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A Model System for Rheological Simulation: Silica-PDMS Colloids in Low Molecular Weight Silicone Oil

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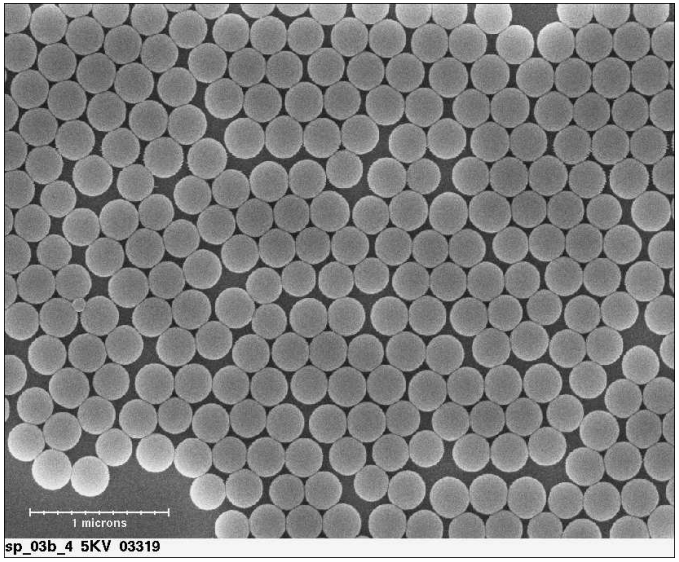
Overview

- Colloidal Dispersion Perspective
- Particle Interactions and Surfactants
- Surface Properties of Nanoparticles and Rheology
- Conclusions

Model System Characteristics

- **Spherical Shape**
- **Monodisperse**
- **Controlled surface properties by covalent grafting of poly-dimethylsiloxane (PDMS).**

PDMS force fields are available for simulation and interaction modeling.



Fuso Chemical SP-03B Silica particles
Avg. Diameter: 283.4 nm
Polydispersity: 11.1 nm standard deviation

1. SiO_2 reaction with aminopropylsilane for surface grafting.

2. APS reaction with monoepoxy terminated PDMS chains of varying molecular weight. (NMR shows strong PDMS peak)

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Hamaker Constant for the SiO_2-PDMS system

Application of Lifshitz Theory for summing Van der Waals interactions

Construct imaginary dielectric response functions

$$\varepsilon(i\xi) = 1 + \sum_{j=1}^{N} \frac{C_j}{1 + \left(\xi / \omega_j\right)^2} \qquad C_j = \frac{2}{\pi} \frac{f_j}{\omega_j}$$

Evaluate the difference function between particles and solvent over m up to 3000 and s from 1 to 4 to gain a valid A_{131}.

$$\Delta_{kl} = \frac{\varepsilon_k(i\xi_m) - \varepsilon_l(i\xi_m)}{\varepsilon_k(i\xi_m) + \varepsilon_l(i\xi_m)} \qquad A_{131} = \frac{3kT}{2} \sum_{m=0}^{\infty}{}' \sum_{s=1}^{\infty} \frac{(\Delta_{12}\Delta_{32})^s}{s^3}$$

Hamaker Constant from Lifshitz theory for silica in PDMS fluid gives

$A_H = 0.27 \times 10^{-20}$ J.

Material	IR Peak	IR Frequency	UV Peak	UV Frequency	Index of refraction	Dielectric Constant
SiO_2	0.829	8.67E13	1.098	2.034E16	1.448	3.82
	0.095	1.51E14				
	07.98	2.03E14				
PDMS	0.789	2.03E14	0.961	1.70E16	1.40	2.75

Parameters collected from literature sources (L. Bergstrom, Adv. Coll. Sci, 1997.

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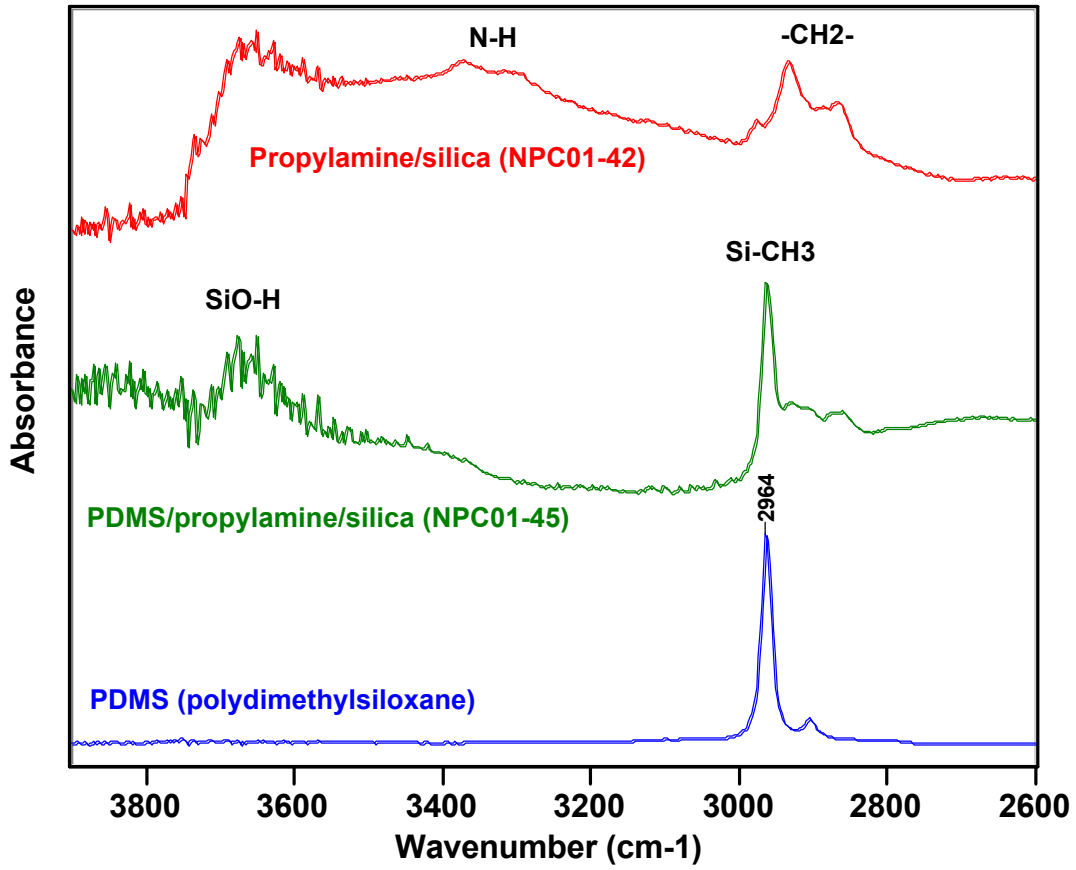
Surface Modification Characterization



