Section II: Intermediate Rheology Methods

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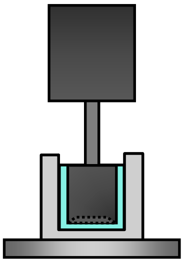
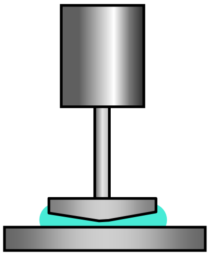
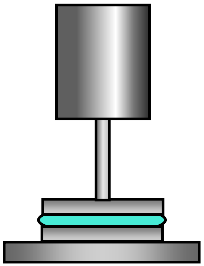
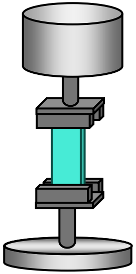
TA Instruments – Waters LLC

Agenda

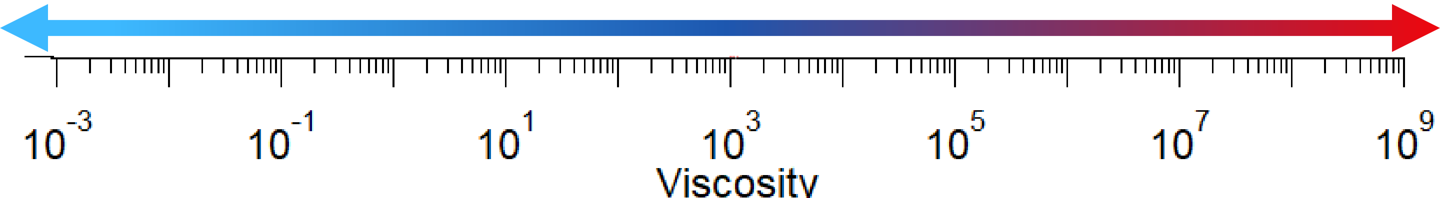
Agenda: Day 2

8:30 - 9:00 AM	Light Breakfast
9:00 - 9:20 AM	I Have a Viscometer... Why do I need a Rheometer?
9:20 - 10:15 AM	Rheological Theory and Introduction to HRx0 and Geometries
10:30 - 10:50 AM	Morning Break with Beverages and Snacks
10:50 - 12:00 PM	Rheology Applications Examples - Basic and Advanced
12:00 - 1:00 PM	Lunch
1:00 - 2:00 PM	DMA Theory and Introduction to DMA 850
2:00 - 3:00 PM	Basic and Advanced DMA Applications

Recall – Rheometer Geometries

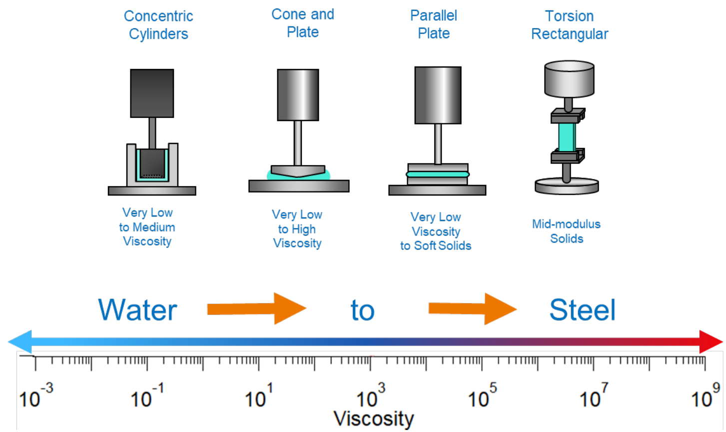
Concentric Cylinders	Cone and Plate	Parallel Plate	Torsion Rectangular
			
Very Low to Medium Viscosity	Very Low to High Viscosity	Very Low Viscosity to Soft Solids	Mid-modulus Solids

Water → to → Steel



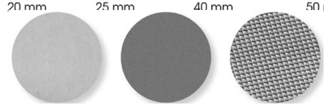
Assess material to test

- How to Select a geometry configuration for a material?
  - Estimate sample viscosity – concentric cylinder, plates, or torsion – plate size
  - Volume requirements- concentric cylinder requires 6-25mL of sample depending on rotor, plates require much less
  - Particle size, settling or mixing necessary – particles must be less than 1/10th of the gap size
  - Loading procedure for structured substances (Pre-shear)
  - Evaporation – seal sample edge, solvent trap, or RH accessory
  - Surface slip and edge fracture – geometry surface: smooth sandblasted, crosshatched



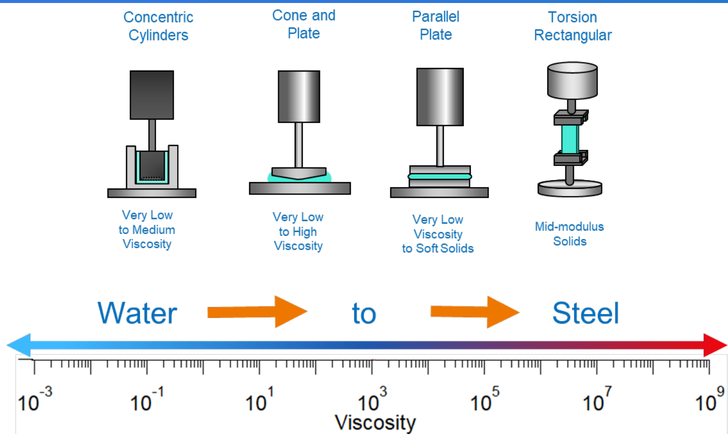
Concentric Cylinders (or Cups) and Rotors (or Bobs)

Cones and Plates



Smooth, Sandblasted, and Cross hatched

Organization of talk

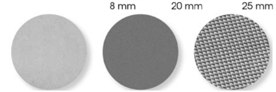


- We will cover applications from low to high viscosity materials
- Geometry and configuration considerations will be highlighted

1. Low Viscosity Solutions, emulsions, suspensions, weak structured fluids →
2. Strong Structured fluids, gels, adhesives →
3. Polymer melts, asphalt, thermosets →
4. Solids

Concentric Cylinders (or Cups) and Rotors (or Bobs)

Cones and Plates



Smooth, Sandblasted, and Cross hatched

Classes of Fluids

- Newtonian – Viscosity is independent of shear rate

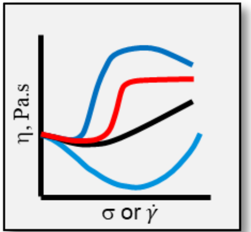
- Non-Newtonian – Viscosity is dependent on shear rate
  - Neat Fluid
  - Polymer melt
  - Structured Fluid
    - Yield stress
    - Thixotropy
    - Viscoelasticity

- <u>Three categories of Structured Fluids</u>
  - <u>Suspension</u> - Solid particles in a fluid
  - <u>Emulsion</u> - Fluid in a fluid
  - <u>Foam</u> - Gas in a fluid (or solid)

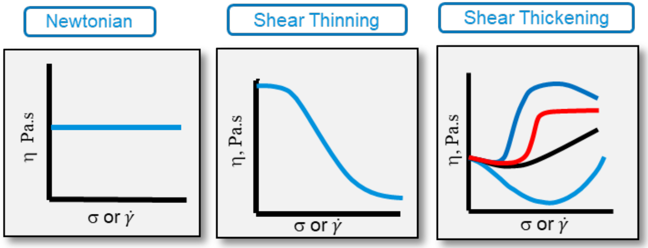
Newtonian

Shear Thinning

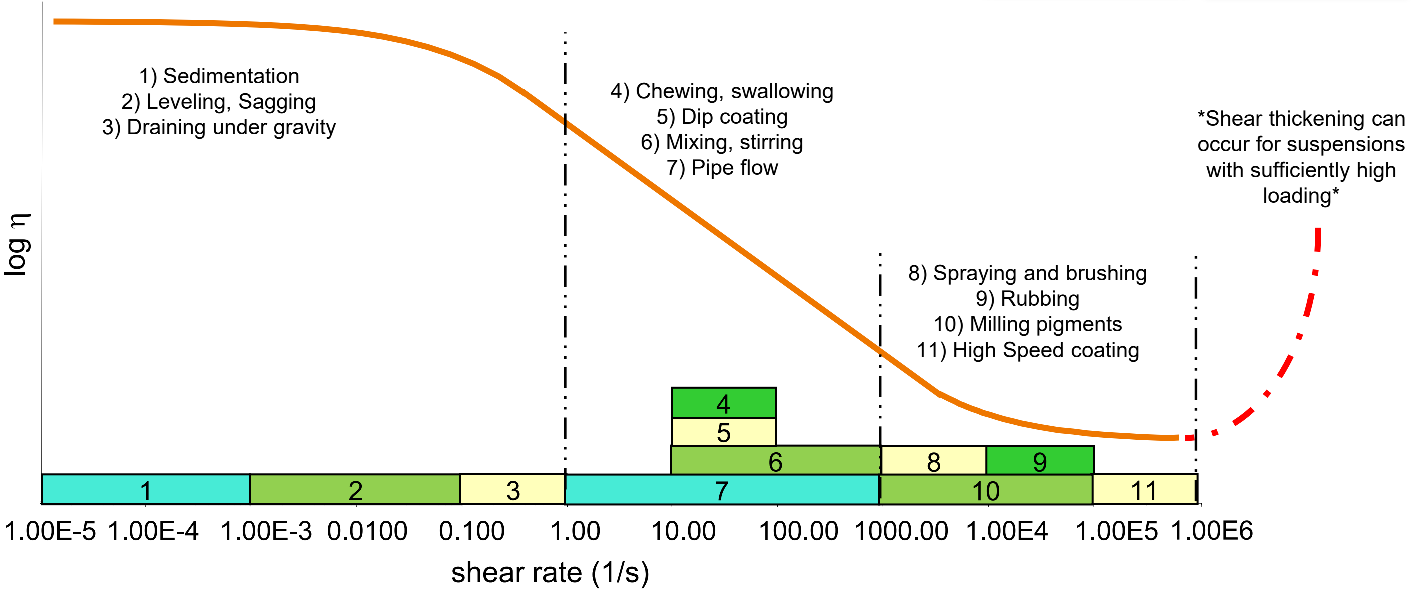
Shear Thickening



Properties of Fluids



- What shear rate?



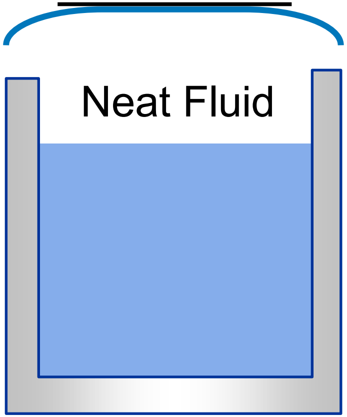
Rheology Applications

Neat Fluids

Classes of Fluids

In the next several examples, I will demonstrate common neat fluids

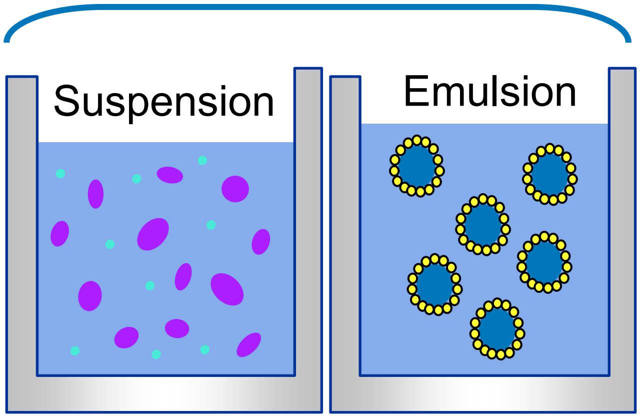
Unstructured



Examples are:

- Water
- Oil
- Honey

Structured



- Three categories of Structured Fluids
  - Suspension - Solid particles in a fluid
  - Emulsion - Fluid in a fluid
  - Foam - Gas in a fluid (or solid)

Examples are:

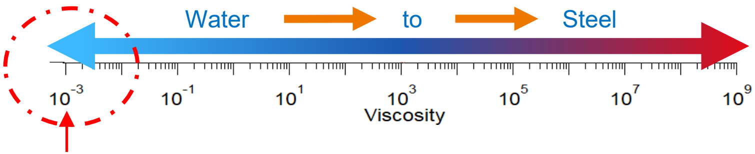
- Paints
- Coatings
- Inks
- Adhesives
- Personal Care Products
- Cosmetics
- Foods

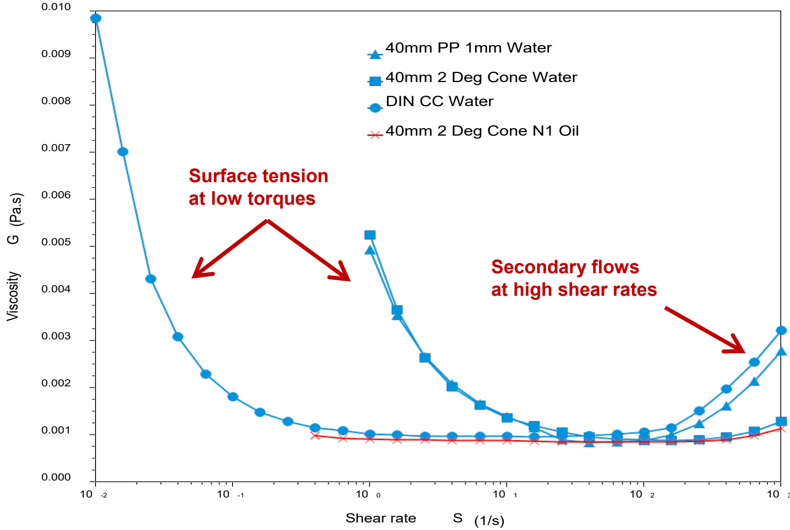
Low Viscosity
Solutions, emulsions, suspensions, weak structured fluids

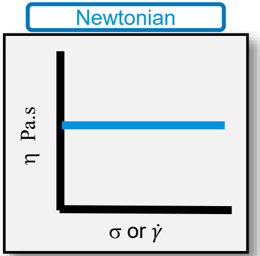
1

Common Neat Fluid - Water

Flow Sweep Experiment

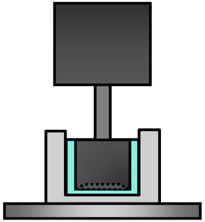






Right tool for the job:

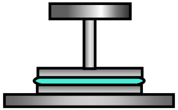
Concentric Cylinders



Very Low to Medium Viscosity

Runner up:

40-60mm parallel plates



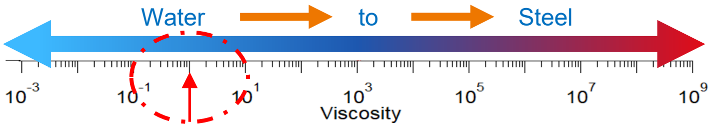
- Water is possibly the most well-known Newtonian fluid
- Viscosity is 1 mPa*s at 20°C
- <u>This is additionally observed for water-based formulations</u>
- For a more complete flow curve, a concentric cylinder geometry is required
- For plates - Use a large diameter geometry with a smaller gap

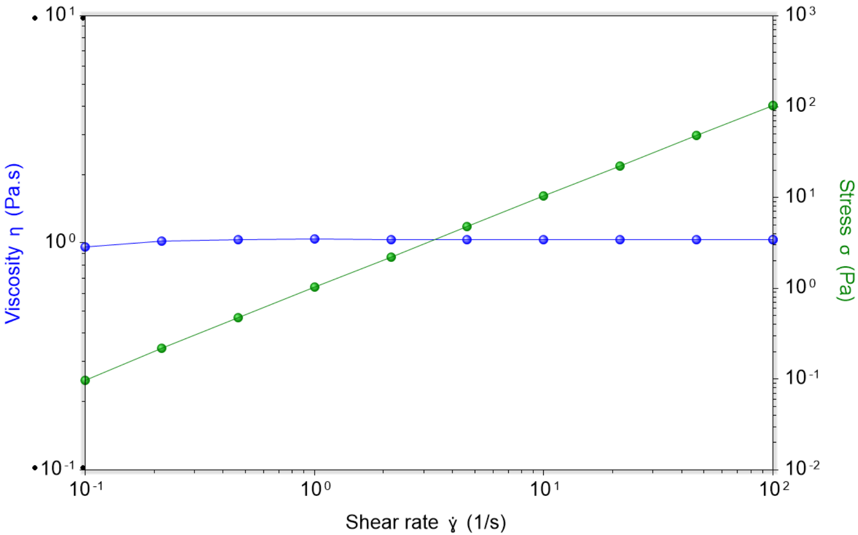
Low Viscosity
Solutions, emulsions, suspensions, weak structured fluids

1

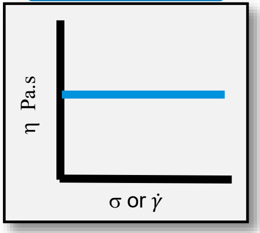
Common Neat Fluid 2 – Olive Oil

Flow Sweep Experiment



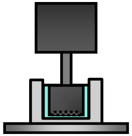


Newtonian



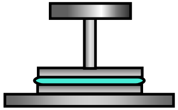
Right tools for the job:

