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ANALYZING & TESTING

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USING RHEOLOGY TO OPTIMIZE COATINGS

Philip Rolfe, Rheology Technical Specialist. Netzsch Instruments Inc

Coatings Trends and Technology Summit, Sept 4th, 2025

Why Rheology?

An ideal coating has a number of rheological attributes including:

- Sag resistance, but good levelling properties
- Sedimentation Stability
- High shear stability – for sprays and roller coatings
- Low extensional viscosity to eliminate longitudinal striations
- Good metering, but with maximum opacity
- High solids loading to reduce drying time

It’s clear that these are flow or rheologically related

Shear Rates of Different Processes

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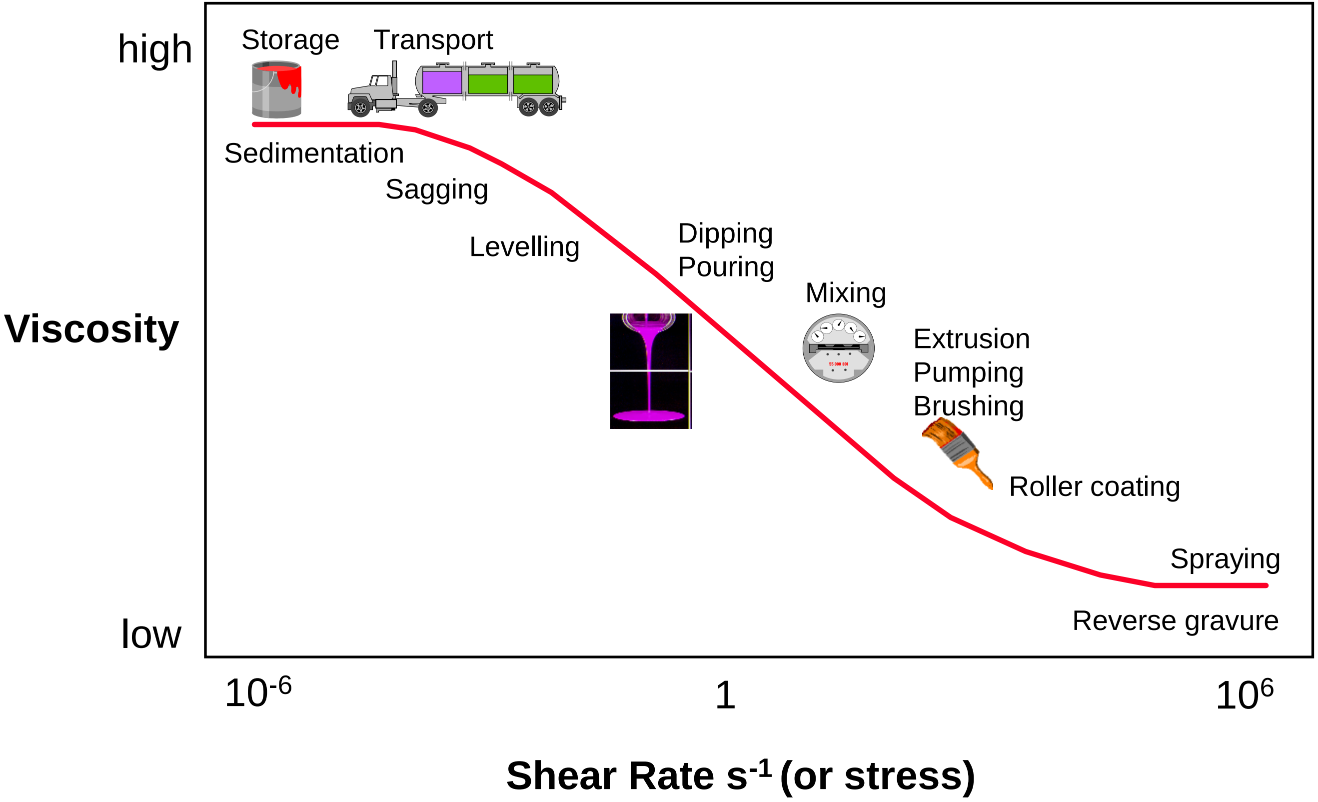

Shear rates of different processes

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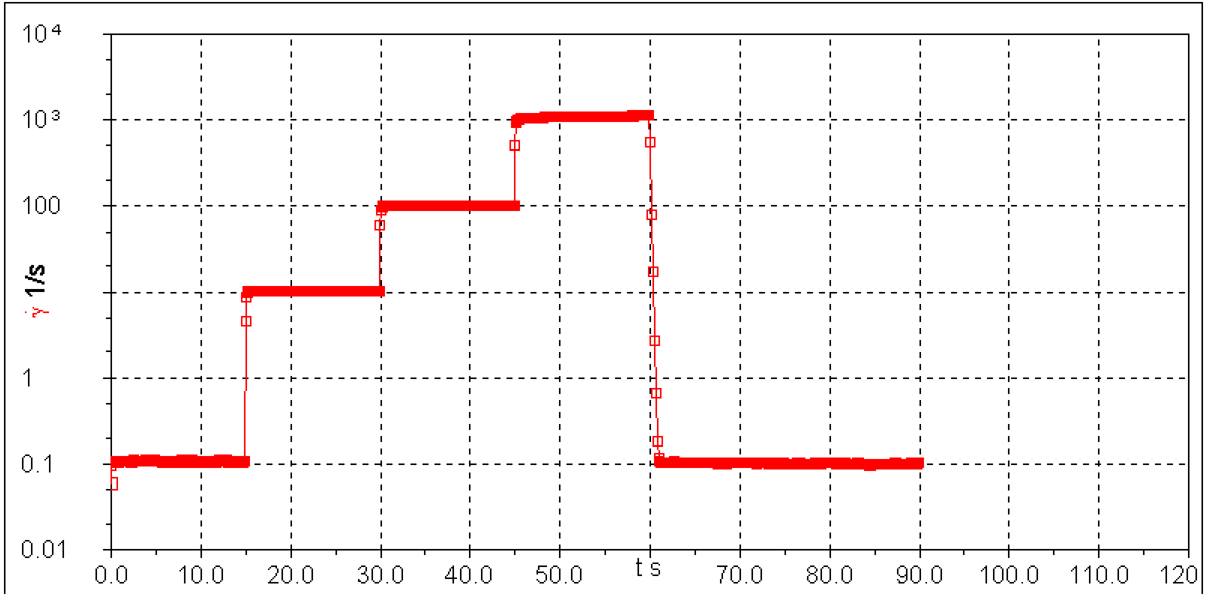
Process	Minimum Shear Rate (1/s)	Maximum Shear Rate (1/s)
reverse gravure	10^5	10^6
spraying	10^4	10^5
blade coating	10^3	10^5
mixing/stirring	10	10^3
brushing	10	10^3
pumping	1	10^3
extrusion	1	10^2
curtain coating	1	10^2
levelling	10^{-2}	0.1
sagging	10^{-2}	0.1
sedimentation	10^{-6}	10^{-2}

Transient Speed Change

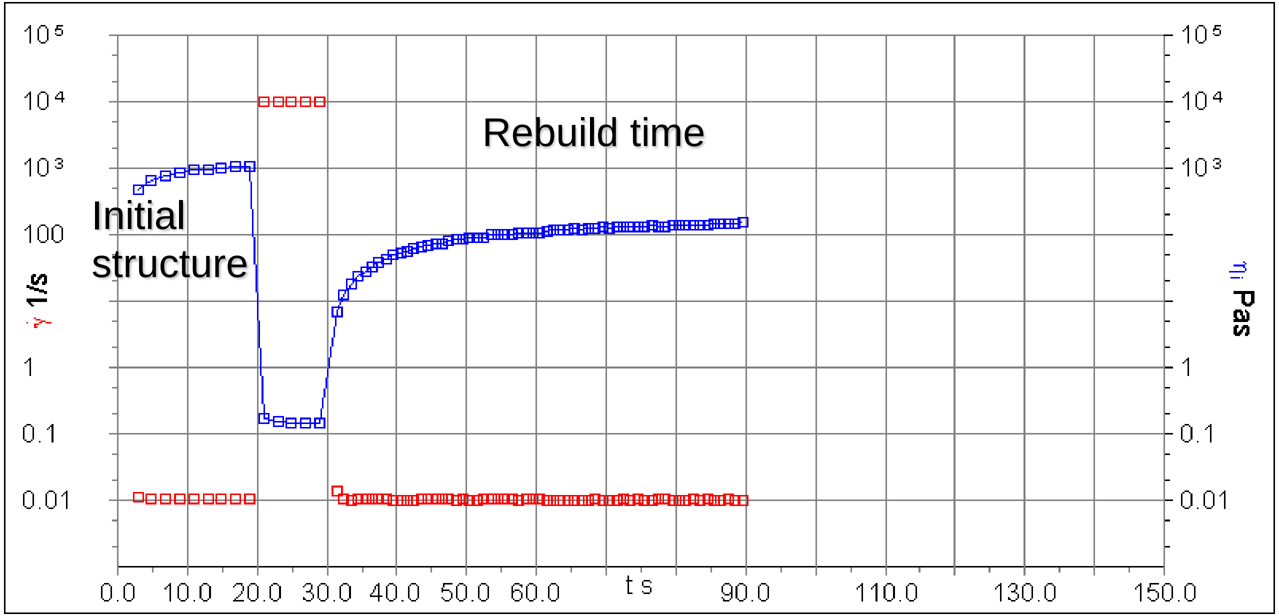


Near instantaneous change of speed

Example shows four orders of magnitude change of speed

Generated by Flow Profile Software

Simulation of Coating

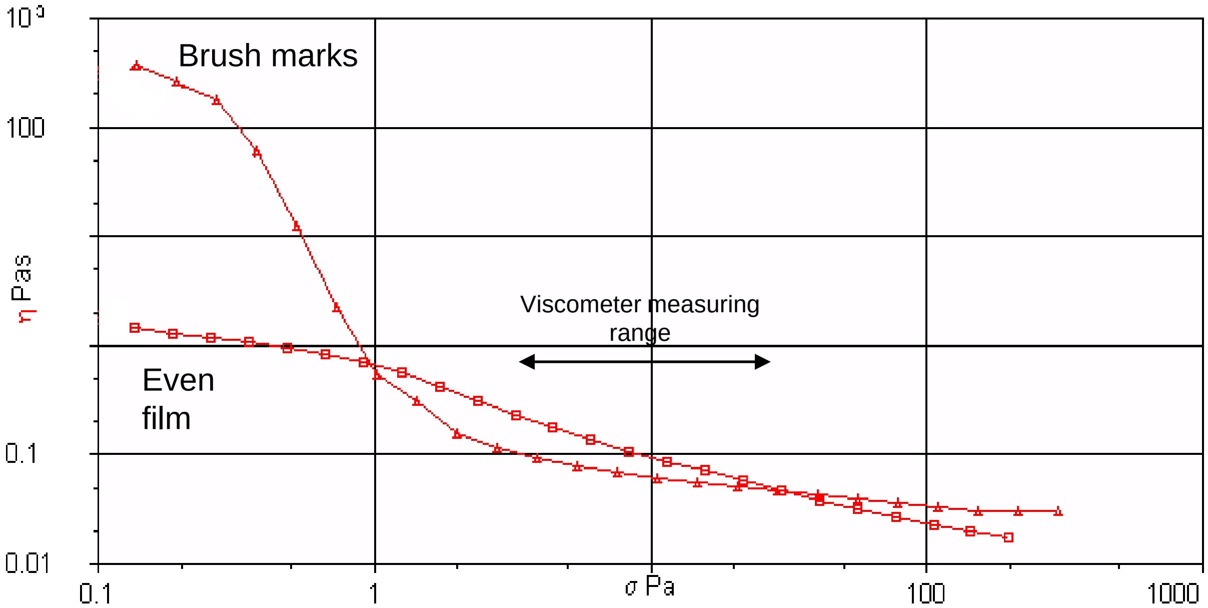


Shear rate profile 0.01s-1 to 1000s-1 to 0.01s-1

Shear thins at high rate & Recovers at low rate

Allows direct simulation of application process

Low shear stress - leveling



Controlled stress measurements enable the user to predict leveling properties of the coating from the value of the low shear stress viscosity

