Material design and synthesis of 3D-printable geopolymers and foams

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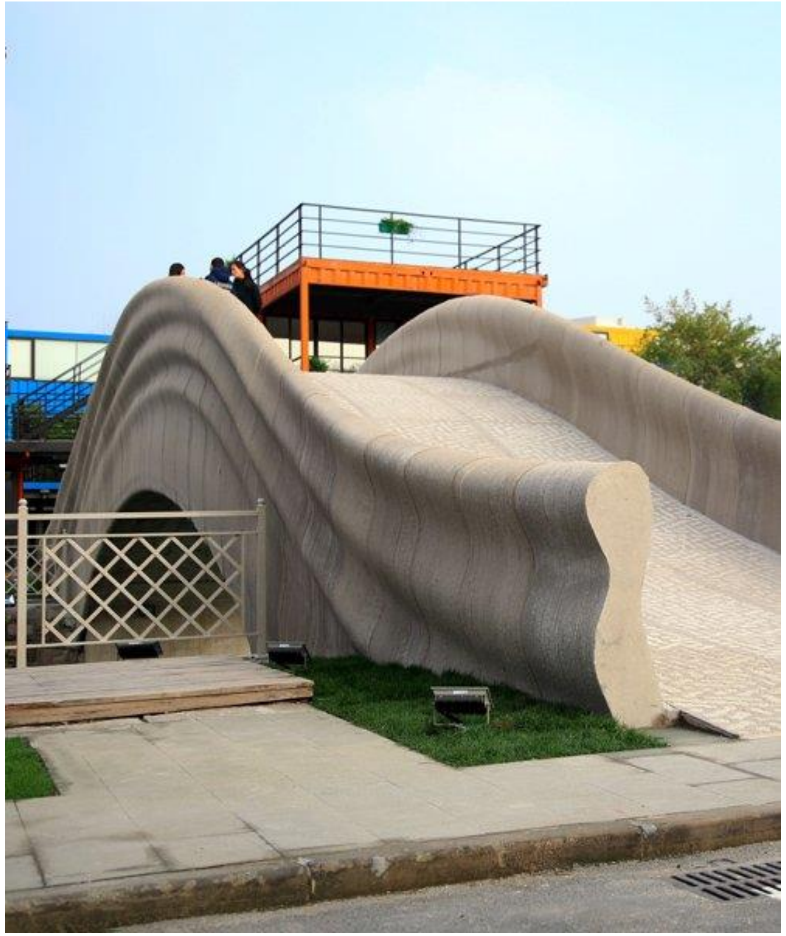
Concrete 3D Printing



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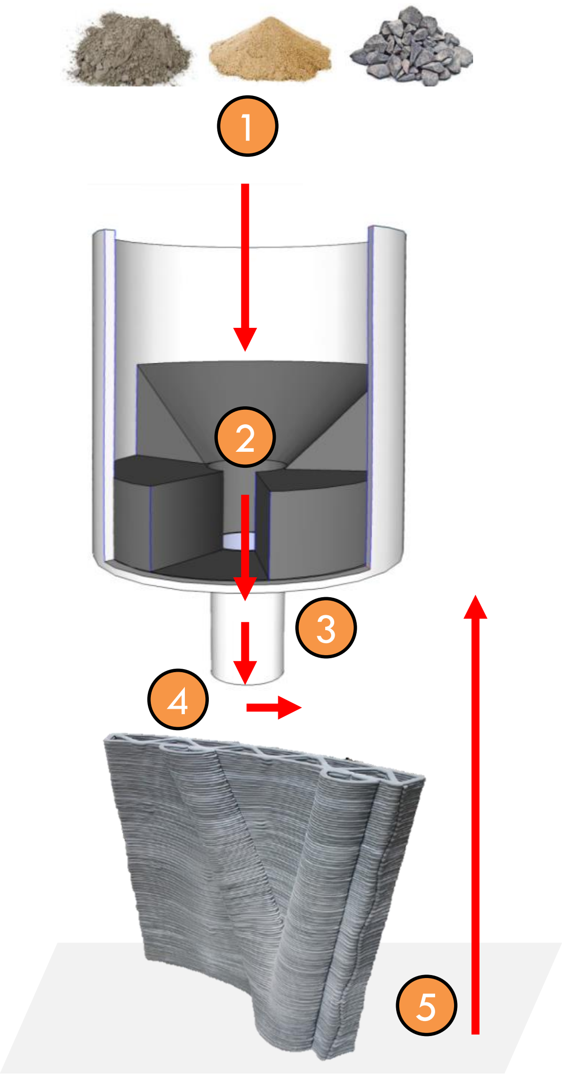
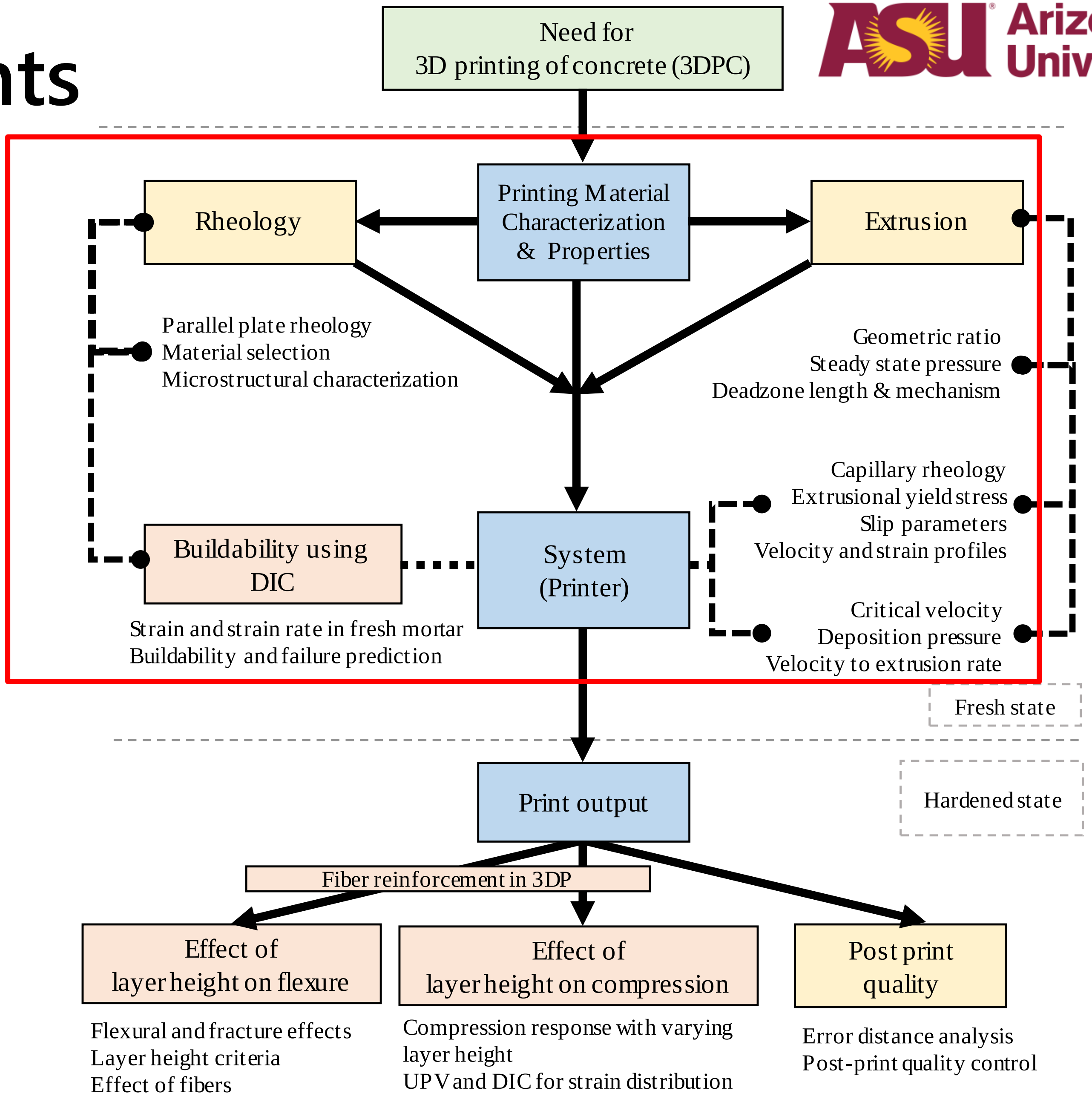
Sustainable 3D printed binder systems

