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The Rheological Effects of additives to Aqueous Cab-O-Sil Dispersions

By

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Finally, without the assistance of Billi Bean and Roberta Porter a printed report would not have been possible.
Many industrial products require additives for rheological adjustment. Additives, such as, fumed silica can enhance the flow properties of paints, and epoxy coatings by stabilizing the the suspension of particles in a dispersion. Fumed silica can impart a yield stress to the system while maintaining a low viscosity. The result is a suspension both stable and easily applied. To gain knowledge and understanding of the mechanisms involved with thickening, an experiment to determine the effects of additives to aqueous dispersions of fumed silica was performed using an analytical rheometer purchased from Bohlin Instruments.

A series of measurements of shear stress vs shear rate for concentrations ranging from 4% to 12% by weight of Cab-O-Sil in water were performed. The solvent used for the experiment was water and additives were NaCl, Sodium Lauryl Sulfate, Cetyltrimethylammonium bromide, and urea. The results from the experiment indicated a critical shear rate was present in the dispersions. At rates higher than the critical rate, the dispersion behaved as a Bingham plastic. In the regions corresponding to Bingham plastic behavior, energy was dissipated by viscous forces. Below the critical point, floc-solution and floc-floc interactions became dominant. At extremely low shear rates, such as .0018 1/s, the floc size approached the size of the container.

Further studies of time dependent relationships and structure as a function of shear rate might add additional insight into the understanding of thickening.
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The Rheological Effects of additives to Aqueous Cab-O-Sil Dispersions

Introduction

Many industrial products require additives for rheological adjustment. Additives, such as, fumed silica can enhance the flow properties of paints, and epoxy coatings by stabilizing the the suspension of particles in a dispersion. Fumed silica can impart a yield stress to the system while maintaining a low viscosity. The result is a suspension both stable and easily applied.

Fumed silica is formed by the hydrolysis reaction of chlorinated silanes such as tetrachlorosilane. One such hydrolysis scheme involves the injection of mixtures of methylated chlorosilanes, air, and hydrogen into a hydrogen flame. The products of the reaction include water, hydrogen chloride gas and fumed silica. Fumed silica consists of agglomerates of silicon dioxide particles. The primary particles are approximately 2 nanometers in diameter and the agglomerate size is approximately 250 nanometers\(^1\). Located on the surface of the particles are three types of hydroxyl groups, isolated, adjacent, and adjacent hydrogen bonded.

Approximately 230 million pounds of fumed silica are produced from four sources each year. The annual production of fumed silica by the Degussa Corporation is 110, the Cabot Corporation is 80, the Wacker Corporation is 30, and the Tokoyama Soda
Corporation is 10 million pounds. Thirty percent of the 80 million pounds produced annually by the Cabot Corporation is used for thickening agents in reinforced plastics, polyester resins, inks, and coatings. Since the current selling price of Cab-O-Sil is approximately $3.08 per pound, the annual sales of fumed silica used for thickening applications is about 210 million dollars. Therefore, knowledge of the mechanism of thickening and the rheology of silica dispersions are extremely important topics.

Theory

According to Bird, Stewart, and Lightfoot, if a Newtonian fluid is placed between two plates and one of the plates is stationary while the other is set in motion, the force per area required to maintain constant velocity of the moving plate is equal to the velocity of the plate divided by the distance between the plates. Upon differentiation the force per area, termed shear stress, is proportional to the velocity gradient perpendicular to the plates. The constant of proportionality is termed viscosity and the velocity gradient is termed the shear rate. Fluids that do not have a linear relationship between shear stress and shear rate are termed Non-Newtonian.

Cab-O-Sil dispersions possess a linear relationship between shear rate and shear stress at high shear rates. However, extrapolation of the data in the linear region indicates a non-zero stress at zero shear rate. This stress is termed the Bingham yield stress. Therefore, most Cab-O-Sil dispersions behave as Bingham plastics at high shear rates. At
Experimental

The experimentation was divided into two parts. First, due to the complex flocculation of the Cab-O-Sil dispersions over time, a strict procedure for sample preparation was developed and followed precisely. Second, the samples were loaded into a rheometer and shear stress vs shear rate measurements were taken.

