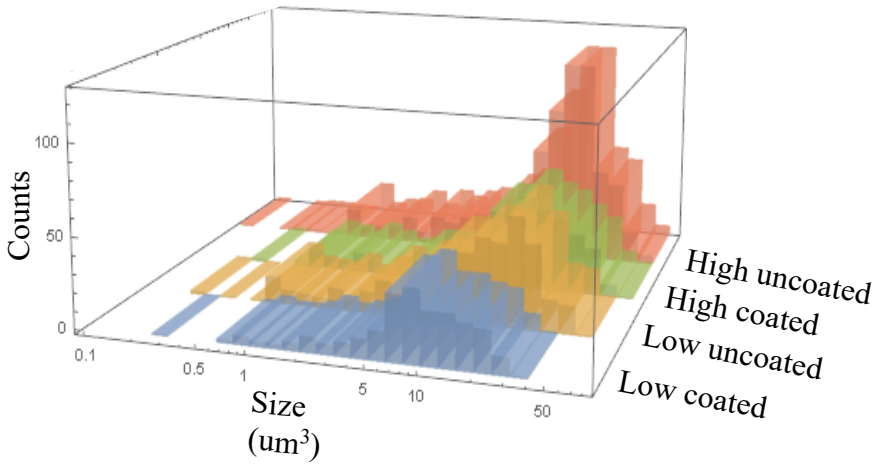
CTAn quantitative Analysis





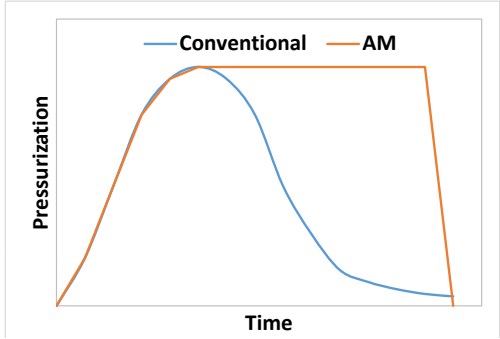
Solids Loading Volume, Particle Size, Coupling Agent – All Matter!

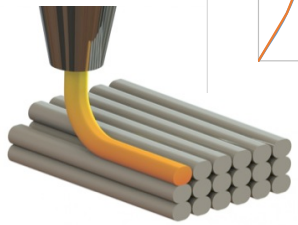


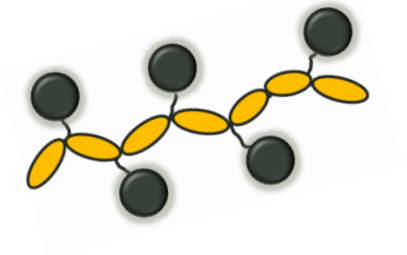


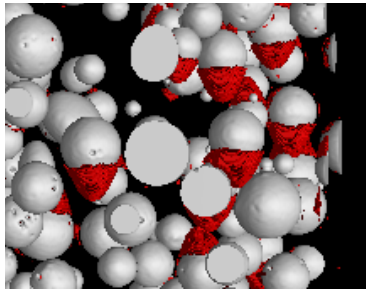
ARL Energetic AM Focus Areas

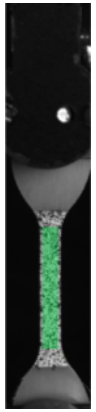
- Applications – gun/rocket propellant, explosives
- Mission – develop feedstocks and processes to enable AM
- AM Processing
  - Techniques: SLA, reactive extrusion
  - Improved resolution of highly loaded polymers (~55-60 vol%)
- Feedstock Development
  - Rapid curing chemistries – photo, Michael Addition, polyurea
  - Energetic (or consumable) binders for AM
- Interfacial Design
  - Solid-binder wetting during processing
  - Tailored interfacial reactivity or improved compatibility
- Mechanical Characterization
  - Key failure mechanisms in highly solids-loaded composites
  - Answer question: “What makes a good binder?”











Acknowledgments

- Polymer AM Team – Dr. John La Scala (Team Leader)
  - Polymer Formulation – Dr. Ian McAninch, Dr. Anthony Clay, Dr. Joshua Orlicki, Dr. Alice Savage
  - Surface Science – Dr. Nichole Zander, Dr. Jennifer Sietins
  - Manufacturing – Mr. David VanOosten, Mr. Joshua Mitchell, Mr. Zach Boelter
- Synthesis – Dr. Joe Banning, Dr. Jesse Sabatini, Dr. Edward Byrd
- Modeling – Dr. Andrew Gaynor, Dr. Efrain Hernandez, Mr. Paul Conroy
- PPG – Ms. Cindy Kutchko