Concentric Cylinders



OR

40-60mm parallel plates



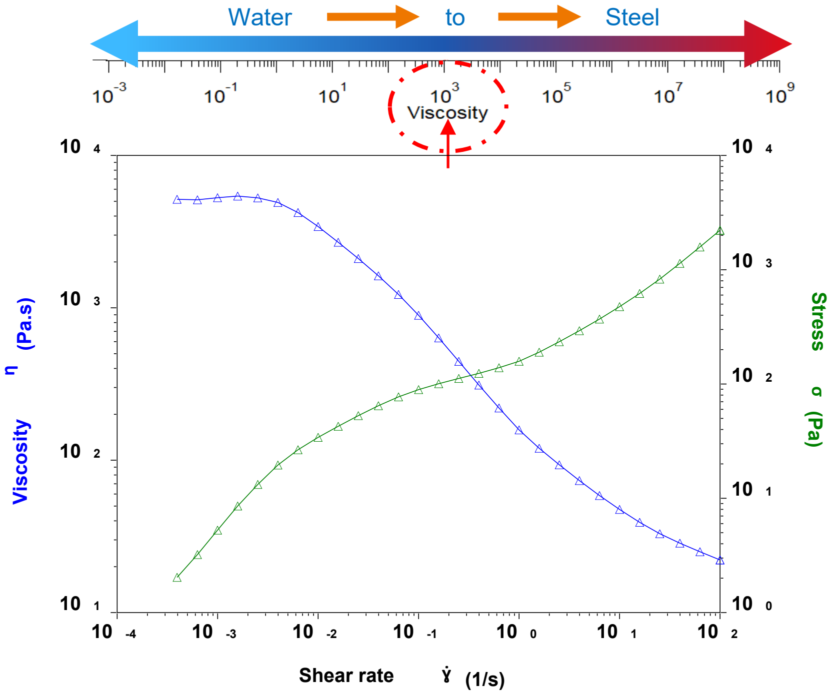
- Viscosity is 1 Pa*s at 20°C
- Oil based fluids typically don't have the same surface tension effects at with water
- Geometry selection will come down to sample volume

Low Viscosity
Solutions, emulsions, suspensions, weak structured fluids

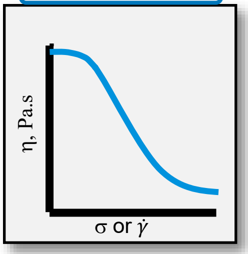
1

Common Neat Fluid 3 – Honey

Flow Sweep Experiment

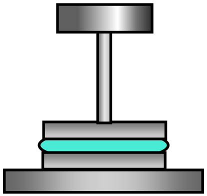


Shear Thinning



Right tool for the job:

20-60mm parallel plates



- Viscosity is approximately 5000 Pa*s at 25°C
- Non-Newtonian Neat Fluid
- Honey is quite viscous and sticky, making it more suited to a plate geometry rather than a concentric cylinder configuration

Rheology Applications

Structured Fluids

Classes of Fluids

Low Viscosity Solutions, emulsions, suspensions, weak structured fluids → Strong Structured fluids, gels, adhesives

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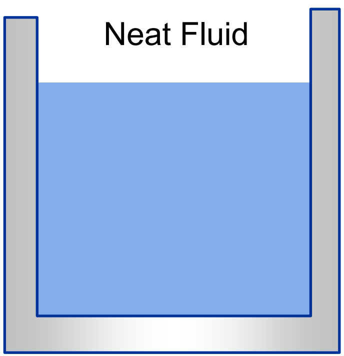
Unstructured

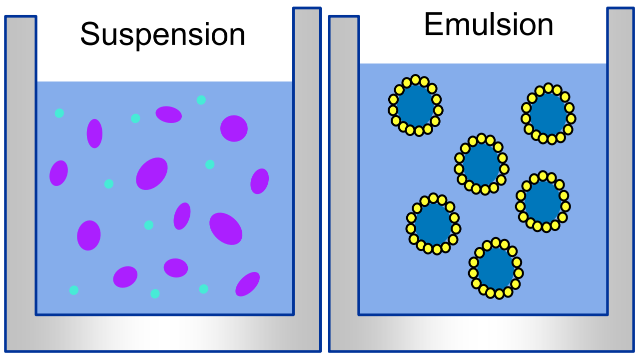


Examples are:

- Water
- Oil
- Honey

We will now turn our attention to structured fluids

Structured



- Three categories of Structured Fluids
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  - Emulsion - Fluid in a fluid
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Examples are:

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- Coatings
- Inks
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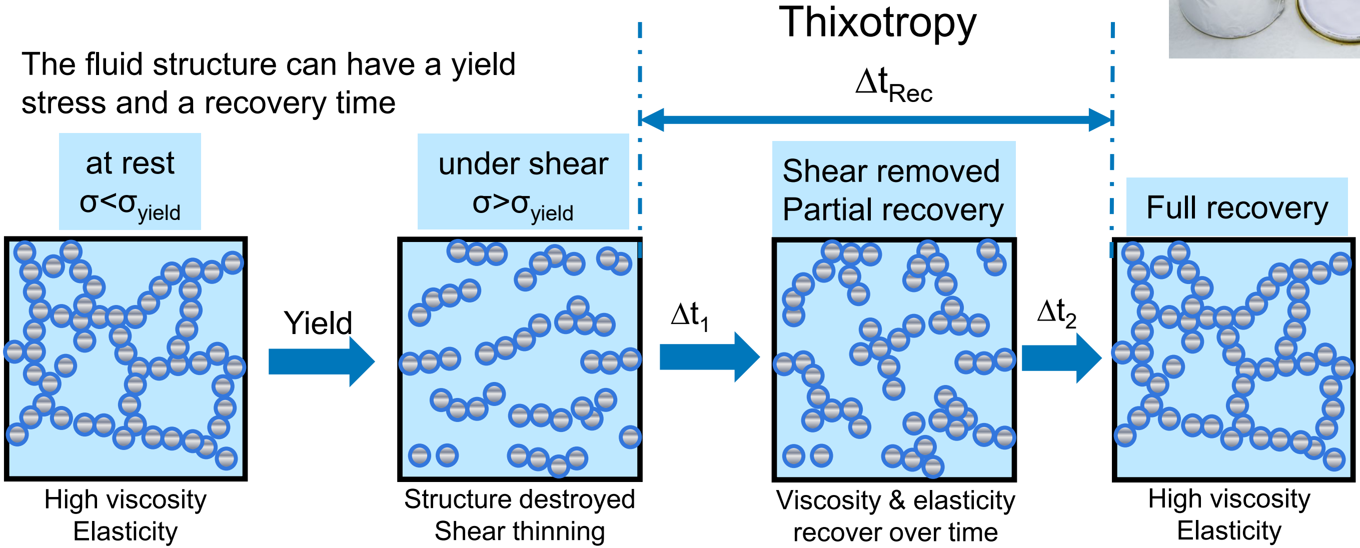
- Personal Care Products
- Cosmetics
- Foods

Properties of Structured Fluids

- Structured fluid properties
  - **Non-Newtonian**
  - **Yield stress**
  - **Thixotropic**
  - **Viscoelasticity**

- The fluid structure can have a yield stress and a recovery time

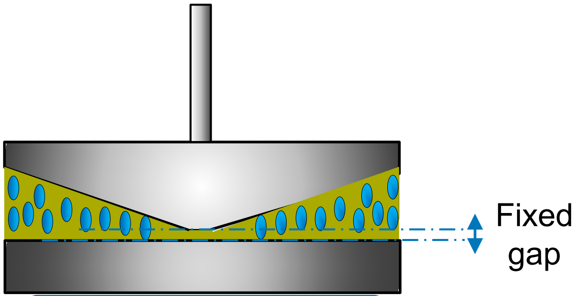


Properties of Structured Fluids

- Considerations for structured fluids
  - **Particle Sizes**
  - Wall Slip
  - Viscosity

- Particle sizes must be less than 1/10th of the gap size
- Parallel Plates are best suited, since the gap can be varied

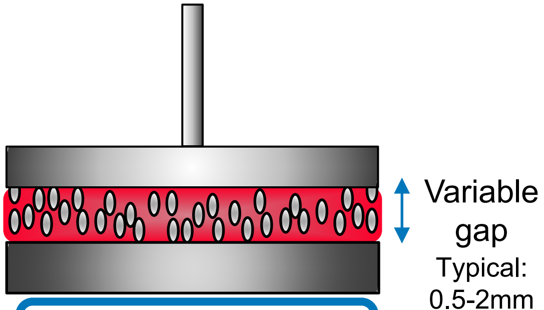
Cone and Plate



Truncation Height = Gap

Cone Angle (°)	Gap (micron)
0.5	18
1	28
2	52
4	104

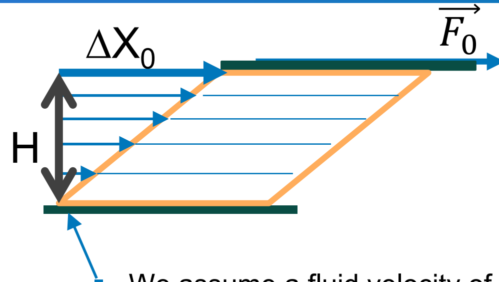
Parallel Plates



Gap can be adjusted
Common gap at 0.5-2mm

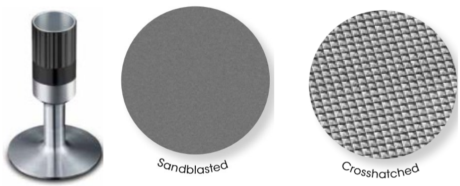
Properties of Structured Fluids

- Considerations for structured fluids
  - Particle Sizes
  - **Wall Slip**
  - Viscosity



- We assume a fluid velocity of zero at the wall
- Slip is the occurrence of non-zero wall velocity

Parallel Plates:



If using parallel plates:
- Use sandblasted or crosshatched plates
- Increase plate gap

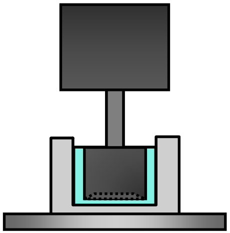
Concentric Cylinder:

If using concentric cylinder:
- Use sandblasted cup and rotor
- Use grooved cup with vane or helical rotor

Properties of Structured Fluids

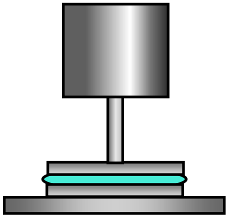
- Considerations for structured fluids
  - Particle Sizes
  - Wall Slip
  - **Viscosity**

Concentric Cylinders



Very Low to Medium Viscosity

Parallel Plate



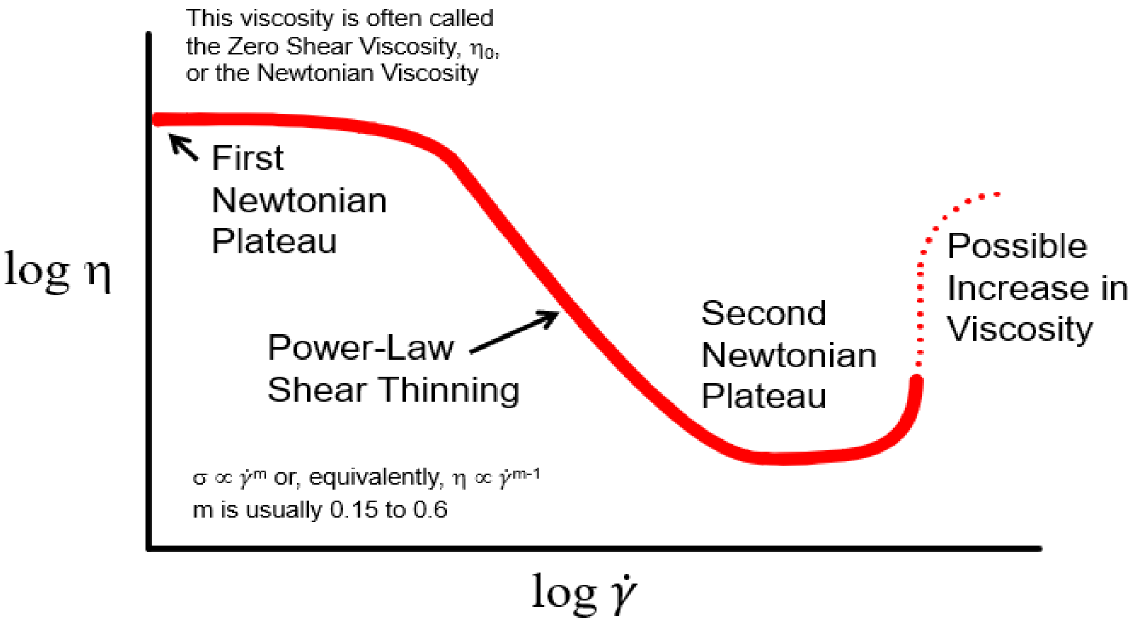
Very Low Viscosity to Soft Solids

- Sample can readily flow:
  - Shampoo
  - Eye drops
  - Infant forumla

- Wide range of samples:
  - Toothpaste
  - Ketchup
  - Paint

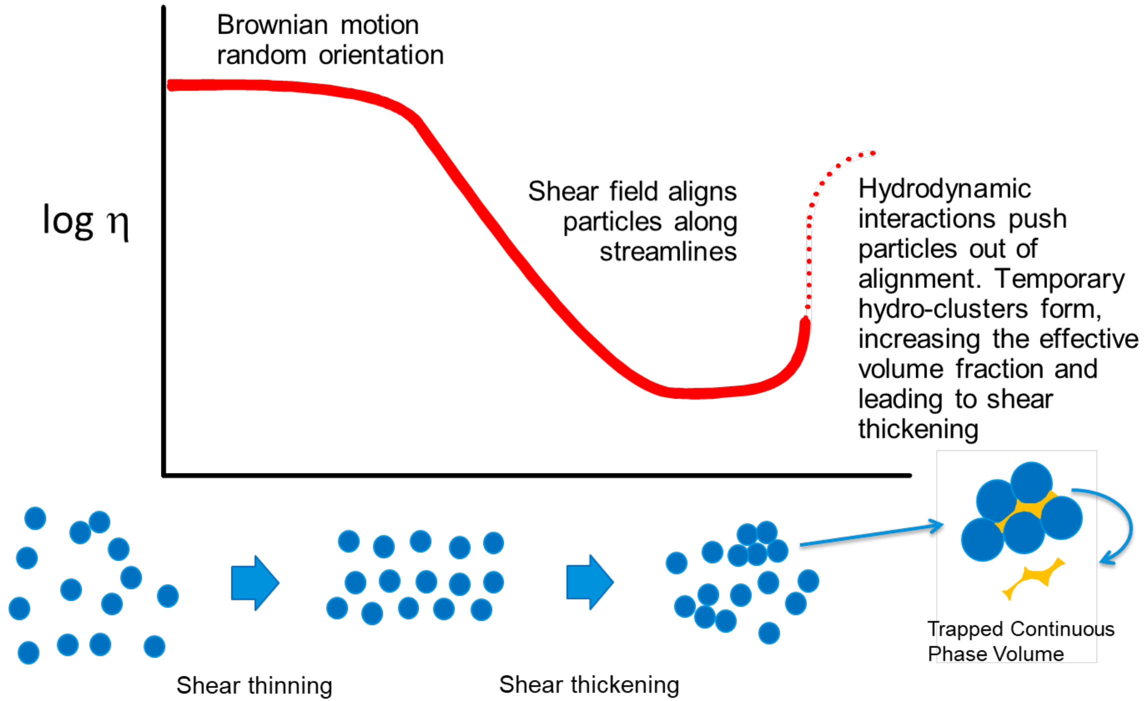
***Additionally noting surface tension effects for parallel plates

General Viscosity Curve for Suspensions



Reference: Barnes, H.A., Hutton, J.F., and Walters, K., An Introduction to Rheology, Elsevier Science B.V., 1989. ISBN 0-444-87469-0

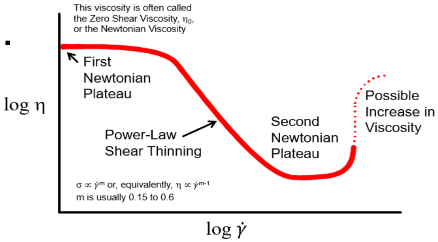
General Viscosity Curve for Suspensions



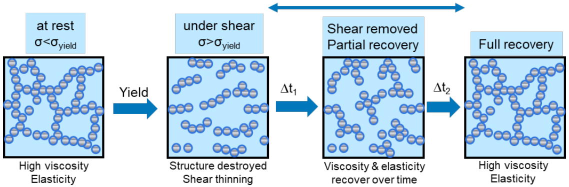
Characterization of Structured Fluids

- Overall, we want to characterize several relevant properties of structured fluids:
  I. Flow Curve (Newtonian or Non-Newtonian)
  II. Yield Stress
  III. Thixotropy
  IV. Viscoelasticity (complex mechanical properties)

I.



II. & III.



IV.