All Cab-O-Sil dispersions were prepared by following a number of steps. First, the mass of Cab-O-Sil, grade PTG, needed for a given weight fraction was calculate according to:

$$C = \frac{(V \cdot d_w \cdot x)}{(1-x)}$$

(1)

where $C$ = wt of Cab-O-Sil, $V$ = volume of water, $d_w$ = density of water, and $x$ = weight fraction. Densities of water were determined from temperature readings and extrapolation of data given in a CRC$^3$. Next, the volume of water used in equation (1) was pipetted into the Cab-O-Sil sample. The mixture was then stirred for 5 minutes, transferred to a glass jar, and sealed with parafilm. Finally, to ensure complete dispersion, the sample was placed in a sonicator box and sonicated for 5 minutes. The sample was then allowed to rest for 24 hours before experimentation.
Experimentation consisted of loading a sample into a 14 mm cup and bob apparatus. This was performed by pipetting the dispersion into the cup to a depth of 12 mm. The sample was then placed in a Bohlin rheometer and the bob was lowered into the cup to a depth corresponding to a .5mm spacing between the cup and bob. The sample was then sheared at 91/s for 5 minutes to break any large flocs. Upon completion of the 5 minute initial shearing measurements of shear stress were taken for various shear rates. The time between measurements was 1.5 minutes and the time during measurements was 30 seconds. All measurements started at high shear rates and continued to low shear rates.

The apparatus consisted of a Bohlin VOR Rheometer. The instrument was purchased from Bohlin instruments of Switzerland. The vor is designed to perform variable shear stress measurements for various shear rates. The instrument measures the torque applied to a torsion bar attached to the bob while spinning the cup at a given angular velocity. The torsion bars used for each of the experiments are listed in appendix A page A.2. All data was collected by an IBM compatible computer and saved as an ASCII file. The ASCII file was then imported into lotus 1-2-3 release 3.0 for analysis and Harvard Graphics release 2.3 for printing. A diagram of apparatus is included in appendix A page A.3.

An additional experiment was performed to determine the effects of bubbles and the reproducibility of the data. This was done by preparing an independent sample according
to the sample preparation procedures and then applying 26 inHg vacuum to the sample. Virtually all the air bubbles were destroyed by this debubbling technique.

Finally, a stress growth experiment was performed by applying a constant shear rate to a 7% Cab-O-Sil in .01M NaCl dispersion. The shear stress was measured with 60 second intervals and 30 second integration time for two hours.

Data Reduction

Data from the rheometer was imported into lotus 1-2-3 spreadsheets. The Bingham yield stress was obtained by regression of the linear portion of the curves at high shear rates. The true yield stress was obtained by regressing the data at low shear rates. The intercepts calculated by lotus were the Bingham yield stress and the true yield stress respectively.

Results and Discussion

According to Funt:\textsuperscript{4}, the rate of energy dissipation per unit volume is equal to the product of the shear stress and the shear rate. That is,

\[ E_{\text{total}} = \tau \text{u} \times R \]
where \( \tau = \text{shear stress} \) and \( R = \text{shear rate} \). The total energy dissipation, according to Firth\(^5\), is equal to the energy dissipation by viscous forces and the energy dissipation due to solute-solvent interactions. So that,

\[
E_{\text{total}} = E_{\text{v}} + E_{\text{s}}
\]

In the linear region of the curves, the dispersion behaves as a plastic so that,

\[
E_{\text{v}} = \tau \cdot R
\]

Since \( \tau = \text{viscosity} (\mu) \cdot R \)

\[
E_{\text{v}} = \mu \cdot R^2
\]

and

\[
E_{\text{s}} = \tau_{\text{s}} \cdot R
\]

then,

\[
E_{\text{total}} = \tau_{\text{s}} \cdot R + \mu \cdot R^2
\]

so that,

\[
\tau_{\text{total}} = \tau_{\text{s}} + \mu \cdot R \tag{2}
\]

