Rheological Characterization of 3D Printable Mixtures Beyond Flow Initiation

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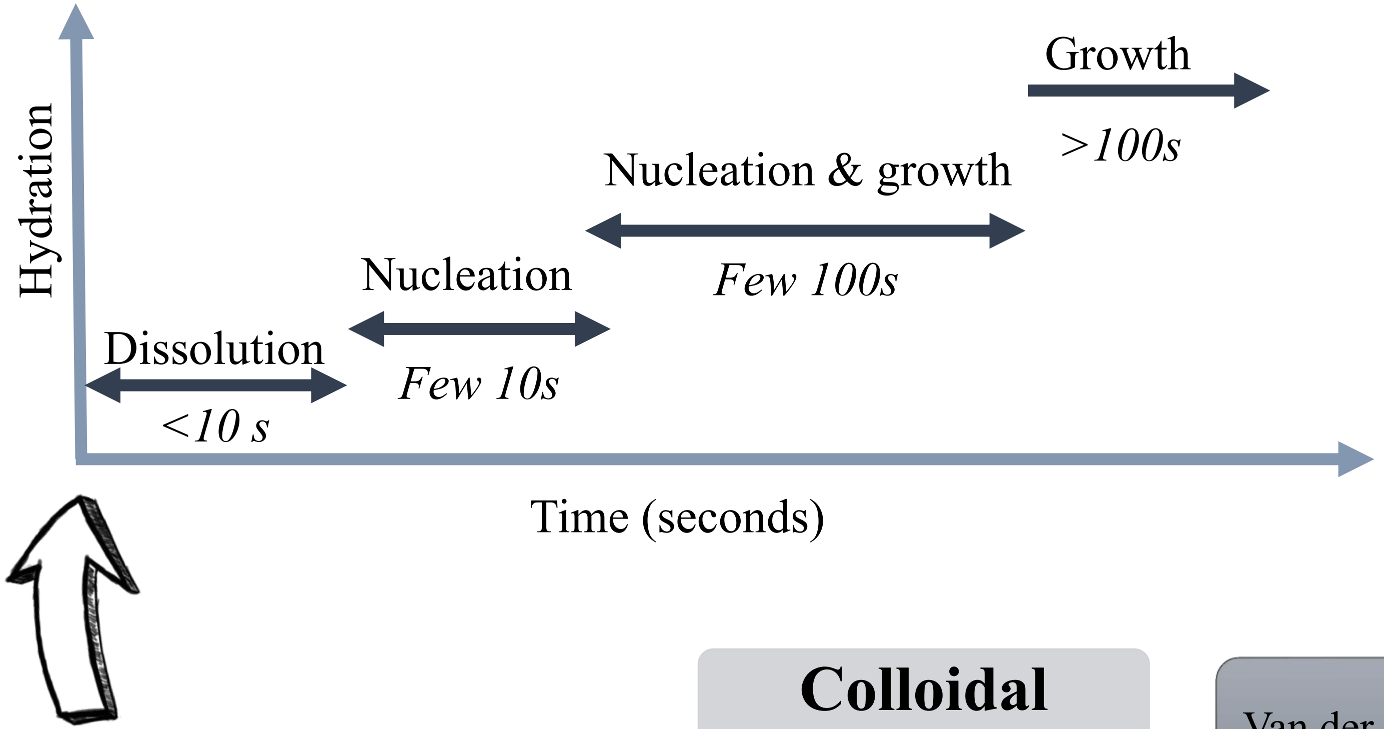
Static yield stress

The stress required to initiate flow

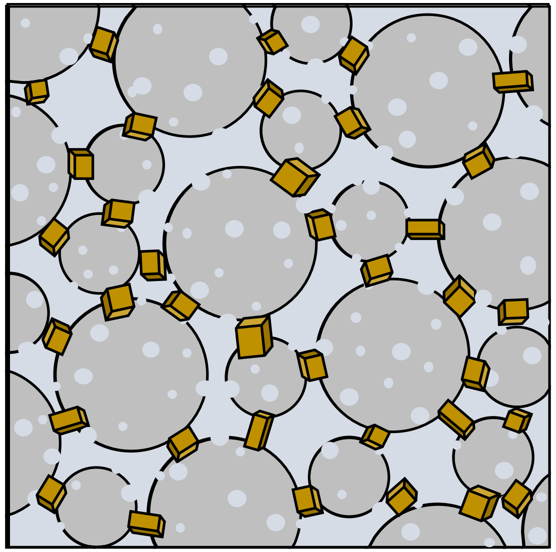
or in other words:

”The stress at which the behavior transitions from **solid** to **fluid** response”

Origins of structuration in cement paste (Based on N.Roussel (2012))



Onset of water-cement reaction



Colloidal structure

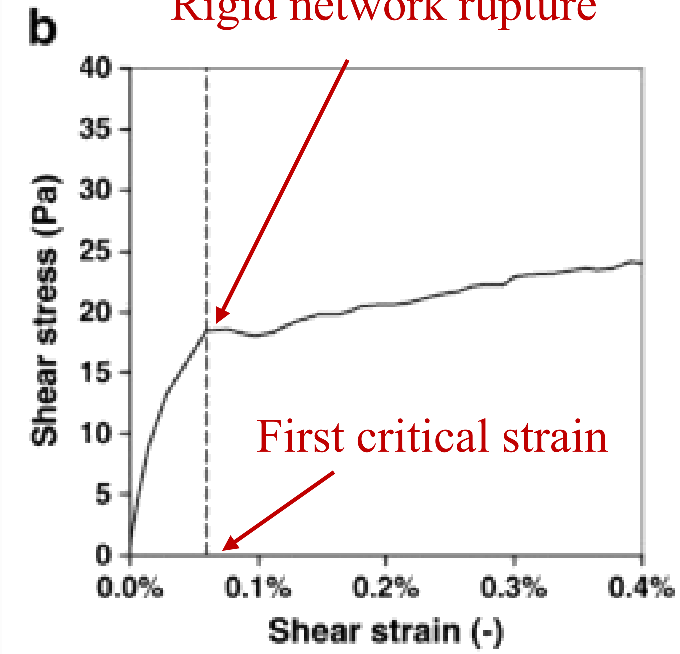
Van der Waals | Electrostatic forces | Ionic forces