Properties of Structured Fluids

- Overall, we want to characterize several relevant properties of structured fluids:
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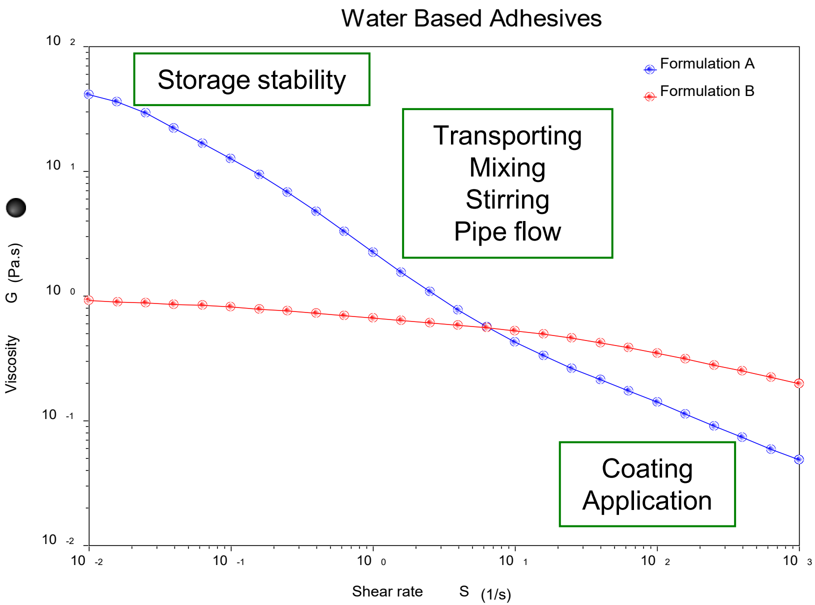
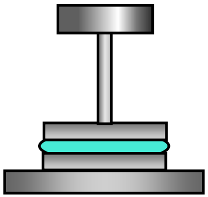


Right tool for the job:

20-60mm parallel plates



Properties of Structured Fluids

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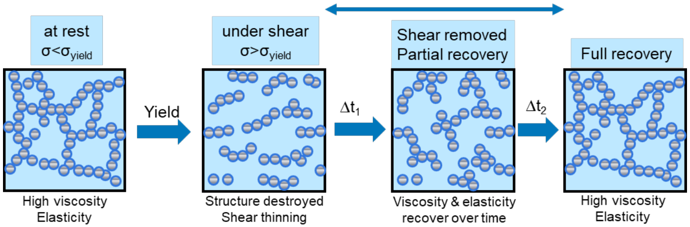

- Common methods
  - Stress ramp → – Ramp between initial and final stress within time interval
  - Stress sweep – Rotational stress is stepped in increments
  - Shear rate ramp – Ramp between initial and final stress within time interval
  - Dynamic stress/strain sweep – Oscillate at strain within LVR, then outside the LVR, and then back inside LVR

Note:
Yield behavior is a time dependent characteristic. Measured yield stress values will vary depending on experimental parameters

Properties of Structured Fluids

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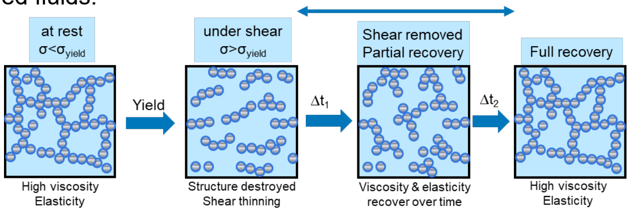
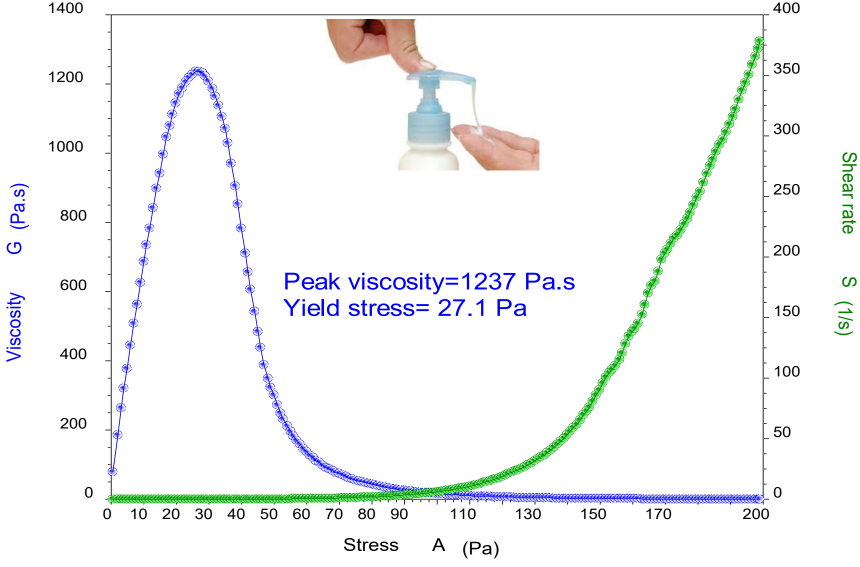
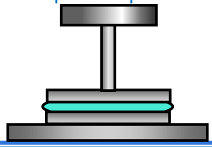


- Common methods
  - **Stress ramp #1**
  - Stress sweep
  - Shear rate ramp
  - Dynamic stress/strain sweep



- Stress ramp from 0 to 200 Pa in 60 seconds
- Yield is determined at the point where viscosity shows a peak

Right tool for the job:
20-60mm sandblasted parallel plates



Properties of Structured Fluids

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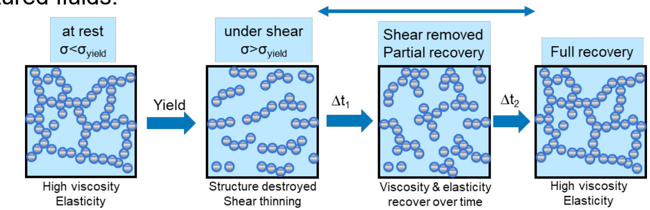
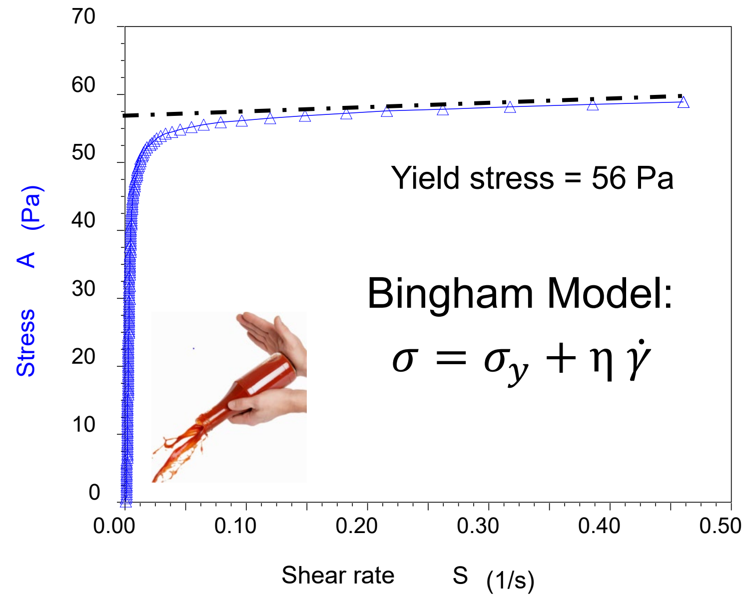
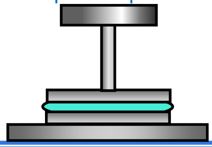


- Common methods
  - **Stress ramp #2**
  - Stress sweep
  - Shear rate ramp
  - Dynamic stress/strain sweep

*Bingham – Yield stress of a Newtonian fluid



Right tool for the job:
20-60mm sandblasted parallel plates



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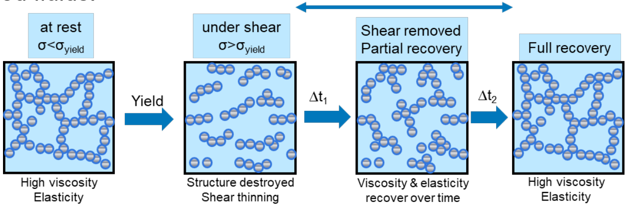
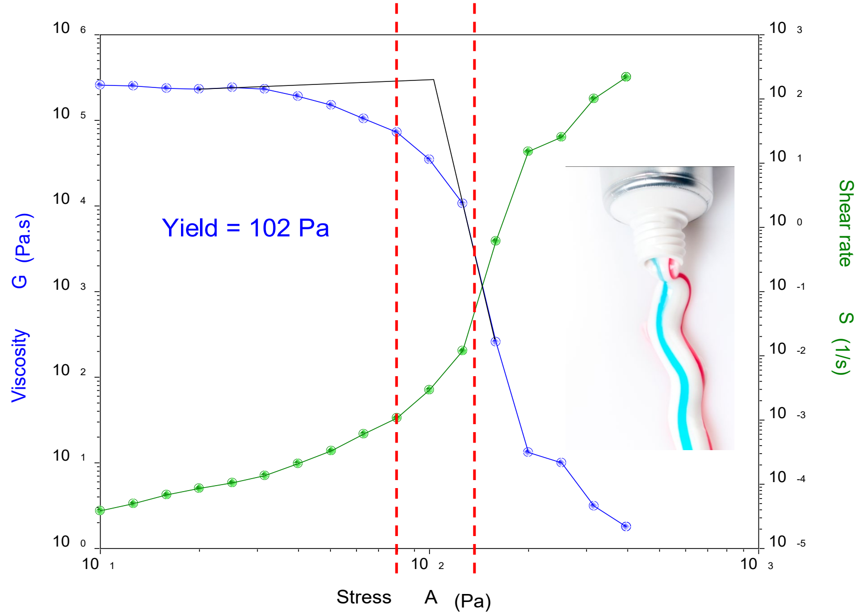
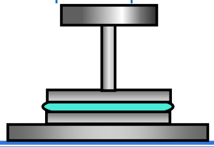


- Common methods
  - Stress ramp
  - **Stress sweep #1**
  - Shear rate ramp
  - Dynamic stress/strain sweep

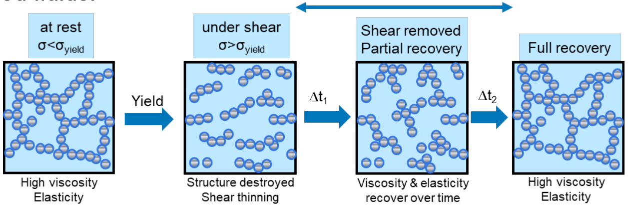


Right tool for the job:
20-60mm crosshatched parallel plates



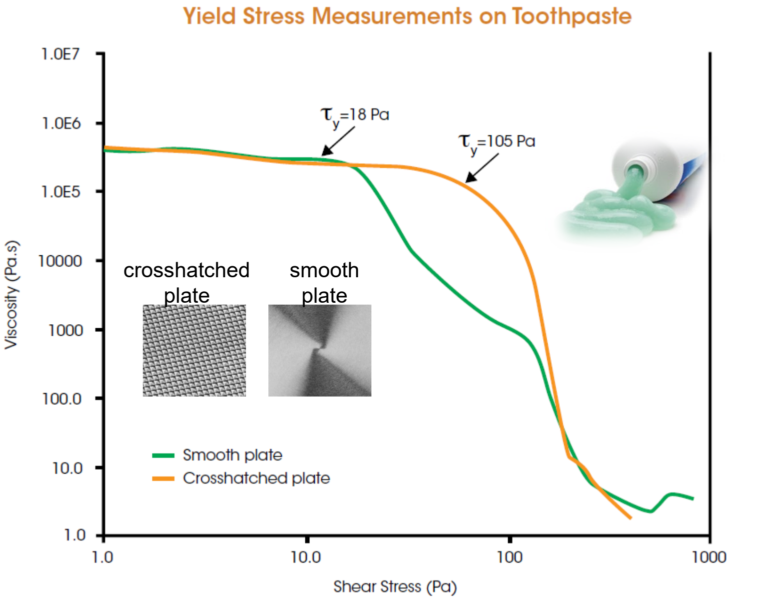
Properties of Structured Fluids

- Overall, we want to characterize several relevant properties of structured fluids:
  - I. Flow Curve (Newtonian or Non-Newtonian)
  - **II. Yield Stress**
  - III. Thixotropy
  - IV. Viscoelasticity (complex mechanical properties)



- Common methods
  - Stress ramp
  - **Stress sweep #2**
  - Shear rate ramp
  - Dynamic stress/strain sweep

- Incidence of wall slip is often observed when testing structured fluids
- Wall slip shows artifact yield



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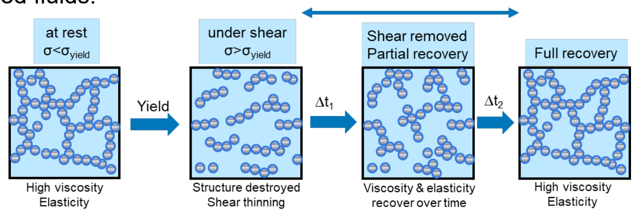
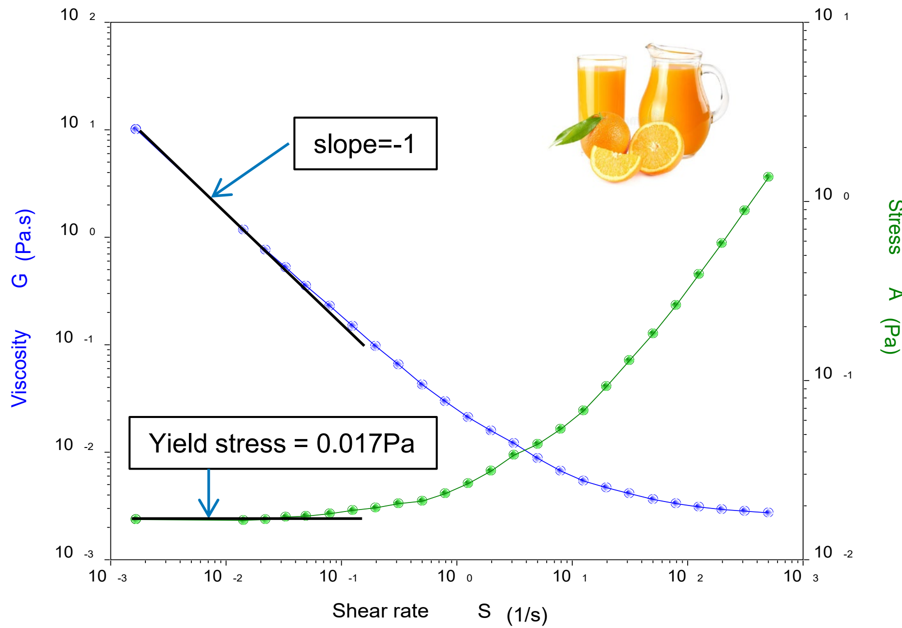


- Common methods
    - Stress ramp
    - Stress sweep #2
    - **<u>Shear rate ramp</u>**
    - Dynamic stress/strain sweep

- Shear rate ramp down from 500 to 0.001 1/s
- Yield is identified by the stress plateau
- Suitable for weak structures



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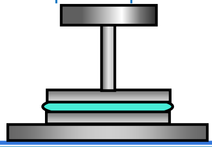

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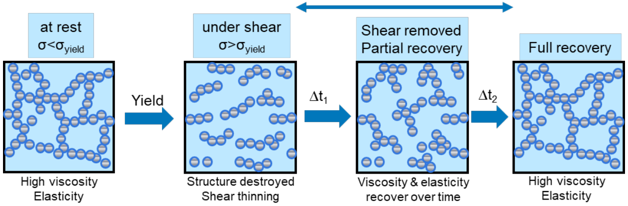

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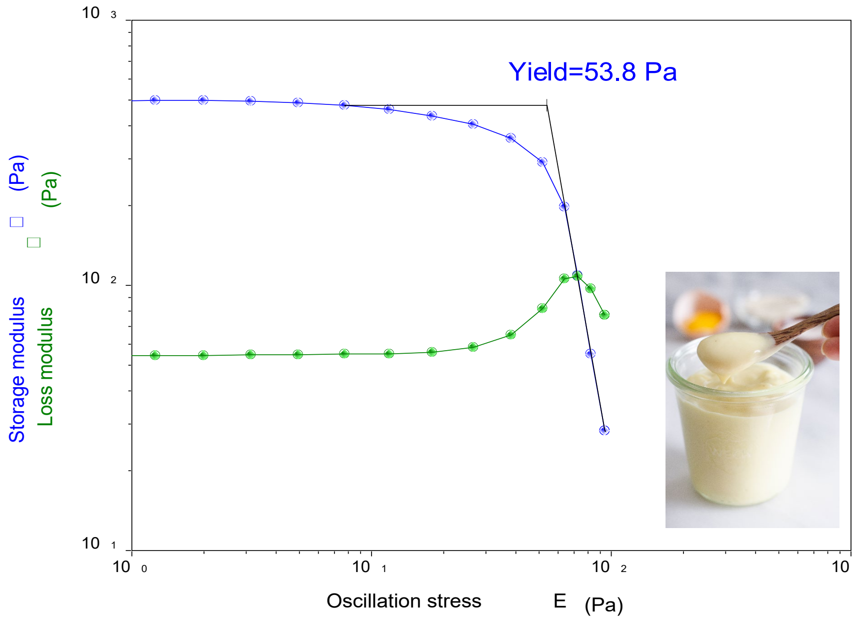

- Dynamic stress/strain sweep test on Mayonnaise
- Yield stress is signified at the onset of G' vs. stress curve
- Yield determined by this method indicates the critical stress at which irreversible plastic deformation occurs

Right tool for the job:
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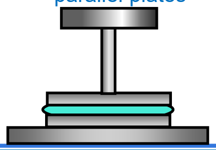

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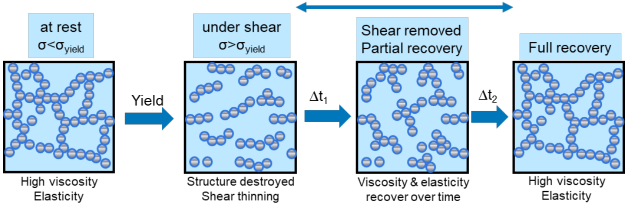