In other words, the shear stress is a linear function of shear rate if no floc-floc interactions occur. Since the experimental data is linear at high shear rates, there is a critical shear rate above which no floc-floc interactions occur. In this region the Mooney equation\(^6\) seems to fit the data for viscosity vs concentration when water is the solvent. The Mooney equation is

\[
\text{plastic viscosity} = \text{solvent viscosity} \cdot \exp(2.5 \cdot f/(1-b \cdot f))
\]
where \( f \) = effective volume fraction of flocs, and \( 1/b \) = maximum packing volume fraction = 1 for Cab-O-Sil dispersions. The effective volume fraction = a constant \( C_{fp} \) * the volume fraction of solids. \( C_{fp} \) is the floc volume ratio and equals approximately 33.8 for Cab-O-Sil dispersions.

Modifying the ionic strength of the dispersion by addition of NaCl increases the solvent particle interactions. This is shown by the increasing Bingham yield stress. From equation (2) if the true yield stress varies while the shear rate and the solvent viscosity are held constant, the shear stress contributions from particle-solvent interactions must vary.

When anionic surfactants are added to the dispersion two effects occur. First, at low concentrations the surfactants interact with the solvent and lower the surface tension and hence the viscosity of the solvent. At higher concentrations, the surfactants interact with the flocs and form micelles. Since the viscosity of the solvent must be lowered by the introduction of a surfactant, the increase in yield stress is due to floc-solvent or floc-floc interactions.

Since the yield stress in cationic surfactants did not show appreciable change, cationic surfactants seem to have little effect on fumed silica-solvent interactions at high surfactant concentrations. However, at low surfactant concentrations, the surfactant interacted with the solvent and lowered the solvent viscosity.
In the regions of low shear rate, solute-solvent interactions are more apparent. This is easily shown from equation (2) and small changes in R. In these cases, the viscous contributions became negligible and the particle-floc interactions become dominant.

When NaCl is added to increase the ionic strength of the solvent, the yield stress increases. Again only floc-floc interactions contribute to the increased yield stress. Thus the floc-floc interactions are most likely due to electrostatic interactions such as hydrogen bonding. When urea was added to the dispersion to eliminated hydrogen bonding, the yield stress approached that of pure water.

The addition of surfactants had very little effect on the shear stress at low shear rates. Thus, the surfactants have little effect on floc-floc interactions.

Conclusions

1. Aqueous Cab-O-Sil dispersions exhibit characteristics of Bingham plastics at high shear rates.

2. At high shear rates, energy dissipation is primarily due to viscous terms.

3. At low shear rates, energy dissipation is primarily due to floc-floc interactions.

4. Addition of anionic surfactants increases the floc-solvent interactions while addition of cationic surfactants does not.
5. Increasing ionic strength increases floc-floc and floc-solvent interactions.

6. The floc-floc interactions are primarily due to hydrogen bonding.

7. The floc size grows to the size of the container as the shear rate approaches zero.

8. The growth rate of the floc is dependent on concentration.

Recommendations

1. Perform structural analysis on dispersions of varying concentrations as a function of shear rate.

2. Develop a model of the dispersions as a function of particle interactions.

3. Investigate the supernomalous behavior of Cab-O-Sil dispersions.

4. Develop time dependent models of Rheology as a function of concentration and neutral and ionic additives.
References


7. 
Appendix A: Experimental Apparatus
Appendix B: Experimental Data
Appendix C: Figures
Shear Stress vs. Shear Rate
Dependency Image

Shear Stress (Pa)

Shear Rate (1/s)

- 5% Cab-O-Sil
- 8% Cab-O-Sil
- 10% Cab-O-Sil
- 8% Cab-O-Sil
- 9% Cab-O-Sil
Shear Stress vs Shear Rate

1M NaCl in Deionized Water

Shear Stress (Pa) vs Shear Rate (1/s)

- 9% Cab-O-Sil
- 8% Cab-O-Care
- 7% Cab-O-Sil
- 6% Cab-O-Sil
- 4% Cab-O-Sil
Shear Stress vs Shear Rate
0.1M SLS in Deionized Water

Shear Stress (Pa)

Shear Rate (s⁻¹)

- 9% Cab-O-Sil
- 8% Cab-O-Sil
- 6% Cab-O-Sil

SLS = sodium lauryl sulfate, Silica
Shear Stress vs Shear Rate
0.01M SLS in Deionized Water

