Rheology: Basic Theory and Applications Training

Section #1

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Agenda

Section 1 (2 hours)

- Basics in rheology and instrumentation
  - Rheology theory
  - How rheometers work and geometry selections
- Introduction to all rheological methods
  - Flow experiments
  - Oscillatory experiments
  - Transient experiments

Section 2 (2 hours)

- Rheology Applications- how to select correct geometries and test methods
  - Structured fluids
    - Low viscosity liquids
    - Creams/slurries/pastes
    - Gels and soft solids
  - Polymers
    - Polymer melts
    - Reactive polymers
    - Solid polymers

Rheology: An Introduction

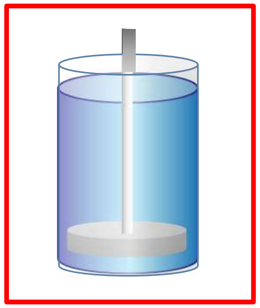



Rheology is the science of *flow*
and *deformation* of matter



What Rheology Measures

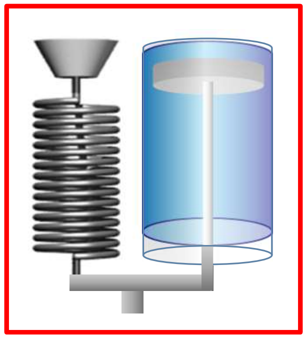
- Viscosity (Liquids)



- Elasticity (Solids)

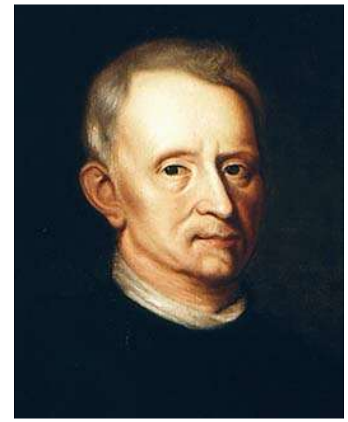


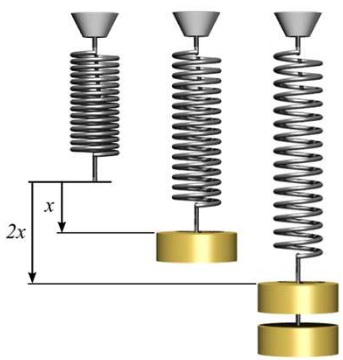
- Viscoelasticity (Liquids to Solids)

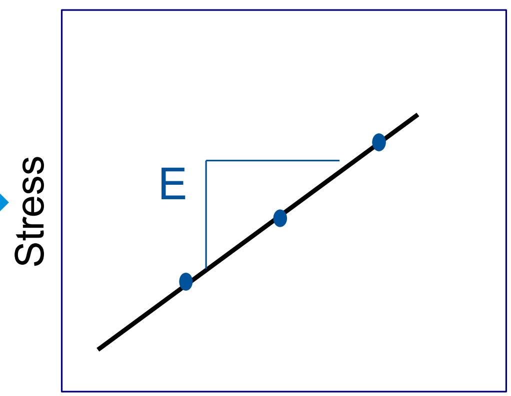



What is Elasticity?

- In 1660, Robert Hooke developed his “True Theory of Elasticity”
  - Model – spring
  - Observations – stress is linearly proportional to the deformation
  - Young’s Modulus is the slope of the stress and strain curve





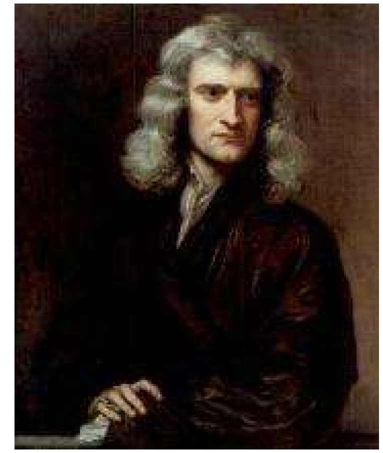


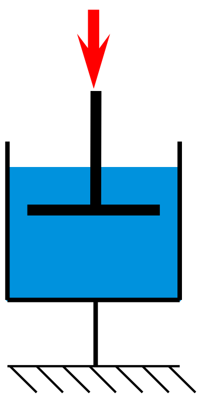
$$\sigma = E\gamma$$

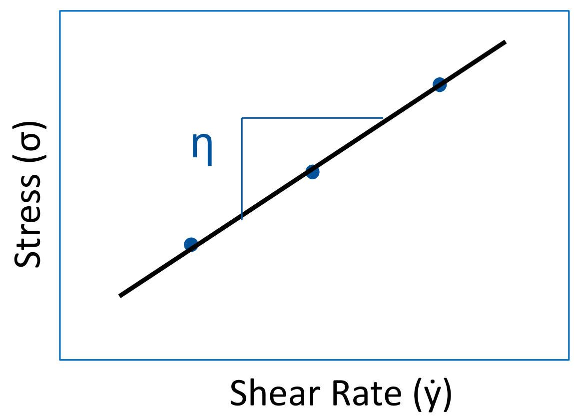
Hooke’s Law of Elasticity

What is Viscosity?

- In 1687, Isaac Newton studied the flow behavior of liquids
  - Model – dashpot
  - Observations – stress is linearly proportional to shear rate
  - Viscosity is – the ratio of the stress and rate curve







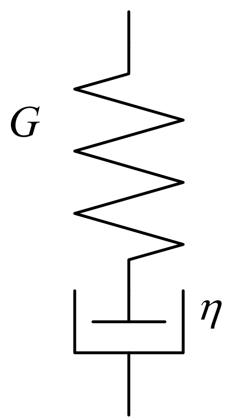
$$\sigma = \eta\dot{\gamma}$$

Newton's Law of Viscosity

How to Describe Viscoelasticity?

- Viscoelastic Materials: Force depends on both deformation and rate of deformation and vice versa

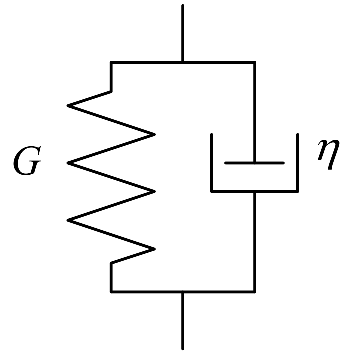
Maxwell Model (Stress Relaxation)



$$\gamma = \frac{\sigma}{G} + \frac{\sigma}{\eta} t$$

$$\frac{d\gamma}{dt} = \frac{1}{G}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

Kelvin-Voigt Model (Creep)



$$\sigma = G\gamma + \eta\dot{\gamma}$$

$$\sigma = G\gamma + \eta \frac{d\gamma}{dt}$$

Instrumentation

Rotational Rheometers by TA

ARES G2

Controlled Strain
Dual Head
SMT

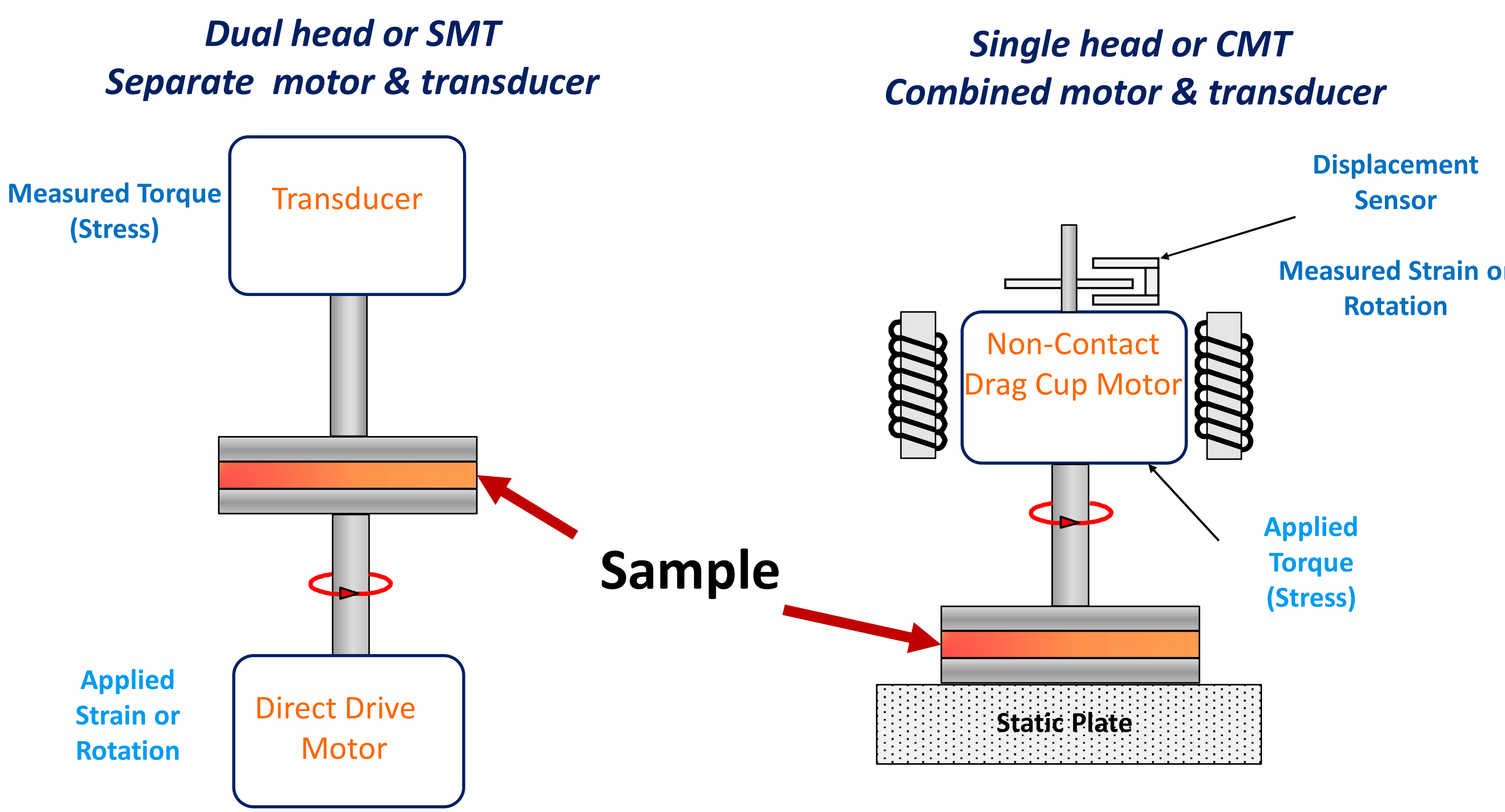
DHR - 1,2,3

Controlled Stress
Single Head
CMT

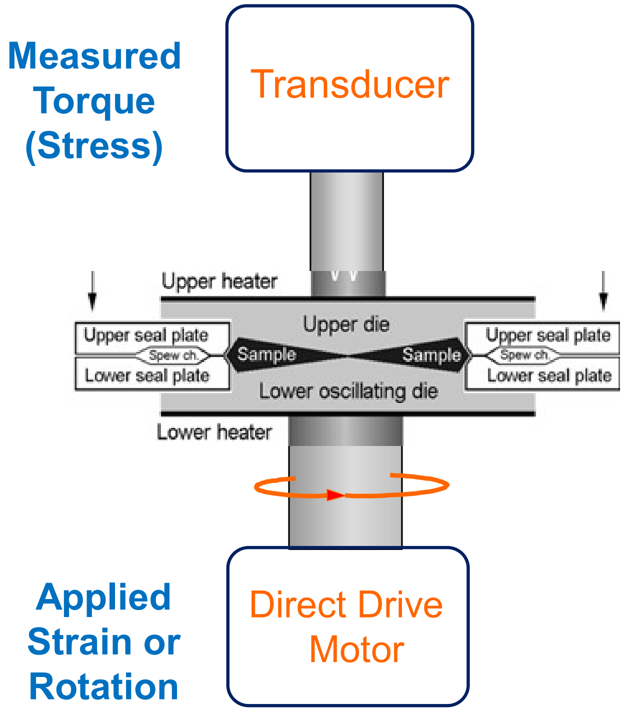
HR – 10,20,30

Controlled Stress
Single Head
CMT

Rotational Rheometer Designs



Closed Die Cavity Rheometer by TA



RPA Elite, RPA Flex and MDR

Controlled Strain
SMT or Dual Head

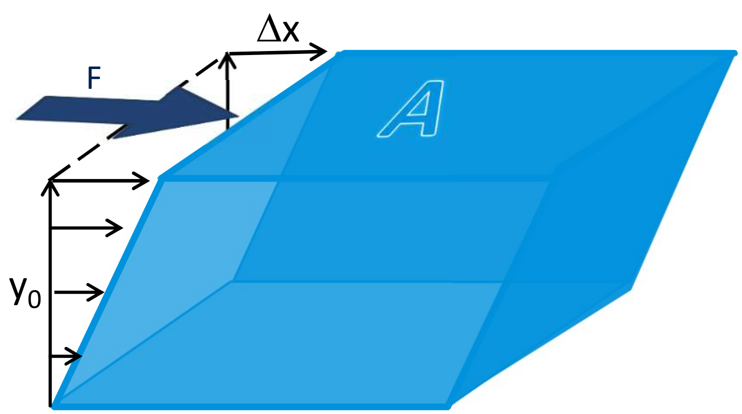
What does a Rheometer measure?

- Rheometer – an instrument that measures both viscosity and viscoelasticity of fluids, semi-solids and solids

- It can provide information about the material's:
  - Viscosity - defined as a material's resistance to deformation and is a function of shear rate or stress, with time and temperature dependence
  - Viscoelasticity – is a property of a material that exhibits both viscous and elastic character. Measurements of G', G", tan δ with respect to time, temperature, frequency and stress/strain are important for characterization.

How do Rheometers Work?

- The study of *stress* and *deformation* relationship



$$\text{Shear stress} \quad \sigma = \frac{F}{A}$$

$$\text{Shear strain}\ \gamma = \frac{\Delta x}{y_0}$$

$$\text{Shear rate} = \dot{\gamma} = \frac{1}{y_0} \cdot \frac{dx(t)}{dt}$$

$$\frac{\text{Stress}}{\text{Shear rate}} = \text{Viscosity}$$

$$\frac{\text{Stress}}{\text{Strain}} = \text{Modulus}$$

How do Rheometers Work?

- In a rheological measurement, stress; strain and strain rate (shear rate) are all calculated signals

- The raw signals behind the scene are torque; angular displacement and angular velocity

Fundamentally, a rotational rheometer will apply or measure:

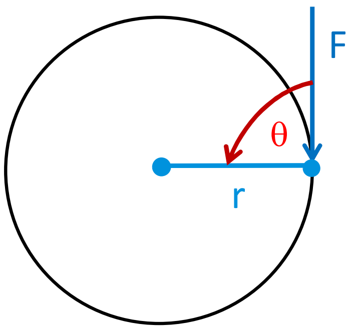
1. Torque (Force)
2. Angular Displacement
3. Angular Velocity

Measured parameter: torque

- Torque (M) is a measure of how much a force (F) acting on an object causes that object to rotate.
  - The object rotates about an axis, called the pivot point
  - The distance (r) from the pivot point to the point where the force acts is called the moment arm
  - The angle (θ) at which the force acts at the moment arm

$$M = r \cdot F \cdot \sin\theta = r \cdot F$$

(for θ = 90° as shown)



Calculated parameter: stress

- Shear stress is calculated from the torque and geometry stress constant

$$\sigma = M \cdot K_\sigma$$

σ = shear stress (Pa or Dyne/cm^2)

M = torque (N·m or gm·cm)

K_σ = stress constant

- The stress constant, K_σ, is dependent on measurement geometry and/or initial sample dimensions

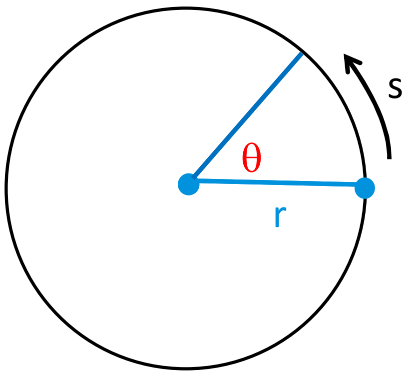
Measured parameter: angular displacement

- Angular displacement (θ) is the angle, in radians, through which an object moves on a circular path

s = arc length (or linear displacement)

r = radius of a circle

Conversion: degrees = radians·180/π



$$\theta = s/r$$

Calculated parameter: strain

- Strain is a measure of deformation representing the angular displacement relative to a reference length

$$\gamma = \theta \cdot K_{\gamma}$$

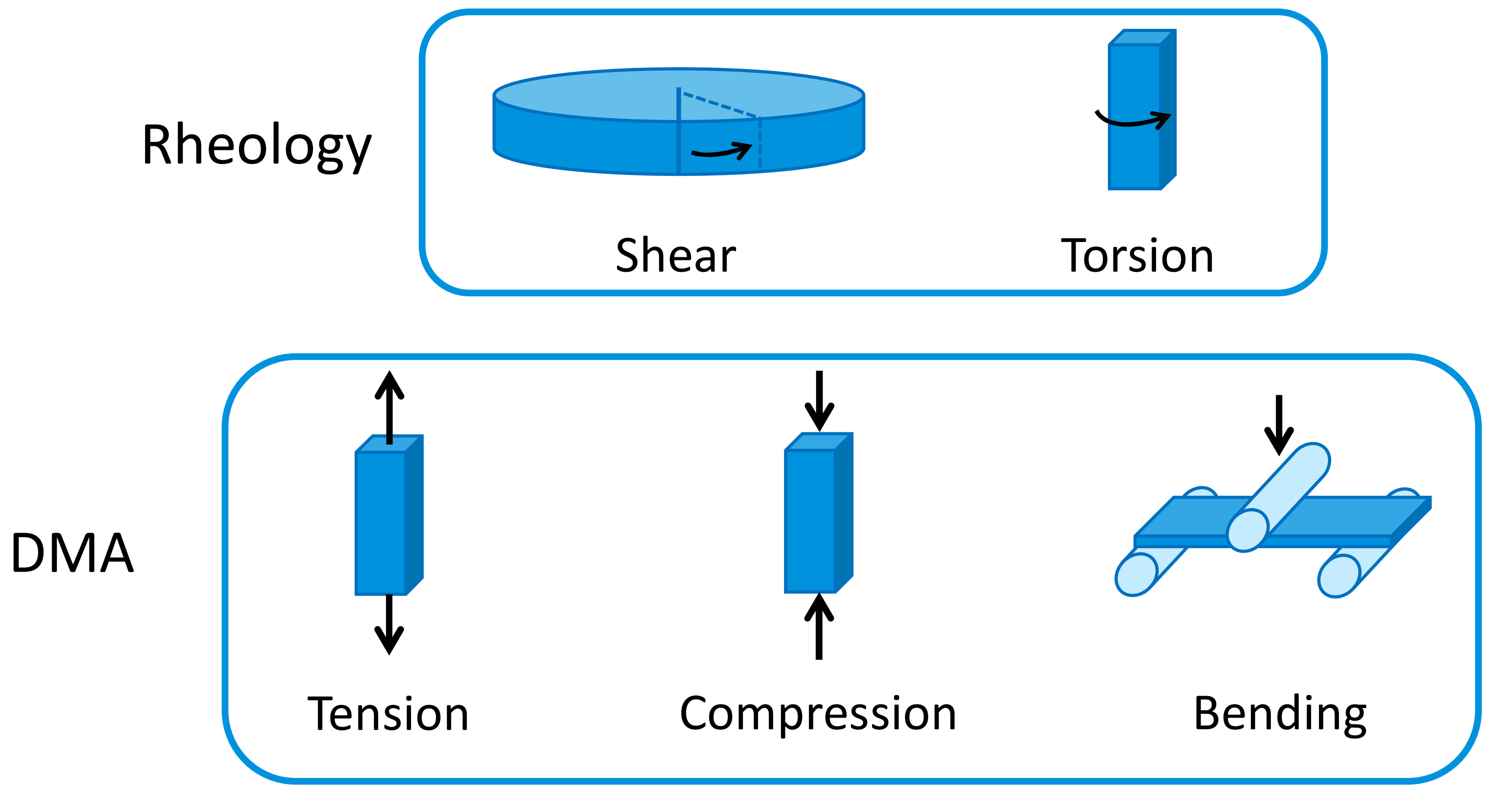
γ = shear strain (no units)

θ = angular displacement (radians)

K_{γ} = strain constant

- The strain constant, K_{γ}, is dependent on measurement geometry and/or initial sample dimensions
- Calculate percent strain (γ%) by multiplying strain by 100

Modes of Deformation



Equation for modulus

$$G = \boxed{\frac{\sigma}{\gamma}} = \frac{\boxed{M} \cdot \boxed{K_\sigma}}{\boxed{\theta} \cdot \boxed{K_\gamma}}$$

Material function

Constitutive equation

Measured signals

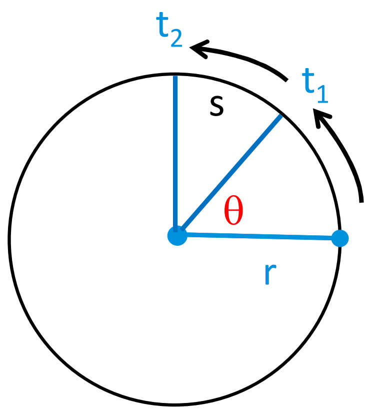
Geometry constants

Measured parameter: angular velocity

- Angular velocity (Ω) is the change in angular displacement (θ) per unit time of measurement

Note: linear velocity $V = \Delta s/\Delta t$

$$\Omega = \Delta\theta/\Delta t$$



Ω = angular velocity (radians/s)

θ = angular displacement (radians)

t = time (s)

Calculated parameter: shear rate

- Shear rate is calculated from the angular velocity and geometry strain constant

$$\dot{\gamma} = \Omega \cdot K_{\gamma}$$

$\dot{\gamma}$ = shear rate (s^{-1})

Ω = angular velocity (radians/s)

K_{γ} = strain constant

- The strain constant, K_{γ}, is dependent on measurement geometry and/or initial sample dimensions

Equation for viscosity

$$\eta = \boxed{\frac{\sigma}{\dot{\gamma}}} = \frac{\boxed{M} \cdot \boxed{K_\sigma}}{\boxed{\Omega} \cdot \boxed{K_\gamma}}$$

Material function

Constitutive equation

Measured signals

Geometry constants

Discovery Hybrid Rheometer Specifications

Specification	HR-3	HR-2	HR-1
Bearing Type, Thrust	Magnetic	Magnetic	Magnetic
Bearing Type, Radial	Porous Carbon	Porous Carbon	Porous Carbon
Motor Design	Drag Cup	Drag Cup	Drag Cup
Minimum Torque (nN.m) Oscillation	0.5	2	10
Minimum Torque (nN.m) Steady Shear	5	10	20
Maximum Torque (mN.m)	200	200	150
Torque Resolution (nN.m)	0.05	0.1	0.1
Minimum Frequency (Hz)	1.0E-07	1.0E-07	1.0E-07
Maximum Frequency (Hz)	100	100	100
Minimum Angular Velocity (rad/s)	0	0	0
Maximum Angular Velocity (rad/s)	300	300	300
Displacement Transducer	Optical encoder	Optical encoder	Optical encoder
Optical Encoder Dual Reader	Standard	N/A	N/A
Displacement Resolution (nrad)	2	10	10
Step Time, Strain (ms)	15	15	15
Step Time, Rate (ms)	5	5	5
Normal/Axial Force Transducer	FRT	FRT	FRT
Maximum Normal Force (N)	50	50	50
Normal Force Sensitivity (N)	0.005	0.005	0.01
Normal Force Resolution (mN)	0.5	0.5	1

