Altering Shear Thickening of Chemical Mechanical Polishing Slurries Through the Addition of Electrolytes and Organic Solvents

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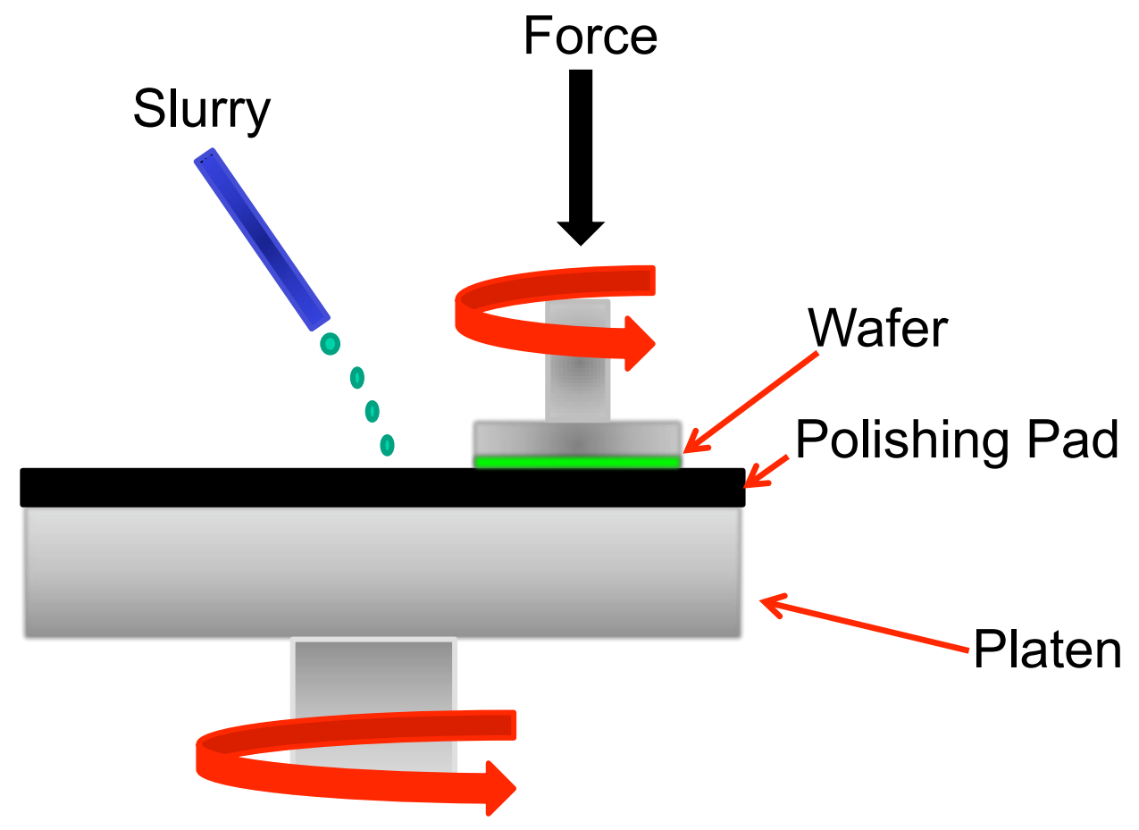
What is CMP?

- Chemical mechanical Polishing (CMP) planarizes and polishes semiconducting materials commonly used in microelectronics[1]
- The CMP process depends highly on the slurry composition, particle size and concentration, pH, and added chemicals , which determine the slurry's stability and effectiveness
- During the CMP process[2], the slurry film thickness (between the polishing pad and wafer surface) can vary from 1-100 µm, with shear rates >10^6 s^{-1}

