



Ultrafast Stiffening of Concentrated Thermoresponsive Polymer-Mineral Suspensions

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Acknowledgements

T R A N S C E N D



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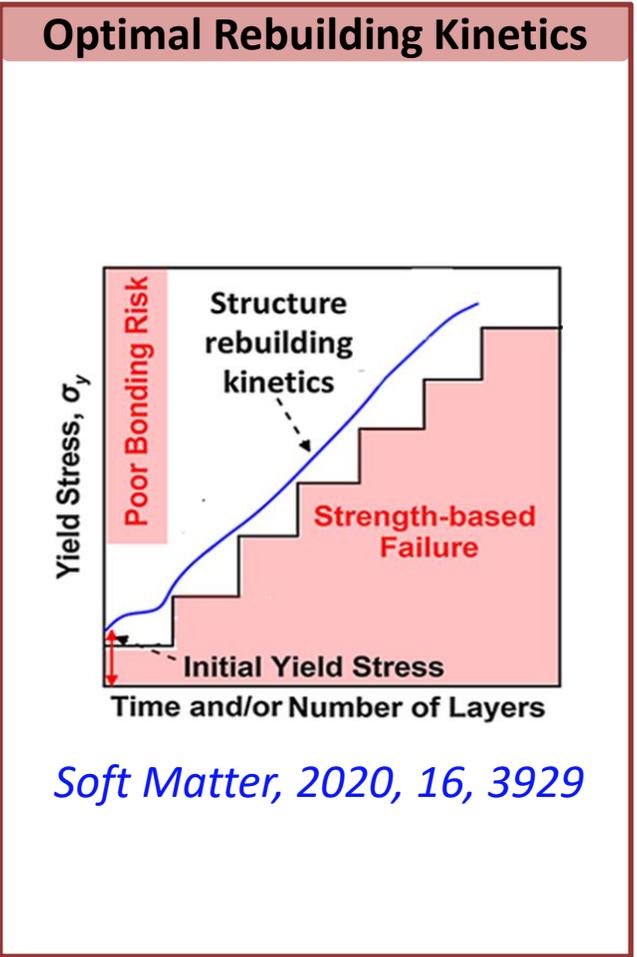
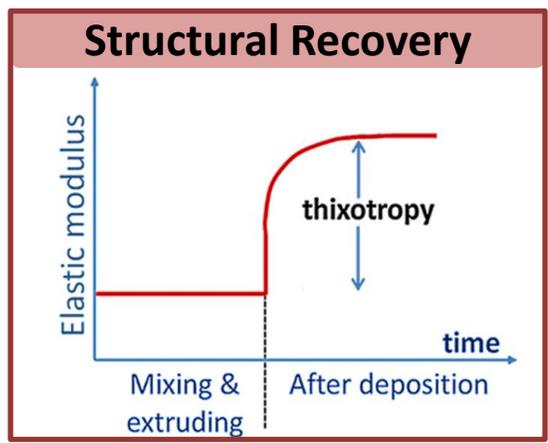
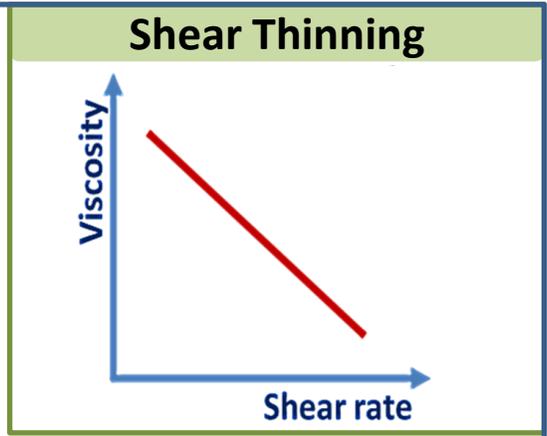
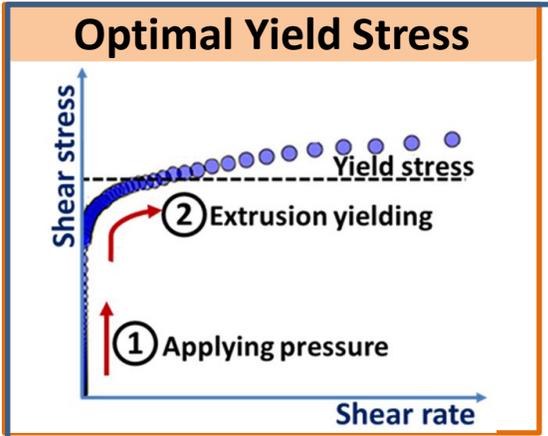




3D Printable Slurries: Rheological Requirements

Pre-printing Requirements

Post-printing Requirements



Soft Matter, 2020, 16, 3929

- Rheology control of printing slurries is crucial
- Optimal rebuilding kinetics is essential to ensure the buildability