DHR - DMA mode (optional)	
Motor Control	FRT
Minimum Force (N) Oscillation	0.1
Maximum Axial Force (N)	50
Minimum Displacement (µm) Oscillation	1.0
Maximum Displacement (µm) Oscillation	100
Displacement Resolution (nm)	10
Axial Frequency Range (Hz)	1 x 10^{-5} to 16

HR 30/20/10 Instrument Features

Specification/ Feature	HR 30	HR 20	HR 10
Bearing Type, Thrust	Magnetic	Magnetic	Magnetic
Bearing Type, Radial	Porous Carbon	Porous Carbon	Porous Carbon
Minimum Torque (nN.m) Oscillation	0.3	1	5
Minimum Torque (nN.m) Steady Shear	1	3	5
Maximum Torque (nN.m)	200	200	200
Optical Encoder Dual Reader	●	●	-
Displacement Resolution (nrad)	2	2	10
DMA Mode	●	○	-
True Position Sensor (TPS)	●	●	●
Controlled Stress (steady, transient, oscillation)	●	●	●
Controlled Strain (steady, transient, iterative oscillation)	●	●	●
Direct Strain (oscillation)	●	●	○
Fast data collection	●	●	-
Normal Force measurements with FRT	●	●	●
Axial and tack testing	●	●	○
One-Touch-Away Display	●	●	●
Integrated Sample Lighting	●	●	●
FastTrack for asphalt testing	●	●	●
AutoPilot	○	○	○

DMA Mode Specifications	
Motor Control	Force Rebalance Transducer
Minimum Force in Oscillation	3 mN
Maximum Axial Force	50 N
Minimum Displacement in Oscillation	0.01 µm
Maximum Displacement in Oscillation	100 µm
Axial Frequency Range	6×10^{-5} rad/s to 100 rad/s (10^{-5} Hz to 16 Hz)

ARES-G2 Rheometer Specifications

Force/Torque Rebalance Transducer (Sample Stress)	
Transducer Type	Force/Torque Rebalance
Transducer Torque Motor	Brushless DC
Transducer Normal/Axial Motor	Brushless DC
Minimum Torque (μN.m) Oscillation	0.05
Minimum Torque (μN.m) Steady Shear	0.1
Maximum Torque (mN.m)	200
Torque Resolution (nN.m)	1
Transducer Normal/Axial Force Range (N)	0.001 to 20
Transducer Bearing	Groove Compensated Air

Driver Motor (Sample Deformation)	
Maximum Motor Torque (mN.m)	800
Motor Design	Brushless DC
Motor Bearing	Jeweled Air, Sapphire
Displacement Control/ Sensing	Optical Encoder
Strain Resolution (μrad)	0.04
Minimum Angular Displacement (μrad) Oscillation	1
Maximum Angular Displacement (μrad) Steady Shear	Unlimited
Angular Velocity Range (rad/s)	$1x\ 10^{-6}$ to 300
Angular Frequency Range (rad/s)	$1x\ 10^{-7}$ to 628
Step Change, Velocity (ms)	5
Step Change, Strain (ms)	10

Orthogonal Superposition (OSP) and DMA modes	
Motor Control	FRT
Minimum Transducer Force (N) Oscillation	0.001
Maximum Transducer Force (N)	20
Minimum Displacement (μm) Oscillation	0.5
Maximum Displacement (μm) Oscillation	50
Displacement Resolution (nm)	10
Axial Frequency Range (Hz)	1×10^{-5} to 16

Geometries

Geometry Options

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

Solids

Water → to → Steel

Assess material to test

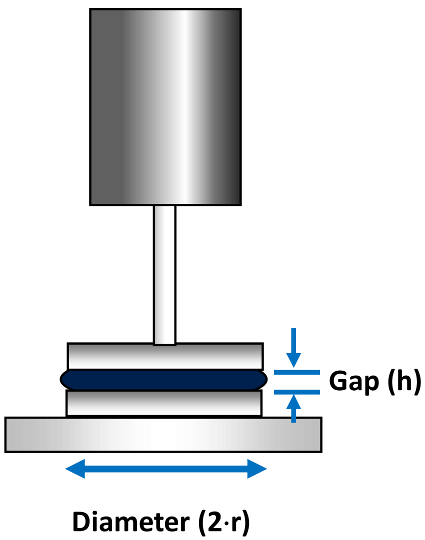
- Geometry - material of construction, size and surface
- In general, lower viscosity use larger diameter or larger contact area and higher viscosity or more solid-like smaller diameter
- Consider:
  - Volume requirements
  - Particle size, settling or mixing necessary
  - Loading procedure for structured substances (Pre-shear)
  - Evaporation – seal sample edge, solvent trap, or RH accessory
  - Surface slip and edge fracture

Cones and Plates

Smooth, Sandblasted, and Cross hatched

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

Parallel Plate



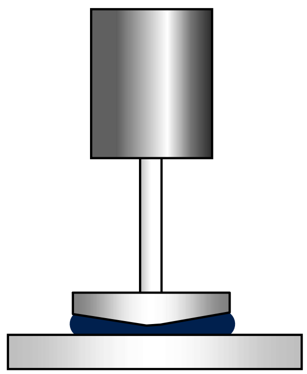
Strain Constant: $$K_\gamma = \frac{r}{h}$$

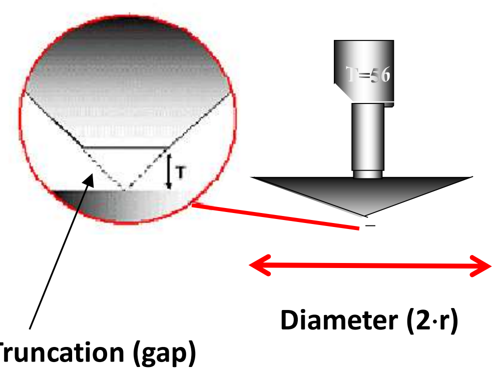
(to convert angular velocity, rad/sec, to shear rate, 1/sec, at the edge or angular displacement, radians, to shear strain (unitless) at the edge. The radius, r, and the gap, h, are expressed in meters)

Stress Constant: $$K_\sigma = \frac{2}{\pi r^3}$$

(to convert torque, N·m, to shear stress at the edge, Pa, for Newtonian fluids. The radius, r, is expressed in meters)

Cone and Plate





Strain Constant: $K_\gamma = \frac{1}{\beta}$

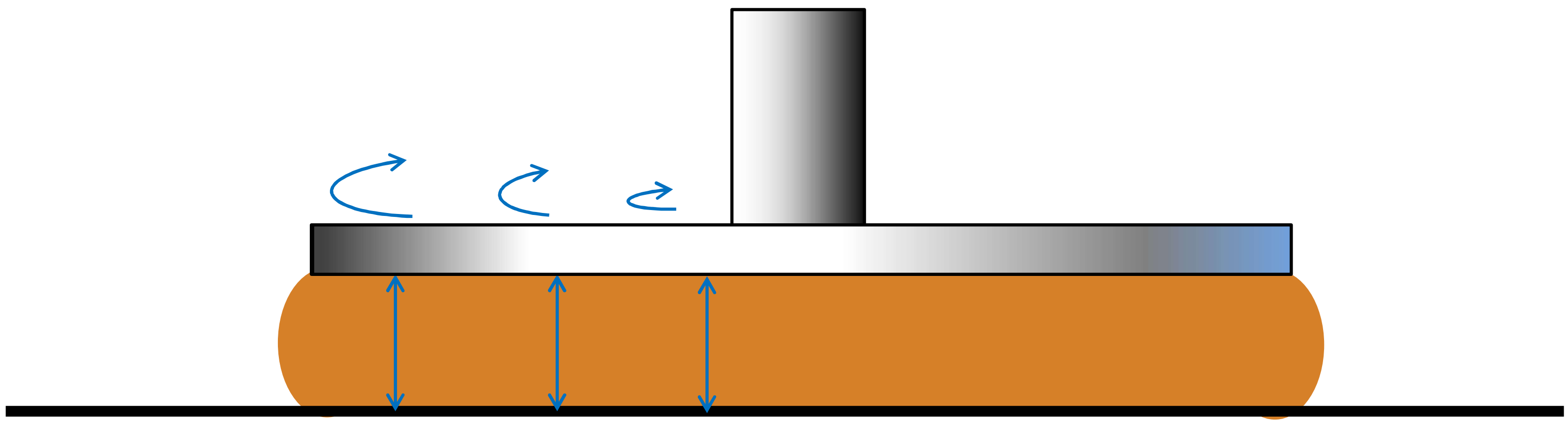
(to convert angular velocity, rad/sec, to shear rate. 1/sec, or angular displacement, radians, to shear strain, which is unit less. The angle, β, is expressed in radians)

Stress Constant: $K_\sigma = \frac{3}{2\pi r^3}$

(to convert torque, N·m, to shear stress, Pa. The radius, r, is expressed in meters)

Effective Shear Rate Varies Across a Parallel Plate

- For a given angle of deformation, there is a greater arc of deformation at the edge of the plate than at the center



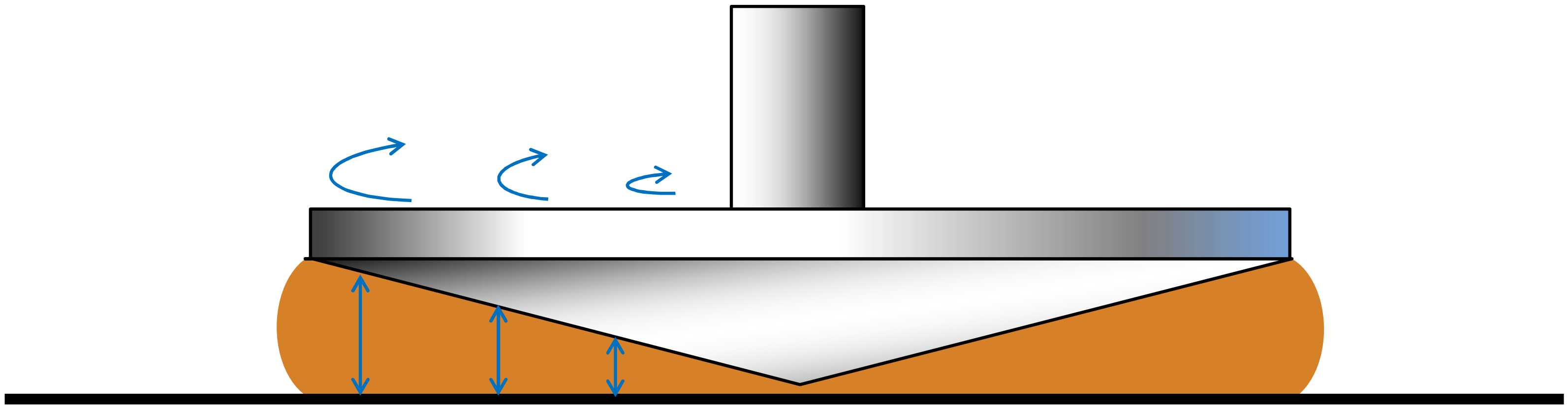
$$\gamma = \frac{dx}{h}$$

dx increases further from the center,
h stays constant

Single-point correction for the parallel plate geometry (0.76 radius)
[M.S. Carvalho, M. Padmanabhan and C.W. Macosko, *J. Rheol.* 38 (1994) 1925-1936]

Shear Rate is Normalized across a Cone

- The cone shape produces a smaller gap height closer to inside, so the shear on the sample is constant



$$\gamma = \frac{dx}{h}$$

h increases proportionally to *dx*, γ is uniform

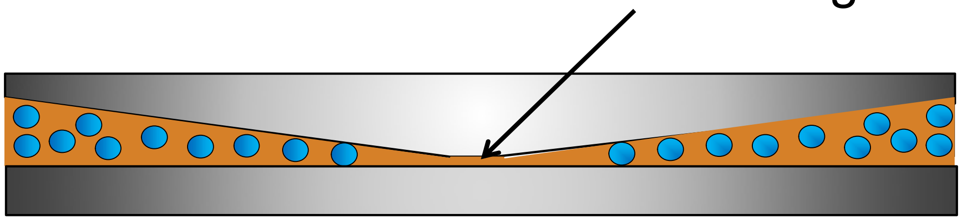
Limitations of Cone Plate

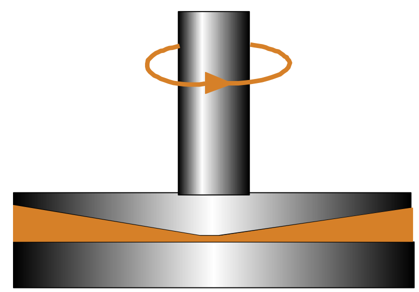
- Cone geometries have small truncation gaps
- Using the cone and plate to measure a sample that has large particles could result in artifacts since the particles could be ground between the cone and the plate

Typical Truncation Heights:

1° degree ~ 20 - 30 microns
2° degrees ~ 60 microns
4° degrees ~ 120 microns

Truncation Height = Gap

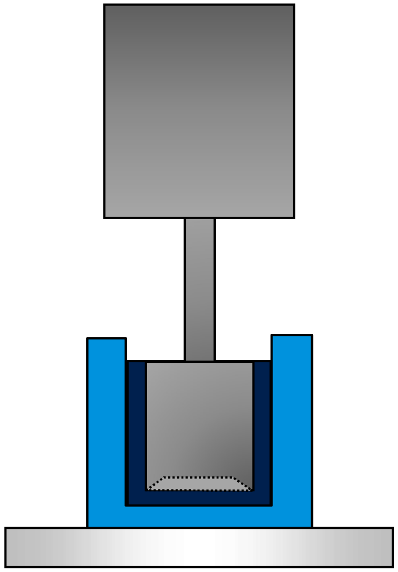




Cone & Plate

Gap must be > or = 10 x particle size

Concentric Cylinder



Strain Constant:

$$K_{\gamma} = \frac{1 + \left(\frac{r_2}{r_1}\right)^2}{\left(\frac{r_2}{r_1}\right)^2 - 1}$$

(to convert angular velocity, rad/sec, to shear rate, 1/sec, or angular displacement, radians, to shear strain (unit less). The radii, r_1 (inner) and r_2 (outer), are expressed in meters)

Stress Constant:

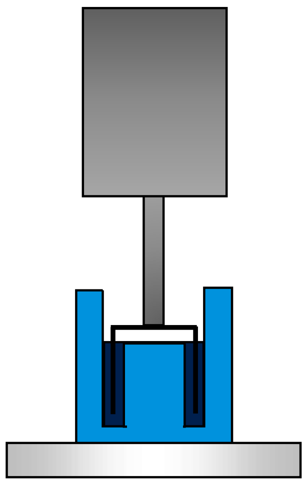
$$K_{\sigma} = \frac{1}{4\pi l}\left[\frac{1 + \left(\frac{r_2}{r_1}\right)^2}{c_l {r_2}^2}\right]^{*}$$

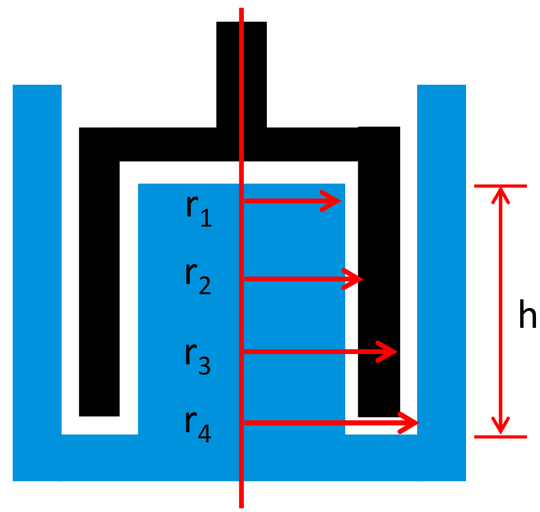
(to convert torque, N·m, to shear stress, Pa. The bob length, l, and the radius, r, are expressed in meters)

c_l is the face factor

Double Wall

- Use for very low viscosity systems (e.g. <1 mPas)





Strain Constant: $K_\gamma = \frac{(r_1{}^2 + r_2{}^2)}{(r_2{}^2 - r_1{}^2)}$

Stress Constant: $K_\sigma = \frac{(r_1{}^2+r_2{}^2)}{4\pi h\cdot \,{}_2{}^2(r_1{}^2+r_3{}^2)}$

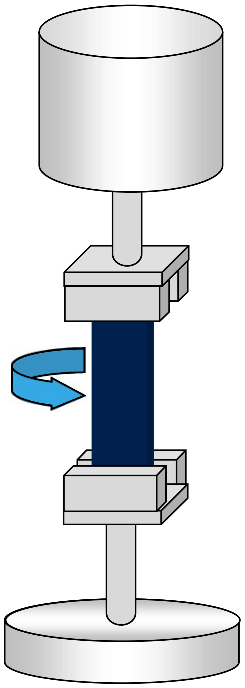
Peltier Concentric Cylinders

Double Gap Rotor & Cup
DIN Rotor & Standard Cup
Starch Pasting Impeller & Cup
Helical Rotor & Cup
Vane Rotor & Grooved Cup

Concentric Cylinder Cup and Rotor Compatibility Chart

Cup/Rotor	DIN	Recessed End	Starch Impeller	Vane	Wide Gap Vane	Double Gap	Helical Rotor
Standard (rad= 15 mm)	●	●		●	●		
Large Diameter (rad= 22 mm)	●	●	●	●	●		●
Starch (rad= 18.5 mm)	●	●	●	●	●		●
Grooved				●	●		
Double Gap						●	
Helical (rad= 17 mm)							●

Torsion Rectangular



Stress constant: $K_\tau = \frac{\left(3 + \frac{1.8}{w}\right)}{(w \cdot t^2)}$

Strain constant: $K_\gamma = \frac{t}{l\left[1 - 0.378\left(\frac{t}{w}\right)^2\right]}$

w = Width

l = Length

t = Thickness

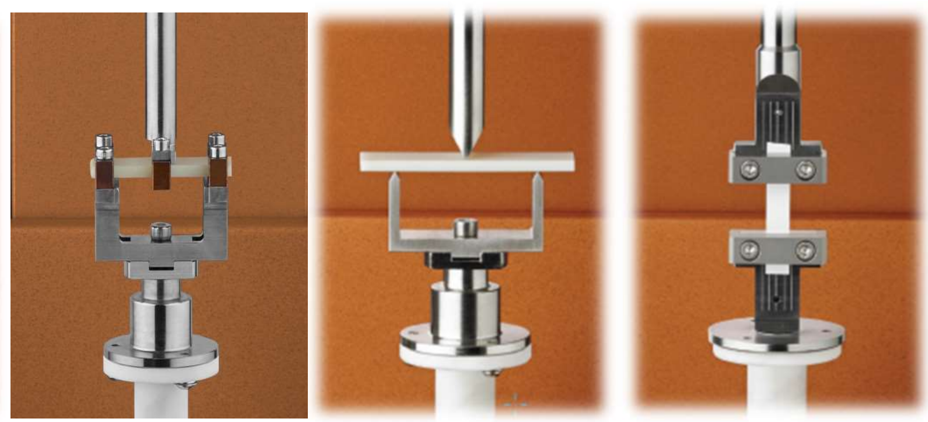
Advantages:	Disadvantages:
• High modulus samples • Small temperature gradient • Simple to prepare	• No pure Torsion mode for high strains

Torsion and DMA Measurements

- Torsion and DMA geometries allow solid samples to be characterized in a temperature-controlled environment
  - Torsion measures G', G", and Tan δ
  - DMA measures E', E", and Tan δ
    - ARES G2 DMA is standard function (50 μm amplitude)
    - DMA is an optional DHR function (100 μm amplitude)

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

Rectangular and cylindrical torsion



DMA cantilever, 3-point bending and tension clamps

Experimental Designs
1. Flow Tests

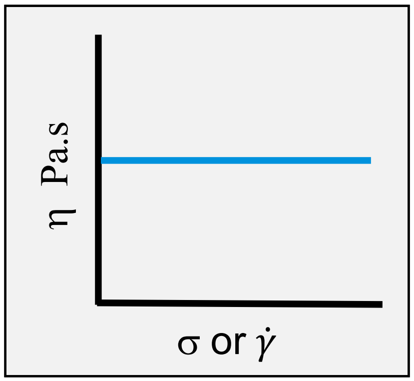
Viscosity Values

Materials	Viscosity η (Pa.s)
Air /Gas	0.00001
Water	0.001
Milk/ Coffee	0.01
Olive oil	0.1
Glycerol	1
Liquid Honey	10
Molasses	100
Polymer Melt	1000
Asphalt Binder	100,000

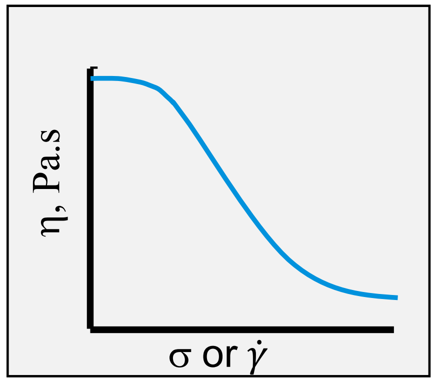
Viscosity Behaviors

- Newtonian and non-Newtonian

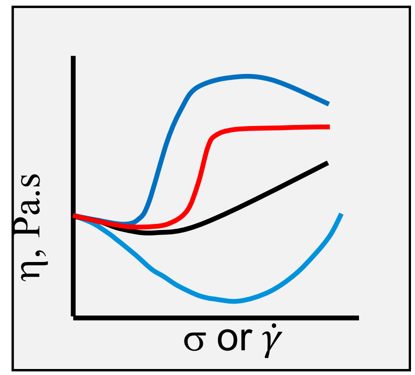
Newtonian



Shear Thinning

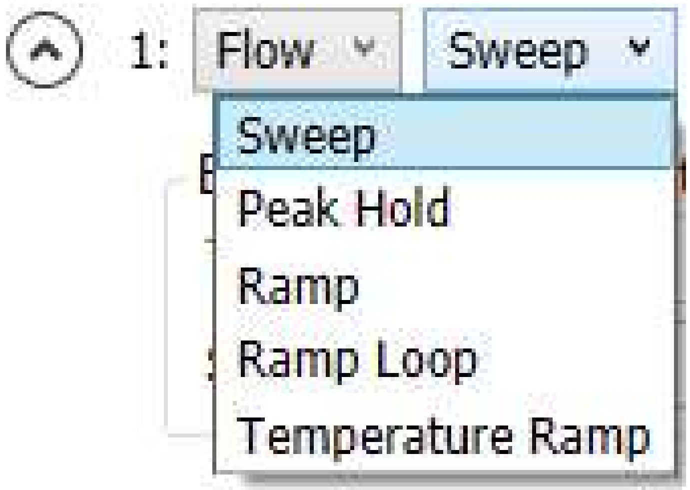


Shear Thickening

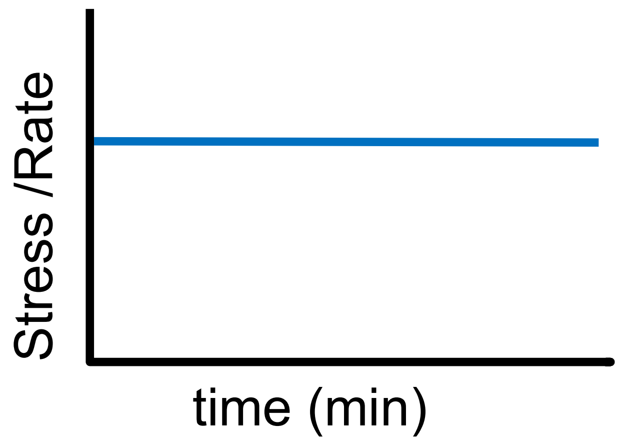


Rheological Methods

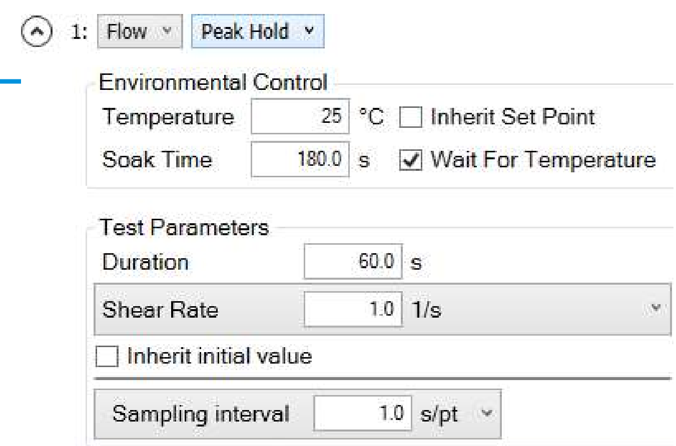
- Common rheological methods for measuring viscosity of liquids
  - Single rate/stress flow
  - Continuous rate/stress ramp
  - Stepped or steady state flow
  - Flow temperature ramp