- Generally mortars are printed – higher cement content
- Use of cement-free binders as a potential option
- Evaluation of the material design parameters and rheology
- Linkage between material design and processing parameters
- Special formulations using geopolymers (e.g., foams) for insulation

Critical Elements





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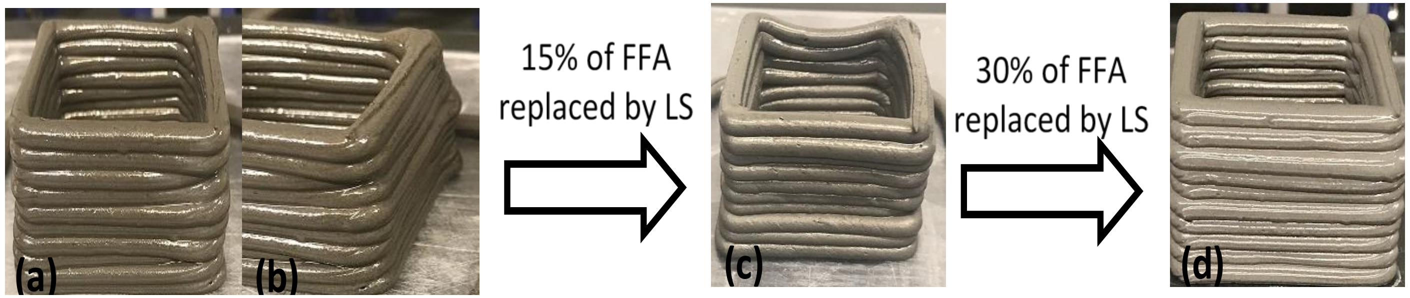
Material design for printability

- Ease of extrusion through a tapered nozzle, and the stability of the printed shape

Table 2: Binder proportions for the final printable mixtures

Mixture ID	FFA (%)	Slag (%)	OPC (%)	LS (%)	Al powder (%)	Alkali activator (%) NaOH (%)	Alkali activator (%) Na_2SO_4 (%)	Liquid/powder ratio
$F_{85}L_{15}$	85			15		5		0.27
$F_{70}L_{30}$	70			30		10		0.27
$F_{50}C_{30}L_{20}$	50		30	20		1	2	0.30
$F_{50}S_{30}L_{20}$	50	30		20		5		0.35
$F_{50}S_{30}L_{19}A_1$	50	30		19	1	n=0.05*, M_s=1.5**		0.30

* n= Na_2O/total powder (mass based); NaOH is the source of Na_2O.
** M_s= SiO_2/Na_2O (molar based), Sodium silicate solution is the source of SiO_2.



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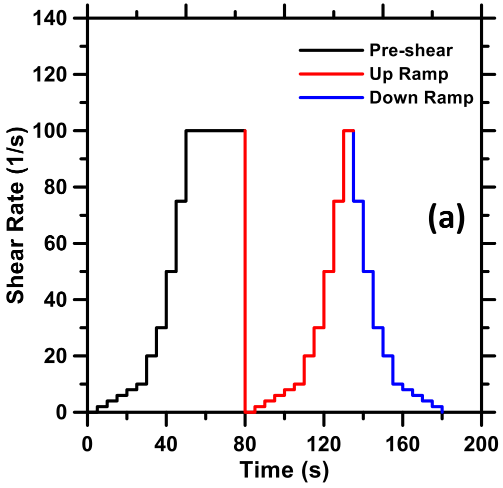
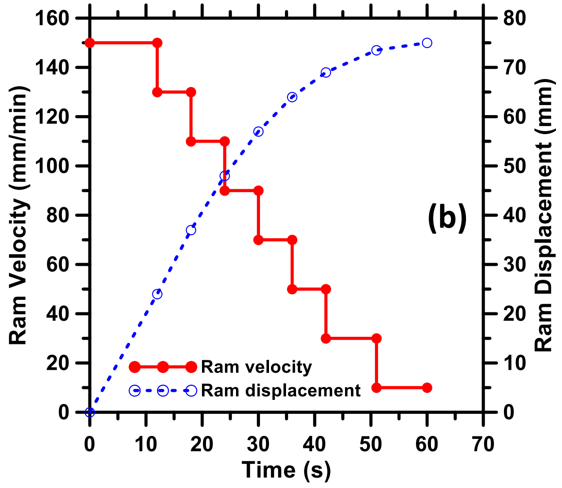
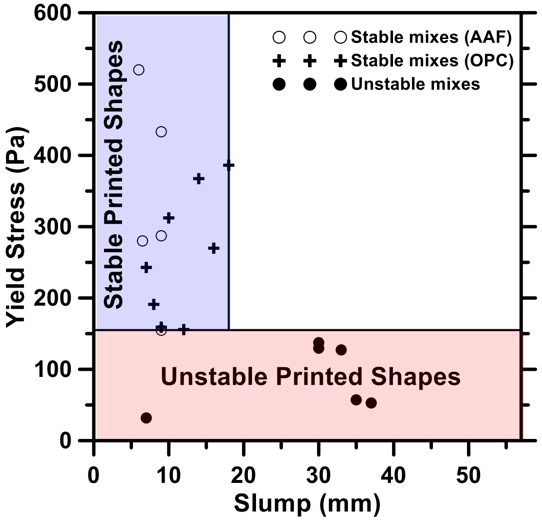
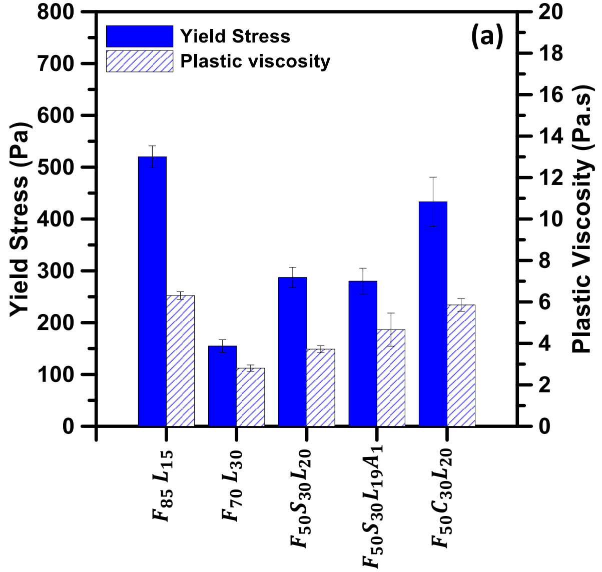
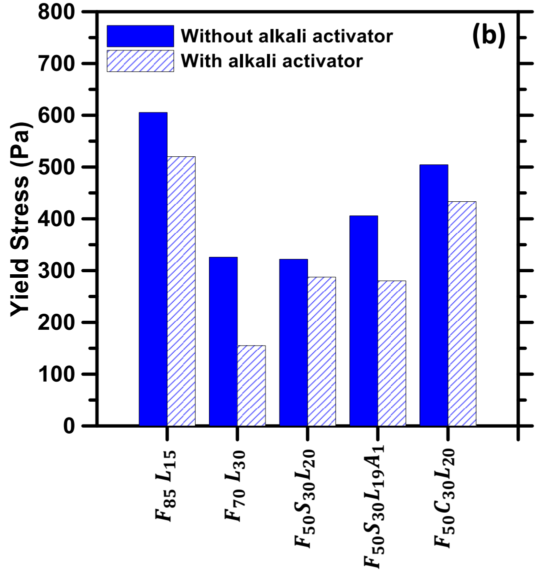
Rotational and Extrusional Rheology