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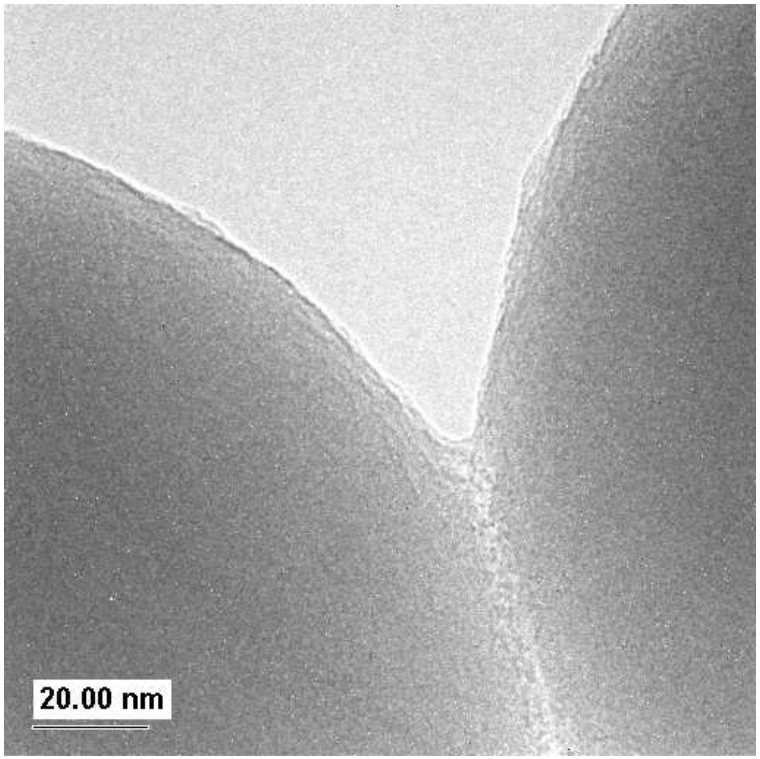
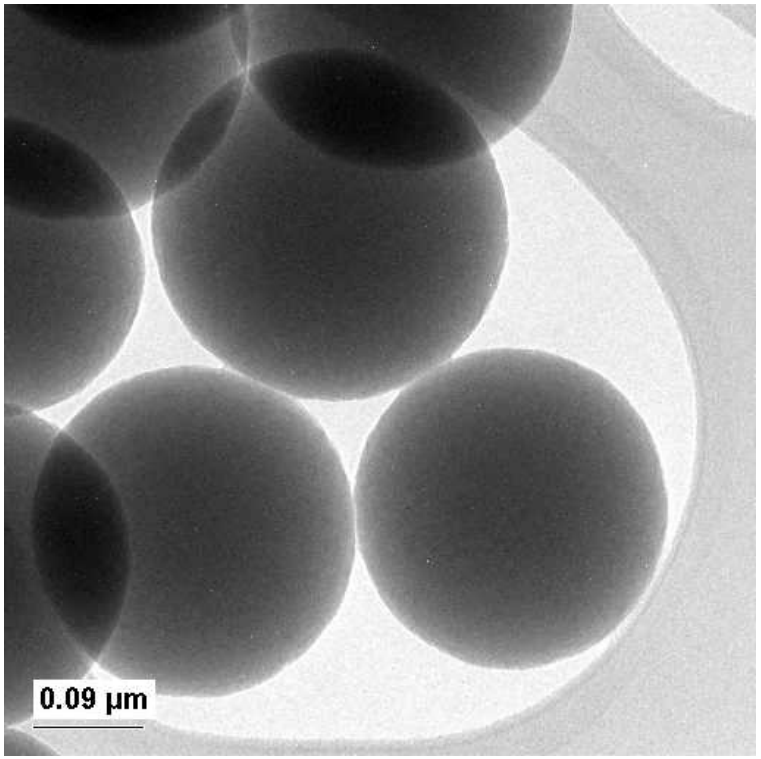
TEM of Model Particles

SiO_2-$PDMS_{5000}$
Mol. Wt. PDMS chain attachment



SiO_2-$PDMS_{800}$
Mol. Wt. PDMS chain attachment



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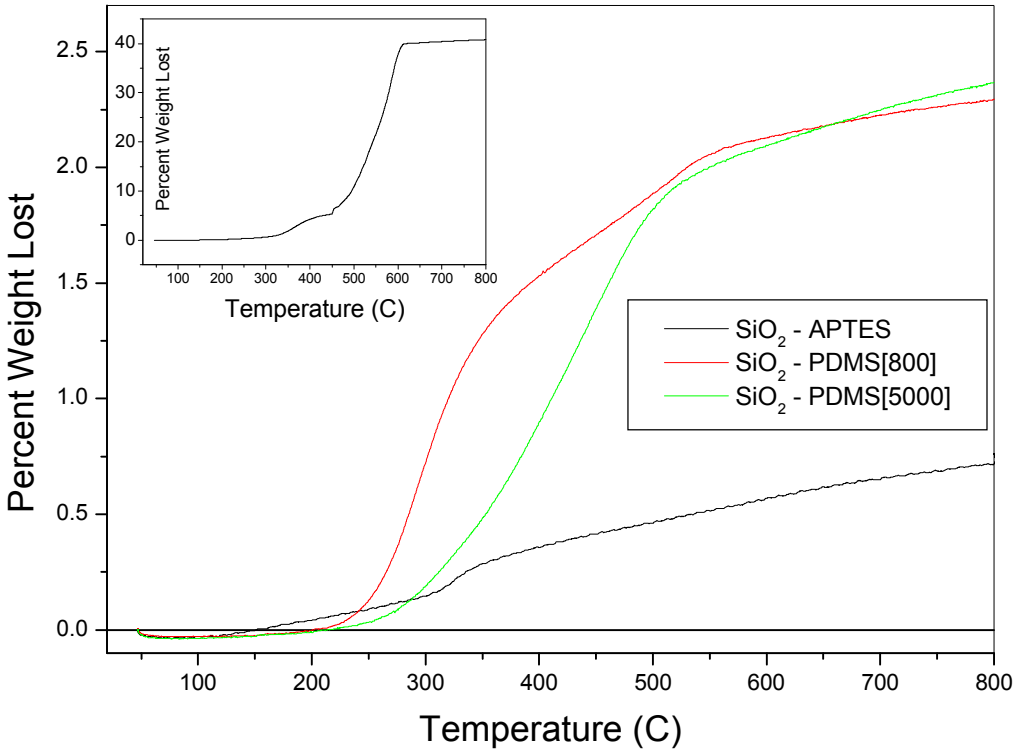
Surface Coverage of PDMS



TGA grafted mass calculations were corrected for the degradation of PDMS by studying TGA of PDMS separately, and assuming the remaining silica fraction is consistent.