Simulating Reverse Gravure with Flow Reversal

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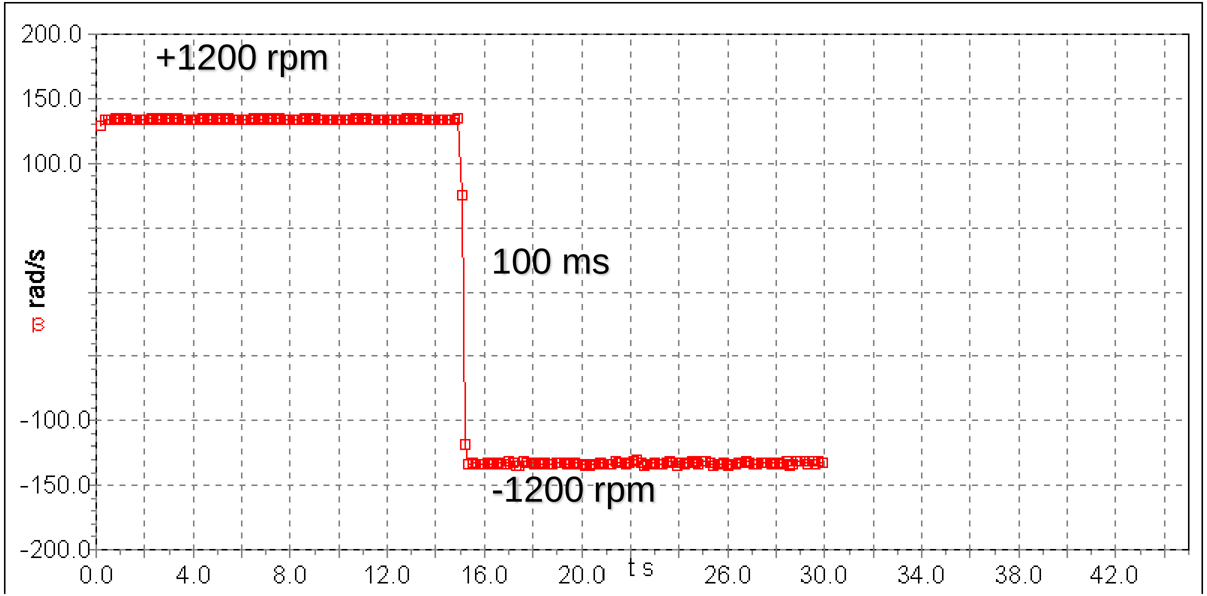
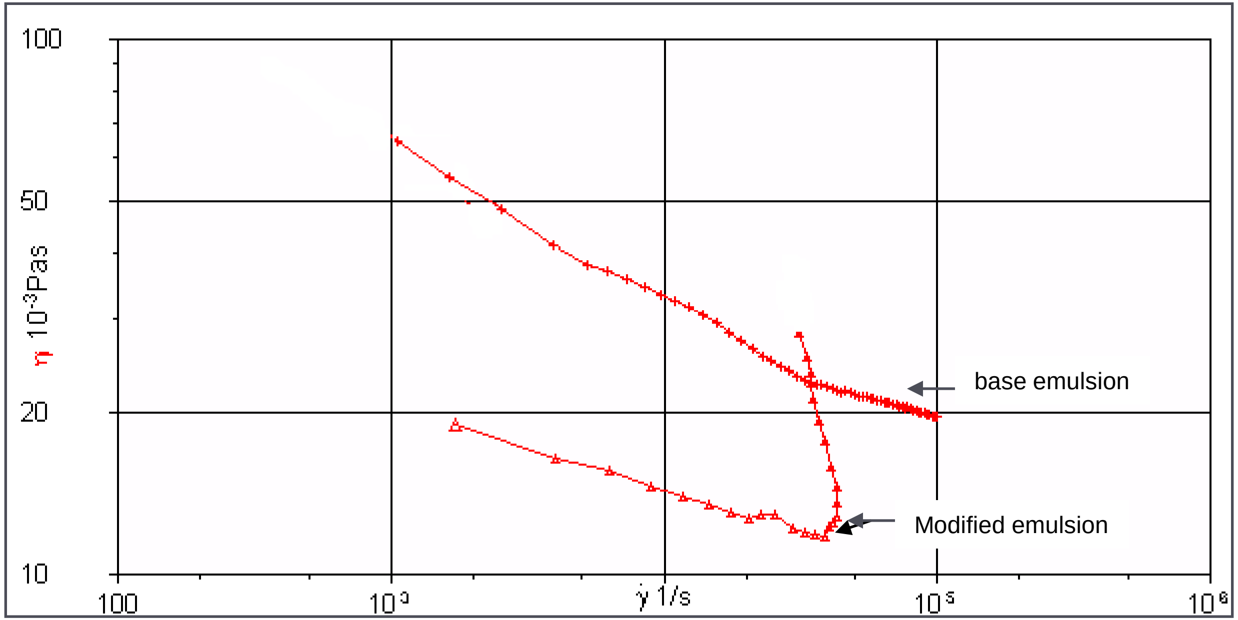


+100 to -100 rad/s in approximately 100 ms

No speed overshoot during reversal of flow

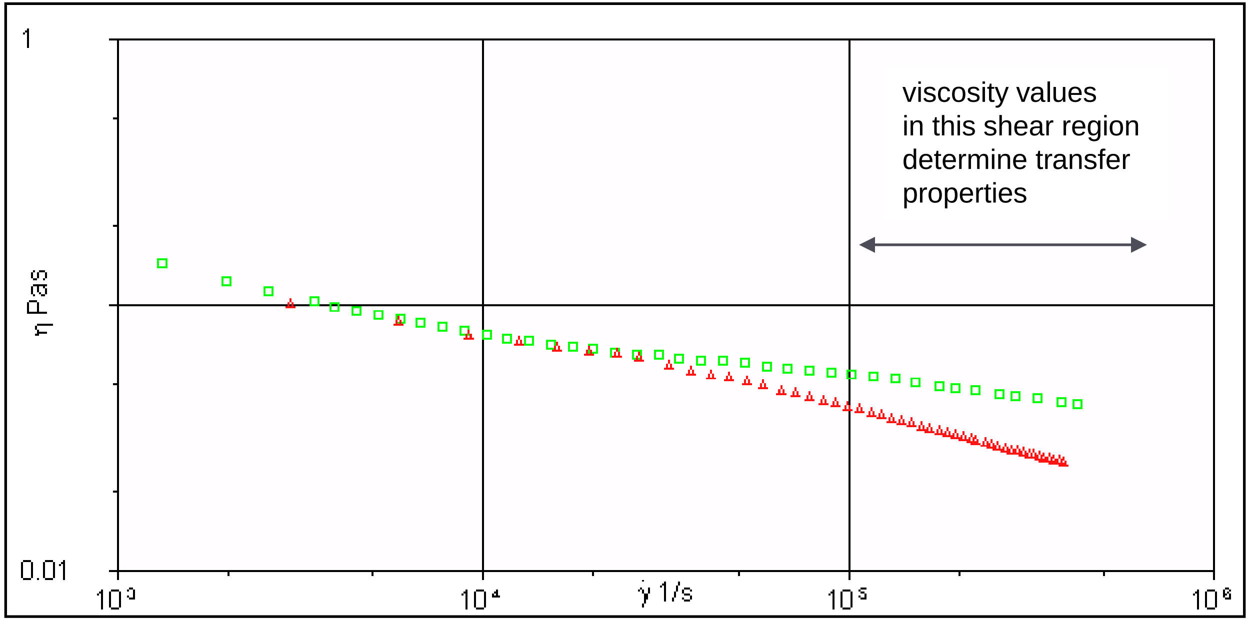
Allows simulation of industrial roller coating processes

Some flow problems - High shear instabilities



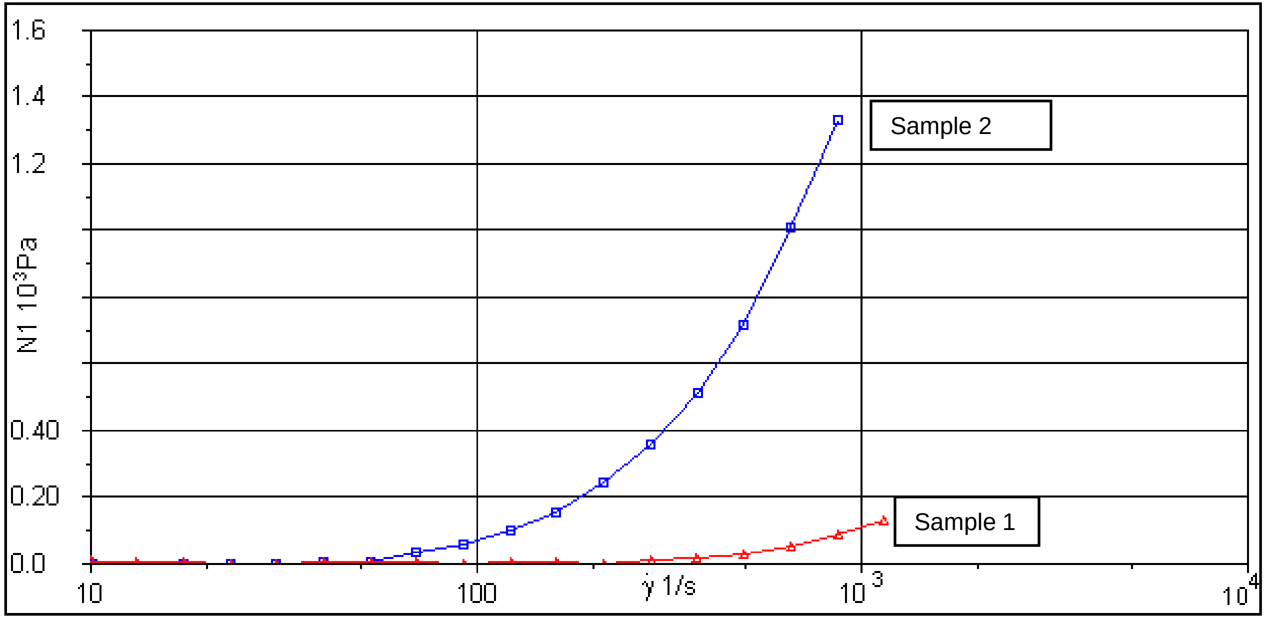
Measurements at high shear rate show the modified emulsion is unstable and breaks down. The base emulsion is mechanically more stable under high shear conditions.