Single Rate/Stress Test



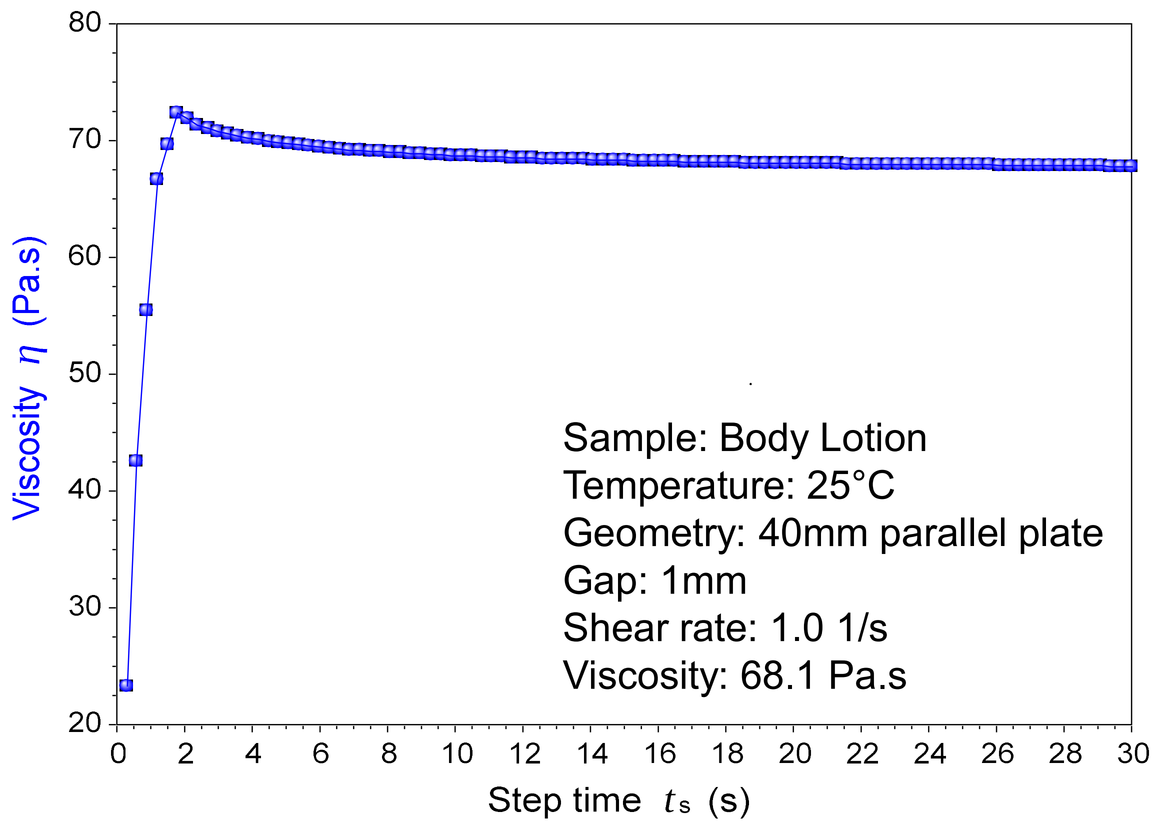
- Isothermal temperature
- Constant rate vs. time
- Constant stress vs. time
- On HR or DHR: peak hold
- On ARES G2: stress growth



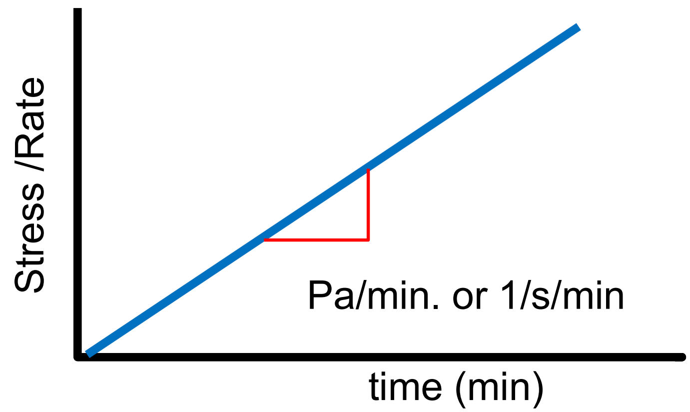
USES

- Single point testing
- Scope the time for steady state under certain rate

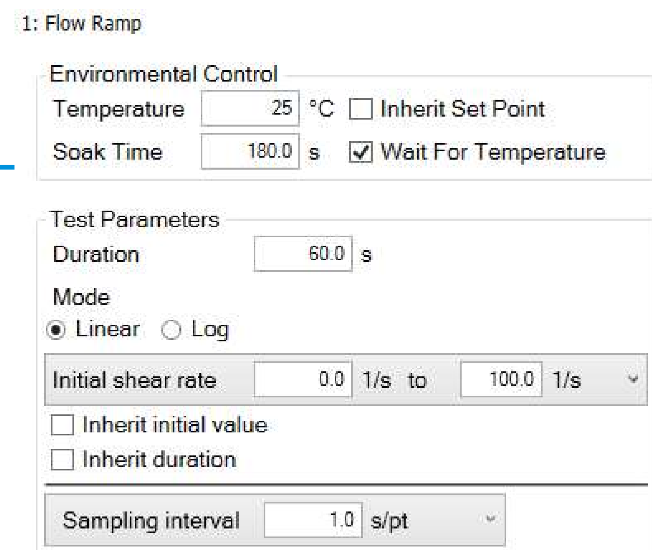
Body Lotion: Single Rate Test



Continuous Ramp



- Isothermal temperature
- Ramp stress or shear rate at a constant speed
- In TRIOS: Flow - Ramp

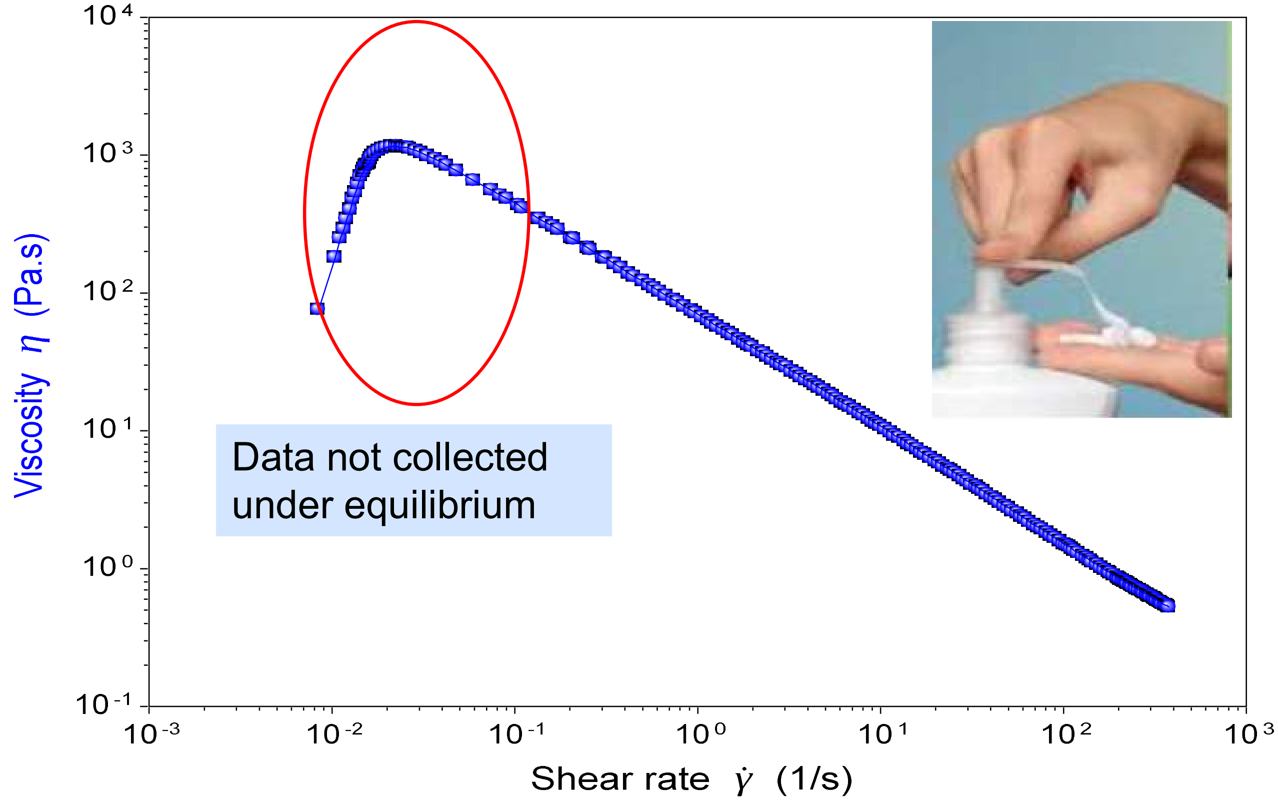


<u>USES</u>

- Scouting viscosity over wide range of shear
- Measure yield stress or thixotropy

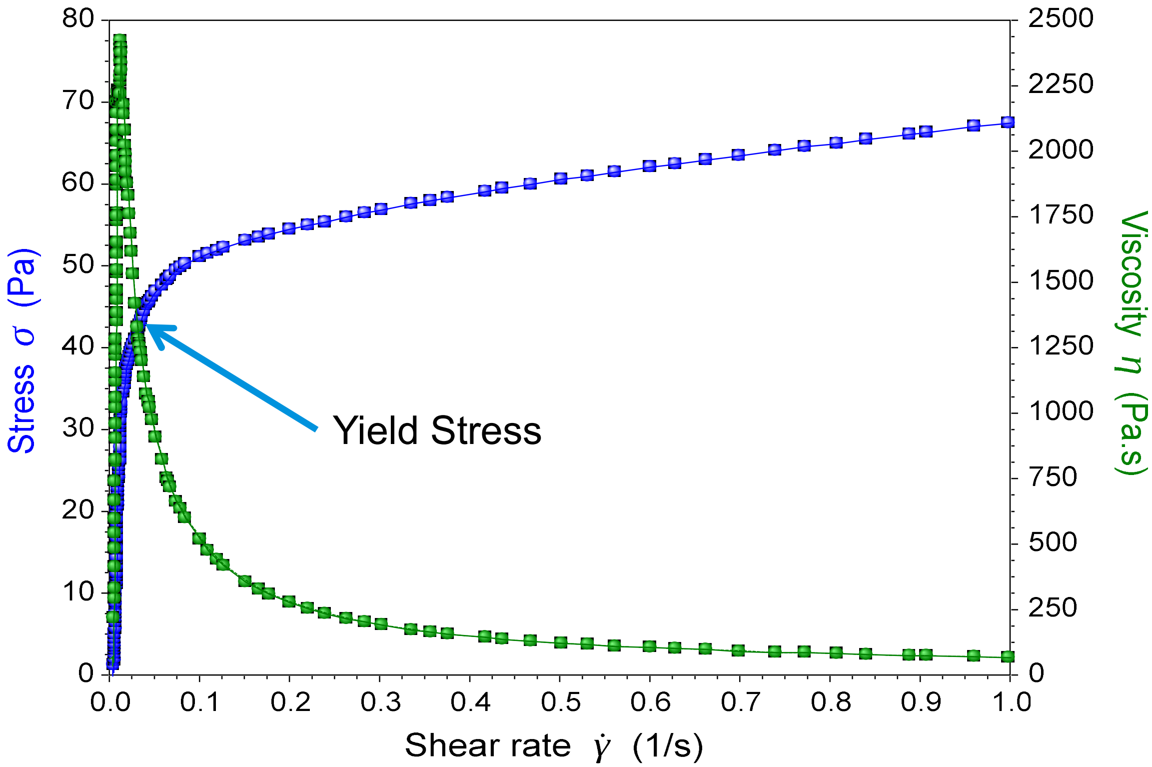
Viscosity of a Body Lotion

- Stress ramp from 0 to 200 Pa within 60 seconds.

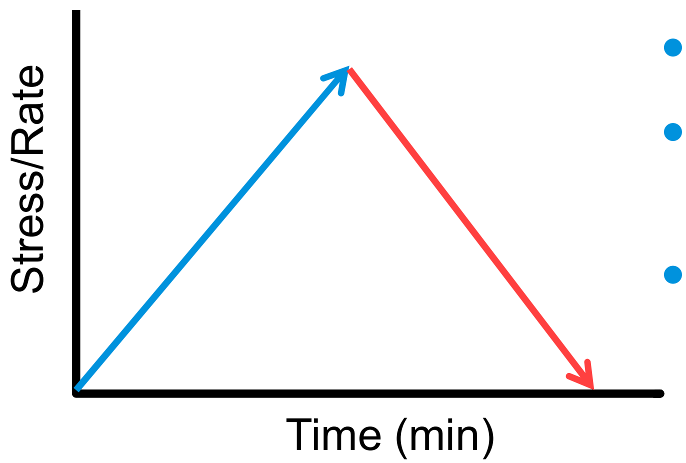


Measure Yield Stress of a Body Lotion

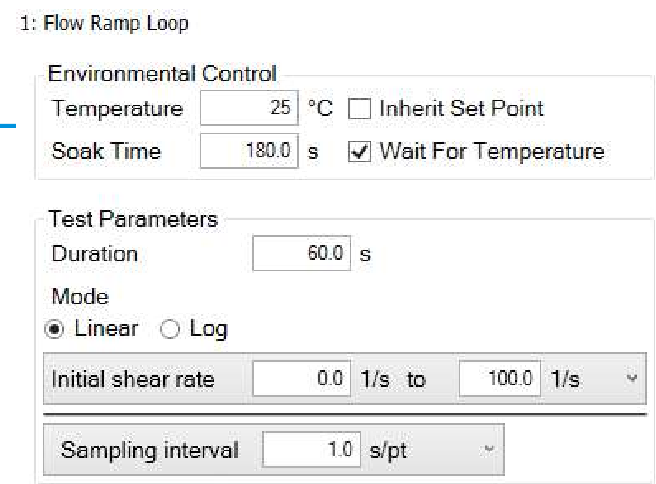
- Body lotion does not flow unless the applied stress exceeds a certain value – the yield point.



Continuous Ramp Up and Down



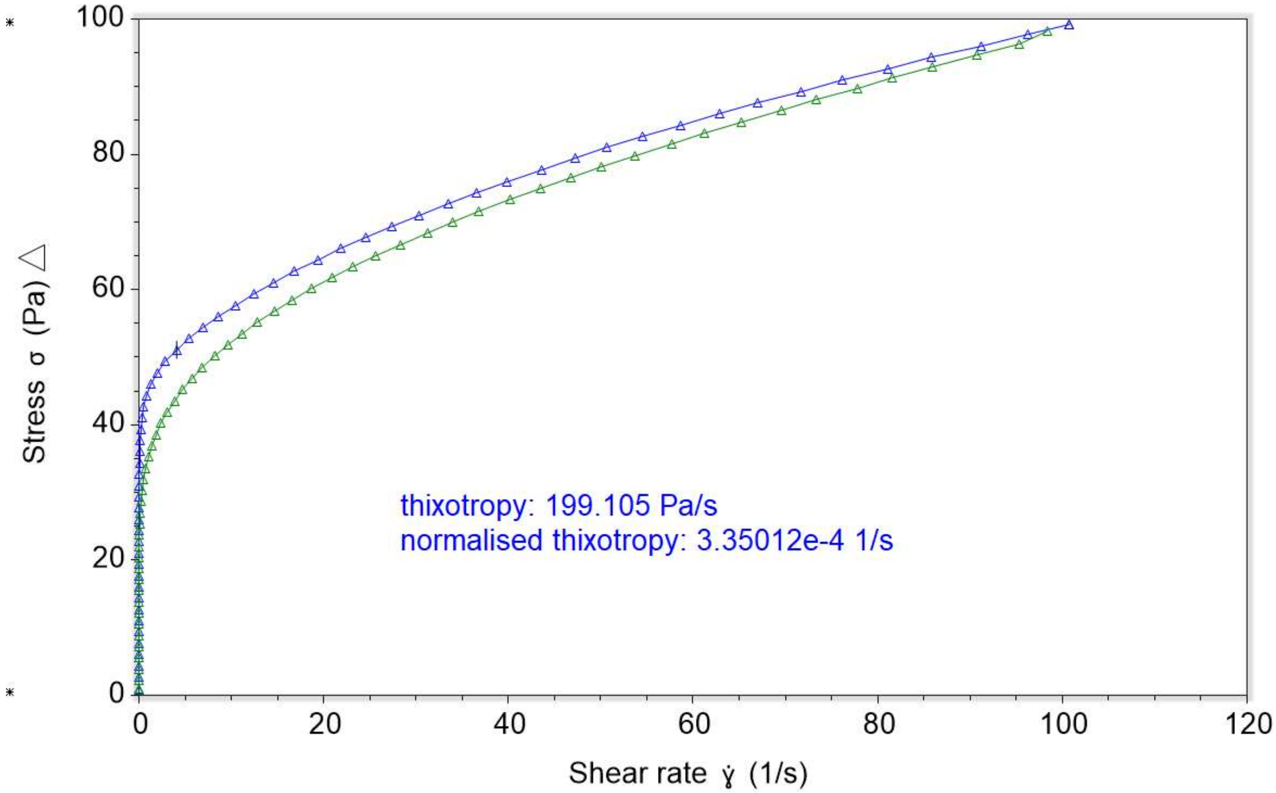
- Isothermal temperature
- Ramp stress or shear rate at a constant speed
- In TRIOS: Flow – Ramp or Loop



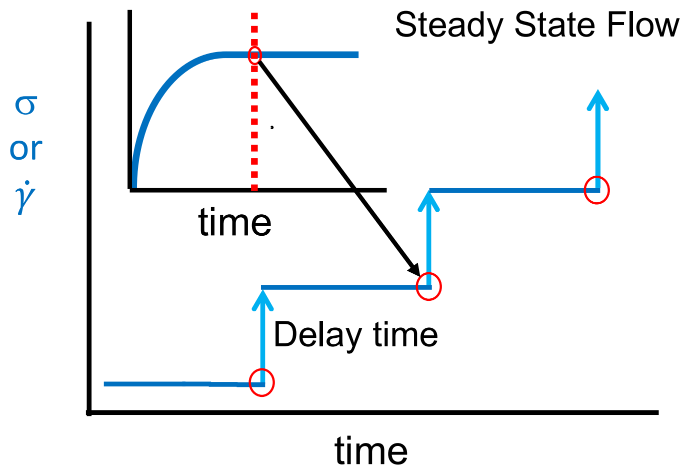
USES

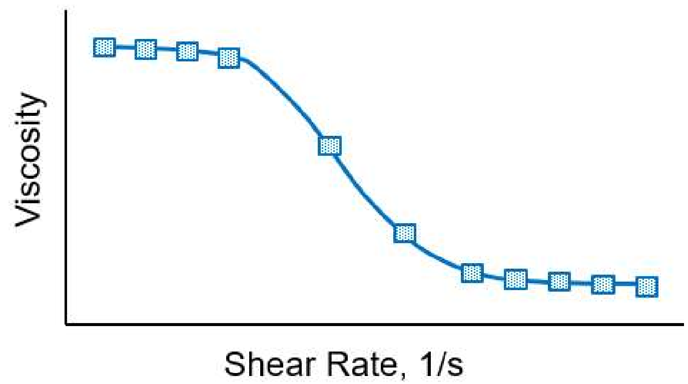
- Scouting viscosity over wide range of shear
- Measure yield stress or thixotropy

