Pacific Heat and Wave Flow: Day II

Section II: Intermediate Rheology Methods

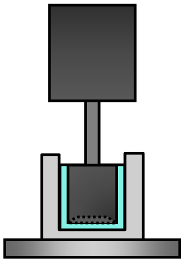
Keith Coasey PhD

Rheology Applications Engineer

TA Instruments – Waters LLC

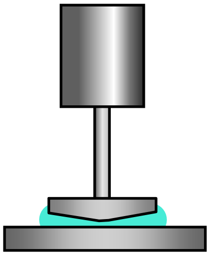
Recall – Rheometer Geometries

Concentric Cylinders



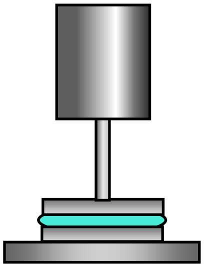
Very Low to Medium Viscosity

Cone and Plate



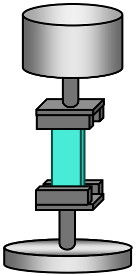
Very Low to High Viscosity

Parallel Plate

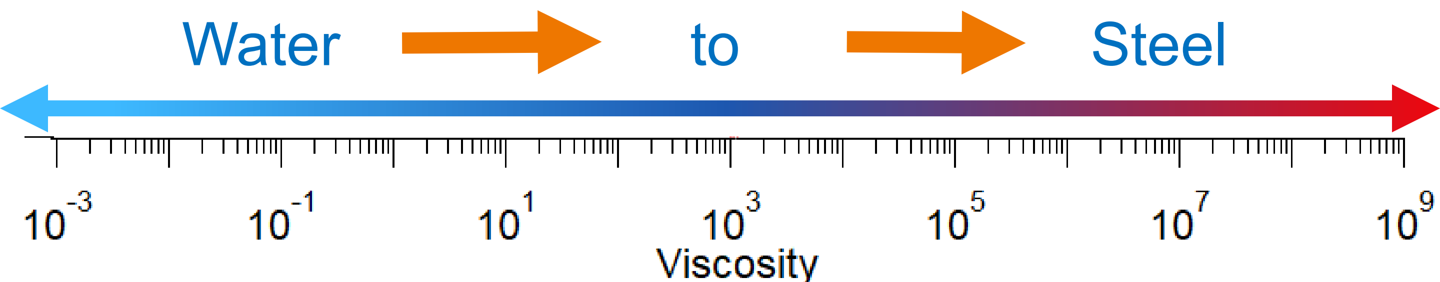


Very Low Viscosity to Soft Solids

Torsion Rectangular

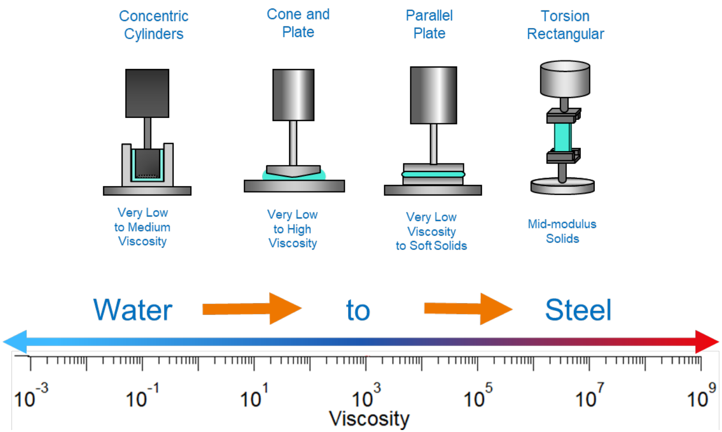


Mid-modulus Solids



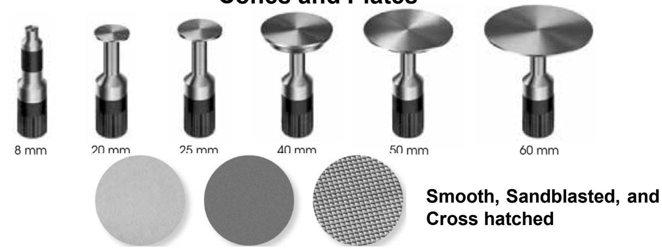
Assess material to test

- 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



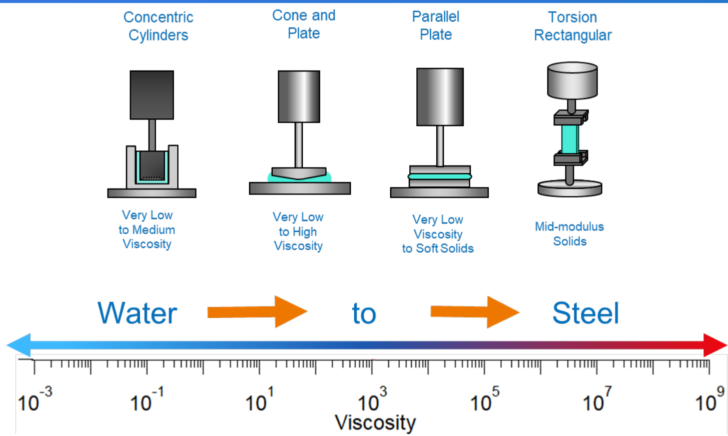
Concentric Cylinders (or Cups) and Rotors (or Bobs)

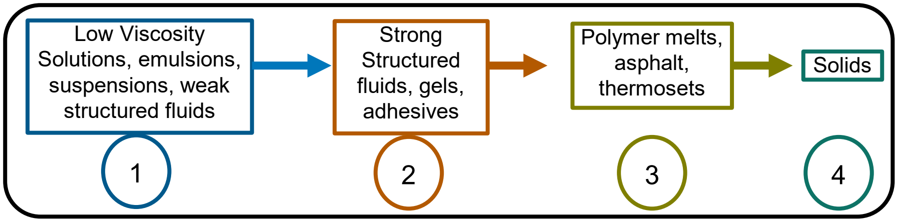
Cones and Plates



Organization of talk

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





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

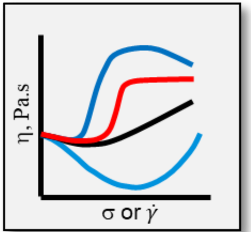
- Non-Newtonian – Viscosity is dependent on shear rate
  - Neat Fluid
  - Polymer melt
  - Structured Fluid
    - Yield stress
    - Thixotropy
    - Viscoelasticity

- <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)

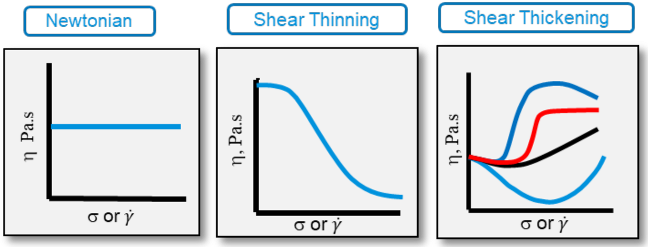
Newtonian

Shear Thinning

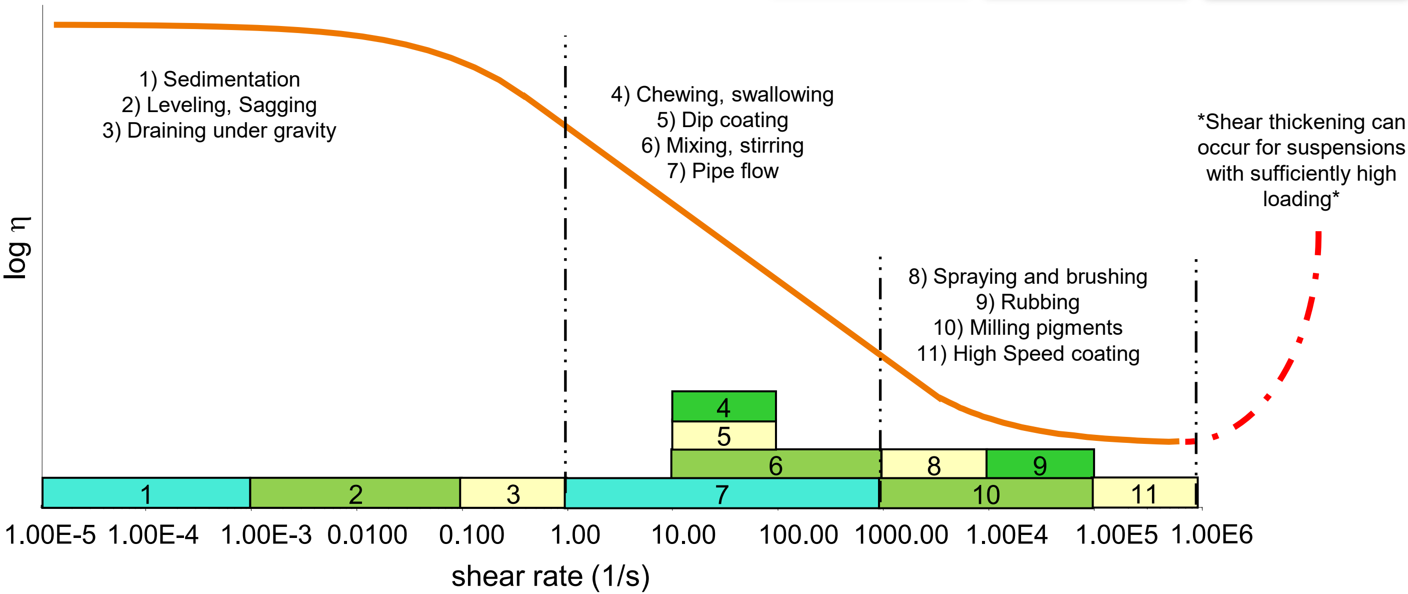
Shear Thickening



Properties of Fluids



- What shear rate?



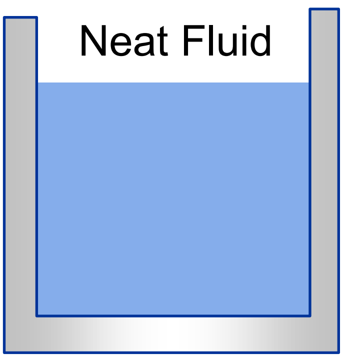
Rheology Applications

Neat Fluids

Classes of Fluids

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

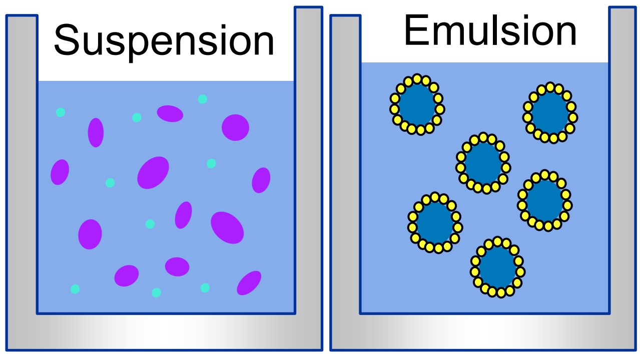
Unstructured



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:

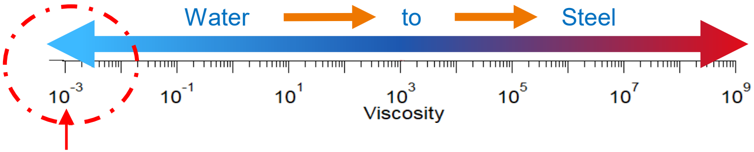
- Paints
- Coatings
- Inks
- Adhesives
- Personal Care Products
- Cosmetics
- Foods

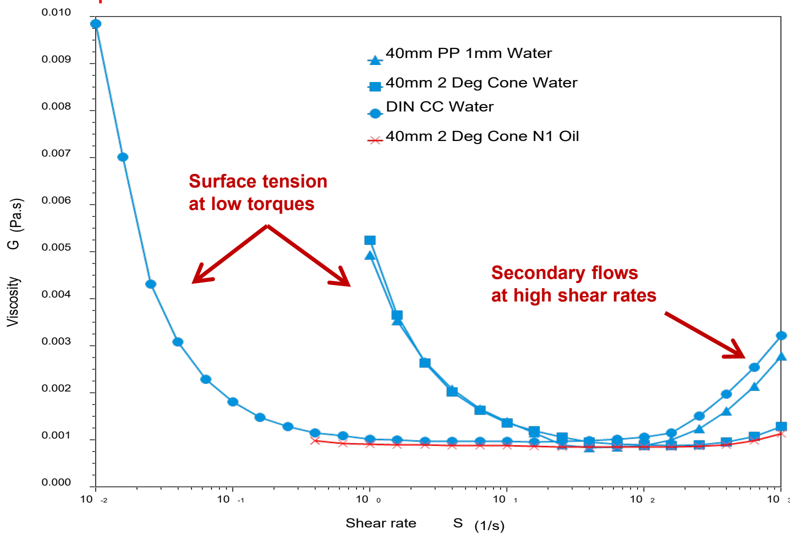
Low Viscosity
Solutions, emulsions, suspensions, weak structured fluids

1

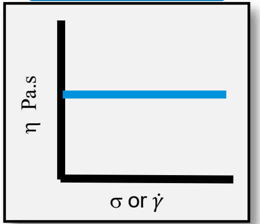
Common Neat Fluid - Water

Flow Sweep Experiment



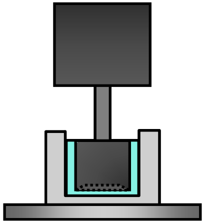


Newtonian



Right tool for the job:

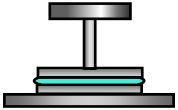
Concentric Cylinders



Very Low to Medium Viscosity

Runner up:

40-60mm parallel plates



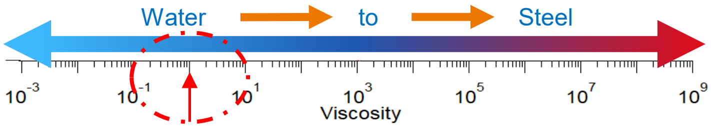
- Water is possibly the most well-known Newtonian fluid
- Viscosity is 1 mPa*s at 20°C
- <u>This is additionally observed for water-based formulations</u>
- For a more complete flow curve, a concentric cylinder geometry is required
- For plates - Use a large diameter geometry with a smaller gap

