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Arizona State University

Enhancing Rheological Properties Through Targeted Nano-Infusions for Better 3D Printing Control

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Presentation Outline

- Introduction: 3D Concrete Printing (3DCP) & Nanomaterials
- Background & Research Objective
- Experimental Program
- Results & Discussions
- Conclusions

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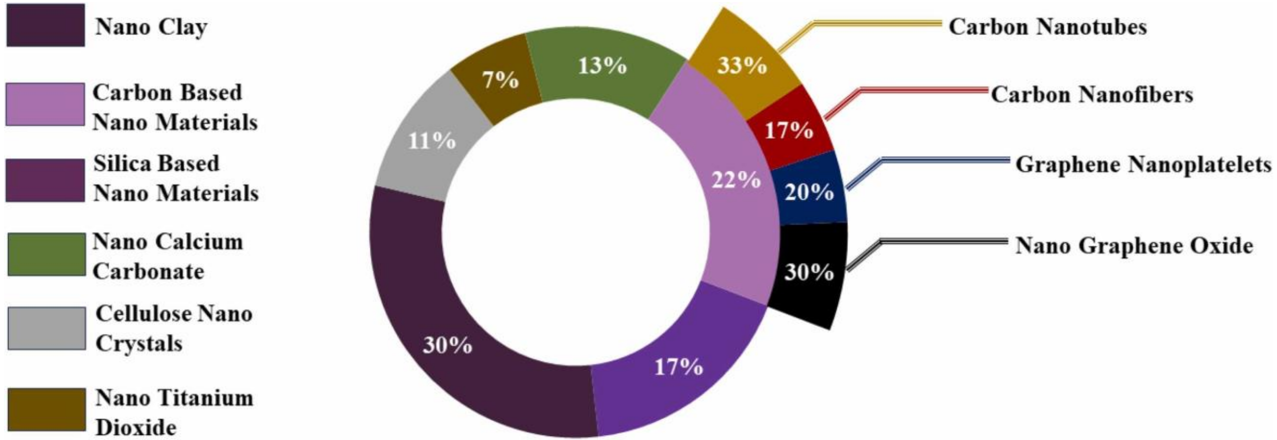
Introduction: 3DCP & Nanomaterials

- 3DCP allows building structures layer-by-layer using 3D printers, offering advantages such as: design optimization; time and cost reduction; waste reduction; enhancing field safety conditions, etc.

- Nanotechnology offers an emerging avenue for developing novel materials featuring superior properties and high-performance characteristics.

- Nanomaterials are engineered materials, 1 to 100 nm in size, produced through either bottom-up or top-down manufacturing methods



Nanomaterials used so far in 3D-Printable CBMs (Khan et al., 2024)

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Background & Research Objective

- Implementation of 3D printing cement-based materials (CBMs) presents a unique set of challenges: necessitating a ***fine equilibrium*** between ***PUMPABILITY – BUILDABILITY – RHEOLOGY*** of the mixture.
- Nanomodification of CBMs involves a bottom-up approach with ***alterations*** in the ingredients of cementitious mixes on a ***nanoscale***, ultimately influencing its final ***physio-mechanical properties*** and durability.
- Challenges associated with nanomodification of CBMs for 3DCP – dispersion and alterations in rheological characteristics.

Research Objective:

*Examine the **fundamental rheological characteristics** of **fractal and reactive-graphene modified binary and ternary blends** containing Portland cement, limestone, and fly ash.*

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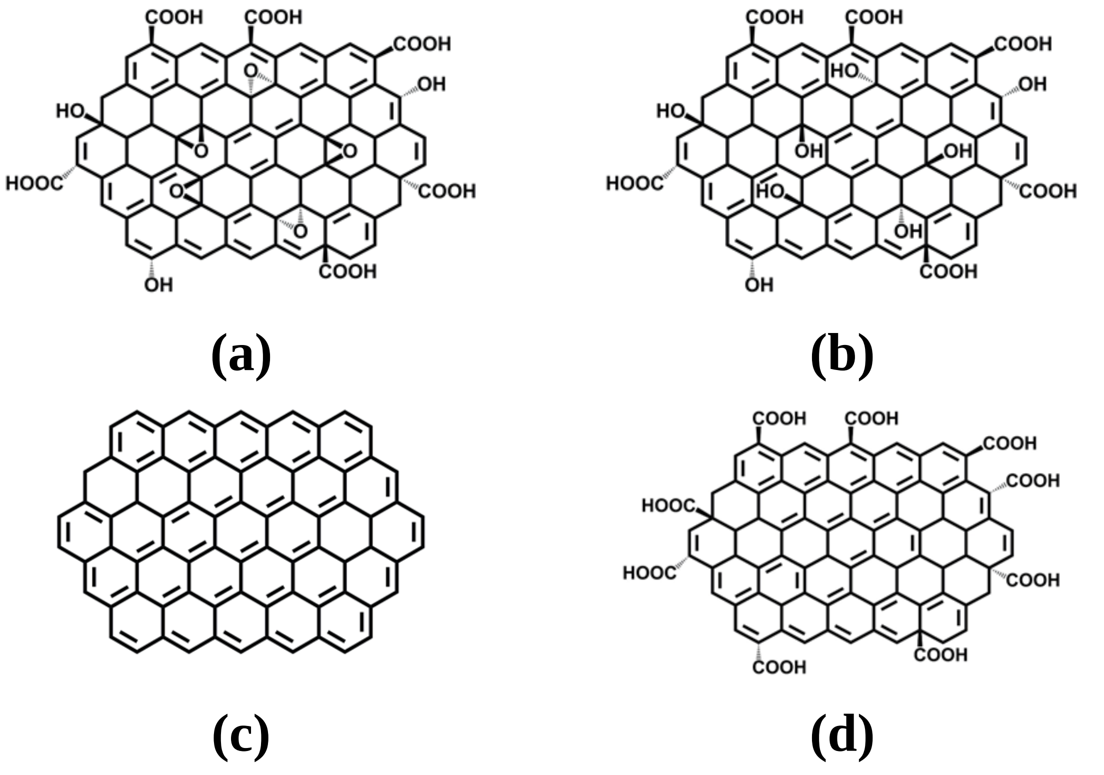
Experimental Program