High shear rates - adhesive transfer



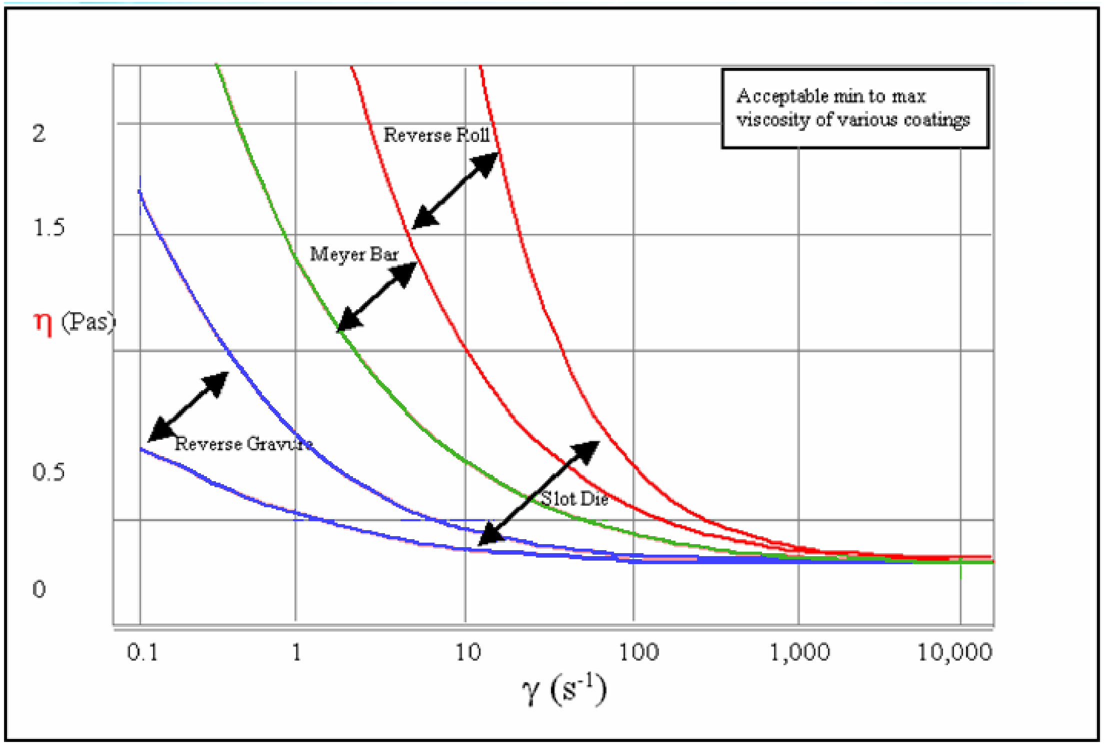
Measurements at high shear rate on two PSA's show differences in viscosity above 2 x 10^4 s^{-1}. This explains variations in transfer properties during gravure coating.

Normal force - paper coatings



Two coating samples with similar viscosity profile. Coating weight cannot be controlled easily with sample 2 (sample 1 is the control and can be coated satisfactorily). Normal force at high shear rates pushes coating blade away from the paper surface

Viscosity profiles for adhesives



Acceptable viscosity ranges for several common coating processes (courtesy of H B Fuller)

How do we get there?
– the effect of particle loading

The Krieger-Dougherty equation (Eq 1, below)[i] shows that for hard spheres the rheological properties are directly related to the volume occupied by the particles.

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$

η - Viscosity of the suspension,
η_0 – viscosity of the medium,
ϕ - Volume fraction of solids in the suspension,
ϕ_m – maximum packing fraction (63% for random close packing).
$[\eta]$ – Intrinsic viscosity (2.5 for spheres)

Equation 1 – The Krieger-Dougherty equation

[i] I M Krieger and T Dougherty, Trans. Soc. Rheol. 3, 137 (1959).

Effect of increasing latex solids loading

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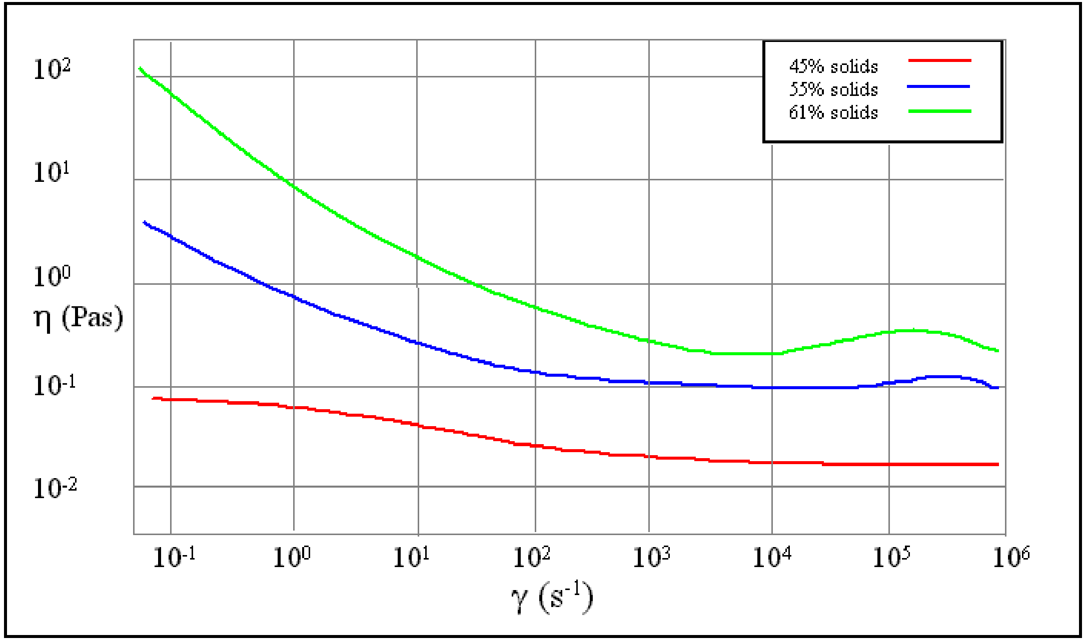

Increasing the solids content increases the viscosity. At high solids contents, shear thickening may be observed at high shears.

Effect of adding Coarse Talc to an Epoxy

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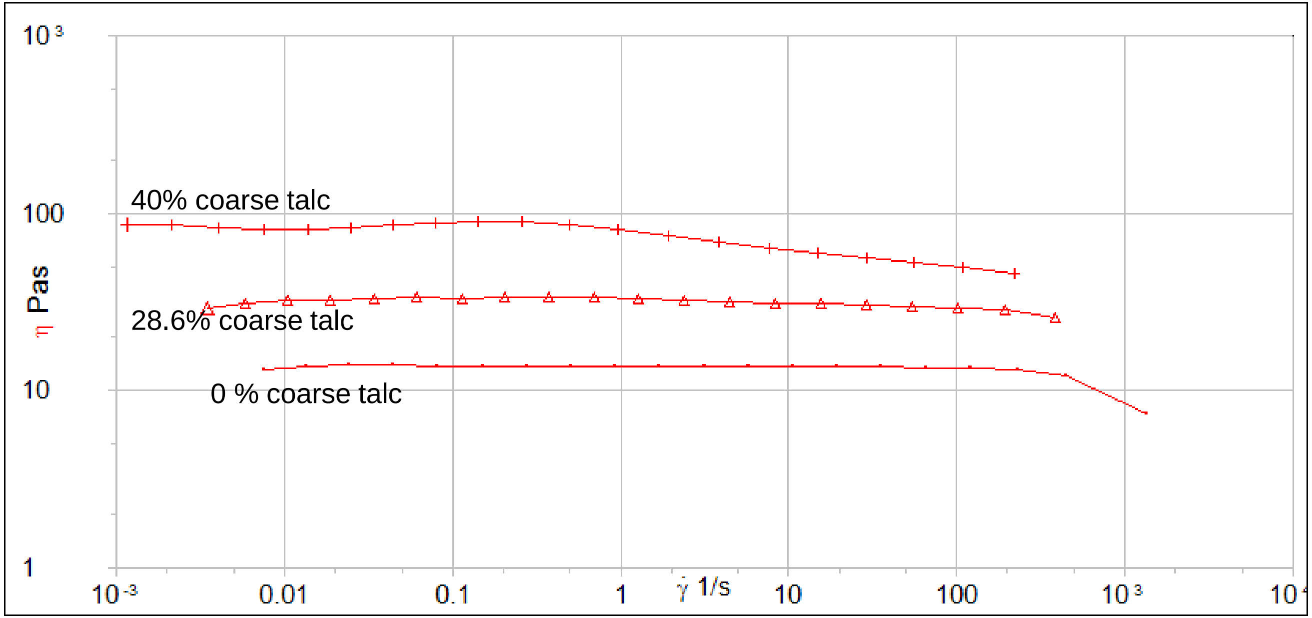
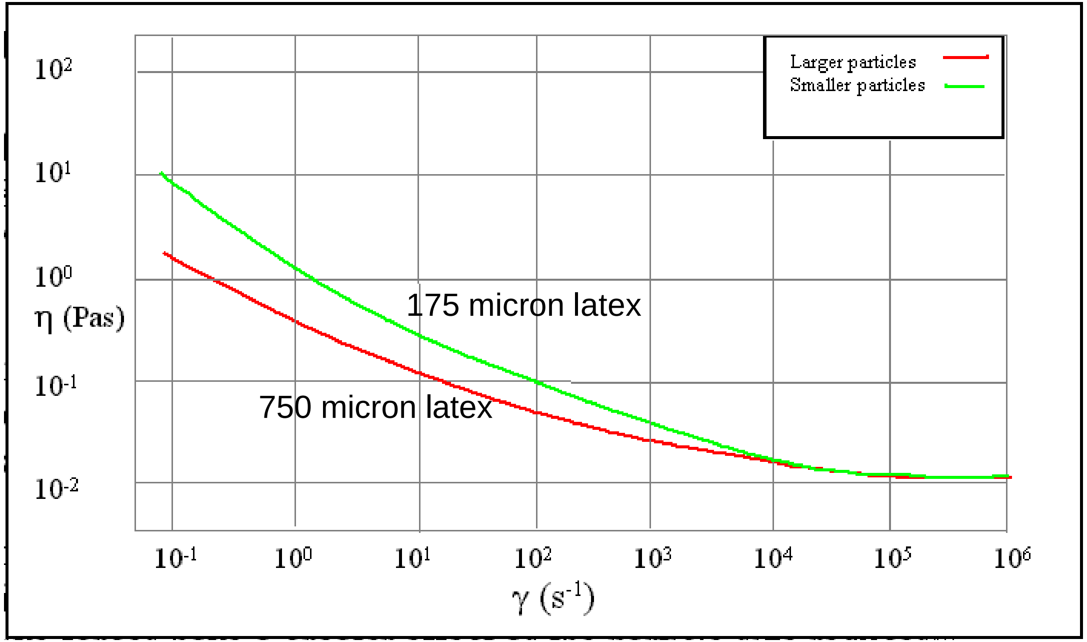
This talc had a volume mean diameter of 19 microns.

