Rheology
Theory and Applications

Course Outline

- Basics in Rheology Theory
- TA Rheometers
  - Instrumentation
  - Choosing a Geometry
  - Calibrations
- Flow Tests
  - Viscosity
  - Setting up Flow Tests
- Oscillation
  - Linear Viscoelasticity
  - Setting up Oscillation Tests
- Transient Testing
- Applications of Rheology
  - Polymers
  - Structured Fluids
  - Advanced Accessories

Basics in Rheology Theory

Rheology: An Introduction





Rheology: The study of
stress-deformation relationships





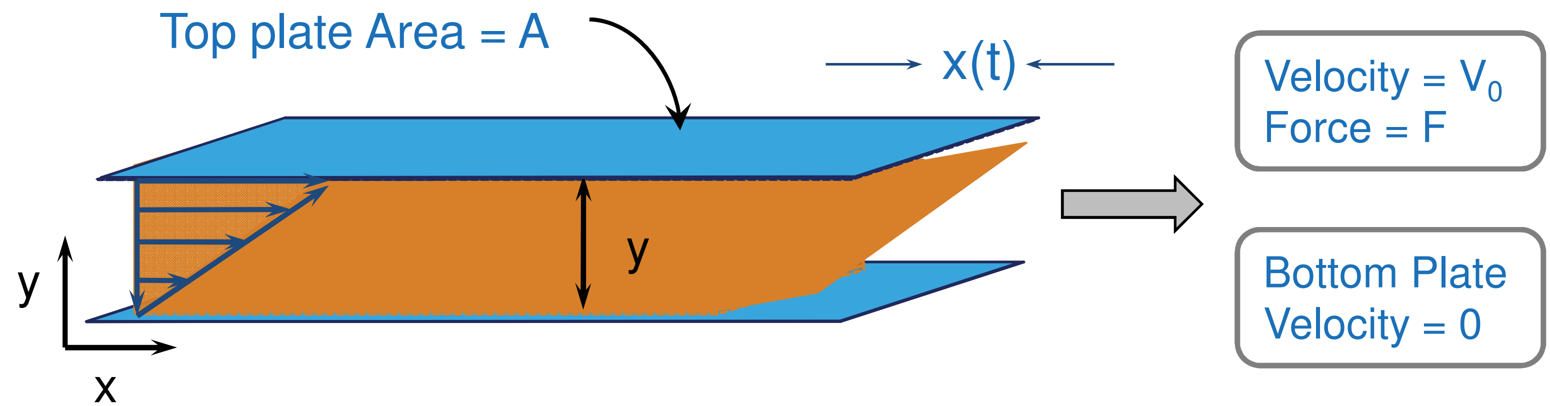
Rheology: An Introduction

- Rheology is the science of flow and deformation of matter
  - The word ‘Rheology’ was coined in the 1920s by Professor E C Bingham at Lafayette College in Indiana
- Flow is a special case of deformation
- The relationship between stress and deformation is a property of the material

