The Importance of Dilution Process and Solvent Selection on Particle Size Measurements

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RSC Particle Dispersion in Liquid Formulations - Online

Introduction – Silica dispersed in silicone fluid

Both liquid silicone rubber (LSR) and antifoam compounds are often composed of a silica dispersed into a silicone polymer matrix. The silica dispersion state can vary widely, from 10-100 micron agglomerates to submicron aggregates, and the size distribution of these particles is an important indicator of product quality

Liquid silicone rubber – durable silicone elastomers

Agglomerates affect shelf life and performance

- Ideally target particle size of all fines (no agglomerates)

Image: https://www.dow.com/en-us/product-technology/pt-elastomers-rubber/pg-elastomers-lsr.html

Antifoam compounds - reduces the formation of foam

Both large and small particles can play a role

- Hydrophobic silica particles help destabilize and penetrate the foam film (1)

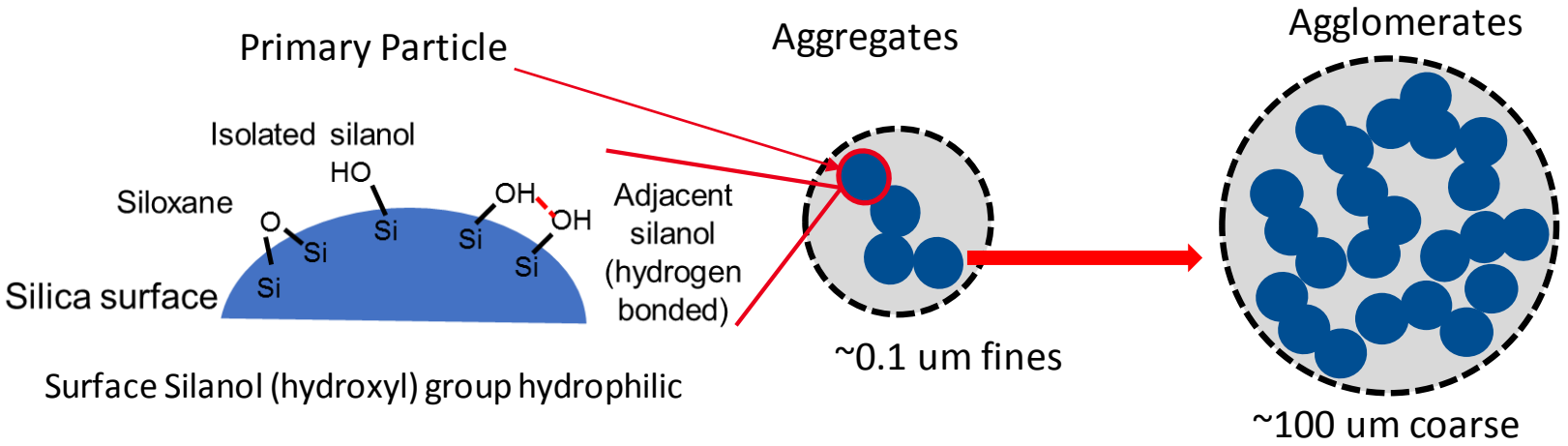
(1) Denkov (2004). Mechanisms of foam destruction by oil-based antifoams. *Langmuir*, 20, 9463-9505.

Image: https://www.dow.com/en-us/product-technology/pt-antifoams/pg-antifoams-antifoams-defoamers-industrial/antifoams-home-care-in-wash.html

FUMED/PRECIPITATED SILICA – MULTIPLE SIZE SCALES

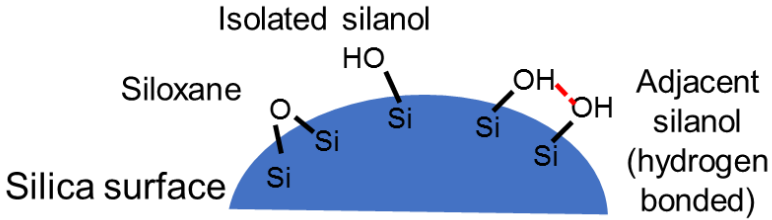
Both fumed and precipitated silica have structural features on multiple size scales:

1) Primary particle of silica, which when untreated has siloxane and silanol groups on the surface
2) Aggregates - submicron chain structure of fused primary particles
3) Agglomerates - clusters of physically bound aggregates