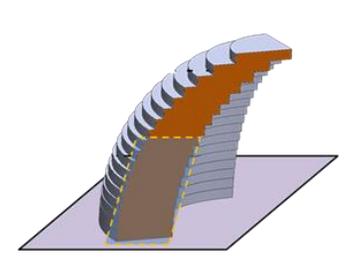
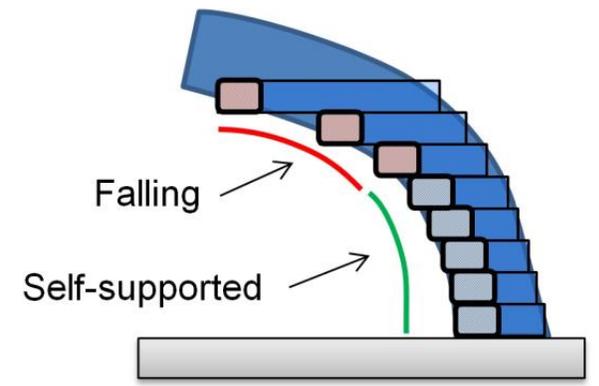
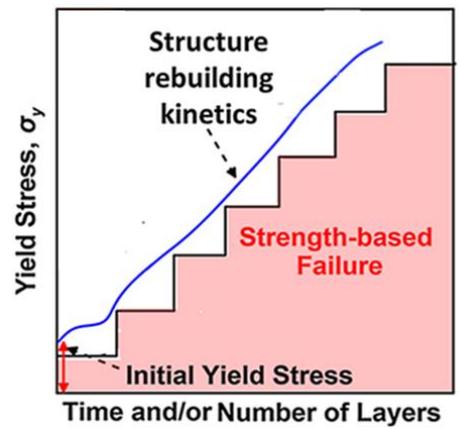


3D Printable Slurries: Requirements & Challenges

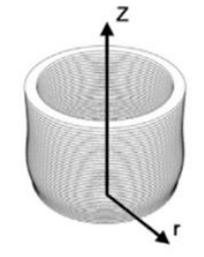
- Slow fluid-to-solid transition greatly restricts:
 - Printing speed
 - Print height
 - Maximum possible overhang
 - Print Fidelity

- Controllable rapid stiffening:
 - ensure the buildability of the structure
 - enables overcoming the limitations of layer wise printing

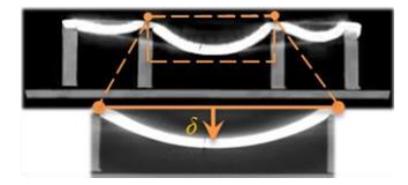
- Selected slurry systems: Quartz, Calcite, Portlandite, Binary & Tertiary mixtures



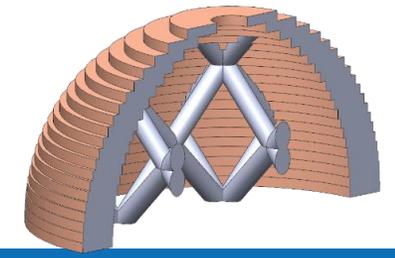
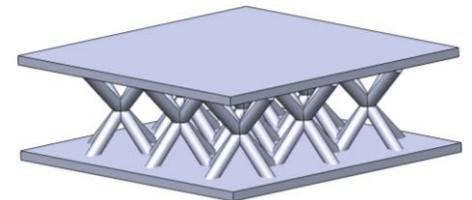
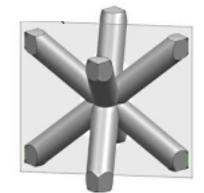
Higher overhangs