Materials - Graphene:

- ❖ Graphene used in this study is produced through a novel, cost-effective, eco-friendly, one-step method that involves controlled detonation of an acetylene-oxygen mixture in a chamber under a spark of 10 kV from an industrial step-up transformer.
- ❖ Two types of graphene used – fractal graphene and reactive graphene.
- ❖ Reactive graphene (RG) is produced from fractal graphene (FG) by functionalizing it with COOH groups on the surface alone.



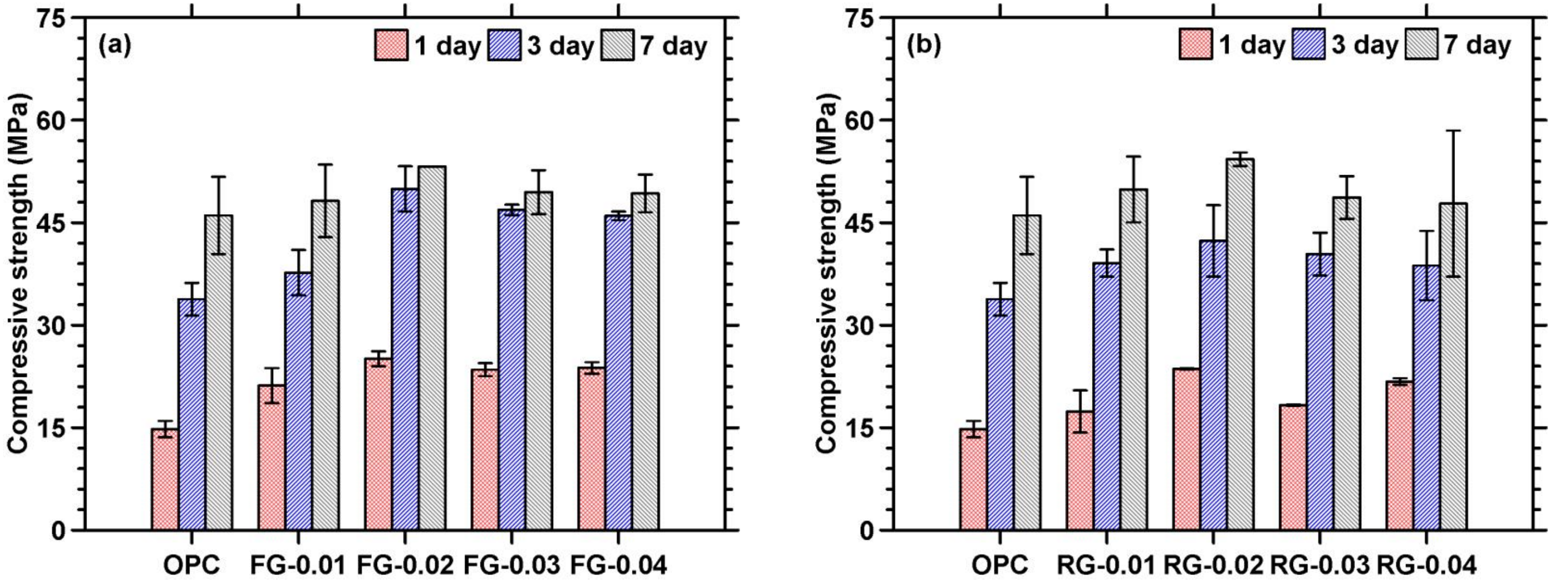
(a) (b)

(c) (d)

Structure of (a) graphene oxide and (b) reduced graphene oxide and (c) fractal graphene and (d) reactive graphene

Experimental Program

- Graphene dosages from 0 to 0.02% by mass of cementitious powder were used based on our previous work.
- Fly ash and limestone were used to replace cement either alone or in combination to prepare binary and ternary blends.



Compressive strengths of: (a) FG-modified mortars, and (b) RG-modified mortars until an age of 7-d. The numbers next to FG and RG indicate the fractal or reactive graphene dosage as a % by mass of cement.