Thickness Estimations for PDMS layers
Weight Loss by TGA
(5000 MW) – 4.17% w/w
(800 MW) – 3.85 % w/w

Chain Density Determination
(5000 MW) A_{chain} ~2.33 /nm^2
(800 MW) A_{chain} ~0.41 /nm^2

	Surface Separation	R_g
(5000 MW)	1.53 nm	1.875 nm
(800 MW)	0.64 nm	0.75 nm

Surface Layer Thickness
$L \sim n^{3/5} l$ where l = 1.64 Å
(5000 MW) L_{800} = 0.69 nm
(800 MW) L_{5000} = 2.06 nm

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Interaction Energy Modeling

Van der Waals Interaction

$$V_A(D) = -\frac{A_{eff}(D)}{6}\left[\frac{2a^2}{D^2-4a^2} + \frac{2a^2}{D^2} + \ln\left(\frac{D^2-4a^2}{D^2}\right)\right]$$

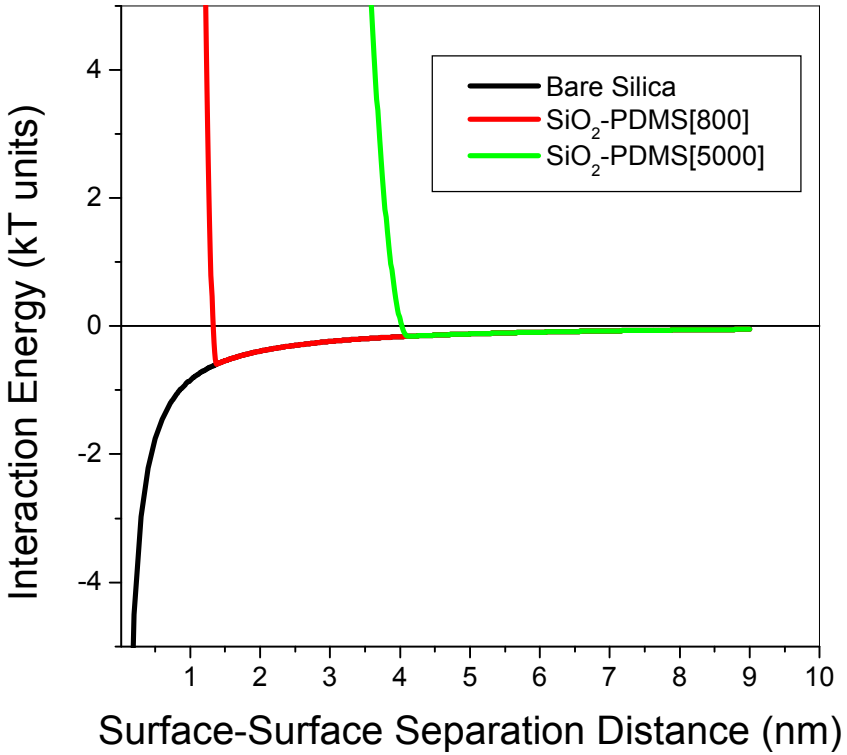
$$A_{eff}(D) = \frac{3}{4}kT\left(\frac{\varepsilon(0)_1 - \varepsilon(0)_3}{\varepsilon(0)_1 + \varepsilon(0)_3}\right)^2 \frac{3h\omega(n_1^2 - n_3^2)^2}{32\pi\sqrt{2}(n_1^2 + n_3^2)^{1.5}} F(D)$$

$$F(D) = \left\{1 + \left[\frac{\pi n_3}{4\sqrt{2}}(n_1^2 + n_3^2)^{0.5}(D-2a)\frac{\omega}{c}\right]^{1.5}\right\}^{-2/3}$$

Steric Interaction

$$V_s(D) = \frac{\pi akT}{\bar{V}_3}\bar{\phi}_2^2(0.5-\chi)(2\delta + 2A - D)^2$$

valid for $\delta < (D-2a) < 2\delta$



L. Bergstrom, *J. Chem. Soc. Faraday Trans.*, **88** *(1992)* pp. 3201-3211.

The PDMS[800] system has attraction of ~ 1kT, whereas PDMS [5000] has minimal attraction.

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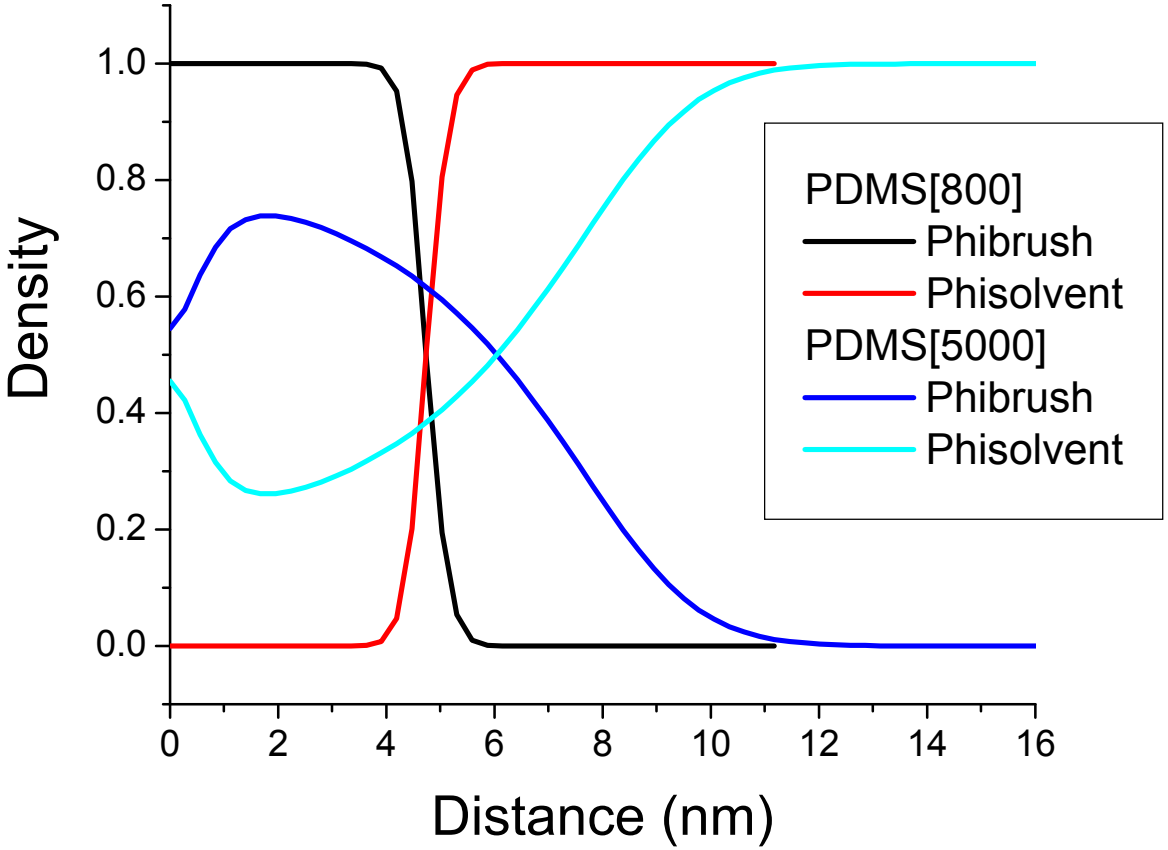
Density Functional Theory Modeling of Grafted PDMS Layers



- The PDMS[5000] layer is penetrated by solvent molecules and is a wet brush.
- The PDMS[800] layer is collapsed and excludes solvent molecules, to give a dry brush.

