Understanding the Link between Particle Properties and Rheology of Suspensions
Overview

• Introduction to Rheology Terms
• Impact of Particle Size
• Impact of Particle Size Distribution
• Impact of Particle Volume Fraction
• Impact of Fluid Additives
Introduction to Terms

› Rheology describes and predicts how a substance will behave under applied outer forces
› We will focus on viscosity – a material’s resistance to flow.
› To measure viscosity, rotational or capillary rheometers can be used.
Shear Viscosity Flow Curves

› Describes a material's resistance to flow ("thickness") against shear rate.

› Shear rate is an indication of how fast you are deforming a material.

Spraying $10^6$ s$^{-1}$ : Brushing $10^2$ s$^{-1}$ : Pumping $10^1$ s$^{-1}$ : Levelling $10^{-1}$ s$^{-1}$

- Newtonian; where the material does not change with shear.
- Shear thinning; where the structure within the material breaks down with shear.

› Most particle containing samples are shear thinning.
Part I – Particle size & distribution

› Effect of increasing size.
› Dependence on volume fraction
› Changing the particle size distribution
› How does this affect rheology?

Mastersizer 3000 by Malvern Instruments

Kinexus Rheometer by Malvern Instruments
Effect of particle size - non-colloidal systems

› For non-Colloidal particles the effect of particle size on viscosity should be minimal as shown below.
› The most critical factor governing viscosity is the volume fraction of particles in suspension.

Effect of particle size on relative viscosity at various volume fractions of spherical particles (Lewis and Nielsen).

Colloidal Suspension Rheology Jan Mewis, Norman J. Wagner, 2012
Effect of particle size - colloidal systems

- For small particles colloidal effects can be significant
  - Brownian motion
  - Attractive/Repulsive forces
- Inter-particle forces dominate at low shear rates giving a large increase in shear stress and hence viscosity
- Hydrodynamic (fluid) stresses dominate at high shear rates, hence particle size effects are minimised
Effect of particle loading – Dilute systems

› Einstein equation

\[ \eta = \eta_{\text{medium}} \left(1 + 2.5\phi\right) \]

- $\eta$ – viscosity of the suspension
- $\eta_{\text{medium}}$ – viscosity of the medium
- $\phi$ – volume fraction of solids in the suspension

› Einstein equation assumes minimal interaction between particles – hence low volume fractions only

› Two main contributions to viscosity
  - Distortion of flow lines around individual particles
  - Friction at particle surface
Effect of particle loading – Concentrated systems

› Krieger-Dougherty equation

\[
\frac{\eta}{\eta_{medium}} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}
\]

› \( \phi_m \) – max vol. fraction of solids in suspension
› \([\eta]\) – intrinsic viscosity (2.5 for spheres)

› Complex particle and fluid interactions give a non-linear viscosity dependence with particle concentration
› This behavior has shown to be well characterized using an equation of this form
Effect of particle loading

› As volume fraction ($\phi$) increases...

\[
\frac{\eta}{\eta_{medium}} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}
\]

› Then viscosity ($\eta$) increases.
› Packing more particles makes flow more difficult.
Controlling flow behaviour

- Changing the volume fraction...

Newtonian: $\phi/\phi_m < 0.1$
Shear Thinning: $0.1 < \phi/\phi_m < 0.5$
Shear Thickening: $\phi/\phi_m > 0.5$
Practical example

› Increase the quantity of latex particles in a pressure sensitive adhesive.
› Particle interactions give high viscosity at low shear rates but can cause thickening under high shear

*Figure 4 - Effect of solids loading on viscosity. Graph shows viscosity vs. shear rate for a monomodal polymer dispersion of 280 nm.*

Application Note: “An Overview of the Use of Rheology for Adhesive Manufacturers”, Malvern Instruments

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Spraying of a Dispersion Adhesive

⇒ Shear Thickening at High Shear Rates
Why? Colloidal microstructure and Viscosity

Colloidal Suspension Rheology Jan Mewis, Norman J. Wagner, 2012
Effect of particle size distribution

› We can keep the volume fraction ($\phi$) the same.
› Now, change the particle size distribution…
› What happens to the viscosity?
Effect of distribution on maximum packing fraction

As the particle size distribution increases, this allows a greater packing fraction.

\[ \phi_m \approx 0.62 \quad \text{Random monodispersed close packing} \]
\[ \phi_m \geq 0.74 \quad \text{Random polydisperse close packing} \]
Effect of maximum packing fraction

› As maximum packing fraction increases…

\[
\frac{\eta}{\eta_{\text{medium}}} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}
\]

› Then viscosity (\(\eta\)) decreases.
› Allows more free flowing particles (self lubricating)
Practical example

› Different sized talc added to an epoxy
› Mixture of particle sizes gives the lowest viscosity suspension – more effective packing
Impact of Additives

Xanthan Solution - measured with Cone Plate and Double Gap

Mw = 2,400,000 g/mol

\[ \frac{\eta_p}{c} = [\eta] + k_h [\eta]^2 c \]

\[ M = \frac{10 \pi}{3} \cdot N_A \cdot \frac{R^3}{[\eta]} \]

Strong Impact on Zero Shear Viscosity for Xanthan thickener
Further Impact on Rheology of Suspensions

- Laser Diffraction
- Spray Particle Analyzer
- Digital Microscopy
- Light Scattering
- Size and Zeta
- Electrostatic interactions
- Steric Hindrance
- Particle shape

Volume fraction, $\phi$

Particle size

Particle size distribution

Wet

Dry

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Conclusions

› Particle Size
  ▪ non-Colloidal suspensions: viscosity is not affected
  ▪ Colloidal Suspensions: significant due to colloidal interactions

› Volume fraction
  ▪ most critical factor for the flow behaviour of suspensions especially at high concentrations
  ▪ Dilute Suspensions: Einstein equation
  ▪ Concentrated Suspensions: Krieger-Dougherty equation

› Particle Size Distribution
  ▪ Wide particle size distributions: lower suspension viscosity
  ▪ Narrow particle size distributions: higher suspension viscosity
Thank you for your attention!

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