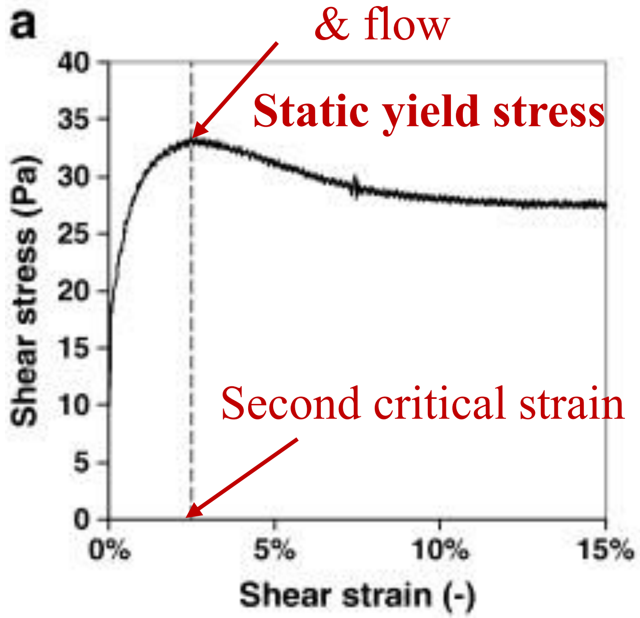
Rigid structure

Nucleation | Rigidification/ Growth

N.Roussel et al., cemconres 2012

Static yield stress of “normal” cement paste





N.Roussel et al., cemconres 2012

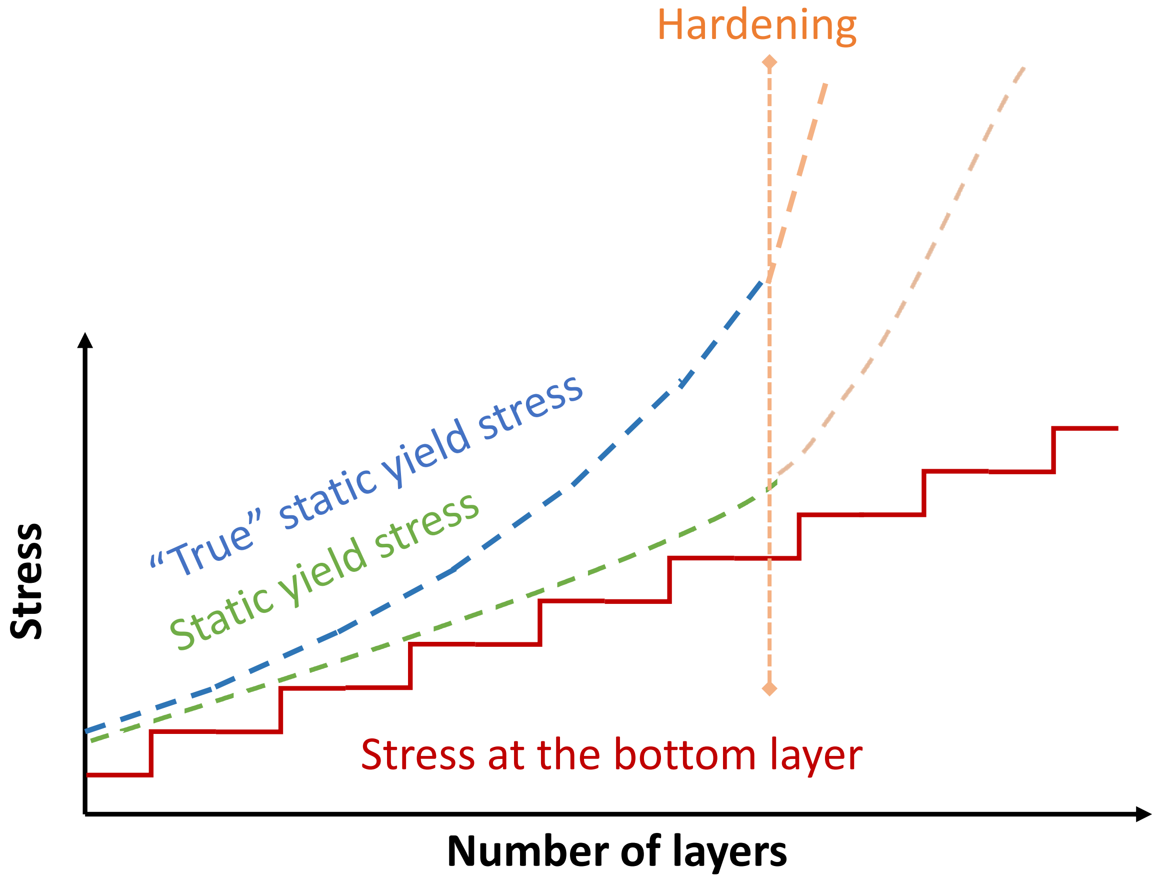
Rigid structure

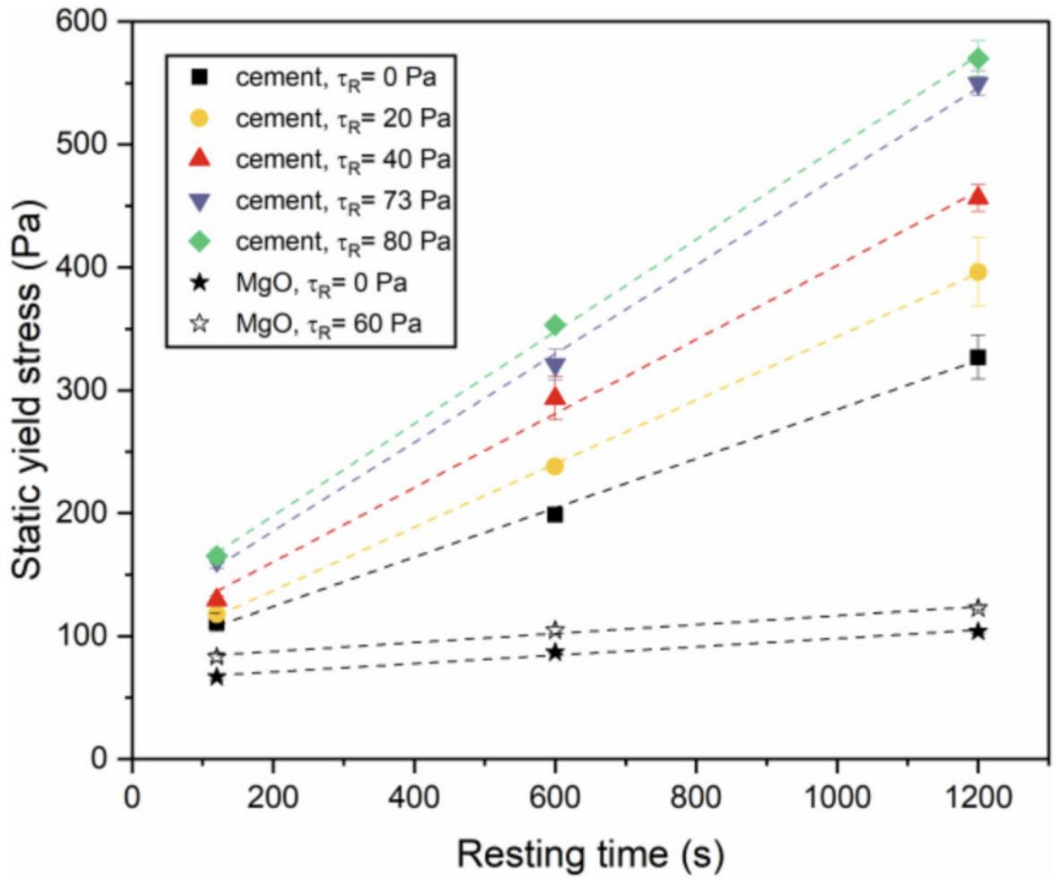
- Nucleation
- Rigidification/ Growth

Colloidal structure

- Van der Waals
- Electrostatic forces
- Ionic forces

Static Yield Stress in 3D printing

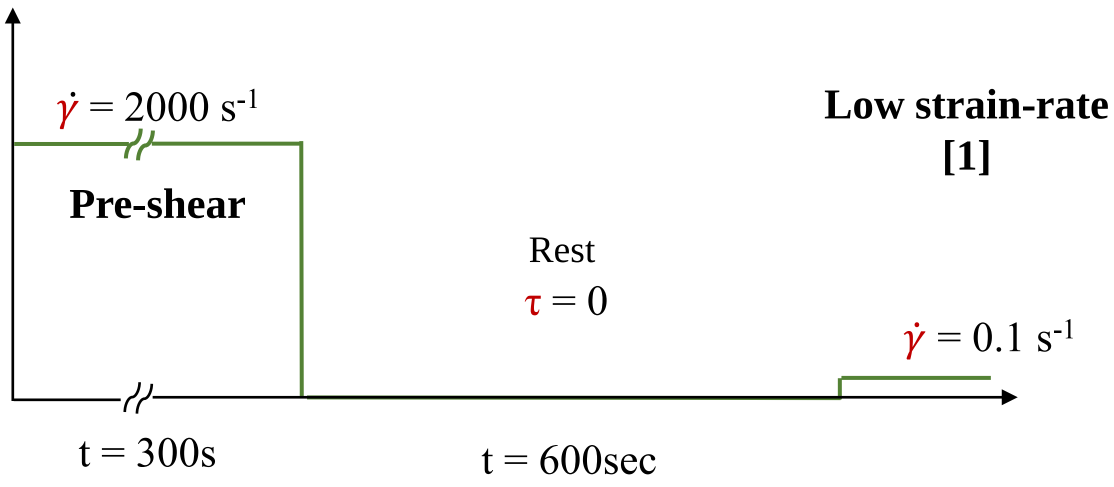




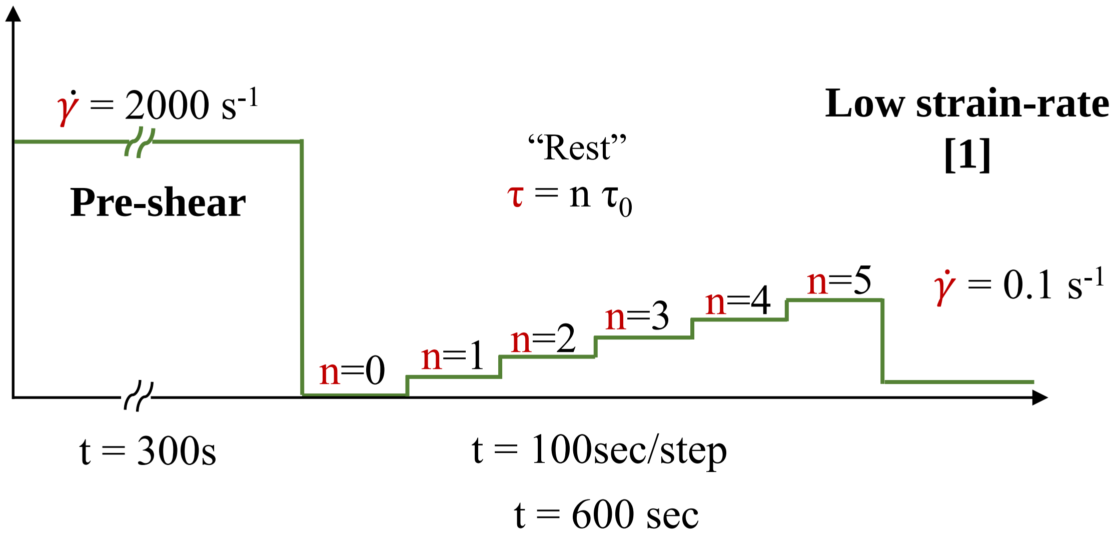
S. Ma & S. Kawashima, JofRheo, 2020

Rheological protocol

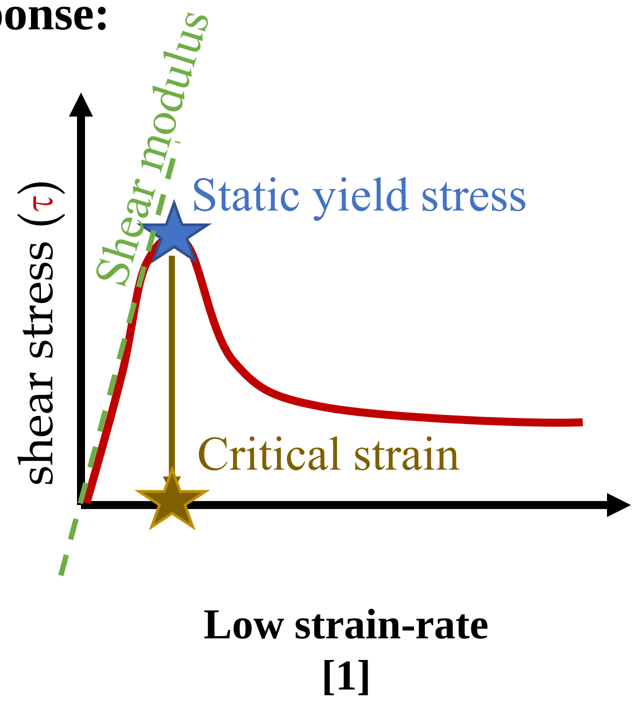
Applied:
- Shear stress (τ)
- strain rate ($\dot{\gamma}$)



Applied:
- Shear stress (τ)
- strain rate ($\dot{\gamma}$)



Response:

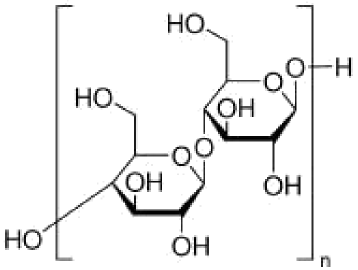


Mortar mixes

0.4 water/cement (w/c)
0.25 sand/cement (s/c)

Mix 1 (reference): 2 wt.% VMA

- Low molecular weight cellulose ether
- Added as dry powder
- Previously shown to enhance bleeding resistance

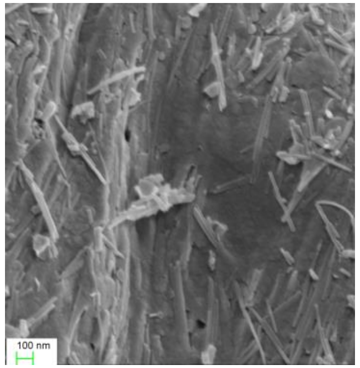


Mix 2 : 2 wt.% VMA + 0.3 vol.% PVA

- 6mm long polyvinyl alcohol fibers
- Previously shown to enhance the static yield stress and expected to enhance tensile properties or reduce shrinkage cracking

Mix 3 : 2 wt.% VMA + 1 wt.% NC

- Nanoclays or attapulgite nanorods with 30nm diameter and 1.5-2 µm length
- Previously shown to enhance static yield stress without significantly impact dynamic properties
- Water dispersible