Experimental Program

Chemical composition and physical properties of the mixture components used:

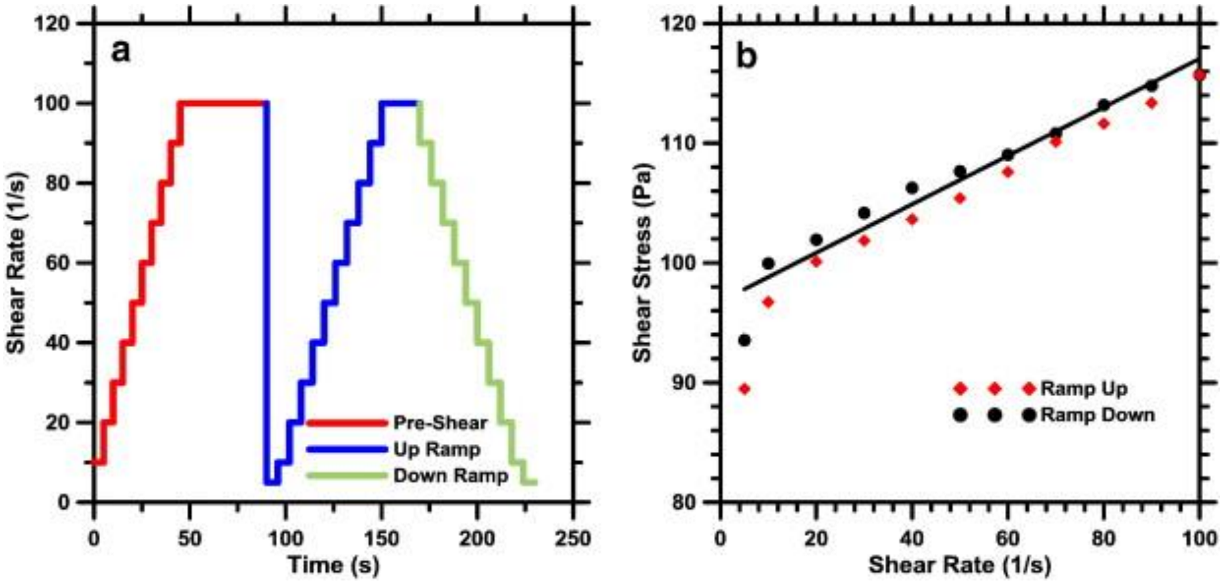
Components of the binders	Chemical composition (% by mass)									Specific gravity
	SiO_2 (%)	Al_2O_3 (%)	SO_3 (%)	Fe_2O_3 (%)	MgO (%)	Na_2O (%)	K_2O (%)	CaO (%)	LOI* (%)	
OPC	21.3	3.78	2.88	3.75	1.77	0.25	0.17	63.83	1.34	3.24
Fly ash (F)	58.40	23.80	3.04	4.19	1.11	-	-	7.32	2.13	2.31
Limestone (L)	$CaCO_3$ >99%									2.80

Mixture proportions used in the study:

Mixture ID	Mass fraction of ingredients			Water-to-powder (w/p) ratio, by mass
	OPC	Fly ash (F)	Limestone (L)	
OPC_{-S}	1.0	0	0	0.34
$F_{15}L_{15\text{-}S}$	0.7	0.15	0.15	0.32
$F_{10}L_{20\text{-}S}$	0.7	0.10	0.20	0.32
$L_{30\text{-}S}$	0.7	0	0.30	0.35
Superplasticizer (% by mass of powder) – 0.25 for fractal graphene-modified blends; 0.15 for reactive graphene-modified blends.				

Experimental Program

- Rheological experiments were carried out on pastes using TA instruments AR 2000EX rotational rheometer with a vane-in-cup geometry .
- Shear rate ramp study (strain-controlled) study was conducted to evaluate the yield stress and plastic viscosity of the mixtures.
- Small amplitude oscillatory shear study (stress controlled) was used to determine the storage and loss moduli of the pastes. An oscillatory stress was applied from 0.01 Pa to 1000 Pa at a frequency of 1 Hz.



A schematic representation of the rheological procedure, and (b) a typical shear rate–shear stress relationship showing the ascending and descending curves. The linear fit of the data in the descending curve is used to extract the yield stress and plastic viscosity.