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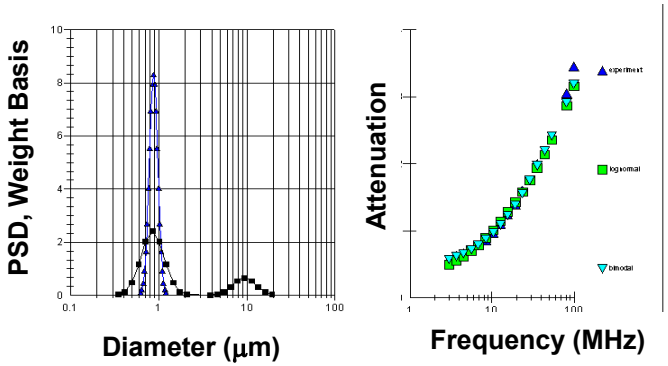
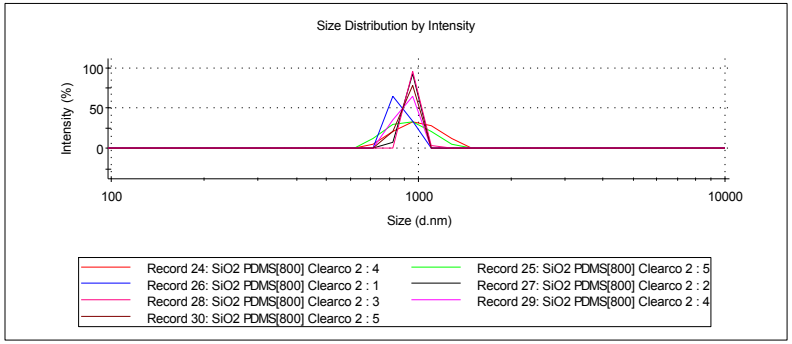
Dispersion Characterization
Acoustic and DLS Methods

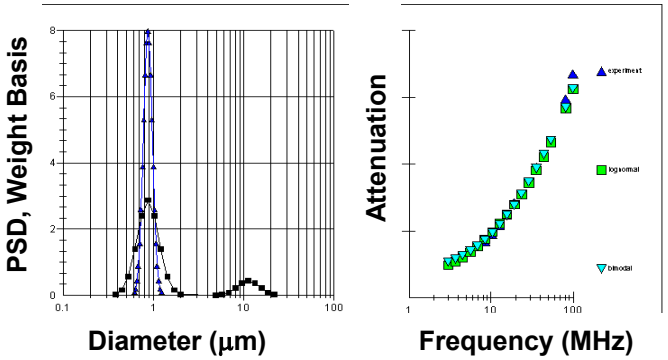
PDMS [800]
Monomodal
Peak Size = 858 nm
Bimodal Peaks
1 – 770 nm
2 – 9.1 mm



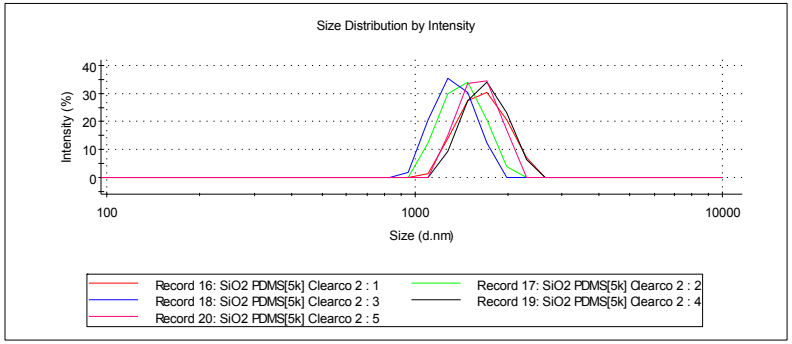
SiO_2-PDMS[800]
Average peak size: 1104 nm Standard Deviation: 65.37 nm



PDMS [5000]
Monomodal Peak
Size = 846 nm
Bimodal Peaks
1 – 872 nm
2 – 11.8 mm



SiO_2-PDMS[5000]
Average peak size: 1905 nm Standard Deviation: 228.5 nm



- Both methods detect aggregates in each system.
- A weakly attractive rheology model should be compared to stress testing.

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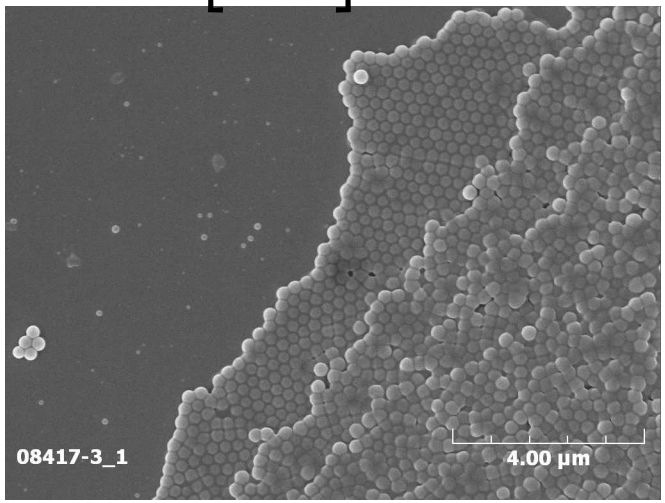
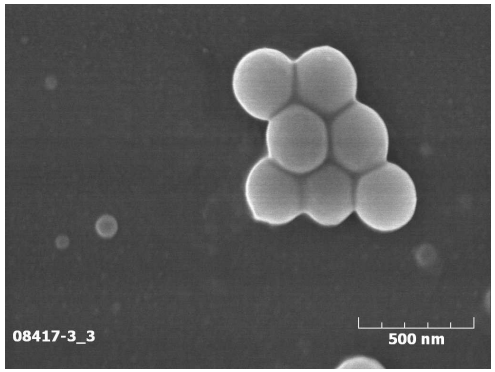
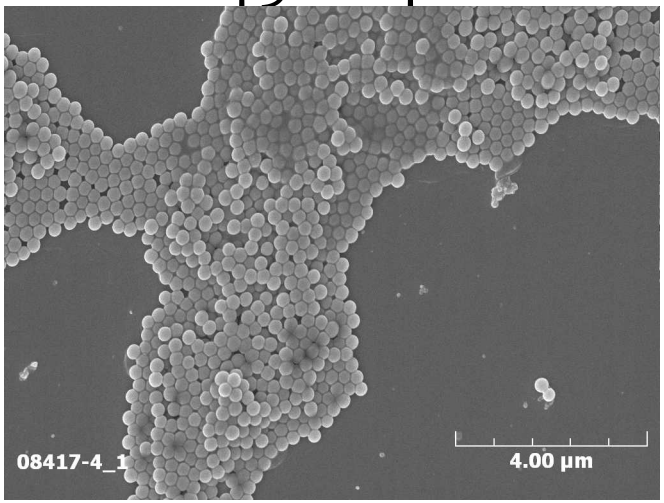
Convective Assembly Characterization - Hexanes