Low Viscosity
Solutions, emulsions, suspensions, weak structured fluids

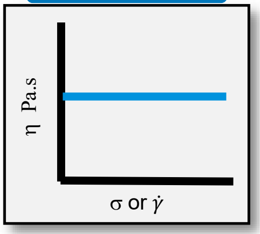
1

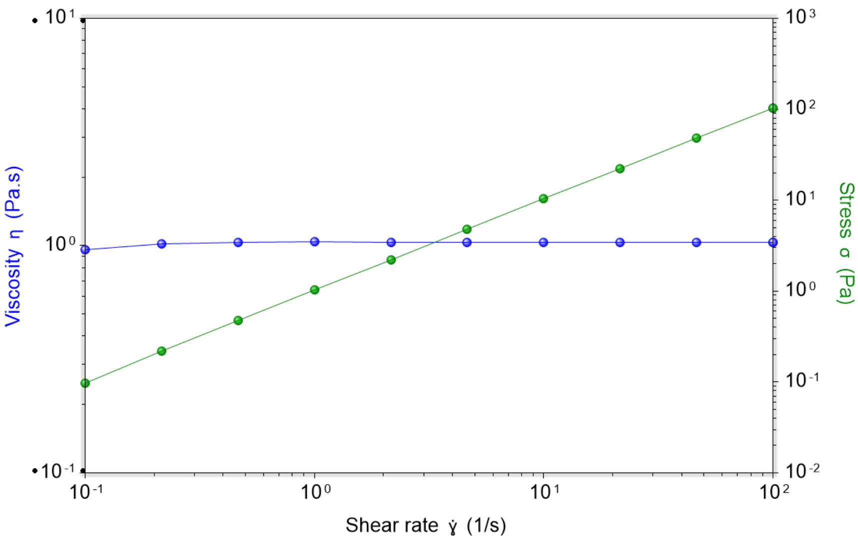
Common Neat Fluid 2 – Olive Oil

Flow Sweep Experiment



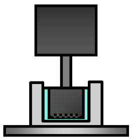
Newtonian





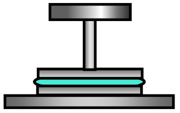
Right tools for the job:

Concentric Cylinders



OR

40-60mm parallel plates



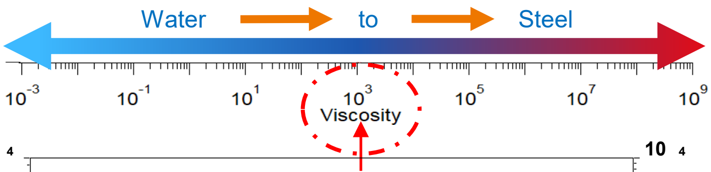
- Viscosity is 1 Pa*s at 20°C
- Oil based fluids typically don't have the same surface tension effects at with water
- Geometry selection will come down to sample volume

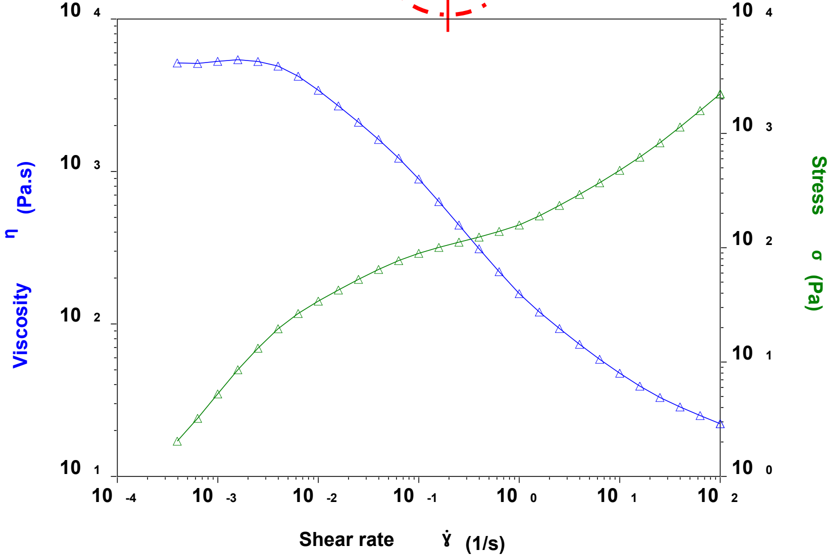
Low Viscosity
Solutions, emulsions, suspensions, weak structured fluids

1

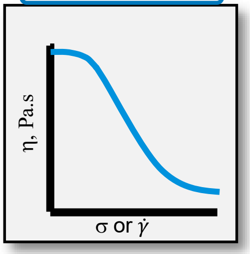
Common Neat Fluid 3 – Honey

Flow Sweep Experiment



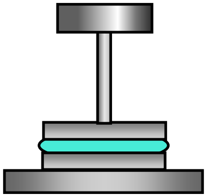


Shear Thinning



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

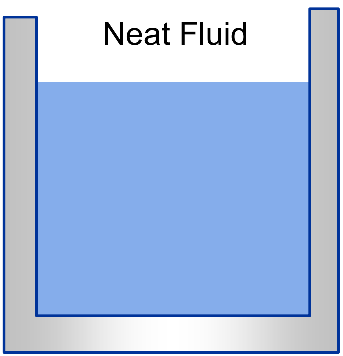
Structured Fluids

Classes of Fluids

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

We will now turn our attention to structured fluids

Unstructured



Examples are:

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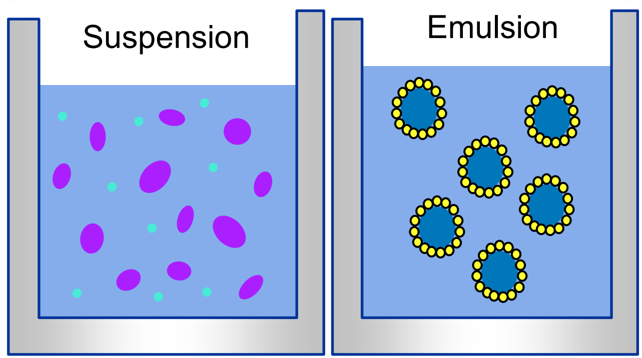
- Oil
- Honey

Structured



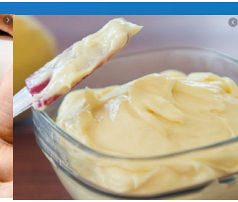
- Three categories of Structured Fluids
  - Suspension - Solid particles in a fluid
  - Emulsion - Fluid in a fluid
  - Foam - Gas in a fluid (or solid)

Examples are:

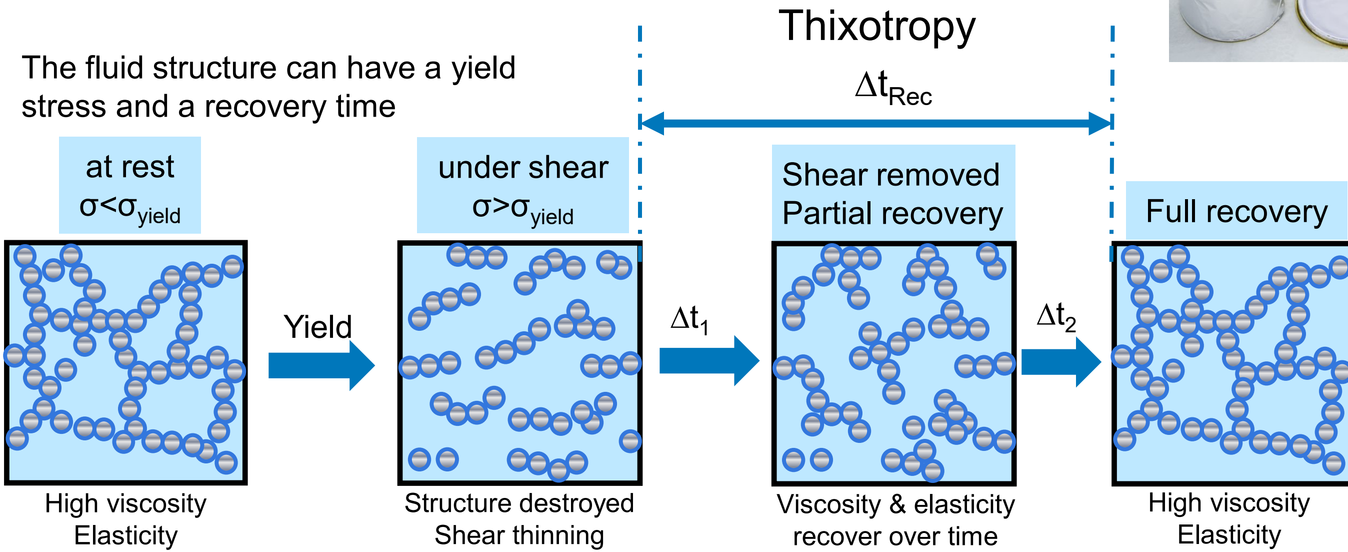
- Paints
- Coatings
- Inks
- Adhesives
- Personal Care Products
- Cosmetics
- Foods

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

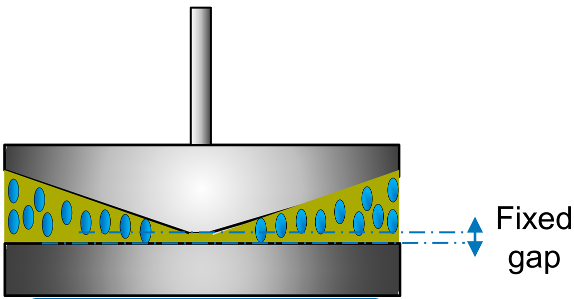


Properties of Structured Fluids

- 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

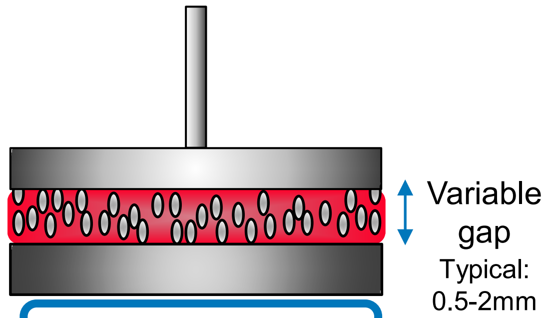
Cone and Plate



Truncation Height = Gap

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

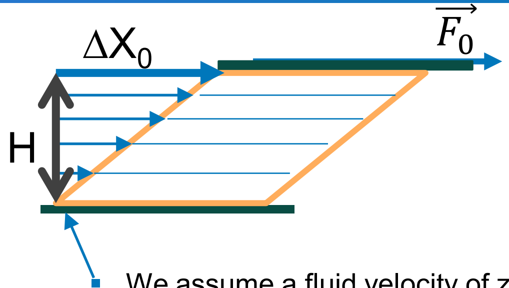
Parallel Plates



Gap can be adjusted
Common gap at 0.5-2mm

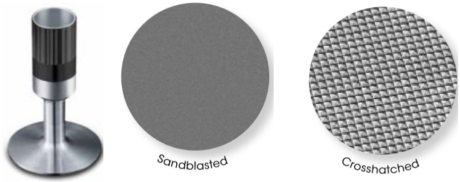
Properties of Structured Fluids

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



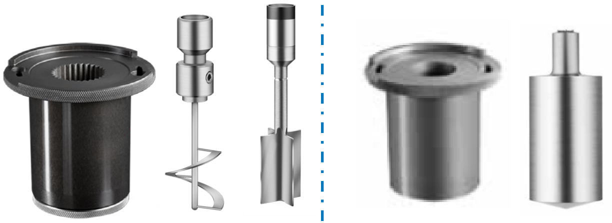
- We assume a fluid velocity of zero at the wall
- Slip is the occurrence of non-zero wall velocity

Parallel Plates:



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

Concentric Cylinder:

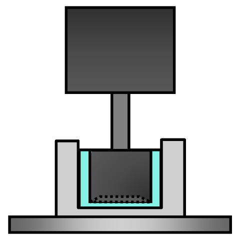


If using concentric cylinder:
- Use sandblasted cup and rotor
- Use grooved cup with vane or helical rotor

Properties of Structured Fluids

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

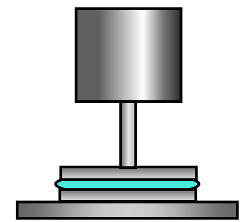
Concentric Cylinders



Very Low to Medium Viscosity

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

Parallel Plate

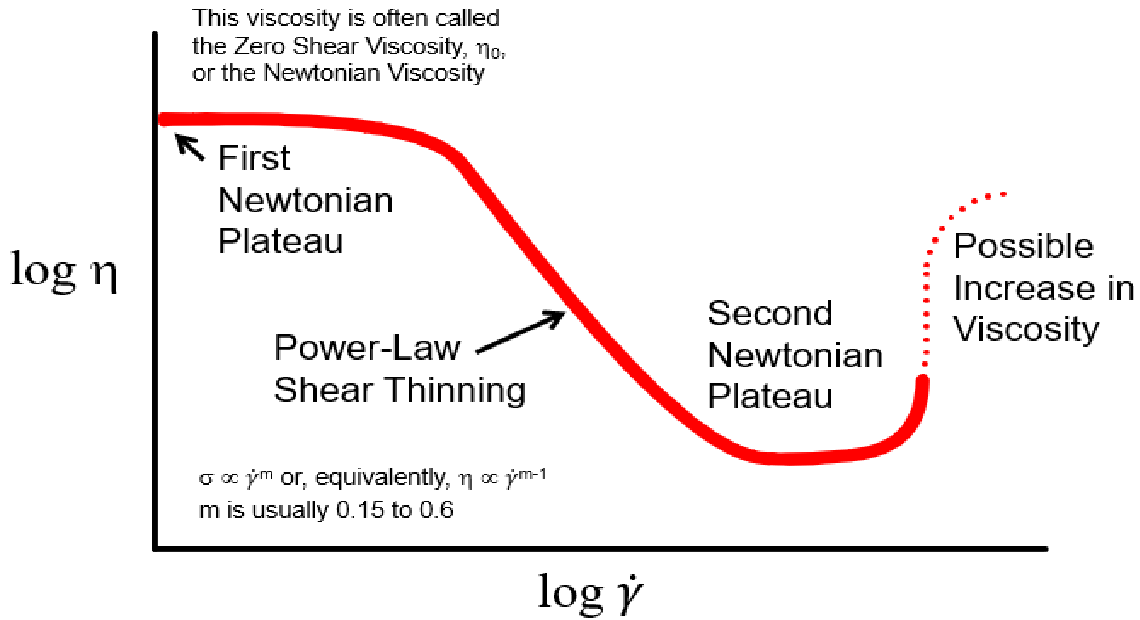


Very Low Viscosity to Soft Solids

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

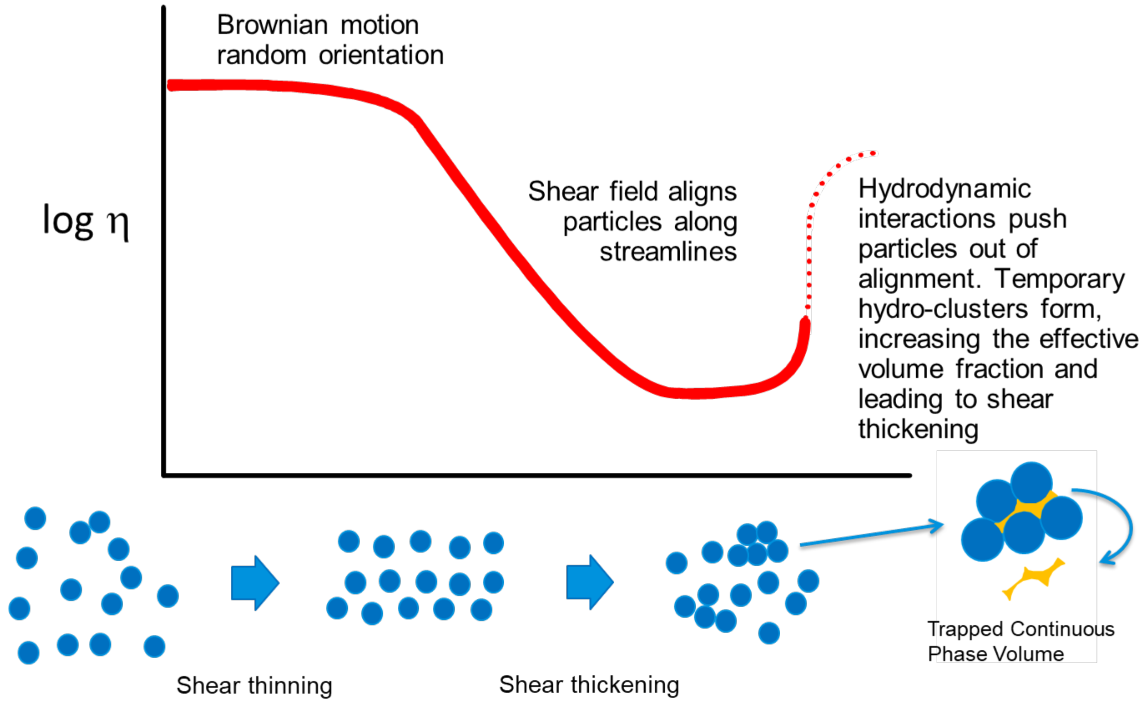
***Additionally noting surface tension effects for parallel plates