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

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

Simple Steady Shear Flow



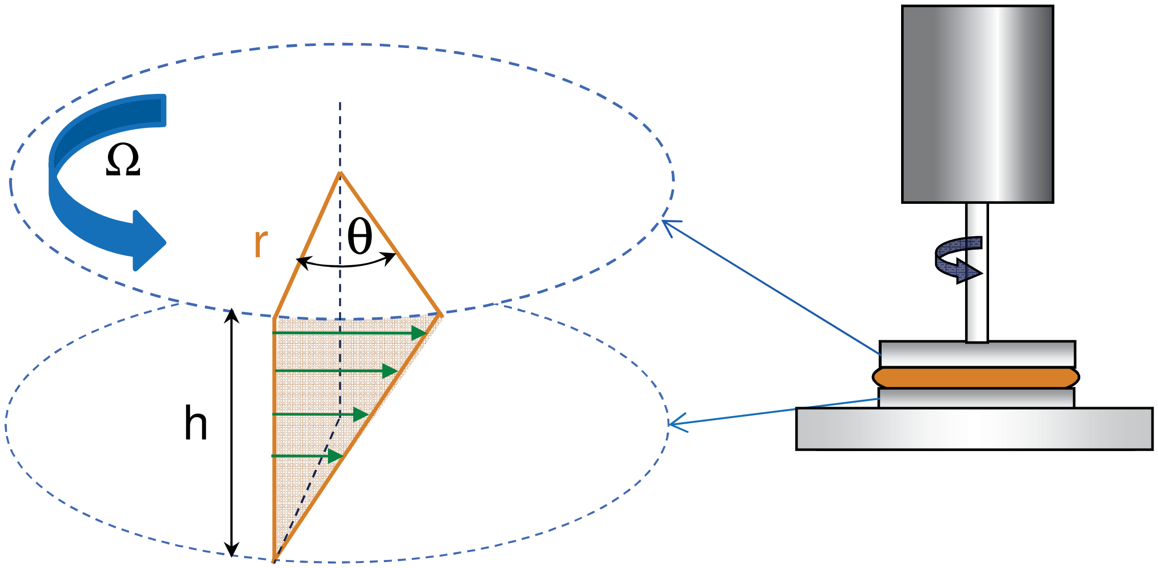
Shear Stress, Pascals $\sigma = \dfrac{F}{A}$

Shear Strain, % $\gamma = \dfrac{x(t)}{y}$

Shear Rate, sec^{-1} $\dot{\gamma} = \dfrac{\gamma}{t}$

$\eta = \dfrac{\sigma}{\dot{\gamma}}$ Viscosity, Pa·s

Torsion Flow in Parallel Plates



r = plate radius
h = distance between plates
M = torque (μN.m)
θ = Angular motor deflection (radians)
Ω= Motor angular velocity (rad/s)