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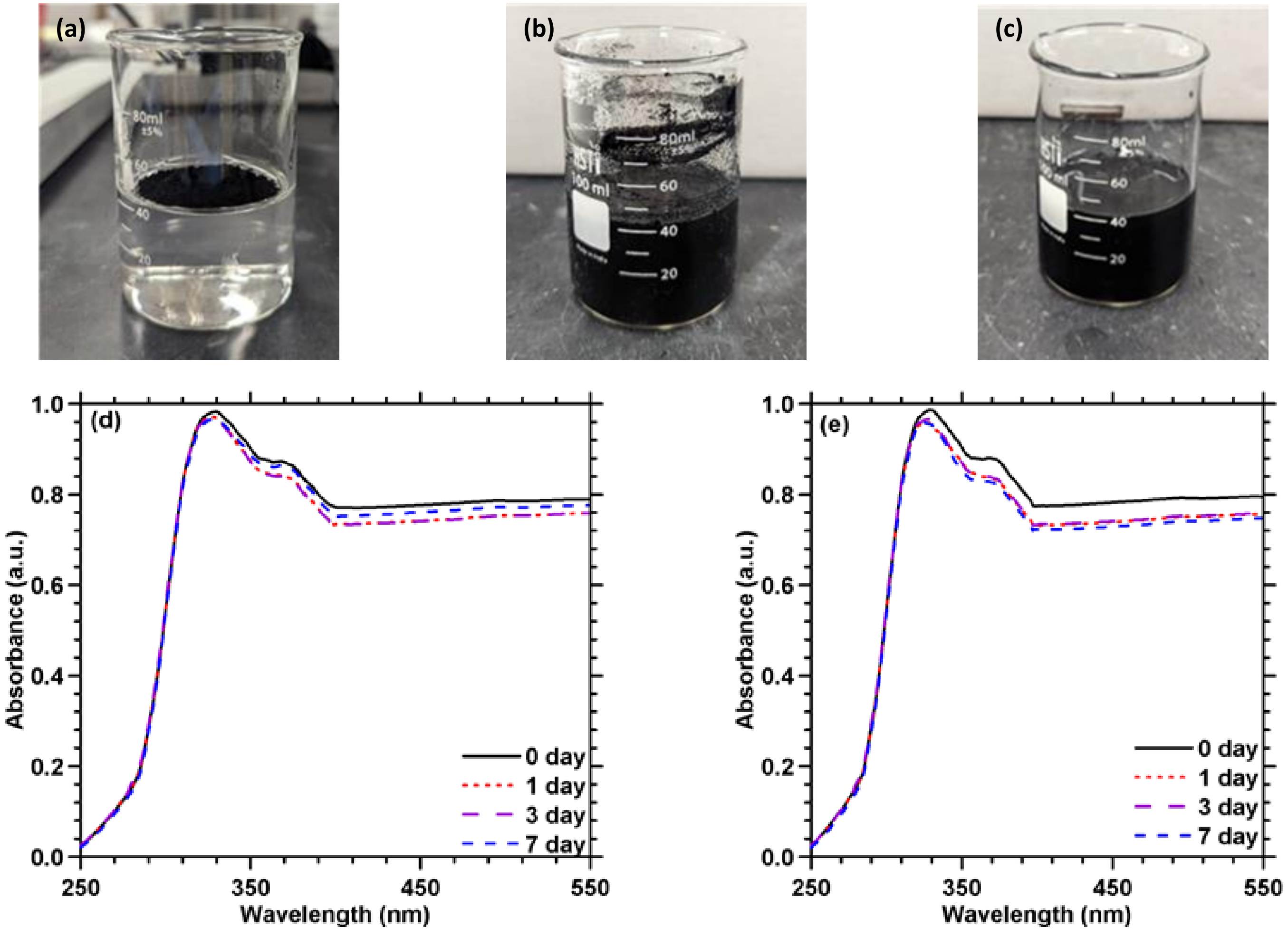
Results & Discussions

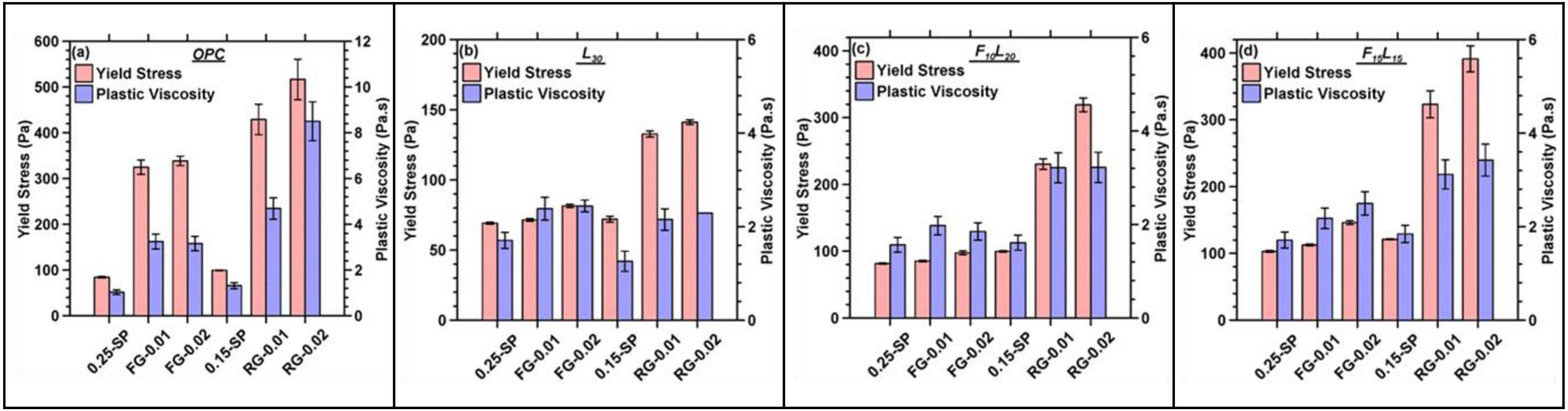
Dispersion of fractal graphene and reactive graphene in water:



Graphene dispersion process: (a) addition of graphene in DI water; (b) after homogenization for 2 minutes, and (c) at the end of ultrasonication process (3 h) (1:1 superplasticizer by mass of graphene was added in the middle of ultrasonication). UV–Vis spectra of graphene dispersed solution at different ages for: (d) fractal graphene (FG), and (e) reactive graphene (RG). 0 d indicates measurement soon after completion of the dispersion procedure.