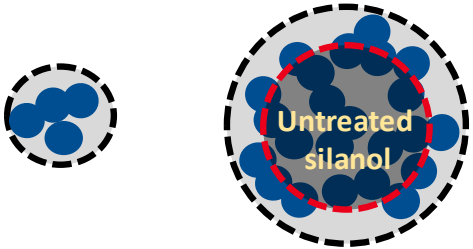


TREATED VERSUS UNTREATED SILICA SURFACES CAN AFFECT PERFORMANCE

Untreated silica is hydrophilic due to silanol



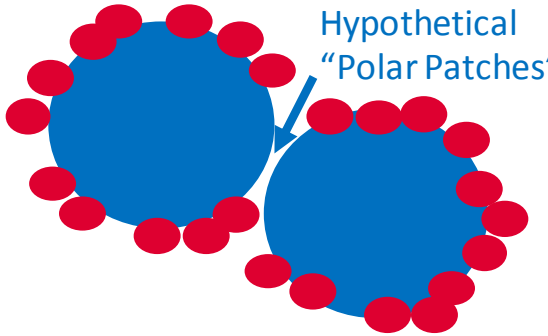
Size of silica agglomerates vs aggregates during silica treatment process can affect level of coverage



Hydrophobically treated surfaces

Hydrocarbon modified silica surface more compatible with hydrophobic silicone matrix

Nonpolar Surface Treatment Groups



Silica treatment process chemically modifies or covers polar surfaces with nonpolar groups, but imperfectly

Effectiveness of treatment and amount of residual hydrophilic surfaces can affect material behavior and resulting performance quality

Particle Size Measurements

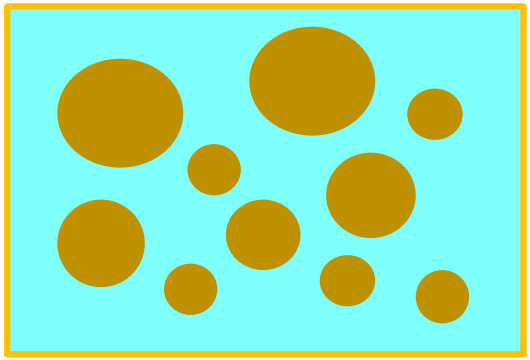
Particle size distribution of filler agglomerates and aggregates can reflect quality of treatment in LSRs and antifoams in addition to final product performance

Consider the physics of the process.
Physical properties will affect interactions and the behavior of materials

- Viscosity
- Solubility
- Glass transition temperature
- …

How do we measure the filler dispersion without artificially changing the distribution due to the nature of processing it for the measurement?

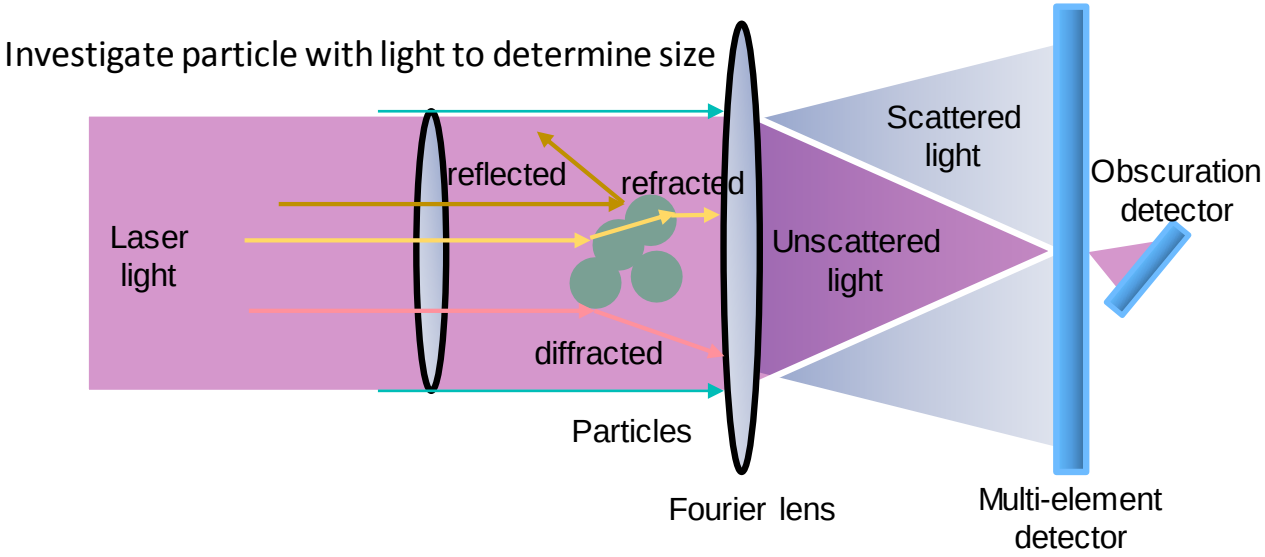
Example Application :
Emulsions – size of droplets
Fillers in polymer – particle size



Current work will only focus on wet dispersion of solids

Laser Diffraction to Measure Particle Size Distribution

Laser diffraction is the commonly used method to measure the apparent particle size distributions and distinguish process condition performance at silica dispersion, but it requires the original dispersion to be sufficiently diluted in a low viscosity solvent; as a result, there are concerns that the dilution process may alter the measurement from its undiluted value.