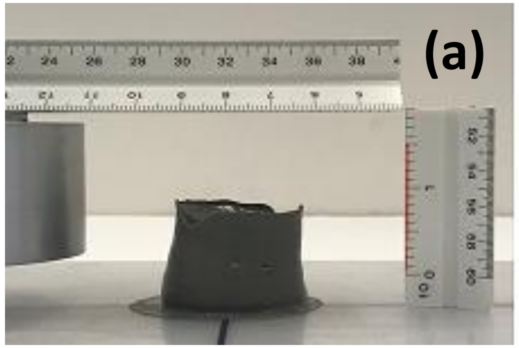








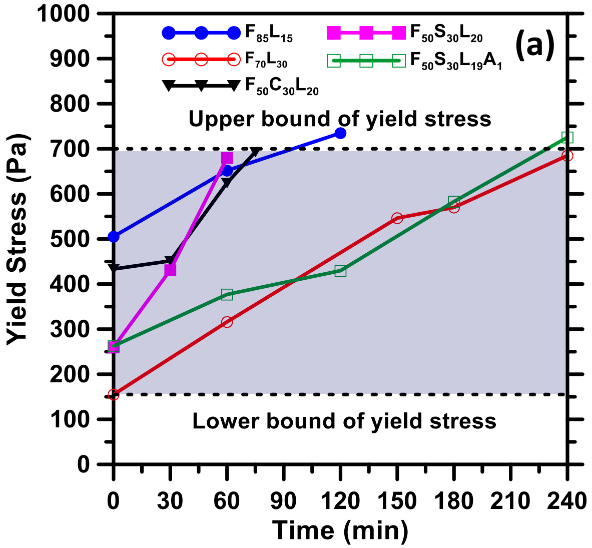


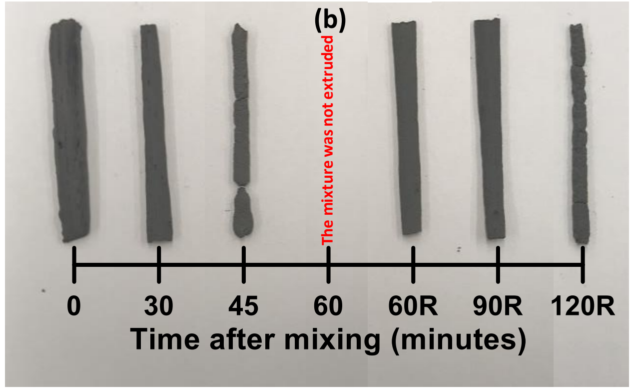


Water

10% NaOH

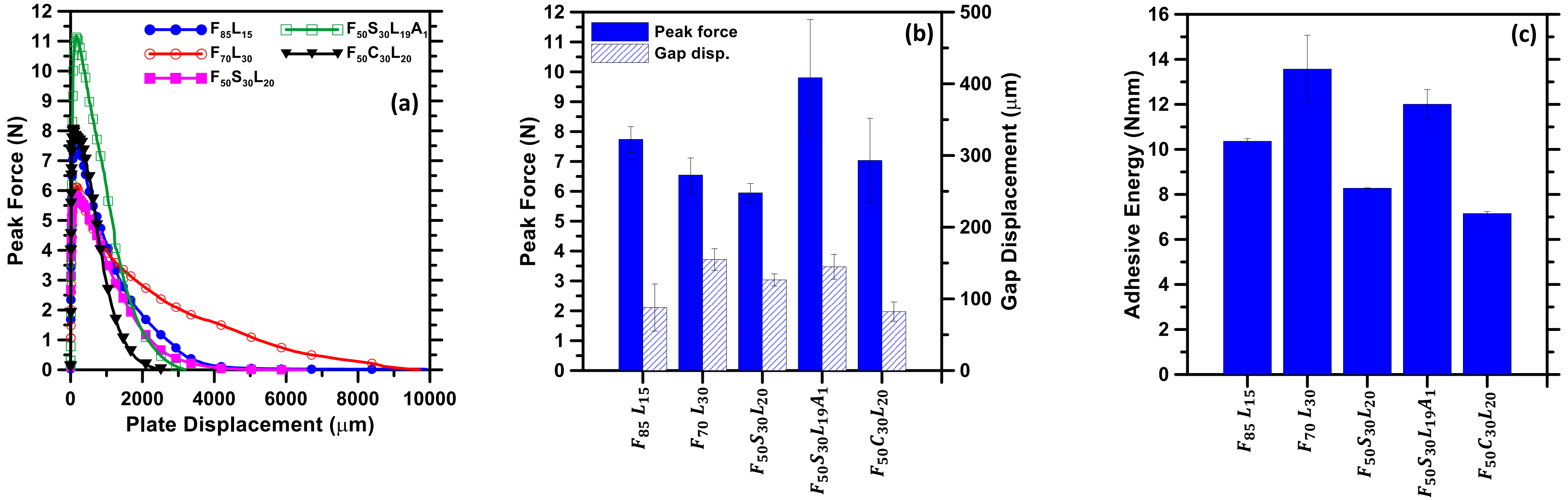
Yield stress and time dependence





- Printability window – based on YS
- Yield stress corresponding to the final time beyond which it cannot be extruded and printed – upper bound
- Printability window found to scale relatively well with the initial setting time of the pastes - setting time could be used as a surrogate parameter to estimate the printability window