Stress (σ) $\sigma = \frac{2}{\pi r^3} \times M$

Strain (γ) $\gamma = \frac{r}{h} \times \theta$

Strain rate ($\dot{\gamma}$) $\dot{\gamma} = \frac{r}{h} \times \Omega$

TA Instruments Rheometers

Rotational Rheometers at TA

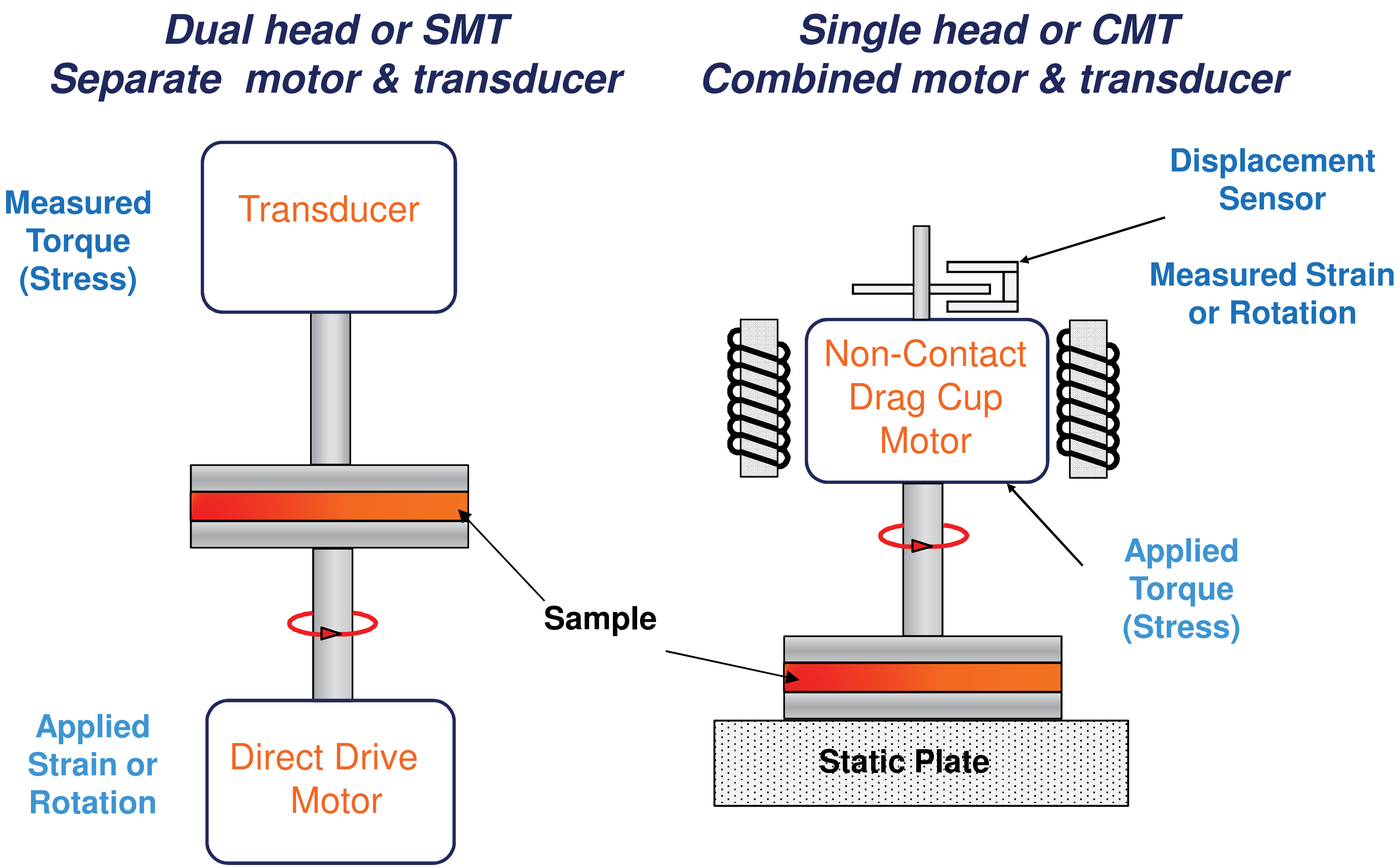
ARES G2

Controlled Strain
Dual Head
SMT

DHR

Controlled Stress
Single Head
CMT

Rotational Rheometer Designs



Note: With computer feedback, DHR and AR can work in controlled strain/shear rate, and ARES can work in controlled stress.

What does a Rheometer do?

- 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.

- A Rheometer works simply by relating a materials property from how hard it's being pushed, to how far it moves
  - by commanding torque (stress) and measuring angular displacement (strain)
  - by commanding angular displacement (strain) and measuring torque (stress)

How do Rheometers work?

From the definition of rheology,

the science of flow and deformation of matter
or
*the study of <u>stress</u> (**Force / Area**) – <u>deformation</u>*
*(**Strain or Strain rate**) relationships.*

Fundamentally a rotational rheometer will apply or measure:

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

Torque → Shear Stress

- In a rheometer, the stress is calculated from the torque.

- The formula for stress is: $\sigma = M \times K_\sigma$

  Where σ = Stress (Pa or Dyne/cm^2)

  M = torque in N·m or gm·cm

  K_σ = Stress Constant

- The stress constant, K_σ, is a geometry dependent factor

Angular Displacement → Shear Strain

- In a SMT Rheometer, the angular displacement is directly applied by a motor.

- The formula for strain is: $\gamma = K_\gamma \times \theta$

$$\%\gamma = \gamma \times 100$$

where γ = Strain

K_γ = Strain Constant

θ = Angular motor deflection (radians)

- The strain constant, K_γ, is a geometry dependent factor

Equation for Modulus

In Spec

Describe Correctly

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

Rheological Parameter

Constitutive Equation

Raw rheometer Specifications

Geometric Shape Constants

The equation of motion and other relationships have been used to determine the appropriate equations to convert machine parameters (torque, angular velocity, and angular displacement) to rheological parameters.