Improved print height and print fidelity

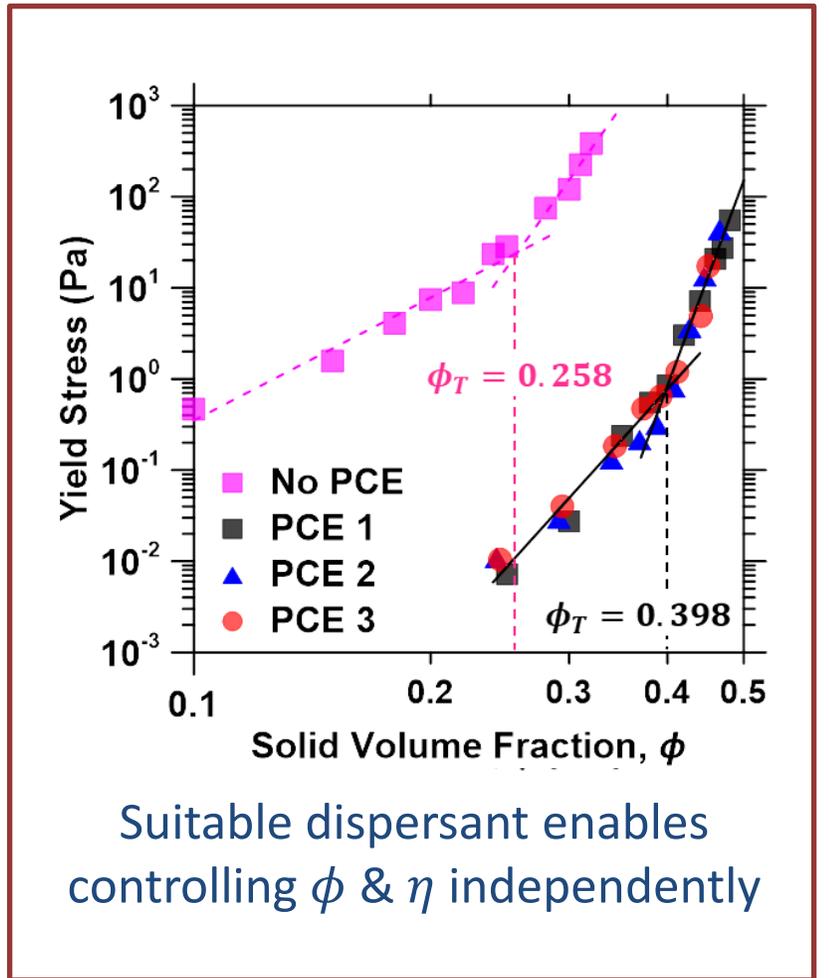
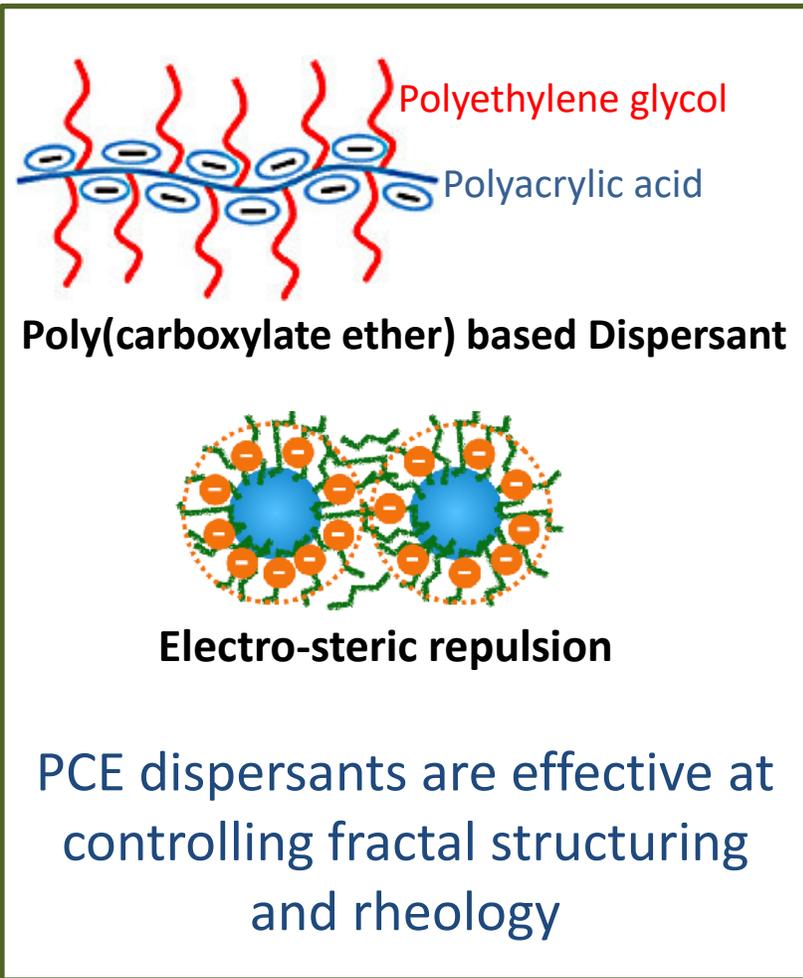
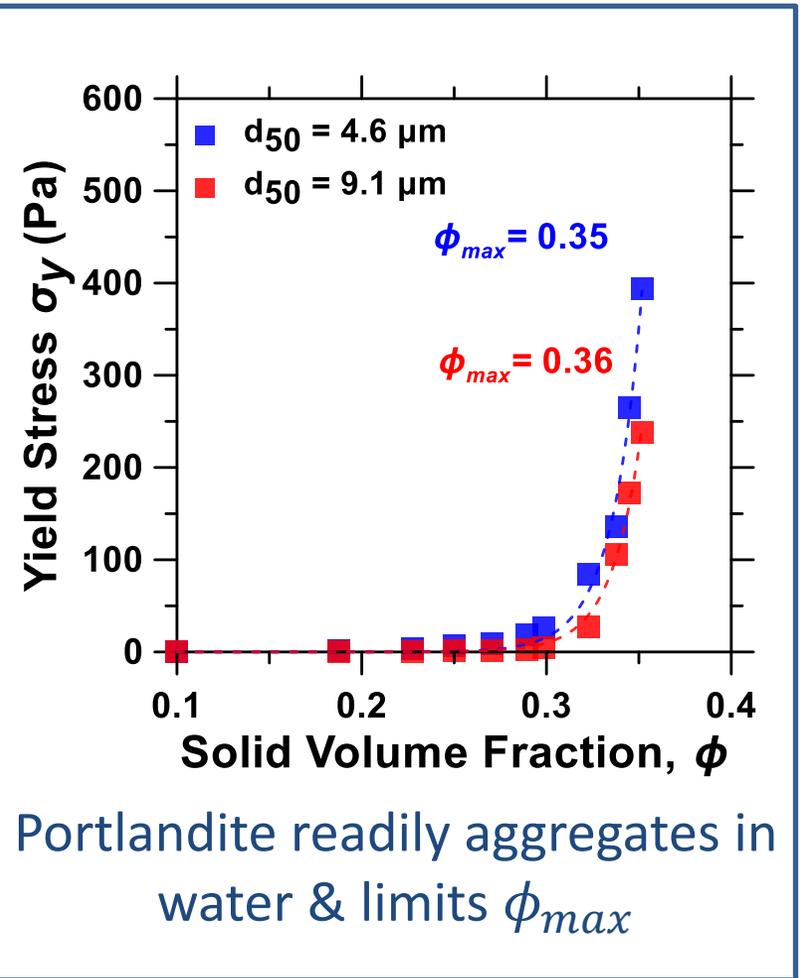