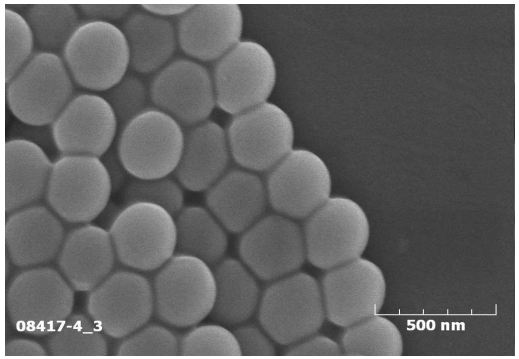
PDMS[800]





PDMS[5000]





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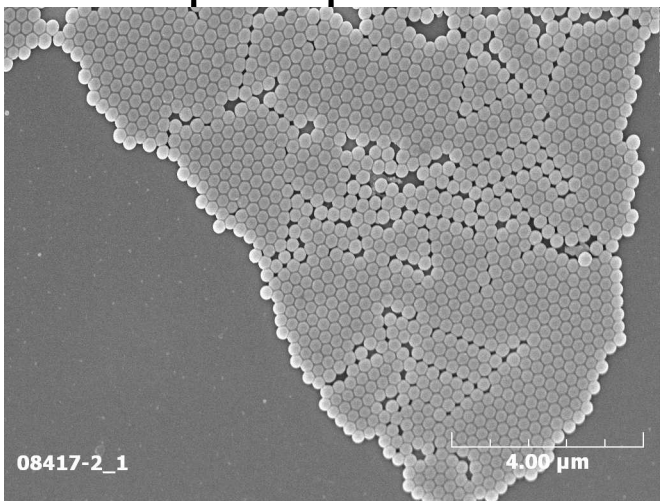
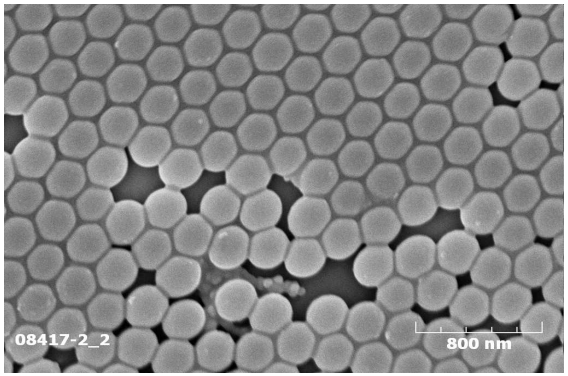
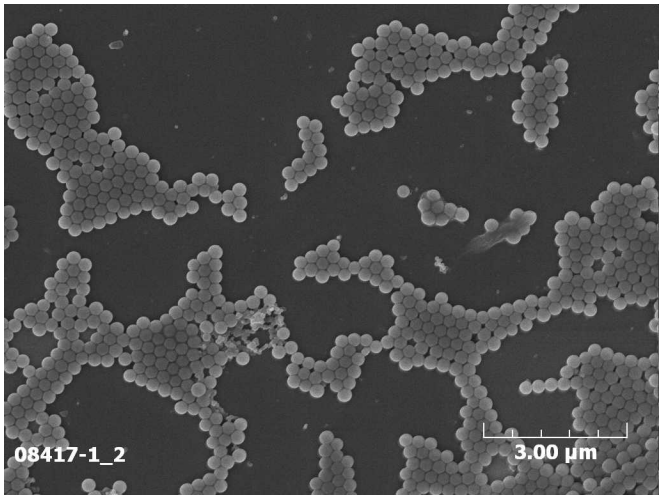
Convective Assembly Characterization - Isopropanol

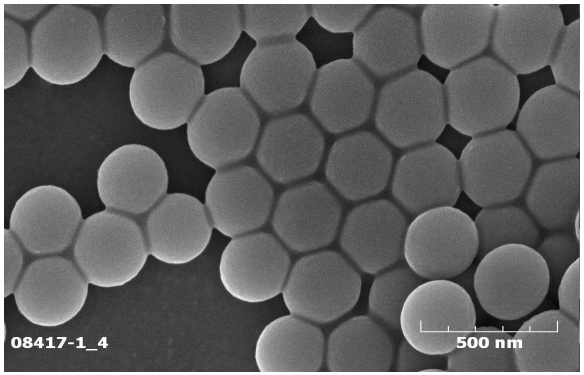
PDMS[800]





PDMS[5000]





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Contact Angle and Surface Properties of PDMS-modified Materials

	PDMS[800]	PDMS[5000]
Formamide	87.6	88.8
Water	101.5	106.0
Methylene Iodide	79.0	79.4
Clearco 20	12.3	10.9

Van Oss Parameters

PDMS[800]	PDMS[5000]
$\gamma^- = 0$	$\gamma^- = 0$
$\gamma^+ = 0.175$	$\gamma^+ = 0$
$\gamma^{LW} = 18.004$	$\gamma^{LW} = 17.979$