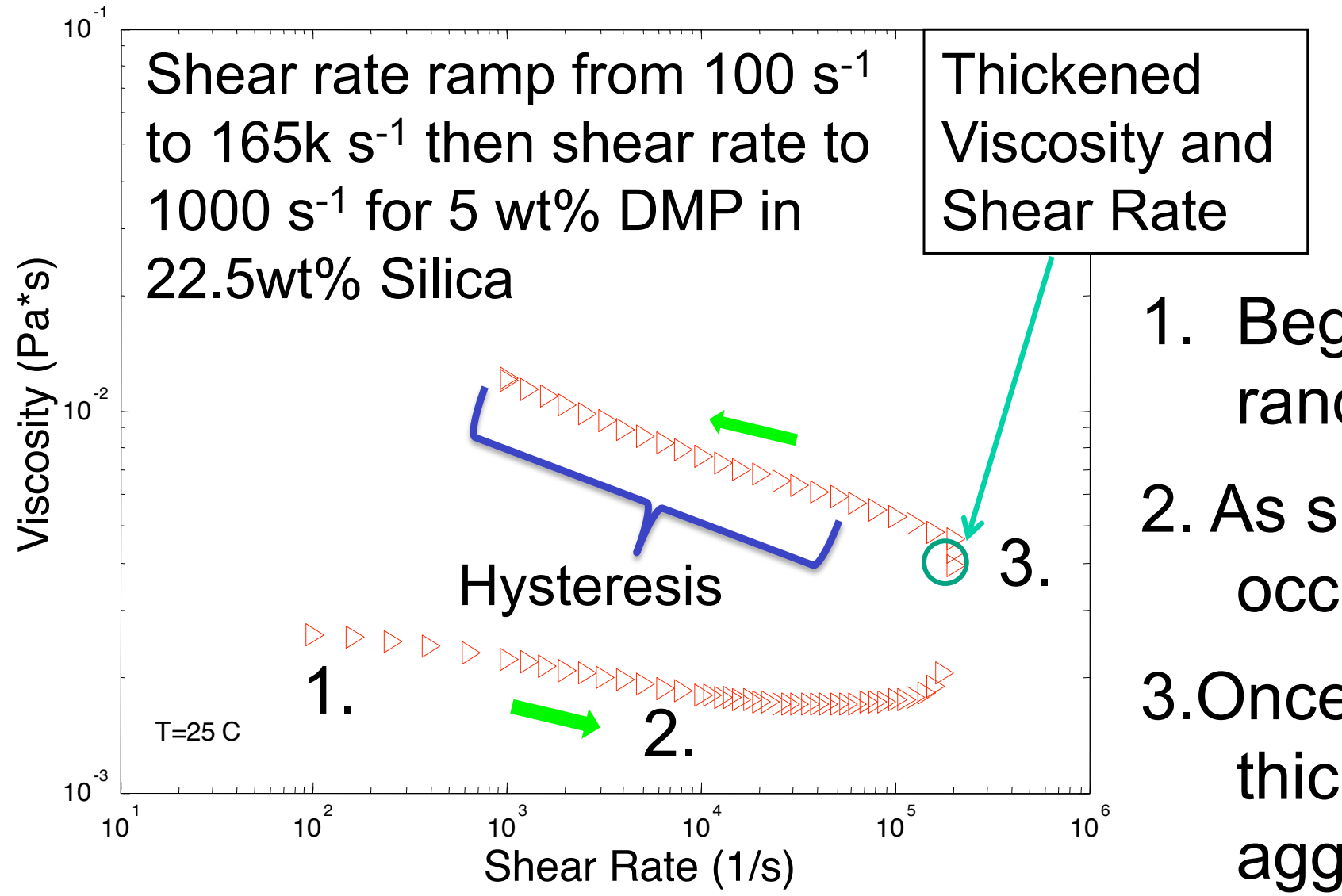


- It is hypothesized that particles agglomerate during the polishing process, leading to structural damages on the wafer surface (i.e., scratches, gouges, pits, etc.), which costs the semiconductor industry billions of dollars[3]

1. Sorooshian A., Ashwani R., Choih K., Moinpour M., Oehler A. and Trequb A.; *Materials Research Society,***2004**, 816, 125-131
2. Lortz W.,Menzel F., Brandes R., Klaessig F. Knothe T, and Shibasaki T.; *Material Research Society,***2003**, 767, F1.7.1 -F1.7.10
3. Basim G., Adler J., Mahajan U., Singh R., and Moudgil B.; *Journal of the Electrochemical Society;* **2000**, 147, 3523-3528

What is Shear Thickening?

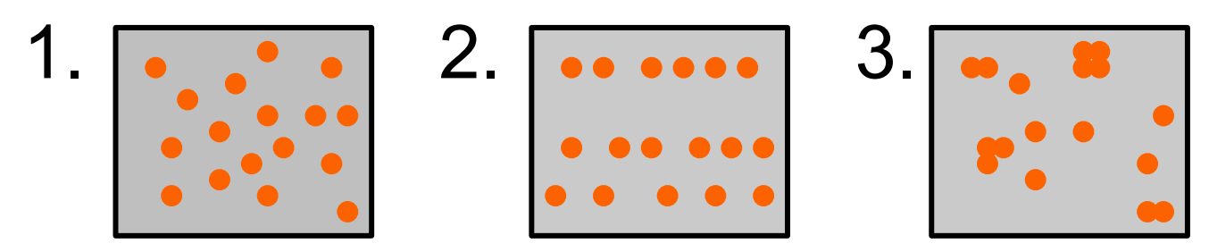
- Shear thickening is a non-Newtonian flow response defined as an increase in viscosity with increasing shear rate or stress
- Commonly, shear thickening is witnessed in mixtures of corn starch and water, allowing for-the mystical ability to walk on water
- Hysteresis (i.e., memory or irreversibility) is found with the thickened slurry