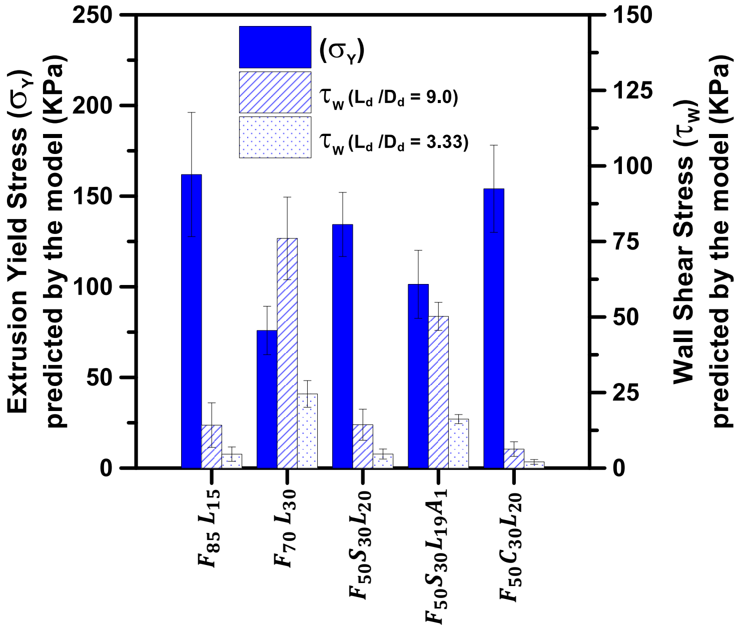
Extensional rheology

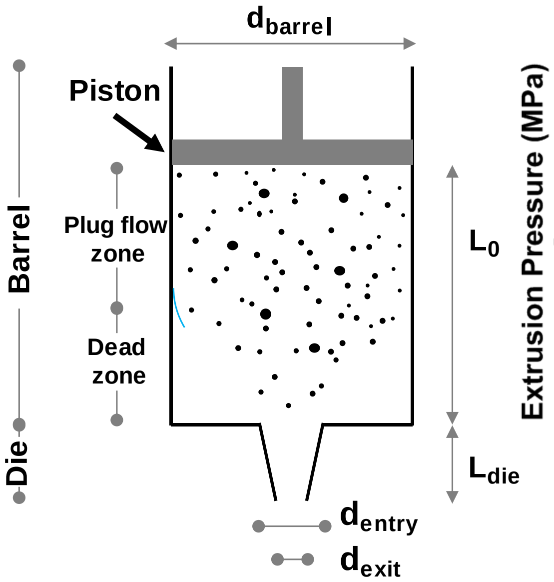


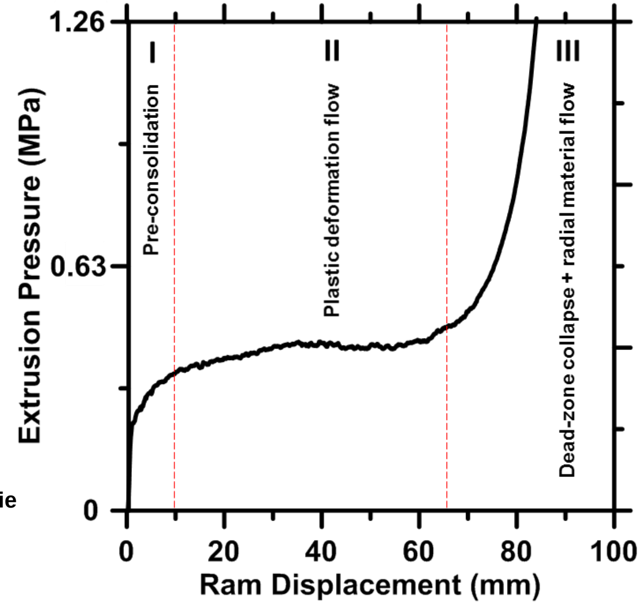
- Quantifying adhesive (tendency to stick to a surface) and cohesive (internal strength at rest) nature of the pastes – influences interlayer bond
- Determined using absolute value of peak force and displacement
- Energy required to separate the paste under a normal tensile force indicative of the influence of material composition on the bonding capacity
- Adhesive energy scales with the alkalinity of the activator - >2X adhesive energy for OPC pastes

Extrusion rheology

- A plasticity approach to analyze the extrusion rheology of dense suspensions
- Benbow-Bridgwater model $$P_{ext} = P_1 + P_2 = (\sigma_0 + \alpha V_{ext}^m) \ln\left(\frac{A_b}{A_d}\right) + \frac{ML}{A_d}(\tau_0 + \beta V_{ext}^n) = \sigma_Y \ln\left(\frac{A_b}{A_d}\right) + \frac{ML}{A_d}\tau_w$$





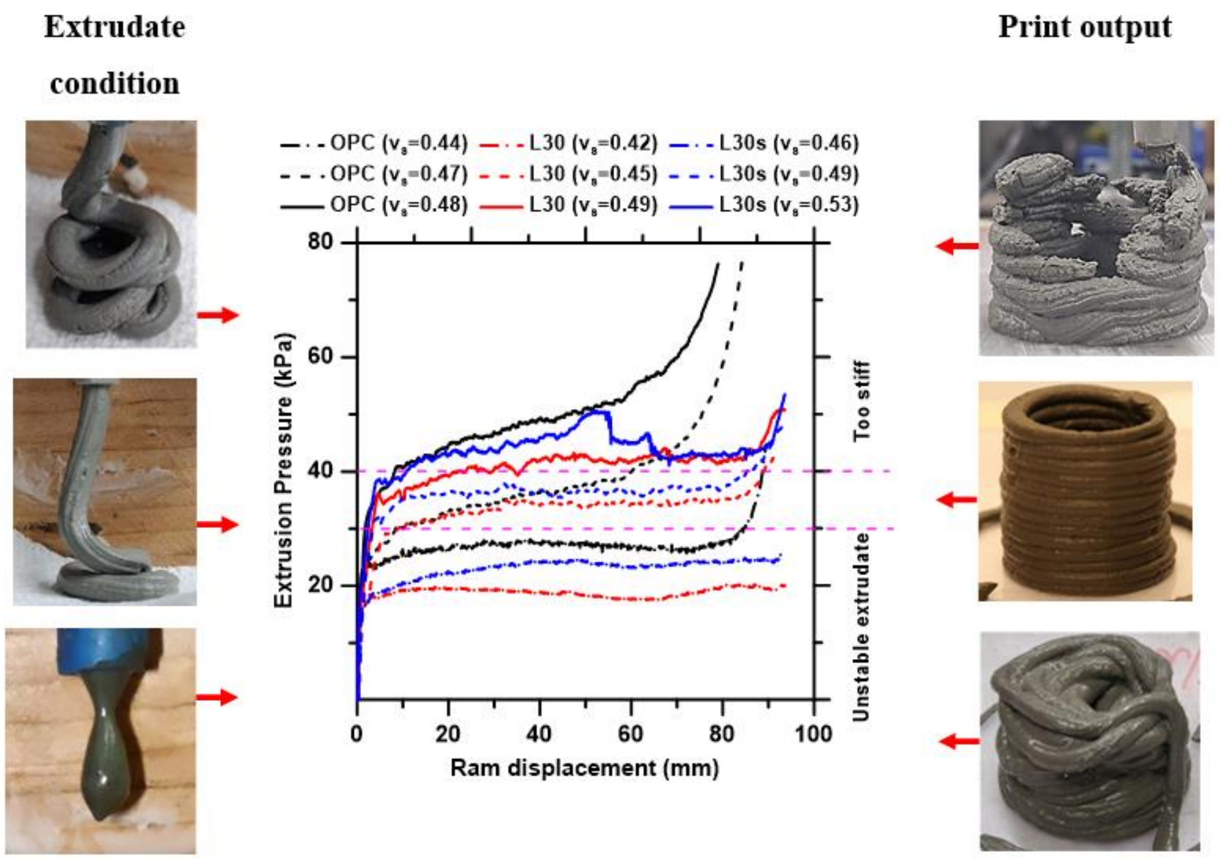


Nair et al. J. Amer. Cer. Soc. 2021

Nair et al. Cem. Concr. Compos. 2022

Extrusion rheology

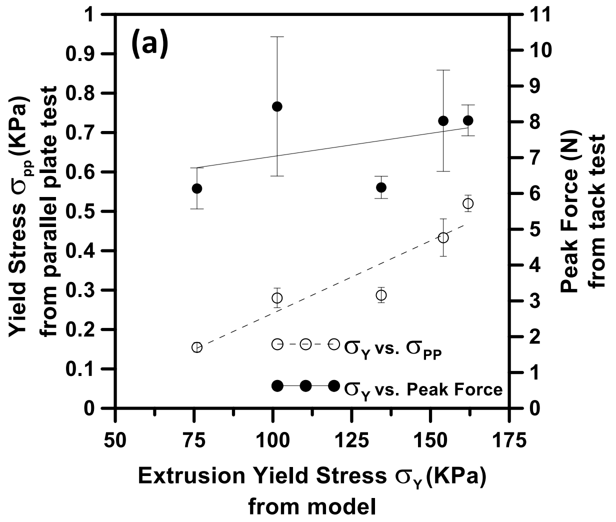
- Mixture characterization approach
- Pressure-displacement relationships
- Related to shear rheology, but represents different mechanics of flow, more relevant to extrusion-based 3D printing
- Time dependence well captured