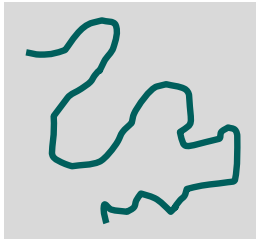
Light collected over large range of angles

Use optical models to interpret data and understand physical system

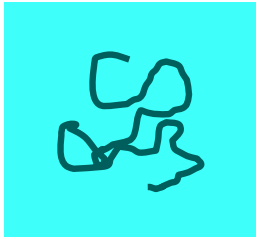
Choice of Solvent

Considerations	Heptane	Silicone fluid
solvent interaction/ compatibility with silicone matrix	good solvent to silicone polymer	theta solvent to silicone polymer
solvent interaction with particles	compatible with silicone-capped silica	same interaction as matrix to particles
viscosity of solvent	0.55 cSt	2 cSt

Polymer expands in a good solvent



Polymer behaves as an ideal chain in a theta solvent



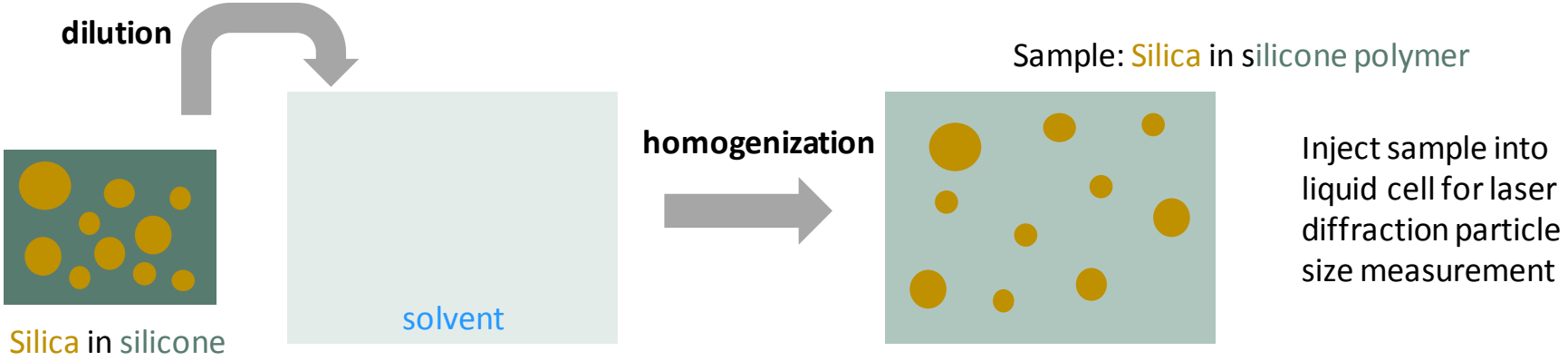
Interactions with particles drive settling speed

Shear stress drives agglomerate breakup:
Shear stress ~ **viscosity** × shear rate

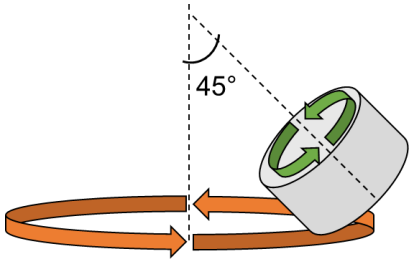
DOES SAMPLE DILUTION PROCESS MASK DIFFERENTIATING SIGNALS?

Sample needs to be diluted in a solvent before measurement in laser diffraction instrument

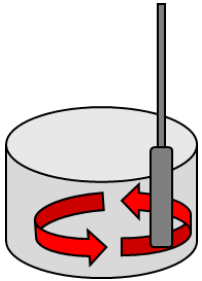
- Ensure flowability of sample in liquid cell
- Dilute down solid concentration for better size detection