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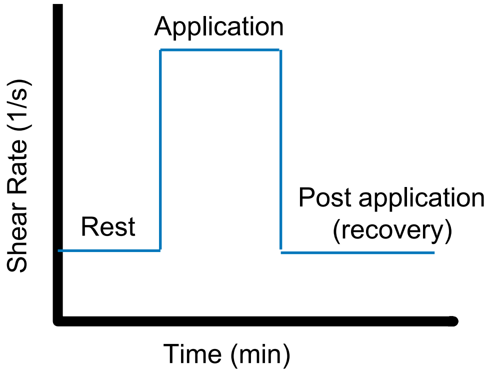
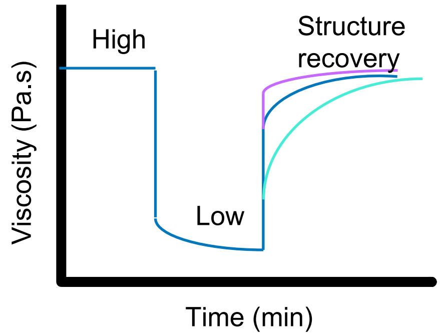
Stepped Flow (3 step)





Experimental:

Step 1: Low Shear (e.g. 0.1 1/s), state of rest

Step 2: High Shear (e.g. 10 1/s), structural destruction

Step 3: Low Shear (e.g. 0.1 1/s), structural regeneration

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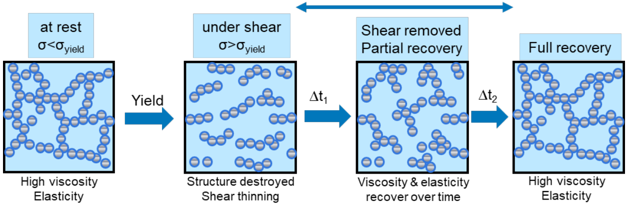

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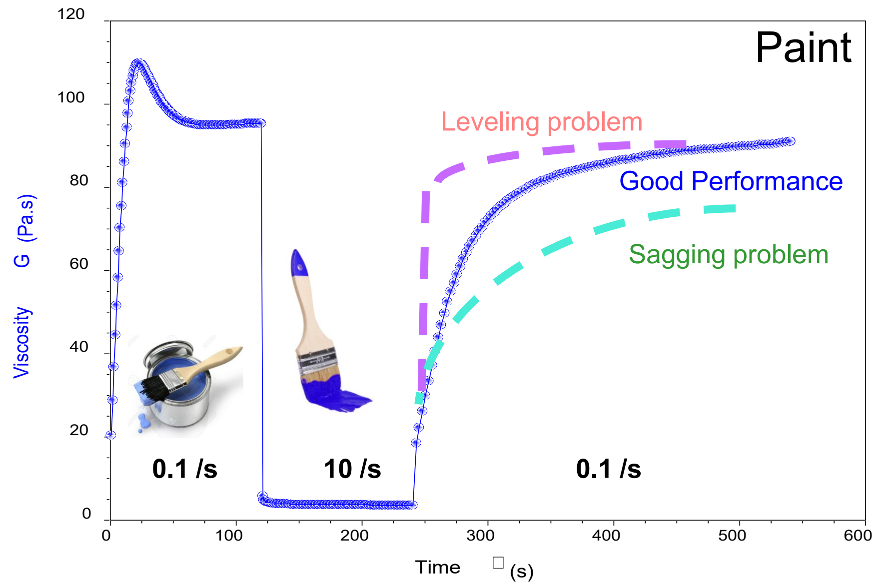

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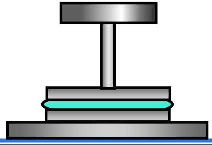

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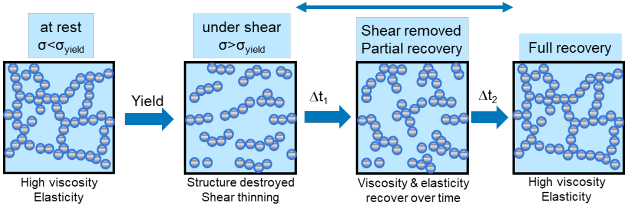

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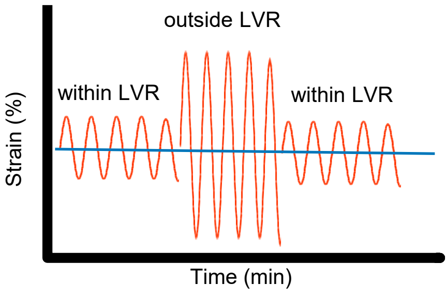

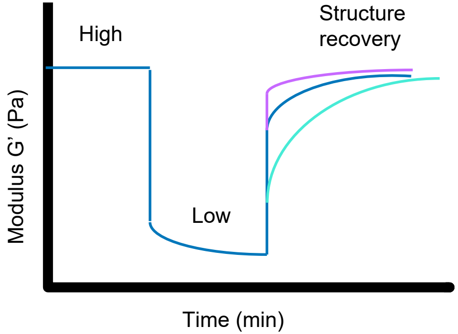

Experimental:
Step 1: Oscillate within LVR, state of rest
Step 2: Oscillate outside LVR, structural destruction
Step 3: Oscillate within LVR, structural regeneration

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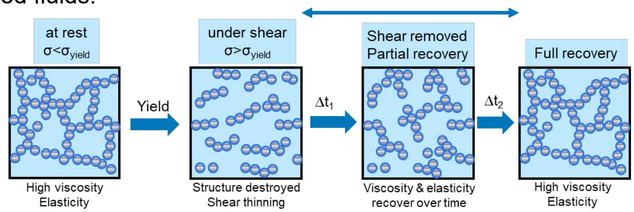

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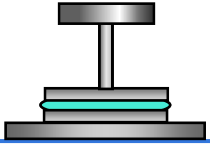

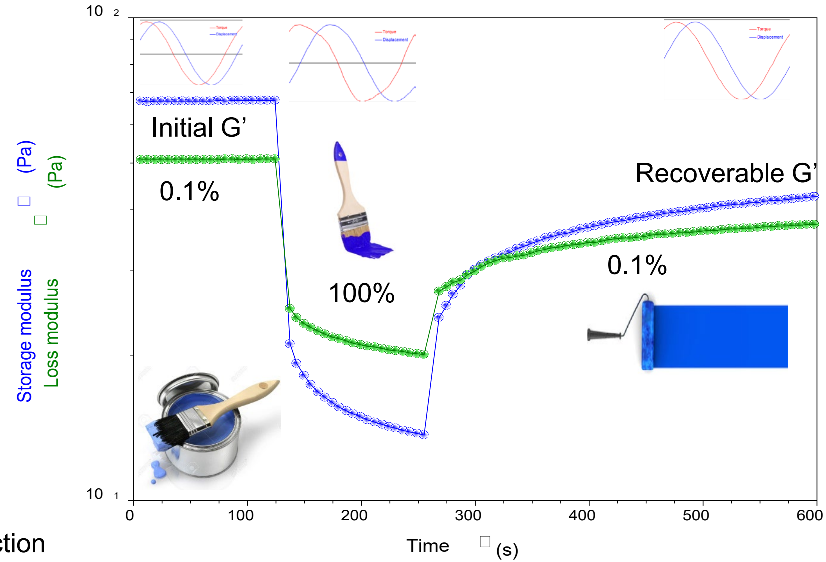

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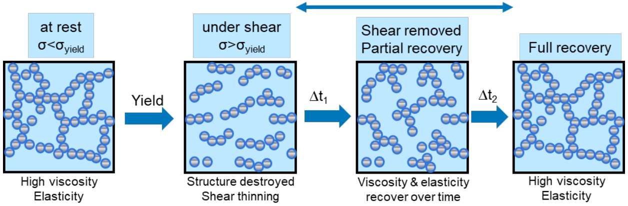

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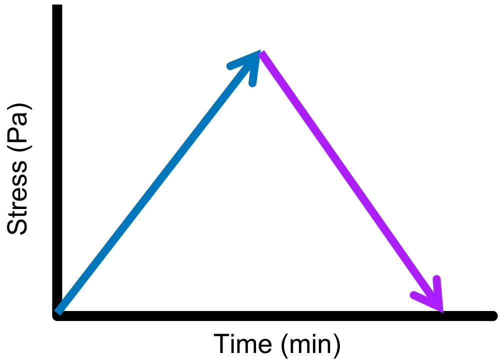

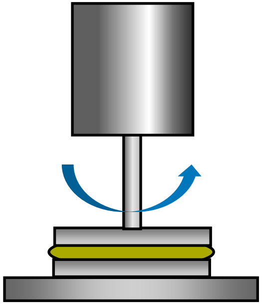

- Ramp shear stress linearly from zero up until sample flows, then ramp stress back down to zero
- Thixotropic index is measured by taking the area between the up and down stress curves
- TA Tech Tip:

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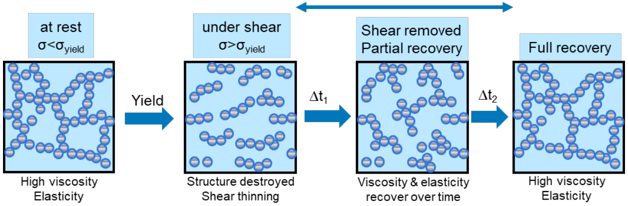

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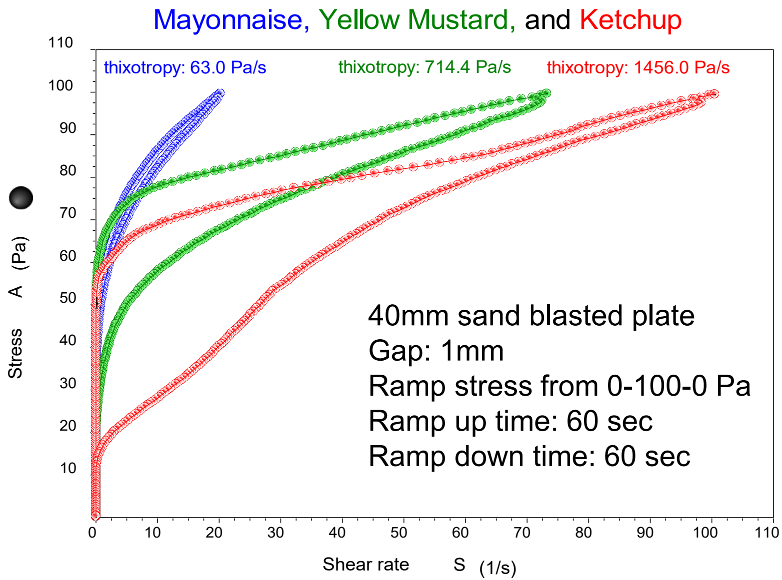

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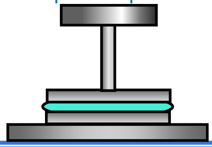

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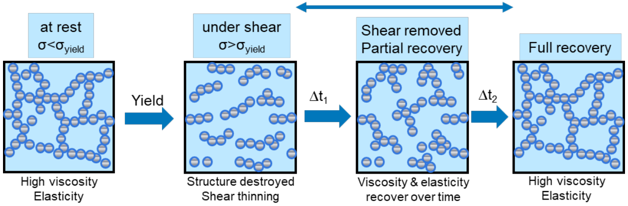

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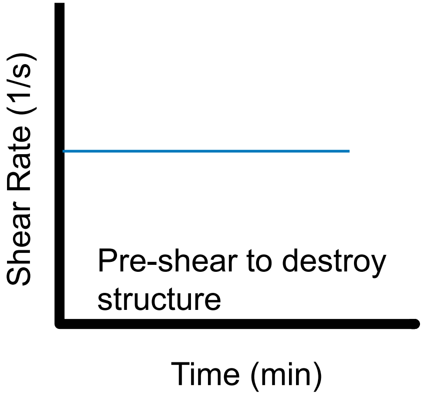
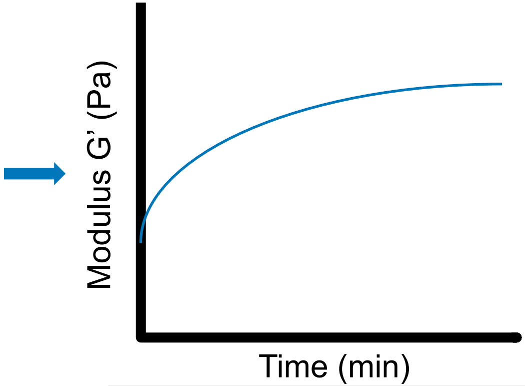
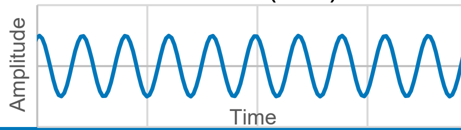




Experimental:

Step 1: Preshear sample for some duration to destroy structure

Step 2: Oscillation time (strain within LVR) to observe recovery



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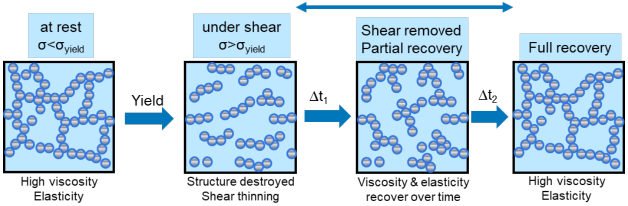

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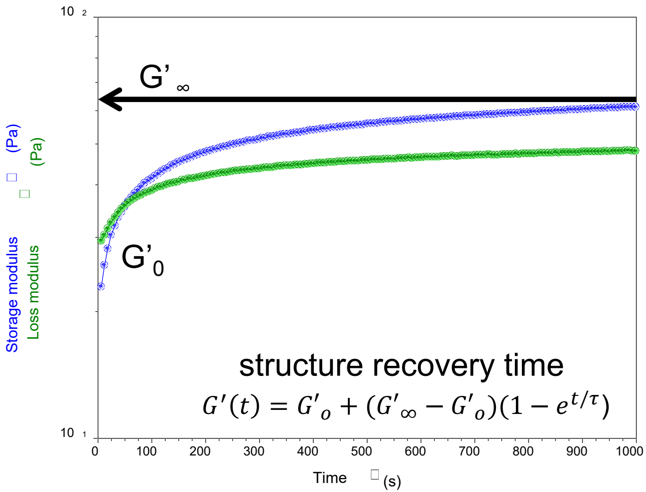

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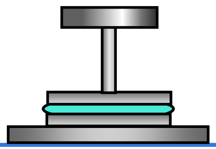

- Monitor the increase of the G' as a function of time.
- Thixotropic recovery is described by meausring the recovery time (τ)

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- Common methods
  - **<u>Creep Recovery</u>**
  - Normal Stress
  - Oscillation Frequency Sweep
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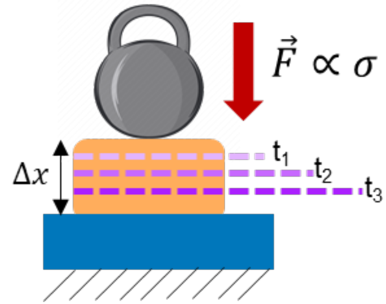
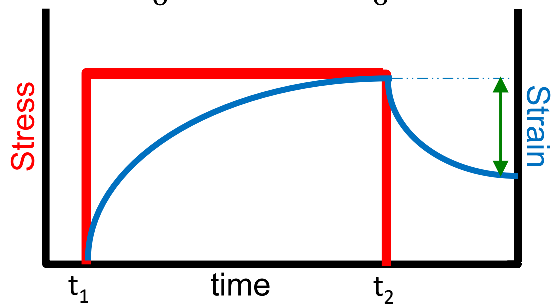


Recall: $G = \frac{\sigma}{\gamma}$

$$J = \frac{\gamma}{\sigma} \qquad J_R = \frac{\gamma_{t_1} - \gamma_r}{\sigma}$$

- Force/Stress is applied for a set duration and strain is measured
- After stress is removed, strain recovery is measured
- The more the strain recovers, the more elastic the sample is



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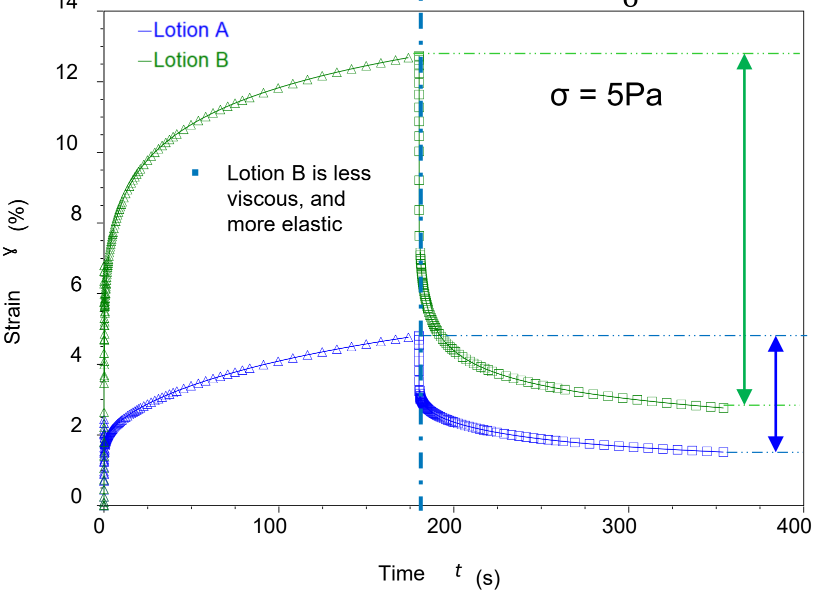

- Compliance and modulus have an inverse relationship
- In creep step – low compliance implies high modulus (low strain at a given stress)
- In recovery step – low recoverable compliance implies high elasticity (sample fully recovers)

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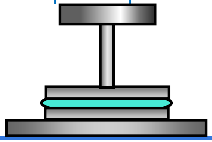