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

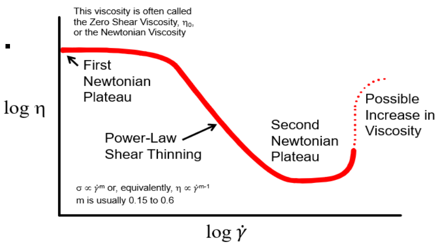
General Viscosity Curve for Suspensions



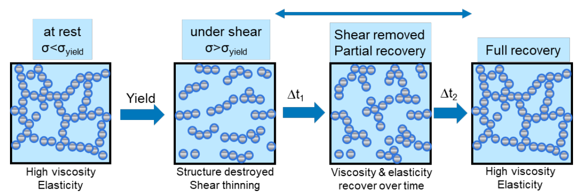
Characterization of Structured Fluids

- 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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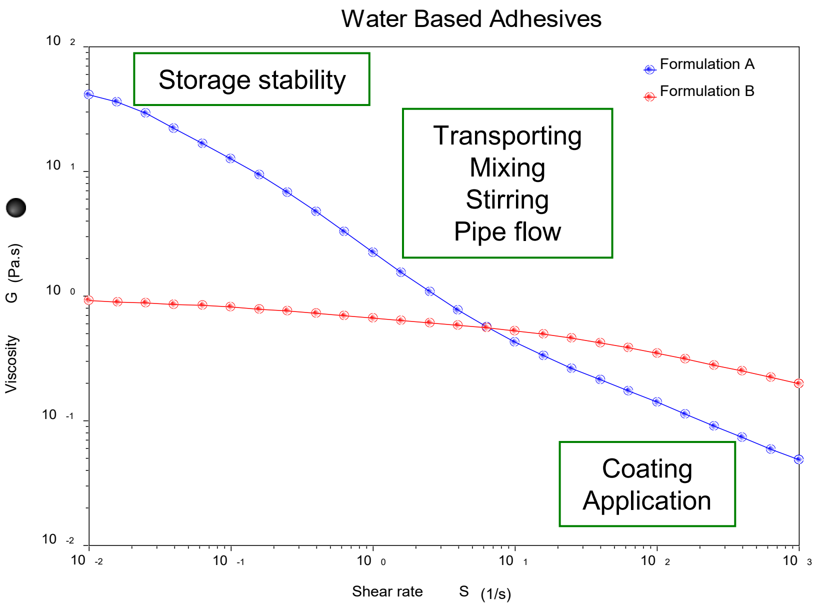

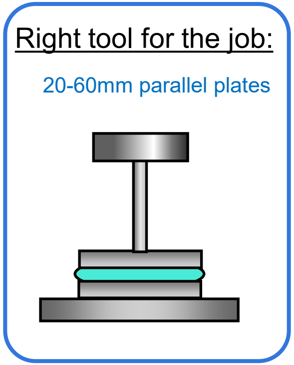

Properties of Structured Fluids

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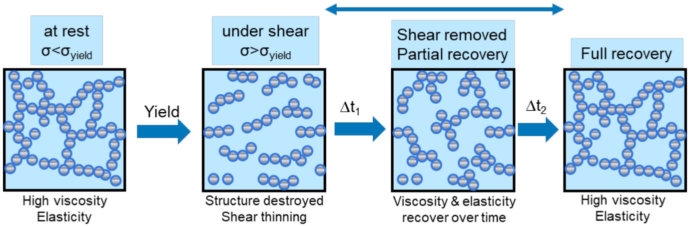

- Common methods
  - Stress ramp → – Ramp between initial and final stress within time interval
  - Stress sweep – Rotational stress is stepped in increments
  - Shear rate ramp – Ramp between initial and final stress within time interval
  - Dynamic stress/strain sweep – Oscillate at strain within LVR,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

- Overall, we want to characterize several relevant properties of structured fluids:
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  - **II. Yield Stress**
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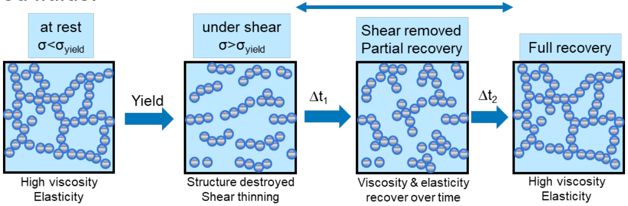
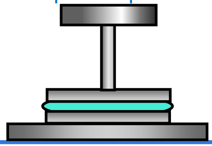
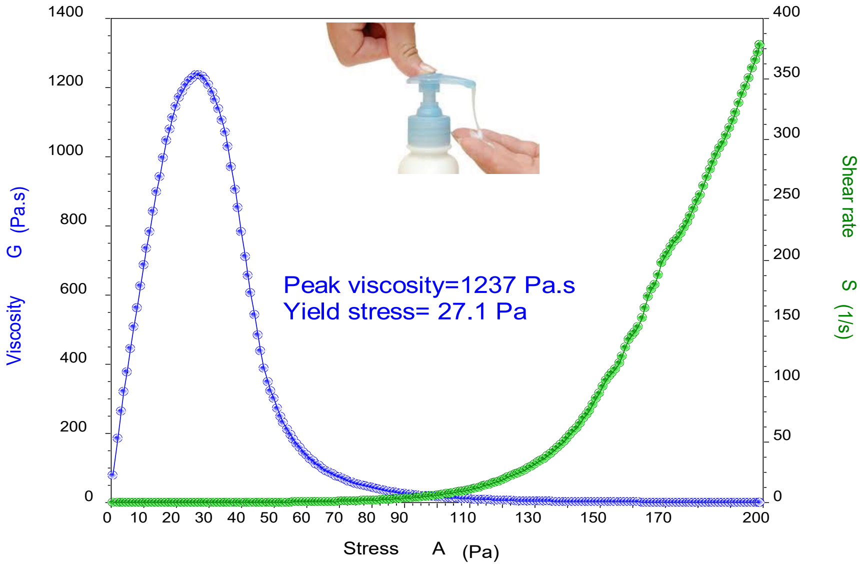


- Common methods
  - **Stress ramp #1**
  - Stress sweep
  - Shear rate ramp
  - Dynamic stress/strain sweep

- 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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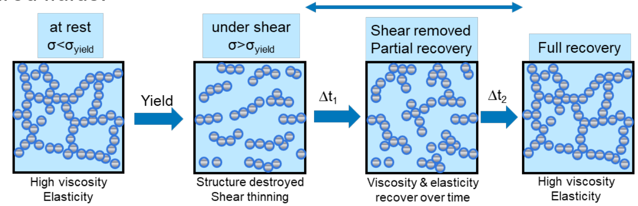
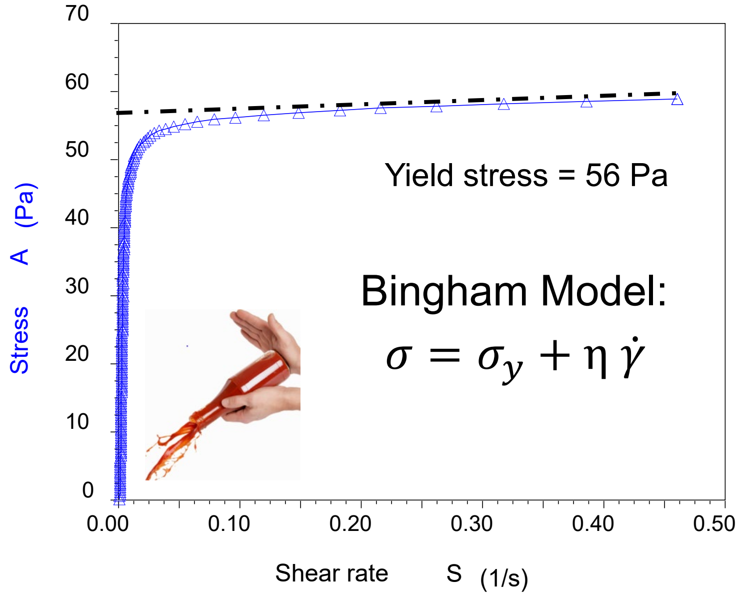
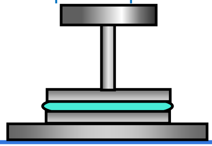


- Common methods
  - **Stress ramp #2**
  - Stress sweep
  - Shear rate ramp
  - Dynamic stress/strain sweep



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



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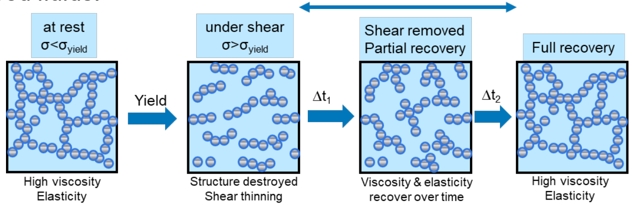
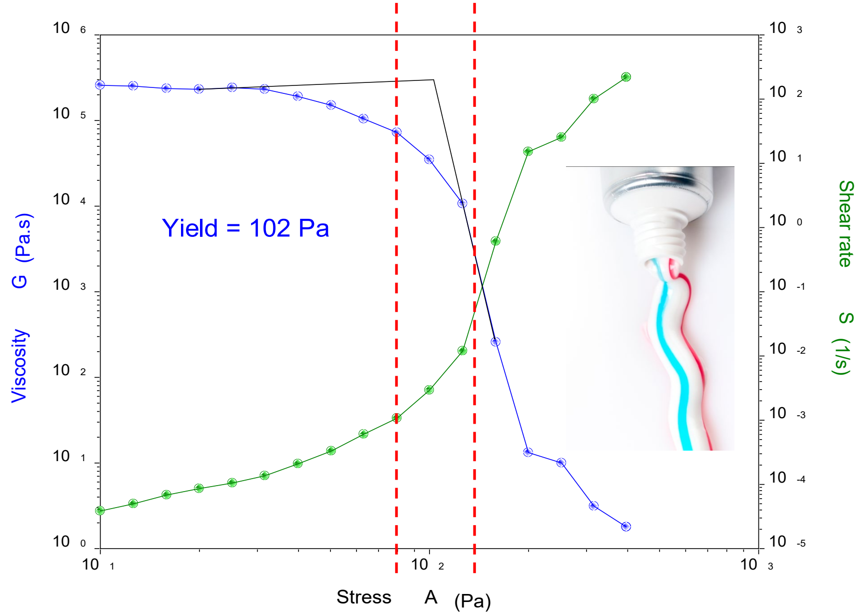
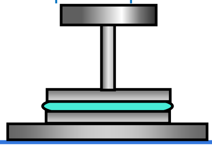


- Common methods
  - Stress ramp
  - **Stress sweep #1**
  - Shear rate ramp
  - Dynamic stress/strain sweep