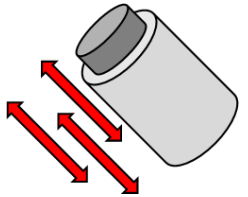
Dual asymmetric centrifugal mixing



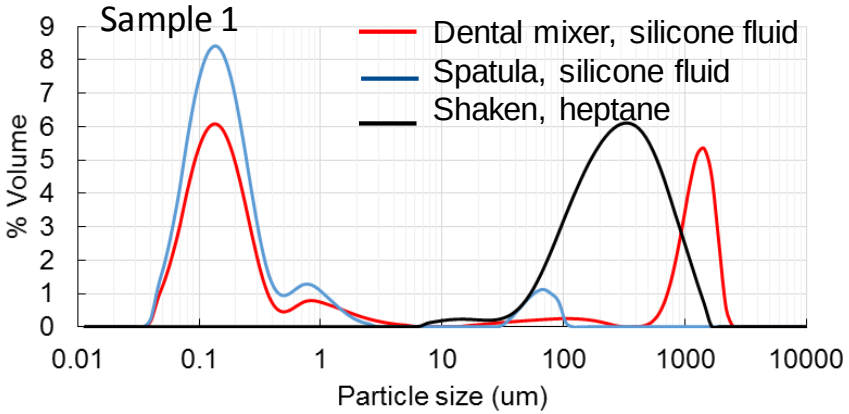
Mixing with spatula

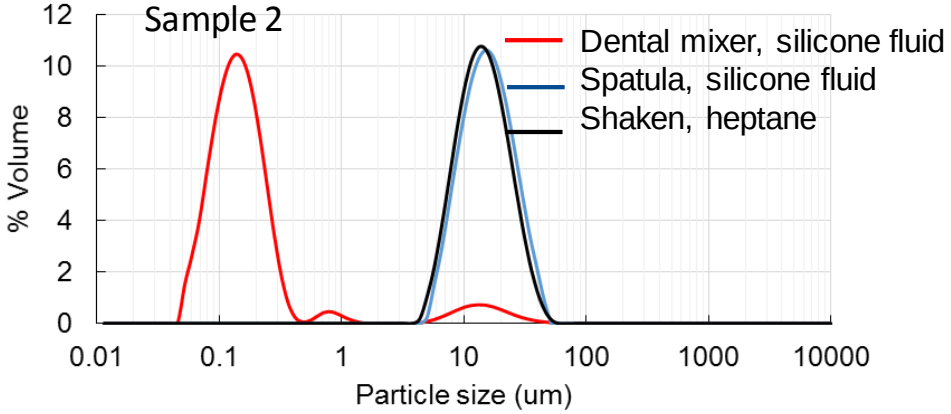


Wrist shaking



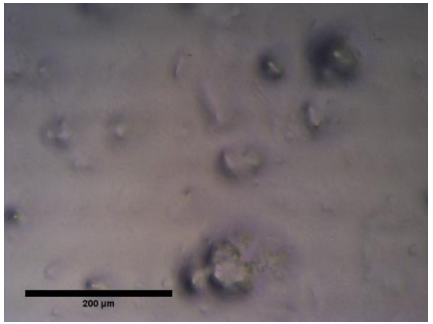
Effect of Sample Dilution into Solvent



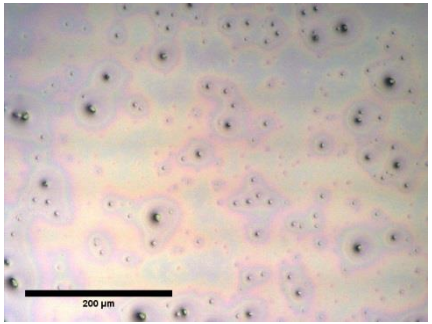


Sample dissolved in different solvents by different means give significantly different apparent particle size distributions, which is also supported by optical microscopy

Handshaken sample 1 after volatilization of solvent



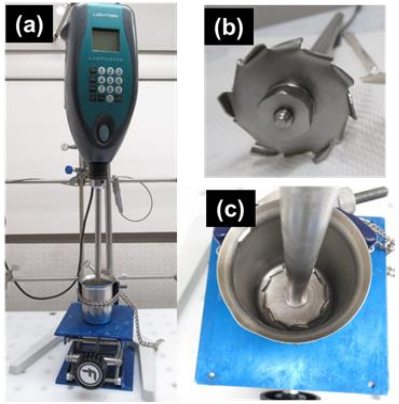
Handshaken sample 2 after volatilization of solvent



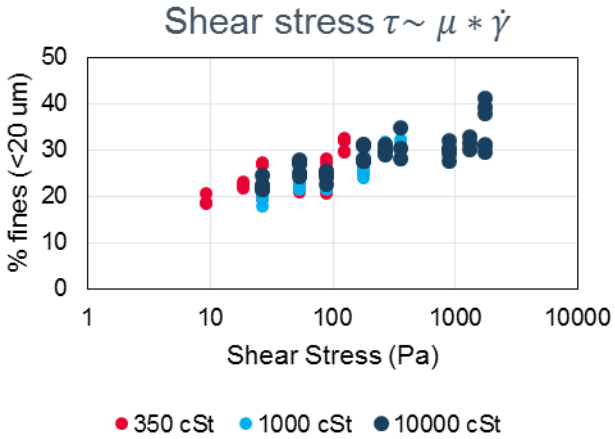
Dental mixed samples tend toward more fines (0.1 µm)

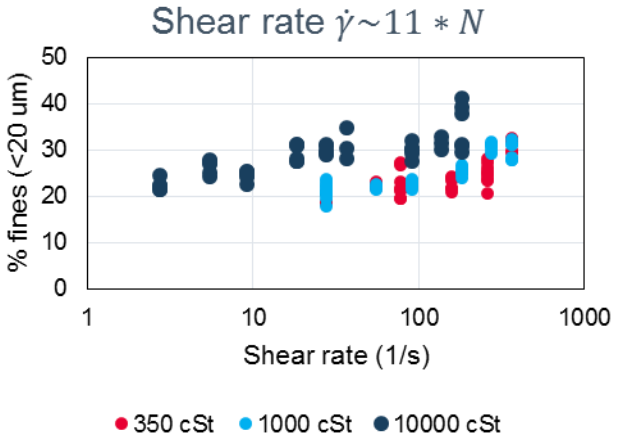
Handshaken samples tend toward more coarse (>10 µm)