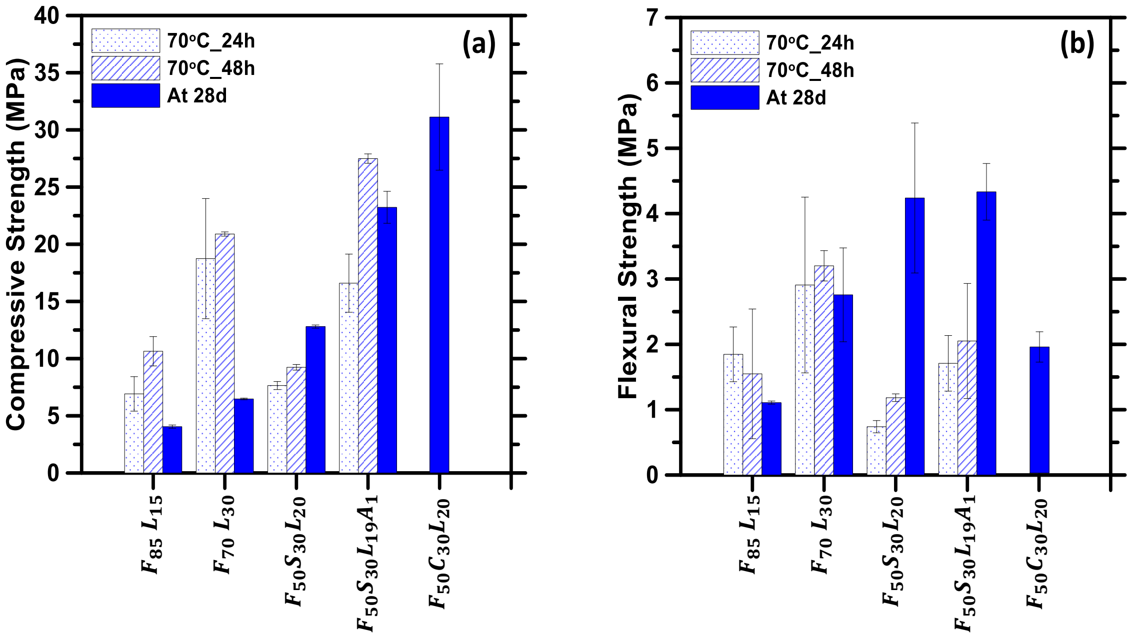
Nair et al. J. Amer. Cer. Soc. 2021
Alghamdi Et al. Mat and Design 2021

Extrusion rheology

- Extrusion yield stress (σ_Y) and the wall shear stress (τ_w) predicted by Benbow-Bridgewater model can be considered as the extrusion process-related parameters and used to design mixtures
- Shear YS measured through rotational rheology is correlated to extrusion YS
- Extrusion YS > 20 kPa for shape stability
- Extrusion YS useful in the apriori determination of the effectiveness of chosen mixture compositions and geometry in ensuring efficient extrudability and printability



Compressive and Flexural Strengths



- Temperature effects in compressive strength
- Slag/cement incorporation for better 28-day strengths of ambient cured specimens
- Strengths for several commercial applications achieved

Porous geopolymeric matrices for 3D printing

- A physical foaming process using surfactants – better bubble stability under 3D printing
- Control of the foam volume: foam volume fraction < jamming transition (0.64 for 3D disordered foams) are flowable and thus not printable.
- Control of skeletal density and cohesiveness
- 70% fly ash – 30% limestone powder; SiO_2/Na_2O of the activator = 1.0; Na_2O/total powder = 0.07
- Surfactant : 1-3% by mass of the binder
- Mass-based liquid-to-binder (l/b) ratio of 0.60 (including liquid surfactant and water in the activator)
- Modified mixing procedure to develop a "jammed foam" along with solid skeleton to achieve stability – staged addition of water, surfactant, mixing process

All-at-once addition

Staged addition

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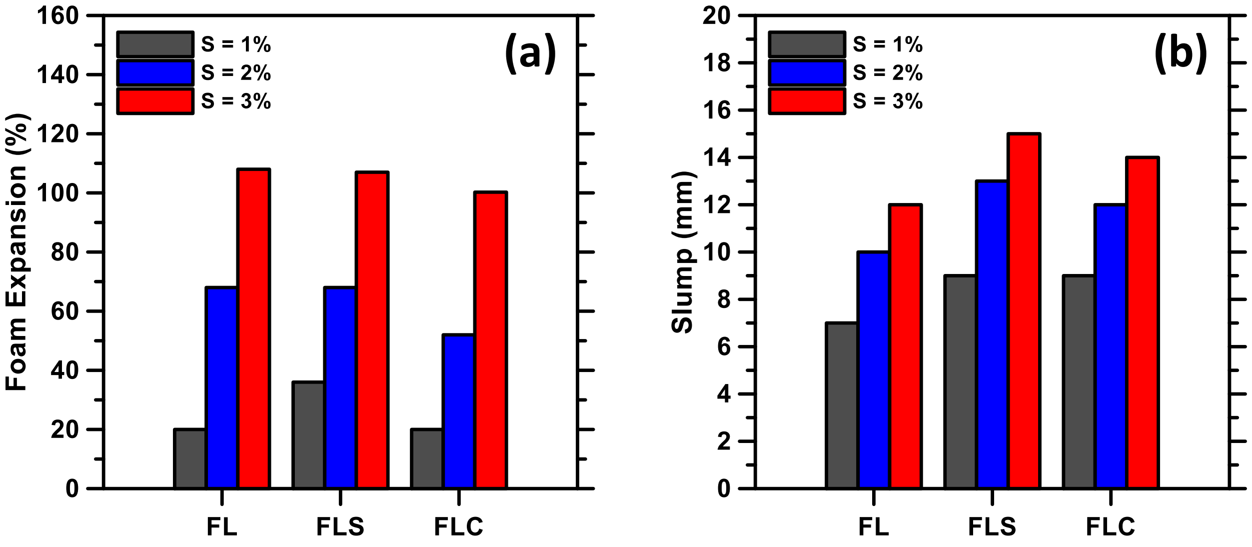
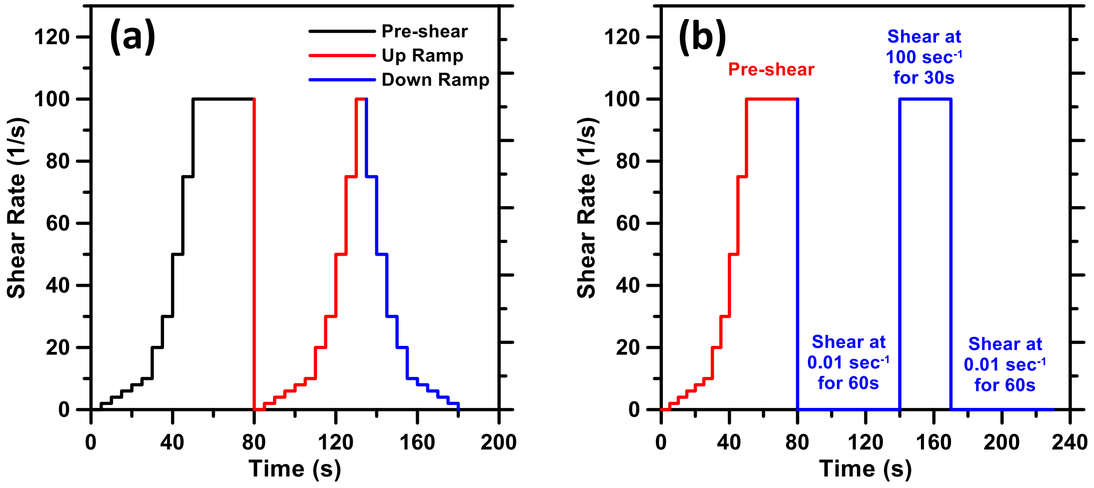
Foam expansion, shape retention