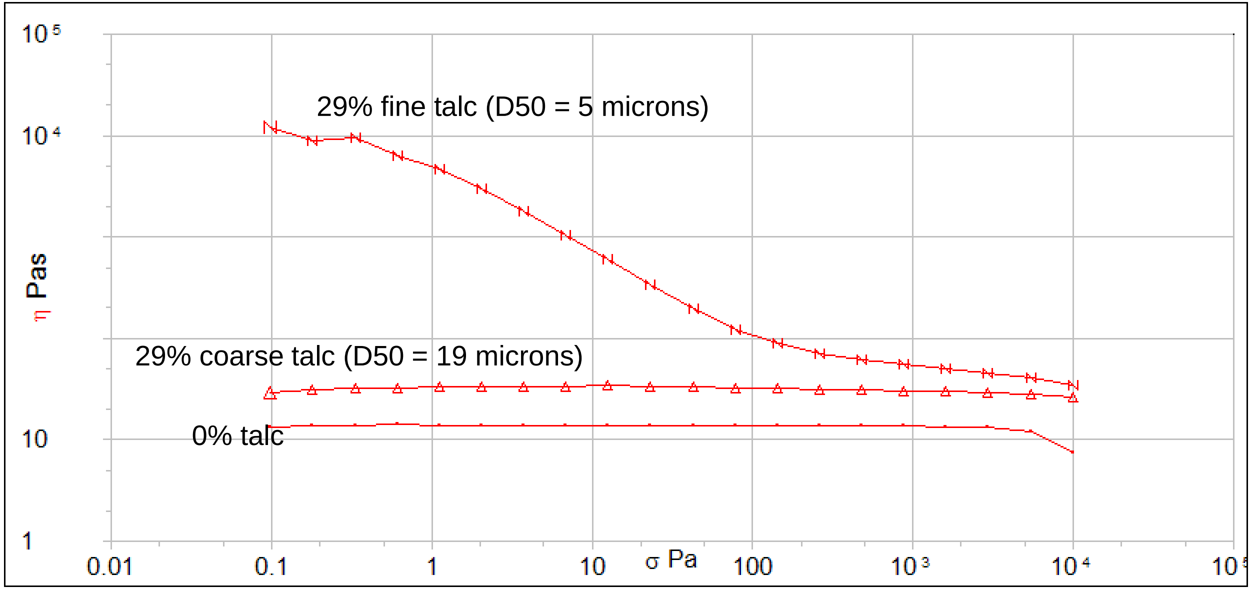


Effect of Mean Latex Particle Size in a PSA



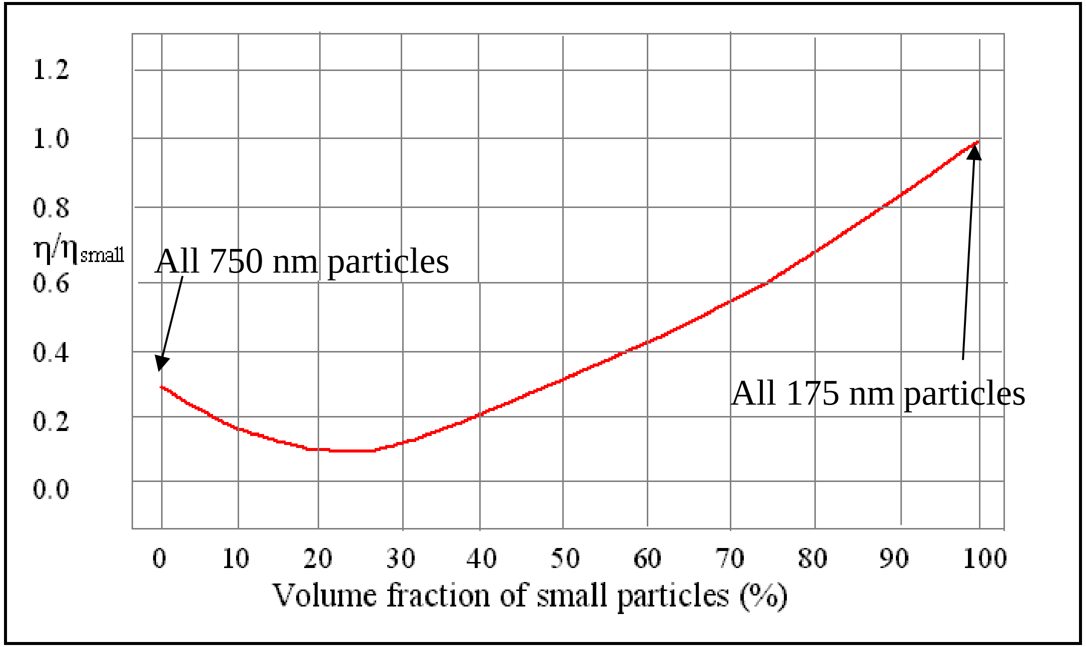
A smaller particle size usually increases the low shear viscosity, due to the colloidal repulsion. Viscosity is often independent of particle size at higher shear rates, as here hydrodynamic forces dominate

Effect of Mean Particle Size for Talc in Epoxy



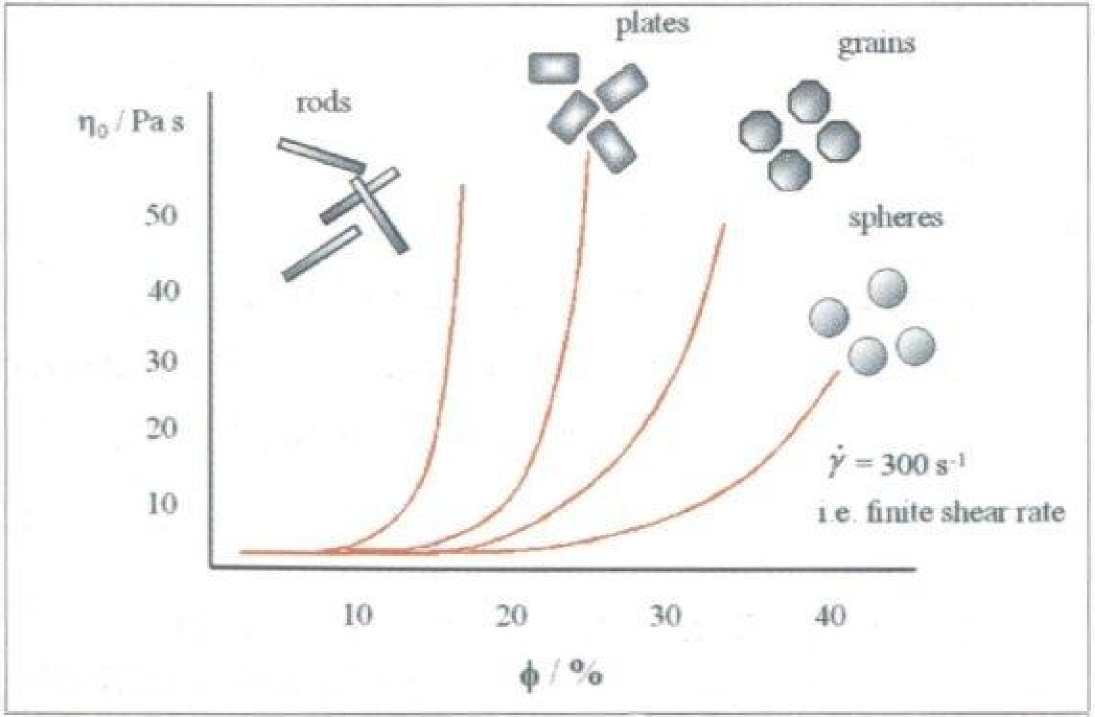
A smaller particle size usually increases the low shear viscosity, due to the colloidal repulsion. Viscosity is often independent of particle size at higher shear rates, as here hydrodynamic forces dominate

Effect of Particle Size Distribution



A wide particle size distribution usually gives a lower viscosity than narrow due to better particle packing. For this bimodal colloid mix of 175 nm in 750 nm, a small to large ratio of 1:4 gave lowest viscosity

Effect of Filler Shape



Storage Stability – Two Common Problems!

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Sedimentation – Particles falling to the bottom of a dispersion due to gravity

Syneresis - the contraction of a gel accompanied by the separating out of liquid.

Reviving An Old Separated Can Of Paint (54) Reviving An Old Separated Can Of Paint – YouTube Amelia Newcomb

Sedimentation Stability and Yield Stress

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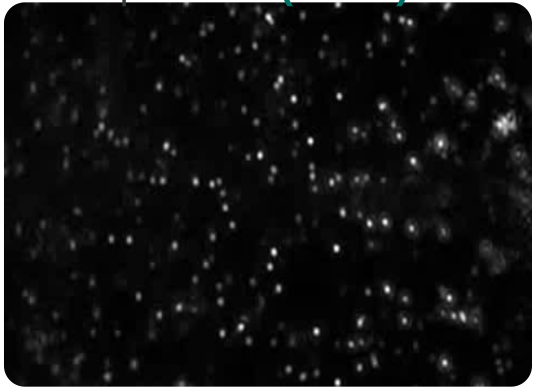
Effect Of Particle Size

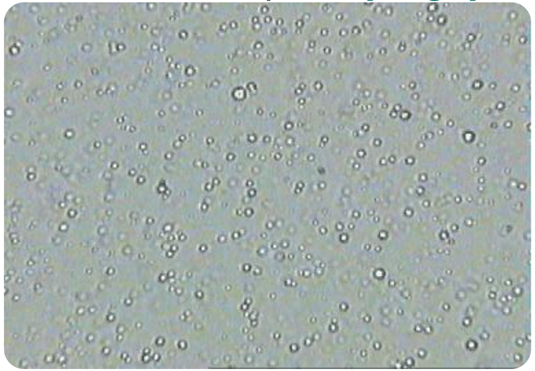
- For **small** particles (<~1um) colloidal effects on rheological properties can be significant:
- Large specific surface area so
  - more electrostatic attractive / repulsive colloidal forces
- Brownian motion is very fast

- For **larger** (>~1um) particles the surface charge effect on rheology is much less
- The affect is more related to the associated change in volume fraction

Nanoparticles **(small)**



Emulsion Droplets **(large)**



Stability: Which Method? ……….It Depends!!

- **Particle radius** (a) will have a large bearing on suspension stability
- For **sub micron** particles **Brownian motion** is usually significant and exceeds the effects of gravity
- For **larger particles** **gravity dominates** if there is a significant density difference (*Δρ*)

Gravitational Forces $a^4 \Delta\rho g$

$k_B T$ **Brownian Forces**

Usually, Only Particles Over 1 Micron in Diameter Will Settle

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Table 7.2 Comparison of Brownian movement displacement and gravitational settling displacement

Particle diameter (μm)	Displacement in 1.0 second (μm) in air at 70°F (1 atm) due to Brownian movement*	due to gravitational settling†	in water at 70°F due to Brownian movement*	due to gravitational settling†	in water at 70°F γ	$k = \frac{100\,\gamma}{1+\gamma}$ (%)
0.10	29.4	1.73	2.36	0.005	31.1	96.9
0.25	14.2	6.3	1.49	0.0346	3.15	75.9
0.50	8.92	19.9	1.052	0.1384	0.556	35.7
1.0	5.91	69.6	0.745	0.554	0.0983	5.0
2.5	3.58	400	0.334	13.84	0.00995	1.0
10.0	1.75	1550	0.236	55.4	0.00031	0.03

* Mean displacement given by equation (7.20).
† Distance settled by a sphere of density 2000 kg m^{-3}, including Cunningham's correction.
γ is defined in equation (7.23).