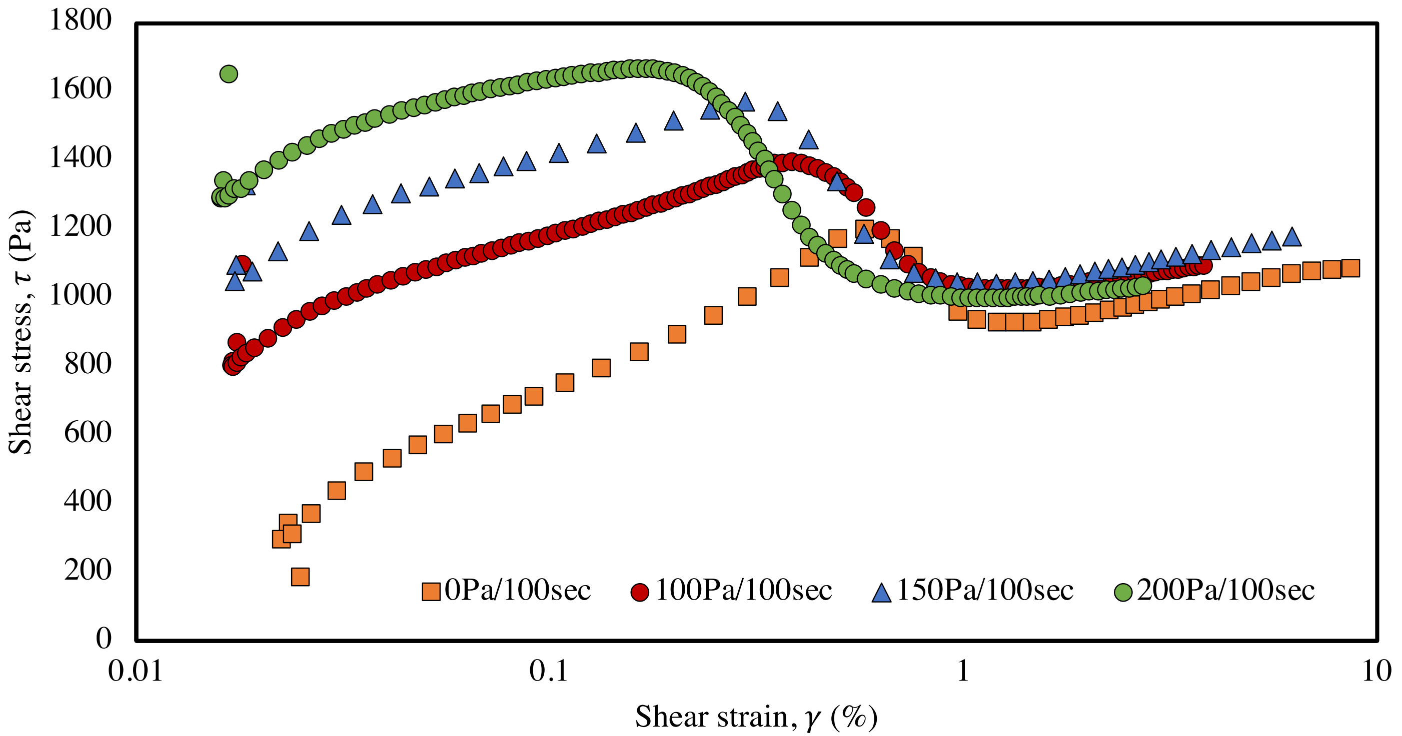


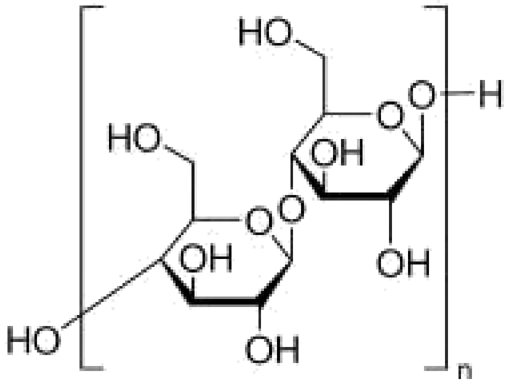
Mix 4 : 2 wt.% VMA + 20% SF

- Added as replacement of Portland cement
- Previously shown to enhance structuration and reduce bleeding

Mortar 1 (reference): 2.0 wt.% VMA

0.4 water/cement (w/c)
0.25 sand/cement (s/c)





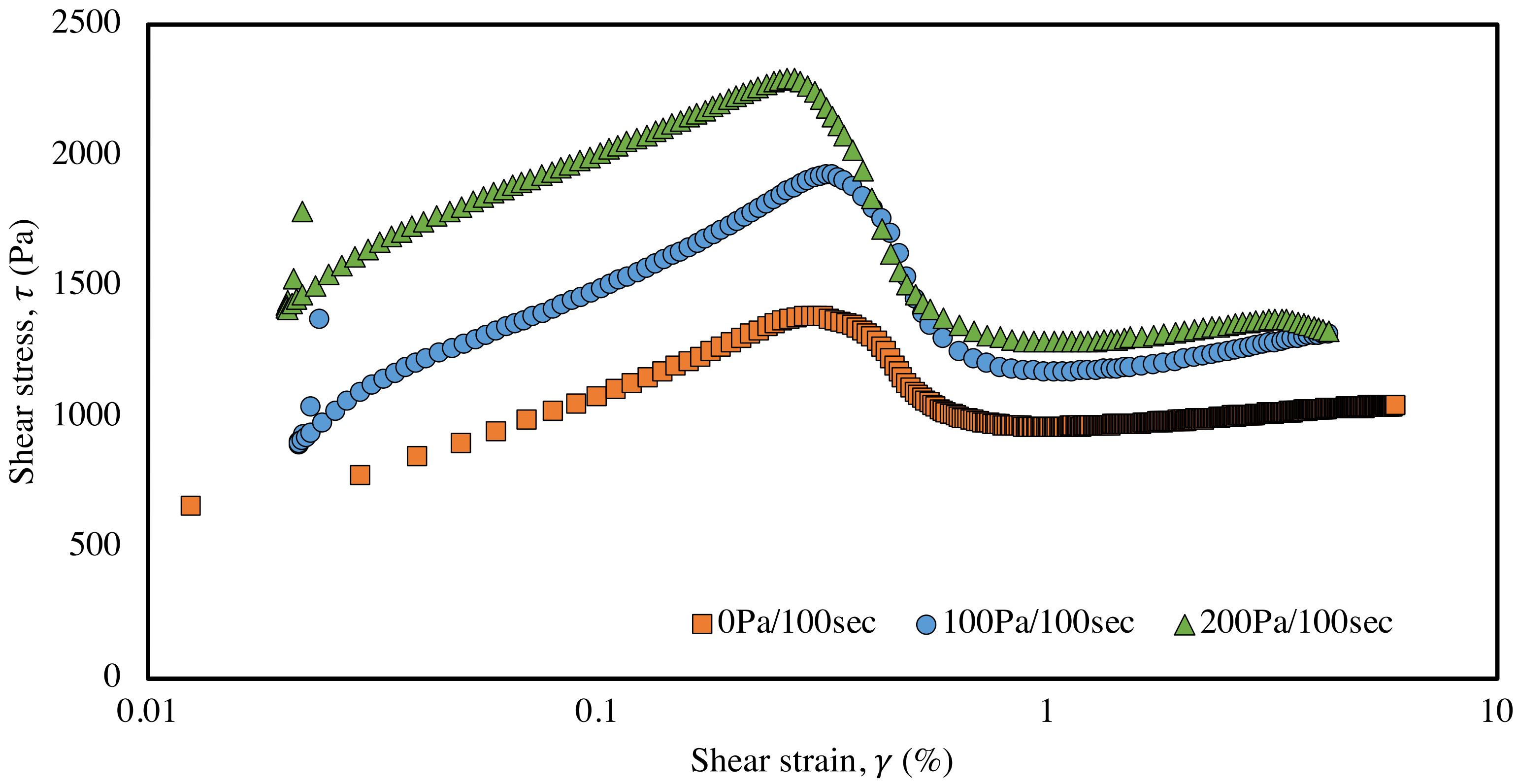
"Rest"
$\tau = n\,\tau_0$

τ_0 (Pa/100 sec)	**Static yield stress (Pa)**	**Critical strain (%)**	**Shear modulus (kPa)**
0	1197 (τ_{s0})	0.58%	111
100 (8% τ_{s0})	1393 (+16%)	0.39% (-33%)	84 (-25%)
150 (13% τ_{s0})	1571 (+31%)	0.30% (-49%)	83 (-25%)
200 (17% τ_{s0})	1665 (+39%)	0.17% (-71%)	60 (-46%)

Mortar 2: 0.3 vol% PVA + 2.0 wt.% VMA

0.4 water/cement (w/c)
0.25 sand/cement (s/c)