INCREASING SHEAR STRESS INCREASES NUMBER OF FINES



- 5 wt% silica in varying solvent viscosity: 350, 1000, and 10000 cSt silicone fluid.
- Shear rate is proportional to varying shear rate via agitation speed (rpm)





Metzner-Otto correlation:

$$\dot{\gamma} = K_{MO} N$$

N = rpm

K_{MO} = geometry dependent constant

- Increasing shear stress (viscosity x shear rate) correlates with more particle breakdown and more fines
- Weak trend between shear rate and % fines

When designing the dilution process, both the bulk experienced viscosity and mixing shear rate need to be considered

Using Solvent to Probe Surface Treatment Level

Recall: Untreated silica is hydrophilic due to silanol

Hypothesis: Particle size measurements in different solvents may distinguish different surface treatment levels

- Unfavorable interaction between particles and solvent will lead to particle agglomeration and sedimentation.
- Favorable interaction leads to deagglomeration and dispersion of particles in solvent.

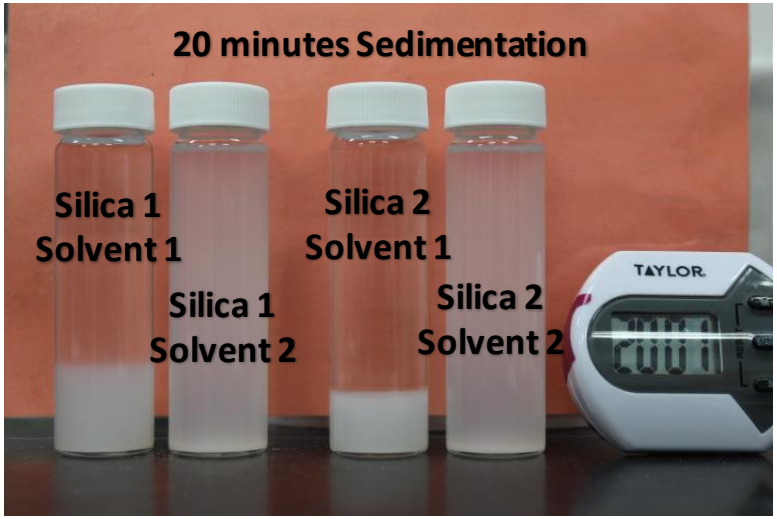
Solvent Selection for Sedimentation

Vary solvent **polarity** at approximately constant

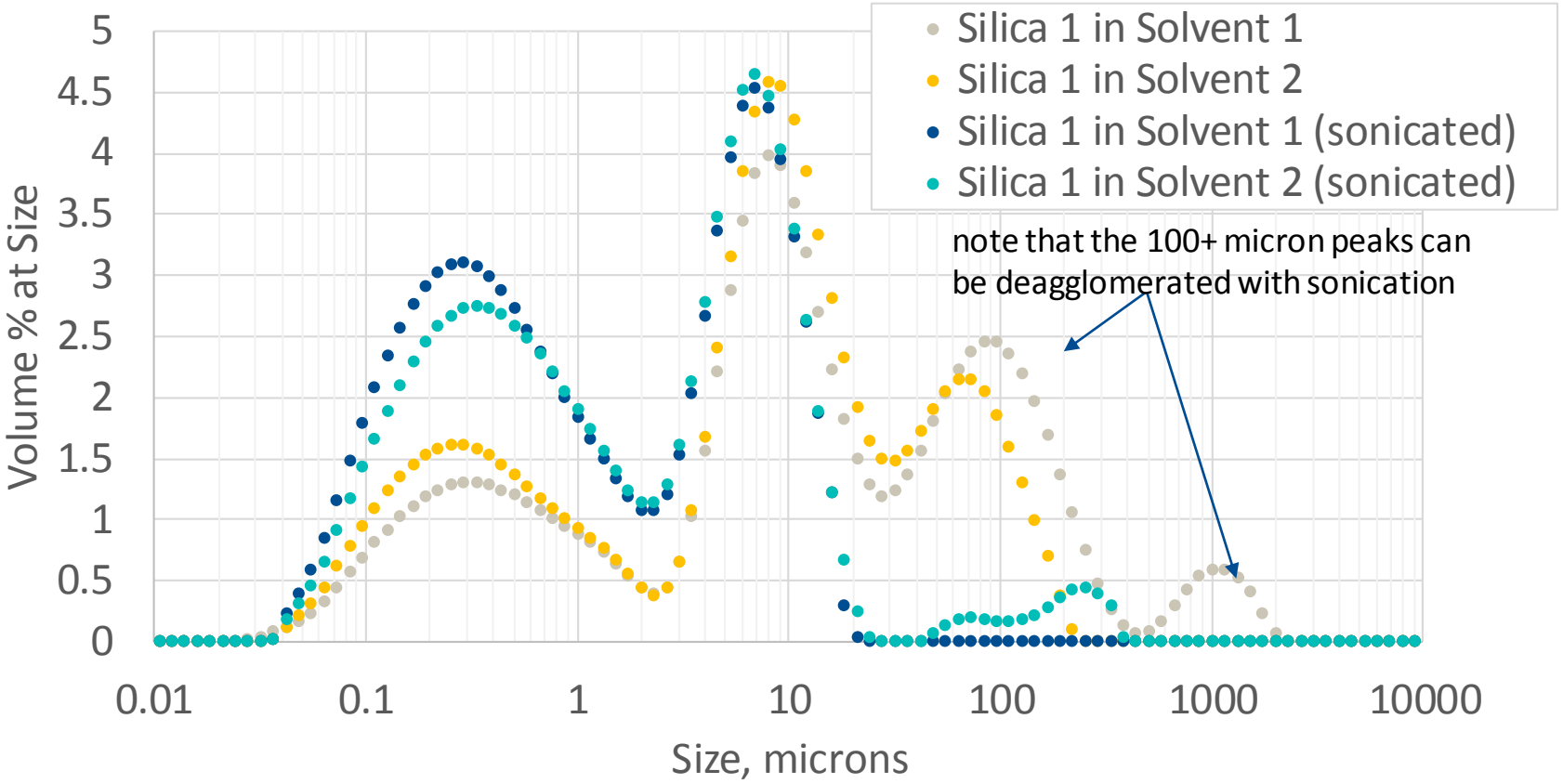
- miscibility with silicone fluids
- specific gravity
- viscosity