Shear rate ramp from 100 s^{-1} to 165k s^{-1} then shear rate to 1000 s^{-1} for 5 wt% DMP in 22.5wt% Silica

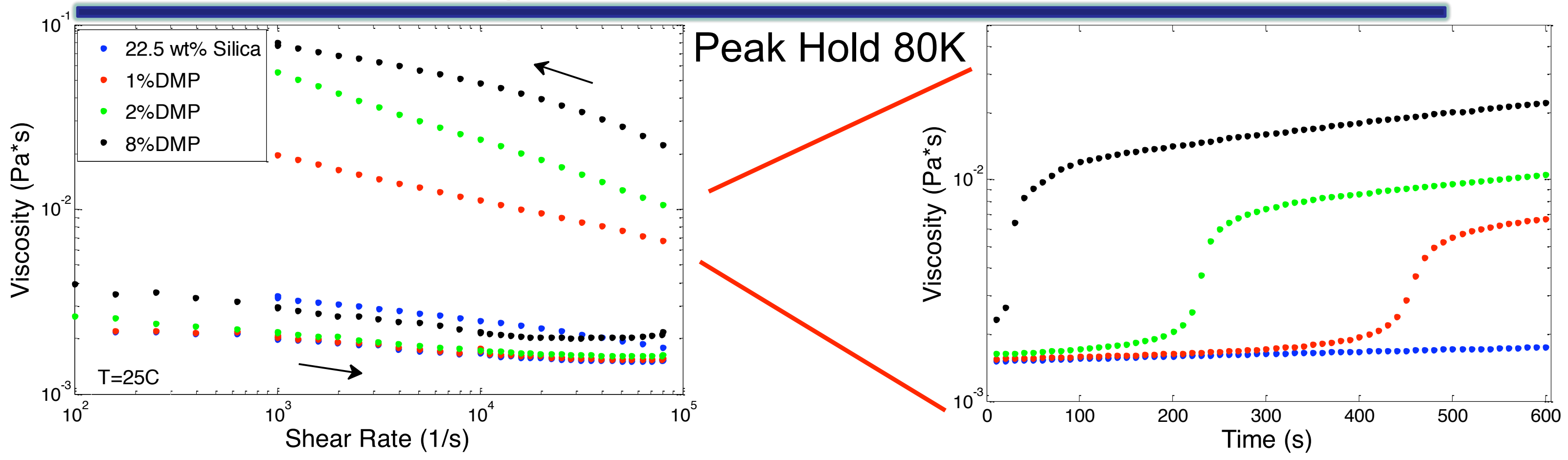
Thickened Viscosity and Shear Rate

Particles During Shearing



1. Beginning of experiment, particles remain randomly dispersed due to Brownian motion
2. As shear rate increases, shear thinning occurs with particle alignment
3. Once the shear rate is high enough, shear thickening arises coupled with particle agglomeration

Organic Solvent Effect



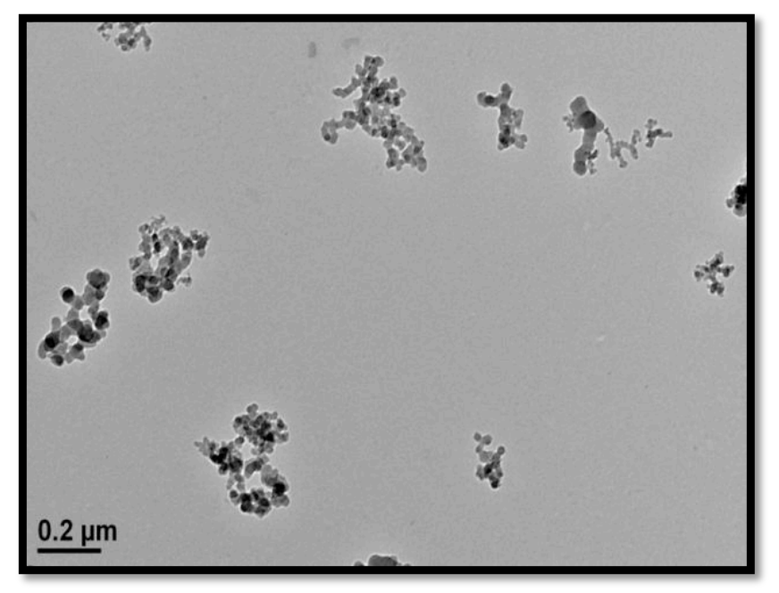
- CMP slurry with DMP displays time dependent behavior