Shelf Life and Sedimentation Stability

- Particles larger than 1 µm will likely sediment

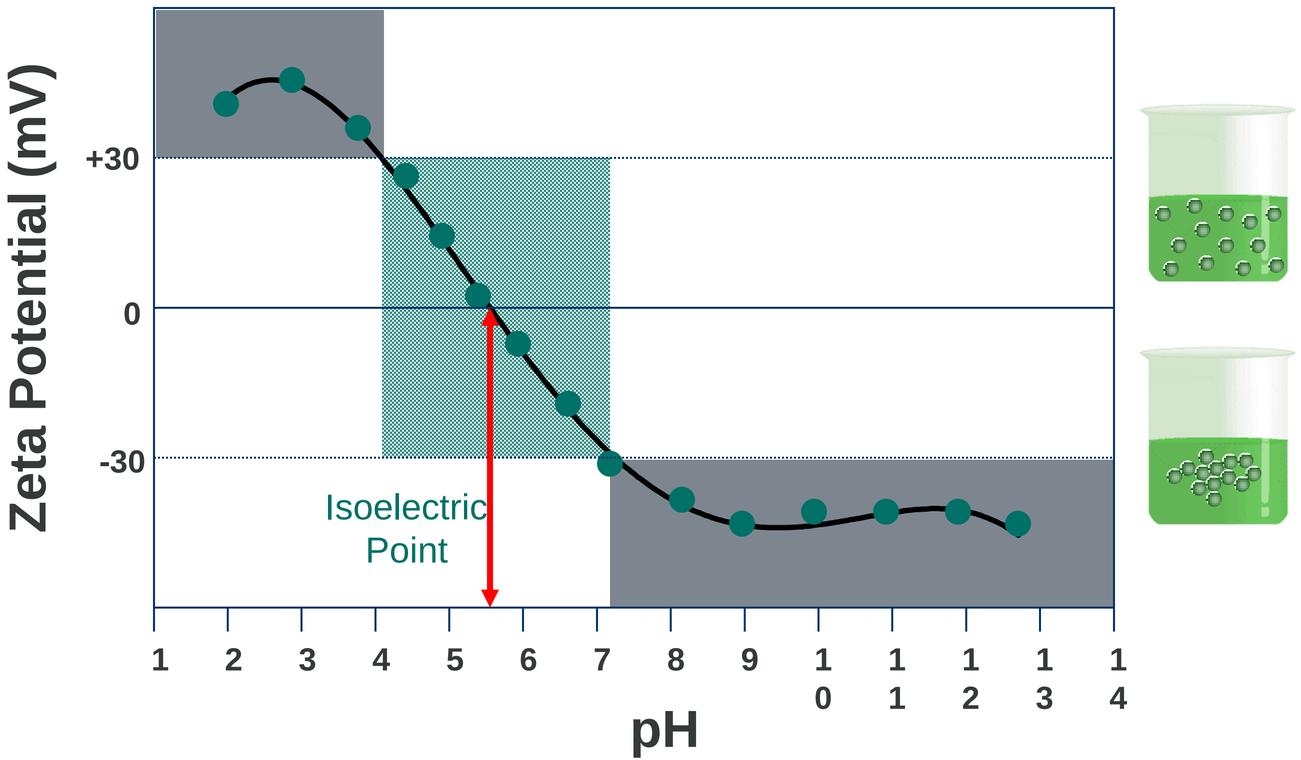
Unless:

- They are **density matched** with the suspending medium

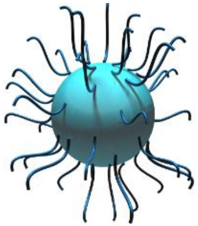
Or:

- There is some **“structure”** in the sample to prevent sedimentation

Less Charged Particles Flocculate Due to Van-der-Waals Forces



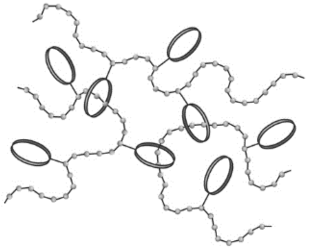
Shelf Life and Sedimentation Stability



- If the **primary** particle size is sub micron - prevent coagulation through **inter-particle repulsion**

- Or we can slow down sedimentation by **increasing viscosity** of continuous phase

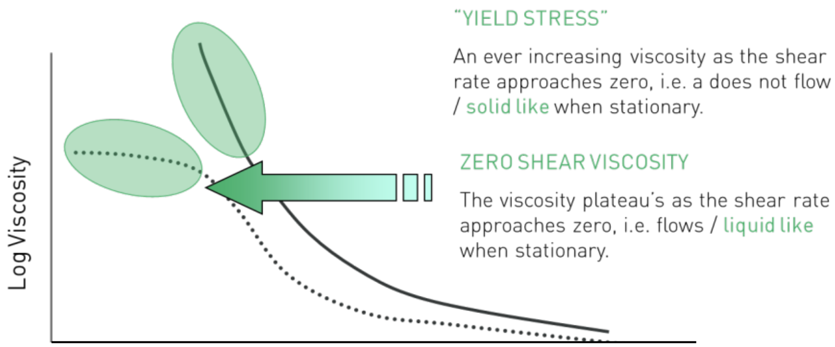
- Make it gel-like by creating a **network structure**



Effect of Viscosity (Dilute Systems)

- Stokes law can be used to predict **settling velocity** (*V*) of a dilute suspension within a continuous phase; viscosity (*η*)

$$V = \frac{2\Delta\rho g a^2}{9\eta}$$



- Velocity increases with **the square of particle size** making this the most critical parameter
- To slow down sedimentation rate:
  - Decrease particle size
  - Match density of dispersed and continuous phases
  - Increase low shear viscosity

Yield Stress : Predicting Sedimentation

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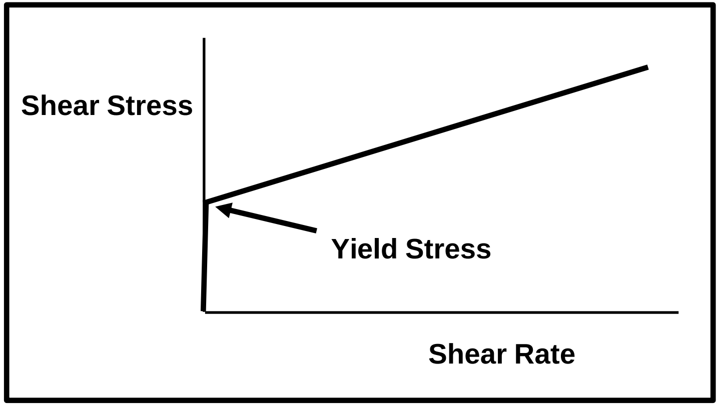
https://www.youtube.com/watch?v=r06S127HM40

"The shear stress where the sample just starts to flow."

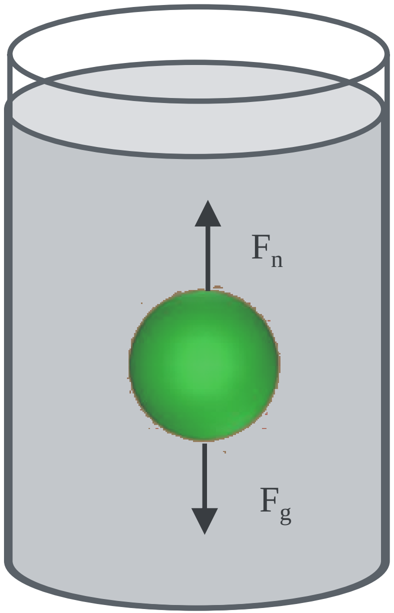


1. Determines whether a sample is likely to settle in-situ
2. Determines whether it will be difficult to start pumping or stirring.
3. Enhance customer perception of the mouth feel – thicker / creamier

What Yield Stress is Sufficient?

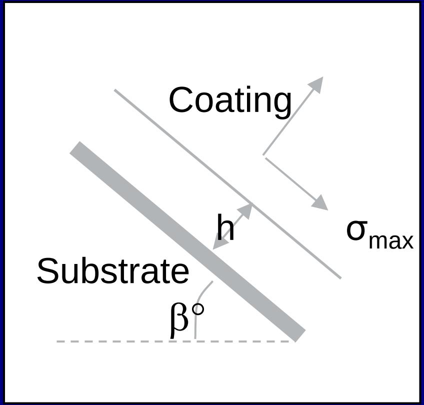
- For a particle to stay suspended, the yield stress must exceed the gravitational force acting on the particle
- The following equation can be used for most systems:

$$\sigma_s = \frac{(\rho_D - \rho_C)rg}{3}$$



- Calculation is made for the largest particle and it is also important to account for external stresses which can be much greater than particle stresses eg. transportation

Sagging due to the action of gravitational forces on a coating can be modelled as shown here.



The maximum shear stress is at the surface is:

$\sigma_{max} = \rho g h \text{ Sin } ß$

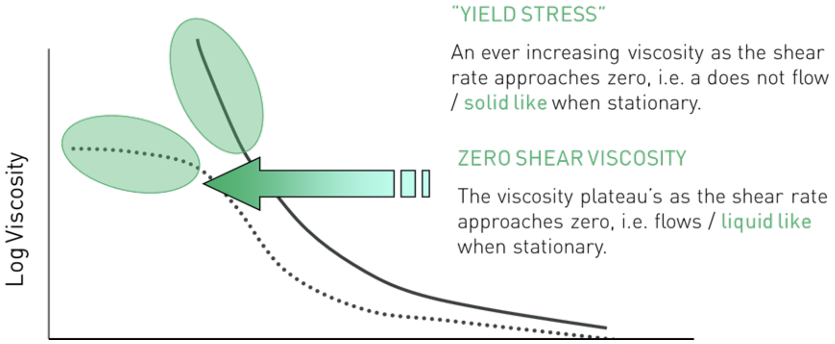
Therefore sagging will not occur for coatings with yield stresses greater than σ_{max}.

Syneresis

Syneresis is caused by the coating have too much gel structure, such that it contracts exuding the liquid from within it.

Optimal rheology for a gel stabilized network subject to sedimentation is therefore “just enough” structure.