Despite similarity of solvent properties, sedimentation behavior is vastly different:

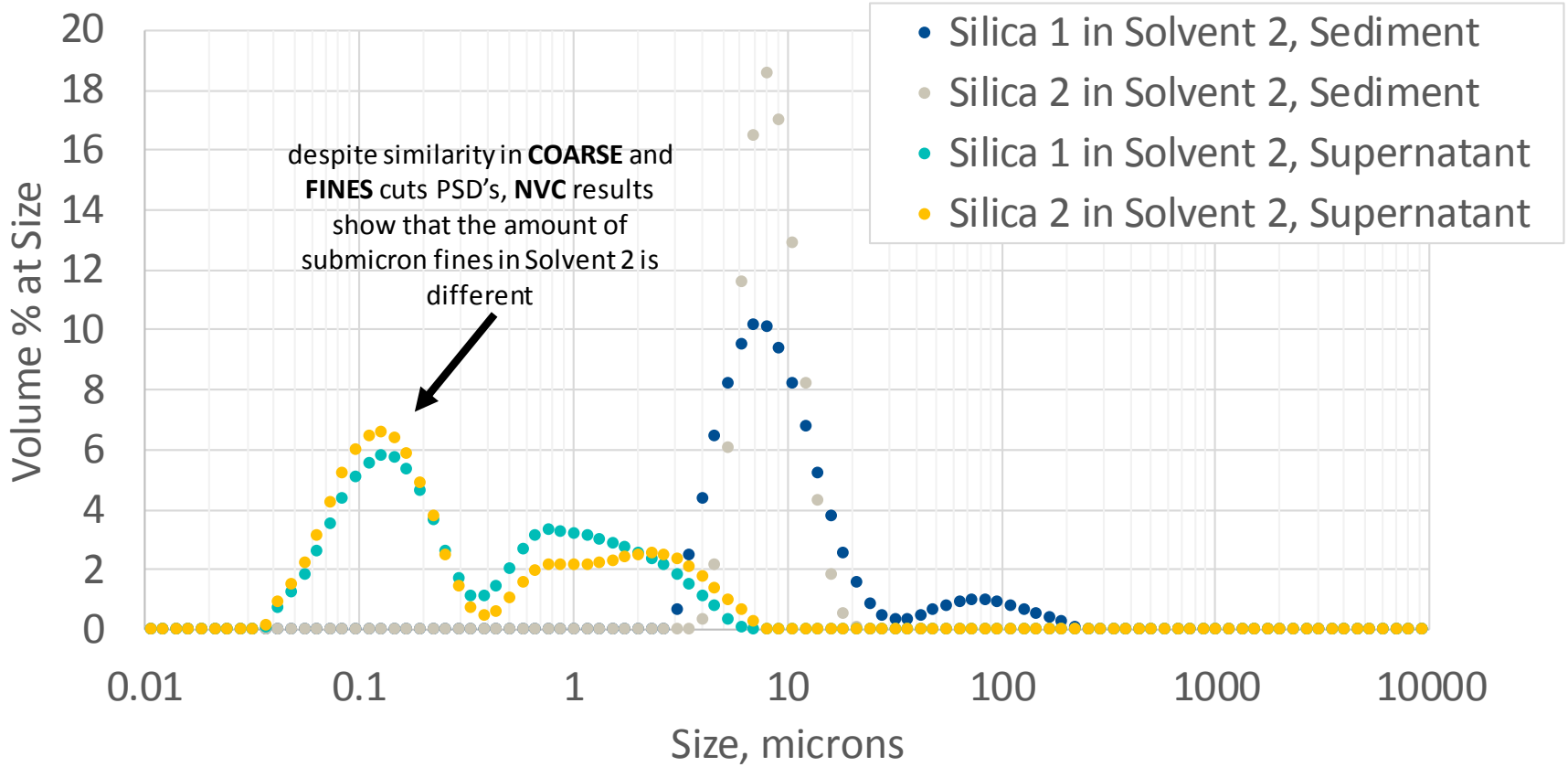
Observation	Solvent 1	Solvent 2
Predicted Sedimentation time (10 μm single particle)	~10 min	~10 min
Observed Sedimentation Time	10-20 min	> several days