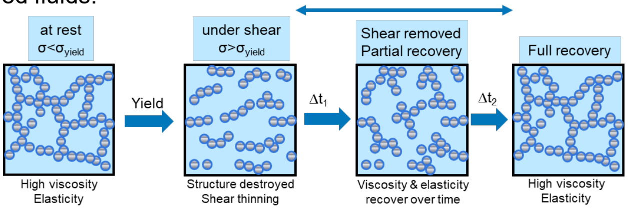


Right tool for the job:
20-60mm crosshatched parallel plates



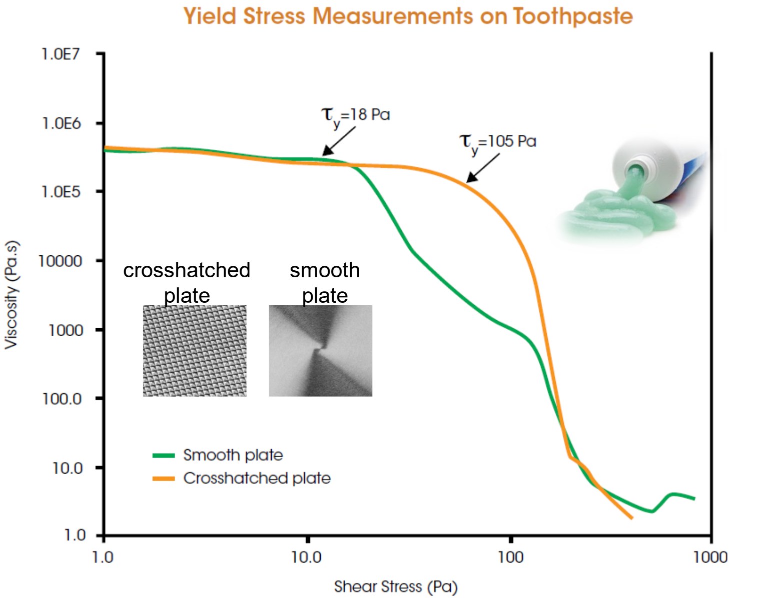
Properties of Structured Fluids

- 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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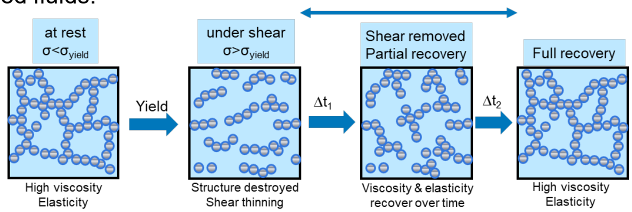
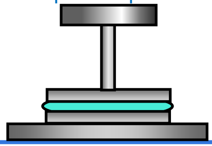
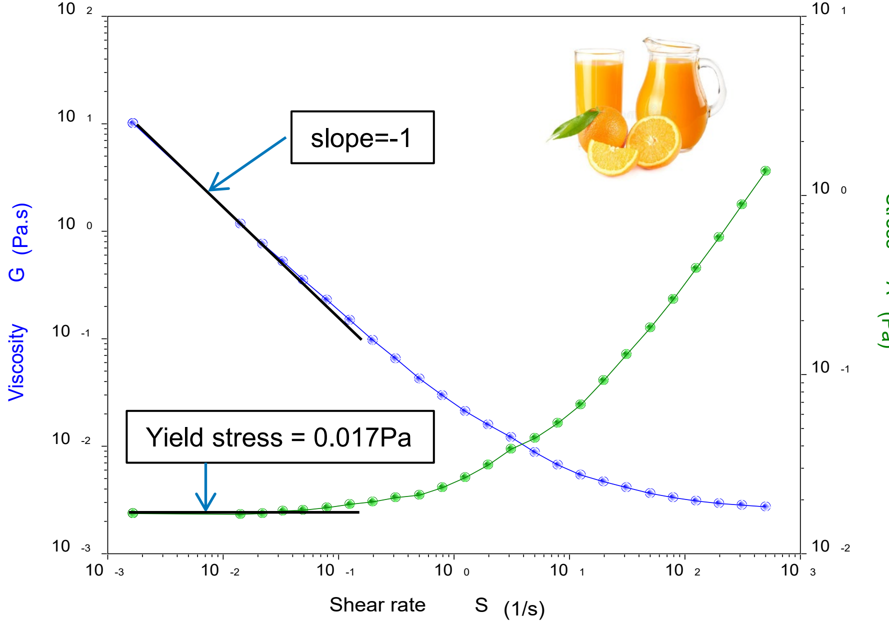


- Common methods
  - Stress ramp
  - Stress sweep #2
  - **Shear rate ramp**
  - Dynamic stress/strain sweep

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

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





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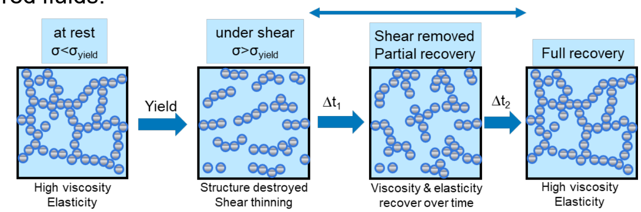
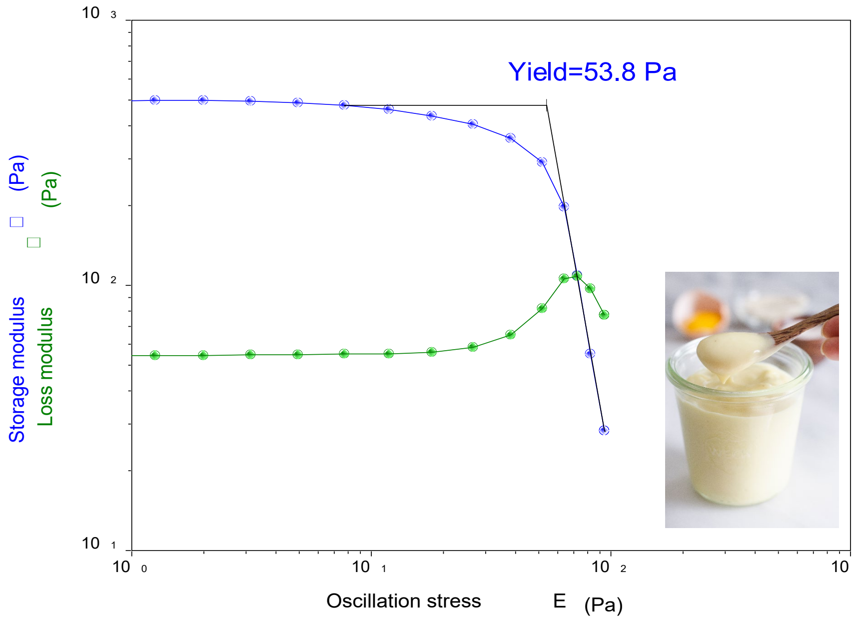


- Common methods
  - Stress ramp
  - Stress sweep #2
  - Shear rate ramp
  - **<u>Dynamic stress/strain sweep</u>**

> - 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



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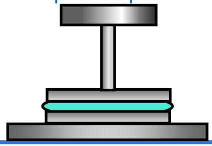

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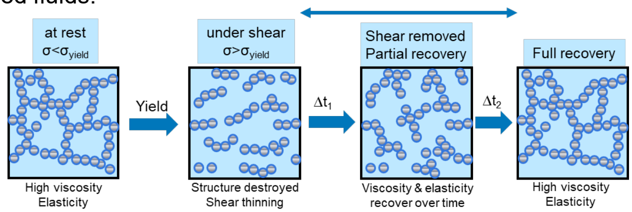

- Common methods
  - **Stepped Flow (3 step)**
  - Stepped Dynamic (3 step)
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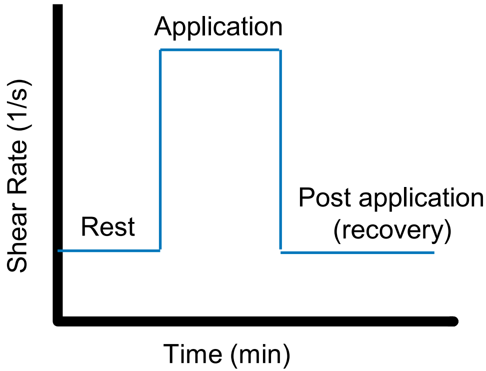
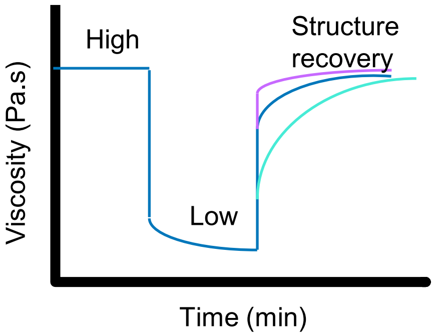
  - Dynamic time sweep after pre-shear

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

Properties of Structured Fluids

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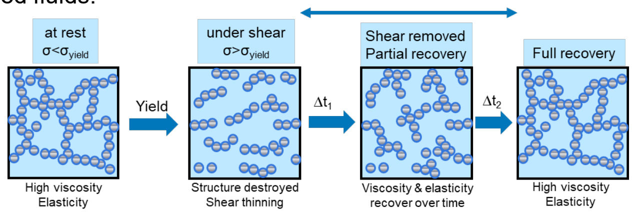

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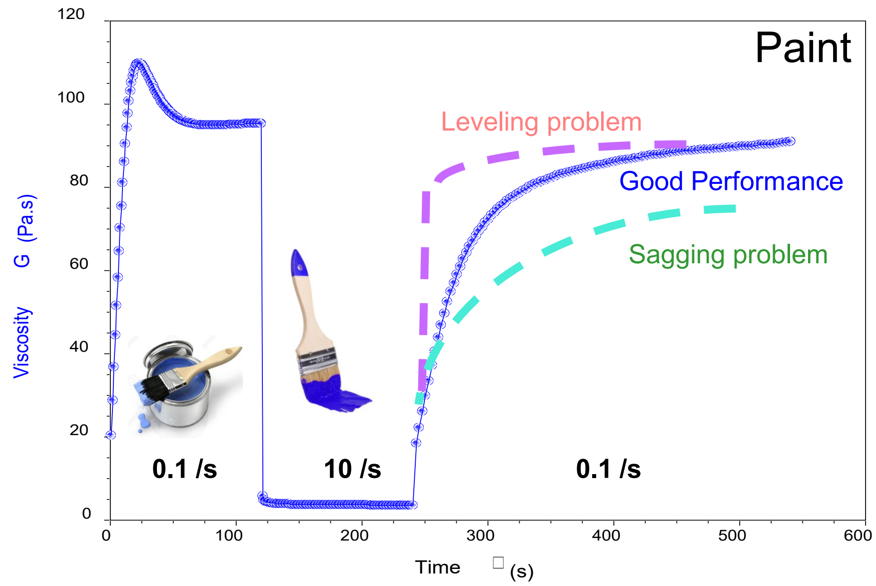

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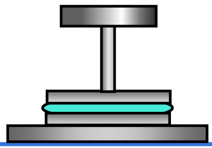

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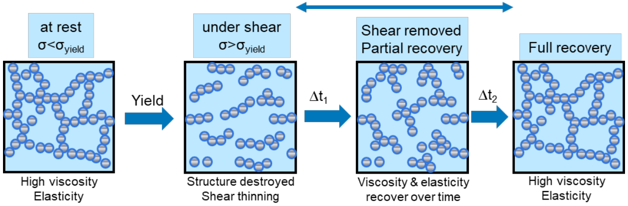

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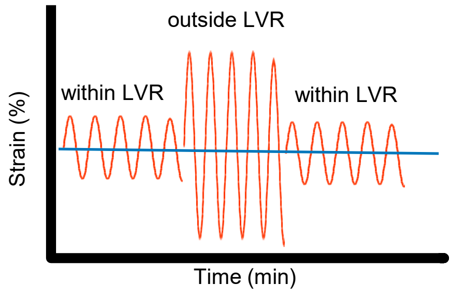
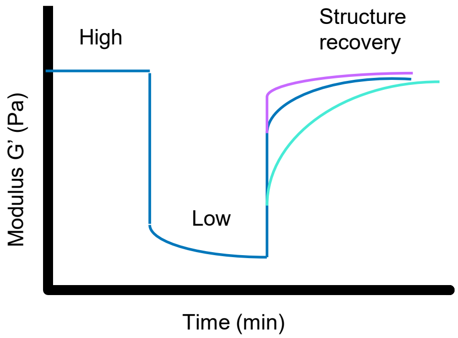
Stepped Dynamic (3 step)





Experimental:

Step 1: Oscillate within LVR, state of rest

Step 2: Oscillate outside LVR, structural destruction

Step 3: Oscillate within LVR, structural regeneration

Properties of Structured Fluids

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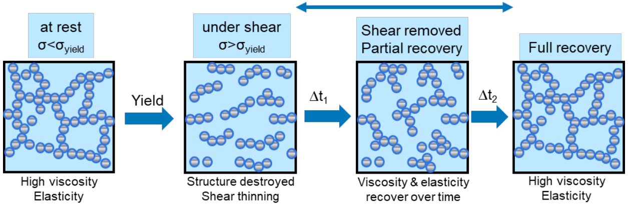

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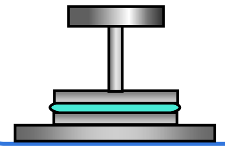

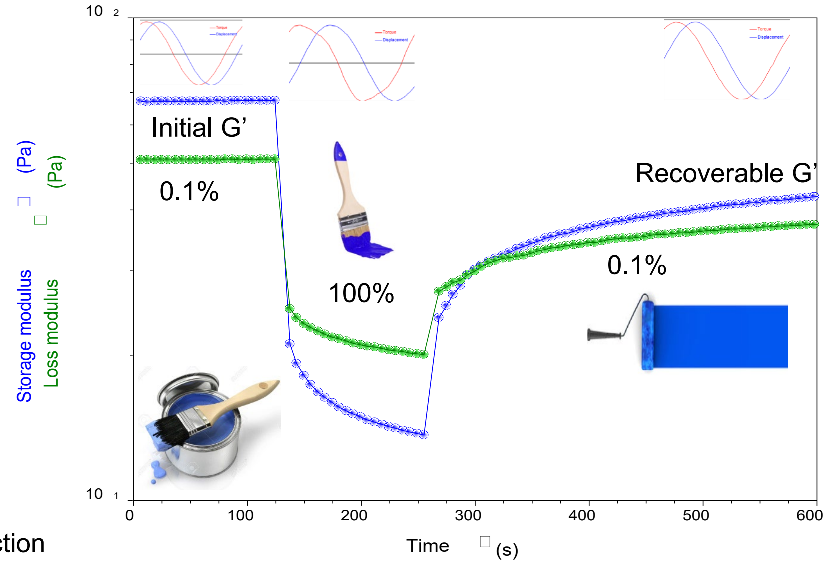

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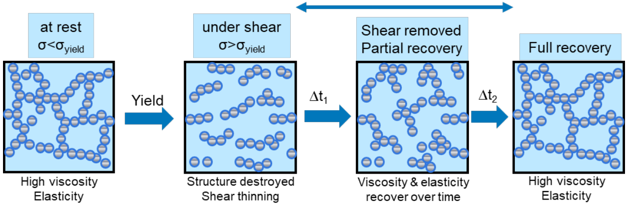

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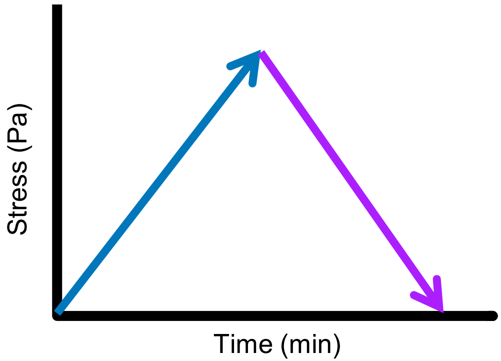

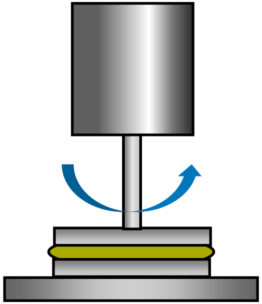

- Ramp shear stress linearly from zero up until sample flows, then ramp stress back down to zero
- Thixotropic index is measured by taking the area between the up and down stress curves
- TA Tech Tip:

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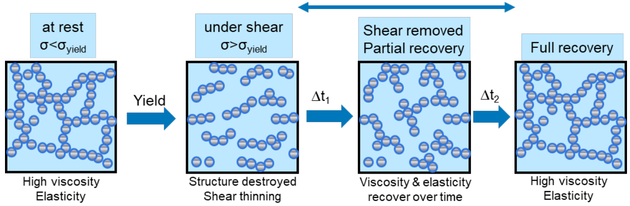