Hamaker Constant Estimate

$A_{[800]} = 3.346 \times 10^{-20}$ J

$A_{[5000]} = 3.346 \times 10^{-20}$ J

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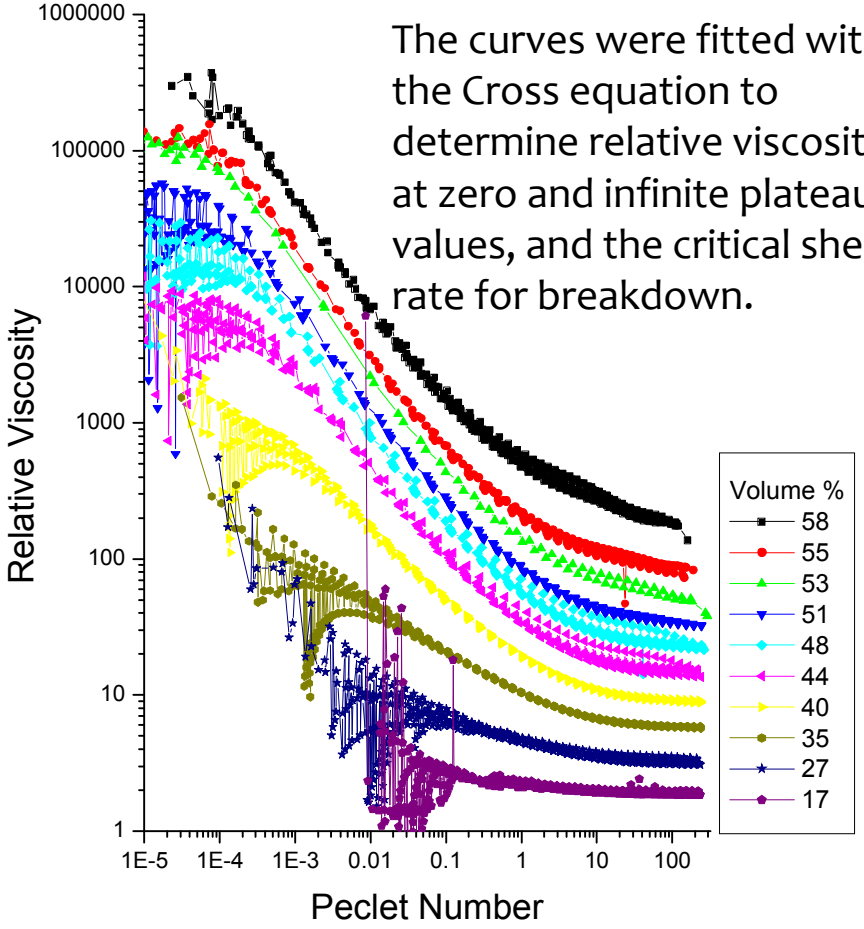
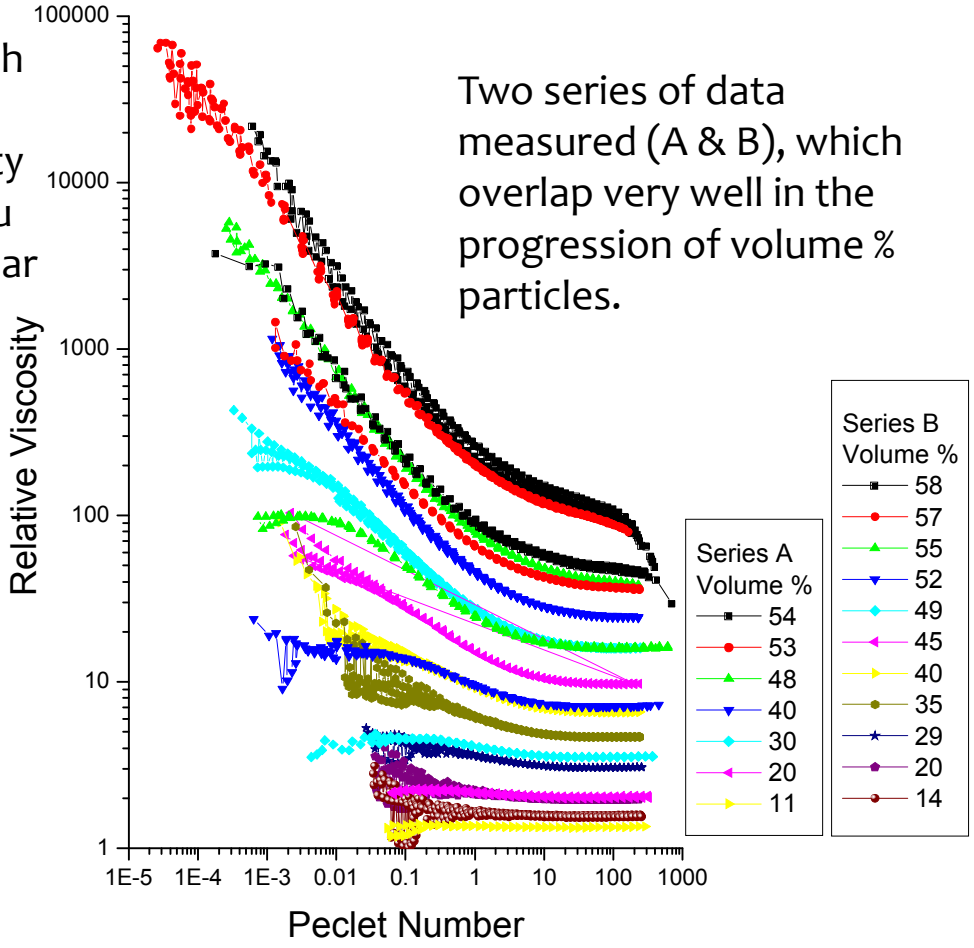
Rate Step Sweep for SiO_2-PDMS of 800 and 5000 Molecular Weight

- **Rate Sweeps vs. Volume Fraction Solids**

The curves were fitted with the Cross equation to determine relative viscosity at zero and infinite plateau values, and the critical shear rate for breakdown.



Two series of data measured (A & B), which overlap very well in the progression of volume % particles.



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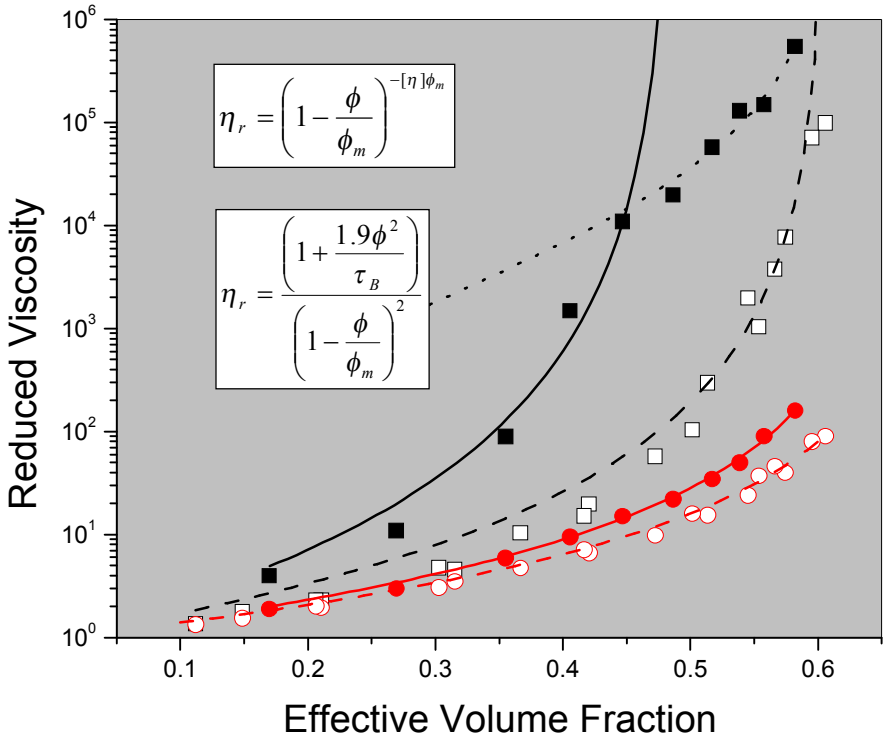
Relative Viscosity and Volume Fraction ϕ

- **Rate Sweeps vs. Volume Fraction Solids**

  A series of tests were performed with a single preparation of these colloids, using dilution with filtered solvent and monitored by mass addition.