Shear Stress (Pa)

Shear Rate (s⁻¹)

- 9% Cab-O-Sil
- 8% Cab-O-Sil
- 7% Cab-O-Sil
- 6% Cab-O-Sil
- 5% Cab-O-Sil

SLS = sodium lauryl sulfate (ammonia)
Shear Stress vs Shear Rate
0.001M SLS in Deionized Water

Shear Stress (Pa)

Shear Rate (1/s)

- 12% Cab-O-Sil
- 10% Cab-O-Sil
- 8% Cab-O-Sil
- 6% Cab-O-Sil
- 7% Cab-O-Sil
- 6% Cab-O-Sil
- 5% Cab-O-Sil

SLS = sodium lauryl sulfate (anionic)
Shear Stress vs Shear Rate
.001M SLS IN DEIONIZED WATER

Shear Stress (Pa)

12% Cab-O-Sil
10% Cab-O-Sil
8% Cab-O-Sil
6% Cab-O-Sil
5% Cab-O-Sil
7% Cab-O-Sil
6% Cab-O-Sil
5% Cab-O-Sil

SLS = sodium lauryl sulfate (anionic)
Shear Stress vs. Shear Rate
0.01M SLS in de-ionized water

Shear Stress (Pa)

Shear Rate (s⁻¹)

- 10% Cab-O-Sil
- 10% Cab-O-Sil + 1% Surfactant A
- 7% Cab-O-Sil + 1% Surfactant A
- 7% Cab-O-Sil + 1% Surfactant B

SLS: Sodium dodecyl sulfate surfactant
Shear Stress vs Shear Rate
0.1M CTAB in Deionized Water

CTAB = Cetyltrimethylammonium bromide

Shear Rate
Shear Stress vs Shear Rate
0.01M CTAB in Deoxygenated Water

CTAB = Cetyltrimethylammonium bromide
Shear Stress vs Shear Rate
0.01 M CTAB in deionized water

Shear Stress (Pa)

Shear Rate (1/s)

9% Cab-O-Sil
8% Cab-O-Sil
7% Cab-O-Sil
6% Cab-O-Sil
5% Cab-O-Sil

Cetyltriethylammoniumbromide
Shear Stress vs Shear Rate
6% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.4M NaCl
- 0.04M NaCl
- 0.004M NaCl
Shear Stress vs Shear Rate
6% Cab-O-Sil Dispersions

Shear Stress (Pa):

Shear Rate (1/s):

- water
- 0.1M NaCl
- 0.01M NaCl
- 0.001M NaCl
Shear Stress vs Shear Rate
6% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.01M SLS
- 0.001M SLS
Shear Stress vs Shear Rate
6% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water  - 0.01M SLS  - 0.001M SLS
Shear Stress vs Shear Rate
6% Cap-O-Stex Dispersion

Shear Stress (Pa):

Shear Rate (1/s):

- water
- 0.01M SLS
- 0.001M SLS
Shear Stress vs Shear Rate
6% Cab-O-Sil Dispersion

Shear Stress (Pa)

Shear Rate (s⁻¹)

- water
- 0.01M OTAB
- 0.001M OTAB
Shear Stress vs Shear Rate
7% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)
Shear Stress vs. Shear Rate
7% CaO-CaSi Dispersions

Shear Stress (Pa)

Shear Rate (1/s)
Shear Stress vs. Shear Rate
7% Cab-O-Sil Dispersions
Shear Stress vs. Shear Rate
7% Carboxylate Dispersion

Shear Stress (Pa)

Shear Rate (1/s)
Shear Stress vs. Shear Rate
7% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- Water
- With 0.5% SDS
- With 0.5% SDS + 40% Urea

Legend:
- Water
- With 0.5% SDS
- With 0.5% SDS + 40% Urea
- Water + SDS
Shear Stress vs Shear Rate
7% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)
Shear Stress vs Shear Rate
7% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- WATER
- 0.05% CTAB
- 0.05% CTAB + WATER
- WATER w/UREA
Shear Stress vs Shear Rate
7% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- WATER
- 0.05% CTAB
- 0.001% CTAB
- WATER w/UREA
Shear Stress vs Shear Rate
8% Cab-O-Sil Dispersion