Improved free standing length





Controlling Pre-printing Slurry Rheology: Ensuring Extrudability

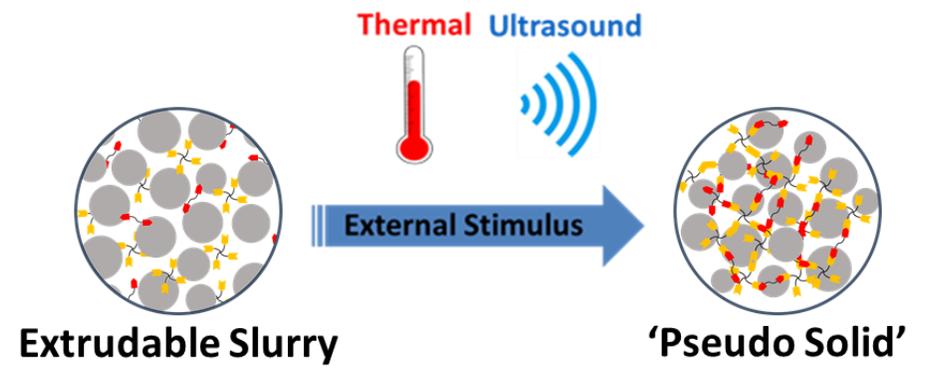


1. S. Kandy et al., *Langmuir* 2020, 36, 10811
 2. S. Kandy, S. Srivastava, G. Sant et al. (2022), *In Preparation*

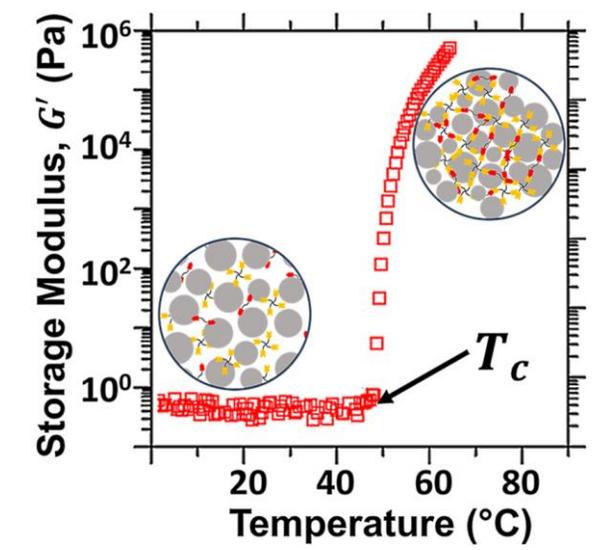
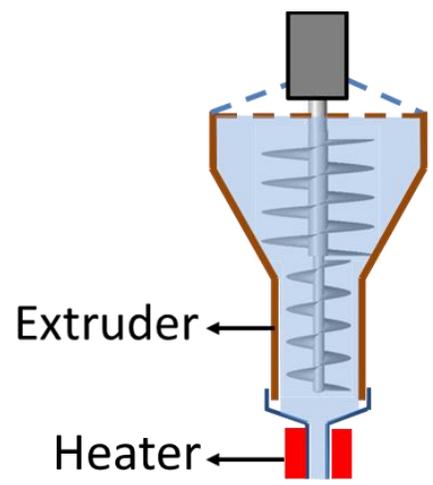
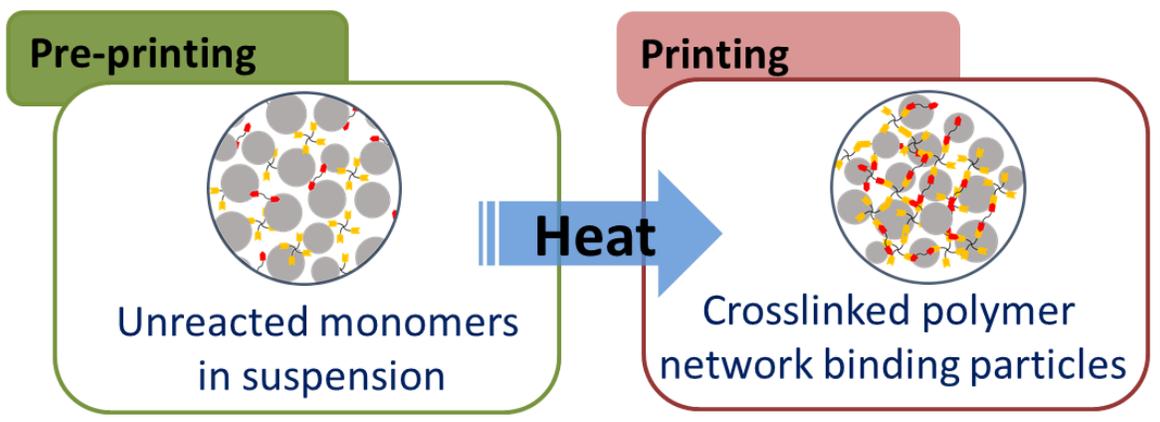


Achieving Rapid Stiffening: Stimuli-Responsive Printing Slurries

- Incorporating a stimuli-responsive secondary binder which can trigger rapid stiffening
- Secondary binder is triggered during and/or after printing to induce rapid stiffening