APPARENT PSD IS SOLVENT-INDEPENDENT



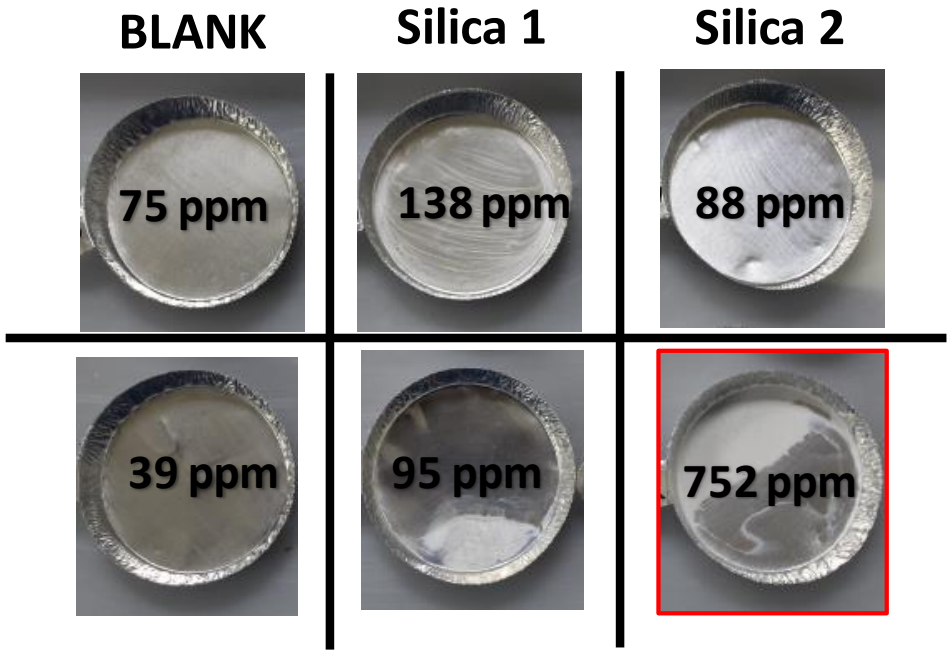
SEDIMENTATION IN SOLVENT 2 ENABLES SUBMICRON PARTICLE ISOLATION



POST CENTRIFUGATION SUPERNATANT NON-VOLATILE CONTENT (NVC)

Silica 1 and Silica 2 are differentiated using their affinity to different polarity solvents

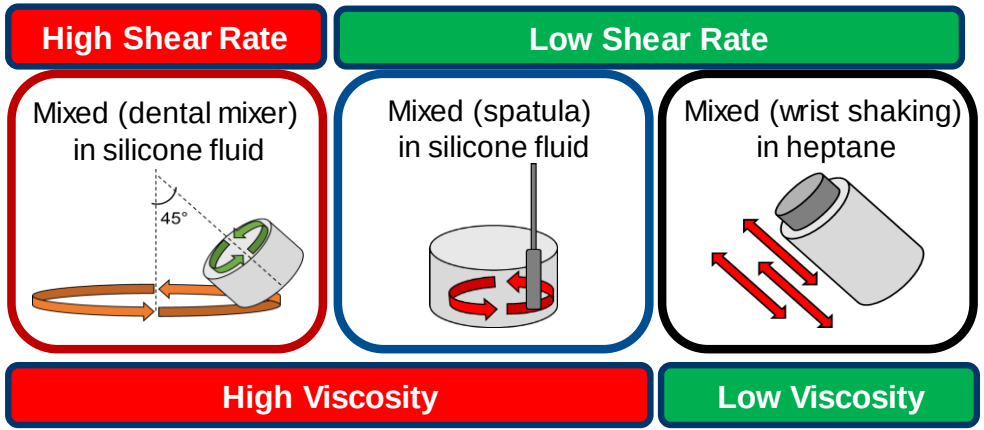
Supernatant of Silica 2 in Solvent 2 has higher NVC