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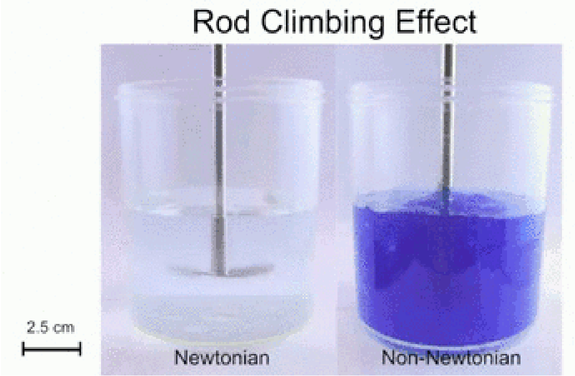

Normal Stress Constant

$$K_Z = \frac{2}{\pi R^2}$$

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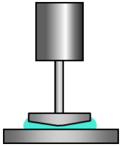
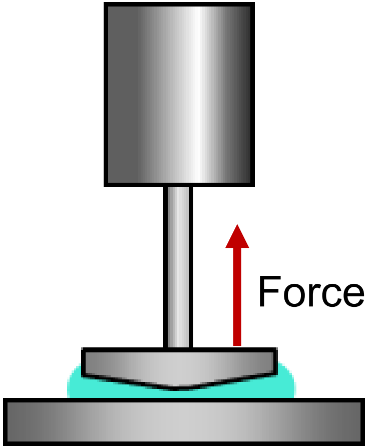
20-60mm Cone and Plate



- Normal stress is measured as a function of shear rate
- Elastic fluids store energy of deformation, and push plates apart



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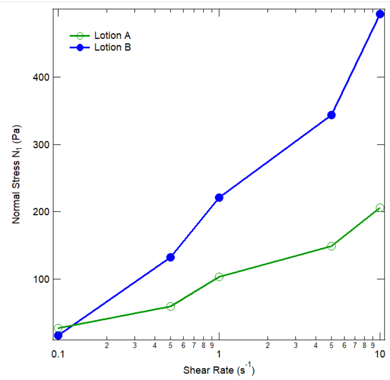

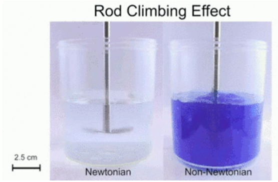

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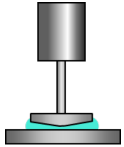

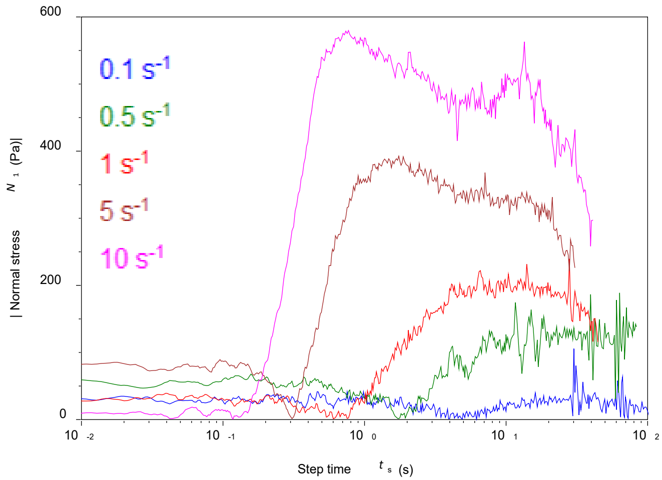

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- The complex viscosity of the two lotions is very similar
- However, the viscoelasticity is very different between the two

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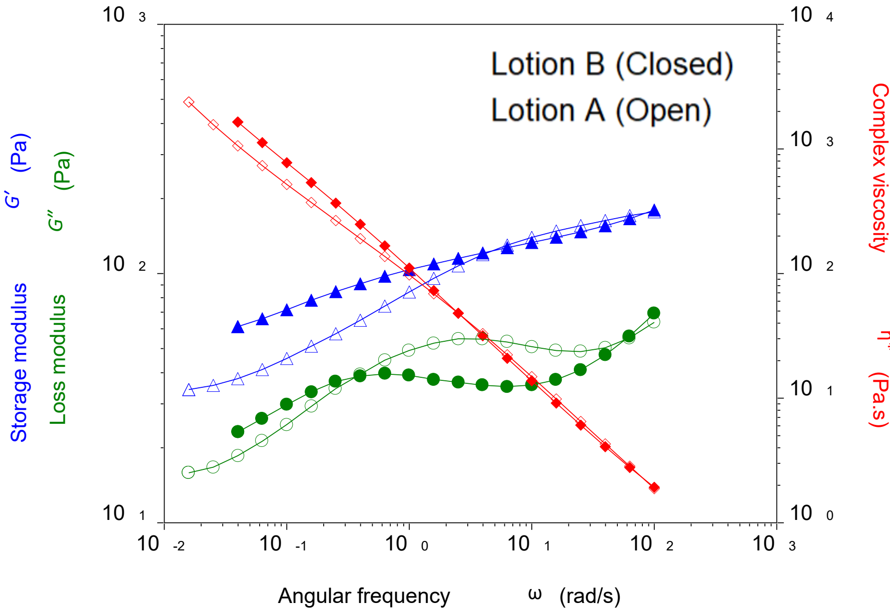

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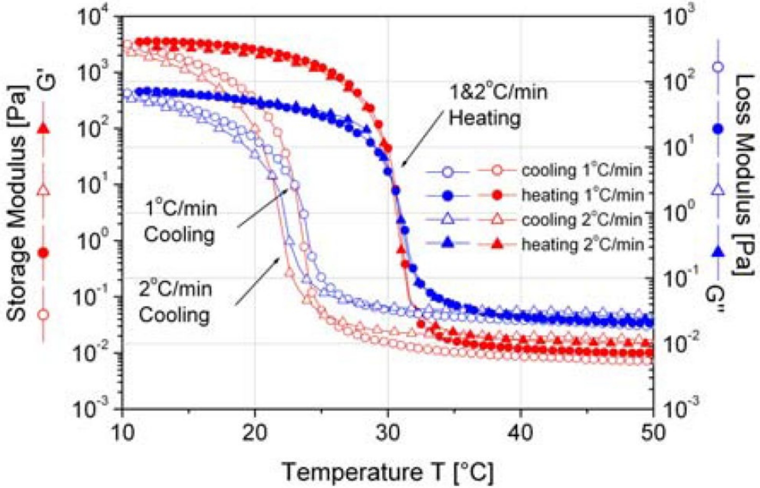
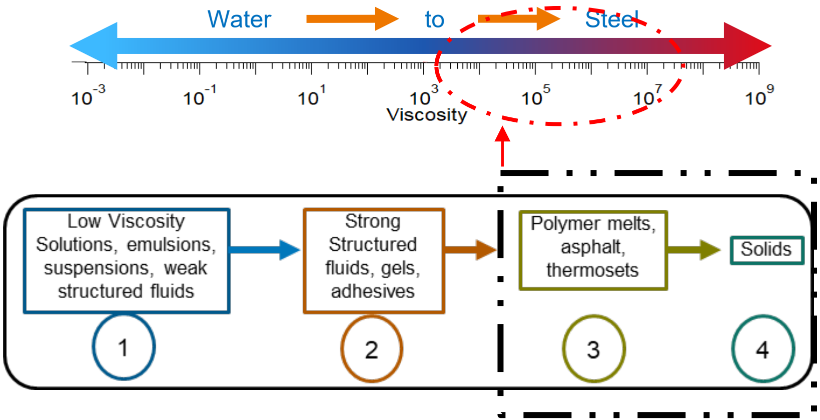


Rheology Applications

Polymers

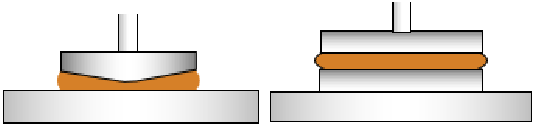
Rheology Applications
2. Polymers



Three main reasons for rheological testing:

- **Characterization**
  MW, MWD, formulation, state of flocculation, etc.
- **Process performance**
  Extrusion, blow molding, pumping, leveling, etc.
- **Product performance**
  Strength, use temperature, dimensional stability, settling stability, etc.

- Polymer melts:
  - 25mm and 8mm parallel plates, and disposable plates (cure)
  - Cone-plate (normal force measurement)
  - Cone partitioned plate (avoid edge fracture, LAOS)
- Polymer solids:
  - Torsion rectangular and cylindric geometry
  - DMA clamps (tension, bending, cantilever, compression)



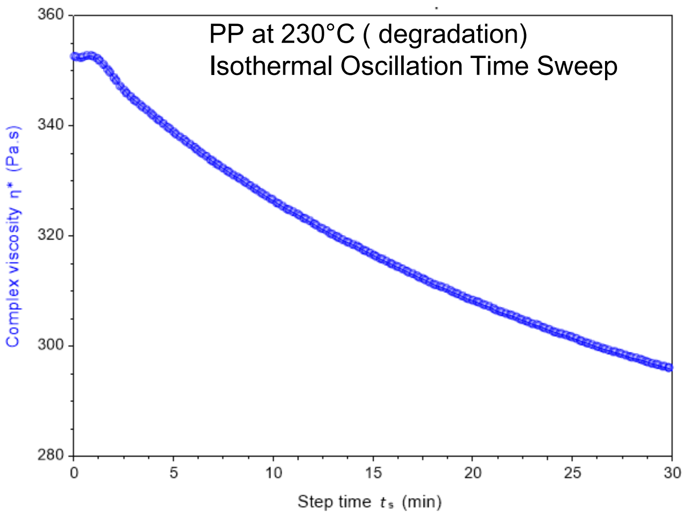
Torsion rectangular and cylindrical clamps

DMA cantilever, 3-point bending and tension clamps

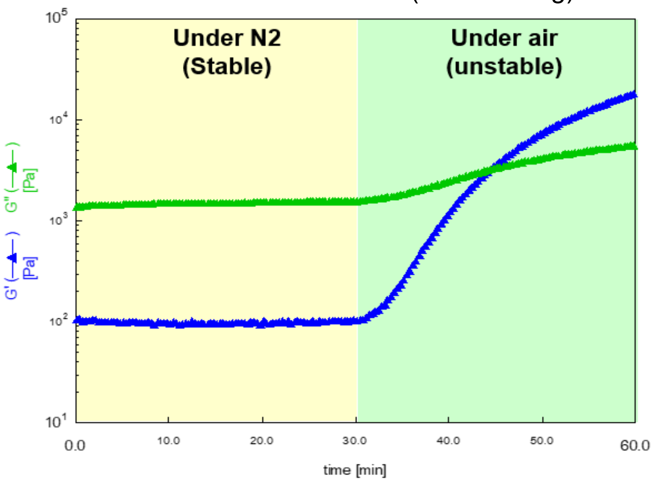
Properties of Polymers

- **Overall, we want to characterize several relevant properties of polymers:**
  - I. **Thermal Stability**
  - II. Flow Curve
  - III. Molecular Weight Effects (Viscoelasticity)
  - IV. Thermosets, Curing, Gelation

- Determines if properties are changing over the time of testing
  - Degradation
  - Molecular weight building, crosslinking



PEEK at 400°C (crosslinking)



Melt Flow Testing Considerations

- Overall, we want to characterize several relevant properties of polymers:
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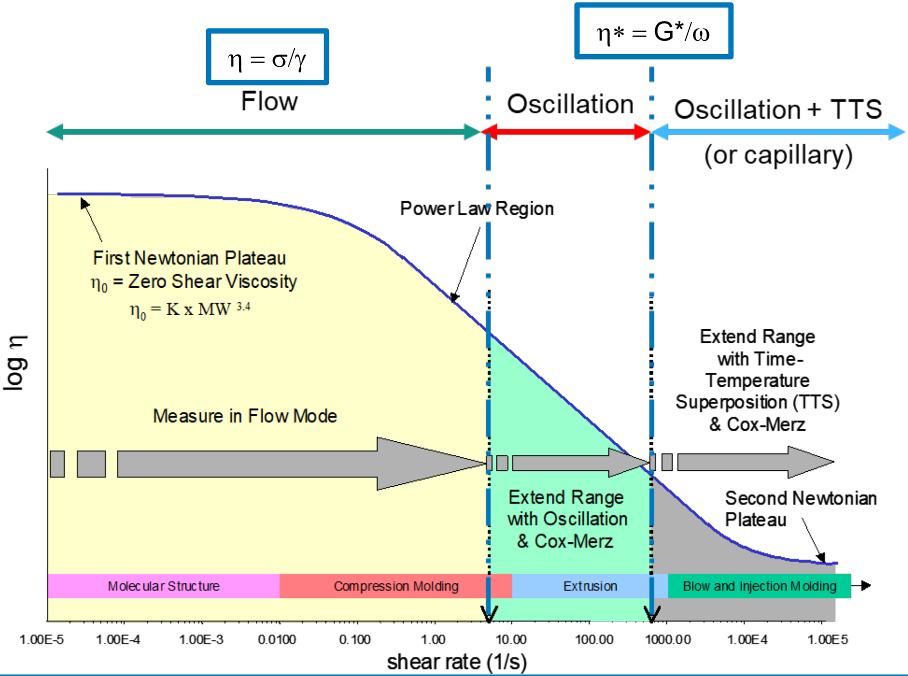
  - **II. Flow Curve**
  - III. Molecular Weight Effects (Viscoelasticity)
  - IV. Thermosets, Curing, Gelation



- **Edge Fracture:**

Sample leaves gap because of normal forces

- **Cox-Merz Rule**

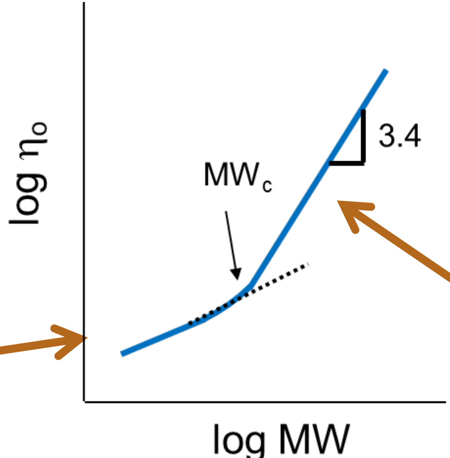
An empirical relationship between a dynamic complex viscosity and steady shear viscosity. It has been observed working with many polymer melt systems

$$\eta(\dot{\gamma}) \equiv \eta^*(\omega)$$

Molecular weight and Viscoelasticity

- Overall, we want to characterize several relevant properties of polymers:
  I. Thermal Stability
  II. Flow Curve
  III. Molecular Weight Effects (Viscoelasticity)
  IV. Thermosets, Curing, Gelation

- Sensitive to Molecular Weight, Mw
- For Low MW (no Entanglements) η_0 is proportional to Mw
- For MW > Critical Mw_c, η_0 is proportional to $Mw^{3.4}$



$\eta_0 = K \cdot Mw$

$\eta_0 = K \cdot Mw^{3.4}$

Time and Temperature Relationship (Viscoelasticity)

- Overall, we want to characterize several relevant properties of polymers:
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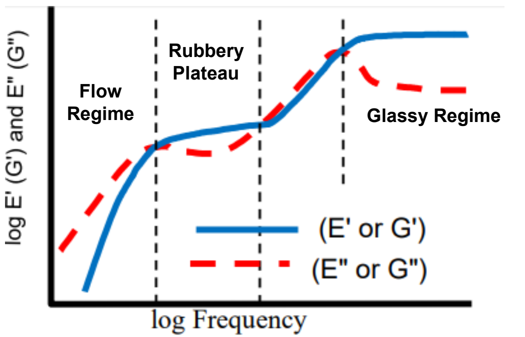

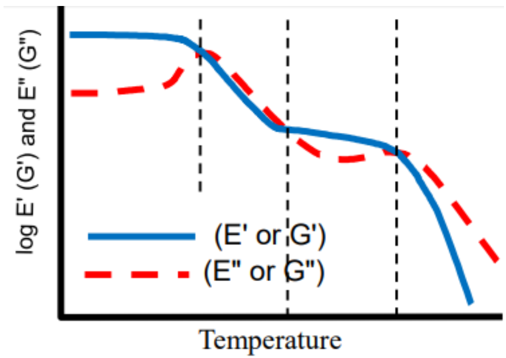

- At low frequencies molecular relaxation is at large time scales- **large length scales**
- At high frequencies molecular relaxation is at short time scales – *small length scales*
- At low temperatures molecular relaxation is slow – the diffusion is limited to *small length scales* and small time scales
- At high temperatures molecular relaxation is fast – the diffusion is predominately **large length scales** and large time scales

- Commonality between Frequency and Temperature is the timescale of molecular relaxation (Polymer chains diffusing)

Molecular weight and Viscoelasticity

- Overall, we want to characterize several relevant properties of polymers:
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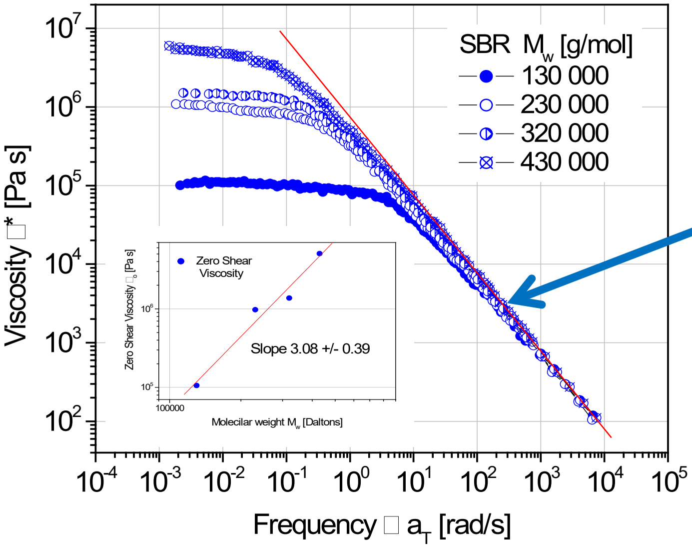
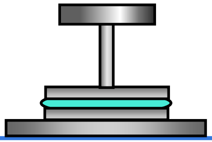
  - **III. Molecular Weight Effects (Viscoelasticity)**
  - IV. Thermosets, Curing, Gelation

- The zero shear viscosity increases with increasing molecular weight. TTS is applied to obtain the extended frequency range.