Thixotropy of a Blue Paint

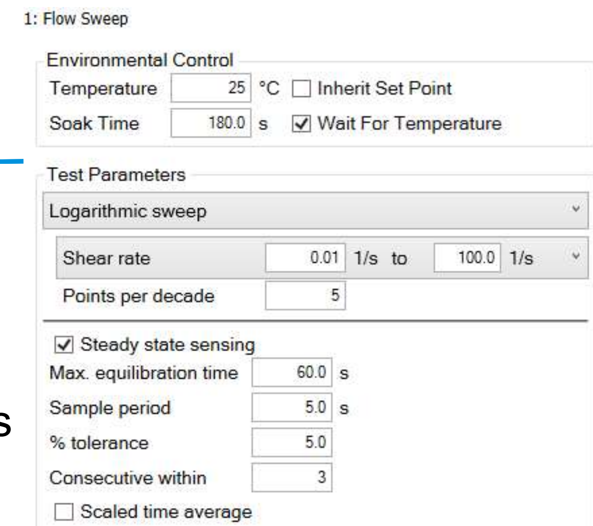


Flow Sweep – Steady State Flow





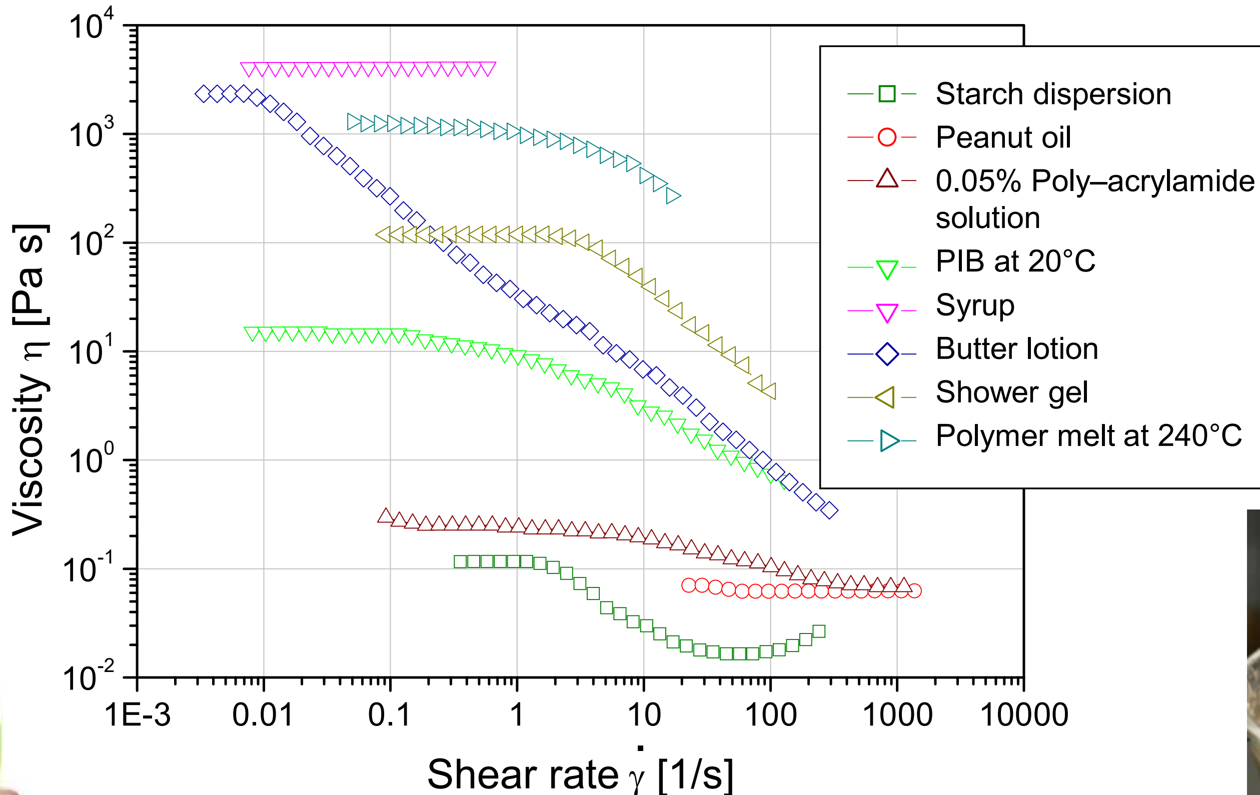
- Step stress or shear rate from low to high on a logarithmic scale
- At each step, viscosity is measured when steady state has been reached
- In TRIOS: Flow - Sweep



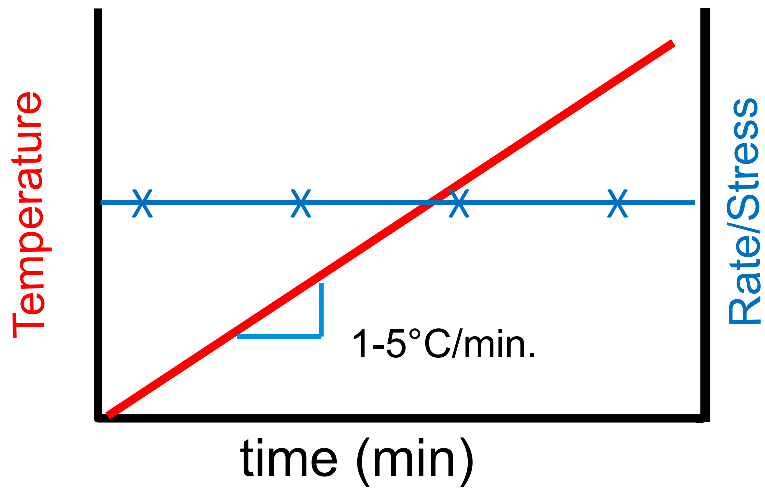
USES

- Viscosity Flow Curves
- Yield Stress Measurements

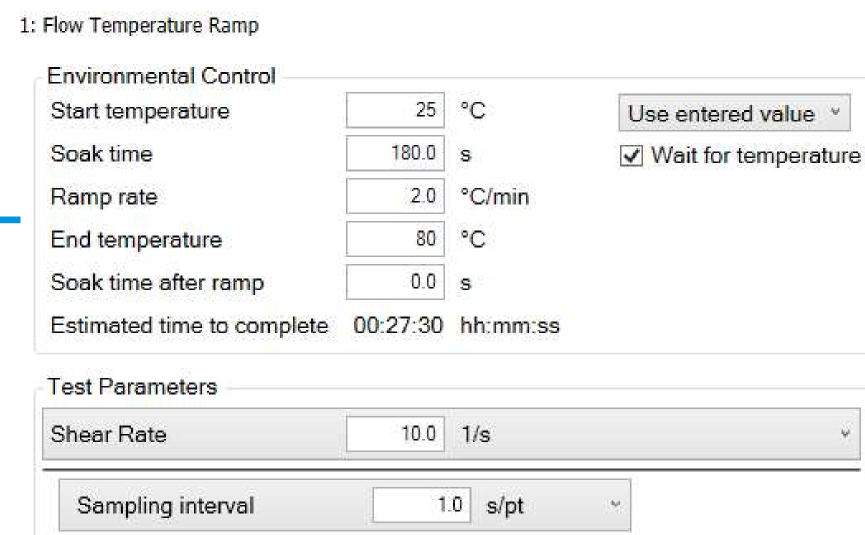
Viscosity Curves of Various Fluids



Flow Temperature Ramp



- Constant shear stress or shear rate
- Ramp temperature
- In TRIOS: Flow – Temp Ramp


1: Flow Temperature Ramp

Environmental Control

Start temperature	25	°C	Use entered value
Soak time	180.0	s	☑ Wait for temperature
Ramp rate	2.0	°C/min	
End temperature	80	°C	
Soak time after ramp	0.0	s	
Estimated time to complete	00:27:30	hh:mm:ss	

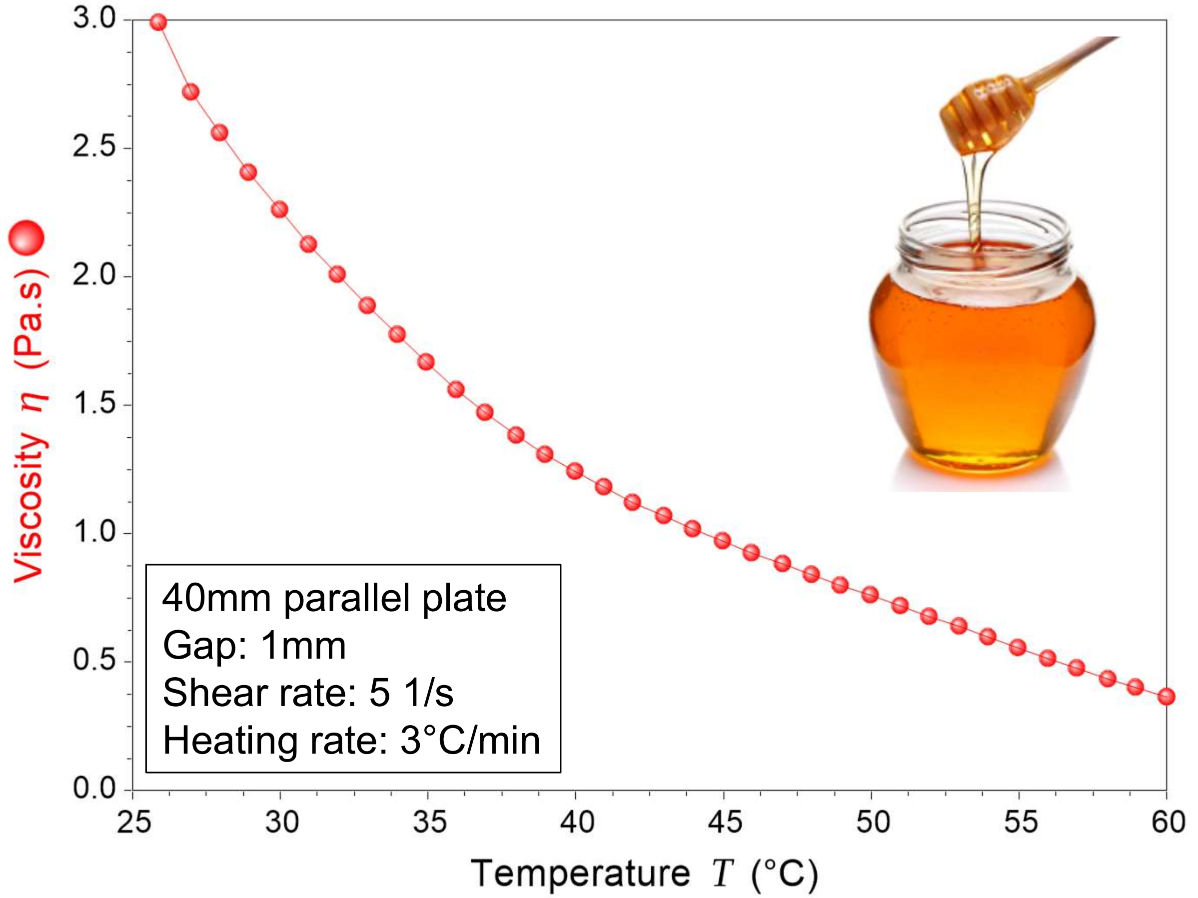
Test Parameters

Shear Rate	10.0	1/s
Sampling interval	1.0	s/pt

<u>USES</u>

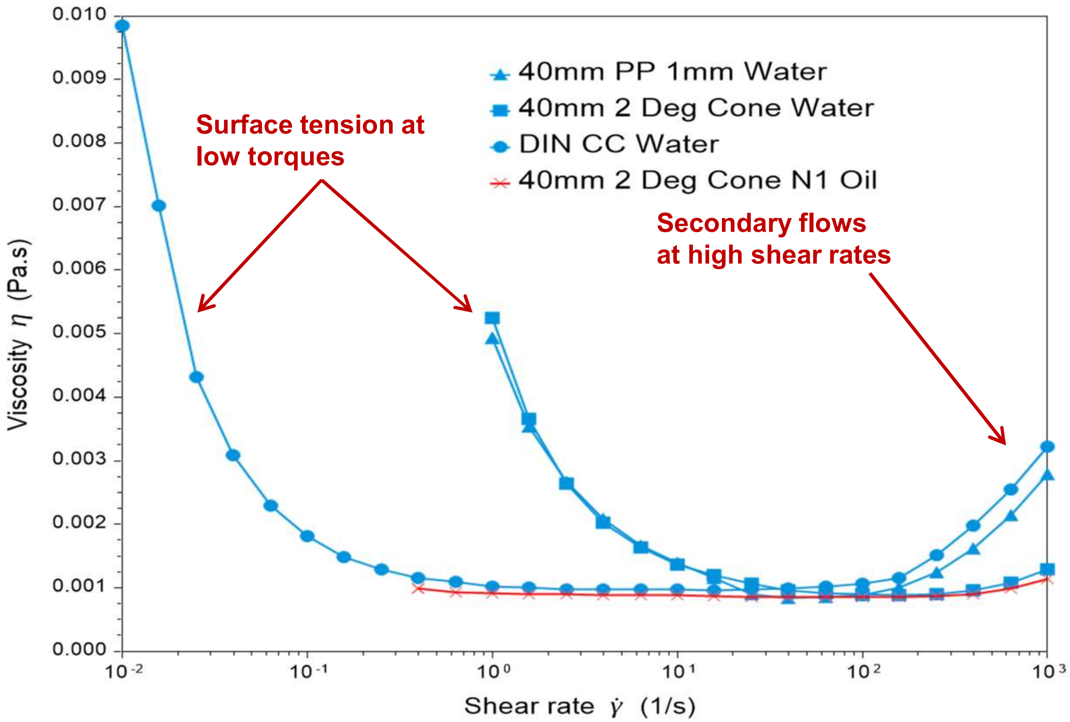
- Measure the viscosity change vs. temperature

Viscosity of Honey: Temperature Dependence



Water is not a Good Viscosity Standard

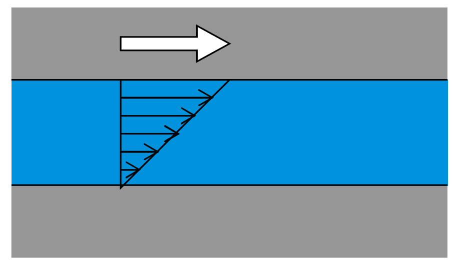
- Surface tension causes artifact shear thinning under low torque
- Secondary flow shows artifact shear thickening under high shear
- Use a large diameter geometry with a smaller gap



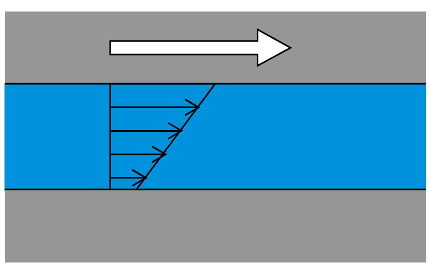
Wall Slip Phenomena

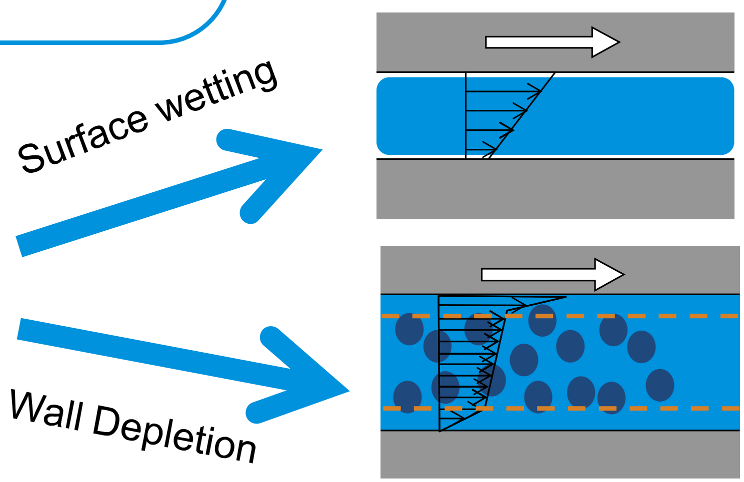
- Wall slip is often observed in flow viscosity measurements
- It can manifest itself in many ways:
  - Artificially low yield stress
  - Early shear thinning
  - Low viscosity

No slip condition
Ideal, Assumed Velocity Profile



Wall Slip
Incorrect Velocity Profile



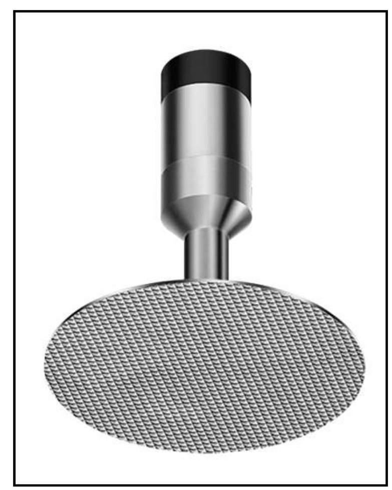


Solutions To Minimize Wall Slip

- Diagnosis method
  - Running the same experiment at different gaps. For samples that don't slip, the results will be independent of the gap

- Solutions
  - Use a grooved cup with vane or helical shape rotor geometry
  - Use a roughened surface geometry

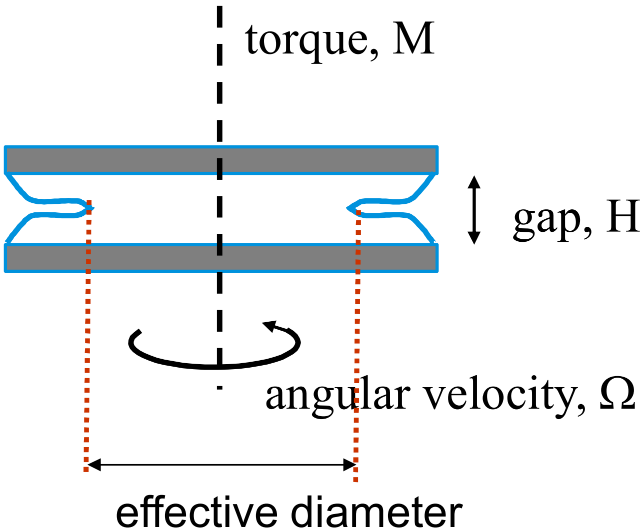


Edge Fracture

- Edge fracture is caused by the elasticity of the fluids
- When shearing a viscoelastic material, a large normal stress difference (created from its elasticity) can lead to a crack formation at the geometry edge. This is called edge fracture.
- Results: decrease in viscosity

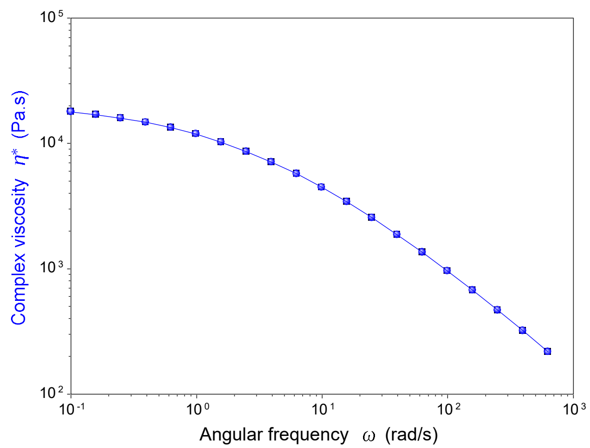
- To minimize edge fracture
  - Decrease measurement gap
  - Use partitioned plate



The Cox-Merz Rule

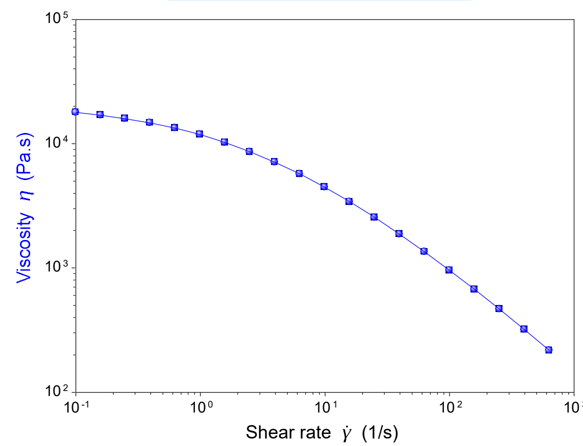
- For materials that exhibit wall slip or edge fracture, one alternative way to obtain viscosity information over shear is to use the Cox-Merz rule
- Cox-Merz “rule” is an empirical relationship. It was observed that in many polymeric systems, the steady shear viscosity plotted against shear rate is correlated with the complex viscosity plotted against frequency

Dynamic frequency sweep



η^* (Pa.s)~ ω (rad/s)

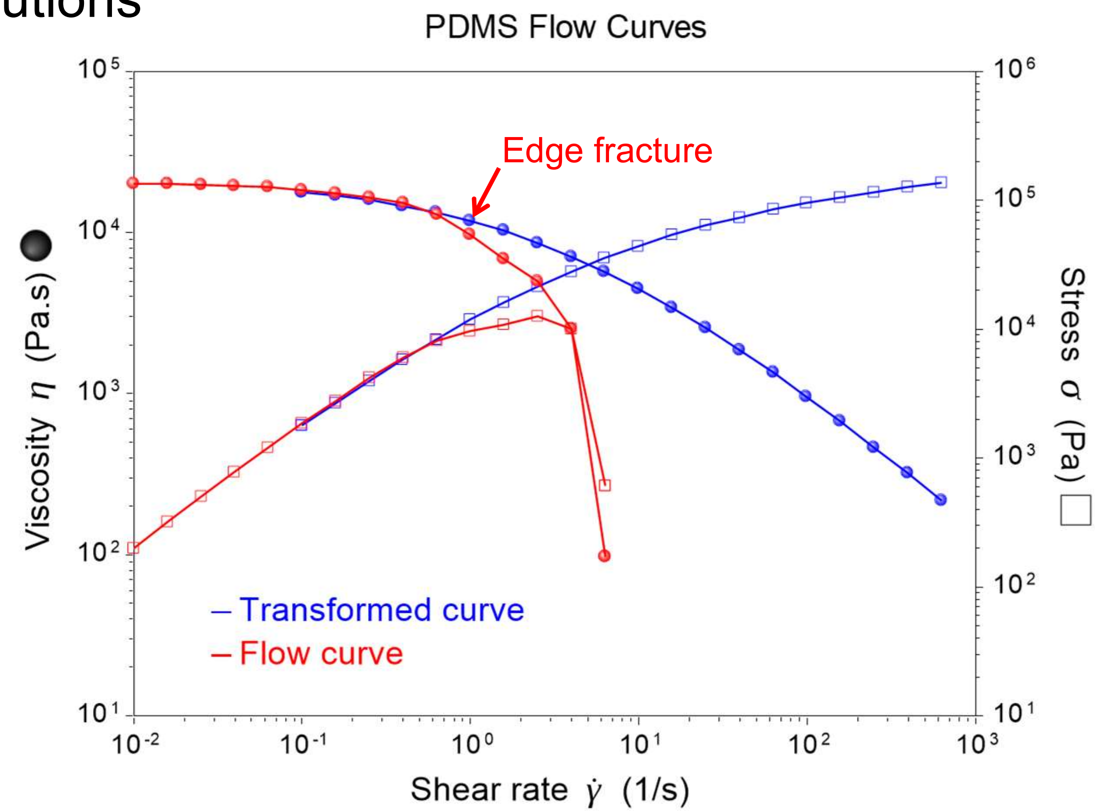
Steady state flow



η (Pa.s)~ $\dot{\gamma}$ (1/s)

Cox-Merz Transformation Benefit

- The Cox-Merz transformation works primarily with polymer melts and polymer solutions



Avoid Testing Artifacts

- TA Webinar - Professor Randy H. Ewoldt

  http://www.tainstruments.com/randy-h-ewoldt-experimental-challenges-of-shear-rheology-how-to-avoid-bad-data-2/

About the Speaker

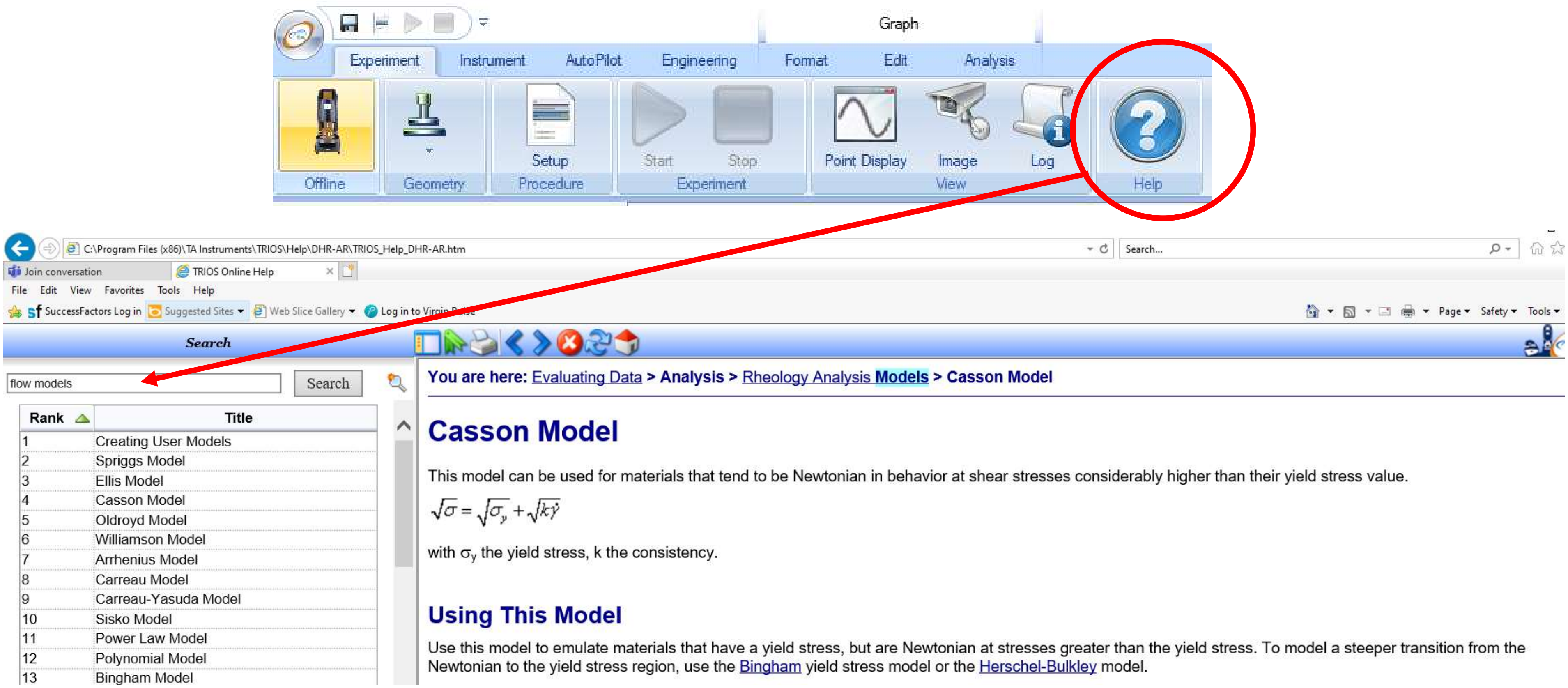
Randy H. Ewoldt is an Assistant Professor in the Department of Mechanical Science and Engineering at the University of Illinois at Urbana-Champaign. He has Ph.D. and S.M. degrees from MIT, and a B.S. degree from Iowa State, all in Mechanical Engineering. Before joining Illinois, he held a post-doctoral fellowship at the University of Minnesota. At Illinois, his research group studies rheology, fluid mechanics, and design of complex fluids; in particular, this includes yield stress fluids, polymer gels, biological materials, and large-amplitude oscillatory shear (LAOS) characterization. His work has been recognized by young investigator awards from NSF, ASME, 3M, DuPont, and The Society of Rheology.