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.1 M NaCl
- 0.01 M NaCl
Shear Stress vs. Shear Rate
by CaCO₃ Oil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

0.002
0.01
0.1
1
10
100
1000

Compositions:
- 0.01 M CaCl₂
- 0.001 M CaCl₂
- 0.0001 M CaCl₂
Shear Stress vs Shear Rate
3% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- Water
- 0.01M SLS
- 0.001M SLS
Shear Stress vs. Shear Rate
8% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- Water
- 0.01M SLS
- 0.001M SLS
Shear Stress vs. Shear Rate
8% Cab-O-Sil Dispersion
Shear Stress vs Shear Rate
8% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.01M CTAB
- 0.001M CTAB
Shear Stress Vs Shear Rate
8% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (s⁻¹)

- Water
- 0.01M CTAB
- 0.001M CTAB
Shear Stress vs. Shear Rate
8% Cab-O-Sil Dispersions

Shear Stress (Pa)

0.001  0.01  0.1  1  10  100  1000
Shear Rate (1/s)

- Water
- 0.01M CTAB
- 0.001M CTAB

Graph shows the relationship between shear stress and shear rate for different concentrations of CTAB in a 8% Cab-O-Sil dispersion.
Shear Stress vs Shear Rate
9% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.1M NaCl
- 0.01M NaCl
Shear Stress vs. Shear Rate
9% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.1M NaCl
- 0.01M NaCl
Shear Stress vs. Shear Rate
9% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.01M SLS
- 0.001M SLS
Shear Stress vs. Shear Rate
9% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.01M SLS
- 0.001M SLS
Shear Stress vs Shear Rate
9% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.01M CTAB
- 0.001M CTAB

Graph showing the relationship between shear stress and shear rate for different concentrations of CTAB in comparison to water.
Shear Stress vs Shear Rate
9% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.01M CTAB
- 0.001M CTAB
Shear Stress vs Shear Rate
9% Cab-O-Sil Dispersions

Shear Stress (Pa)

Shear Rate (1/s)

- water
- 0.01M CTAB
- 0.001M CTAB
Data Reproducibility
6% Dispersions in 0.1M SLS

Shear Stress (Pa)

Shear Rate (1/s)

--- without debubbling

--- with debubbling

Two Independent Samples
Data Reproducibility

6% Dispersions of 1 mM SLS

Stress (Pa)

Shear Rate (1/s)

- without depooling

- with depooling

Existent Samples
Data Reproducibility
6% Dispersions in 0.1M SLS

Shear Stress (Pa)

Shear Rate (1/s)

- without debubbling
- with debubbling

Sample Samples.
Bingham Yield Stress vs Concentration

Bingham Yield Stress

Concentration

Water → 1M NaCl → 0.1M NaCl
Bingham Yield Stress vs Concentration

Bingham Yield Stress

Concentration

Water  IM NaCl  0.5M NaCl
Bingham Yield Stress vs Concentration

Concentration

- Water
- 0.1M SIS
- 0.01M SLS
Bingham Yield Stress vs Concentration
Bingham Yield Stress vs Concentration

Bingham Yield Stress

Concentration

Water 0.1M Ctab 0.01M Ctab
Bingham Yield Stress vs Concentration

Concentration

Water, NaCl, KCl, CaCl2
True Yield Stress vs Concentration

- Water
- 1M NaCl
- 3M NaCl
True Yield Stress vs Concentration

True Yield Stress

Concentration

Water

.01M SIS

.001M SLS
True Yield Stress vs Concentration

True Yield Stress

Concentration

Water

0.1M SIS

0.01M SLS
True Yield Stress vs Concentration

True Yield Stress

Concentration

- Water
- 0.1M Ctaq
- 0.01M Ctaq
Shear Growth Experiment
Shear Stress vs Time

Shear Stress

0  5  10  15  20  25  30  35  40

0  2  4  6  8

time (1000 sec)

--- 8% in 1M NaCl

Constant Shear Rate of 0.01853 [1/s]