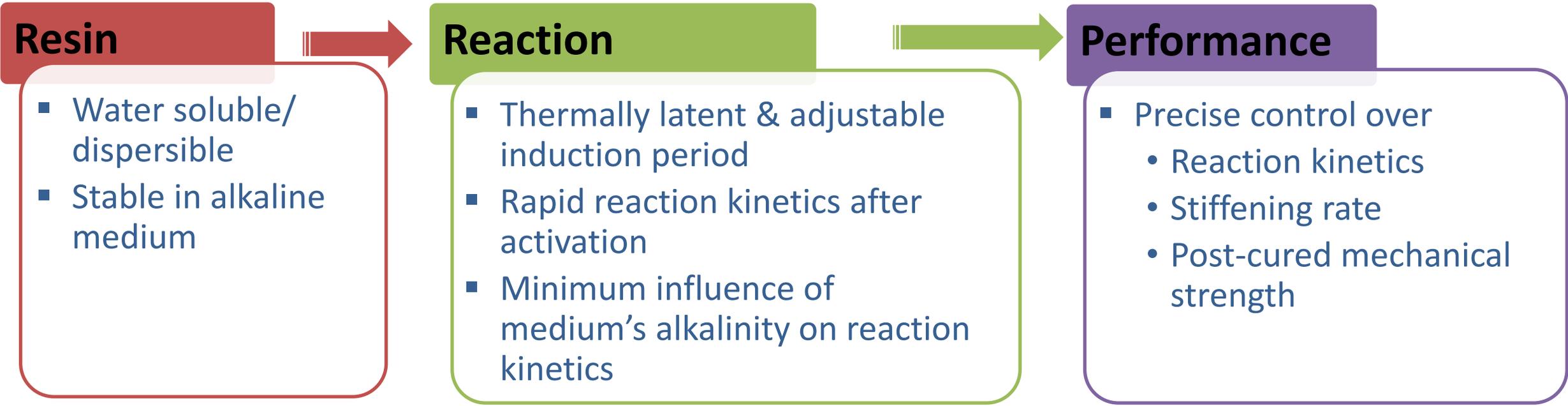
Thermoresponsive Printing Slurries



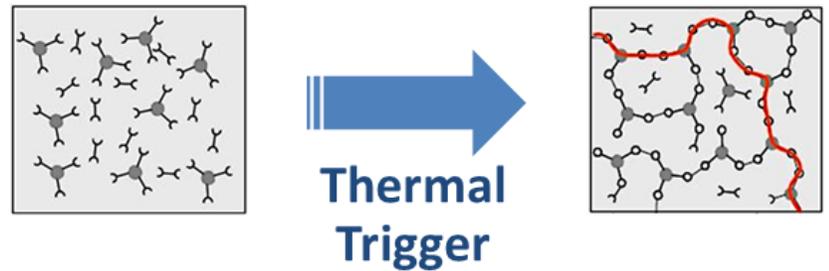
1. S. Kandy et al., Materials & Design, 2021(Under review)
 2. US Patent 17/529763 (Pending)



Thermoresponsive Suspension Formulation: Prerequisite Attributes



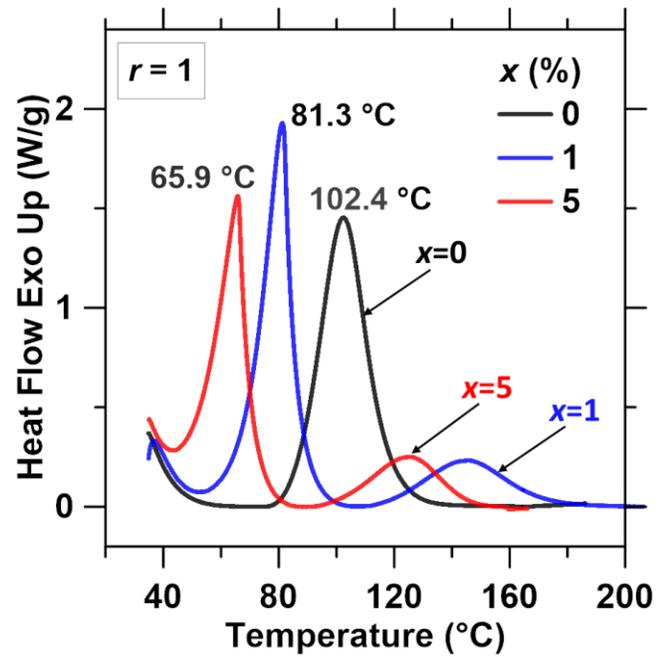
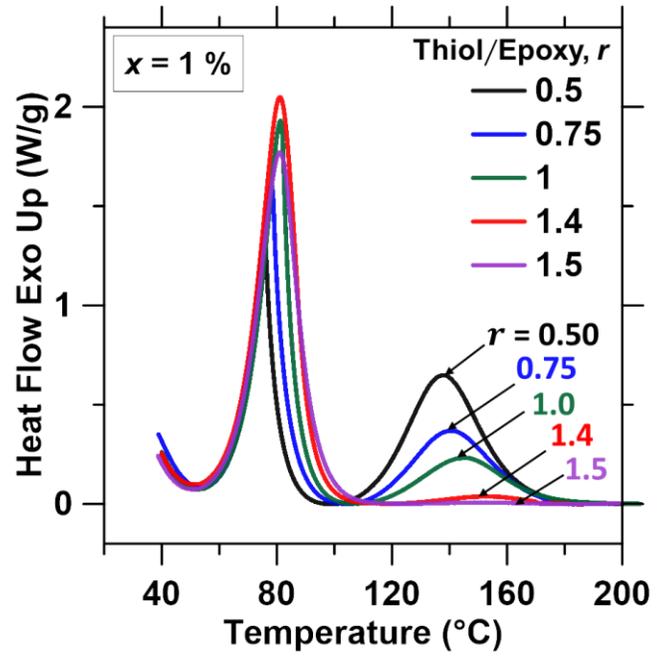
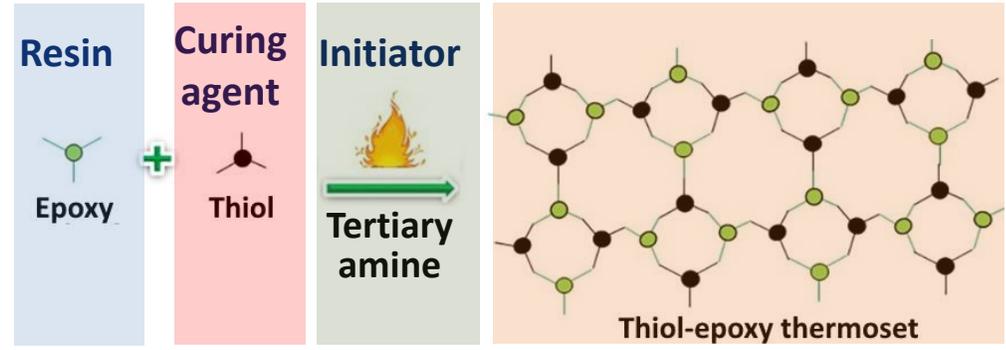
- **Potential thermosetting compositions**
 - Condensation polymerization reactions
 - Free Radical polymerization reaction