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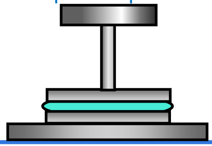
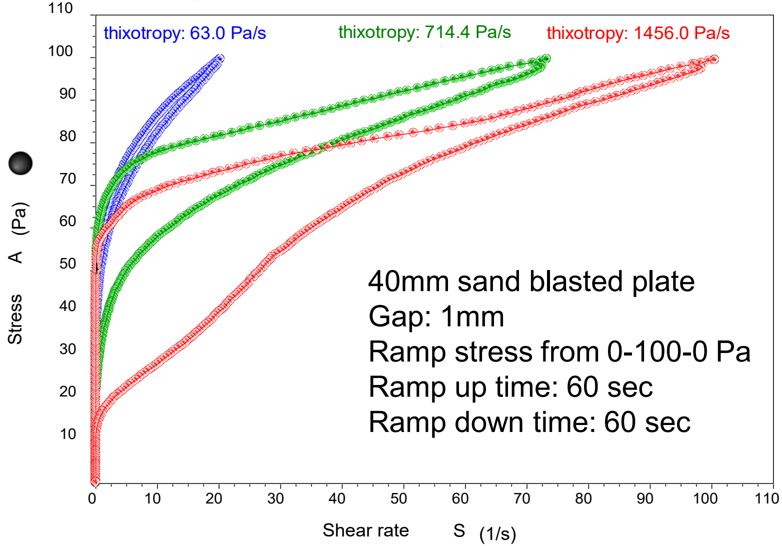


Mayonnaise, Yellow Mustard, and Ketchup



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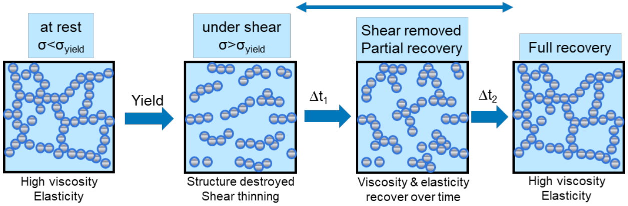

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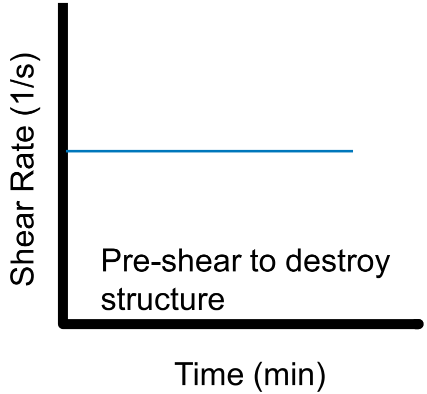

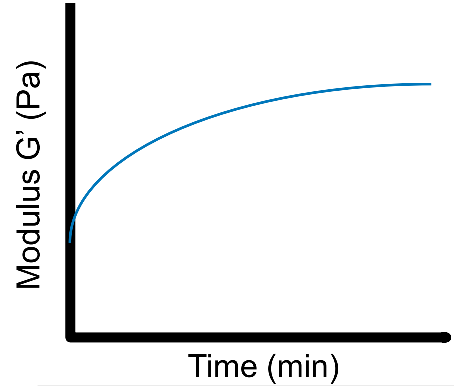

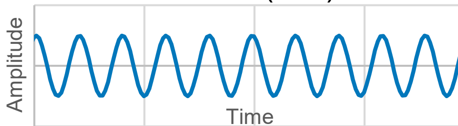

Experimental:

Step 1: Preshear sample for some duration to destroy structure

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

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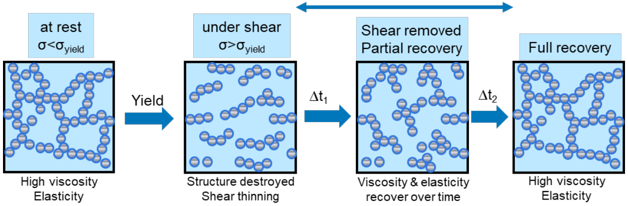

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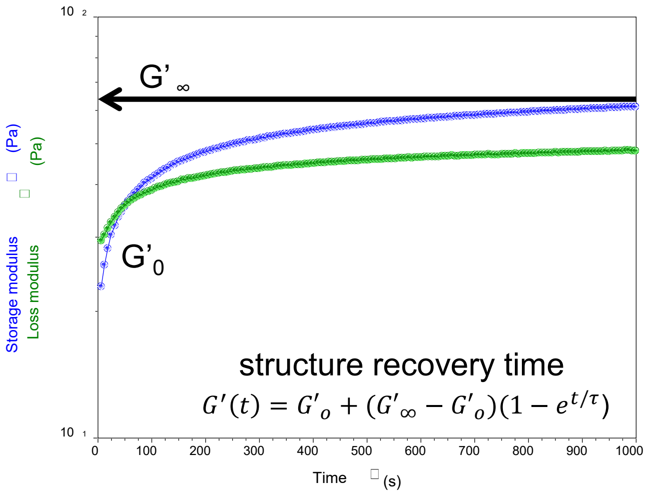

$$G'(t) = G'_o + (G'_\infty - G'_o)(1 - e^{t/\tau})$$

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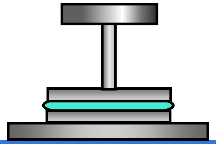

- Monitor the increase of the G' as a function of time.
- Thixotropic recovery is described by meausring the recovery time (τ)

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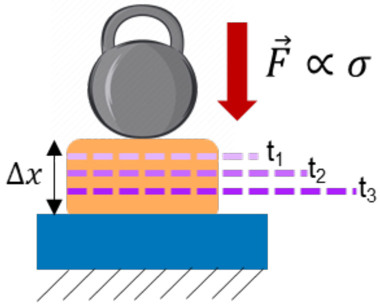
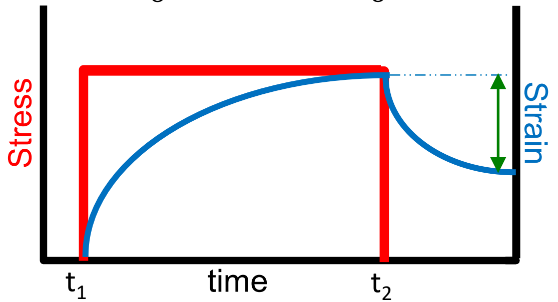
- Common methods
  - **Creep Recovery**
  - Normal Stress
  - Oscillation Frequency Sweep
  - Oscillation Temperature Ramp



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

- Common methods
  - **Creep Recovery**
  - Normal Stress
  - Oscillation Frequency Sweep
  - Oscillation Temperature Ramp

- 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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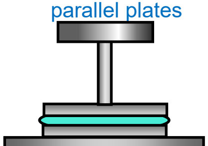

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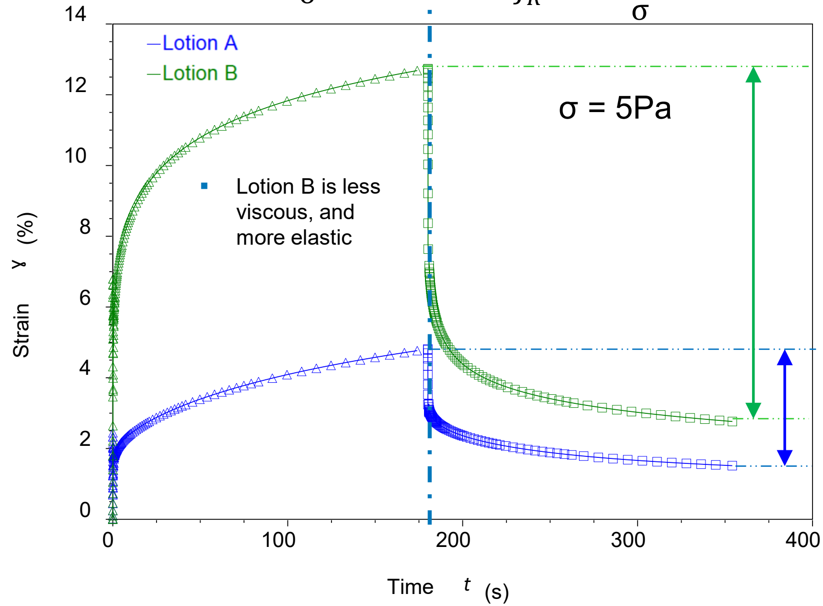

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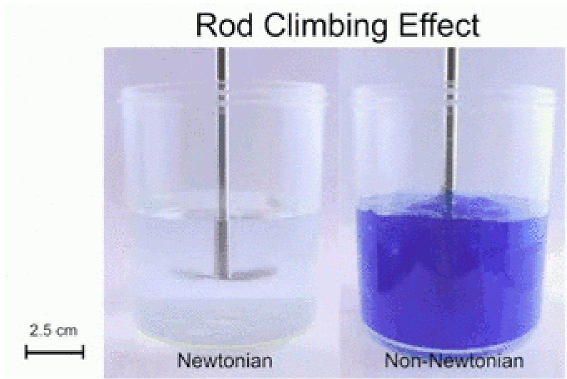
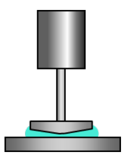


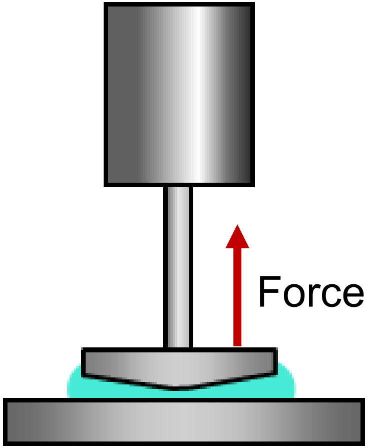
Normal Stress Constant

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

<u>Right tool for the job:</u>
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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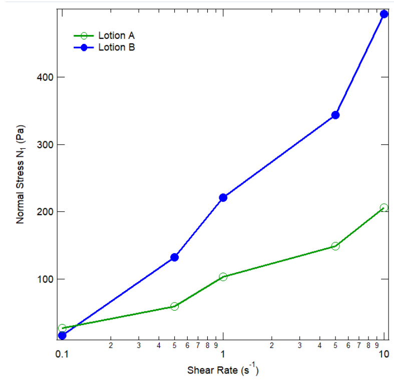

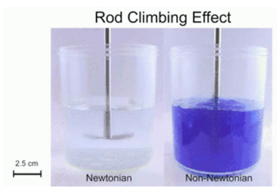

Right tool for the job:

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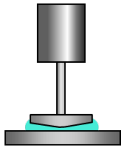

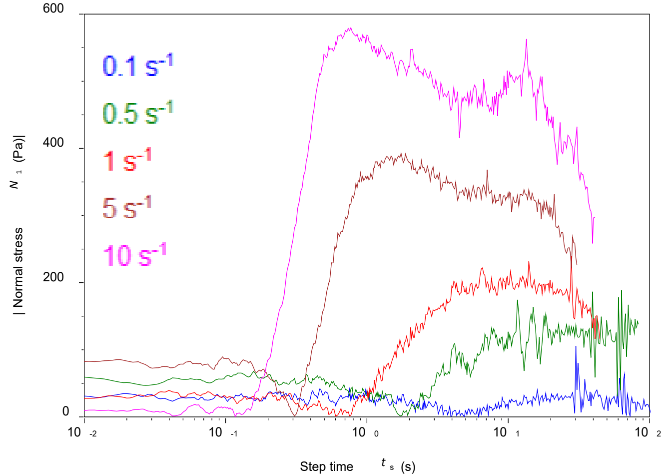

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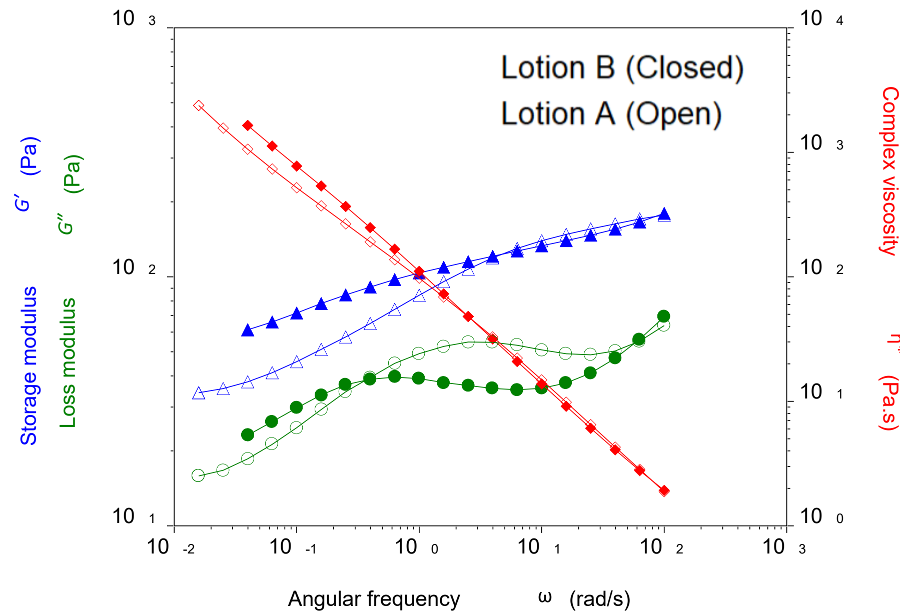

- The complex viscosity of the two lotions is very similar
- However, the viscoelasticity is very different between the two

<u>Right tool for the job:</u>
20-60mm sandblasted parallel plates

Properties of Structured Fluids

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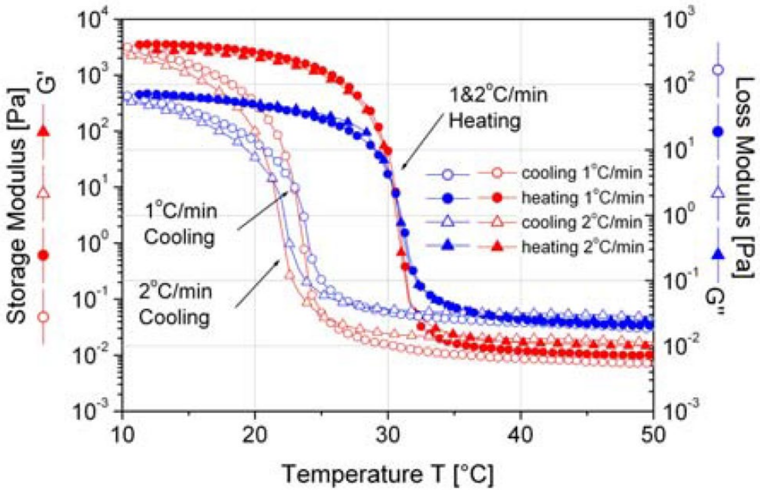
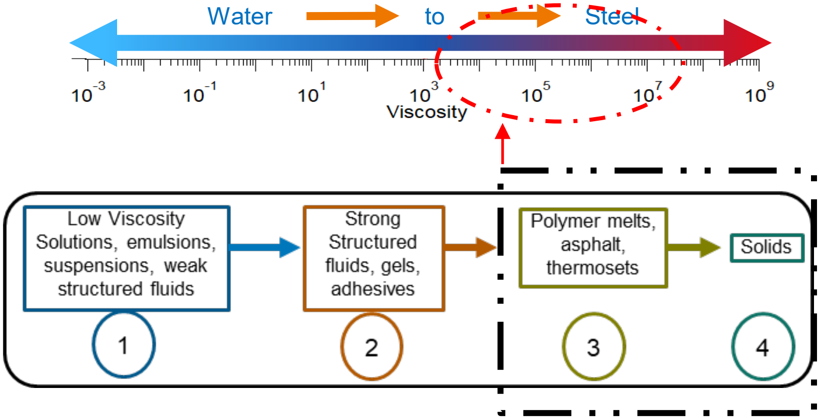


Rheology Applications

Polymers

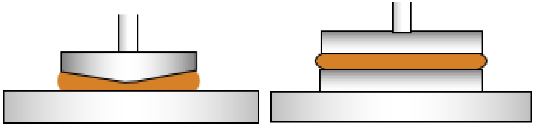
Rheology Applications
2. Polymers



Three main reasons for rheological testing:

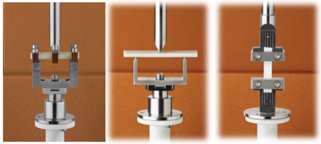
- **Characterization**
  MW, MWD, formulation, state of flocculation, etc.
- **Process performance**
  Extrusion, blow molding, pumping, leveling, etc.
- **Product performance**
  Strength, use temperature, dimensional stability, settling stability, etc.