- Foam expansion: $F_E\ (\%) = \left(\frac{V_F - V_I}{V_I} \times 100\right)$
- YS and Plastic viscosity; Viscosity recovery

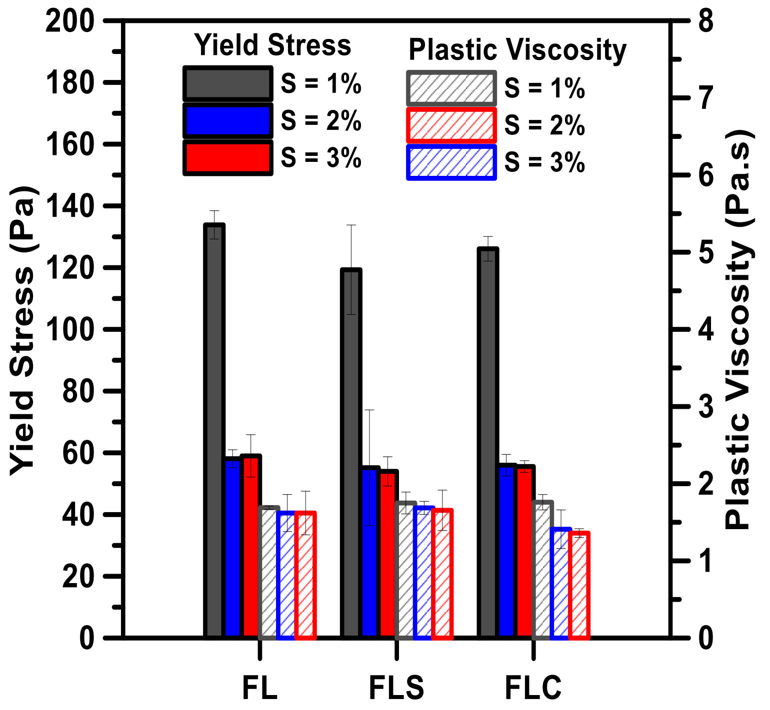




- Excellent consistency and smooth flow during extrusion
- Foamed suspensions with relatively higher slump values were also successful in retaining their shapes because of their low densities

Yield stress, capillary number

- Foams with void volume fractions greater than the jamming transition known to be yield stress fluids, just as conventional cement pastes
- Below the yield stress the foams behave as viscoelastic solids and above the yield stress as non-Newtonian fluids
- Rheological response - competition between the skeleton yield stress that tends to deform the bubbles and the capillary stress acting on the bubble surface that resists this deformation
- Plastic capillary number $C_p = \frac{\tau_y}{(2T/R)}$



Capillary number and foam performance

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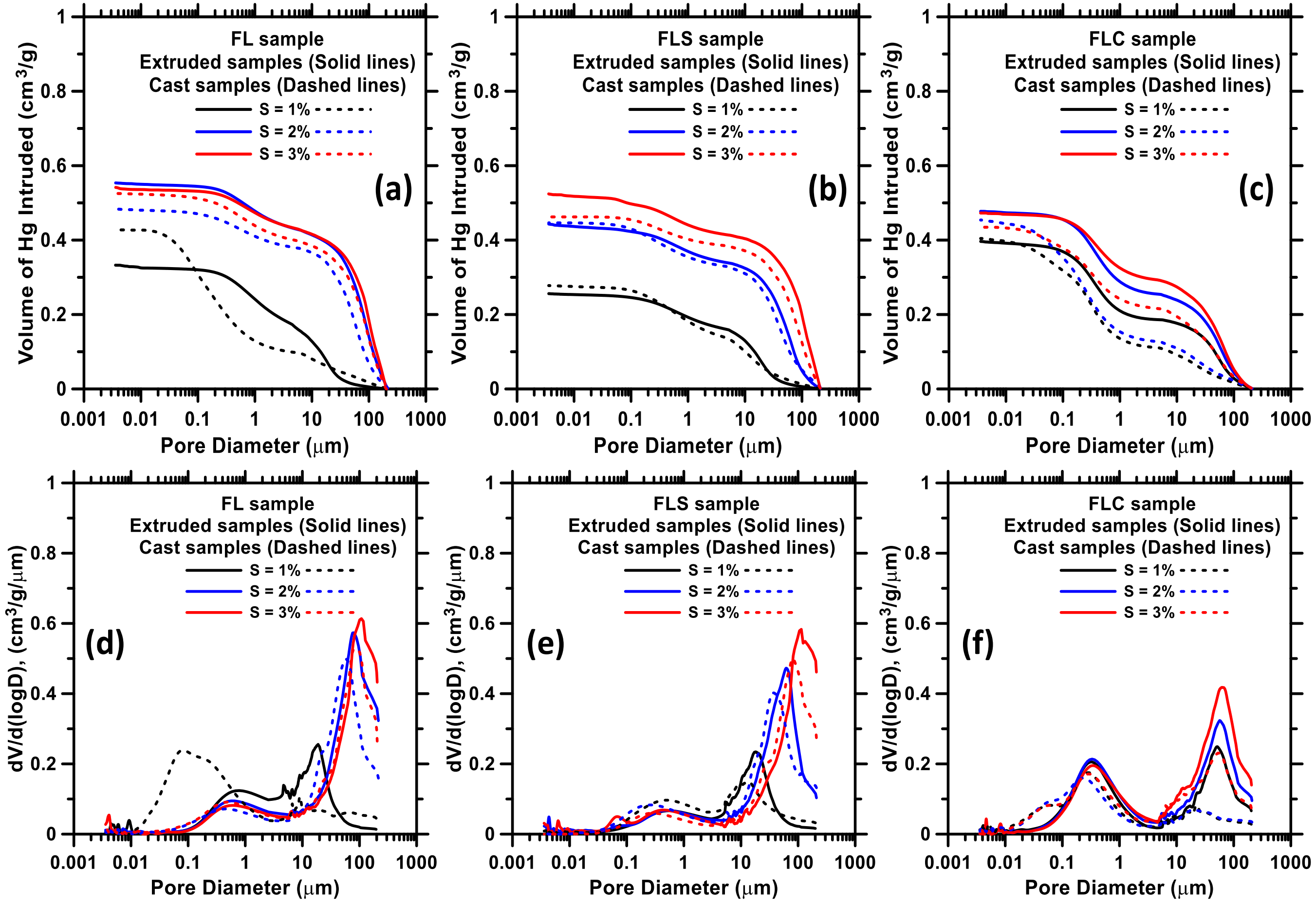
- Rheological response - competition between the skeleton yield stress that tends to deform the bubbles and the capillary stress acting on the bubble surface that resists this deformation
- Plastic capillary number $C_p = \frac{\tau_y}{(2T/R)}$
- Capillary number as a function of time enables an understanding of the rheology of foamed suspensions from those of their skeletal pastes