Thermoresponsive Formulation: Amine Catalyzed Epoxy-thiol 'Click Chemistry'

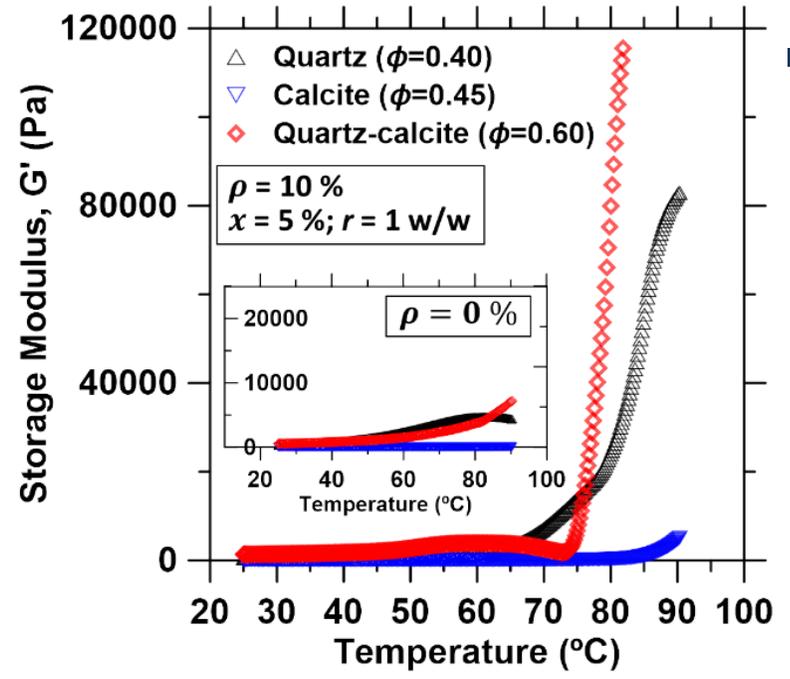
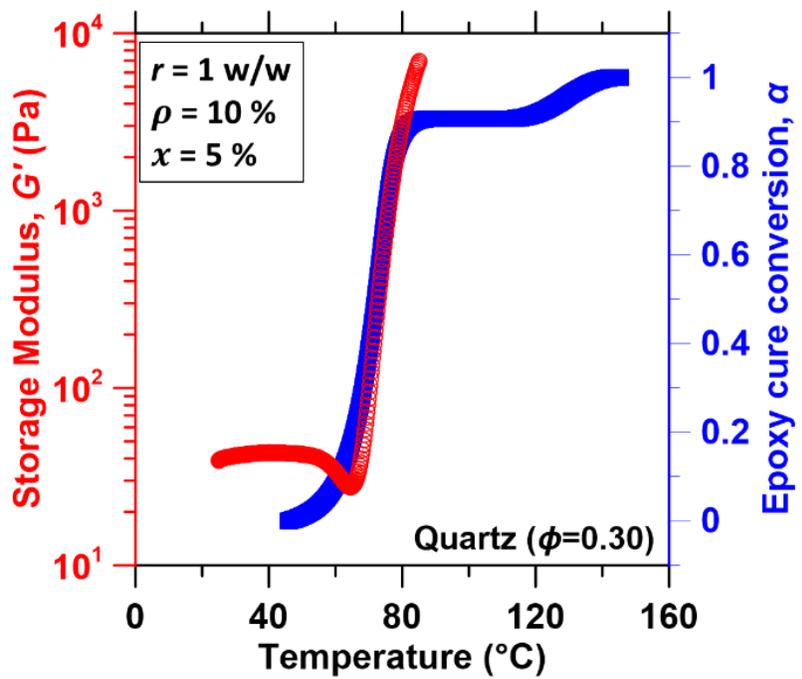
- Fast reaction kinetics & strong auto-acceleration when $T > T_{crit}$
- Tertiary amine catalyzed reactions are thermally latent
- Tunable reaction kinetics & thermal response
 - Resin dosage (ρ)
 - Thiol-to-epoxy mixing ratio (r)
 - Initiator dosage (x)
 - Solid loading (ϕ)





Thermomechanical Behavior of Mineral Suspensions

- At $T > T_c$, polymer network build-up leads to gelation
- Gelation results in rapid shoot up in dynamic moduli and viscosity