- SiO_2-PDMS[800] Low
- SiO_2-PDMS[5000] Low
- SiO_2-PDMS[800] Hi
- SiO_2-PDMS[5000] Hi

Step shear rate fitting was performed with the Cross equation: Low and High shear rate viscosity is plotted for each data set. Fitting of high shear rate data with the Krieger-Doughtery equation

Krieger-Doughtery Equation Parameters

Low SiO_2-PDMS[800] $[\eta] = 7.62$, $\phi_{max} = 0.486$

Hi SiO_2-PDMS[800] $[\eta] = 3.55$, $\phi_{max} = 0.656$

Low SiO_2-PDMS[5000] $[\eta] = 4.99$, $\phi_{max} = 0.606$

Hi SiO_2-PDMS[5000] $[\eta] = 3.11$, $\phi_{max} = 0.688$

Krishnamurthy-Wagner Equation Parameters

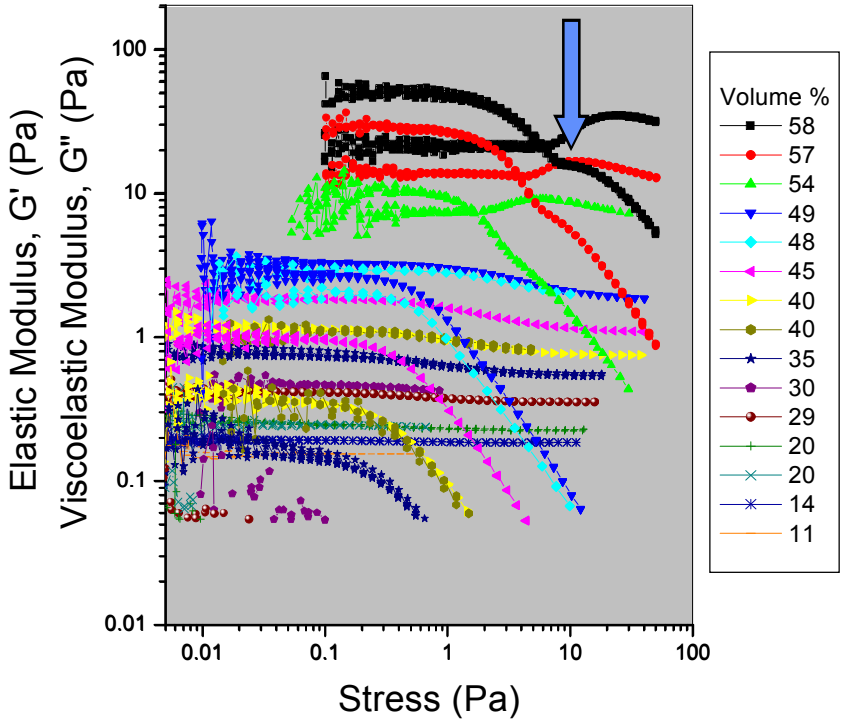
$\phi_{max} = 0.617$

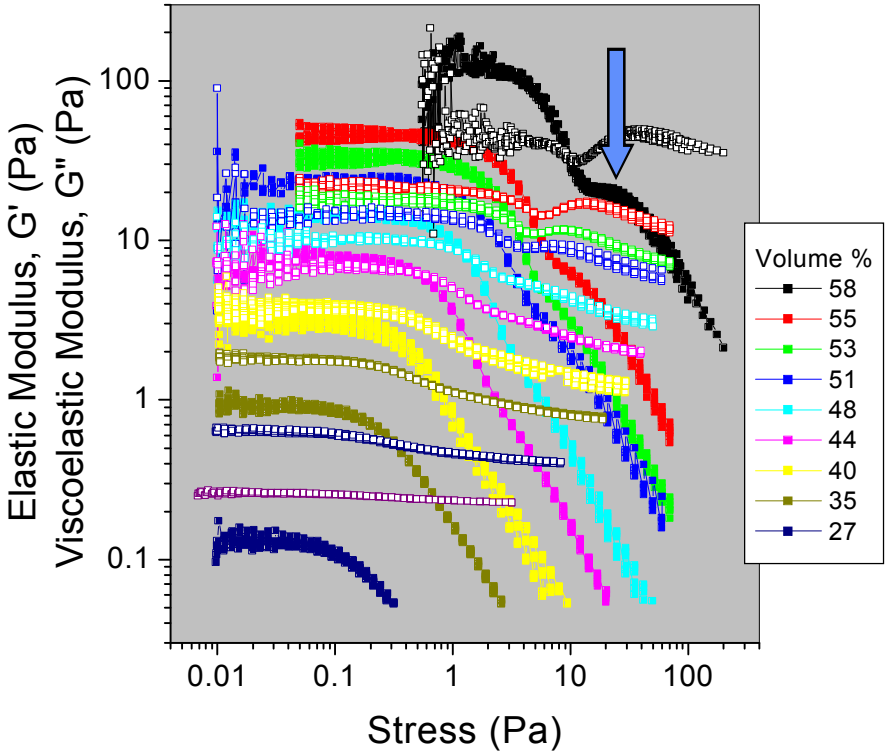
$\tau_B = 0.0004$

Neither the KD equation or the Krishnamurthy-Wagner model for weakly attractive systems fit the low shear viscosity data well.

Oscillation Stress Sweep for SiO_2-PDMS of 800 and 5000 Molecular Weight

- **Stress Sweep vs. Volume Fraction**





- The suspension has a transition to elastic (G') dominant above 49 and below 54 volume %.
- The samples greater than 49% show two breakdown structures as stress is increased.
- G' cannot be measured below 30 volume %.

- Elastic modulus becomes dominant at 44 volume %, in contrast to the PDMS[5000] modified particles.
- This formulation also has a second structural transition in the breakdown of the G' data, indicative of two shear structures.
- G' cannot be measured below 30 volume %.