- 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)

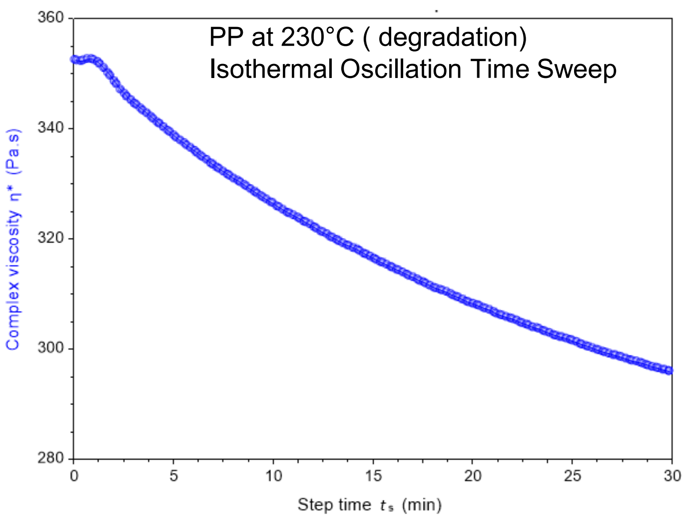
Torsion rectangular and cylindrical clamps



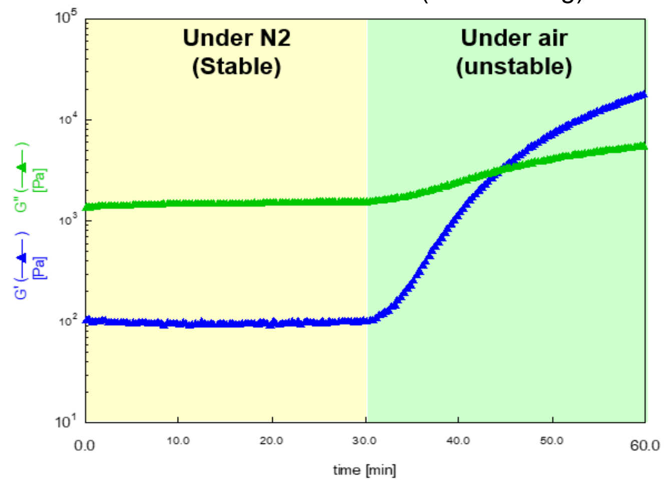
DMA cantilever, 3-point bending and tension clamps

- **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

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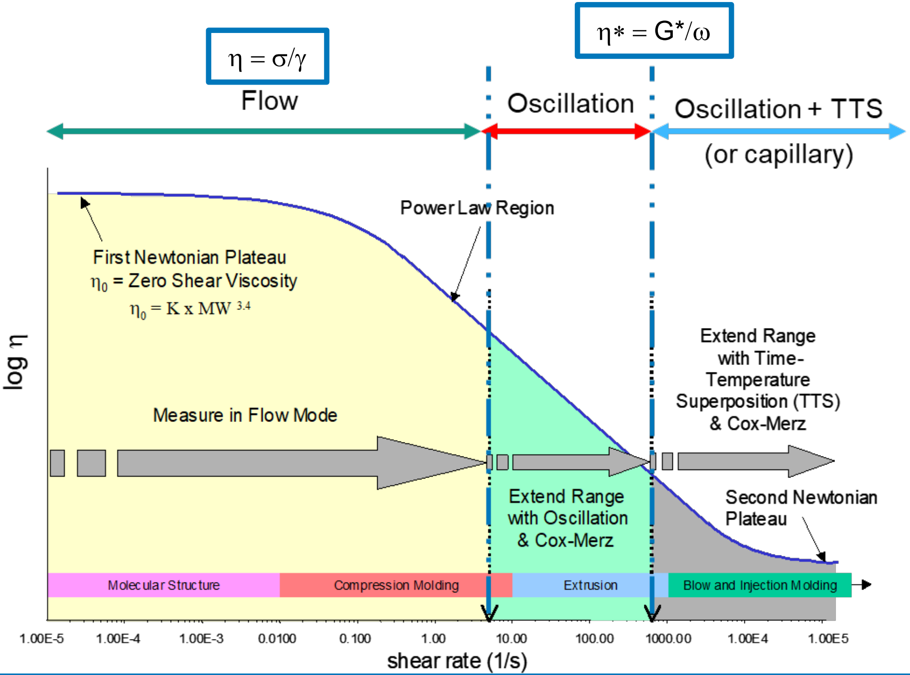

- **Edge Fracture:**

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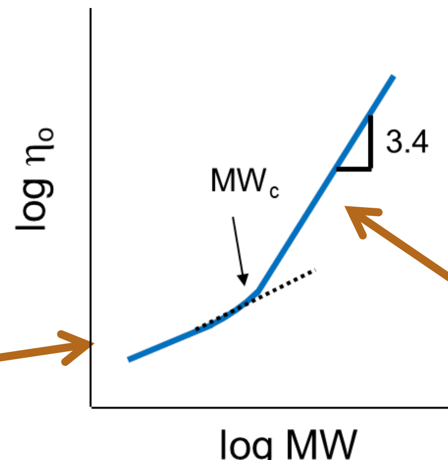
- Sensitive to Molecular Weight, Mw
- For Low MW (no Entanglements) η_0 is proportional to Mw
- For MW > Critical Mw_c, η_0 is proportional to $Mw^{3.4}$



$\eta_0 = K \cdot Mw$

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

Time and Temperature Relationship (Viscoelasticity)

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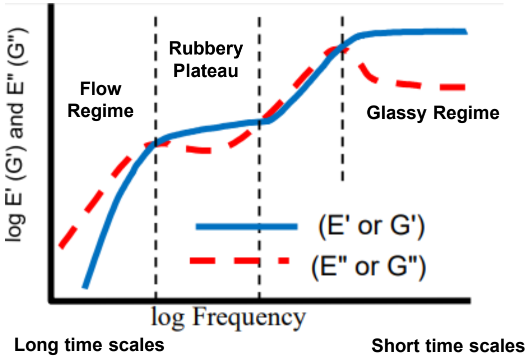

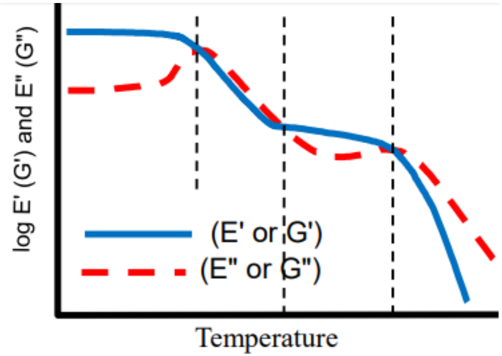

- At low frequencies molecular relaxation is at large time scales- **large length scales**
- At high frequencies molecular relaxation is at short time scales – *small length scales*
- Commonality between Frequency and Temperature is the timescale of molecular relaxation (Polymer chains diffusing)

- 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

Molecular weight and Viscoelasticity

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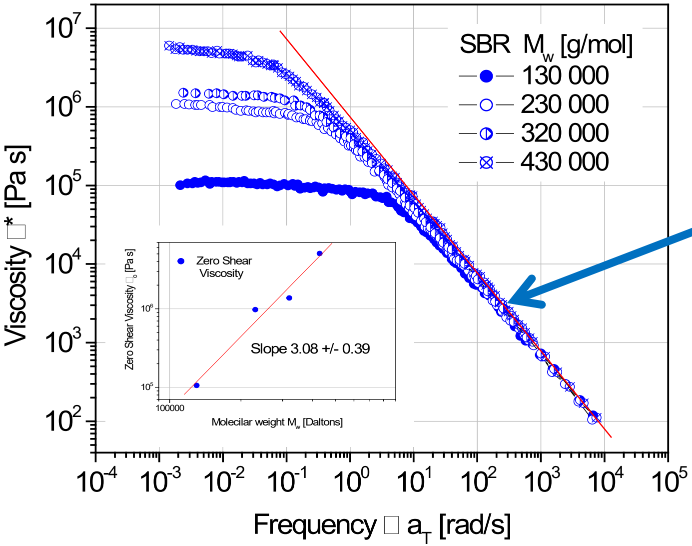
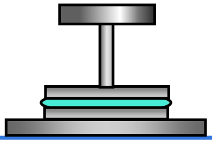
- The zero shear viscosity increases with increasing molecular weight. TTS is applied to obtain the extended frequency range.



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

Right tool for the job:

25mm parallel plates



Molecular weight and Viscoelasticity

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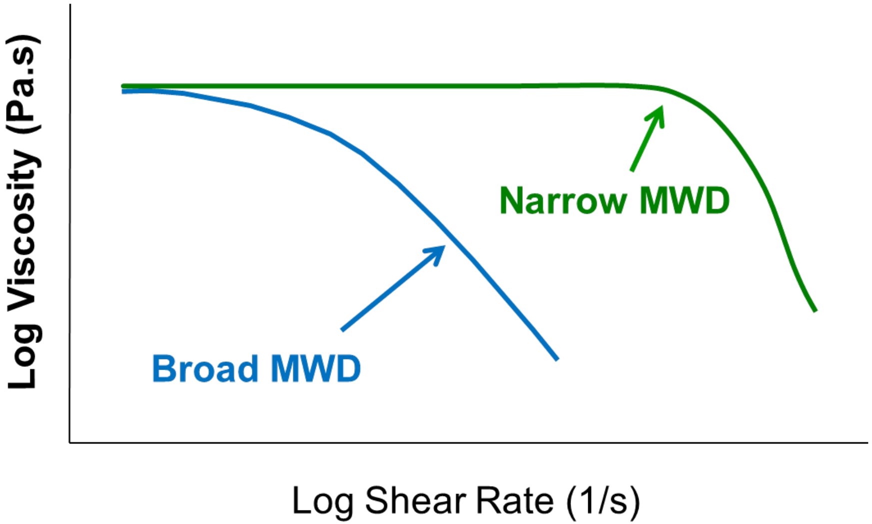
- A Polymer with a broad MWD exhibits non-Newtonian flow at a lower rate of shear than a polymer with the same η_0, but has a narrow MWD.



Molecular weight and Viscoelasticity

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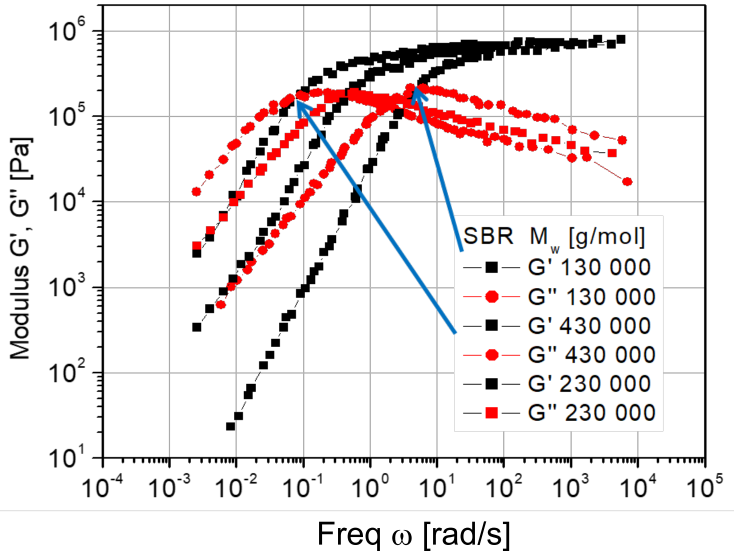
- The G‘ and G“ curves are shifted to lower frequency with increasing molecular weight.