Results & Discussions

Yield Stress and Plastic Viscosity:



Yield stress and plastic viscosity values of FG- and RG-modified pastes: (a) OPC-s, (b) L30-s, (c) F10L20-s, and (d) F15L15-s.

Results & Discussions

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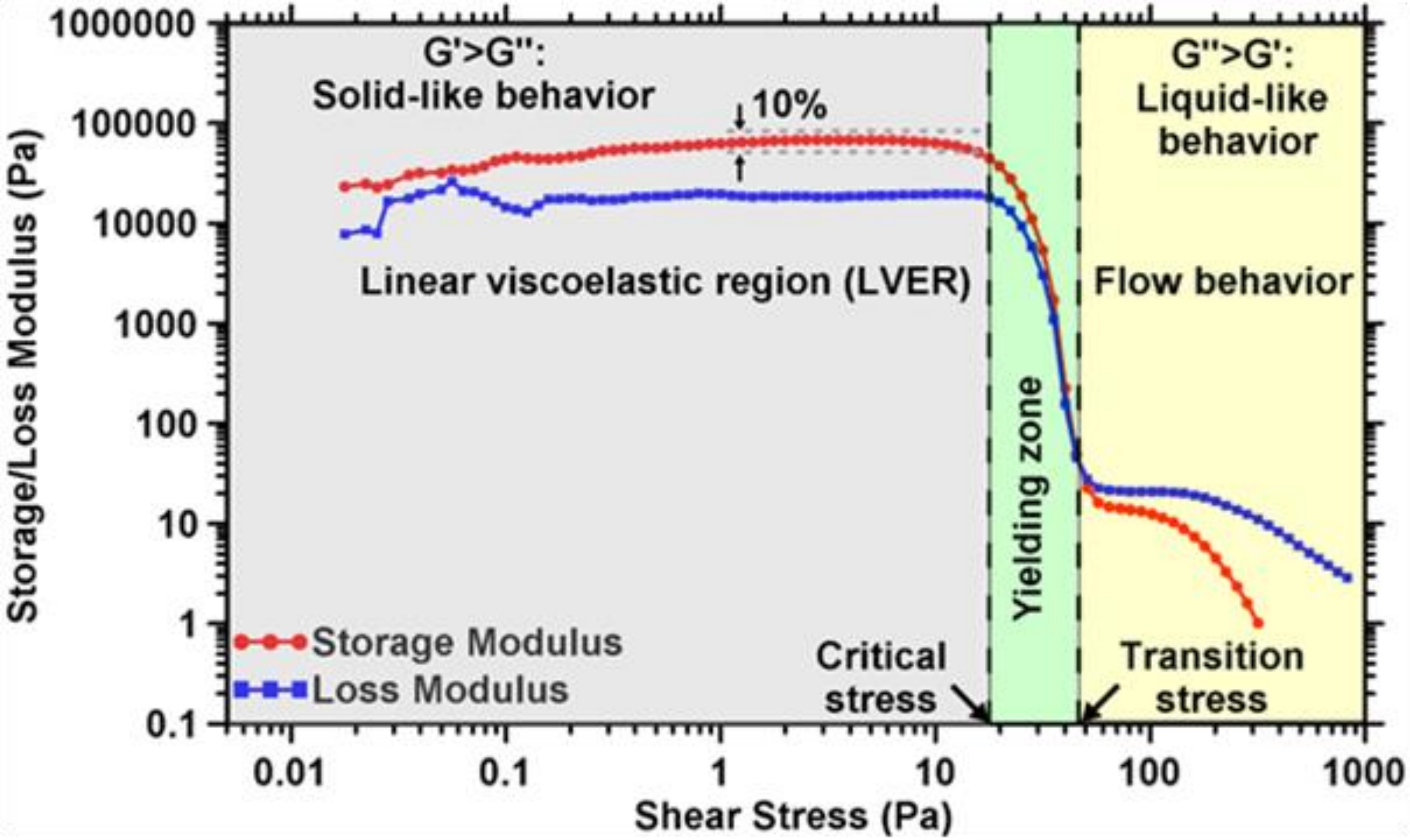
Oscillation rheology – What can we learn?



Typical oscillatory stress sweep measurement result showing the evolution of the storage and loss moduli in three phases