Ewoldt R.H., Johnston M. T., Caretta L.M., "Experimental challenges of shear rheology: how to avoid bad data", in: S. Spagnolie (Editor), *Complex Fluids in Biological Systems*, Springer (2015) 1-36

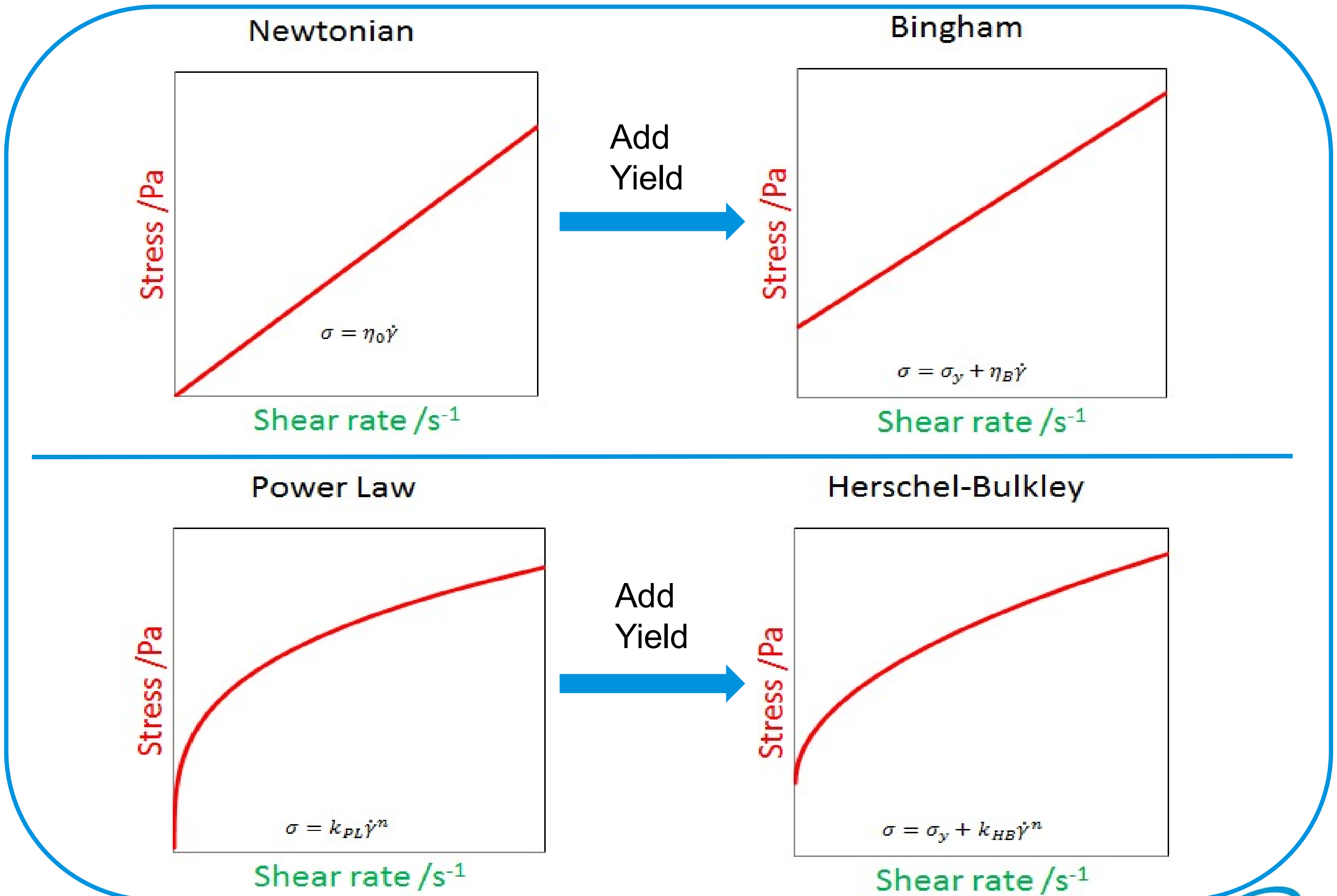
Flow Models

- Fit viscosity curves with mathematical models
  - Newtonian model
  - Power law model
  - Bingham model
  - Williamson model
  - Sisko model
  - Herschel-Bulkley model
  - Cross model
  - Carreau model
  - Carreau-Yasuda model
  - Casson model
  - Ellis model
- Extrapolate to zero shear and infinite shear viscosity
- Calculate viscosity at a specific point

Where to Find Model Equations

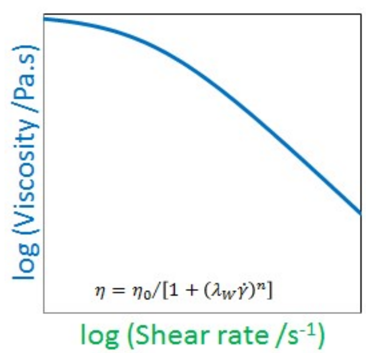


Flow Model Equations



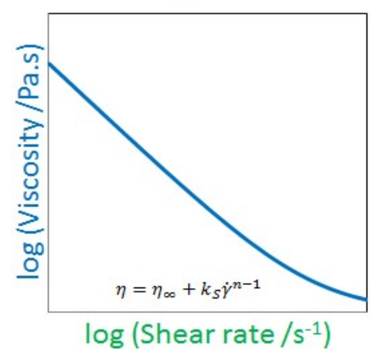
Flow Model Equations – Continued

Williamson



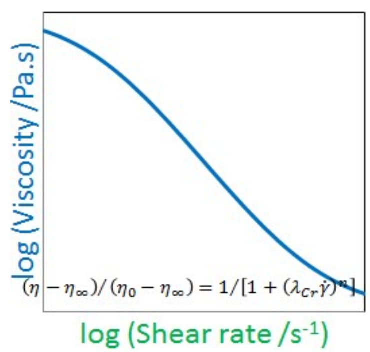
- **Zero Shear Viscosity**

Sisko

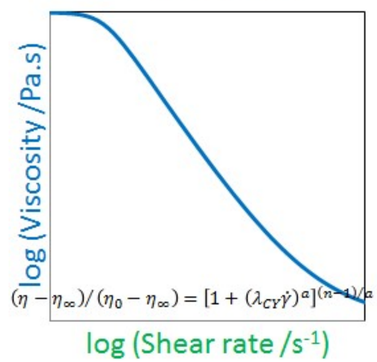


- **Infinite Shear Viscosity**

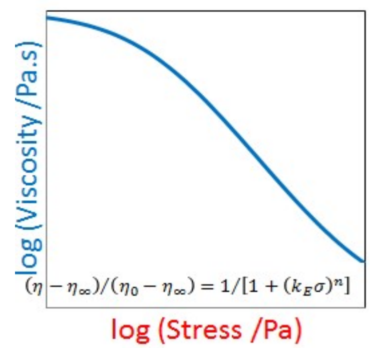
Cross



Carreau-Yasuda

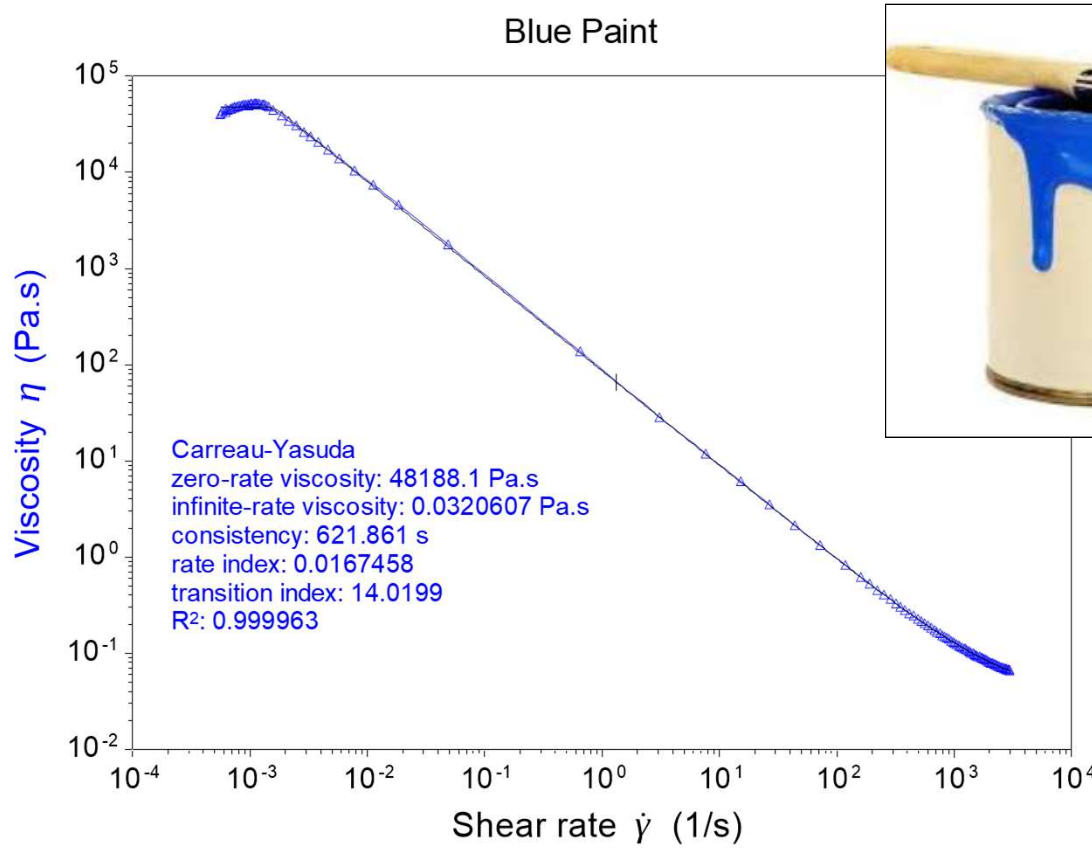


Ellis



- **Both Zero Shear and Infinite Shear Viscosity**

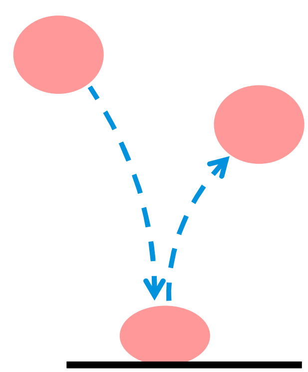
Fit Your Flow Data with a Model

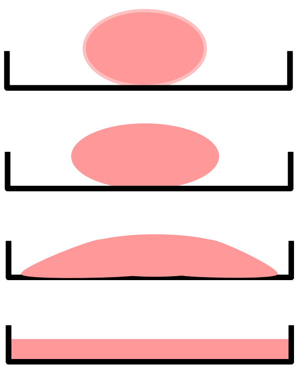


Experimental Designs
2. Oscillation Tests

Not Everything Flows

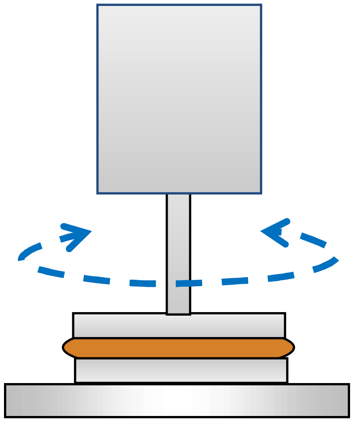
- **Liquid** - flows freely, remains at constant volume and takes the shape of its container
- **Solid** - has a fixed shape and volume, no flow
- **Semi-solid** – shows both viscous and elastic behavior. May flow under certain temperature or time scale

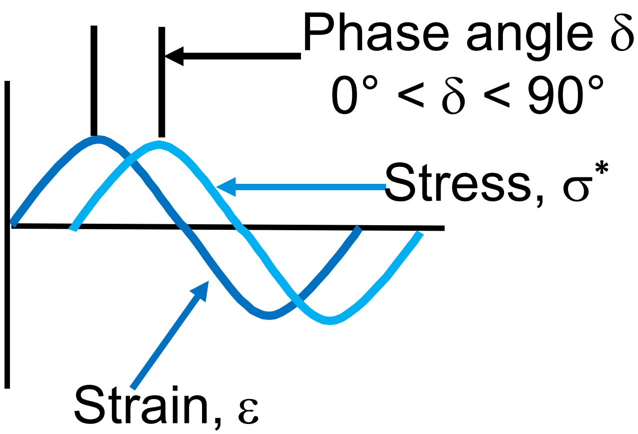




Dynamic Oscillatory Tests

- Apply a sinusoidal strain to the sample at a certain frequency
- Monitor sample response in stress
- The shift between the input strain and output stress is the phase angle





$$\gamma = \gamma_0 \cdot \sin(\omega t)$$
$$\sigma = \sigma_0 \cdot \sin(\omega t + \delta)$$

Viscoelastic Parameters

Complex Modulus: Measure of materials overall resistance to deformation

$$G^* = \left(\frac{\text{Stress}^*}{\text{Strain}}\right)$$

Elastic (Storage) Modulus: Measure of elasticity of material and ability to store energy

$$G' = \left(\frac{\text{Stress}^*}{\text{Strain}}\right) \cos\delta$$

Viscous (loss) Modulus: The ability of the material to dissipate energy

$$G'' = \left(\frac{\text{Stress}^*}{\text{Strain}}\right) \sin\delta$$

Tan Delta: Measure of material damping

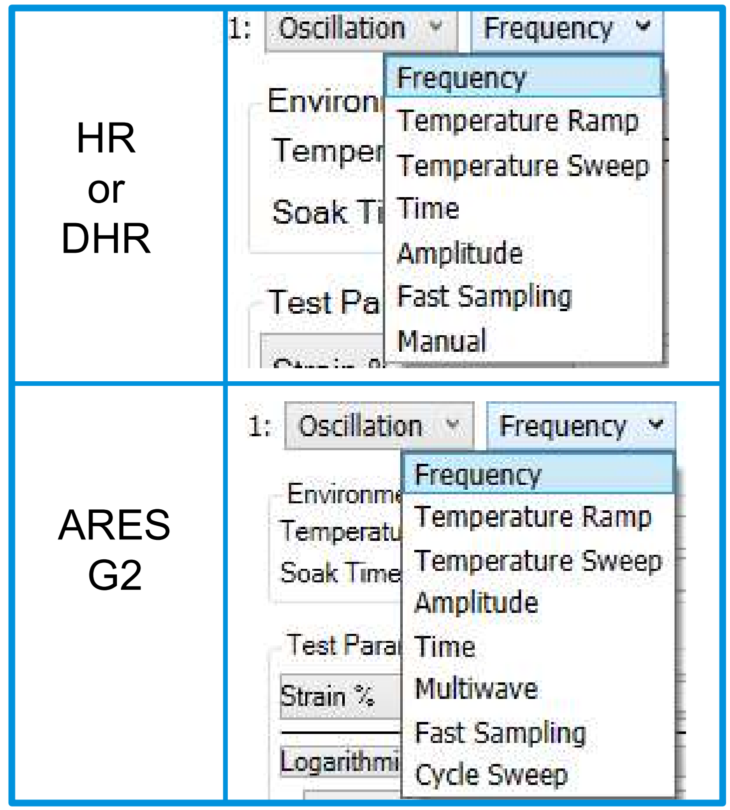
$$\tan\delta = \left(\frac{G''}{G'}\right)$$

Complex Viscosity: Viscosity measured in an oscillatory experiment (ω in rad/s)

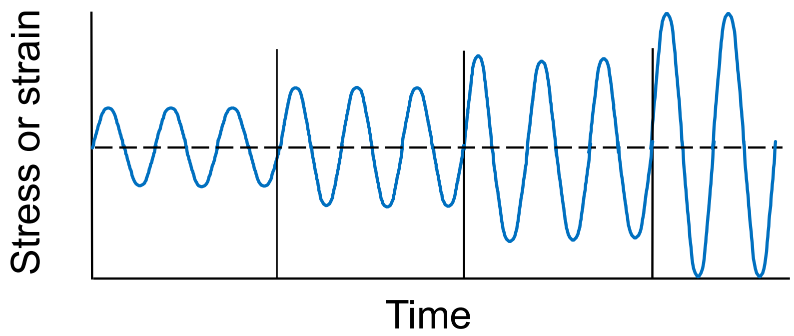
$$\eta^* = \left(\frac{G^*}{\omega}\right)$$

Dynamic Oscillation Methods

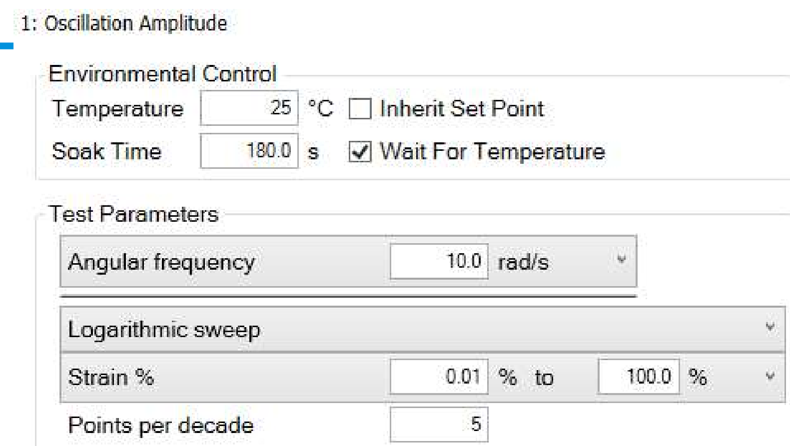
- Stress, strain, or amplitude sweep
- Time sweep
- Frequency sweep
- Temperature ramp
- Temperature sweep (or step)
  - Time temperature superposition (TTS)



Dynamic Strain or Stress Sweep



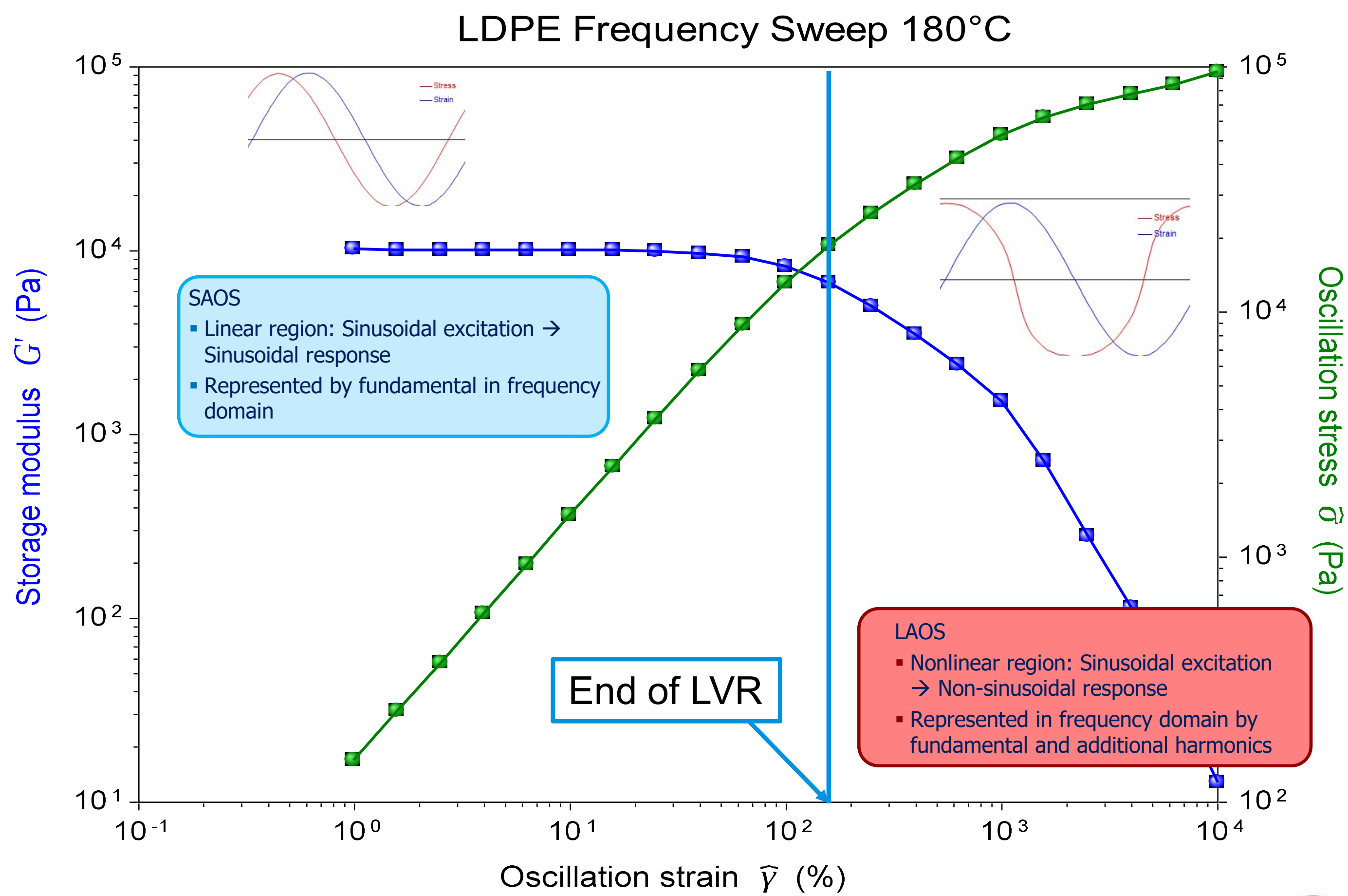
- The material response to increasing deformation amplitude (strain or stress) is monitored at a constant frequency and temperature
- In TRIOS: Amplitude