The high frequency behavior (slope -1) is independent of the molecular weight

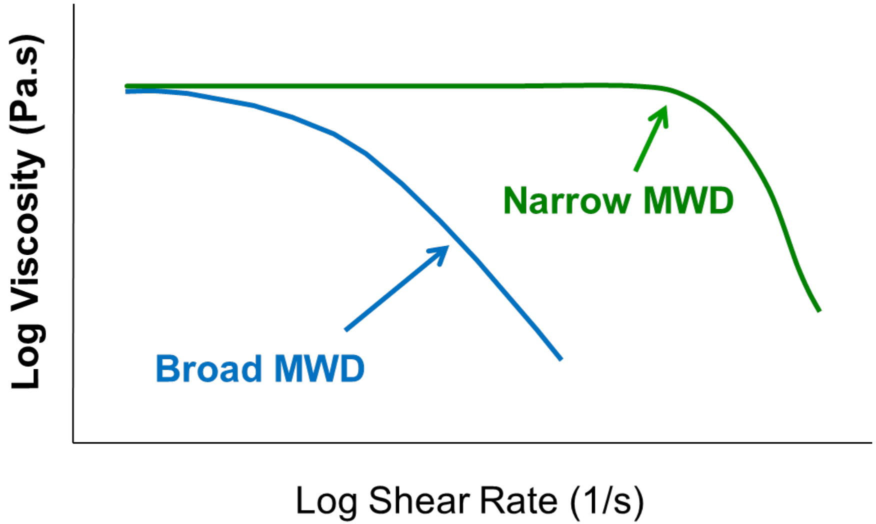
Right tool for the job:
25mm parallel plates



Molecular weight and Viscoelasticity

- Overall, we want to characterize several relevant properties of polymers:
  I. Thermal Stability
  II. Flow Curve
  III. **Molecular Weight Effects (Viscoelasticity)**
  IV. Thermosets, Curing, Gelation

- A Polymer with a broad MWD exhibits non-Newtonian flow at a lower rate of shear than a polymer with the same η_0, but has a narrow MWD.



Molecular weight and Viscoelasticity

- Overall, we want to characterize several relevant properties of polymers:
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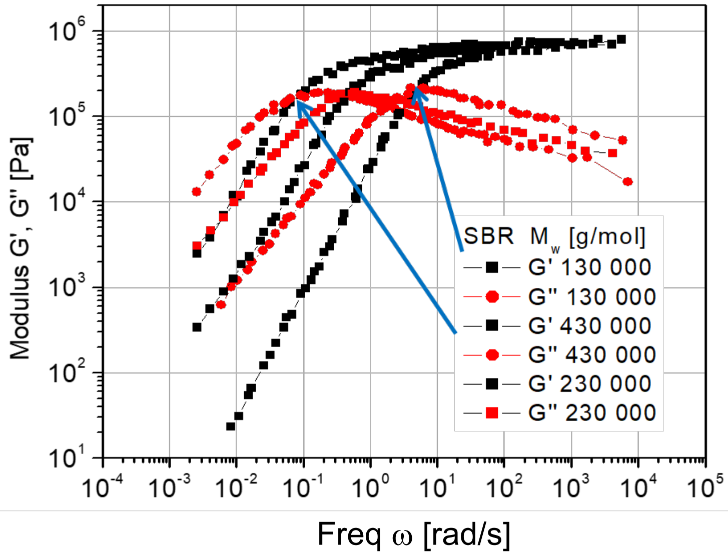
  III. Molecular Weight Effects (Viscoelasticity)
  IV. Thermosets, Curing, Gelation

- The G‘ and G“ curves are shifted to lower frequency with increasing molecular weight.



TA Instruments Webinar

Professor Chris Macosko – Analyzing Molecular Weight Distribution w/ Rheology

Molecular weight and Viscoelasticity

- Overall, we want to characterize several relevant properties of polymers:
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  - II. Flow Curve
  - **III. Molecular Weight Effects (Viscoelasticity)**
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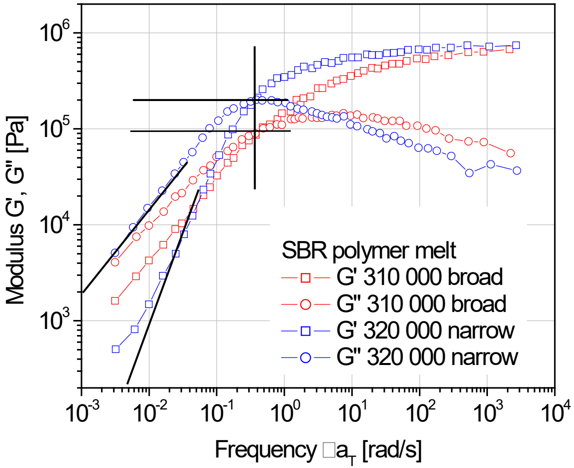
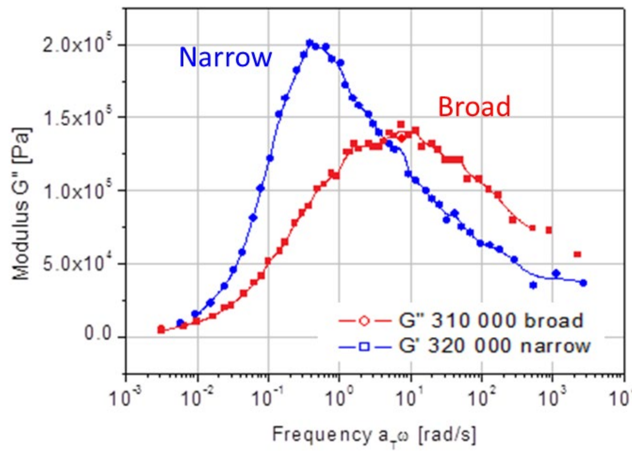


- The maximum in G" is a good indicator of the broadness of the distribution



Higher crossover frequency : lower M_w

Higher crossover Modulus: narrower MWD

(note also the slope of G" at low frequencies – narrow MWD steeper slope)

Molecular weight and Viscoelasticity

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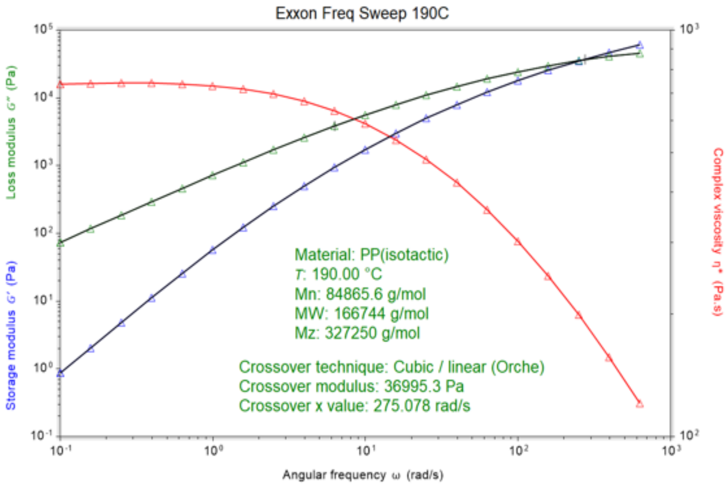
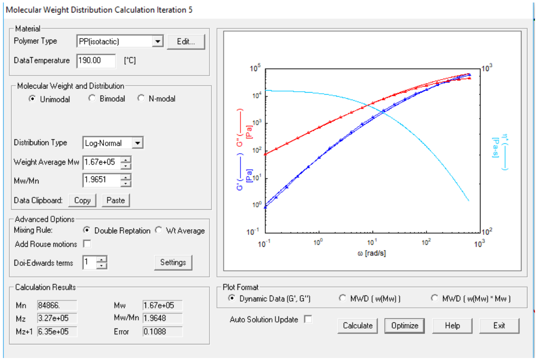


- Using rheological measurements to quantify molecular weight and molecular weight distribution



[João Maia: The Role of Interfacial Elasticity on the Rheological Behavior of Polymer Blends]
[Chris Macosko: Analyzing Molecular Weight Distribution w/ Rheology]

Molecular weight and Viscoelasticity

- Overall, we want to characterize several relevant properties of polymers:
  I. Thermal Stability
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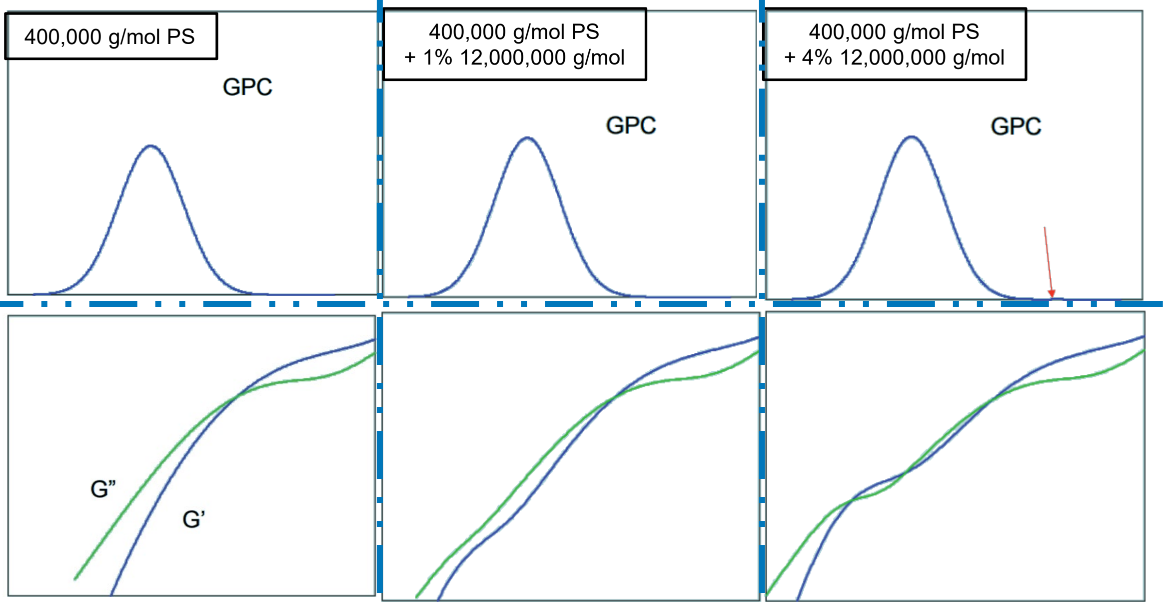
  III. **Molecular Weight Effects (Viscoelasticity)**
  IV. Thermosets, Curing, Gelation

Frequency Sweep

- Small amounts of ultra high MW PS increases entanglement of the polymer. It shows much more effect on the terminal region compared to the GPC data.



Macosko, TA Instruments Users' Meeting, 2015

Molecular weight and Viscoelasticity

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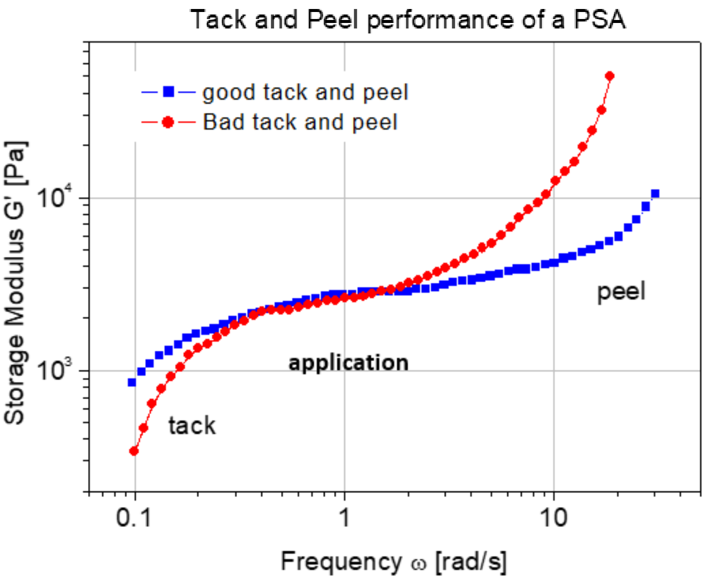
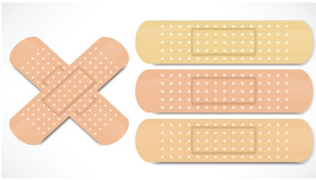


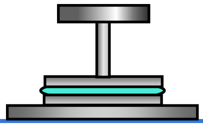
Tack and Peel of Pressure Sensitive adhesive

- Frequency Sweep



- A dynamic frequency sweep test results can correlate to tack and peel performance
- One single frequency sweep test cannot cover the entire frequency range of interest. Use Time-Temperature Superposition (TTS).

Right tool for the job:
25mm parallel plates



Molecular weight and Viscoelasticity

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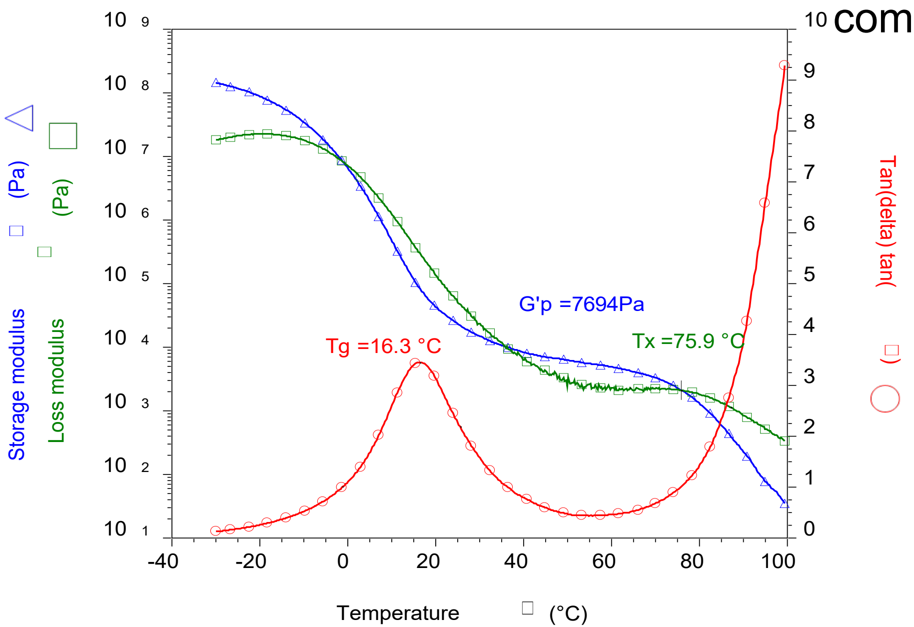
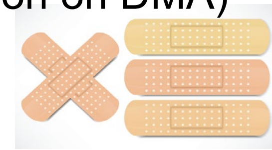


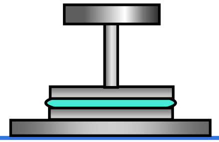
Tack and Peel of Pressure Sensitive adhesive

- Temperature Ramp (more common on DMA)



- A temperature ramp test is an alternative to frequency sweeps for temperature stable polymers

Right tool for the job:
25mm parallel plates



Molecular weight, Viscoelasticity, and Curing

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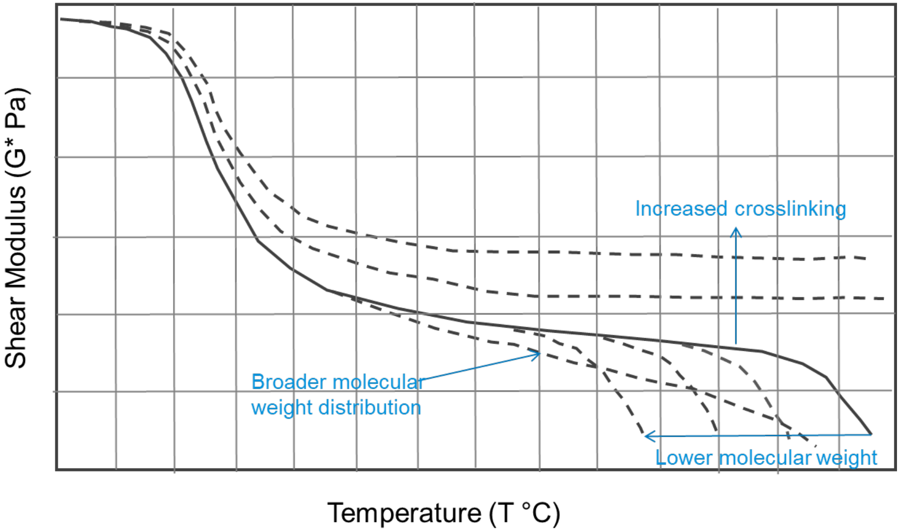

- Temperature Ramp
  - Correlates with polymer molecular structure: Mw, MWD, and crosslinking