Results & Discussions

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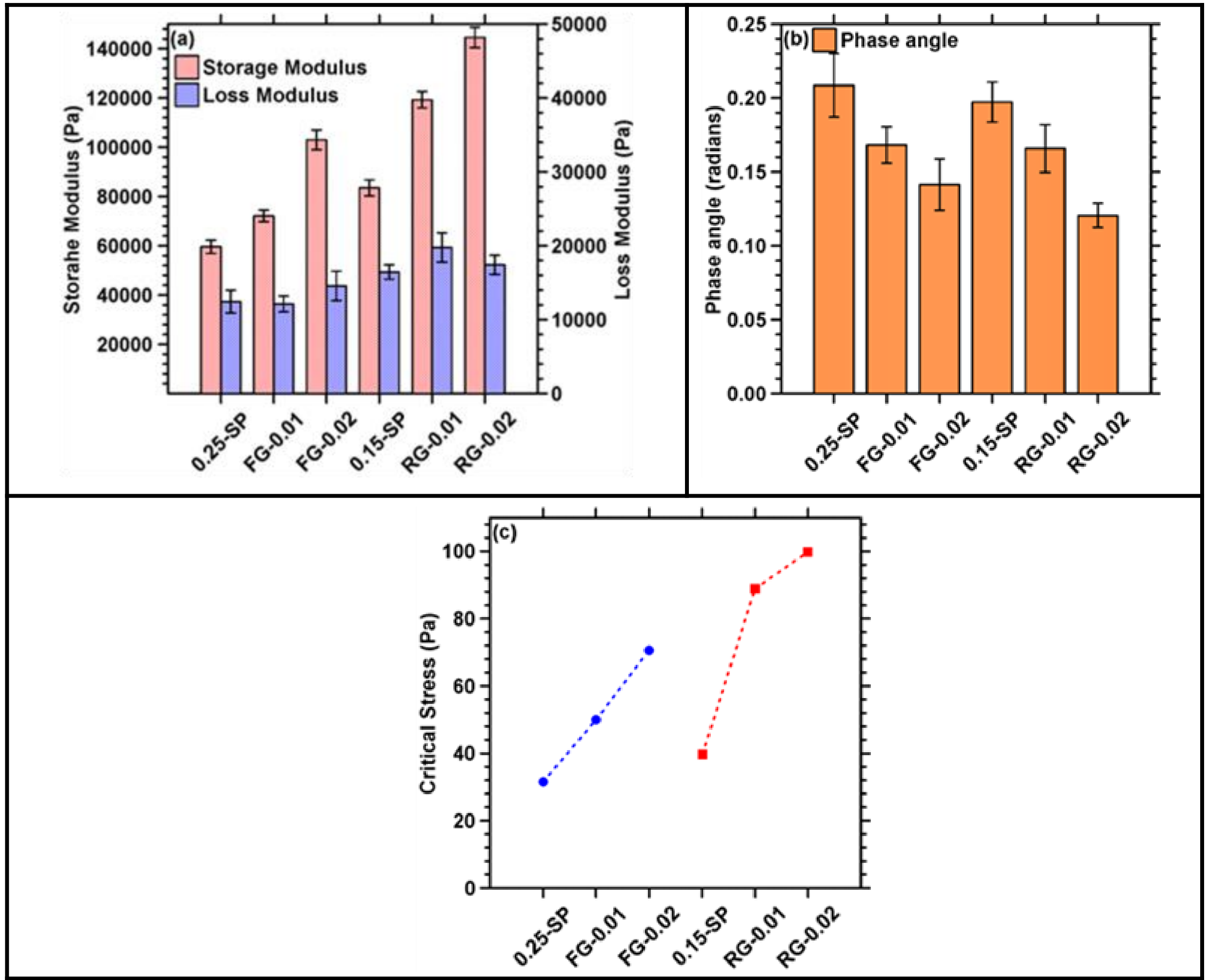
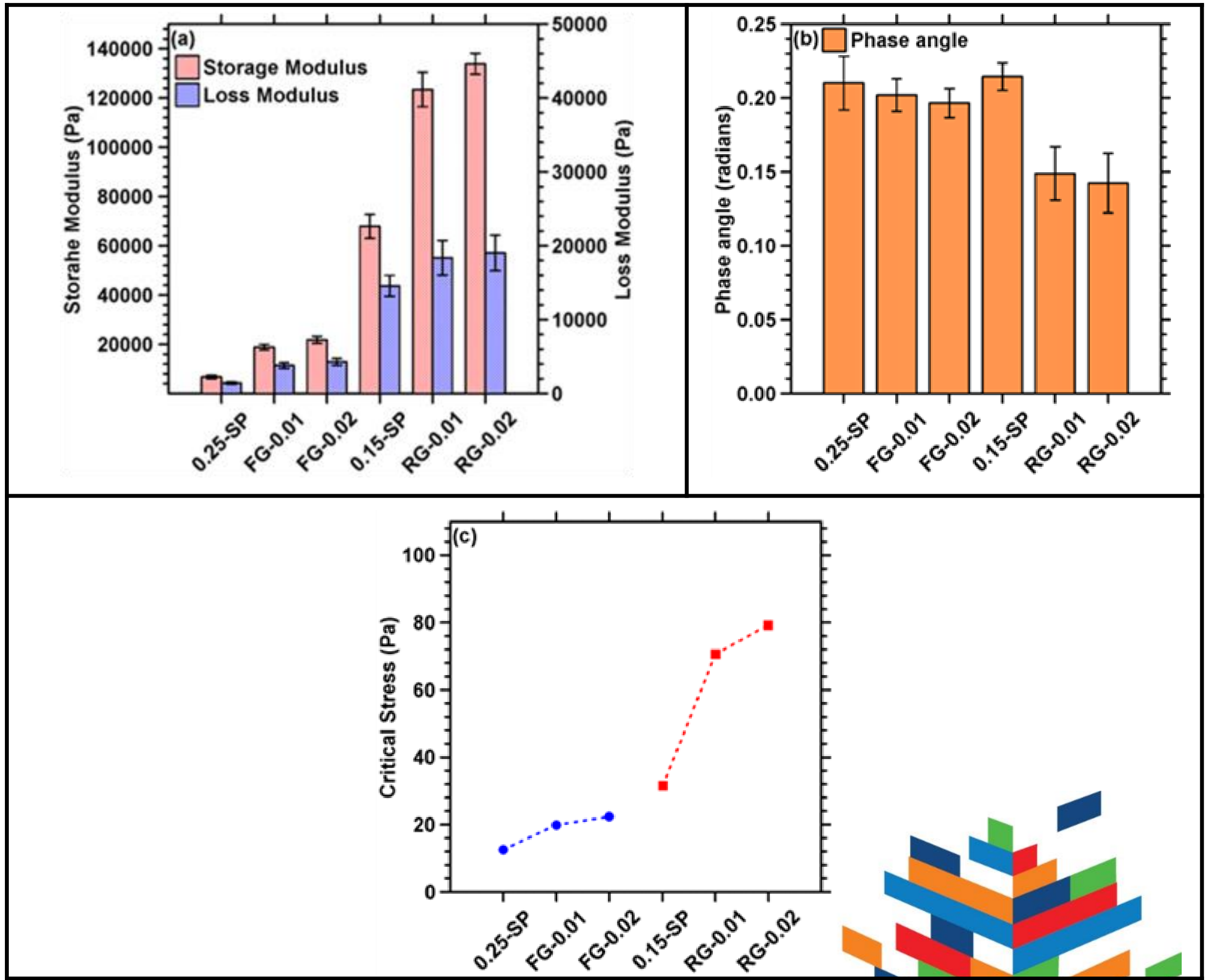
Oscillation rheology – results: (a) Storage and loss modulus, (b) phase angle, and (c) critical stress.