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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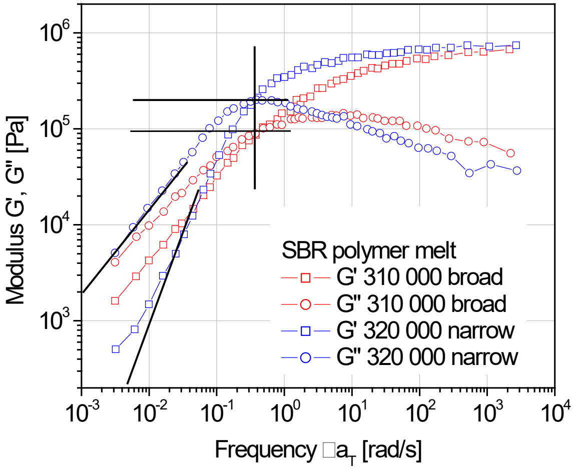
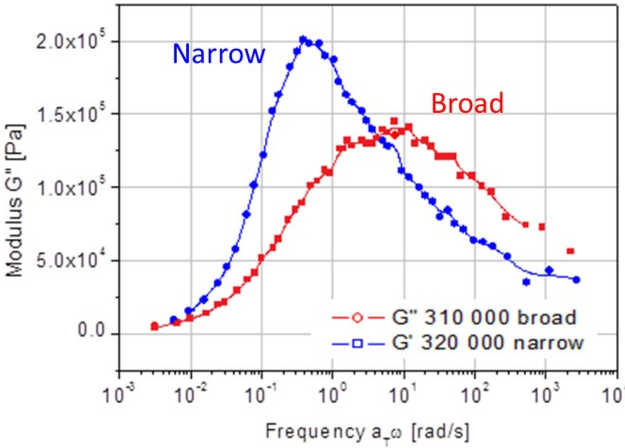


- The maximum in G“ is a good indicator of the broadness of the distribution



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

Waters™ | TA Instruments

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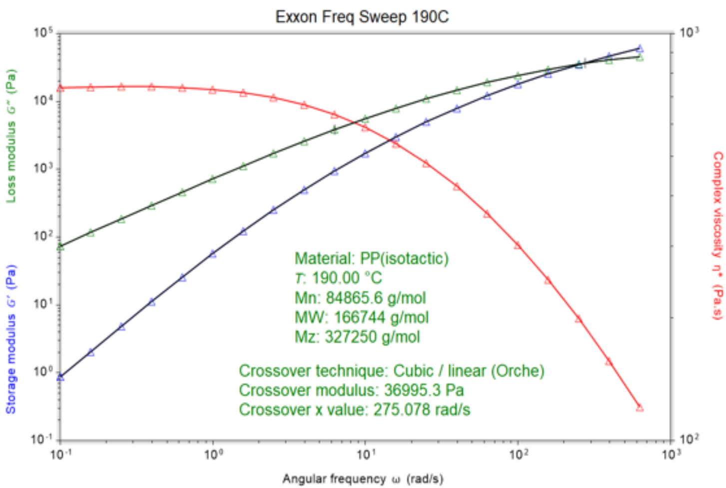
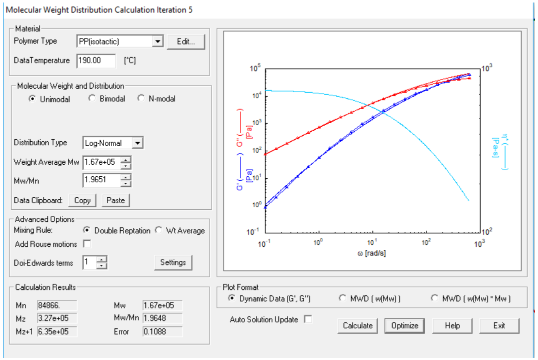


- Using rheological measurements to quantify molecular weight and molecular weight distribution



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

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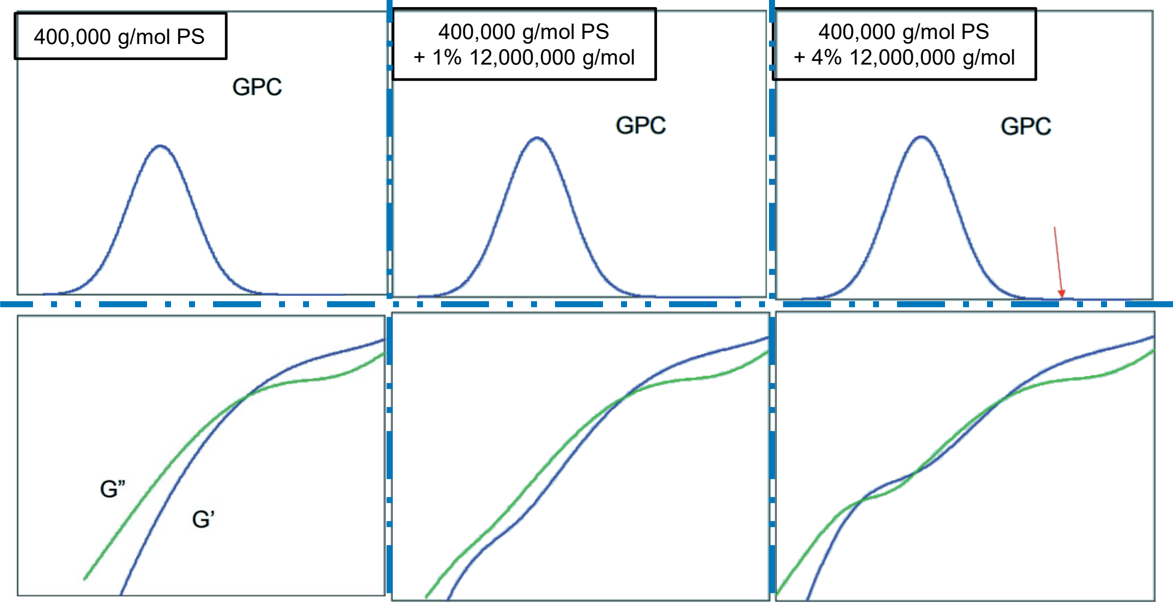
Frequency Sweep

- 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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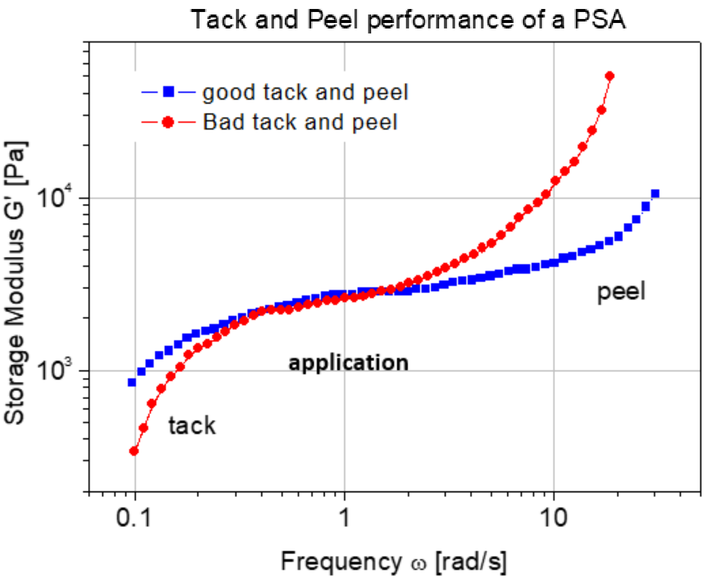
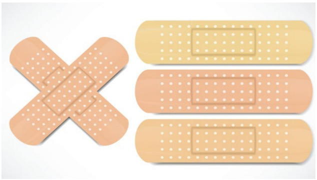


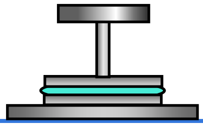
Tack and Peel of Pressure Sensitive adhesive

- 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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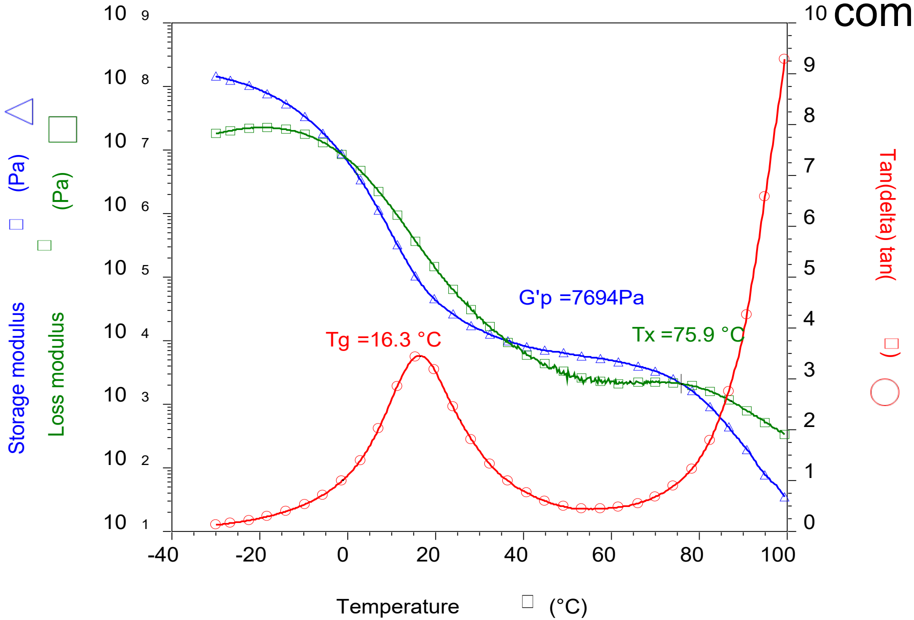
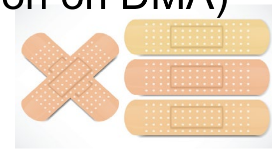
<u>Tack and Peel of Pressure Sensitive adhesive</u>

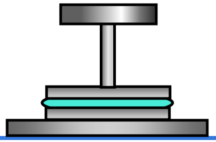
- Temperature Ramp (more common on DMA)





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

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



Molecular weight, Viscoelasticity, and Curing

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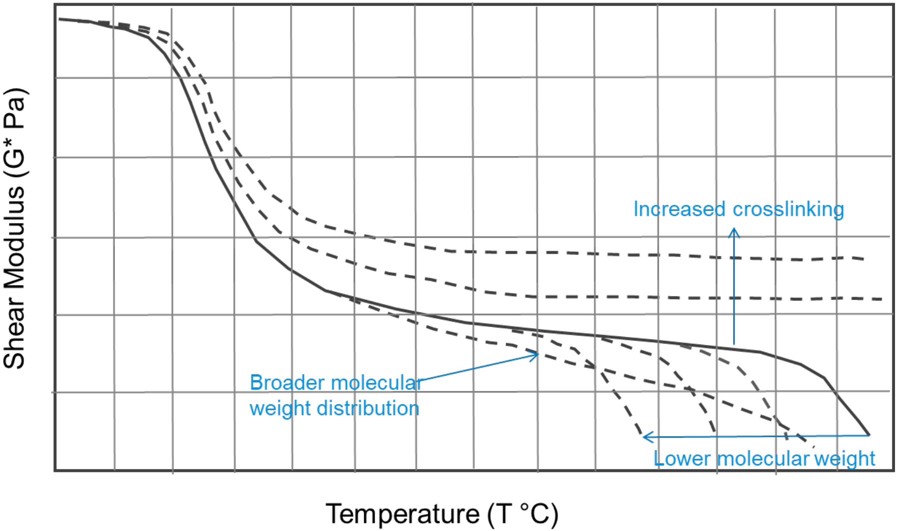

- **Temperature Ramp**
  - Correlates with polymer molecular structure: Mw, MWD, and crosslinking

- **<u>Segway into "Thermosets, curing and gelation" section</u>**

Molecular weight, Viscoelasticity, and Curing

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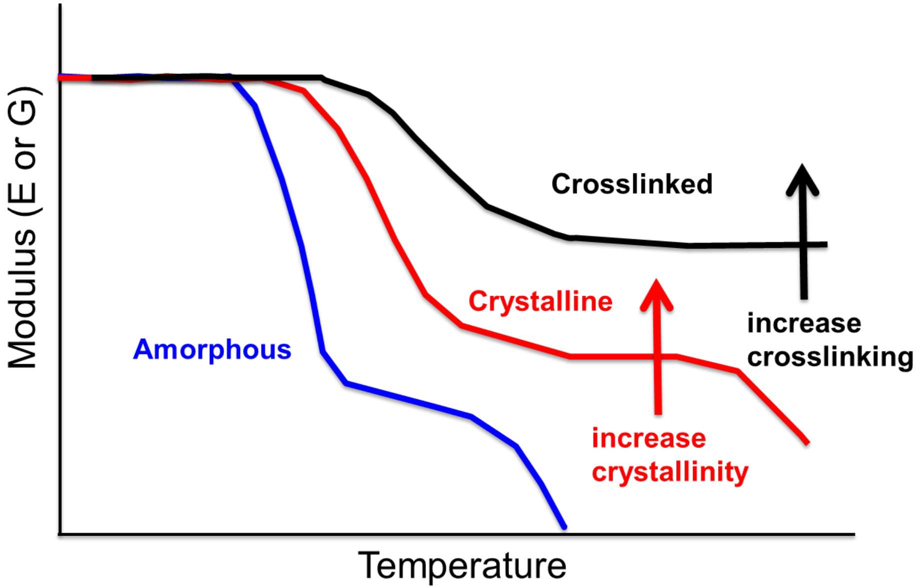

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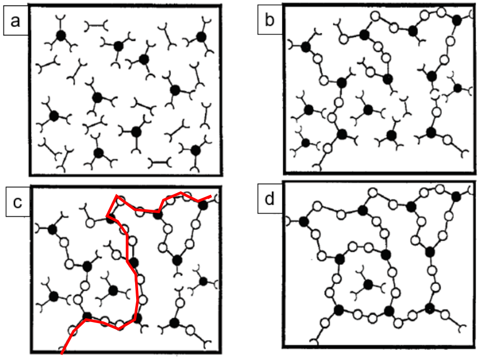
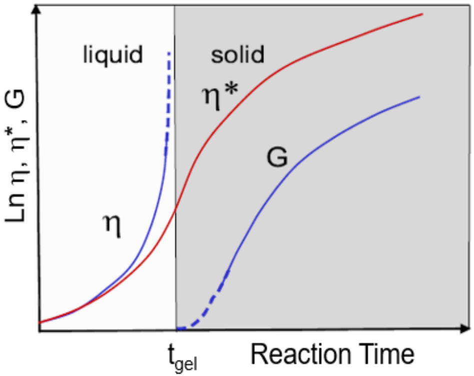
Gelation and Vitrification

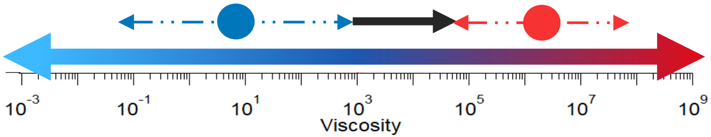


- Formation of network across span of material volume

What Rheology Measures



Viscosity can increase many orders of magnitude over duration of cure



Common Curing Experiments

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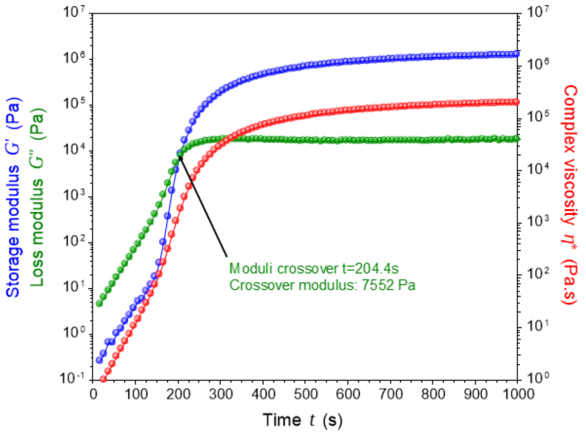
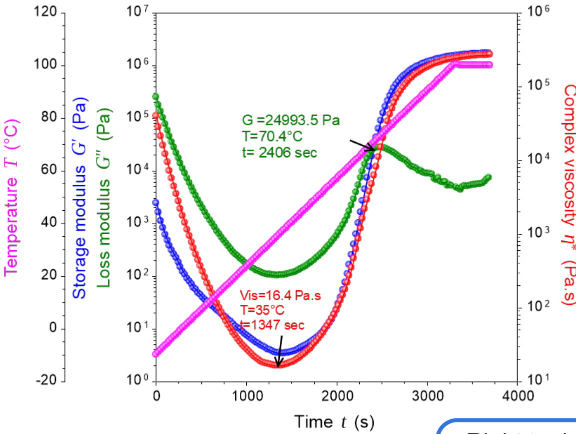
Isothermal Curing (Time Sweep)