ACI CONCRETE CONVENTION

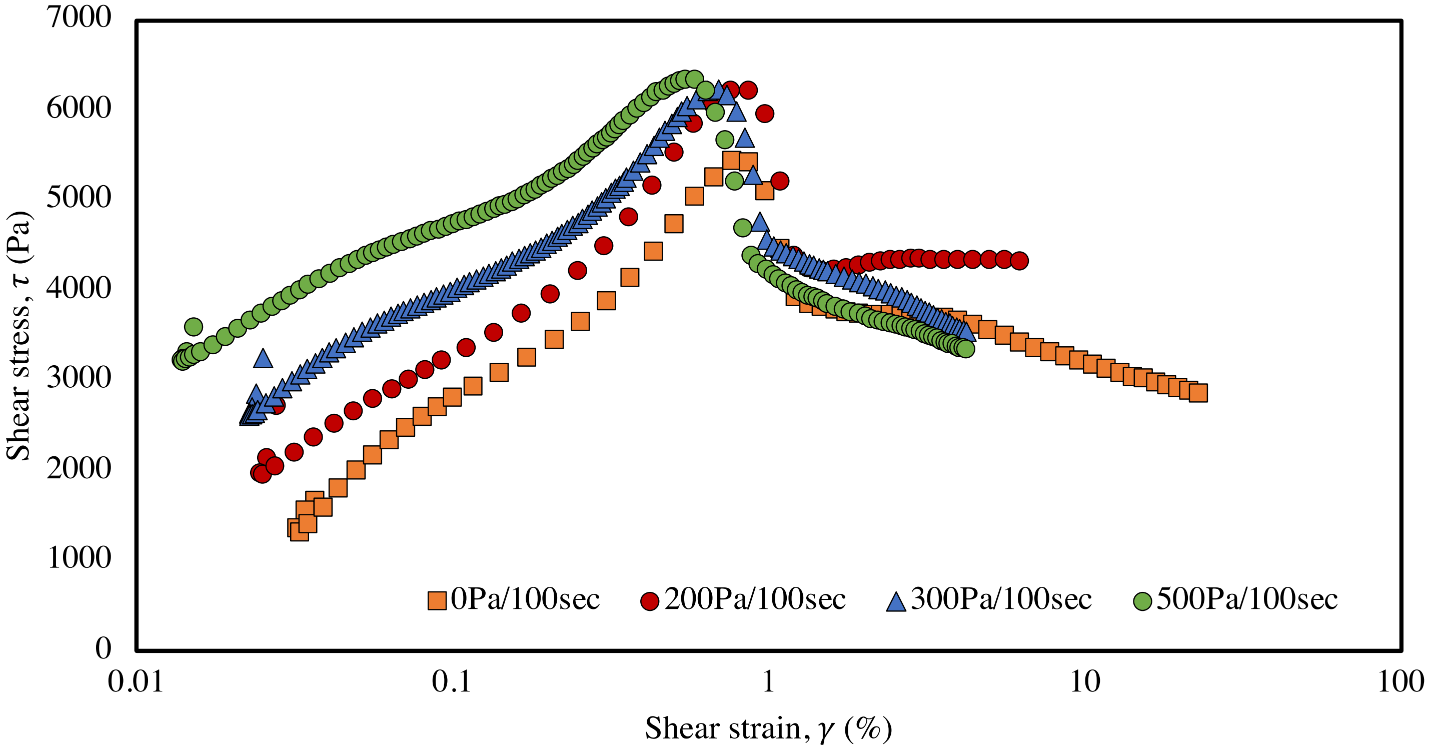


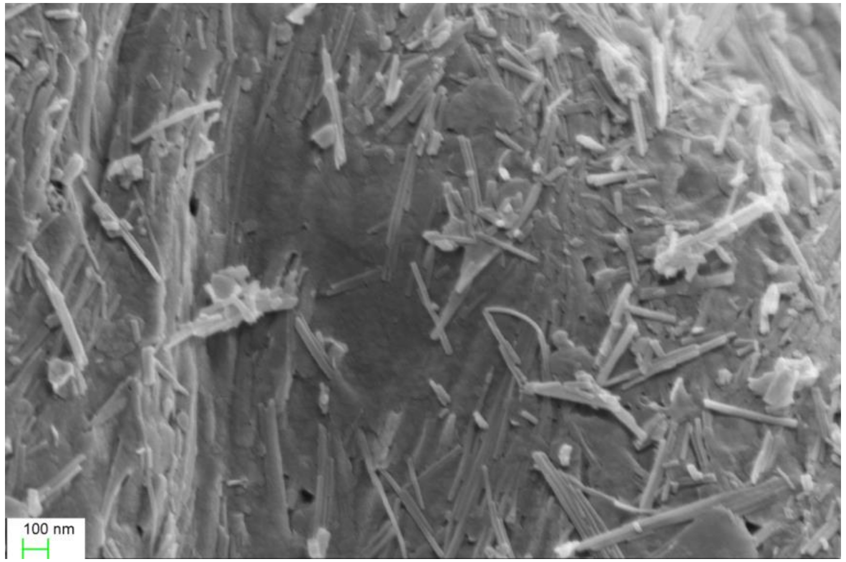
"Rest"
$\tau = n\,\tau_0$

τ_0 (Pa/100 sec)	Static yield stress (Pa)	Critical strain (%)	Shear modulus (kPa)
0	1386 (τ_{s0})	0.30%	212
100 (7% τ_{s0})	1925 (+39%)	0.33% (8%)	210 (-1%)
200 (14% τ_{s0})	2293 (+66%)	0.27% (-8%)	218 (+3%)

Mortar 3: 1.0 wt.% NC + 2.0 wt.% VMA

0.4 water/cement (w/c)
0.25 sand/cement (s/c)



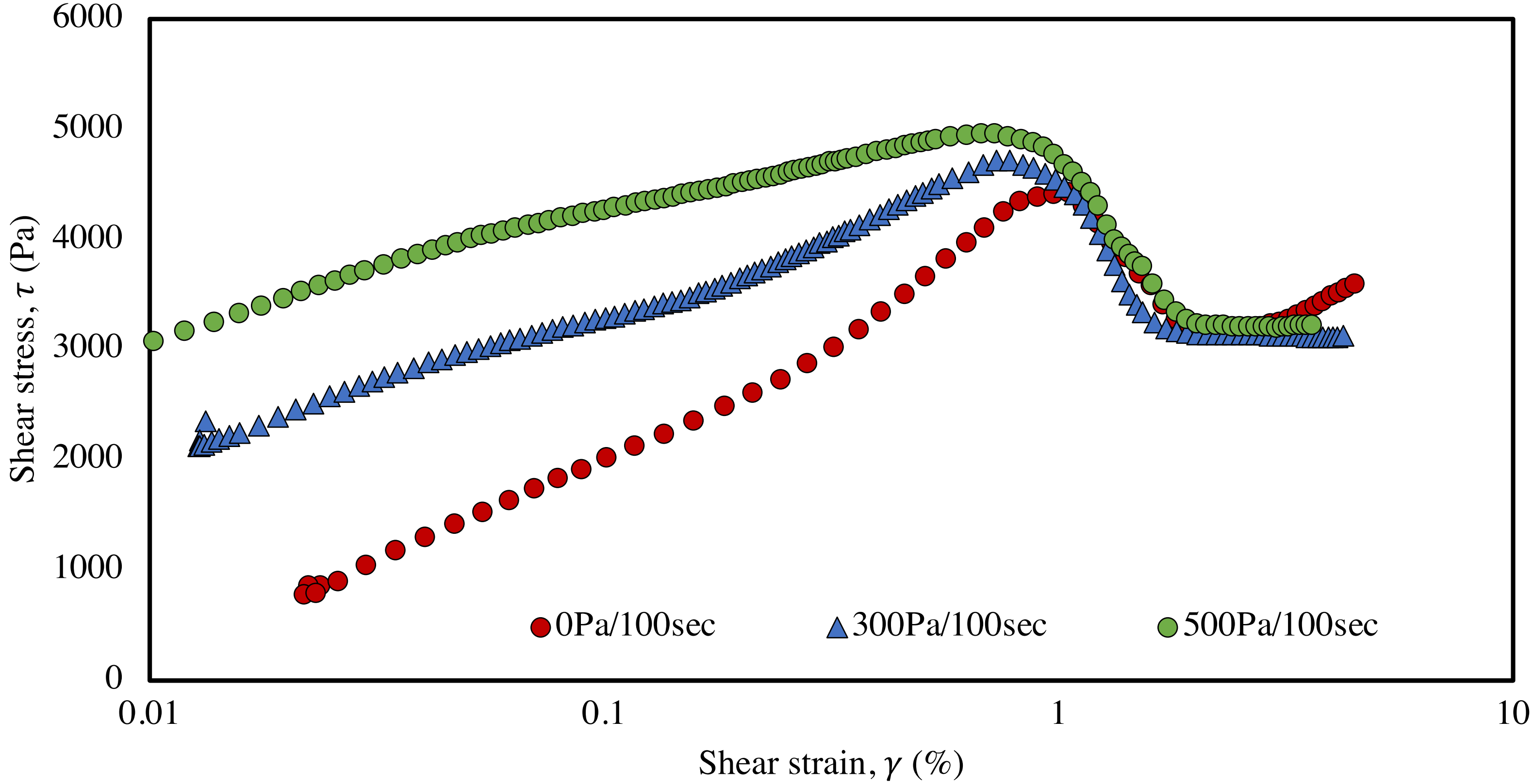


"Rest"
$\tau = n\,\tau_0$

τ_0 (Pa/100 sec)	Static yield stress (Pa)	Critical strain (%)	Shear modulus (kPa)
0	5432 (τ_{s0})	0.77%	450
200 (4% τ_{s0})	6217 (+15%)	0.86% (+13%)	510 (+10%)
300 (6% τ_{s0})	6236 (+15%)	0.69% (-10%)	465 (+3%)
500 (9% τ_{s0})	6333 (+17%)	0.58% (-24%)	443 (-2%)

Mortar 4: 20% SF(substitution) + 2.0 wt.% VMA

0.4 water/cement (w/c)
0.25 sand/cement (s/c)



“Rest”
$\tau = n\,\tau_0$

τ_0 (Pa/100 sec)	Static yield stress (Pa)	Critical strain (%)	Shear modulus (kPa)
0	4428 (τ_{s0})	1.05%	349
300 (7% τ_{s0})	4716 (+7%)	0.73% (-30%)	288 (-17%)
500 (11% τ_{s0})	4954 (+13%)	0.73% (-30%)	145 (-59%)

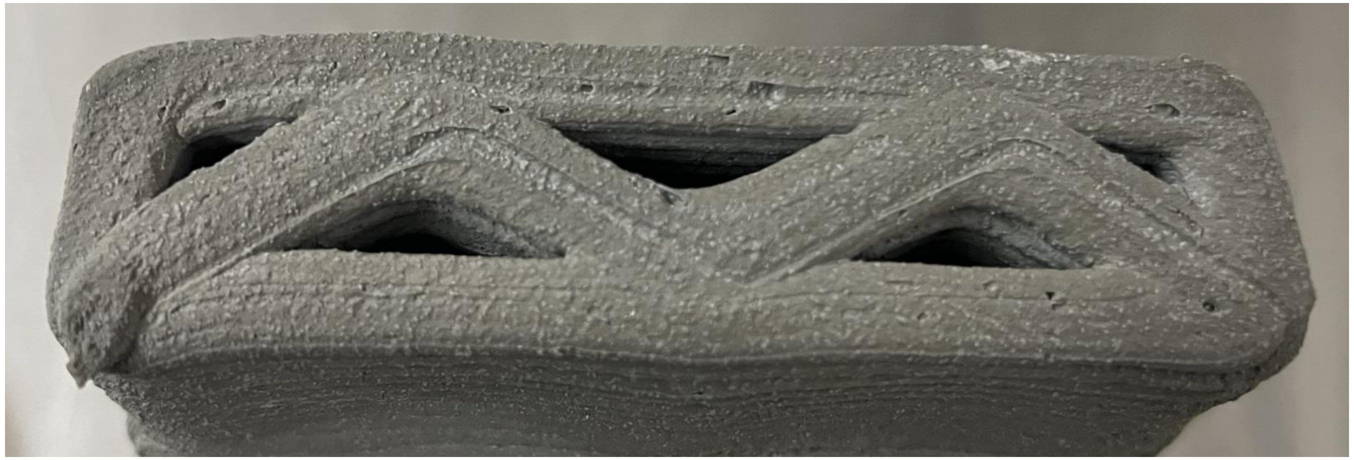
Summary

Mix	2 wt.% VMA	2 wt.% VMA + 0.3 vol% PVA	2 wt.% VMA + 1 wt.% NC	2 wt.% VMA + 20% SF
Static yield stress	↑ (+39%)	↑ (+66%)	↑ (+17%)	↑ (+13%)
Critical strain	↓ (-71%)	-	↑ ~(-24%)	↓ (-30%)
Shear modulus	↓ (-46%)	-	-	↓ (-59%)