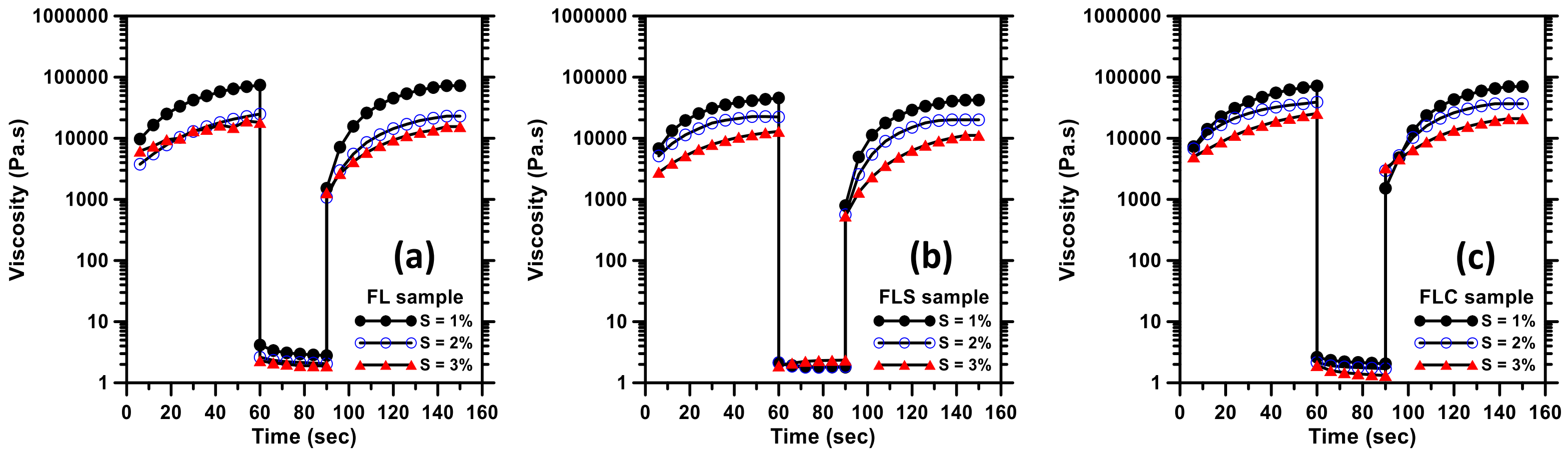
Capillary number and YS

- Surface tension scales between 0.06 N/m and 0.03 N/m between 1% and 3% surfactant dosage, and the bubble size ranges between 25 μm and 100 μm
- C_p for 1% surfactant = 0.02
- C_p for 2%, 3% = >0.10
- C_p < 0.10 – T dominant
- T_y invariant of ϕ; $\phi < 0.50$ (1%S)
- For $\phi > 0.64$ (2% and 3%S) $C_p > 0.10$
- Bubbles behave as softer inclusions
- YS reduced



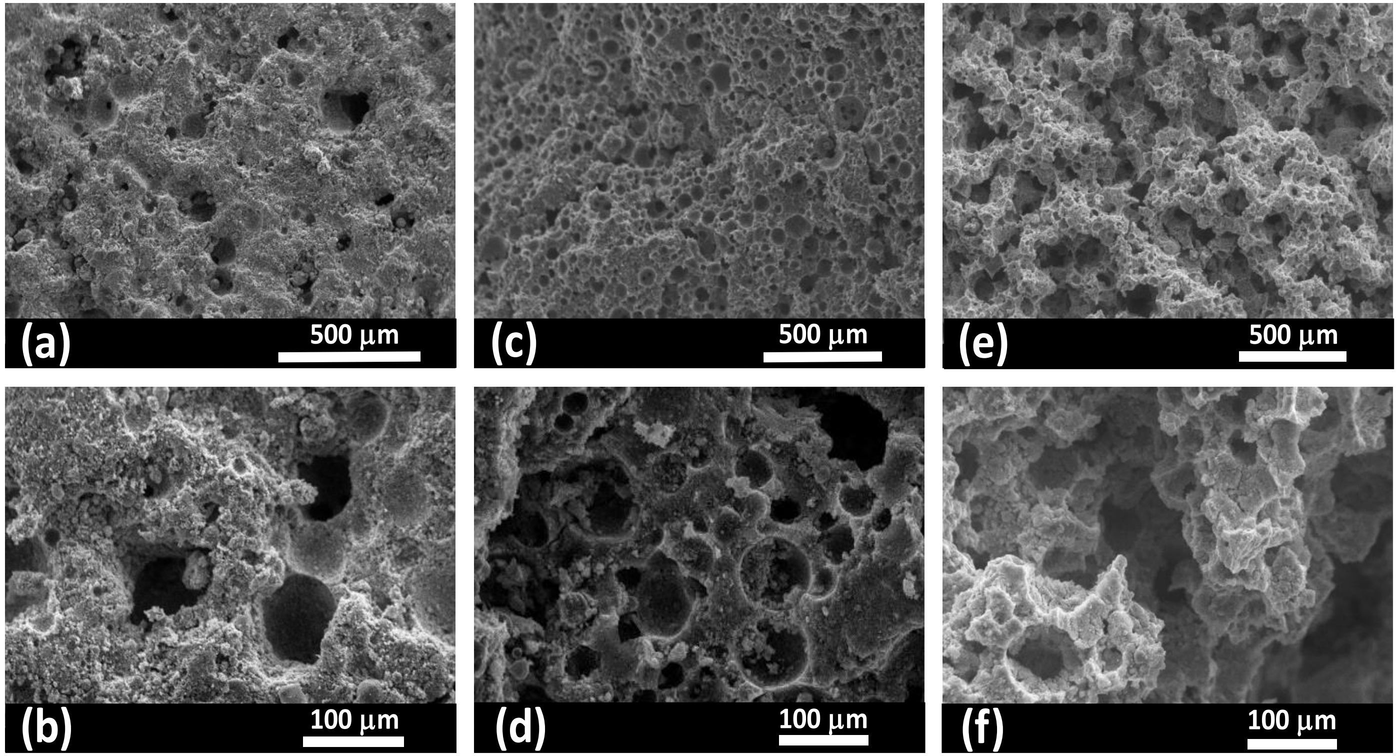
Buildability

- Requires the mixtures to be able to recover most of its initial viscosity after the extrusion effect is simulated