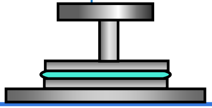


Temperature Ramp Curing



- 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

Right tool for the job:
Disposable 25mm parallel plates



Isothermal Curing Experiments

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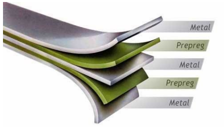

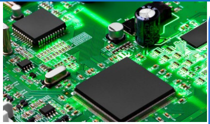

Right tool for the job:
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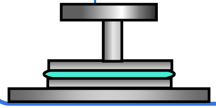
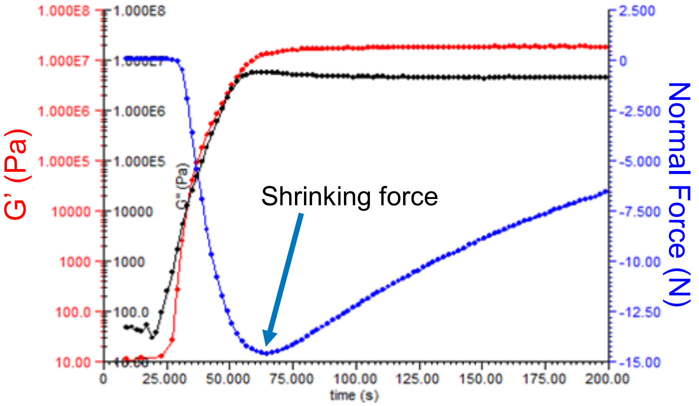
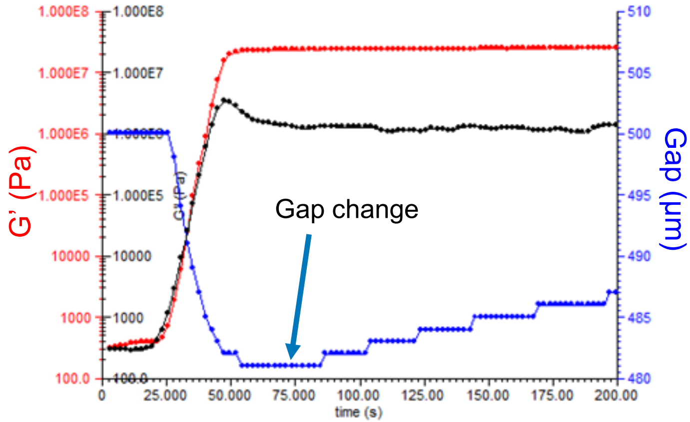


Isothermal Curing (Time Sweep)

Set Gap Constant monitor shrinking force



Set Axial Force = 0
monitor dimension(gap) change



Liquid to Gel to Solid Transition

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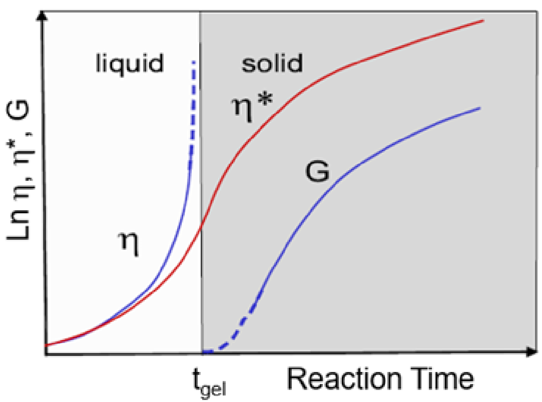
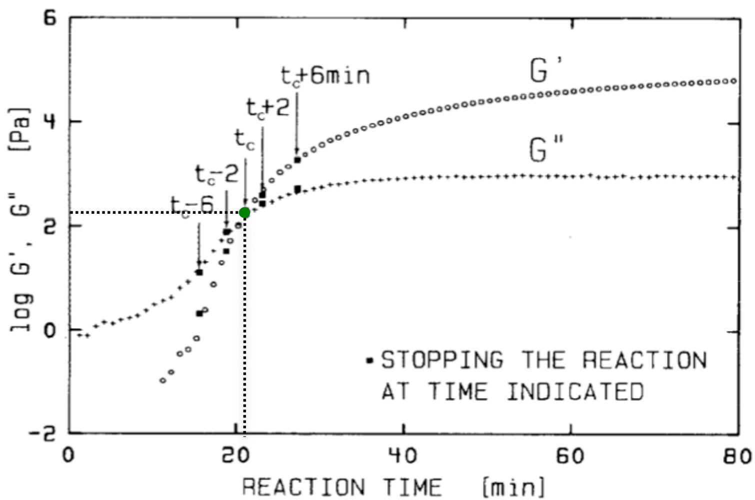
Empiricism of Y. M. Tung and P. J. Dynes (1982)

- 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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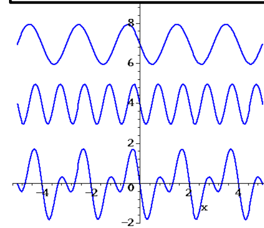
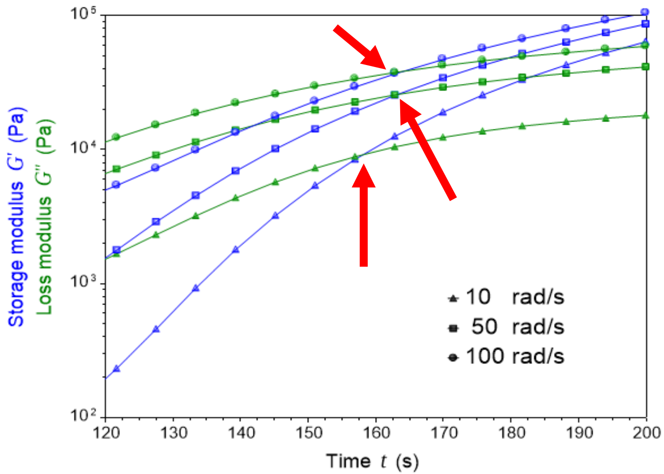
- Multifrequency superposition

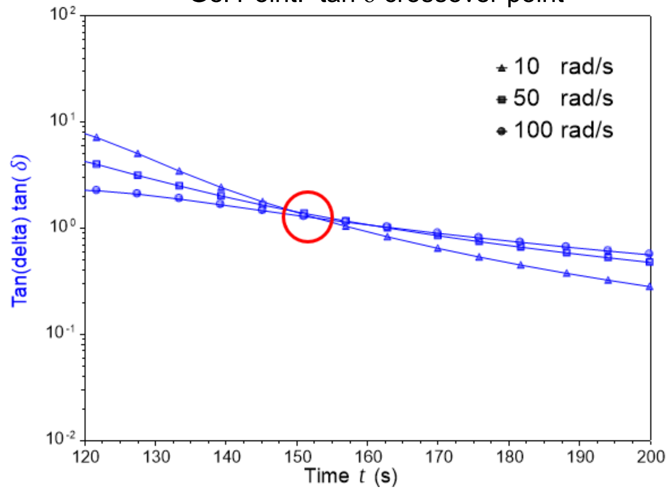


Multifrequency Time Sweep

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

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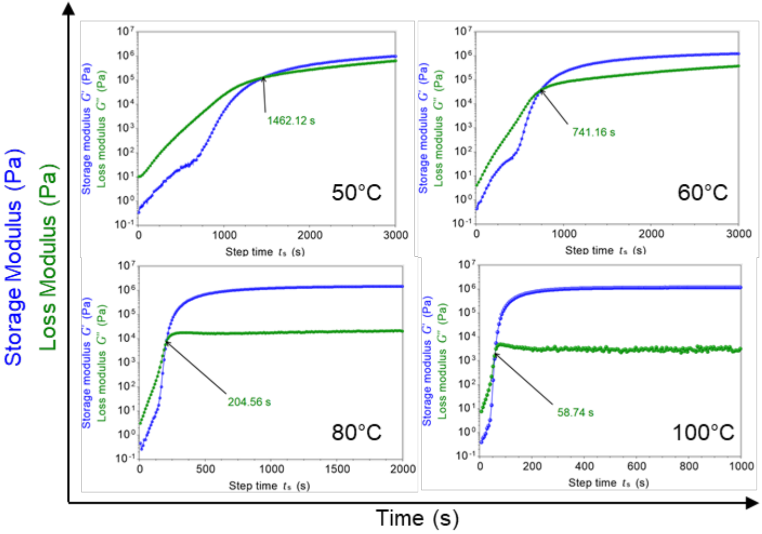
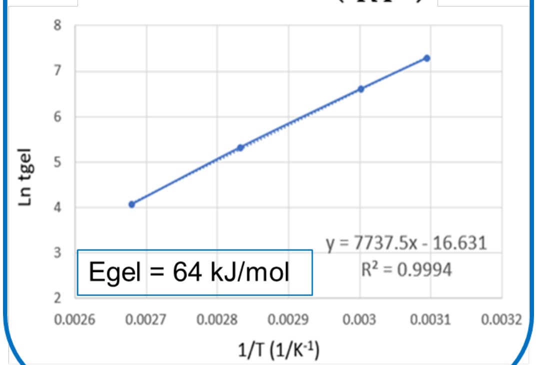
- The gelation kinetics can be described using the empirical Arrhenius model
- Perform isothermal curing at different temperatures



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



Quantifying Crosslink Density Post Cure (DMA)

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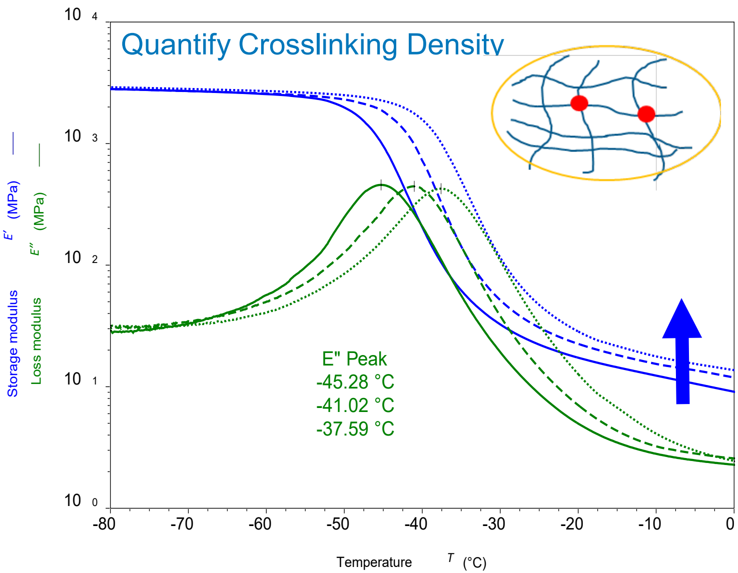

$$M_c = \frac{3RTd}{E'_{rubbery}} \quad \text{or} \quad M_c = \frac{RTd}{G'_{rubbery}}$$

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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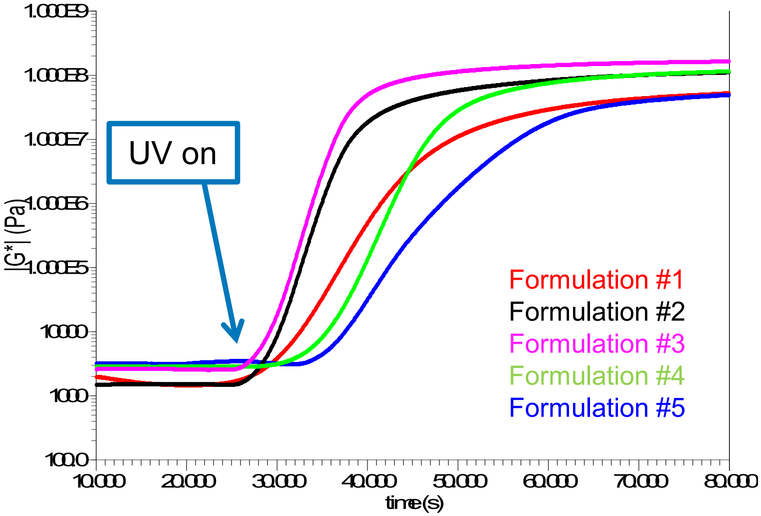
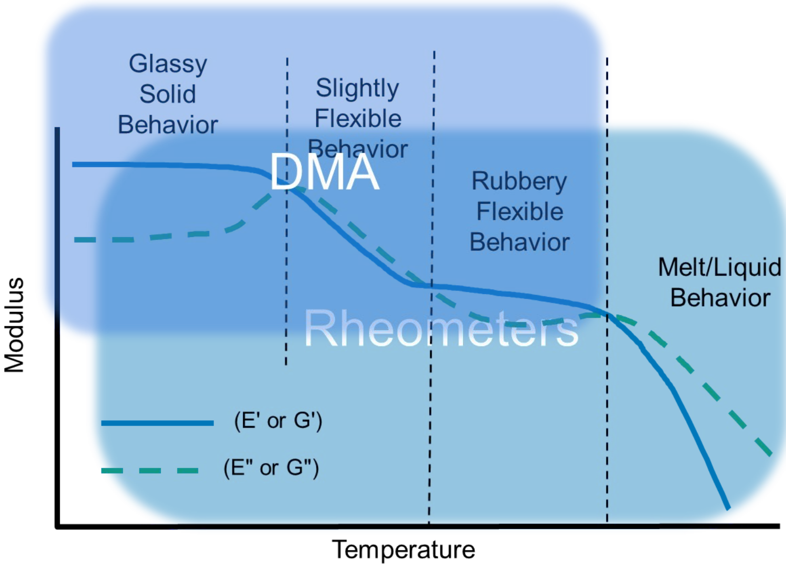
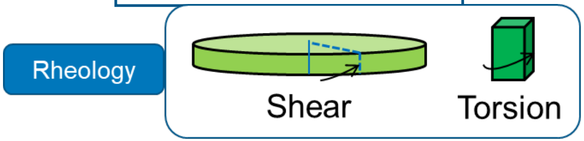


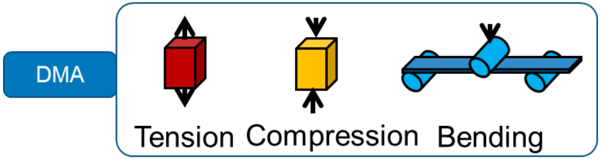
- Monitor UV curing: Dynamic time sweep
- Measure curing time with different formulations, UV intensity and temperature
- Measure cured adhesive modulus

Review



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





Thank You!