Buildability test

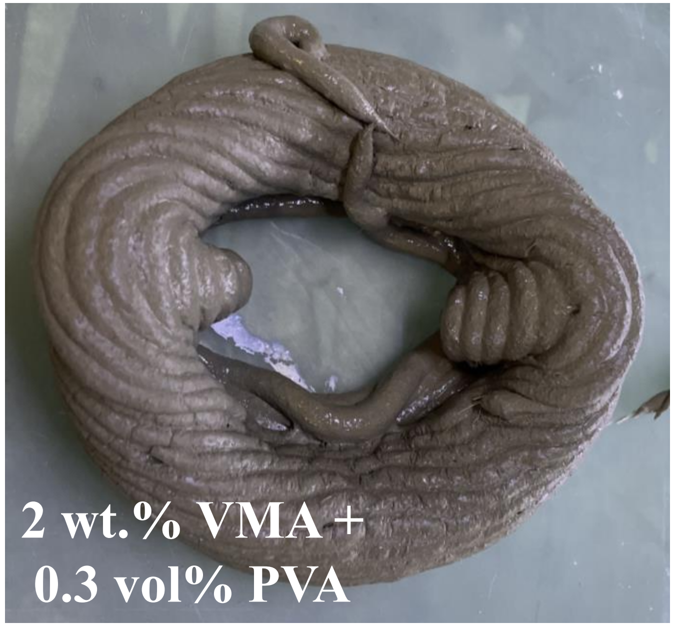
0.4 water/cement (w/c)
0.25 sand/cement (s/c)

100x 20 mm braced wall



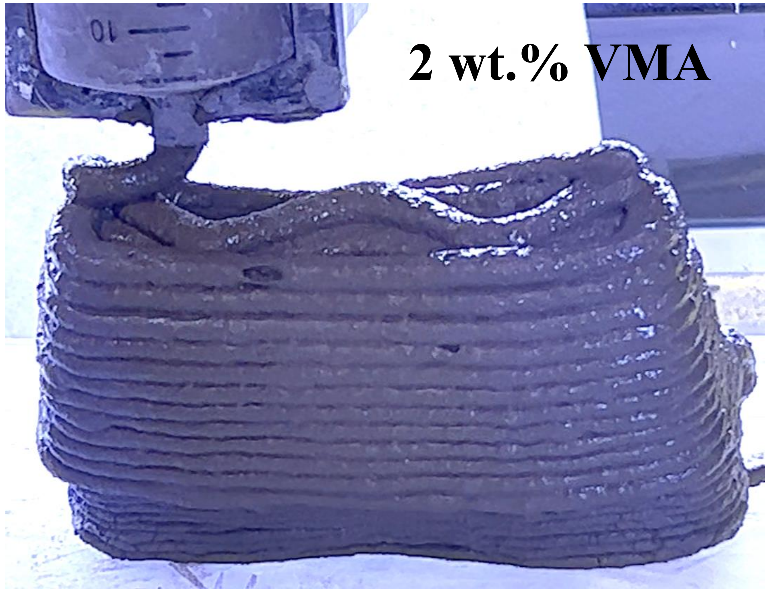
Φ 80mm cylinder

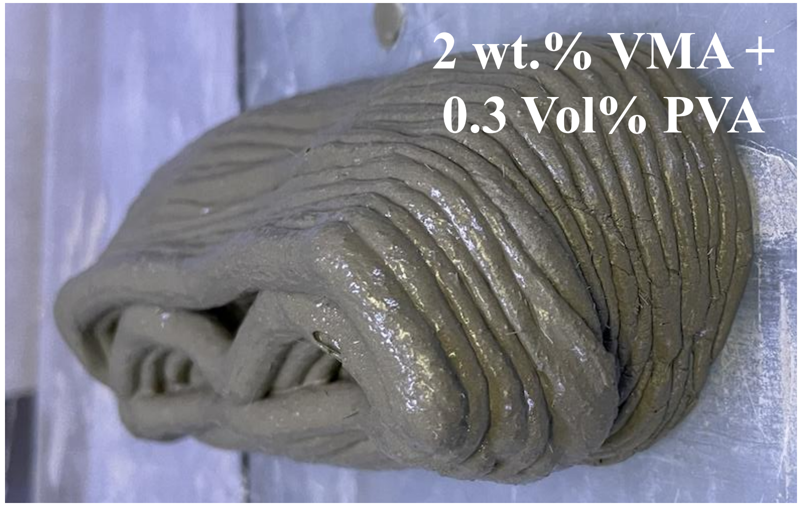
Buildability Test (Φ 80mm cylinder)



Buckling

Buildability Test (100x20 mm wall)





2 wt.% VMA +
20 wt.% SF

2 wt.% VMA +
1 wt.% NC

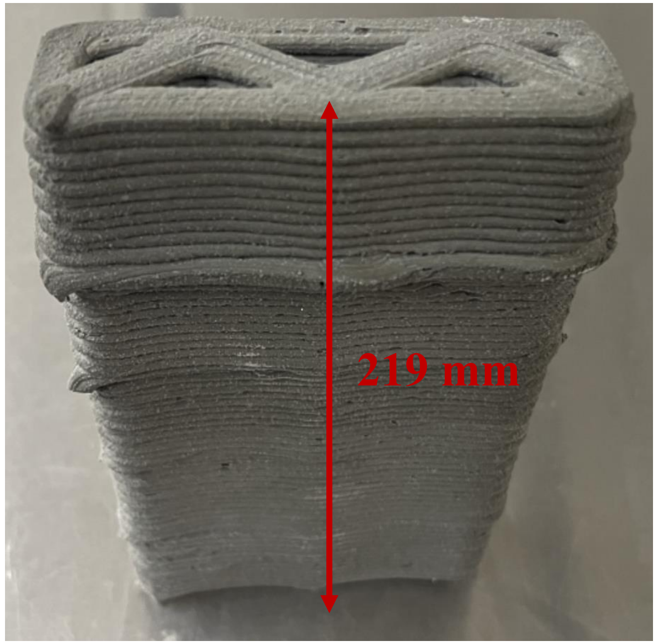
Buildability test results

Mix		2 wt.% VMA	2 wt.% VMA + 0.3 vol% PVA	2 wt.% VMA + 1 wt.% NC	2 wt.% VMA + 20% SF
Shear rheometry at $\tau_0 = 0$		**1197**	**1386**	**5432**	**4428**
Cylinder	Height at failure (mm)	63 mm	63 mm	219 mm	168 mm
	Bottom layer stress (Pa)	1159 Pa (-3%)	1247 Pa (-10%)	4307 Pa	3154 Pa (-29%)
	Mode of failure	***Buckling***	***Buckling***	-	***Buckling***
Wall	Height at failure (mm)	77 mm	75 mm	219 mm	219 mm
	Bottom layer stress (Pa)	1416 Pa (+18%)	1485 Pa (+7%)	4307 Pa	4112 Pa
	Mode of failure	***Bottom collapse***	***Bottom collapse***	-	-

Maximum printing height

Summary

Mix	2 wt.% VMA	2 wt.% VMA + 0.3 vol% PVA	2 wt.% VMA + 1 wt.% NC	2 wt.% VMA + 20% SF
Static yield stress	↑ (+39%)	↑ (+66%)	↑ (+17%)	↑ (+13%)
Critical strain	↓ (-71%) 0.58-0.17 %	- 0.30-0.27 %	↑ ~(-24%) 0.77-0.58 %	↓ (-30%) 1.05-0.73 %
Shear modulus	↓ (-46%) 111-60 kPa	- 210-218 kPa	- 510-445 kPa	↓ (-59%) 349-145 kPa



Slug test

Tensile strength

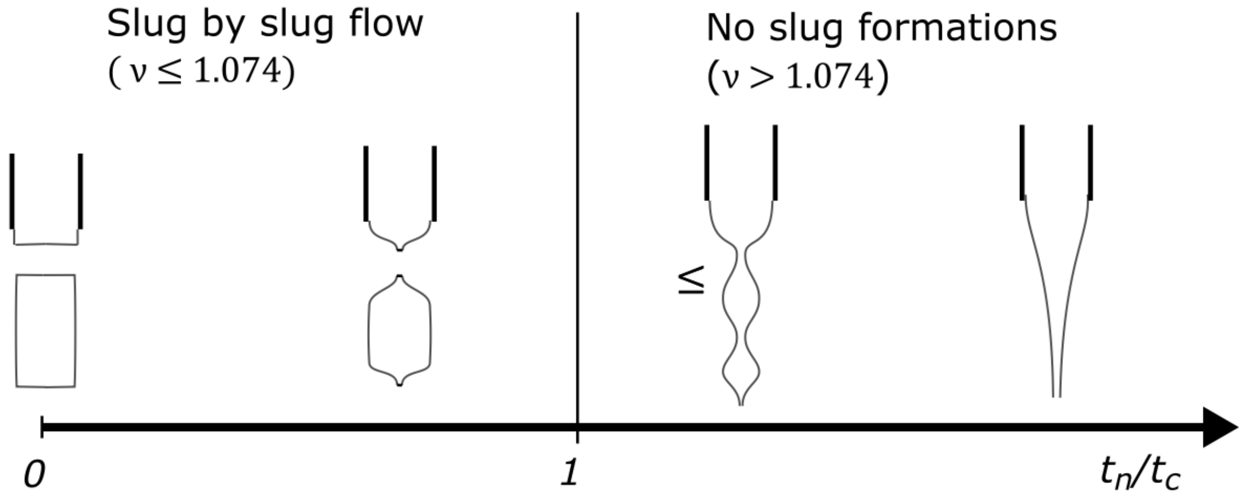
$$\sigma_c = \frac{g}{(\pi R_o^2)} m_s$$

Y. Jacquet et al. RILEMtechlet, 2020

Extensional static yield stress:

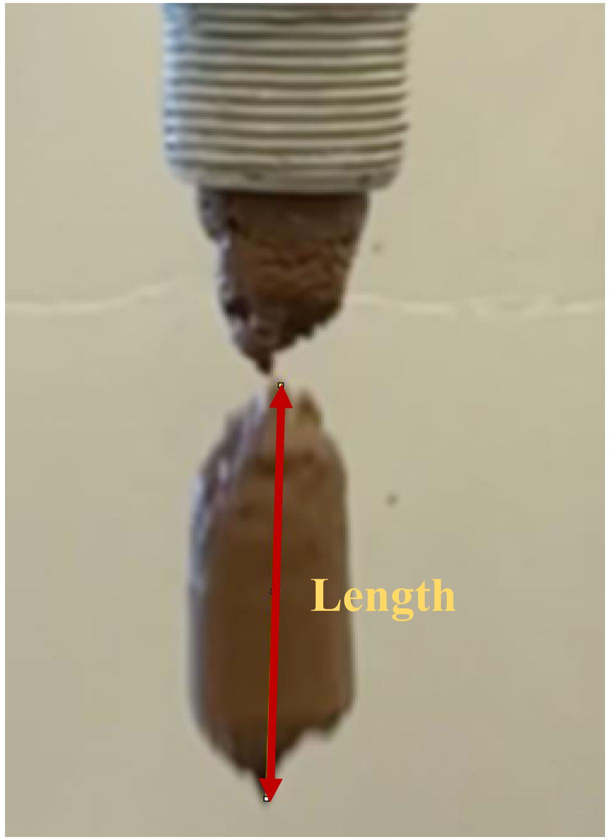
$$\tau_c = \frac{g}{\sqrt{3}\,(\pi R_o^2)} m_s$$

N. Ducoulombier et al. CemConRest, 2021



N. Ducoulombier et al. CemConRest, 2021

Slug test

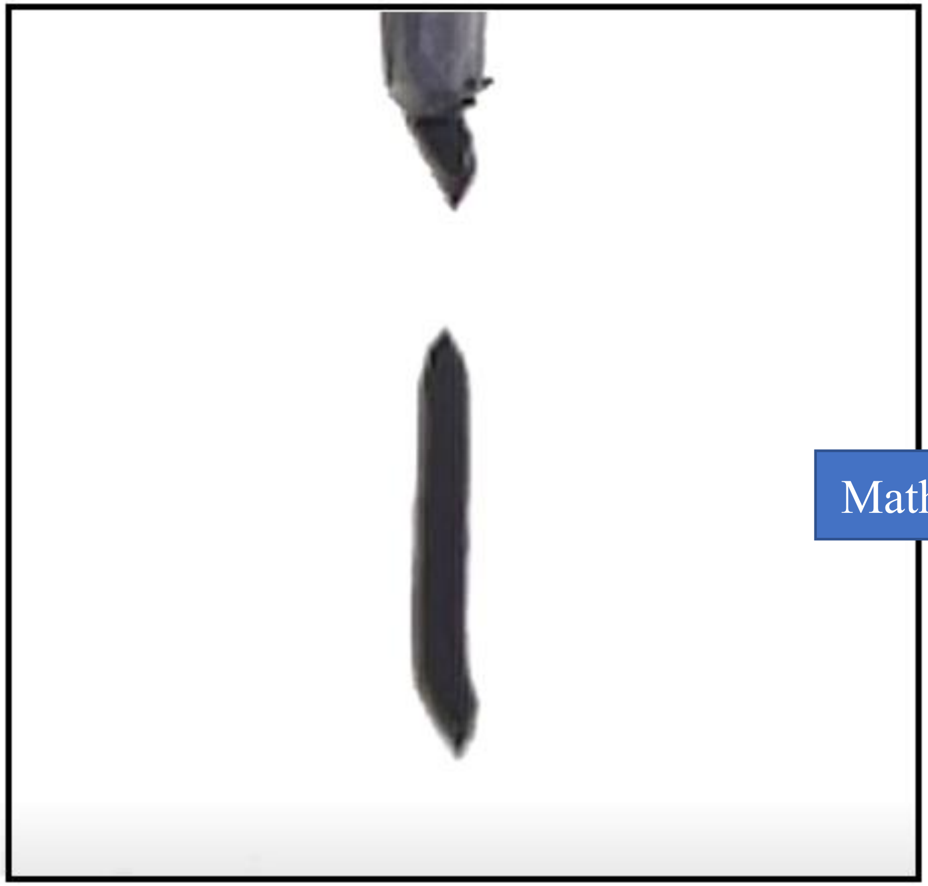


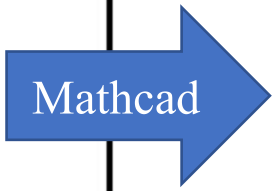
$$\tau_s = \frac{g m_s}{\sqrt{3}\left(\pi R_o^2\right)}$$

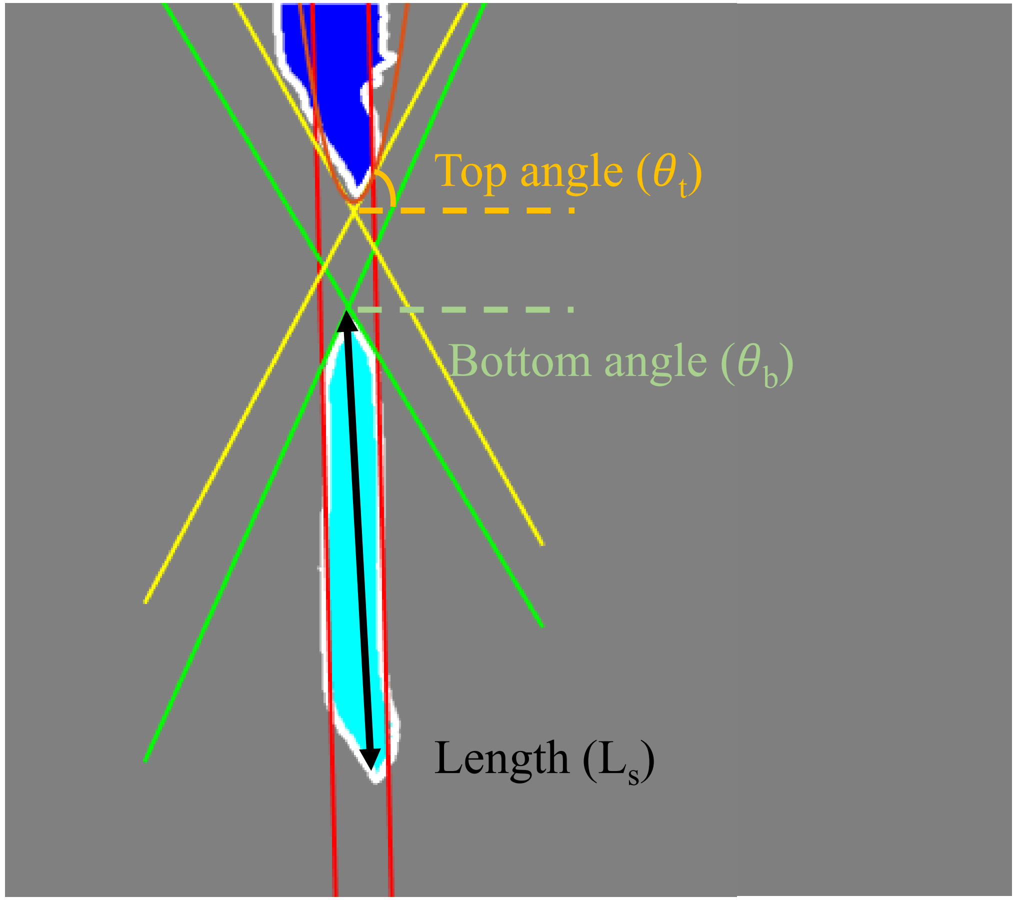
$$\tau_s = \frac{\rho g L_s}{\sqrt{3}}$$