Name	Solubility in Water	γ (s^{-1})	Silica Wt%	Additive Wt%	Rheology Effect of Additive
EG	Completely Miscible	200k	22.5	1,10	10 wt% slightly higher steady increase of viscosity
EG-dm	Completely Miscible	200k	22.5	1, 10wt%	10 wt% very slightly higher steady increase of viscosity
DMP	Slightly Soluble	Varies	22.5	1-10	Stronger thickening in viscosity depending on wt% of DMP
DOP	Very Slightly Soluble	200K	22.5	1, 10	10 wt% slightly higher steady increase of viscosity
DINP	Very Slightly Soluble	200k	22.5	1,5,10	Decrease in viscosity due to loss of sample

Materials

Model CMP Slurry (Provided by Cabot Microelectronics Corporation)

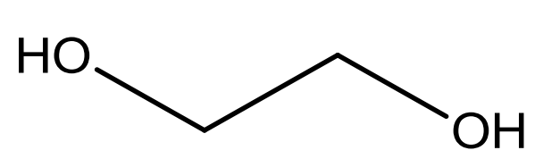
•Fumed silica (0.1-0.2 µm) suspended in water with added KOH to adjust the pH to between 10-11



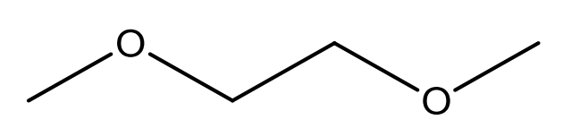
Transmission electron micrograph of the fumed silica particles used in CMP slurries.

Property	Value
Silica Weight Fraction (%)	20-34
Slurry Density with 25 wt% Silica	1.16 g/ml at 25°C

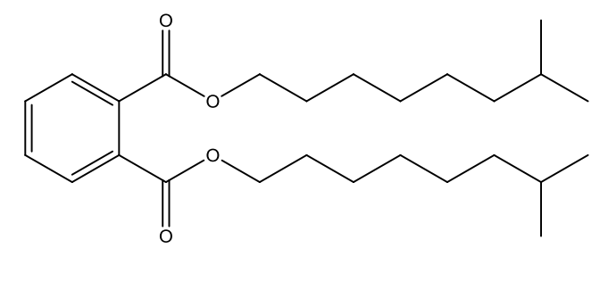
Ethylene Glycol (EG)



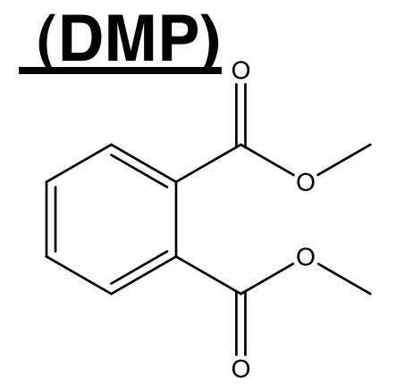
1,2-Dimethoxyethane (EG-dm)



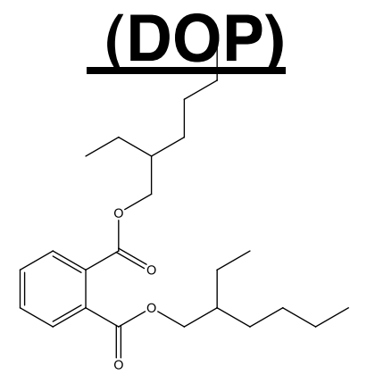
Diisononyl phthalate (DINP)



Dimethyl Phthalate (DMP)



Dioctyl Phthalate (DOP)



Images of Agglomerated Slurry

- 34 wt% fumed silica slurry diluted with 50 mM $CaCl_2$ to 25 wt%
- Particle agglomeration occurs almost immediately