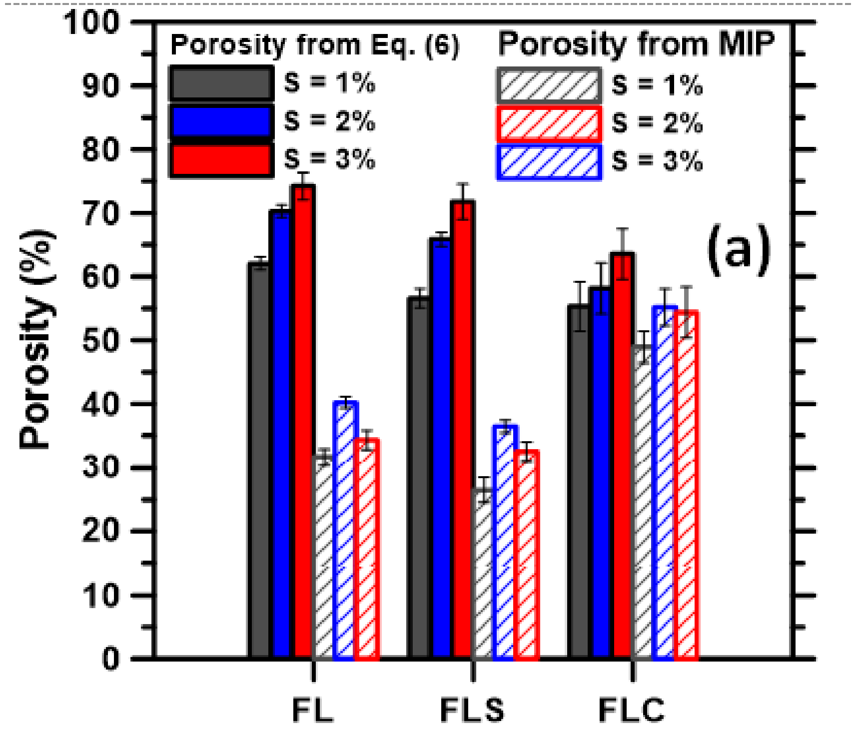


- 3 stages - initial viscosity at rest or before extrusion (before printing; from 0 to 60 s), viscosity during the simulated extrusion process (during printing; 60 s to 90 s), and viscosity of the simulated extruded suspensions (after printing; 90s to 150 s)
- Lower viscosity when shear rate is high; further lowering of shear rate recovers the viscosity (85-95%) – comparable to or higher than that of OPC and geopolymer pastes

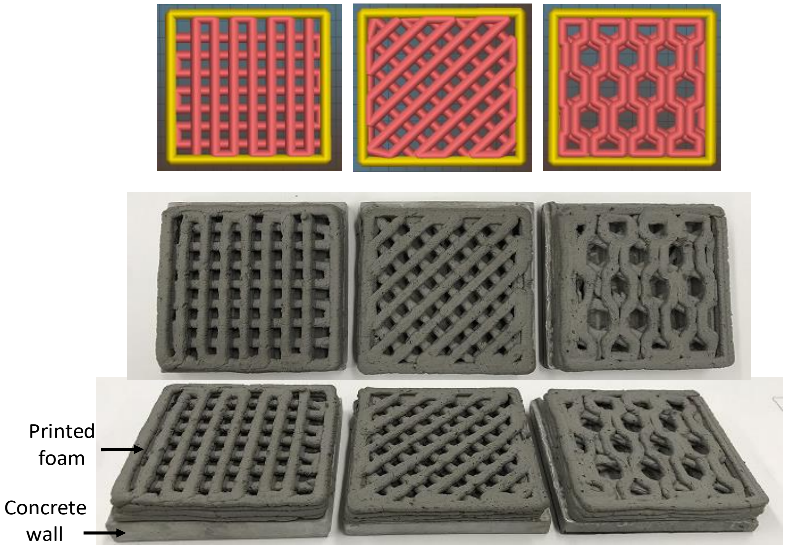
Pore structure

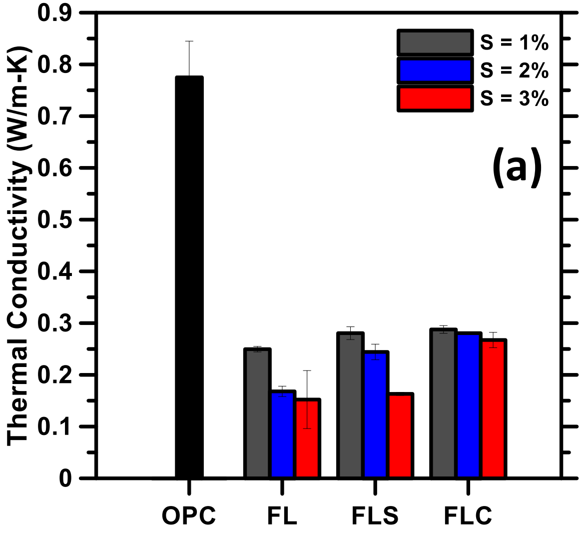


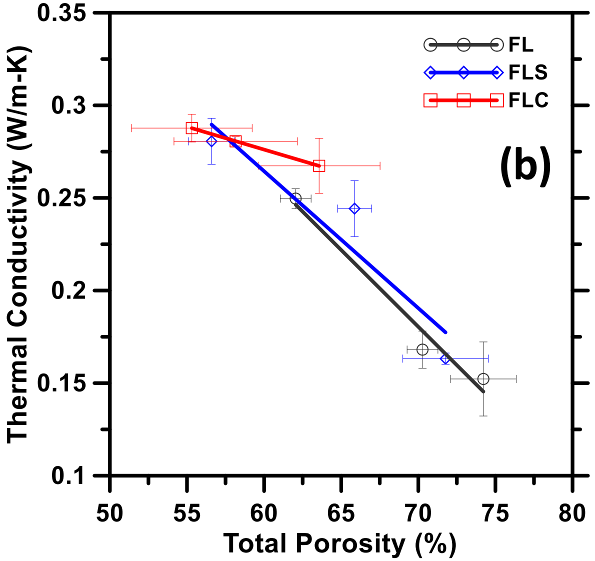
S = 1% S = 2% S = 3%



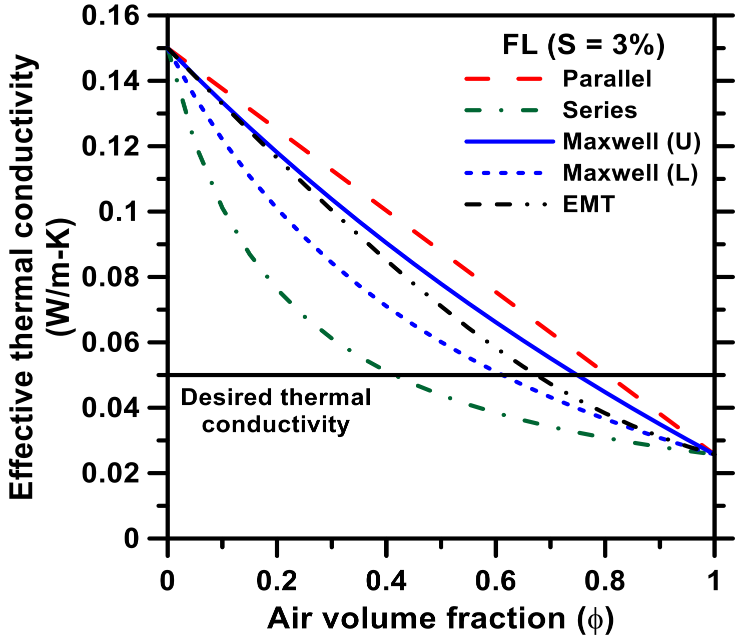
Thermal performance







- At ~70% porosity, thermal conductivity of 0.15 W/m-K (more than that of EPS/XPS – 0.05 W/m-K)
- Can be incorporated with air voids – lattice printing of the foam



Summary

- Use of alkaline activators in lieu of water decreases the shear YS and increases the cohesiveness, similar to the use of a superplasticizer in conventional OPC systems
- A printability window based on concurrent measurement of time-dependent yield stress and extrusion printing of a filament of the paste – scales with the setting time
- Extrusion rheology experiments coupled with the Benbow-Bridgwater model facilitates the extraction of extrusion yield stress - related to shear yield stress and extensional (tack) properties of the virgin paste
- Foamed systems different surfactant contents where foam jamming transition is achieved
- Below the jamming transition (ϕ = 0.64), foams deform, shown through the capillary number
- Viscosity recovery of the chosen foamed matrices were high, demonstrating excellent buildability
- We propose the use of 3D-printed foam layer architecture such that dual-porosity systems - with smaller pores in the foam and larger pores in between the printed paths - can be printed

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