Some Materials Just Need a "Vanishing" Yield Stress



- Alginates
- Methylcellulose
- Acacia gum
- Gellan gum
- Hydroxyethylcellulose
- Bentonite clay

- Laponite clay
- Tragacanth
- Xanthan gum
- Associative Polymers
- Surfactant Lamellar

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Important Properties Imparted By A Thixotropic Agent (Yield Stress)

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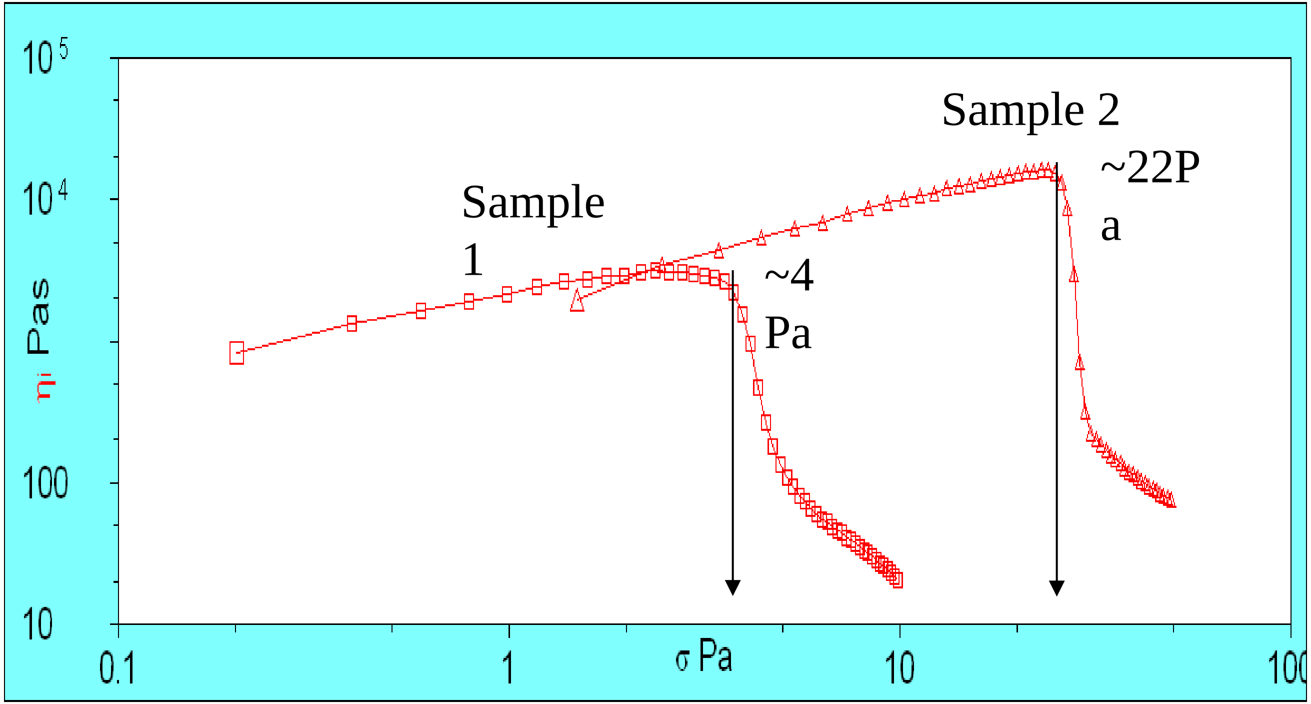
- Flow / Extrusion control
- Anti-settling (storage)
- Anti-sag
- Reinforcement of cured adhesive - cohesive properties such as tear strength
  - Generally the finer the size the greater the tendency towards higher tensile strength at break and tear strength of an elastomer, for example

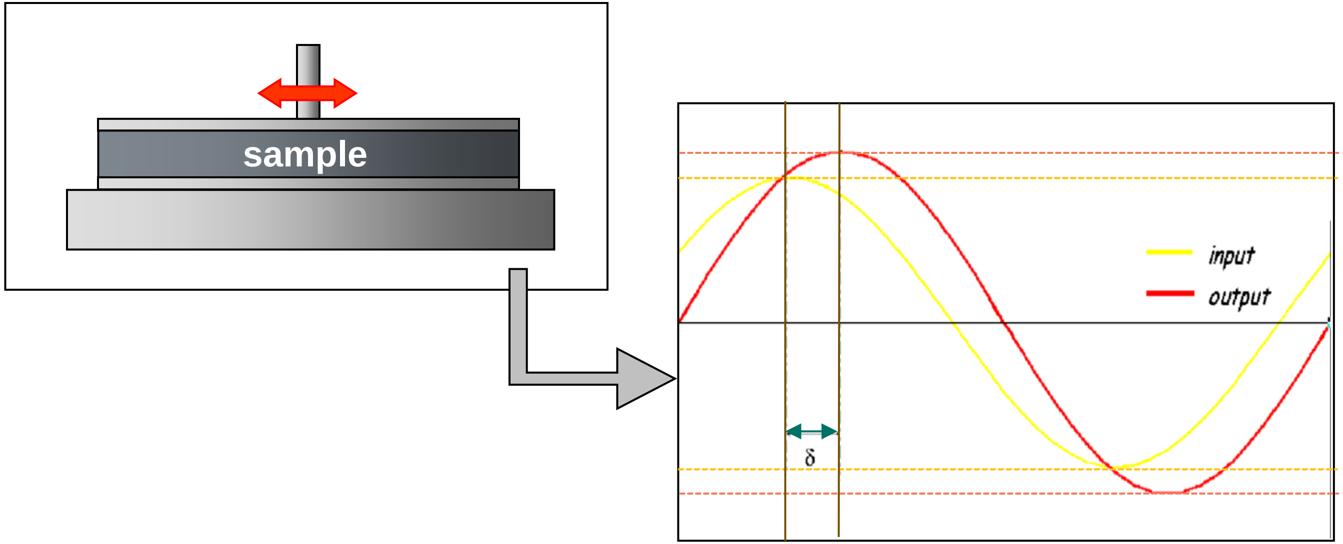
Yield Stress of Dispersions; Sample 1 and Sample 2



- If a sample is sheared significantly, it can break down some of the micro-structure, therefore we use tiny movements to measure the viscoelastic properties:

Oscillation - applies a small oscillating stress or strain

Small Oscillation Measurements



- The complex modulus is the stress amplitude / strain amplitude
- Rheometer applies shear strain sweep (γ) and measures the shear stress required (τ), or vice versa

Oscillation Amplitude Sweep Measurements

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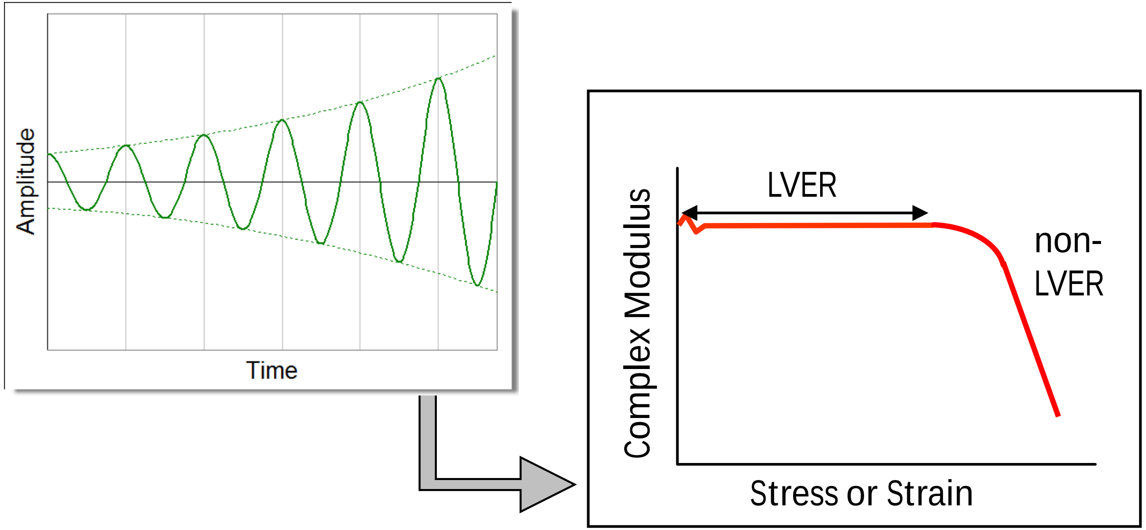
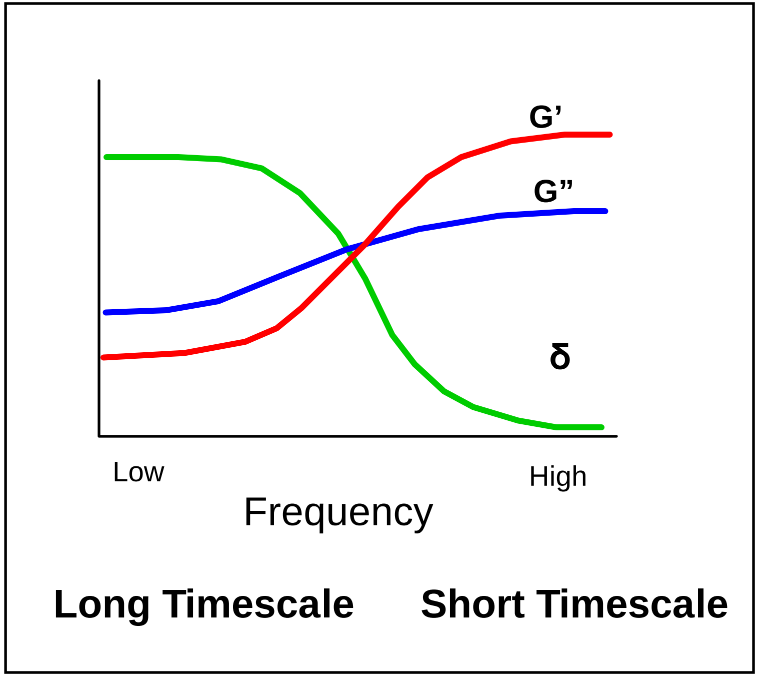


- Experiment – Apply an increasing oscillation amplitude strain
- Determine Linear Viscoelastic Region (LVER) - the length of the linear plateau, before the elastic structure in the bulk material starts to break down

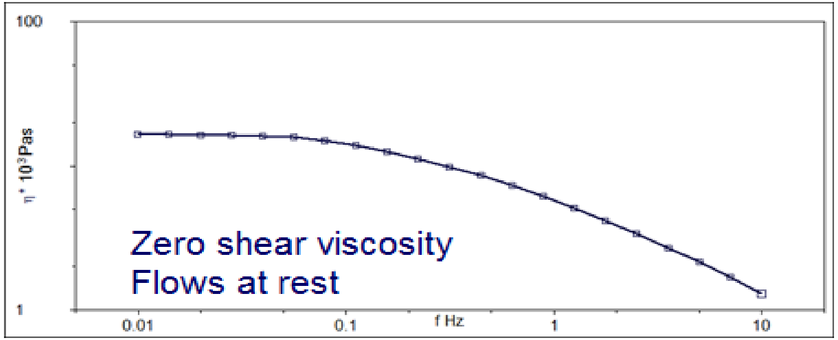
Frequency Sweep

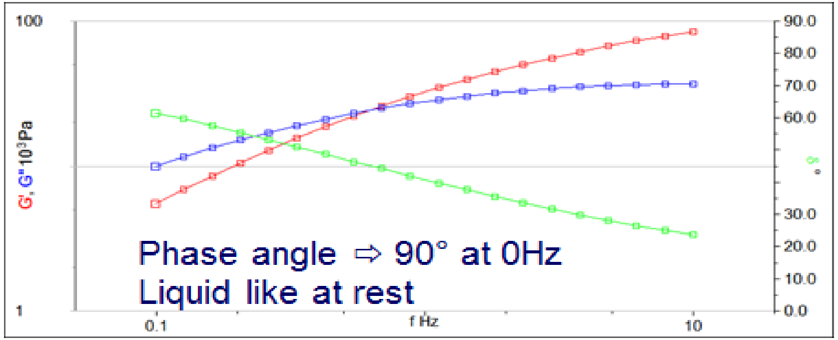


- Oscillate at a strain within the LVER and vary the frequency
- Gives a mechanical spectrum, cf. infra-red spectrum
- Unique fingerprint
- Shows relative process time behavior