Initial 34 wt% Slurry

Seconds After Dilution

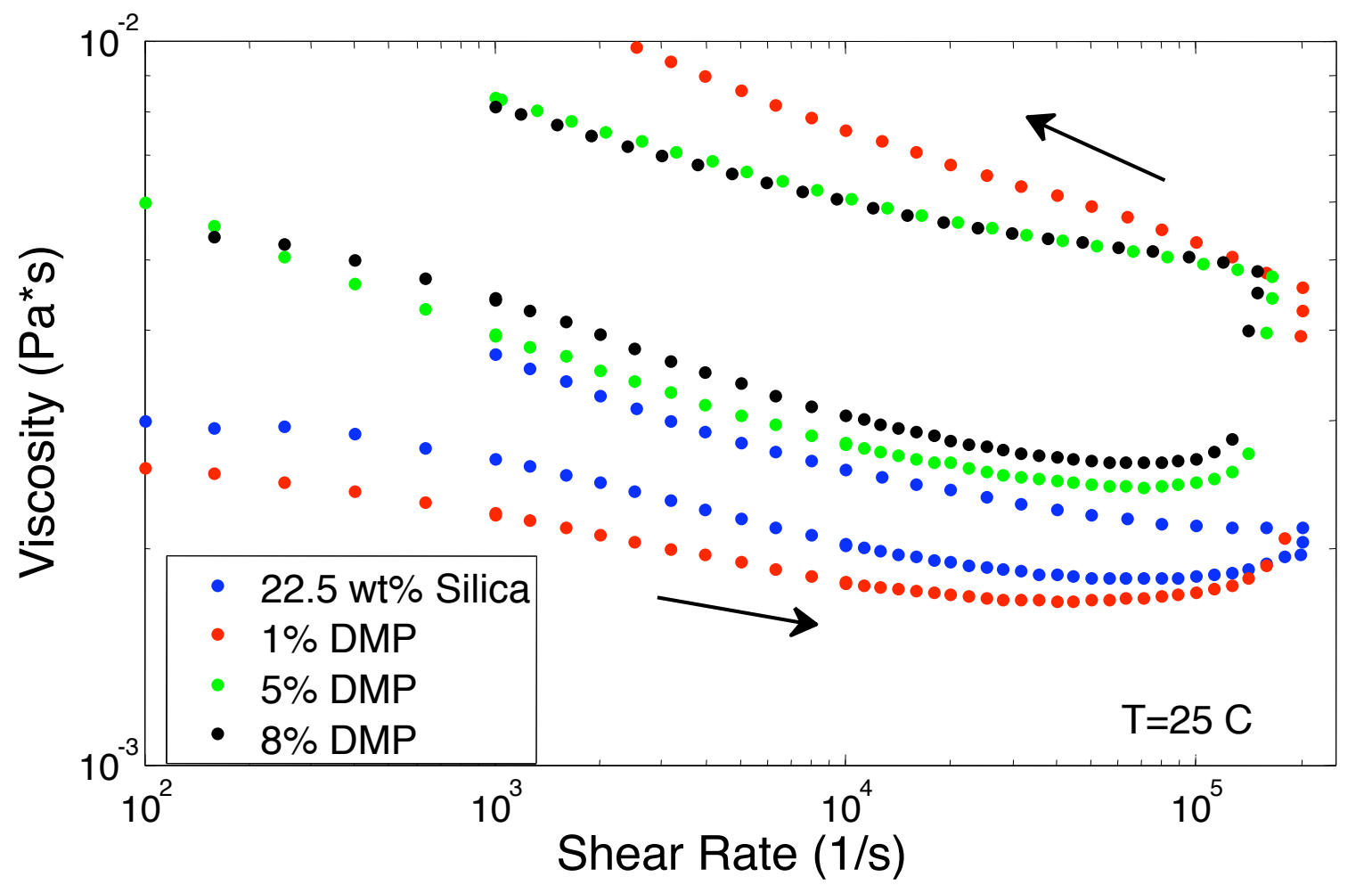
5 Minutes on the Vertical Mixing Wheel After Dilution