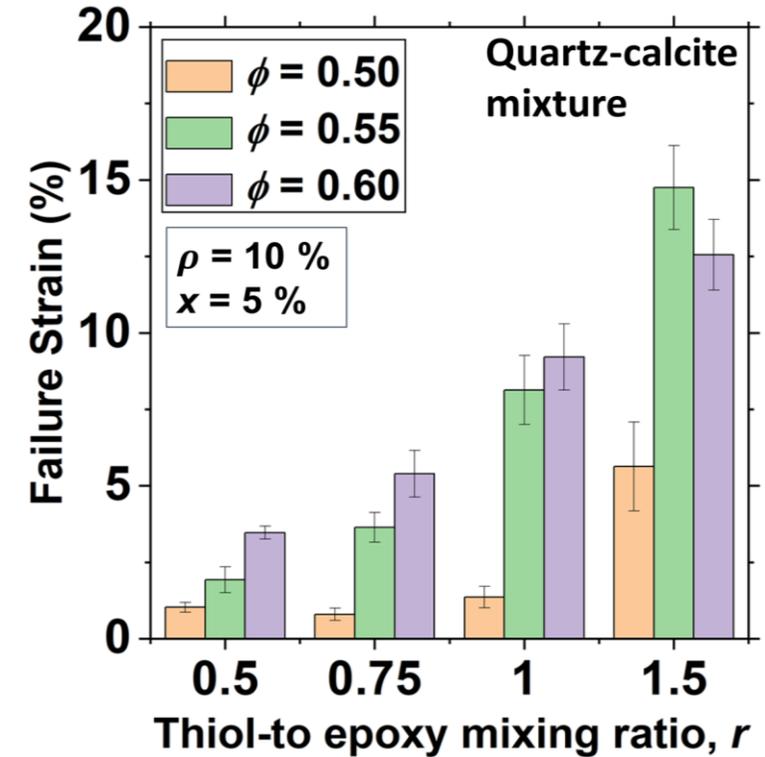
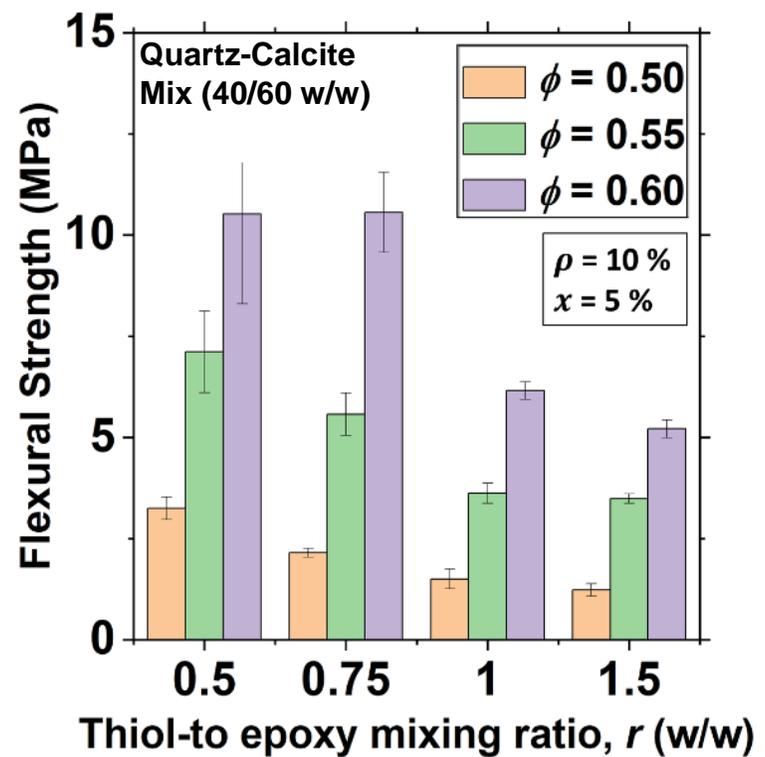
- Controlled Rapid solidification:
 - Average stiffening rate: ~ 500 Pa/s
 - Activation time: $30 \text{ s} < t < 200 \text{ s}$