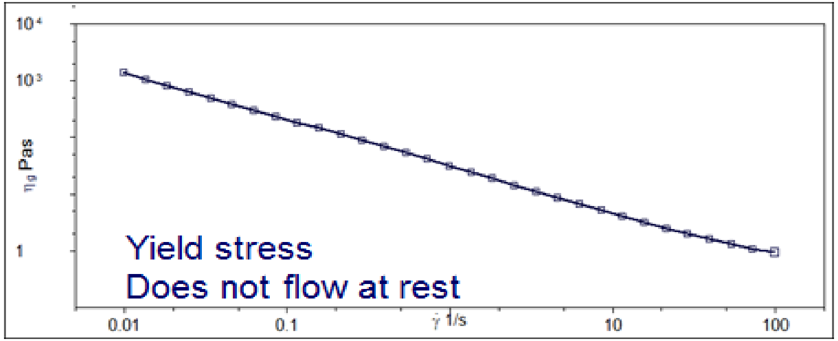
Example Rheology Results

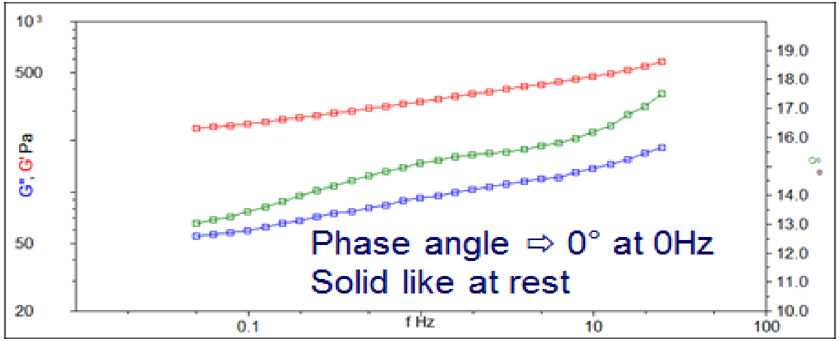
Play Putty = Viscoelastic Liquid





Hand Cream = Viscoelastic Solid





Elastic (G') and Viscous (G") Modulus: Dispersion/Emulsion Dependence

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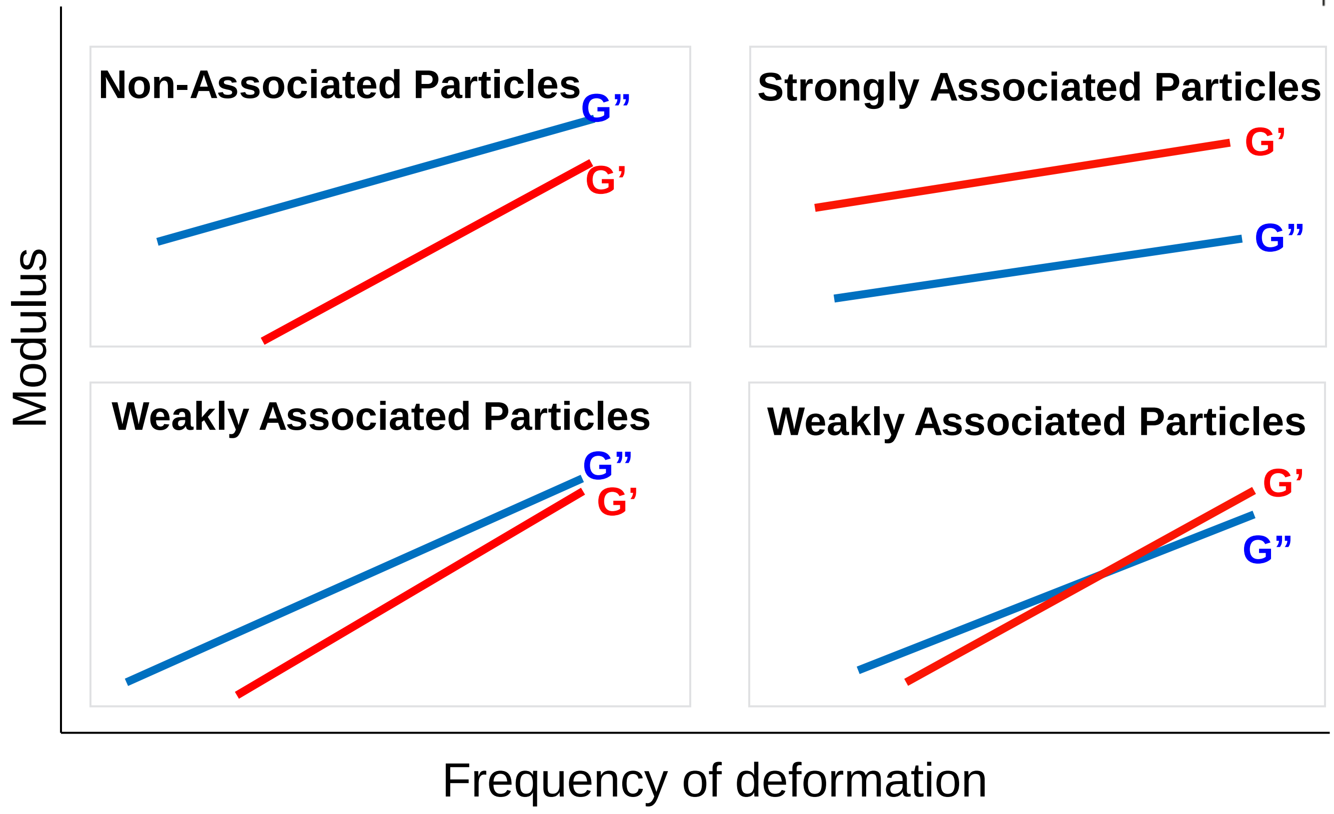
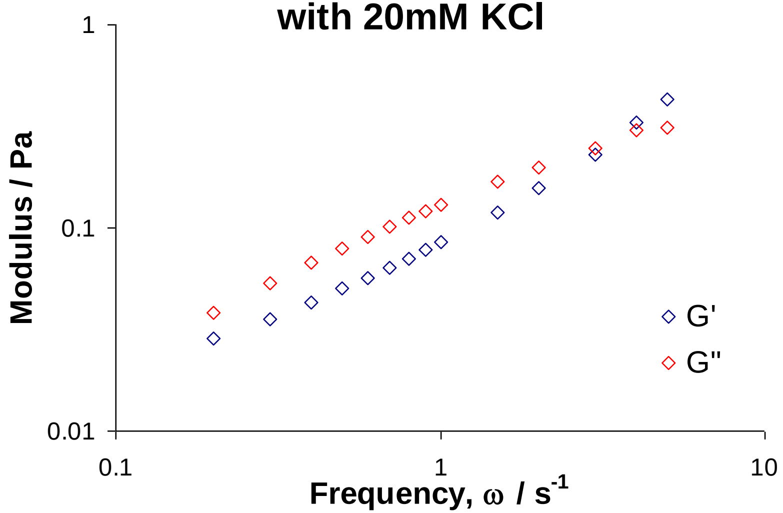
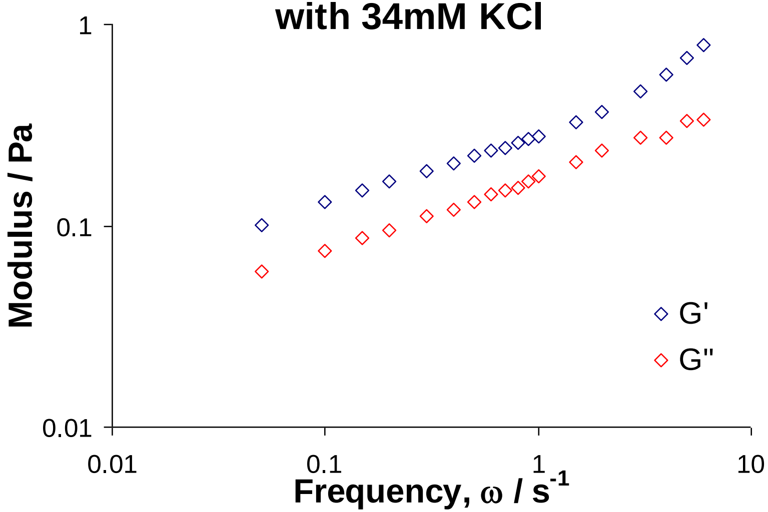


Oscillatory Rheometry of Weak Gels

Frequency sweep of 0.15w% Gellan with 20mM KCl



Frequency sweep of 0.1w% Gellan with 34mM KCl



$\tan\delta = G''/G'$

$\tan\delta > 1$ — **Viscous nature dominates**

$\tan\delta < 1$ — **Elastic nature dominates**

P Laxton and J C. Berg, 78th ACS Colloid and Surface Science Symposium 6/22/2004

http://www.nordicrheologysociety.org/

Sedimentation Behavior & Viscoelastic Character

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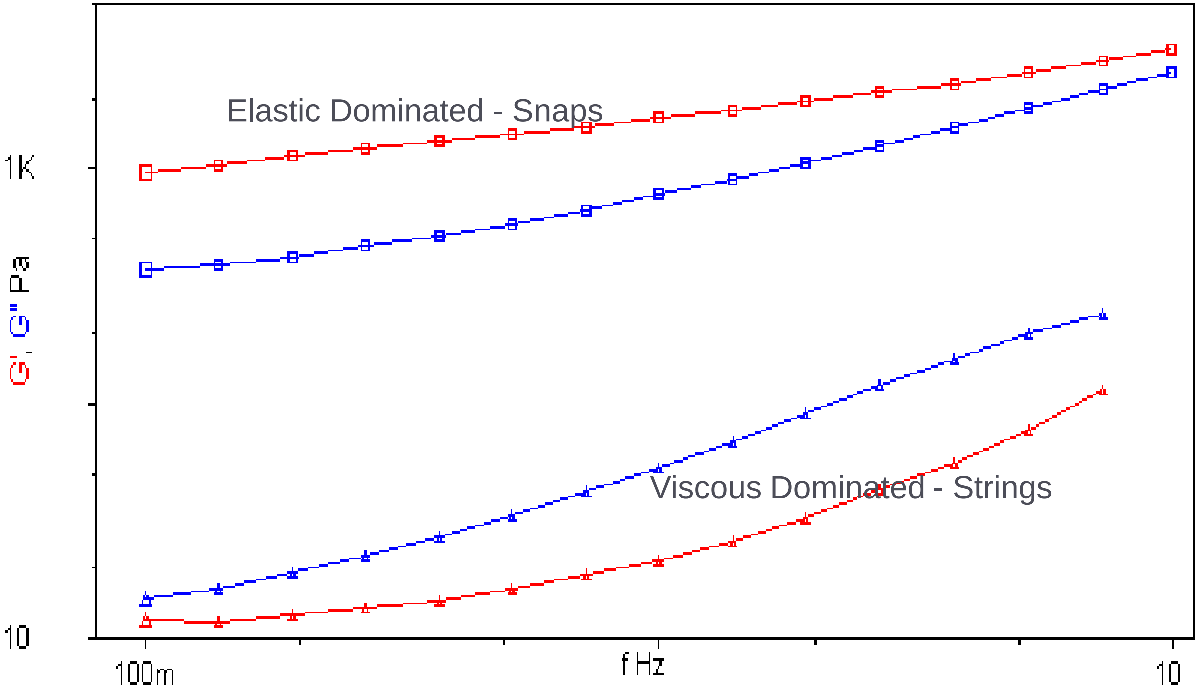
- Note stability required Yield stress of > 0.03 Pa and also tan d < 1