<u>USES</u>

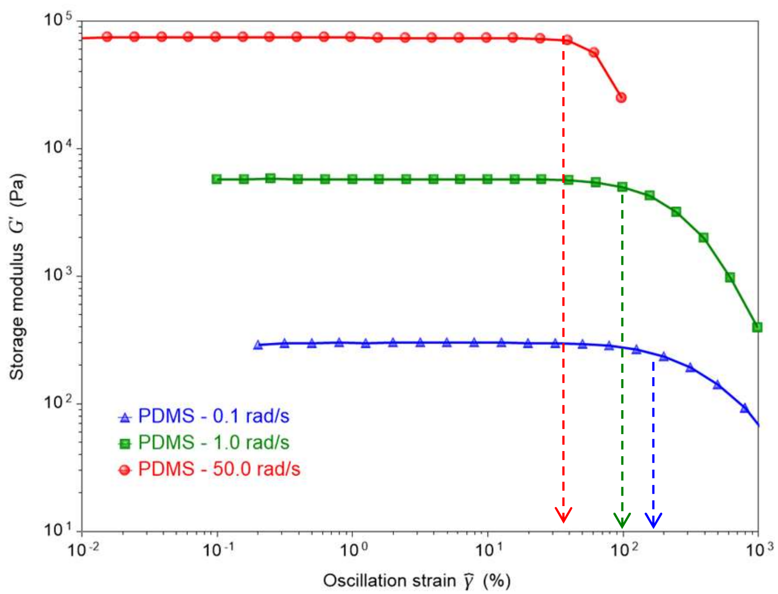
- Measure sample LVE
- Measure yield stress
- Measure non-linear viscoelastic properties (LAOS)

Linear and Non-linear Viscoelasticity

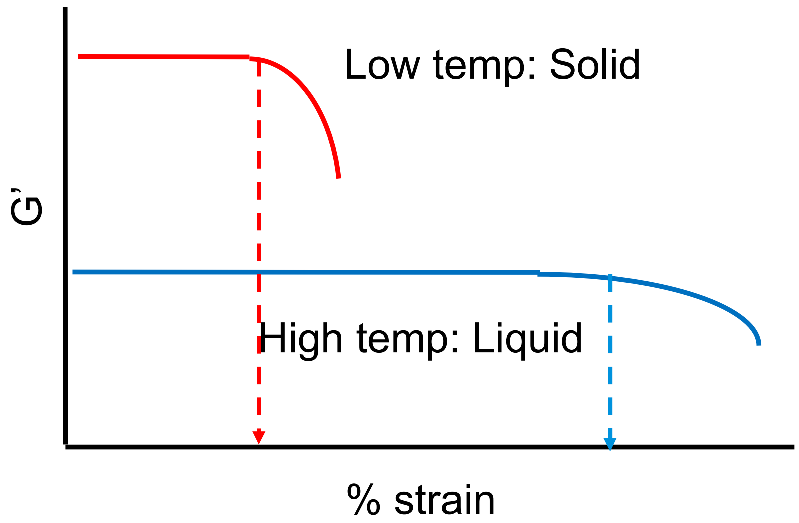


What Affect the LVR

- LVR is sensitive to frequency



- LVR is sensitive to temperature



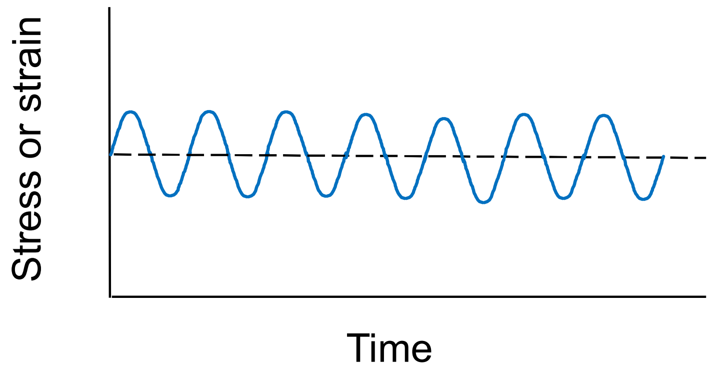
LAOS Webinar

- TA Webinar - Professor Gareth H. Mckinley
  - https://www.tainstruments.com/rheological-fingerprinting-of-complex-fluids-ta-instruments-webinar/

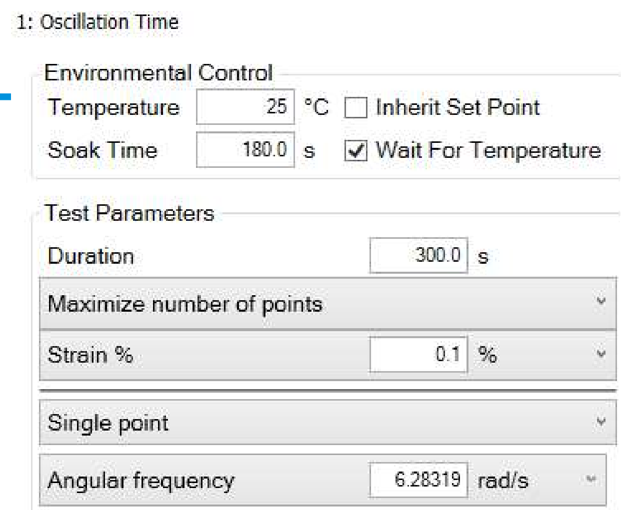
Gareth H. McKinley is Professor and Associate Head of the Department of Mechanical Engineering at MIT. His research interests include extensional rheometry, microfluidic rheometry and non-Newtonian fluid dynamics. He has aided in the development of several rheological techniques for characterizing the extensional rheology of polymer solutions, micellar liquids and other complex fluids. He is a Fellow of the American Physical Society, winner of the 1994 Annual Award of the British Society of Rheology, and this year's Bingham Medalist from the Society of Rheology.

Hyun, K., Wilhelm, M., Klein, C.O., Cho, K.S., Nam, J.G., Ahn, K.H., Lee, S.J., Ewoldt, R.H. and McKinley, G.H., **A Review of Nonlinear Oscillatory Shear Tests: Analysis and Application of Large Amplitude Oscillatory Shear (LAOS)**, *Rev. Poly. Sci*, (2010) **36**, 1697 - 1753; DOI:10.1016/ j.progpolymsci.2011.02.002. GHM164.pdf Abstract

Dynamic Time Sweep



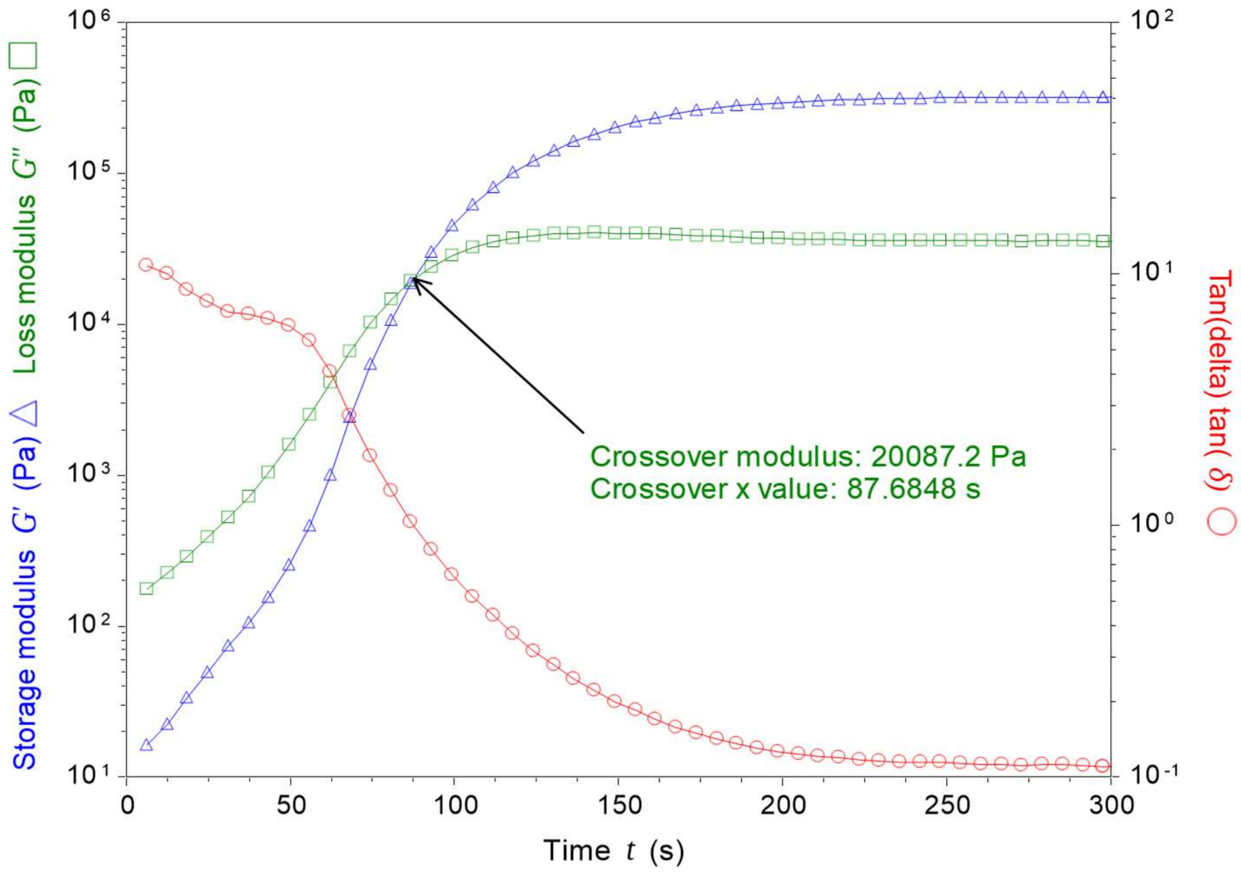
- The material response is monitored at a constant frequency, amplitude and temperature.
- In TRIOS: Time



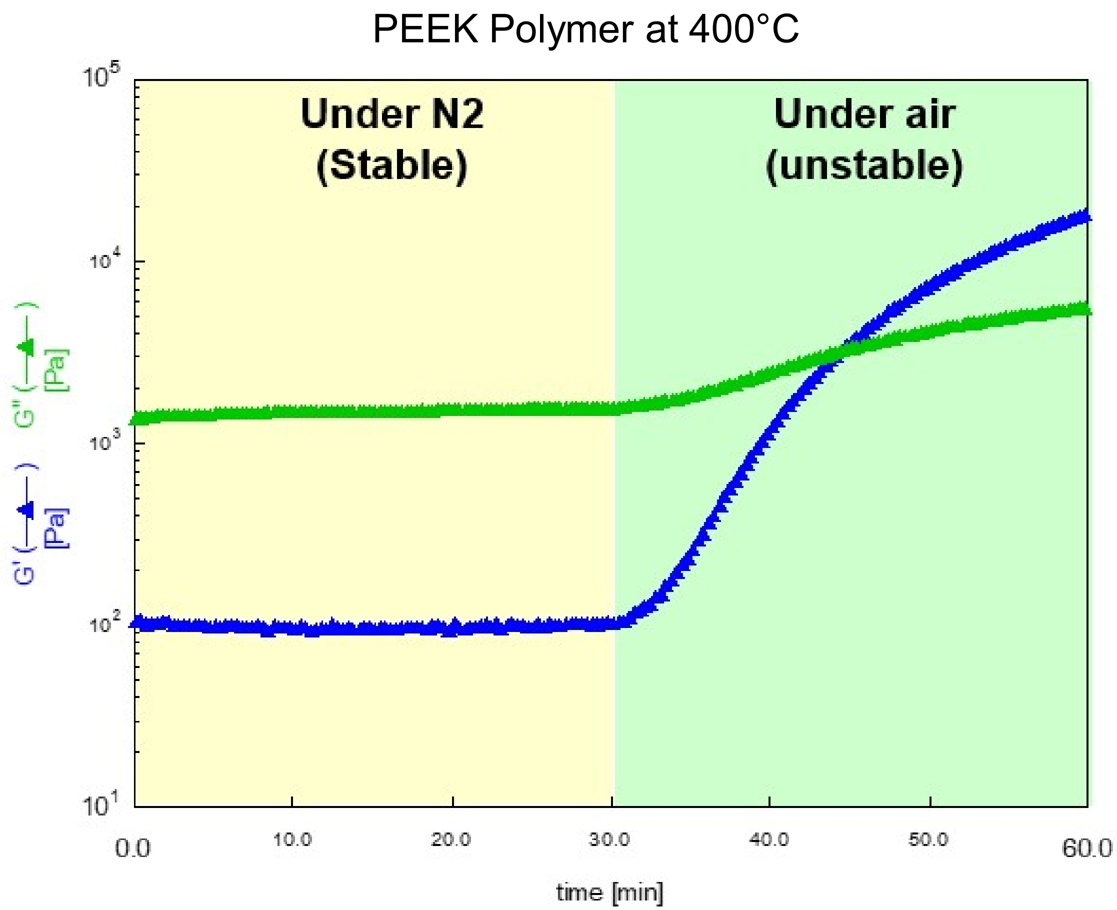
USES

- Cure Studies
- Stability against thermal degradation
- Time dependent Thixotropy

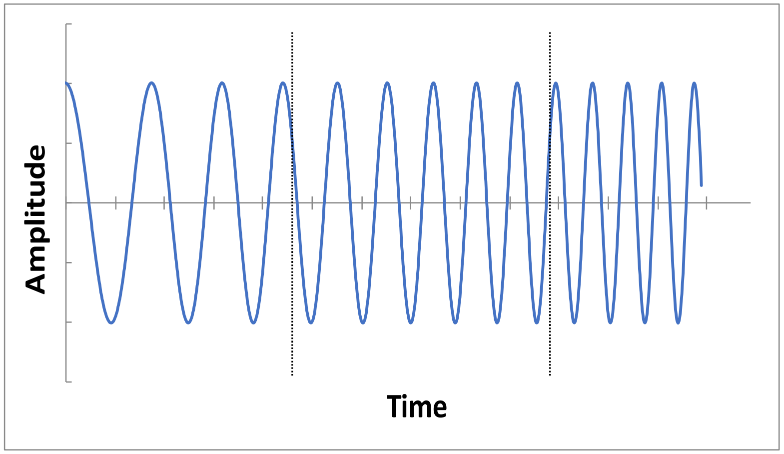
Epoxy Curing



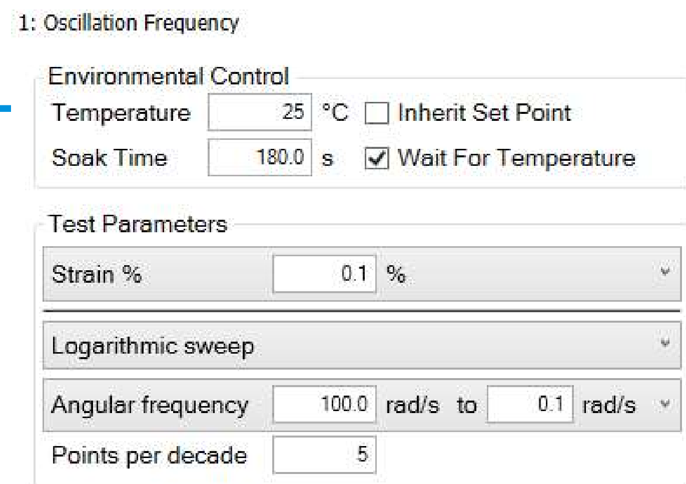
Time Sweep – Polymer Melt Thermal Stability



Frequency Sweep



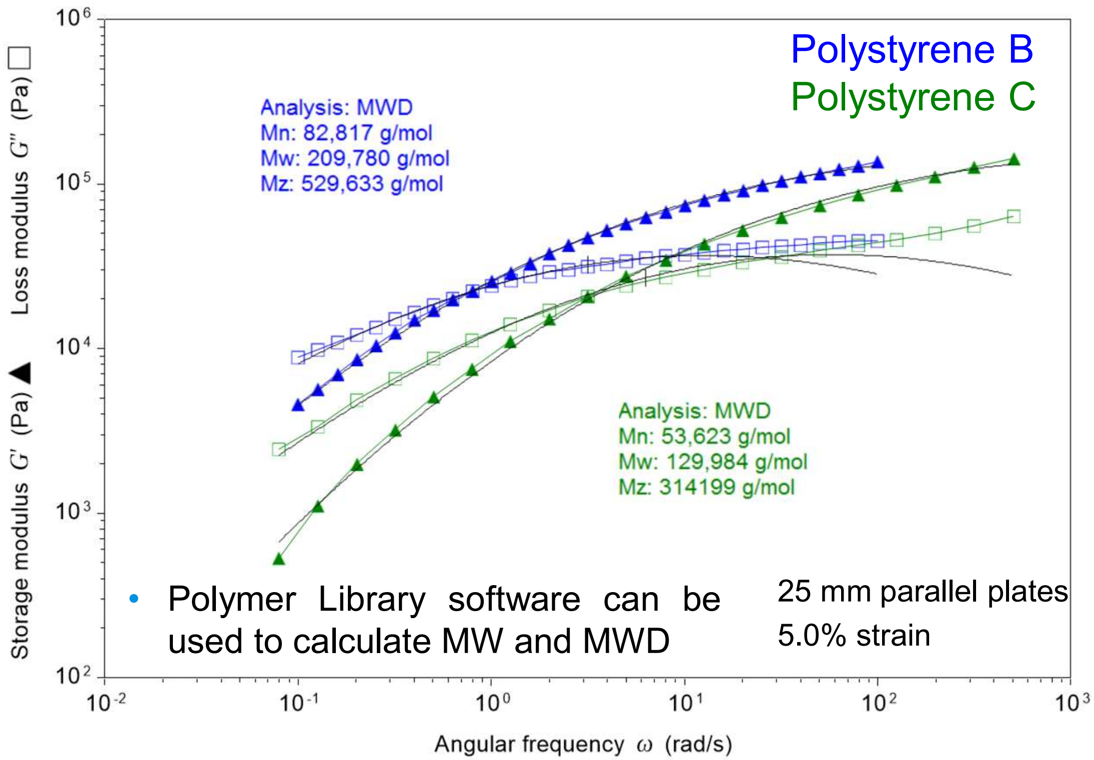
- The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude (strain or stress) and temperature.
- In TRIOS: Frequency



USES

- Measure polymer relaxation
- Measure polymer Mw/ MWD
- Scouting differences of viscoelastic properties between formulations

Frequency Sweep – polymer melt (ASTM D4440)



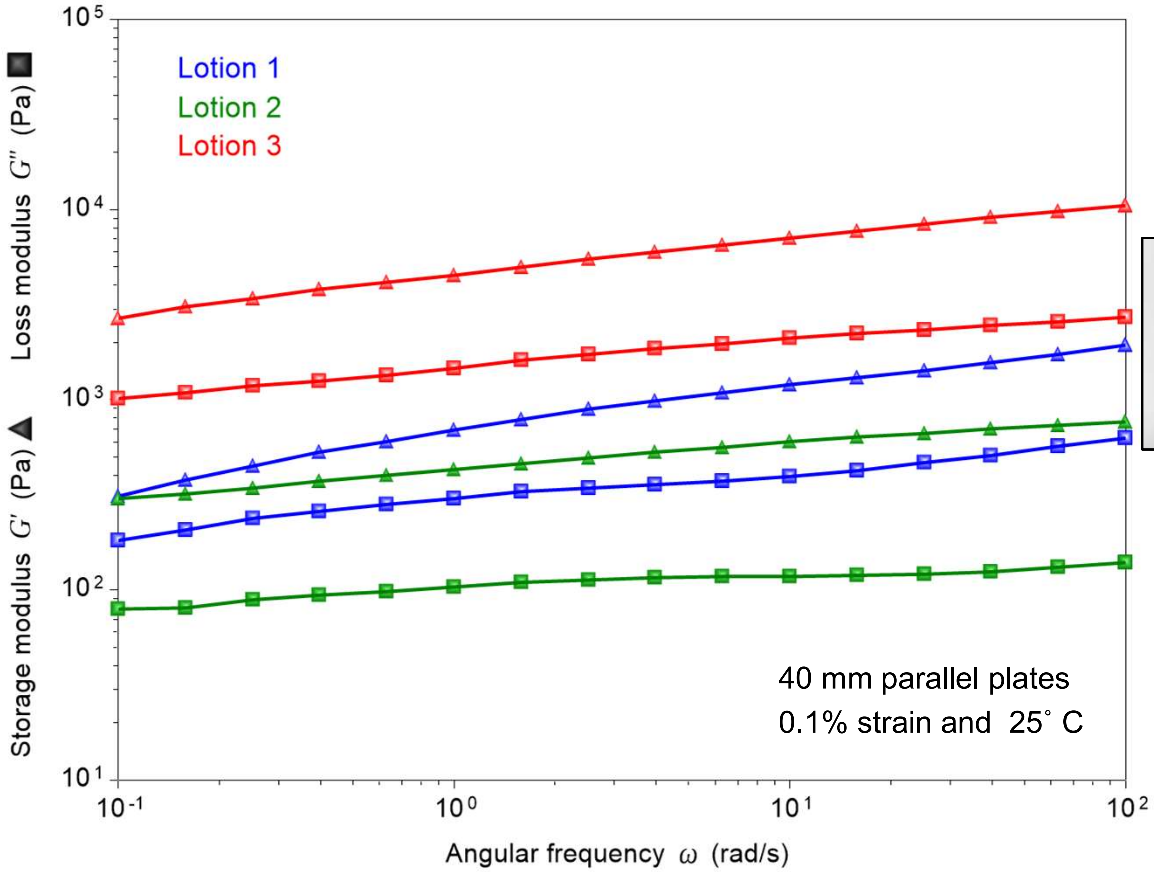
- Polymer Library software can be used to calculate MW and MWD