$$\tau_s = \frac{\rho g V}{\sqrt{3} A}$$

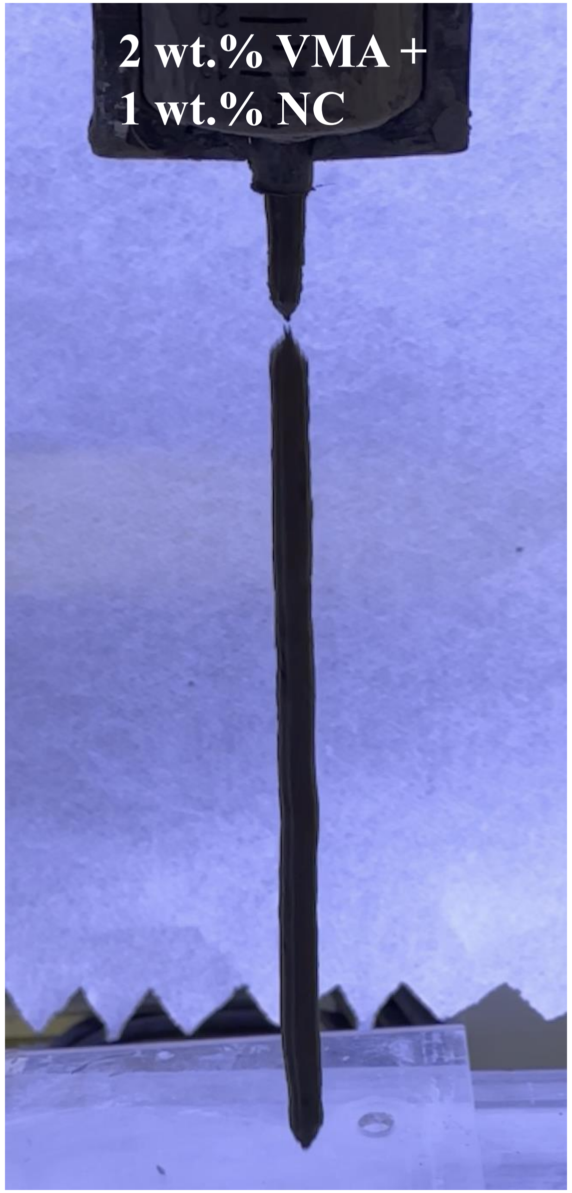
Slug test using image analysis





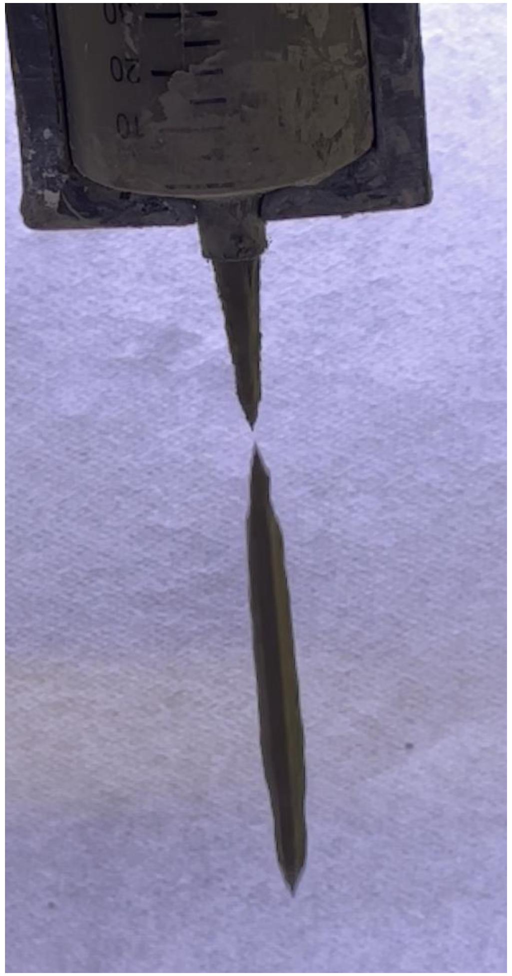


Slug test results



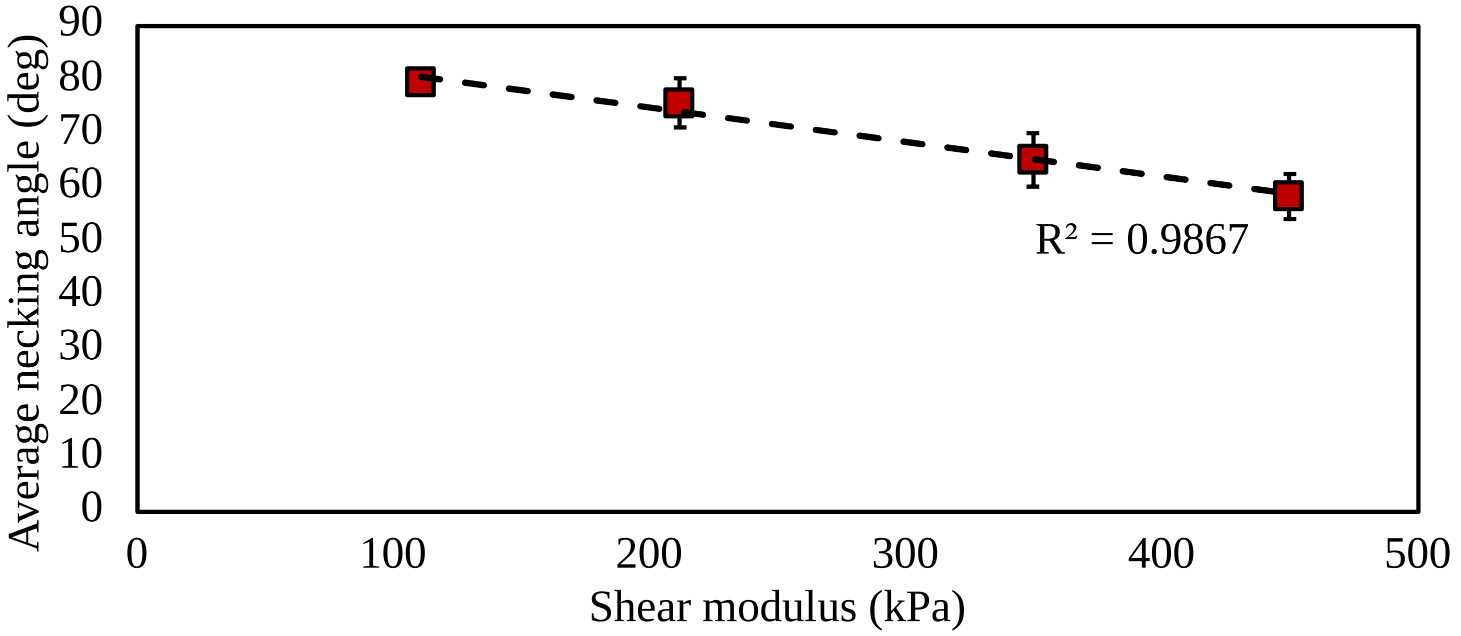
2 wt.% VMA +
0.3 vol% PVA

2 wt.% VMA +
0.3 vol% PVA



2 wt.% VMA

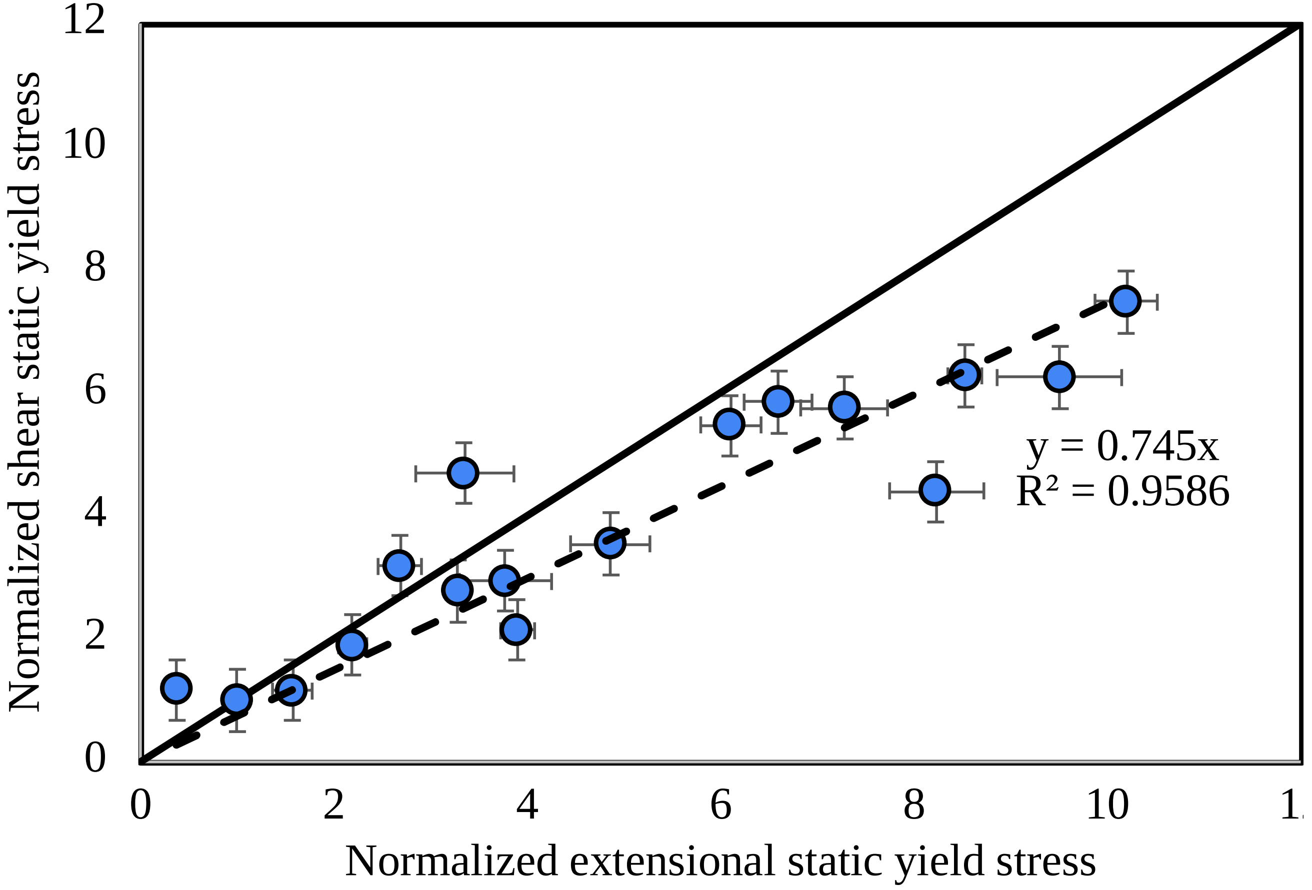
Slug test results

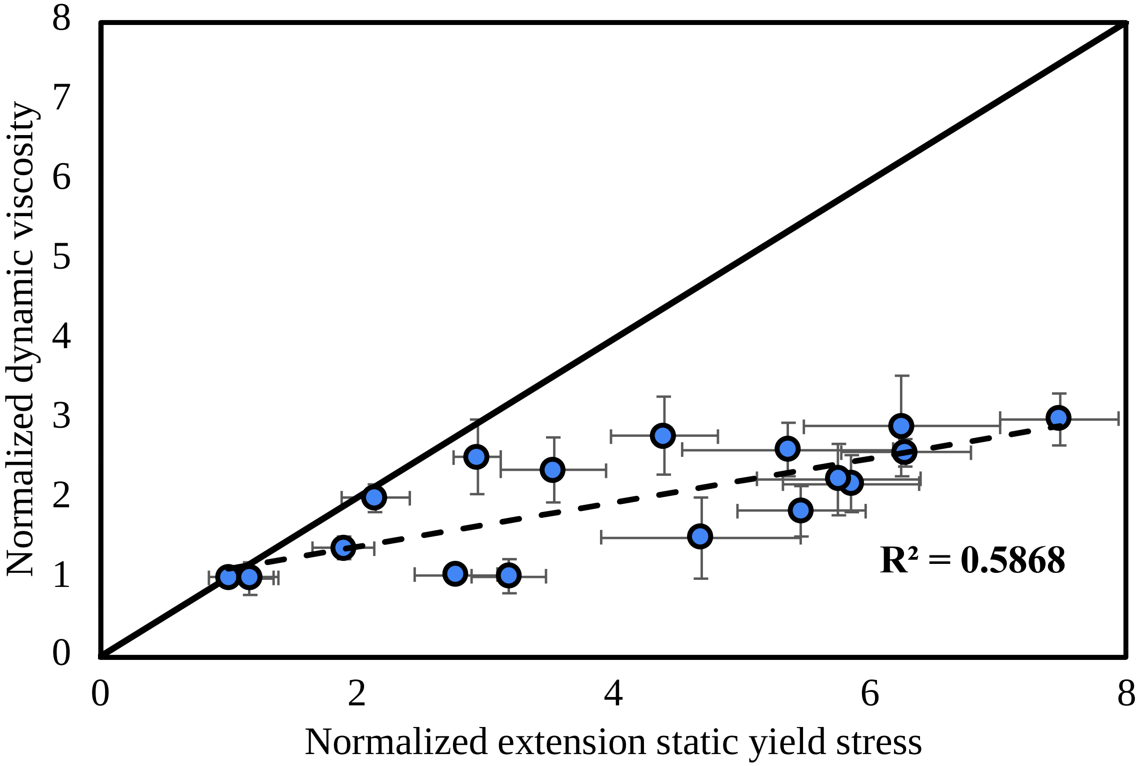


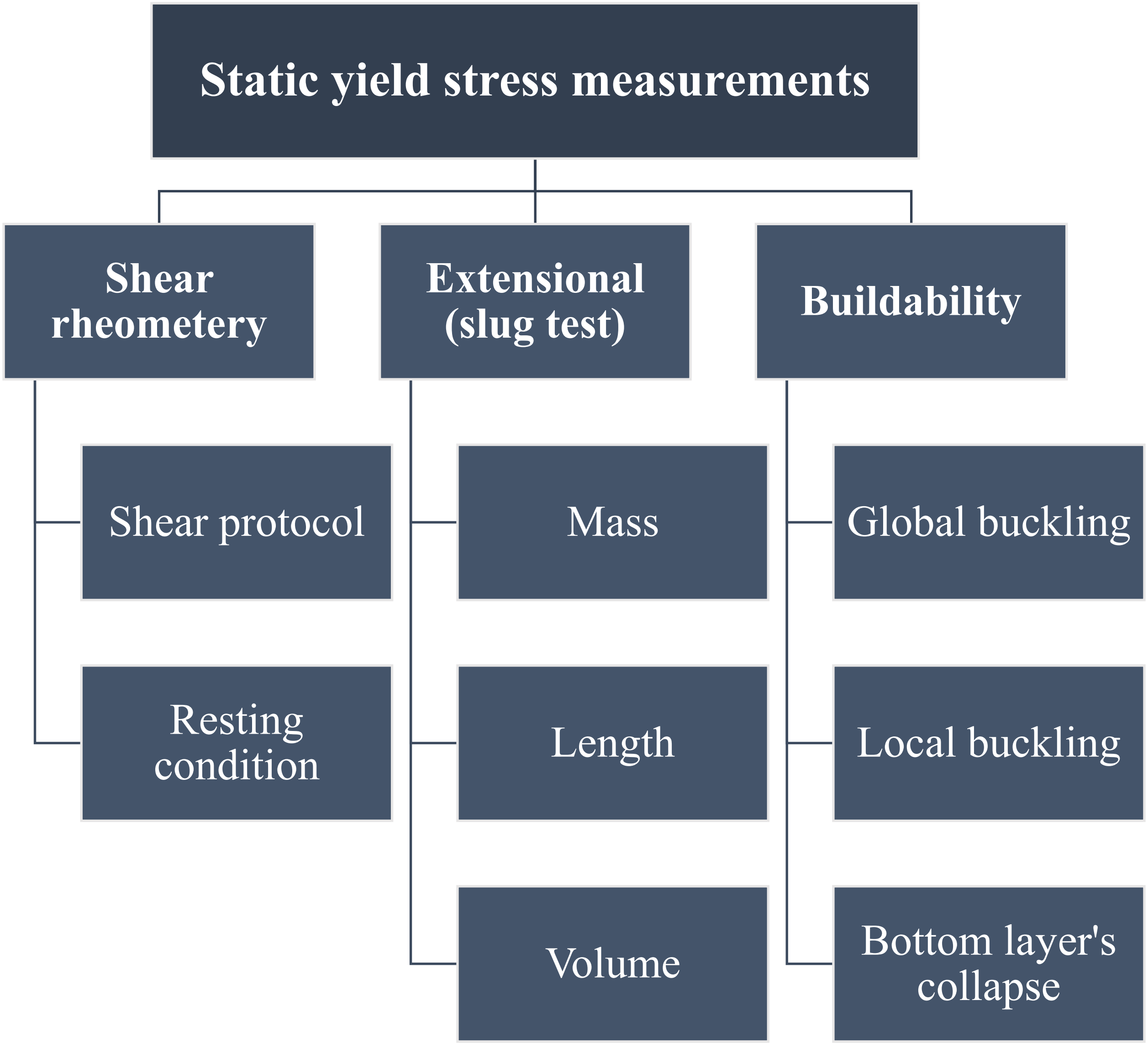
Mix	Static yield stress (Pa)			
	2 wt.% VMA	**2 wt.% VMA + 0.3 vol% PVA**	**2 wt.% VMA + 1 wt.% NC**	**2 wt.% VMA + 20% SF**
Shear rheometry at $\tau_0 = 0$	**1197**	**1386**	**5432**	**4428**
Based on length	2918 (+144%)	3469 (+150%)	5847 (+8%)	3496 (-21%)
Based on volume	1559 (+30%)	1661 (+20%)	4819 (-11%)	3636 (-18%)

Additional study on slugs by mass

- Varying NC (0 – 1.5 wt.%) and VMA (0 – 2.0 wt.%)







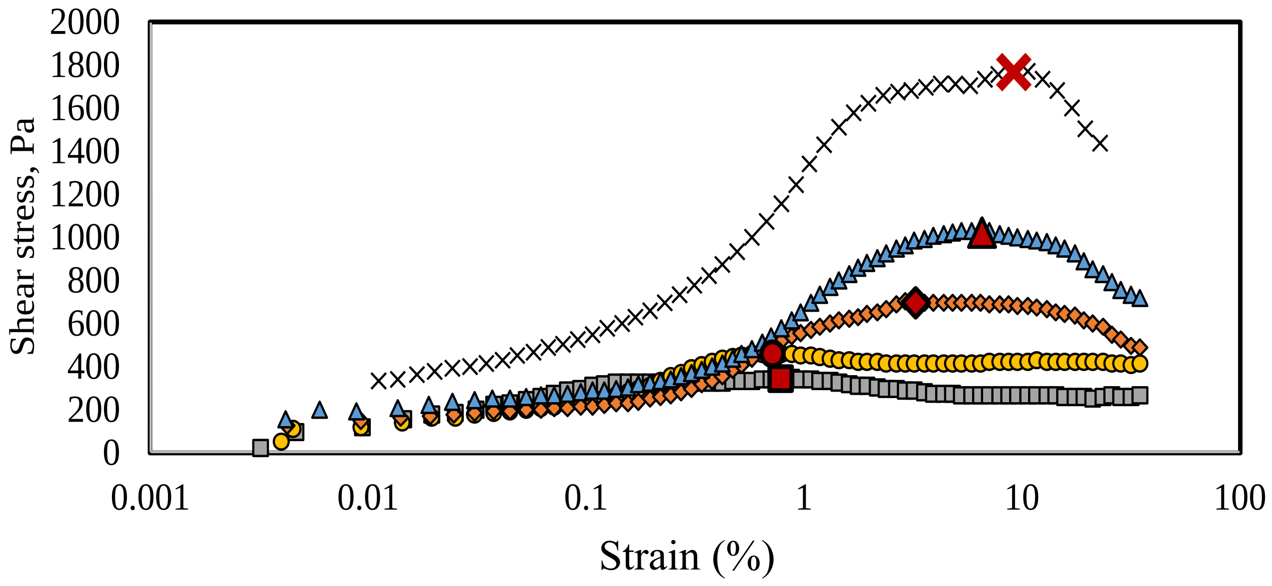
In the context of 3D printing

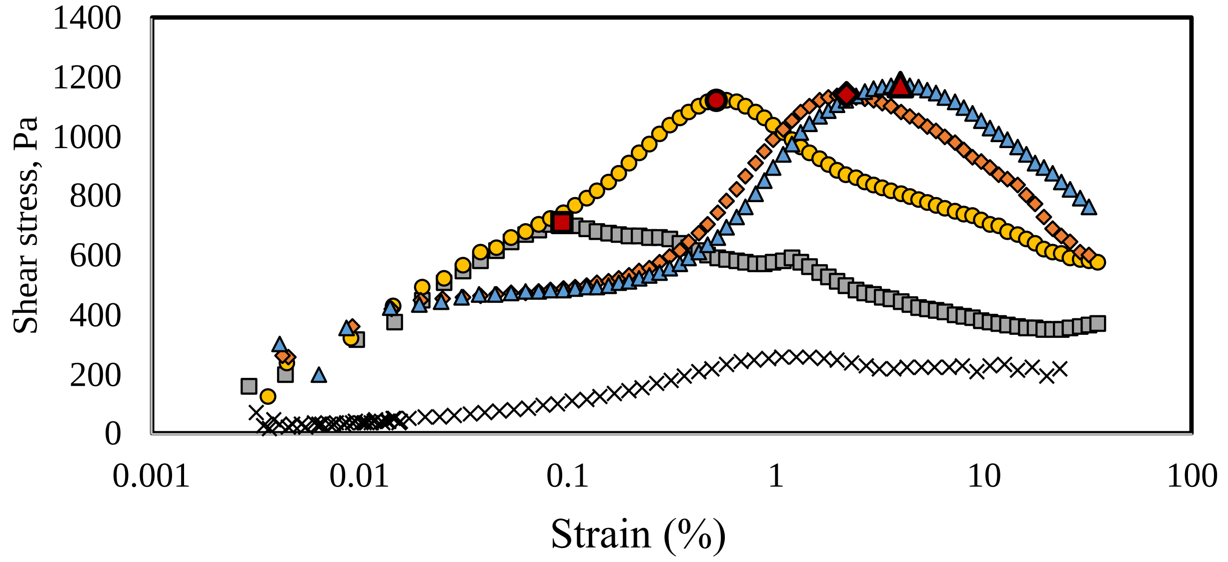
Bottom layer's collapse

How do we measure it:

- On-site during printing?
- In labs during development?

What is the ”true” static yield stress?





Static yield stress:
“The stress required to initiate flow”

But rheologically speaking, it may also be:
“The peak stress prior to or at the onset of flow initiation”

“The stress at which the critical colloidal strain is reached”

“The stress at which the behavior transitions from linear to non-linear during low shear strain rate application”

“The stress at which the colloidal network is damaged enough to result in flow instabilities”

“The maximum shear resistance to extensional flow discontinuity”

Conclusion

- The stress imposed by layer buildup can impact the rheological properties (static yield stress, critical strain and modulus). This effect is sensitive to admixtures and mix design used to enable 3D printing
- Buildability failure can be caused by reaching the static yield stress, critical strain or buckling due to low elastic modulus
- The shear or elastic modulus can be measured using the slug test (extensional rheology)
- Extensional static yield stress has positive correlation to shear static yield stress measured via image analysis or slug masses and can directly be implemented in large-scale 3D printing
- 3D volumetric scanning is required to increase extensional rheological measurements
- The definition of the static yield stress, at least in the context in 3D printing, may require to be updated to include critical strain and elastic modulus

Acknowledgement

LILLIAN GILBRETH POSTDOCTORAL FELLOWSHIP

Dr. Jan Olek's Lab

Dr. Kendra A. Erk's Lab

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Shear rheology measurements of static yield stress