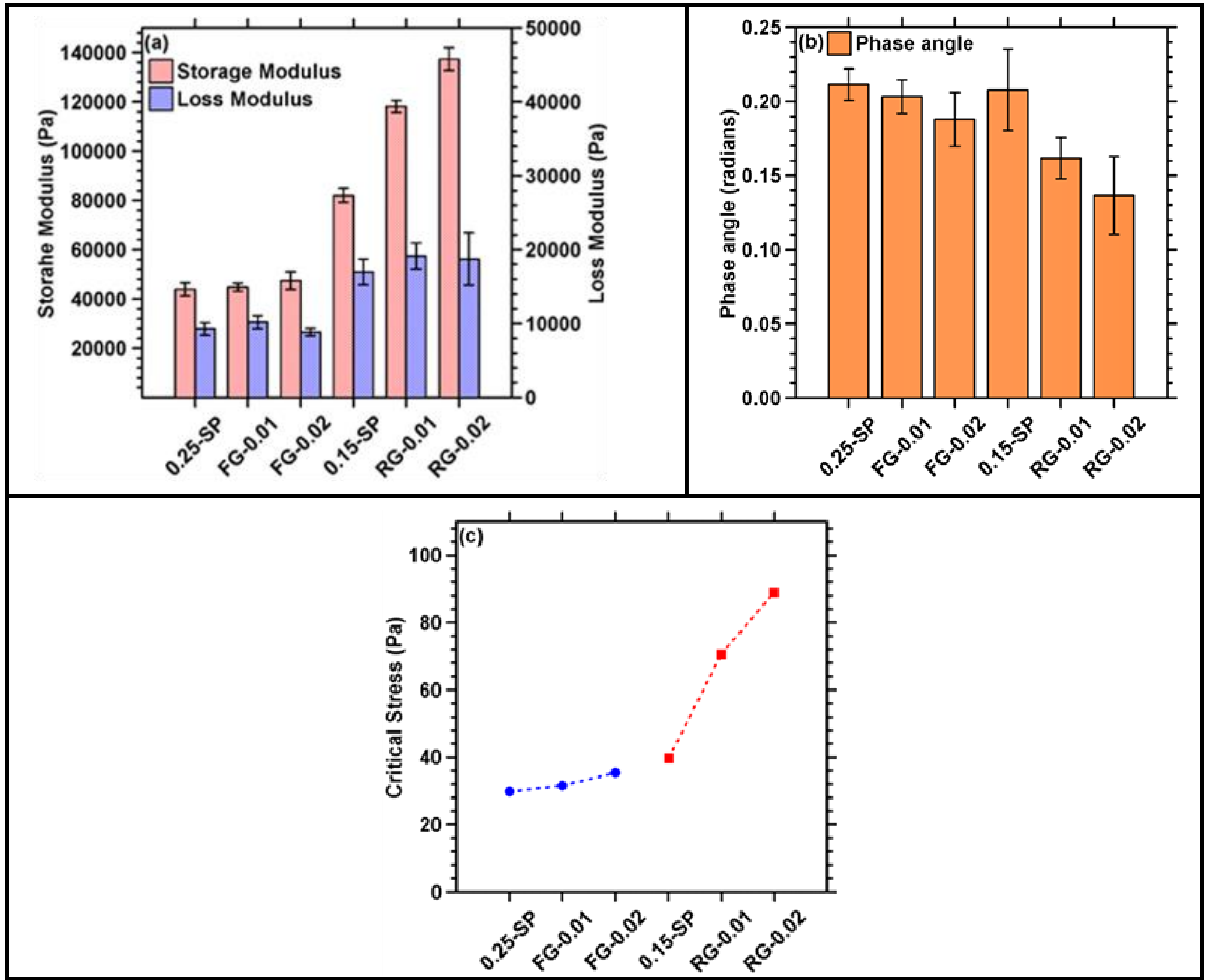
OPC paste



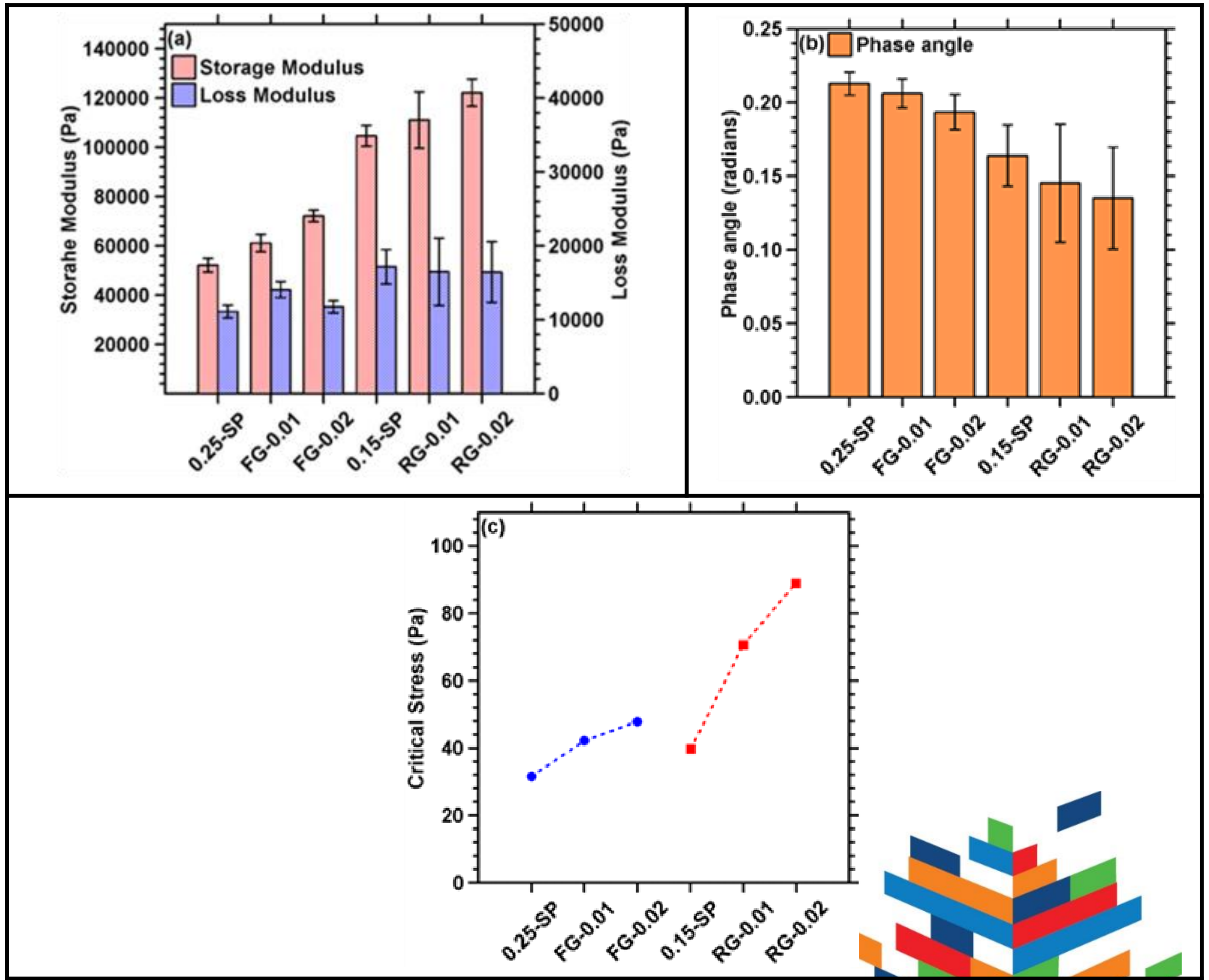
L_{30-s} paste

Results & Discussions

Oscillation rheology – results: (a) Storage and loss modulus, (b) phase angle, and (c) critical stress.



$F_{10}L_{20\text{-}s}$ paste



$F_{15}L_{15\text{-}s}$ paste

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Conclusions

- The graphene-modified pastes exhibit significantly higher yield stress and plastic viscosity as compared to the control paste. Higher yield stress may enhance the buildability of these mixtures.

- Enhanced particle packing with increase in graphene dosage, and higher specific surface area of graphene nanoparticles makes movement of water for the lubrication of cement particles harder.

- Increase in yield stress is more significant in OPC paste compared to binary and ternary blends. This allows optimizing mixture proportions to attain desirable rheological characters along with improvement in microstructure via graphene-modification.

- Oscillation rheology indicate the enhancement in elastic behavior (via higher storage modulus)

- Significant increase in the critical stress of the graphene-modified pastes indicate that these mixtures may retain their microstructure-integrity under higher rotations experienced during extrusion.

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