TA Instruments Webinar

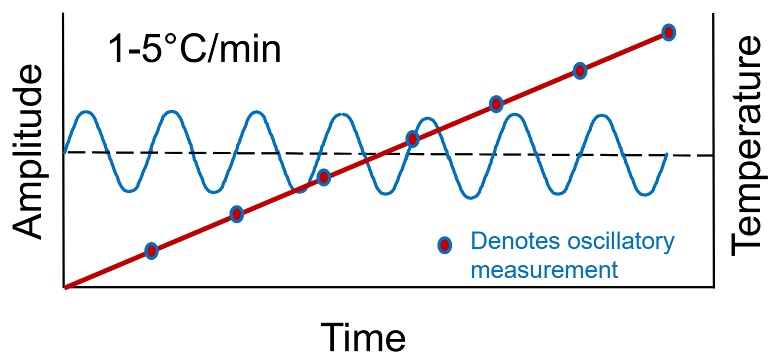
Professor Chris Macosko – Analyzing Molecular Weight Distribution w/ Rheology

https://www.tainstruments.com/analyzing-molecular-weight-distribution-w-rheology/

Frequency Sweep – Lotions



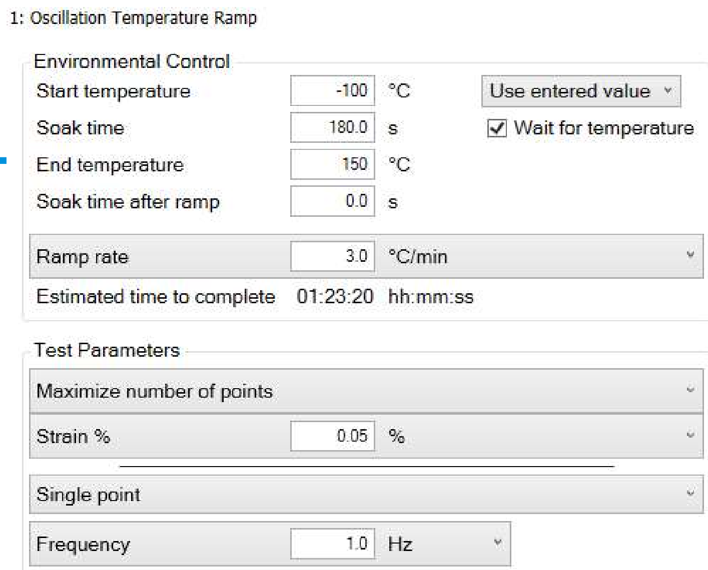
Dynamic Temperature Ramp



USES

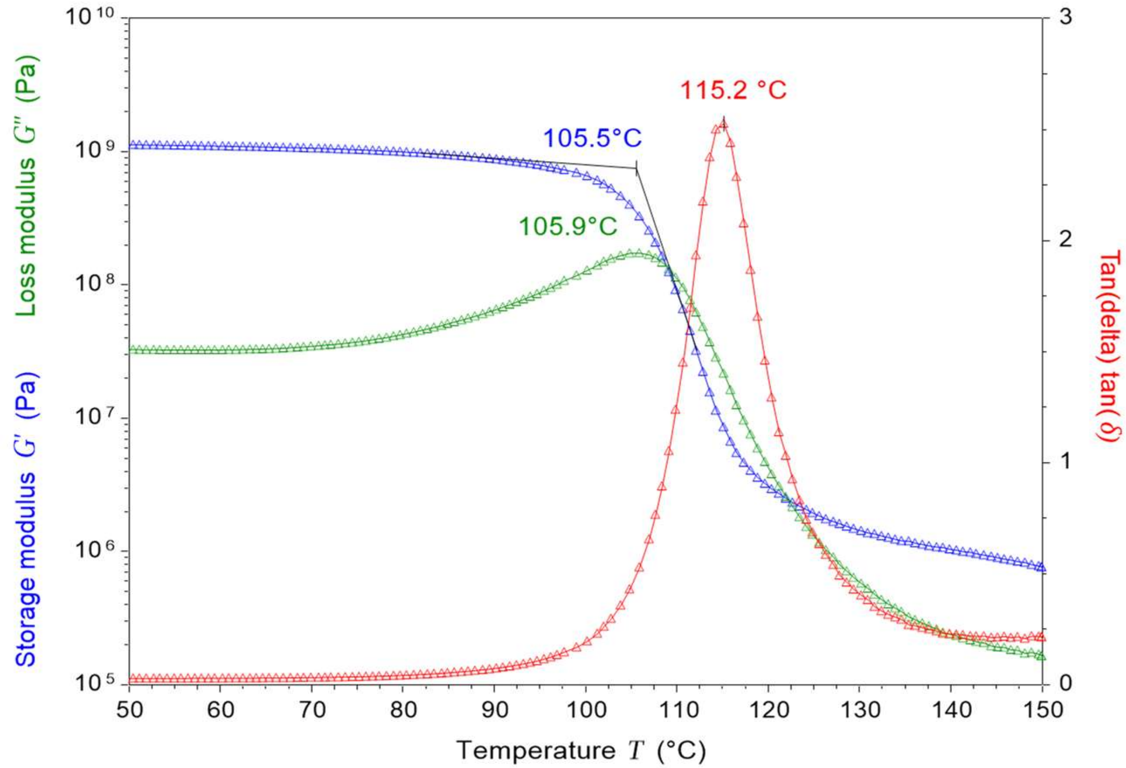
- Measure material's viscoelastic properties vs. temperature
- Measure glass transition and sub-ambient transition temperatures

- Linear heating rate is applied, and the material response is monitored at a constant frequency and constant amplitude
- In TRIOS: Temp Ramp

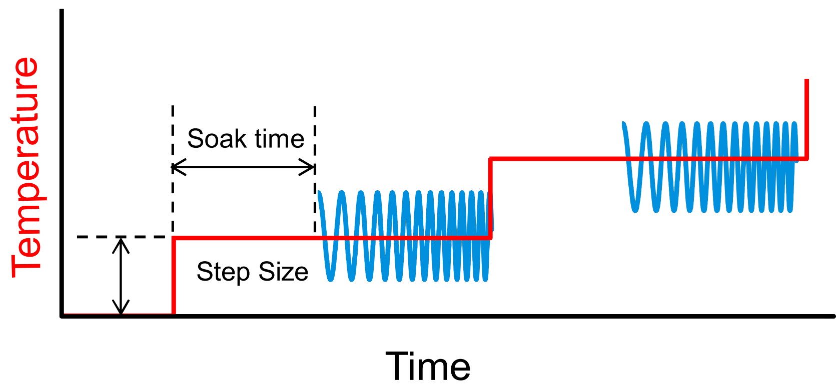


Dynamic Temp Ramp Test on ABS

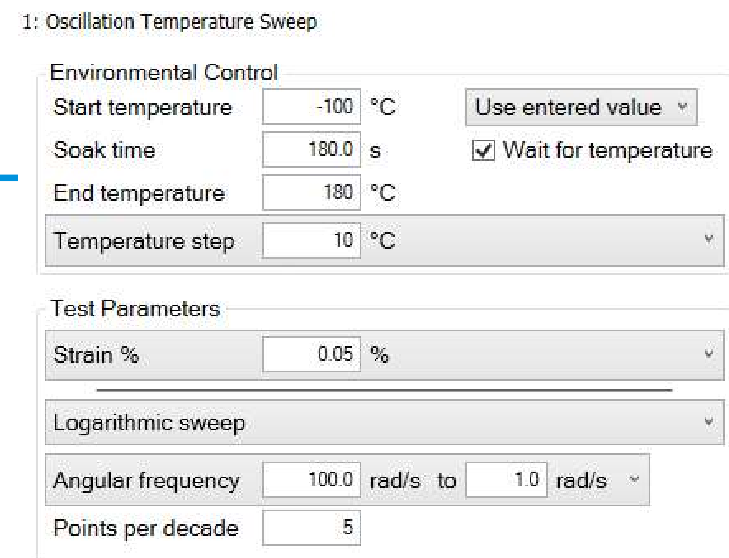
- Measure moduli, tan δ and transitions



Temperature Sweep (or Step)



- Step and hold temperature then monitor material response. No thermal lag
- In TRIOS: Temp Sweep



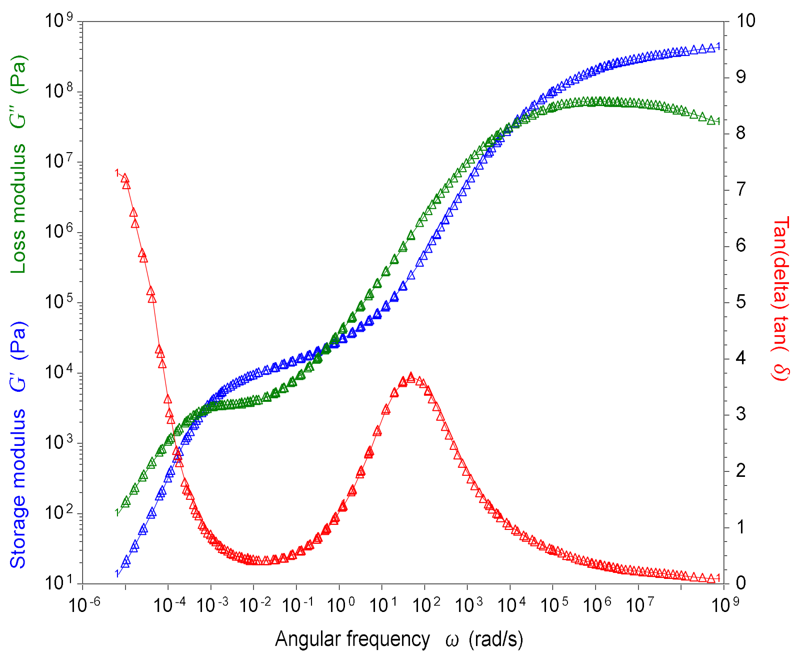
<u>USES</u>

- Measure material's viscoelastic properties vs. temperature
- Time-Temperature Superposition test (TTS)

Time-Temperature Superposition (TTS)

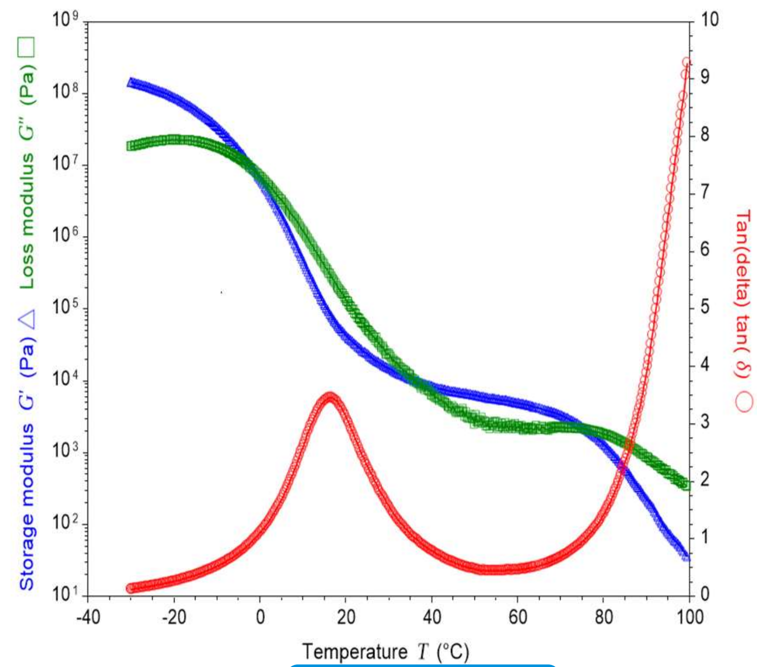
- Rheological measurement results on a non-crosslinked adhesive

TTS master curve generated at 20°C



Time

Dynamic temperature ramp

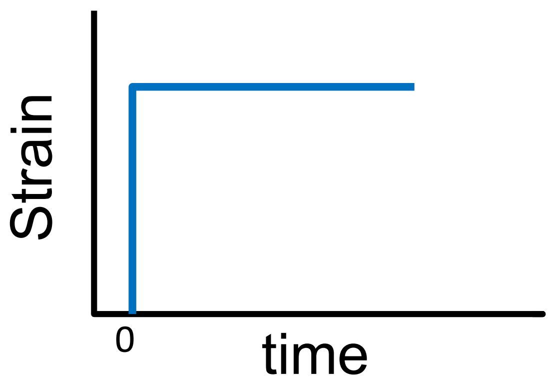


Temperature

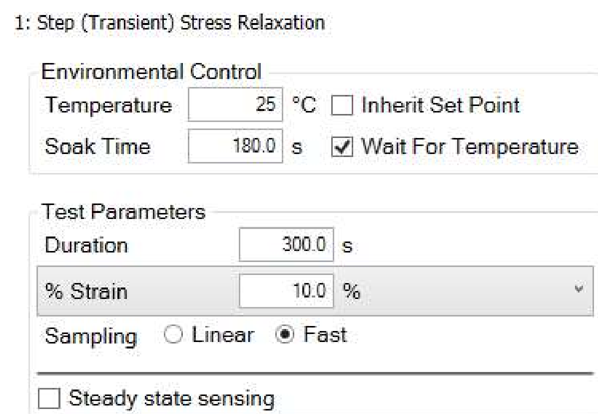
Experimental Designs
3. Transient Tests

Stress Relaxation Experiment

- Strain is applied to sample instantaneously (in principle) and held constant with time.
- Stress is monitored as a function of time $\sigma(t)$.

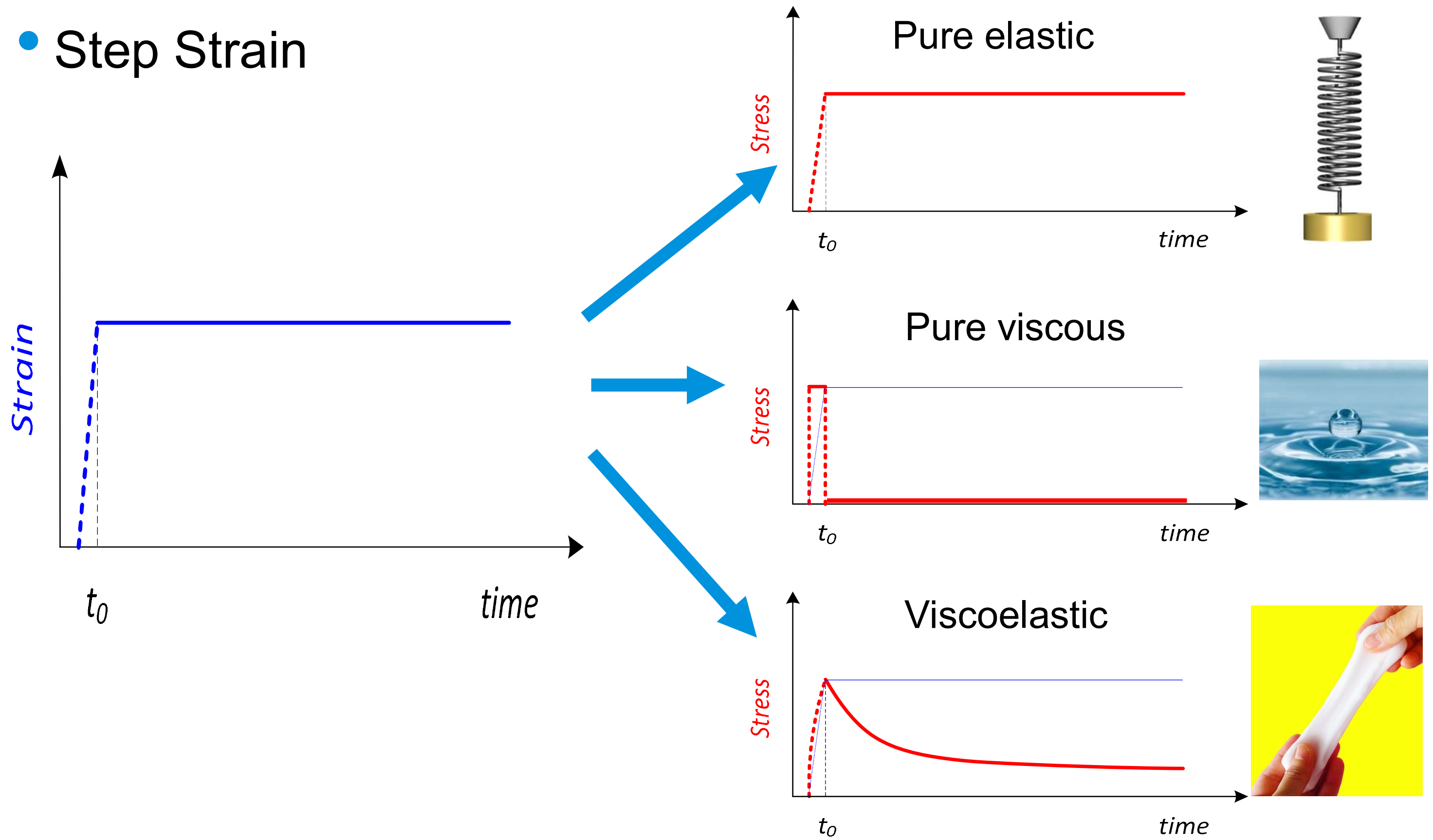


$$\text{Relaxation modulus} = \frac{\text{Stress}}{\text{Strain}}$$



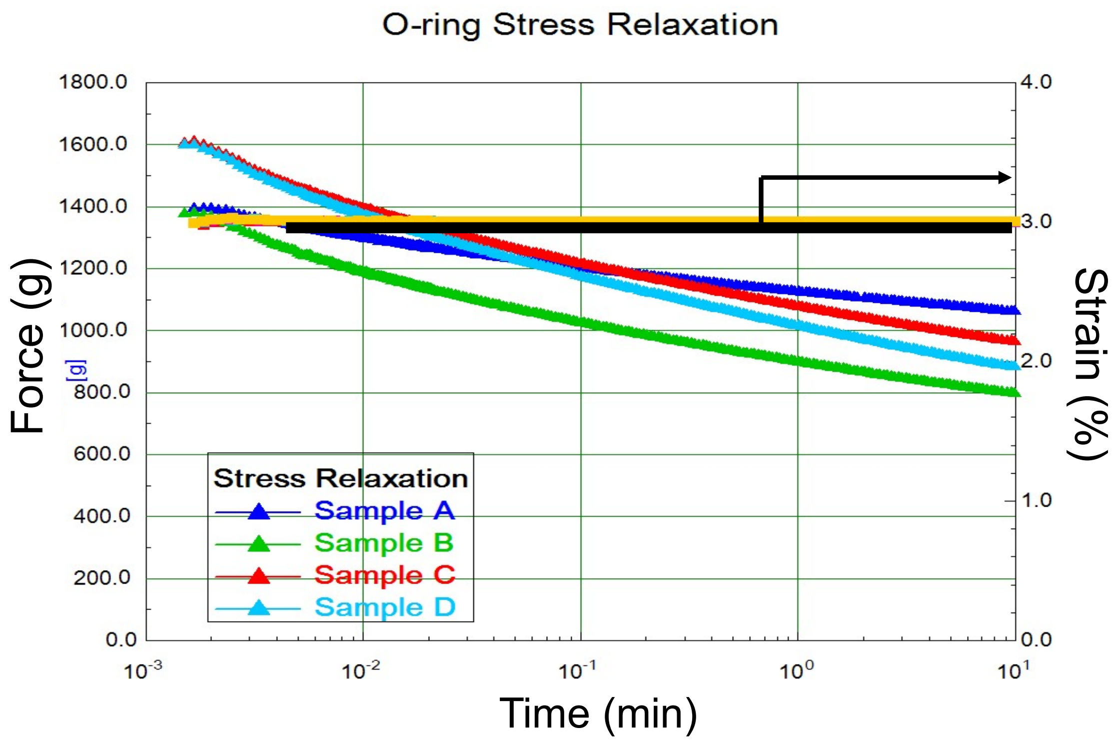
Stress Relaxation- Sample Response

- Step Strain



O-rings: Stress Relaxation

- Squeeze the O-ring to 3% strain. Hold it constant, then measure how long it takes for the force to relax



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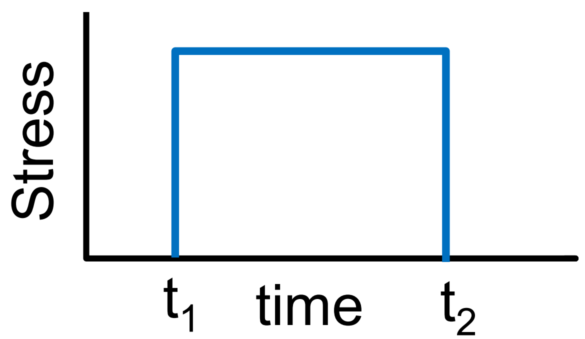
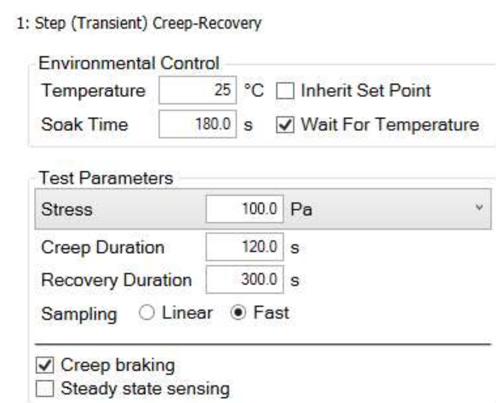
Creep Recovery Experiment

- Creep: Stress is applied to sample instantaneously at t_1, and held constant for a specific period of time. The strain is monitored as a function of time ($\gamma(t)$ or $\varepsilon(t)$)
- Recovery: Stress is reduced to zero at t_2, and the strain is monitored as a function of time ($\gamma(t)$ or $\varepsilon(t)$)