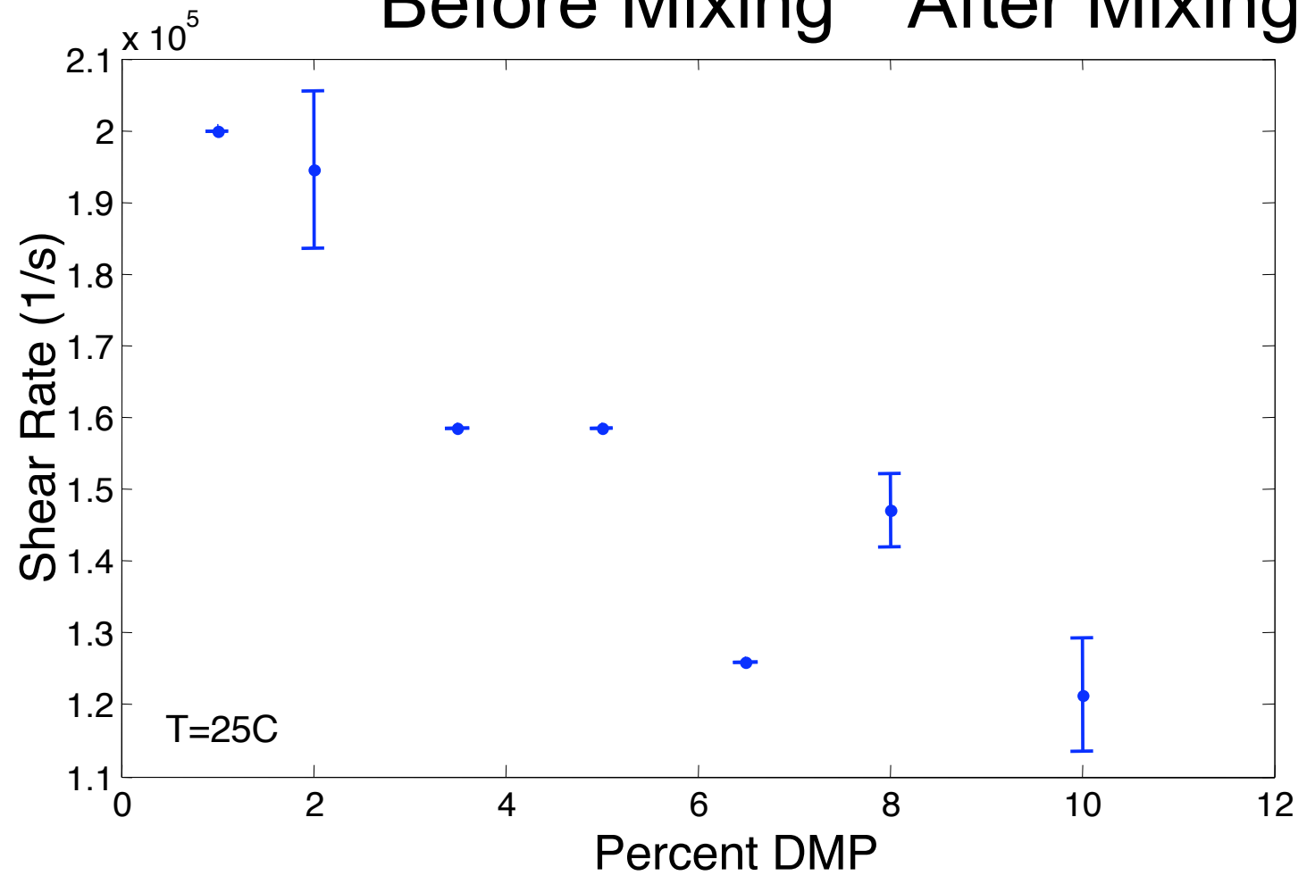
Thickening Enhanced by DMP

- 25 wt% silica slurry diluted to 22.5 wt% with various wt% of DMP
- Thickening shear rate (and shear stress) decreases with increasing weight percent of DMP in slurry
- Solubility of DMP affects stability of samples with higher weight percents of DMP in the slurry

22.5 wt% Silica with 10% DMP

Before Mixing After Mixing





Parallel-Plate Rheology

Experimental Conditions

Temperature: 25°C

Flow experiments-

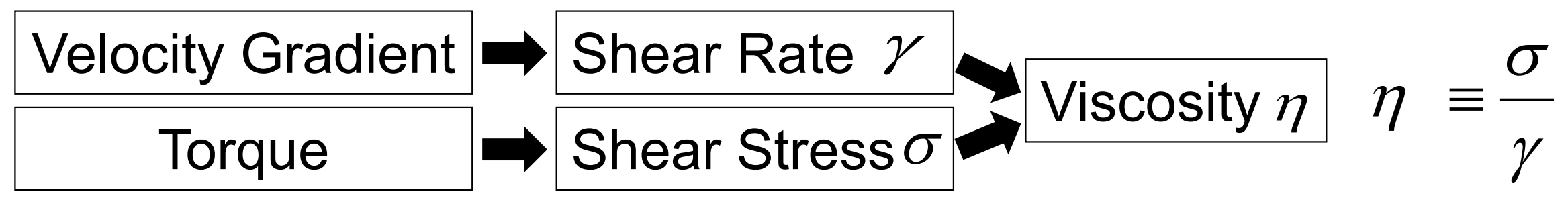
-Steady State Shear Rate Ramp (s^{-1})

-Shear Rate Peak Hold

The rheological experiments were conducted over a short time period (10-40 minutes) to minimize evaporation of solvent.