ρ : Resin dosage; r : Thiol-to-epoxy mixing ratio; x : Initiator dosage



Thermoresponsive Rapid Stiffening in Printing Slurries

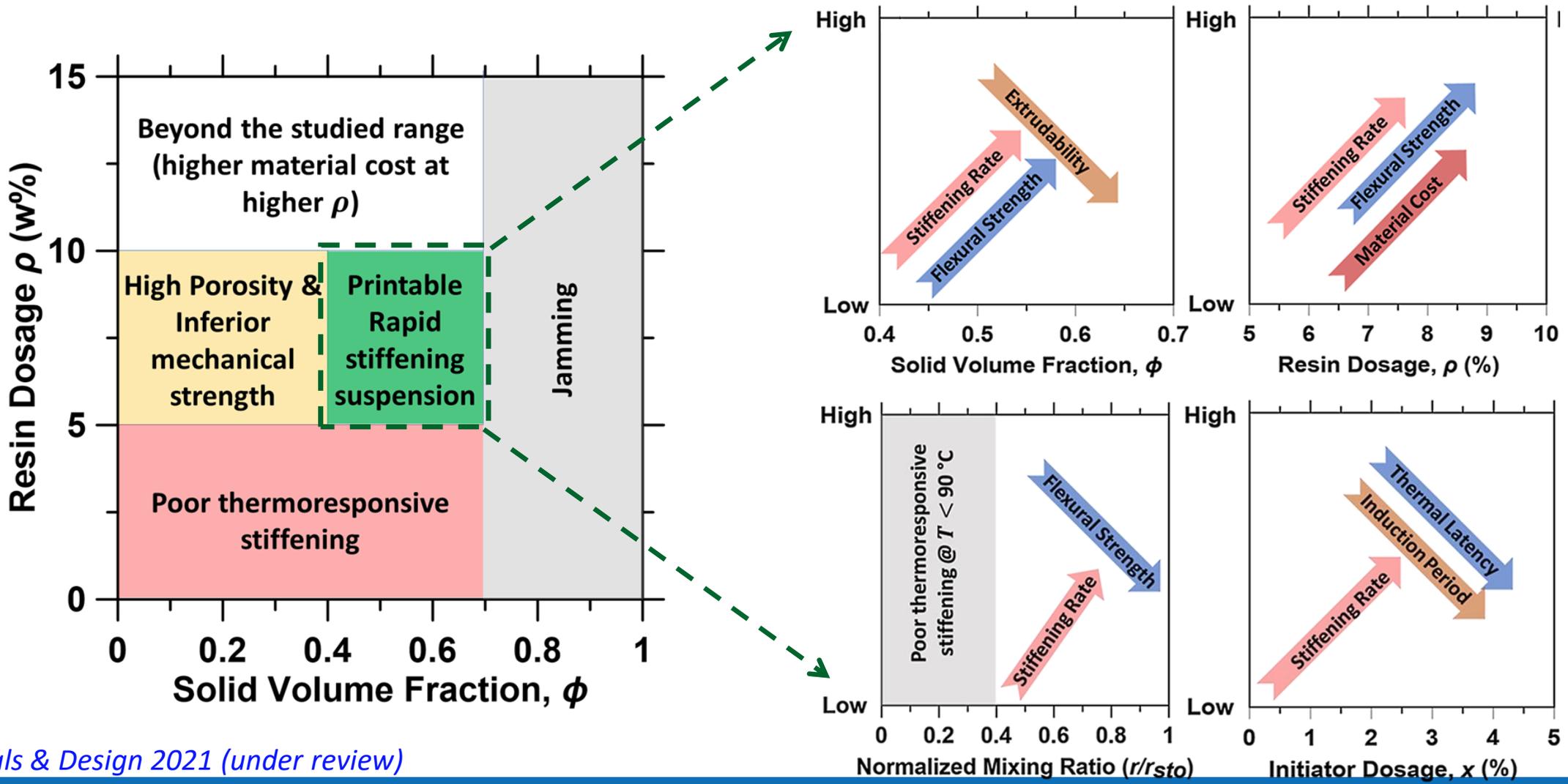
- Achieved a precise control over the suspension rheology:
 - Optimal pre-print rheology ensuring extrudability
 - Controllable induction time and thermal latency
 - Adjustable stiffening rates
 - Enhanced & tunable mechanical strength
- Formulations achieve 1 MPa strength achieved in $t < 2$ min



ρ : Resin dosage; r : Thiol-to-epoxy ratio; x : Initiator dosage



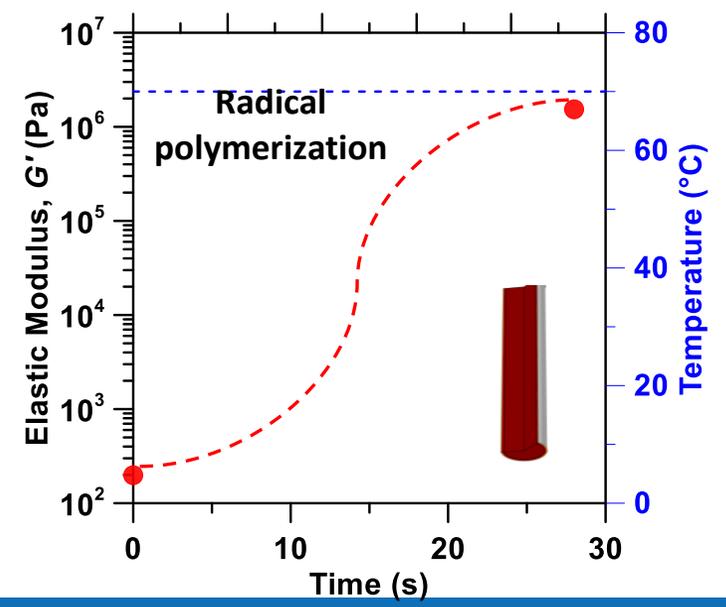
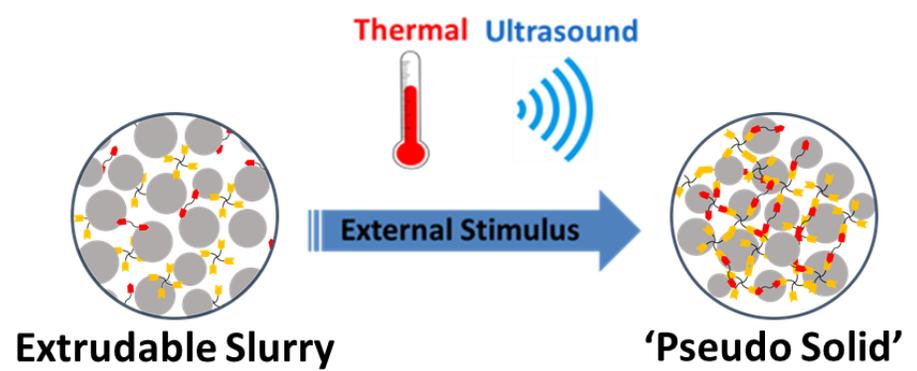
Design Guidelines for Thermoresponsive Suspensions





Conclusions and Takeaways

- Stimuli-responsive rapid stiffening suspensions enables overcoming the limitations 3DCP
- Proposed approach is compatible, economical, and scalable for most structural construction materials
- Formulations provide precise control over the designer compositions
- Rheological response can be adjusted to meet the print requirements
- A facile pathway to expand the design and production space accessible for concrete 3D printing**





Acknowledgements



Gaurav Sant
UCLA



Samanvaya Srivastava
UCLA



Torben Gaedt
TUM

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