- **Segway into "Thermosets, curing and gelation" section**

Molecular weight, Viscoelasticity, and Curing

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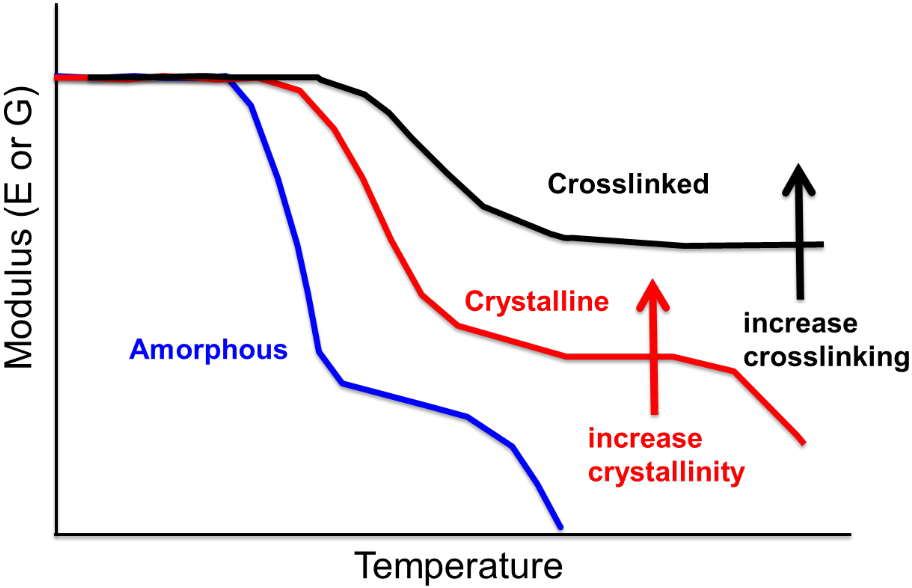

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Molecular weight, Viscoelasticity, and Curing

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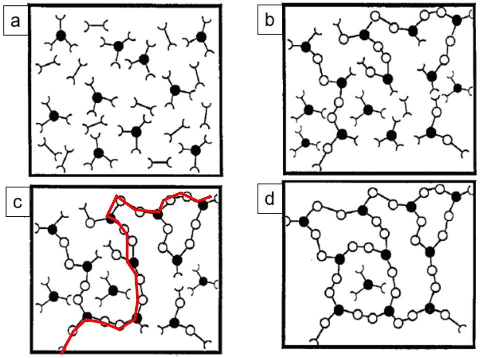
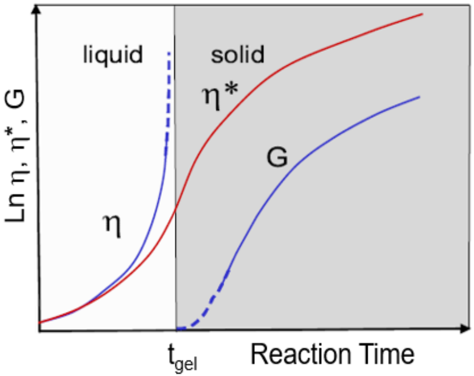
Gelation and Vitrification

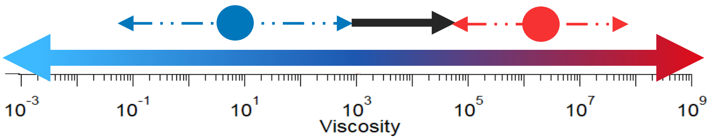


- Formation of network across span of material volume

What Rheology Measures



Viscosity can increase many orders of magnitude over duration of cure



Common Curing Experiments

- Overall, we want to characterize several relevant properties of polymers:
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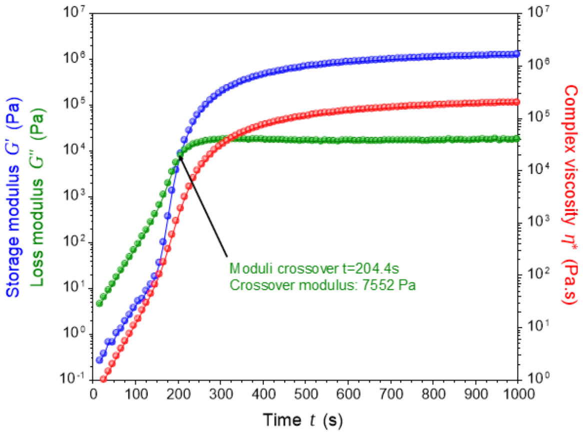
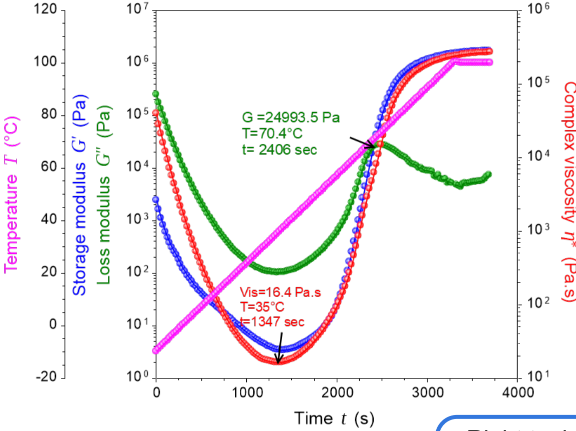
  - **IV. <u>Thermosets, Curing, Gelation</u>**

Isothermal Curing (Time Sweep)

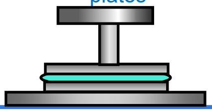


Temperature Ramp Curing



- Measure viscosity change before crosslinking
- Monitor gelation and measure the gel point
- Monitor sample viscoelastic property change (G' and G") during curing
- Evaluate the mechanical properties of the end-use product

<u>Right tool for the job:</u>
Disposable 25mm parallel plates



Isothermal Curing Experiments

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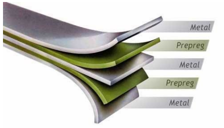
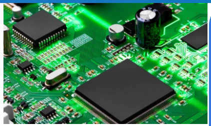
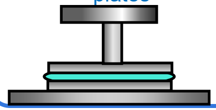


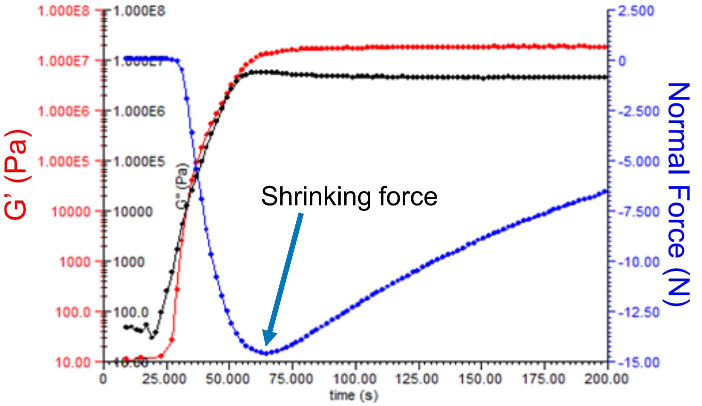


Right tool for the job:
Disposable 25mm parallel plates

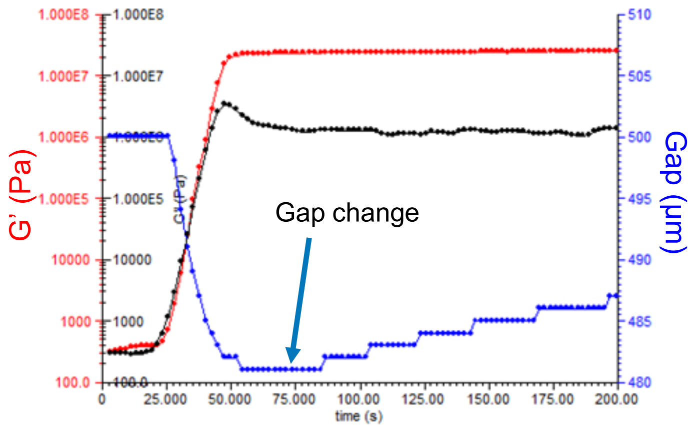


Isothermal Curing (Time Sweep)

Set Gap Constant monitor shrinking force



Set Axial Force = 0
monitor dimension(gap) change



Liquid to Gel to Solid Transition

- Overall, we want to characterize several relevant properties of polymers:
  - I. Thermal Stability
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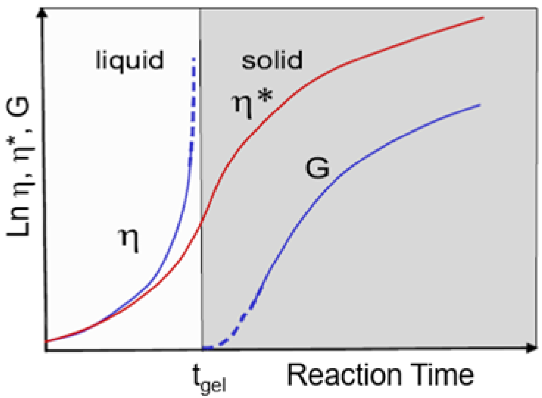
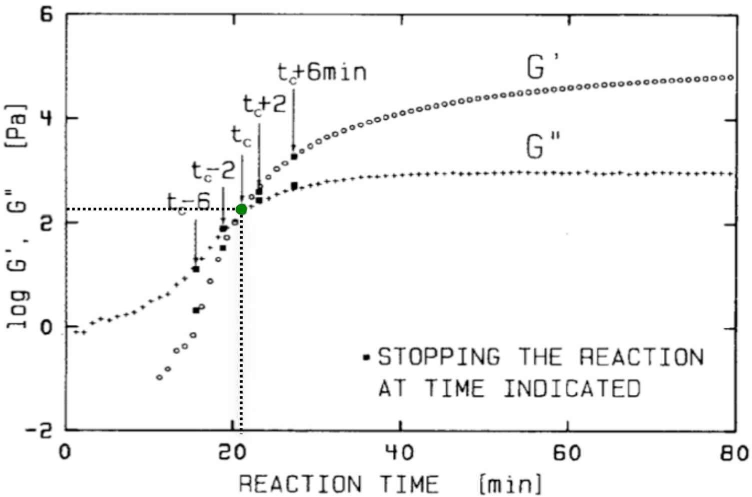
  - **IV. Thermosets, Curing, Gelation**

Empiricism of Y. M. Tung and P. J. Dynes (1982)

- Viscosity goes to infinity
- System loses solubility
- Molecular weight M_w goes to infinity



When G' = G'' and Tan δ = 1



F. Chambon and H. H. Winter (1985)

True Gelation Point (Multifrequency time sweep)

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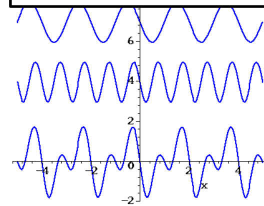
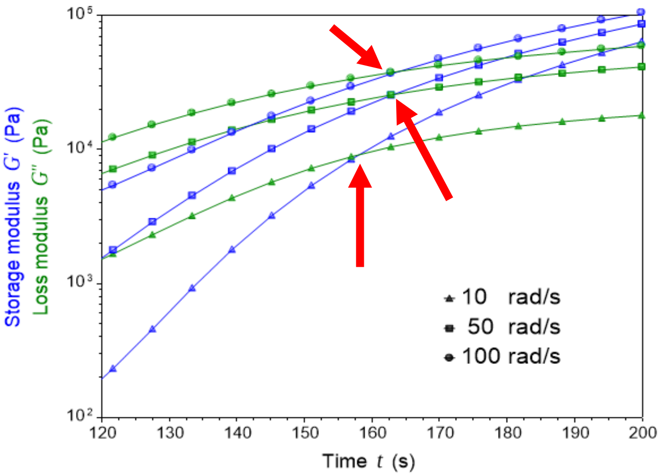
- Multifrequency superposition (ARES G2)

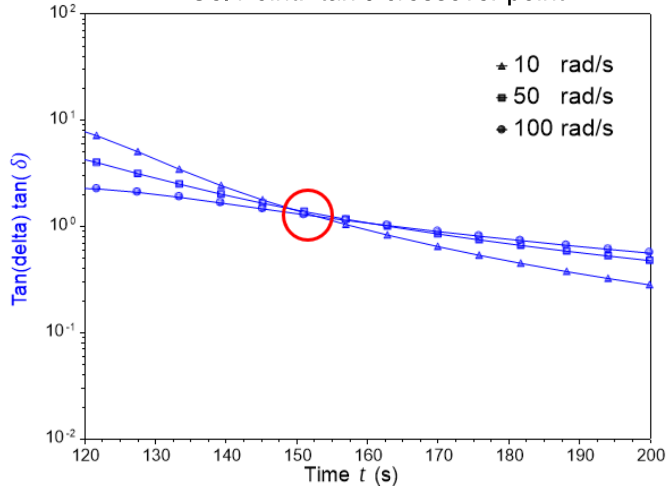


Multifrequency Time Sweep

G'/G" crossover: frequency dependent



Gel Point: tan δ crossover point



G. Kamykowski; T. Chen, **The Use of Multi-wave Oscillation to Expedite Testing and Provide Key Rheological Information. ANTEC, 2020**

Gelation Kinetics

Waters™ | TA Instruments

- Overall, we want to characterize several relevant properties of polymers:
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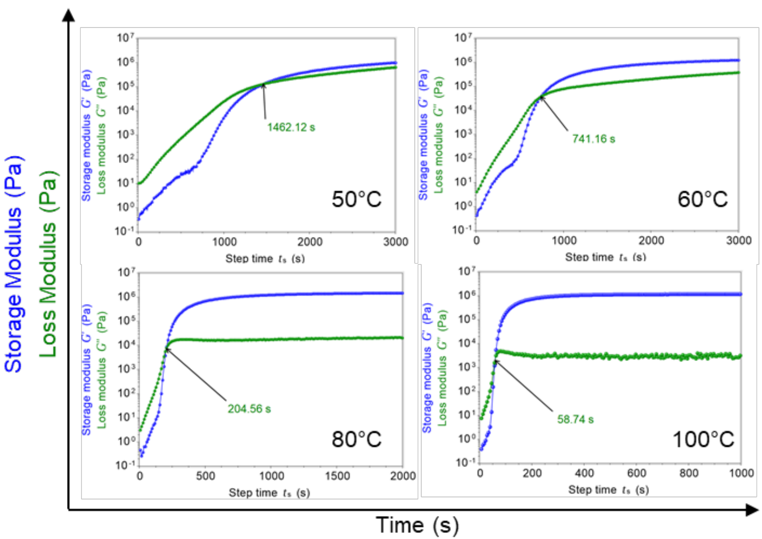
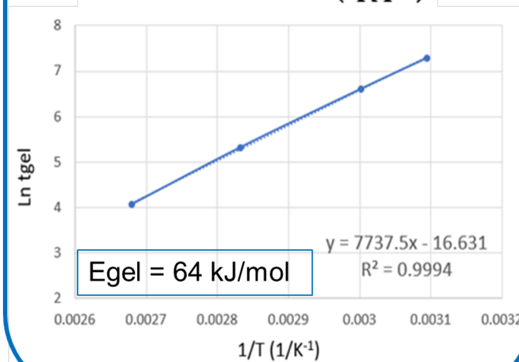
- The gelation kinetics can be described using the empirical Arrhenius model
- Perform isothermal curing at different temperatures



$$t_{gel} = t_{gel}^{\infty} \exp\left(\frac{\Delta Eg}{RT}\right)$$



Quantifying Crosslink Density Post Cure (DMA)

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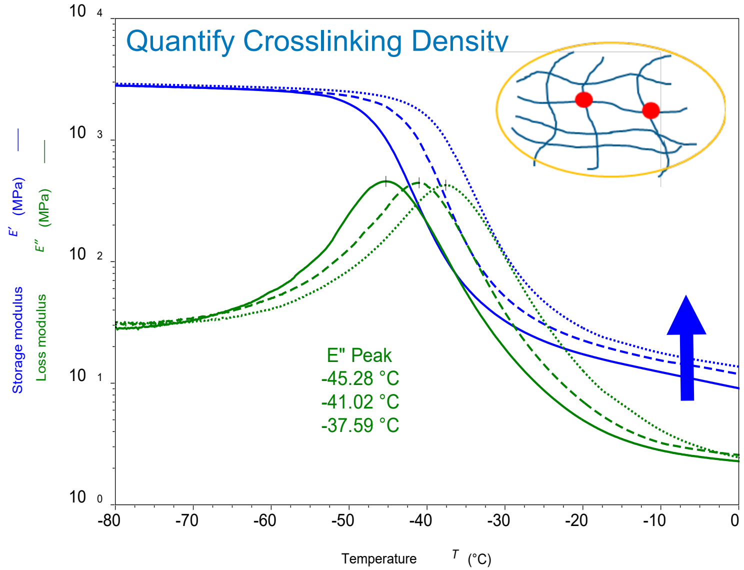
  - **IV. Thermosets, Curing, Gelation**



$$M_c = \frac{3RTd}{E'_{rubbery}} \quad \text{or} \quad M_c = \frac{RTd}{G'_{rubbery}}$$

M_c = Molecular weight between crosslinks
R = Universal gas constant
T = Absolute temperature (K)
d = Polymer density

$$\textit{Crosslinking density}, q = \frac{Mw}{Mc}$$

Mw = Molecular weight of the monomer

- For unfilled polymers, crosslinking density can be quantitatively measured using rheology
- Calculation uses storage modulus in rubber plateau region ($G'_{rubbery}$ or $E'_{rubbery}$)

M. Barszczewska-Rybarak et al; Acta of Bioengineering and Biomechanics, vol 19, 1, 2017.
M. H. Abd-El Salam, J of Applied Polymer Sci, vol 90, 1539-1544, 2003.