- Tests carried out with a:
  - Rotational Rheometer
  - Using a double gap Couette geometry
- Challenges:
  - Slip
    - overcome with roughened tools
  - Shear History Dependence
    - low shear viscosity, h_o
    - yield stress, t_y

Yield stress (Pa)	Tan δ	Result
0.004	2	Sedimented
0.009	1.25	Sedimented
0.024	1.04	Sedimented
0.026	1	Sedimented
0.03	1	Sedimented
0.034	0.71	Stable
0.063	0.91	Stable
0.092	0.85	Stable
0.109	0.74	Stable
0.111	0.58	Stable
0.212	0.4	Stable
0.257	0.51	Stable

P Laxton and J C. Berg, 78th ACS Colloid and Surface Science Symposium 6/22/2004

Using Oscillation Frequency Sweeps to Predict Tailback in dispensing



Case Study

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3 samples of a styrene-butyl acrylate latex with differing levels of tackifier resin added.

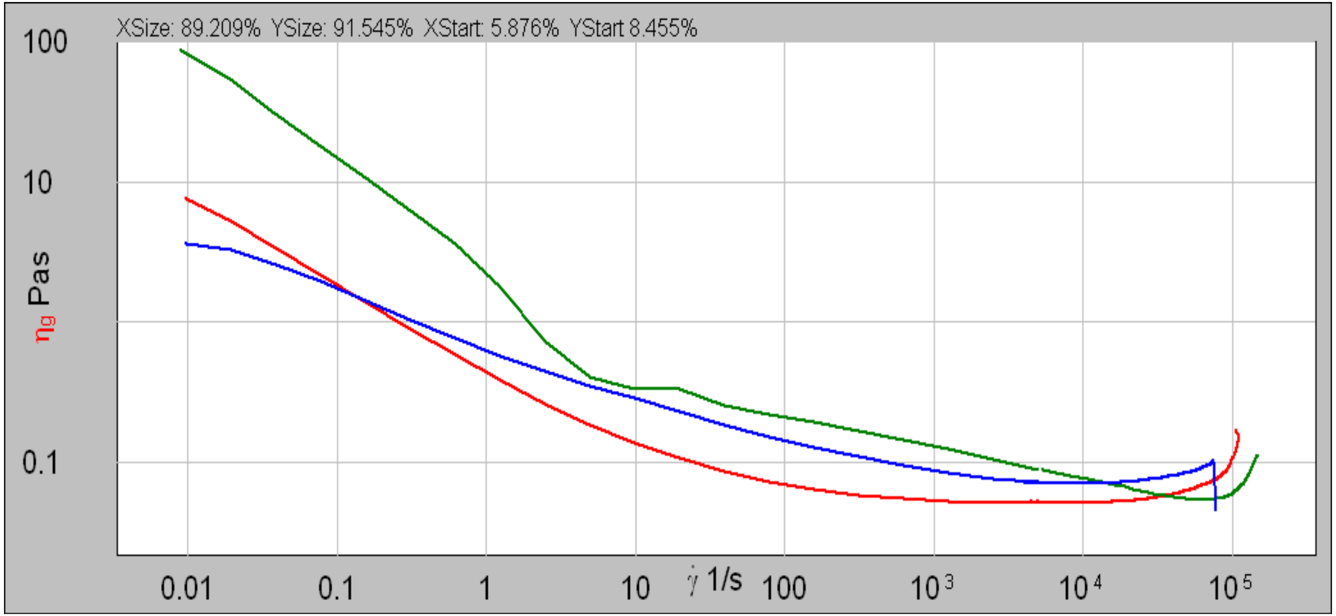
All have similar solids loading

Measured the Shear Viscosity up to the mechanical breakdown (aggregation)

Measured the Zeta Potential

Measured the Particle Size Distribution

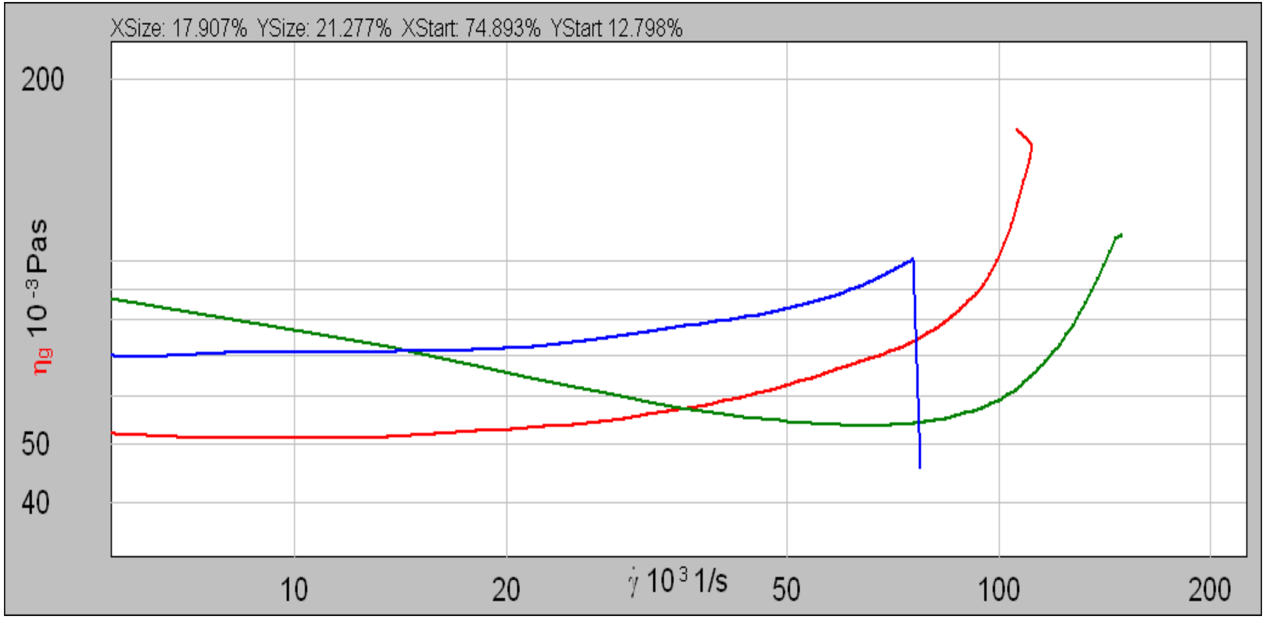
Case Study - Viscosity Flow Curves



Viscosity vs Shear Rate Profiles:

Sample A - Green, Sample B - Red, Sample C – Blue

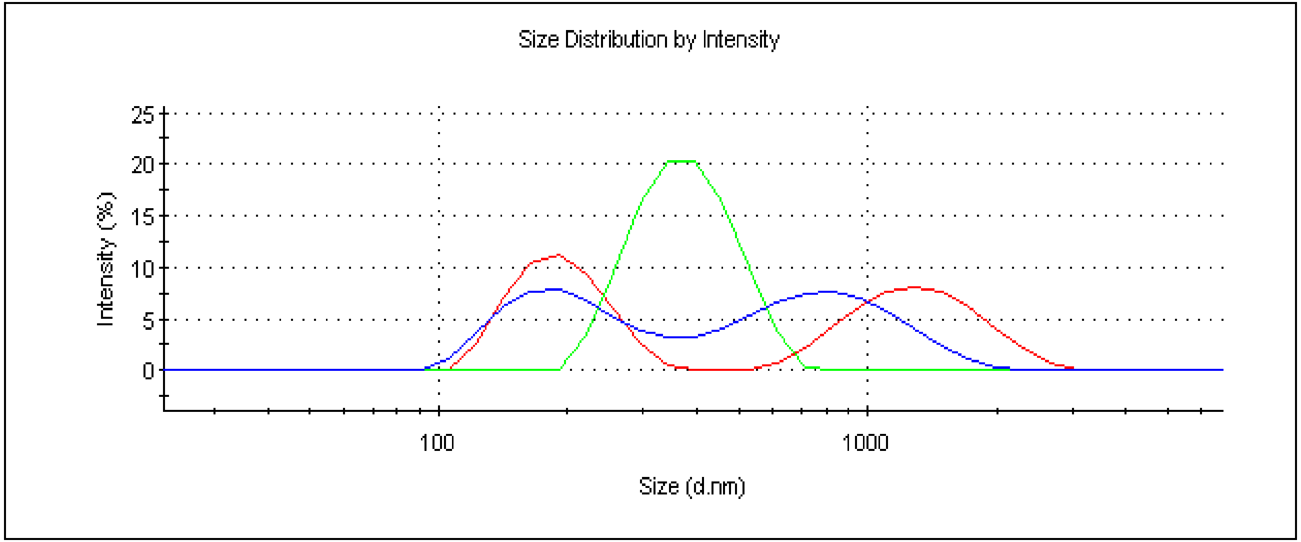
Case Study - Viscosity Flow Curves



Viscosity vs Shear Rate Profiles:

Sample A - Green, Sample B - Red, Sample C – Blue

Case Study - Particle Size Distributions



Light Intensity vs Size (nm):

Sample A - Green, Sample B - Red, Sample C – Blue

Case Study - Summary of Measured Data

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	Sample A	Sample B	Sample C
	Green	Red	Blue
Mean Zeta Potential	**-53.1**	**-51.2**	**-24.5**
Size peak 1	382.2	195	203.3
Size peak 2		1350	806.8
Solids Content (wt%)	59.7	64	58.4
Highest Shear Rate Achieved Before Breakdown	1.47E+05	1.12E+05	7.57E+04
	Thicker at low and moderate shear rates but lower viscosity at high shear	Thinner at most shears but thickened up (aggregated?) sooner	Aggregated at very low shears due to the low zeta potential

Case Study – Conclusions

The Zeta potential was the dominant factor in determining the maximum achievable shear rate

The Particle Size Distribution affected the viscosity most for the three samples where the wider the PSD the lower the viscosity

The Solids Content didn’t appear to have a dramatic effect in these mixtures as they are well below the maximum packing fraction

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