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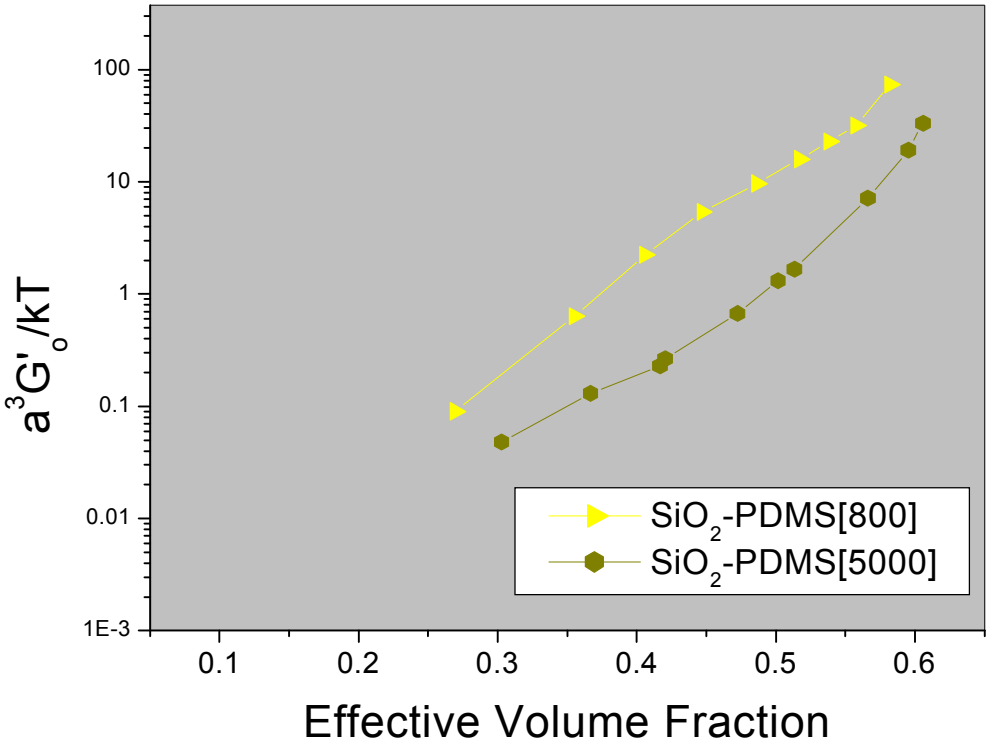
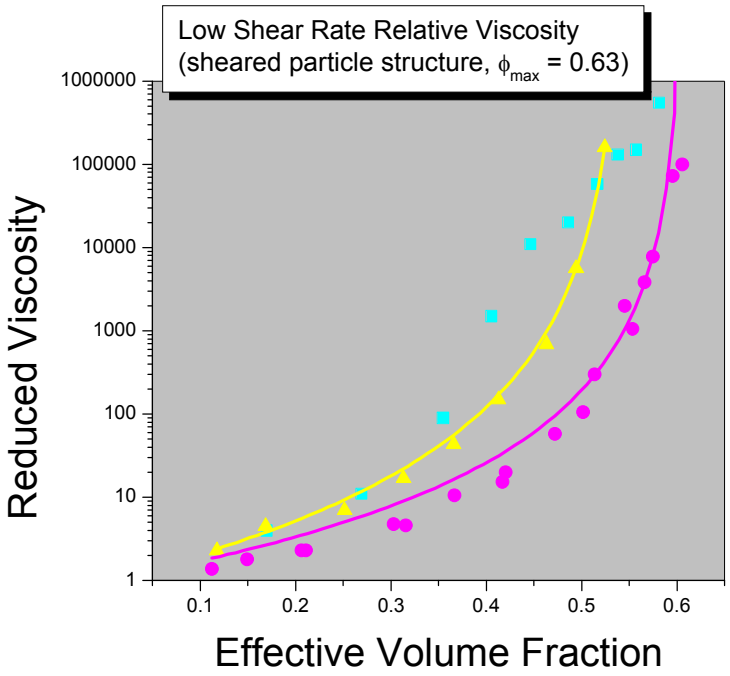
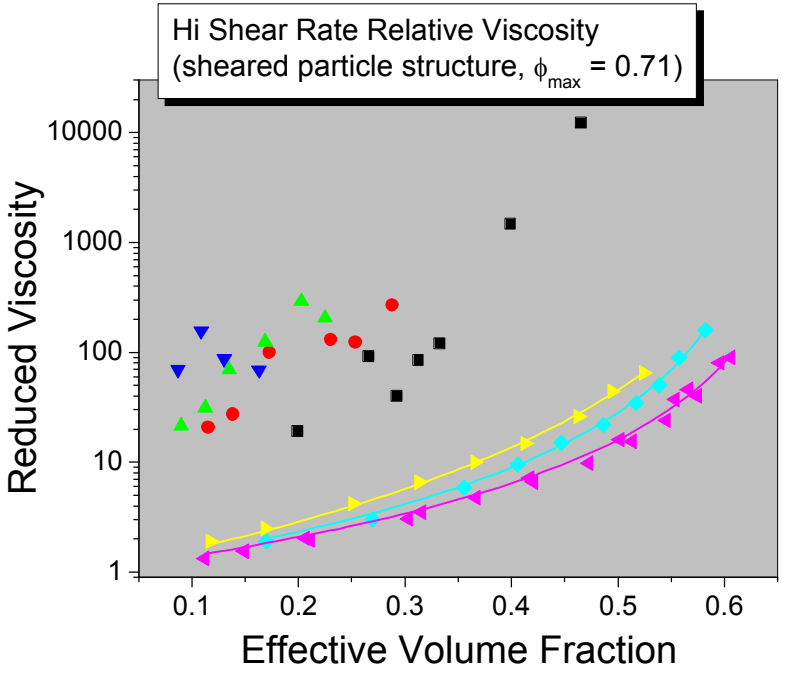
Elastic Modulus vs. ϕ

- G_0 shows the percolating network strength.
- Dispersants which mitigate van der Waals attraction and develop a steric repulsion do not achieve hard sphere behavior.
- Hydrodynamic confinement interactions need to be modeled for suspension properties.

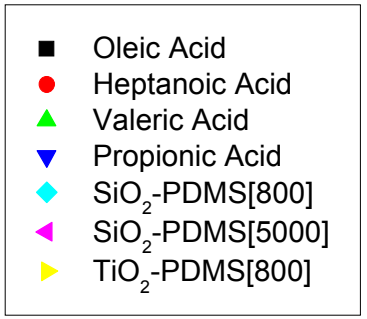


Rheology Characterization





- Dispersant comparison shows grafted chains provide more effective dispersion than adsorbed fatty acids.
- Fatty acids may form bilayer structures, leading to a "wetting" attraction.
- Grafted chain density affects dispersion via polymer wetting interactions.



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Summary

- Analytical Expressions for two particle interaction suggest weak attractions to minimal attraction between the two systems.

- The two systems exhibit weak flocculation. This phenomenon frustrates sedimentation characterization.

- Low and high shear viscosity plateaus are evident for both systems like a hard sphere system. Fitting with the Krieger-Doughtery equation requires flexibility, and the Krishnamurthy-Wagner equation does not fit the data (low shear plateau.)

- The PDMS[5000] is more effective (higher ϕ, lower G') despite lower grafting density.