UV Curing (Rheometer only)

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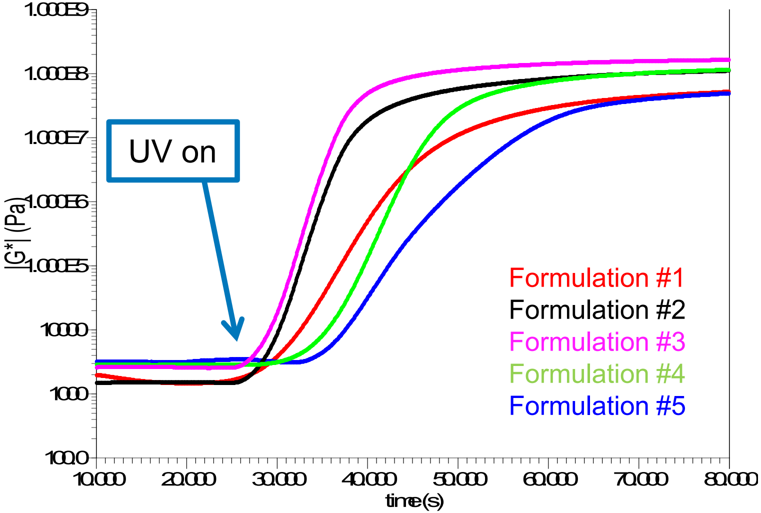


- Monitor UV curing: Dynamic time sweep
- Measure curing time with different formulations, UV intensity and temperature
- Measure cured adhesive modulus

Powder Rheology Kit and Contents

Waters™ | TA Instruments

Powder Rheology Accessory Components

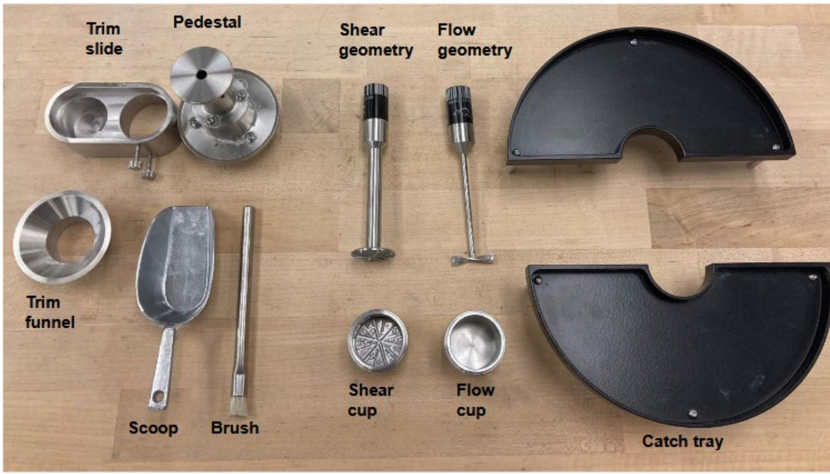
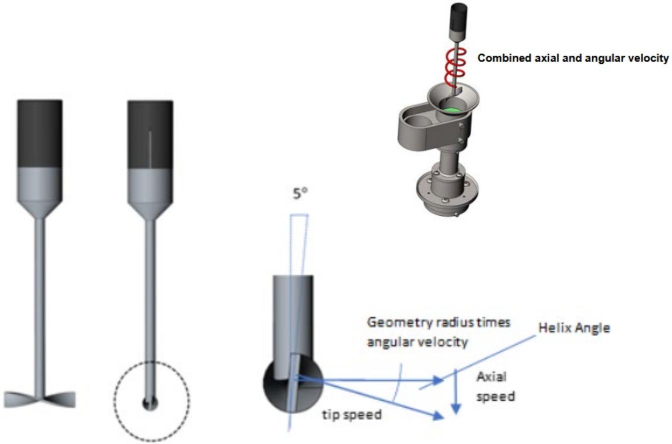


Figure 3 Components.

- We will review a short case study of two powders (for coating applications)

Powder Rheology Testing Modes

Flowability Testing



- Measure confined (downward stroke) and/or unconfined (upward stroke) flow energies
- Measure as a function of time (fixed number of cycles, fixed upward speed, fixed downward speed)
- Measure as a function of tip speed (variable speed)

Shear Testing

- Measure shear properties of powder: cohesion, unconfined yield stress, major principle stress

Flowability Testing Methods

- Fixed Cycles & Constant Speed (properties over time)

2: Powder Flowability

Environmental Control
Temperature 25 °C ☑ Inherit Set Point
Soak Time 0.0 s ☐ Wait For Temperature

Test Range
Upper gap 30.0 mm
Lower gap 5.0 mm

Conditioning Parameters
◉ Tip speed 60.0 mm/s Helix angle 5.0 °
○ Axial speed 5.22934 mm/s Angular speed 4.26941 rad/s

Unconfined Flow Parameters
☑ Enabled
◉ Tip speed up 60.0 mm/s Helix angle 5.0 °
○ Axial speed up 5.22934 mm/s Angular speed 4.26941 rad/s

Confined Flow Parameters
☑ Enabled
◉ Tip speed down 60.0 mm/s Helix angle 5.0 °
○ Axial speed down 5.22934 mm/s Angular speed 4.26941 rad/s

Repeat Count: 7

Data acquisition

- Powder conditioning

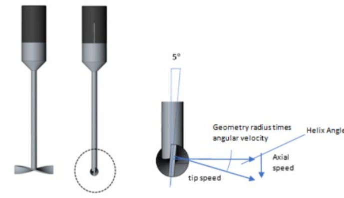
1: Powder Flow Conditioning

Environmental Control
Temperature 25 °C ☑ Inherit Set Point
Soak Time 0.0 s ☐ Wait For Temperature

Test Range
Upper gap 60.0 mm
Lower gap 5.0 mm

Conditioning Parameters
Tip speed 60.0 mm/s

Data acquisition



- Fixed Cycles & variable speed

2: Powder Flowability

Environmental Control
Temperature 25 °C ☑ Inherit Set Point
Soak Time 0.0 s ☐ Wait For Temperature

Test Range
Upper gap 30.0 mm
Lower gap 5.0 mm

Conditioning Parameters
◉ Tip speed 100.0 mm/s Helix angle 5.0 °
○ Axial speed 8.71557 mm/s Angular speed 7.11568 rad/s

Unconfined Flow Parameters
☑ Enabled
◉ Tip speed up 100.0 mm/s Helix angle 5.0 °
○ Axial speed up 8.71557 mm/s Angular speed 7.11568 rad/s

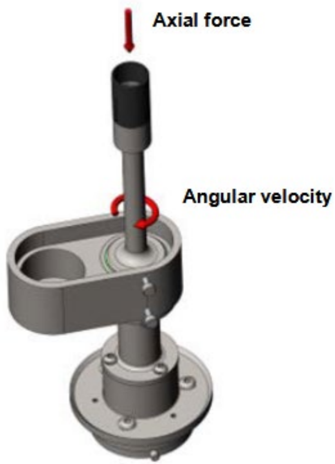
Confined Flow Parameters
☑ Enabled
◉ Tip speed down 100.0 mm/s Helix angle 5.0 °
○ Axial speed down 8.71557 mm/s Angular speed 7.11568 rad/s

Repeat Count: 1

Data acquisition

3: Powder Flowability → 80 mm/s
4: Powder Flowability → 60 mm/s
5: Powder Flowability → 40 mm/s
6: Powder Flowability

Shear Testing Method



- Powder consolidation

X: Powder Consolidation

Environmental Control

Temperature 25 °C ☑ Inherit Set Point

Soak Time 0.0 s ☐ Wait For Temperature

Test Parameters

Constant axial stress 15000.0 Pa

Data acquisition

- Powder Shear Test

1: Powder Shear

Environmental Control

Temperature 25 °C ☑ Inherit Set Point

Soak Time 0.0 s ☐ Wait For Temperature

Test Parameters

Consolidating stress Custom Pa

Test mode Standard

	Normal Stress (Pa)	Velocity (rad/s)	Duration (s)
1st Pre-shear	15000.0	1.0e-3	300.0
Pre-shear	15000.0	1.0e-3	300.0
1	14000.0	1.0e-3	300.0
2	12000.0	1.0e-3	300.0
3	10000.0	1.0e-3	300.0
4	8000.0	1.0e-3	300.0
5	6000.0	1.0e-3	300.0
6	4000.0	1.0e-3	300.0
7	2000.0	1.0e-3	300.0

Add Remove

☑ Repeat initial pre-shear

☑ Steady state detection

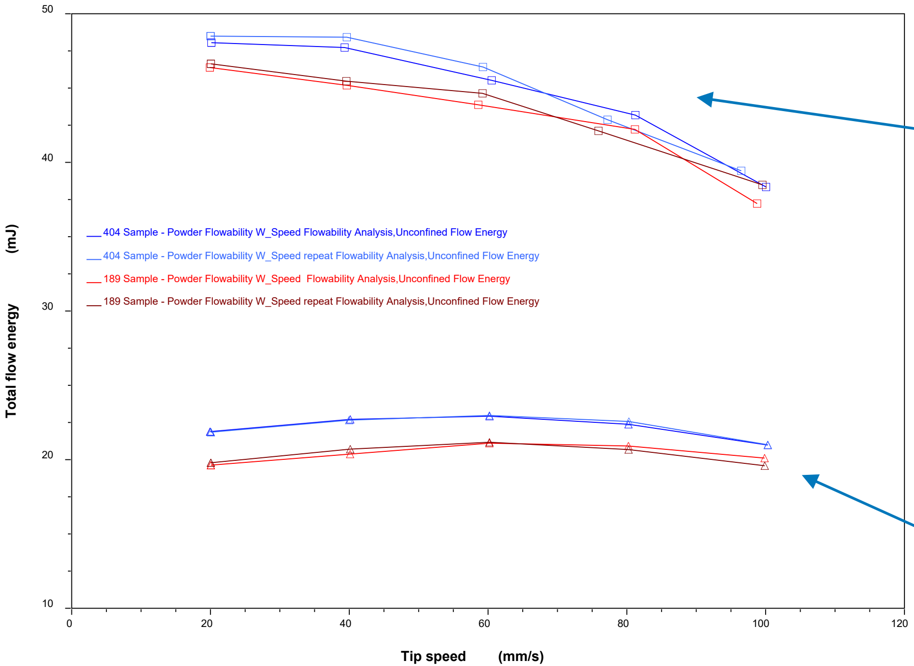
☑ Peak detection

Data acquisition

Advanced

Flowability Testing

- Fixed Cycles & variable speed



Confined Energy

- Sample 189 has 4% lower flow resistance at 20mm/s (low speed)
- Progressively smaller difference with increasing tip speed

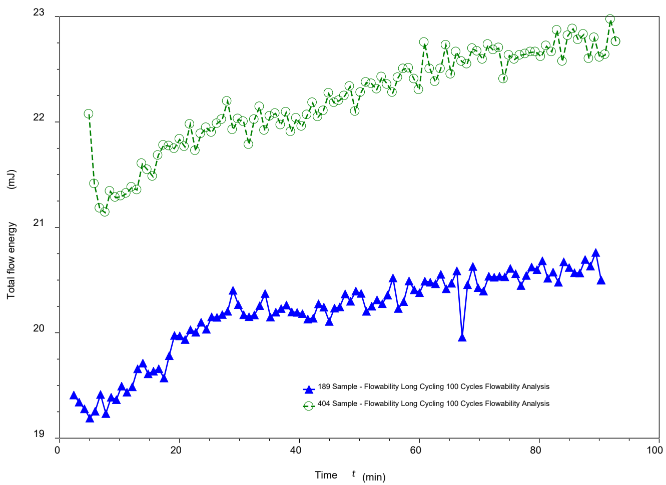
Unconfined Energy

- Sample 189 has 10% lower flow resistance at 20mm/s (low speed)
- Sample 189 has 4% lower flow resistance at 100mm/s (high speed)

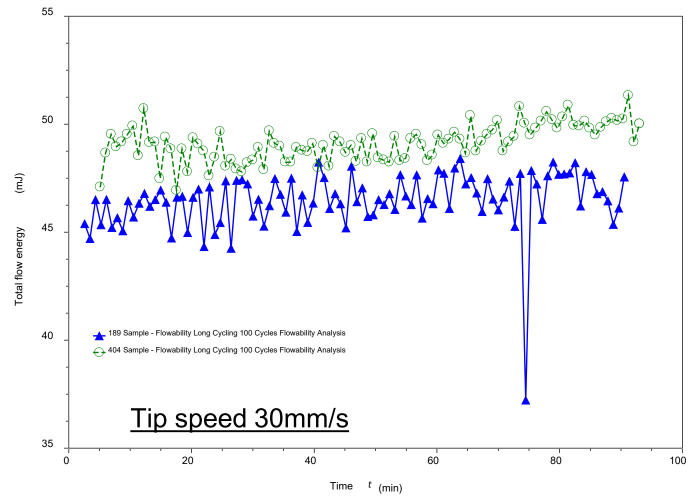
Flowability Testing

- Testing over longer duration (90 minutes)

Unconfined



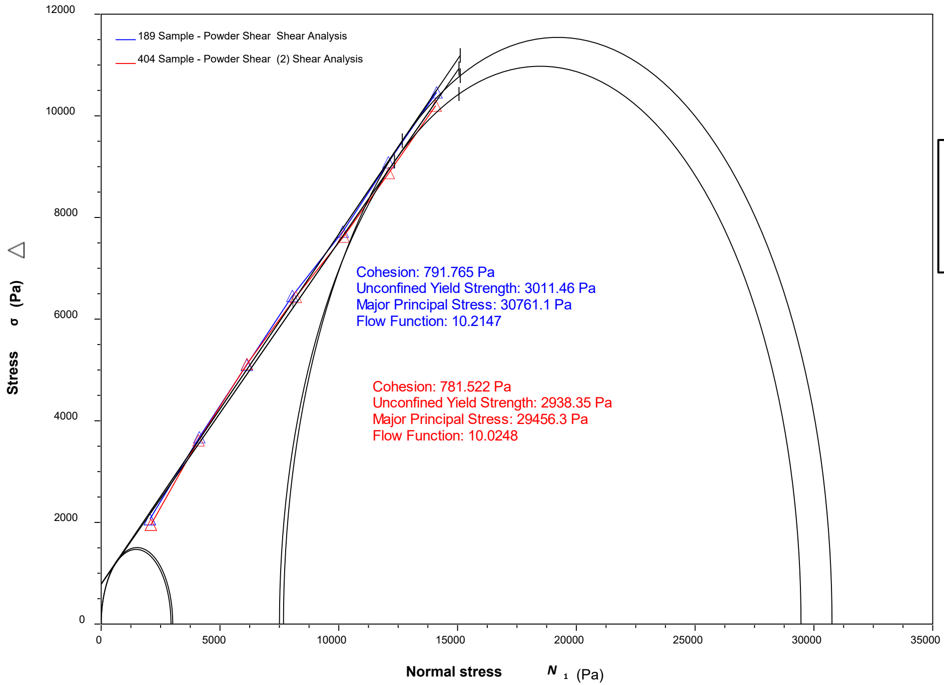
Confined



Unconfined Energy

- Both powders show an appreciable increase in flow resistance over time

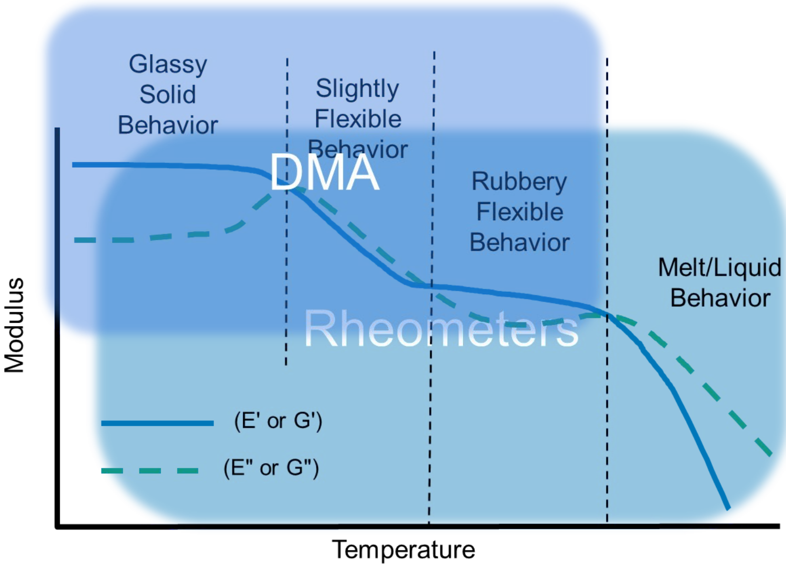
Shear Testing



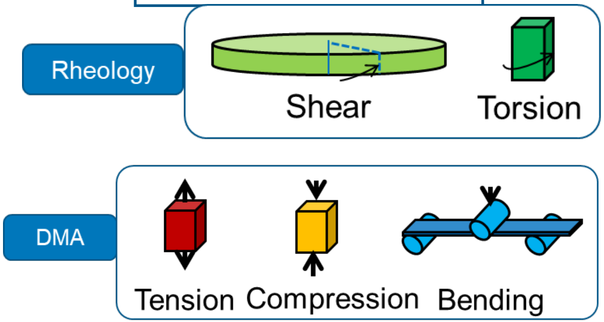
Shear Properties

- Samples have very little difference in shear properties

Review



$$E = 2G(1 + \nu)$$



Thank You!