Silica 2 is deagglomerated to a greater extent in Solvent 2

Conclusion 1: Sample Prep Matters

Careful sample preparation technique is necessary to avoid influencing measured particle size distribution in a way that erases signal differentiating samples with well-dispersed and poorly dispersed silica agglomerates



Shear stress = viscosity × shear rate

$$\tau \sim \mu * \dot{\gamma}$$

High viscosity & high shear rate risk superficially shearing down large agglomerate sizes during sample preparation step

Gentle dilution technique using:

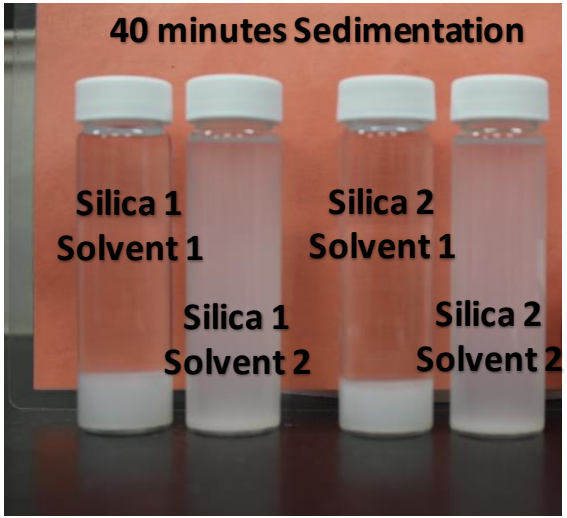
- a low viscosity solvent (good solvent of polymer matrix with sufficient optical contrast between solvent and particles)
- a low shear mixing technique (eg. Lab shaker or rotator) to preserve particle size and avoid shearing down coarse agglomerates into fine aggregates

Conclusion 2: Solvent Selection Matters

Solvent Selection can differentiate particle surface properties by inducing agglomeration (unfavorable interaction) or dispersion (favorable interaction), apparent from changes in sedimentation rate and supernatant NVC

Particle Size	Single-Silica-Particle in Solvent 2 Terminal Velocity v_t		
100 μm*	1.4 cm/s		
10 μm	0.02 cm/s	64 cm/h	
1 μm		0.6 cm/h	153 mm/d
0.1 μm			1.5 mm/d

*100 micron particles are in INTERMEDIATE settling regime, whereas the others are all in the Stokes flow regime.



Terminal velocity calculations used spherical particle drag equations in Perry's Chemical Engineering Handbook 6-50 to 6-51 (Fluid and Particle Dynamics)

$$v_{t,Stokes} = \frac{g\Delta\rho d^2}{18\mu}$$

30 mL vial height ~ 8 cm to shoulder

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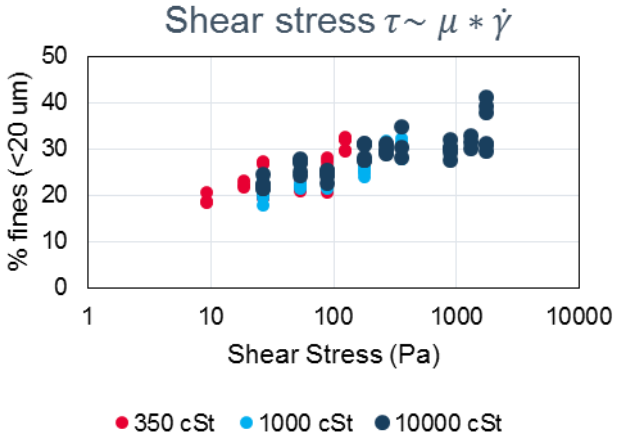

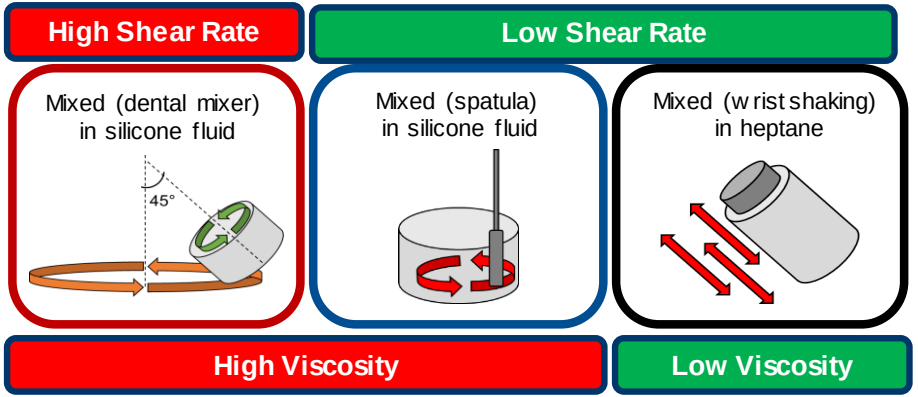

#ShearStressNotShearRate

#SamplePrepMatters

#SolventInteraction

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