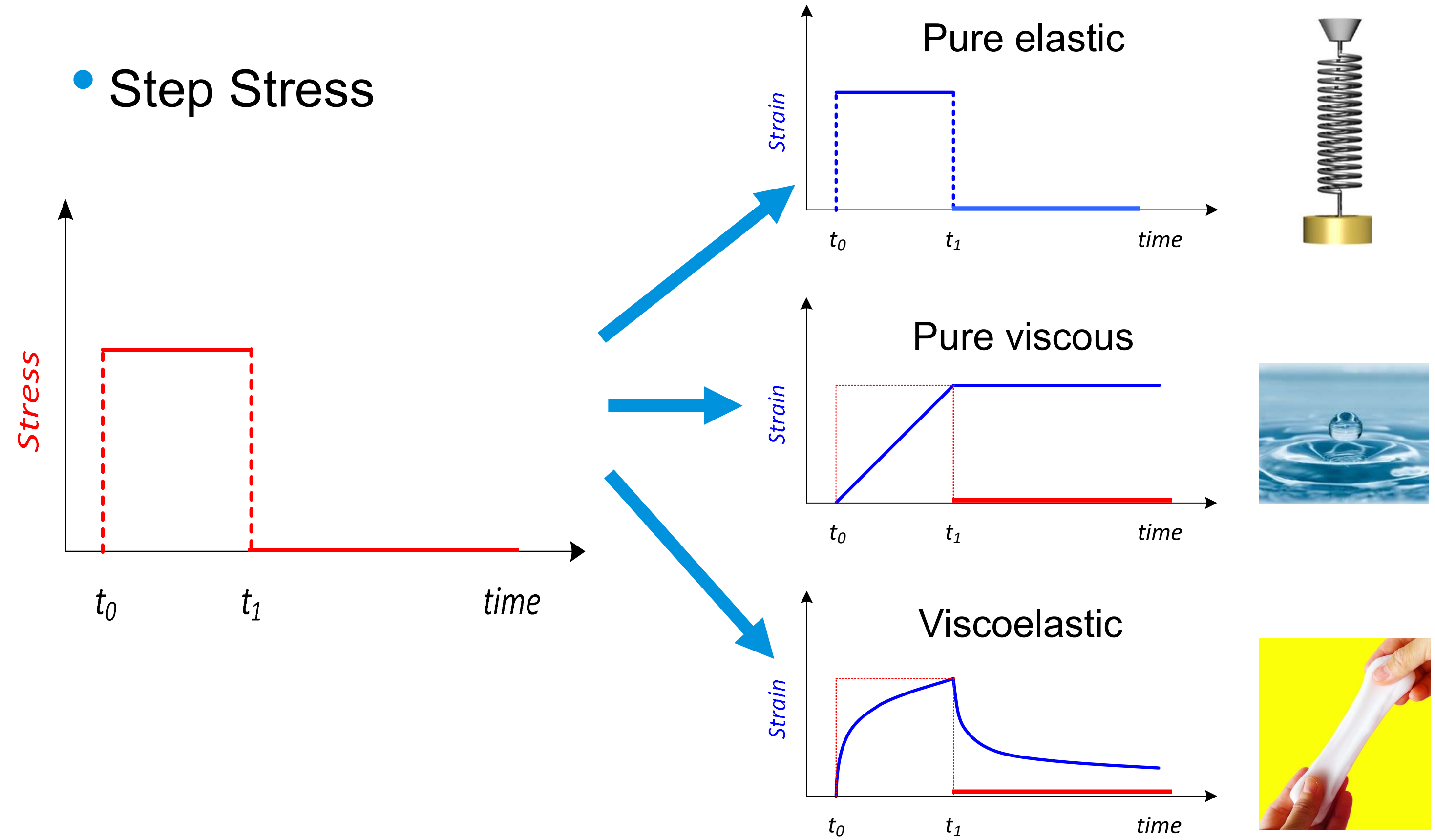
$$\text{Creep compliance } J = \frac{\text{Strain}}{\text{Stress}}$$



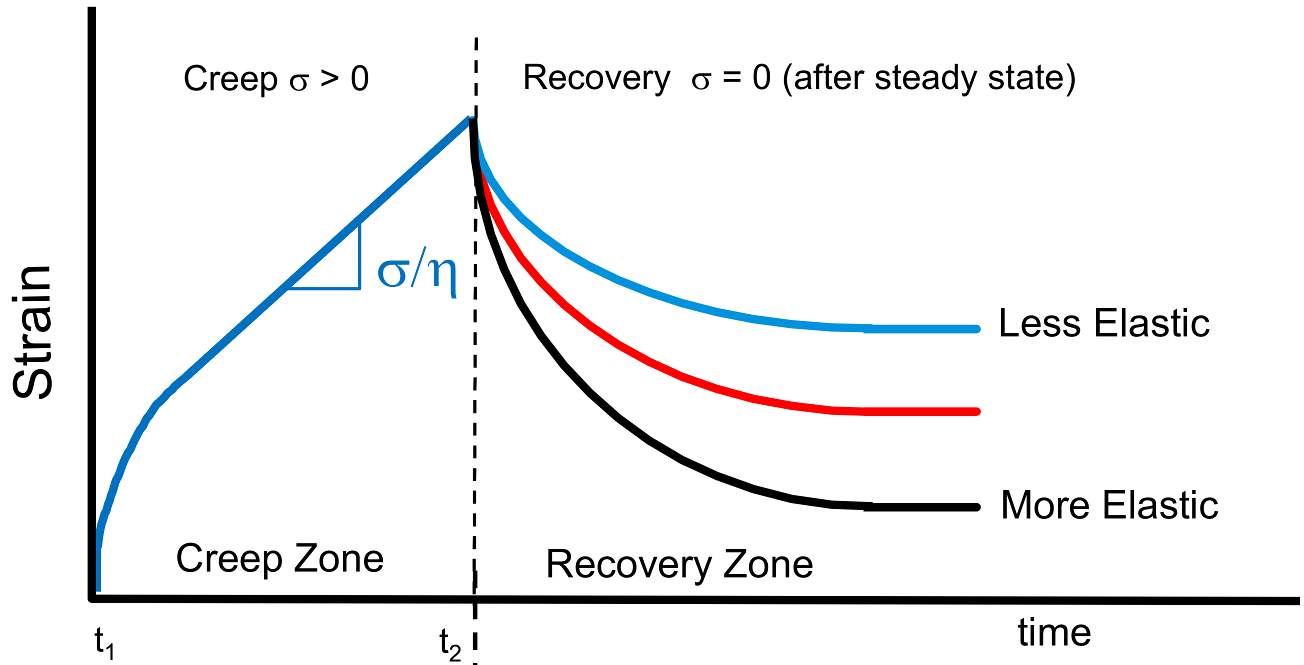


Creep Recovery – Sample Response

- Step Stress



Creep Recovery Experiment

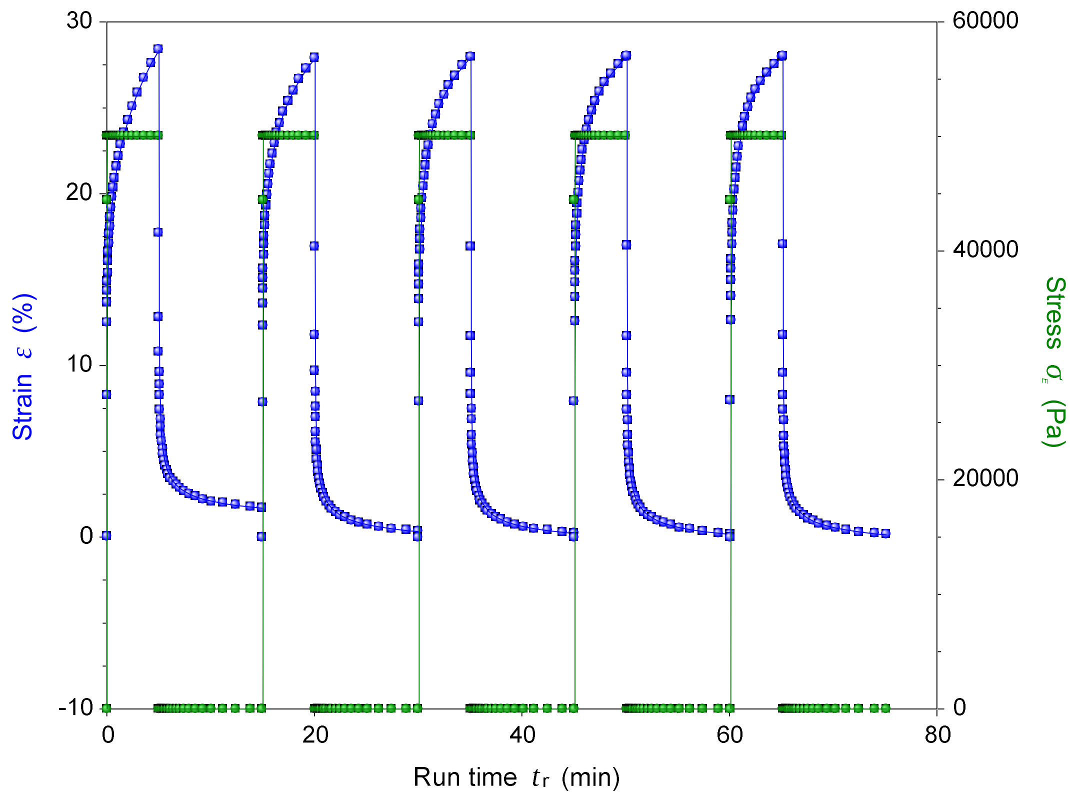


Strain rate decreases with time in the creep zone, until finally reaching a steady state.

In the recovery zone, the viscoelastic fluid recoils, eventually reaching a equilibrium at some small total strain relative to the strain at unloading.

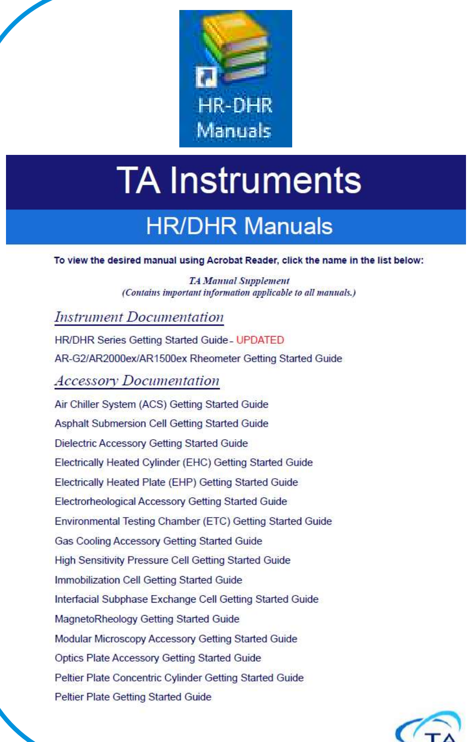
Mark, J., et. al., Physical Properties of Polymers, American Chemical Society, 1984, p. 102.

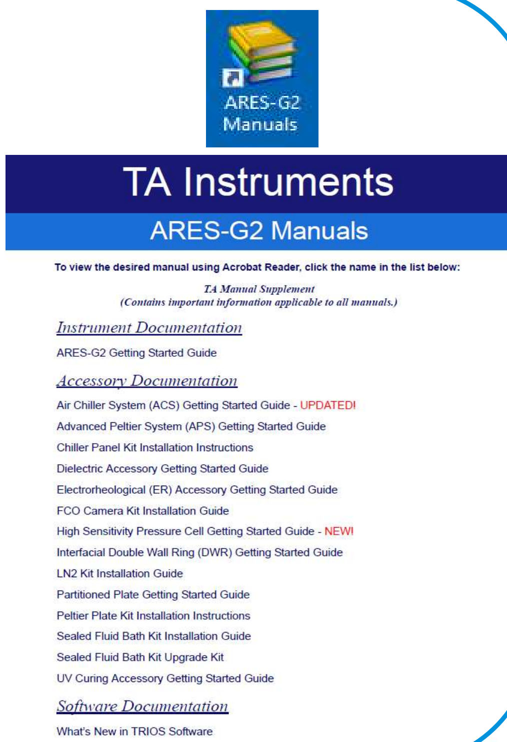
Memory Foam: Multi-Step Creep Recovery



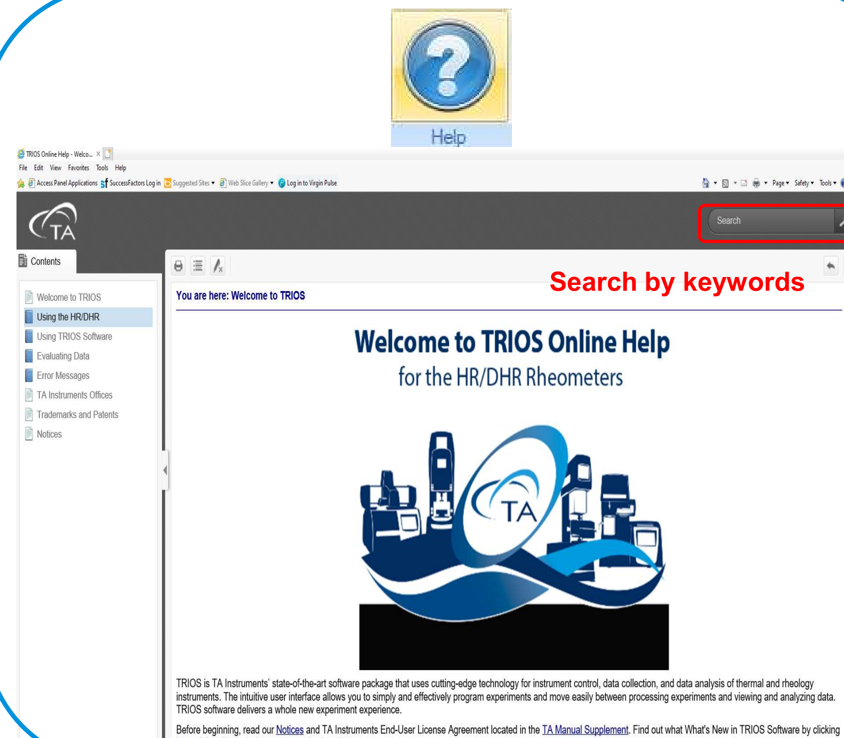
Where to Find Help

On your desktop





In TRIOS



Web Based e-Training Courses

Web based e-Training Courses

TA Instruments offers a variety of training opportunities via the Internet. e-Training opportunities include the following:

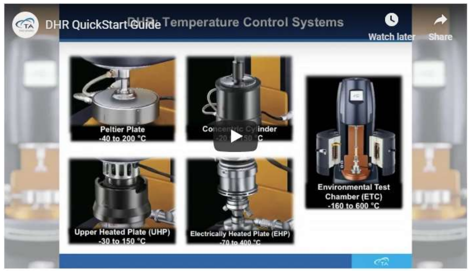
QUICKSTART e-TRAINING COURSES

QuickStart e-Training courses are designed to teach a new user how to set up and run samples on their analyzers. These 60-90 minute courses are available whenever you are. These pre-recorded courses are available to anyone at no charge. Typically these courses should be attended shortly after installation.

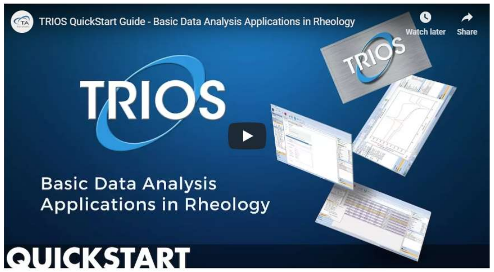
https://www.tainstruments.com/training/e-training-courses/

ARES G2

Discovery HR

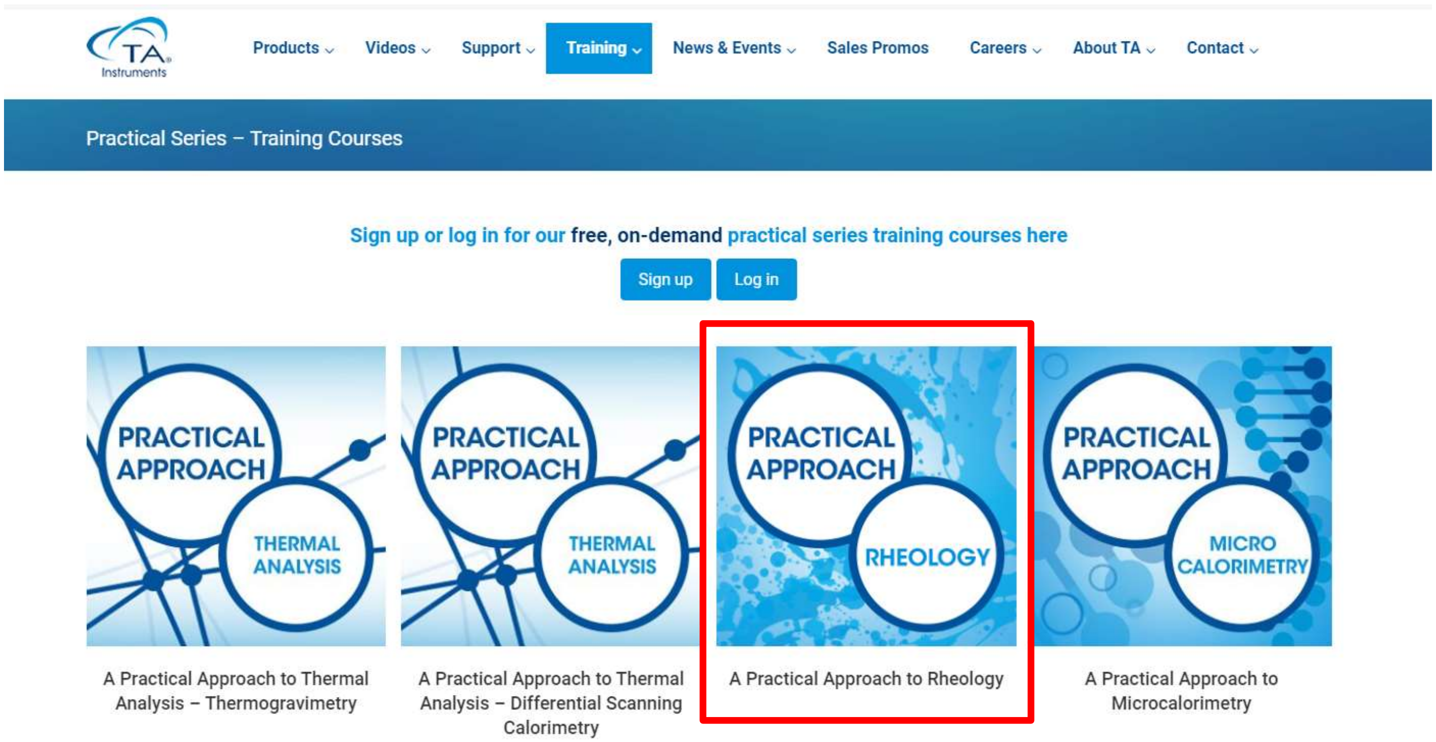


TRIOS Software



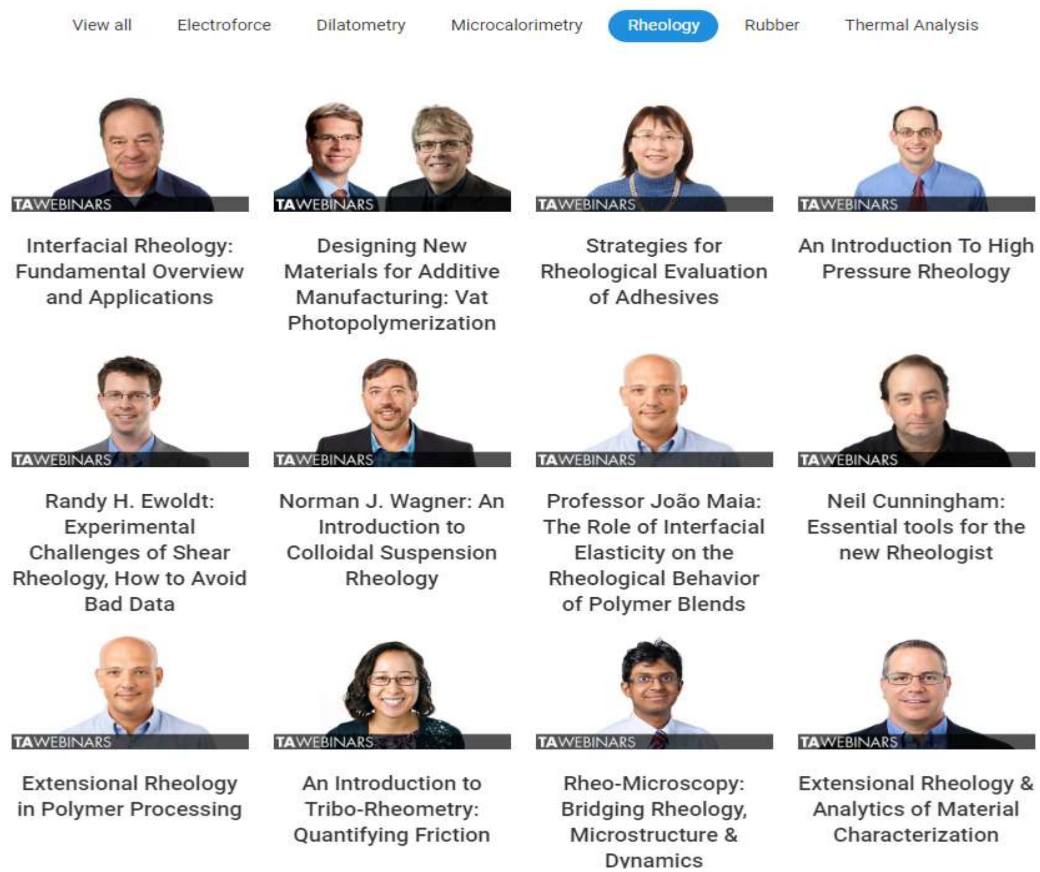
Practical Series Training Course

https://www.tainstruments.com/practical-series-training-courses/



TA Webinars - Rheology

https://www.tainstruments.com/support/webinars/



TA Website – Other Resources

Tech Tips


Installation & Calibration of the Relative Humidity Accessory for the Discovery Hybrid Rheometer


Shear Sandwich Clamp Installation & Calibration for the Discovery DMA 850


Three Point Bend Clamp Installation & Calibration for the DMA850

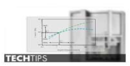

Installation and Calibration for the UV Accessory on the Ares G2 Rheometer


Single Cantilever Installation & Calibration – DMA 850


Dual Cantilever Installation & Calibration – DMA 850


Linear Film Tension Clamp for DMA using the ARES-G2


Loading the Powder Clamp on the Q800 DMA with 35mm Dual Cantilever Clamp


Frequency Sweep Tests for RPA Flex and RPA Elite


Improving Structured Fluid Measurements w/ Pre-Shearing


Measuring Thixotropy Of A Sample- TA TechTips


The Double Wall Ring & Interfacial Measurements – TA

Applications Notes Library

Applications Notes Library

Our instruments are used in a variety of products, in multiple industries. The application notes below provide more detail on specific potential applications. You can search for specific app notes with the search field.

rheology

261 item

Title	Product Category	Ref#	Link
Hot Melt Adhesives	Rheology	AAN001	Download Note
Generating Mastercurves	Rheology	AAN005e	Download Note
Analytical Rheology	Rheology	AAN006e	Download Note
Normal Stresses in Shear Flow	Rheology	AAN007e	Download Note
Mischungsregein Komplexer Polyersysteme	Rheology	AAN008d	Download Note
Mixing Rules for Complex Polymer Systems	Rheology	AAN008e	Download Note
Application of Rheology of Polymers	Rheology	AAN009	Download Note
Synergy of the Combined Application of Thermal Analysis and Rheology Monitoring and Characterizing Changing Processes in Materials	Rheology	AAN010e	Download Note

Seminar Series: Instant Insights

Seminars:

- Thermal Analysis and Rheology
- Medical Device and Biomaterials Testing
- Elastomers and Rubber Compounds
- TRIOS AutoPilot & TRIOS Guardian

Thermal, Rheological and Mechanical Characterizations of Thermoset

Tianhong (Terri) Chen, Ph.D.

Thermosetting materials, such as epoxy, have been widely applied in many areas including automotive, aerospace and electronics industries in the form of surface coating, structural adhesives, advanced composites and packaging materials.

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Advancements in the Characterization of Pharmaceuticals by DSC

Jason Saienga, Ph.D.

Differential Scanning Calorimetry is a simple, yet powerful technique to gain a broad understanding of the characteristics of pharmaceutical materials, from the crystalline structure that exists to the compatibility of a specific formulation.

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Steady State & Flash Methods for Thermal Diffusivity and Thermal Conductivity Determination

Justin Wynn

In this presentation we will demonstrate accurate and high-throughput methods to measure the critical heat transfer properties of thermal diffusivity and thermal conductivity.

View Archive

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- Email rheologysupport@tainstruments.com
- Please put Online Training Questions in the subject line
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