TA Instruments AR-G2 Rheometer

Rheology Basics



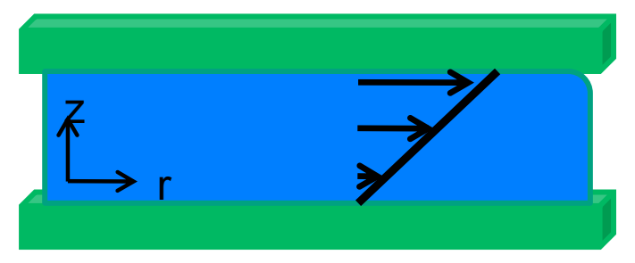
Velocity Gradient → Shear Rate γ

Torque → Shear Stress σ

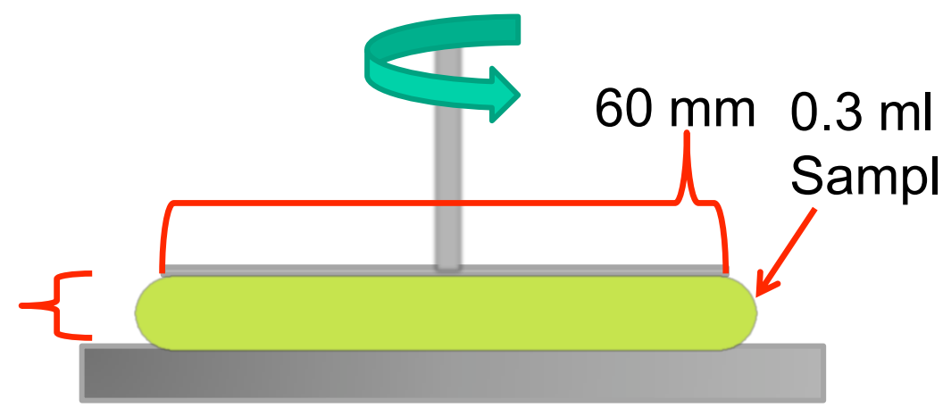
Viscosity η

$$\eta \equiv \frac{\sigma}{\gamma}$$

Velocity Gradient

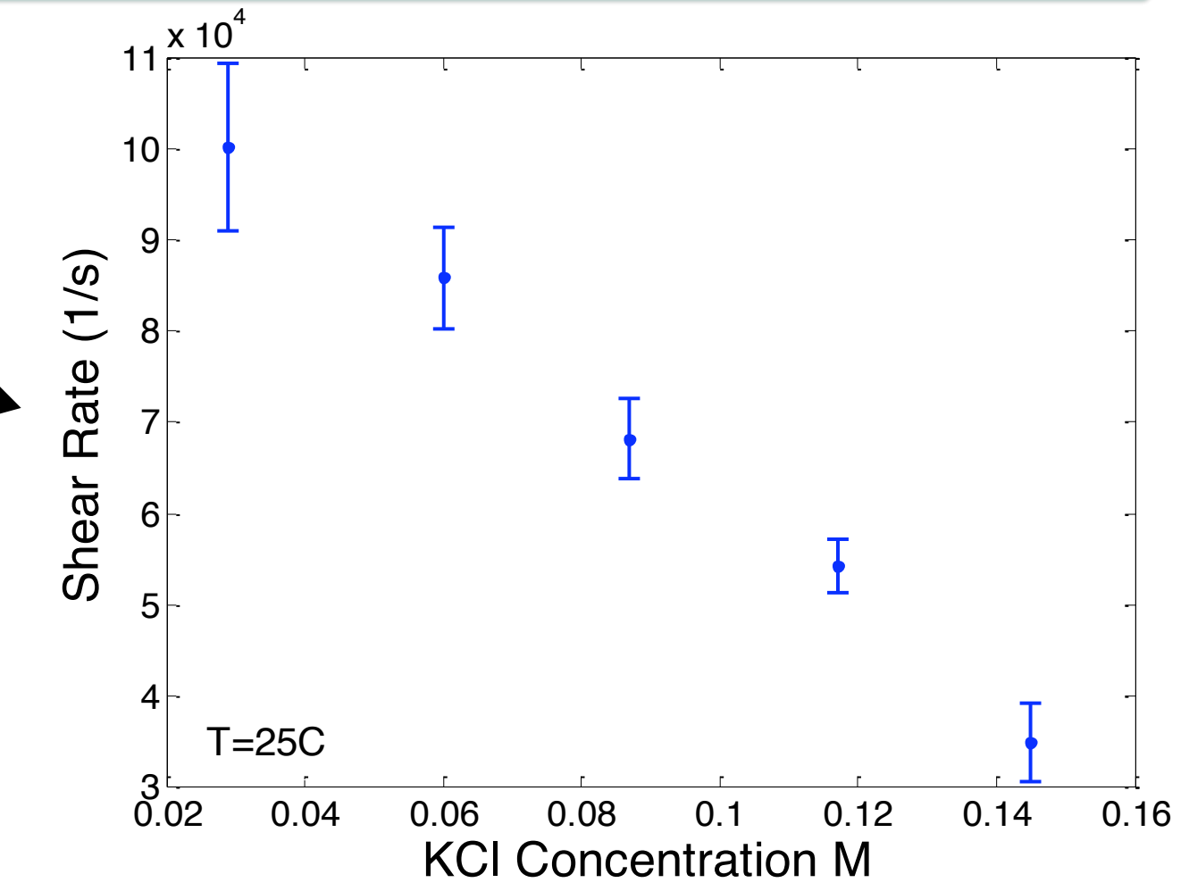


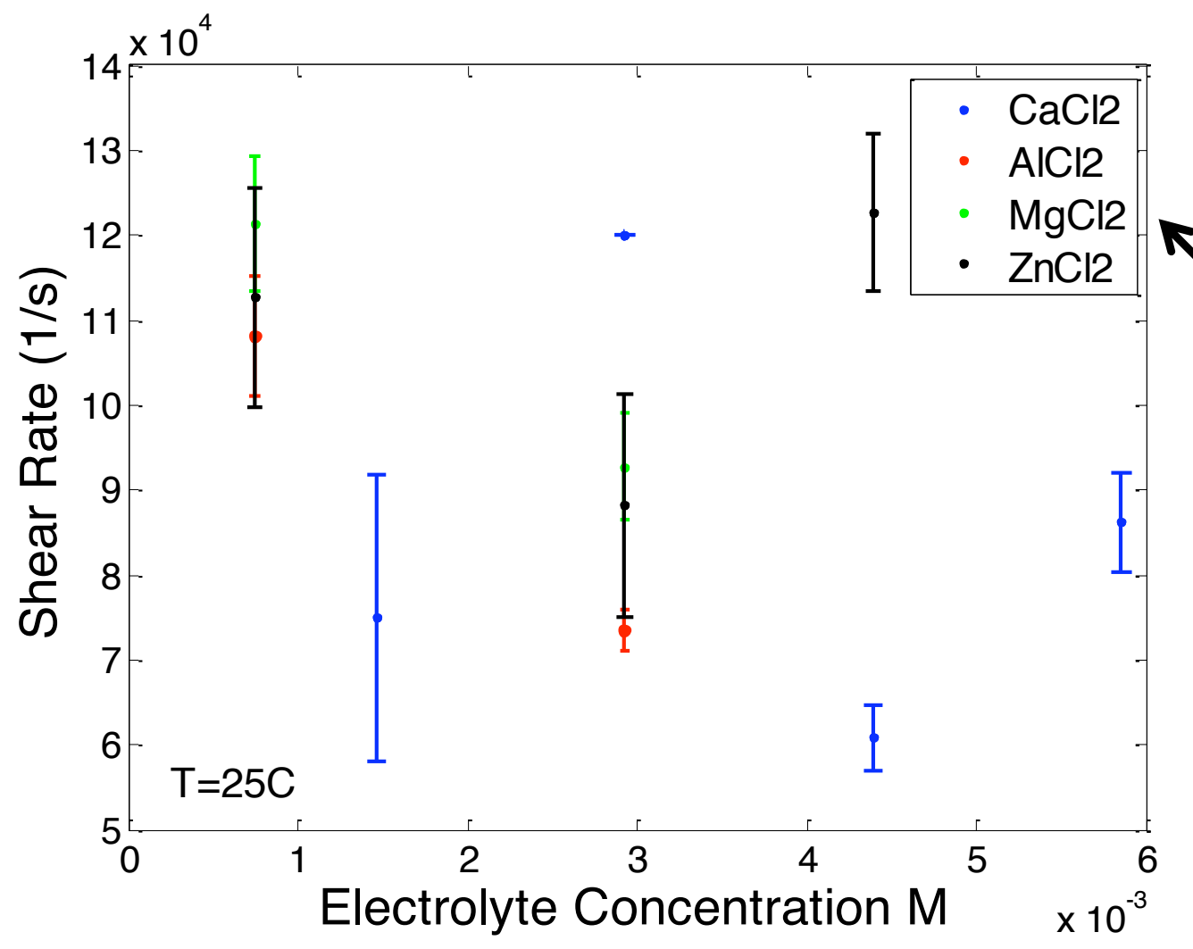
$$\dot{\gamma} = \frac{\partial v_\theta}{\partial z}$$



Di and Trivalent Salt Instability

- Clear linear trend between thickening shear rate (and stress) for the monovalent salts





- Thickening shear rate (and shear stress) show no trend with slurry electrolyte concentration for the di and trivalent cations
- Thickening data for the di and trivalent salts is inconsistent due to particle instability and agglomeration

Summary

- High shear rheology can detect shear thickening in CMP slurry by ramping the shear rate and probing for thickening
- The addition of di and trivalent cations decreased slurry stability and shear thickening events become unpredictable
- The addition of organic solvents had a mild effect of shear thickening with the exception of DMP which enhanced shear thickening similar to adding electrolytes

Future Work: Change functional groups and chain lengths to study the important interactions between the added organic phase and the silica particles that lead to or eliminate shear thickening of the CMP slurry

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