Angular Velocity → Shear Rate

- In a SMT rheometer, the angular speed is directly controlled by the motor).

- The formula for shear rate is:

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

where $\dot{\gamma}$ = Shear rate

K_{γ} = Strain Constant

Ω = Motor angular velocity in rad/sec

- The strain constant, K_{γ}, is a geometry dependent factor

Equation for Viscosity

In Spec

Describe Correctly

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

Rheological Parameter

Constitutive Equation

Raw rheometer Specifications

Geometric Shape Constants

The equation of motion and other relationships have been used to determine the appropriate equations to convert machine parameters (torque, angular velocity, and angular displacement) to rheological parameters.

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

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)	$1\ x\ 10^{-5}$ to 16

Geometry Options

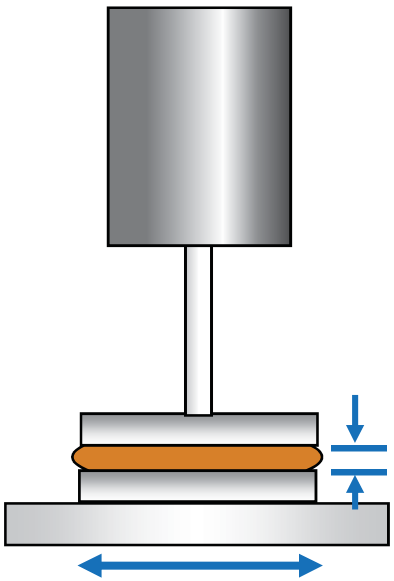
Concentric Cylinders	Cone and Plate	Parallel Plate	Torsion Rectangular
			
Very Low to Medium Viscosity	Very Low to High Viscosity	Very Low Viscosity to Soft Solids	Solids

Water → to → Steel

Choosing a Geometry Size

- Assess the ‘viscosity’ of your sample
- When a variety of cones and plates are available, select diameter appropriate for viscosity of sample
  - Low viscosity (milk) - 60mm geometry
  - Medium viscosity (honey) - 40mm geometry
  - High viscosity (caramel) – 20 or 25mm geometry
- Examine data in terms of absolute instrument variables torque/displacement/speed and modify geometry choice to move into optimum working range
- You may need to reconsider your selection after the first run!

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)

When to use Parallel Plates

- Low/Medium/High Viscosity Liquids
- Soft Solids/Gels
- Thermosetting materials
- Samples with large particles

- Samples with long relaxation time
- Temperature Ramps/ Sweeps
- Materials that may slip
  - Crosshatched or Sandblasted plates
- Small sample volume

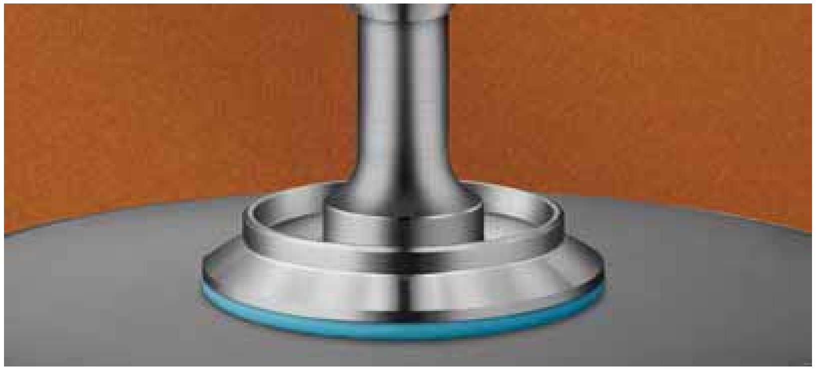
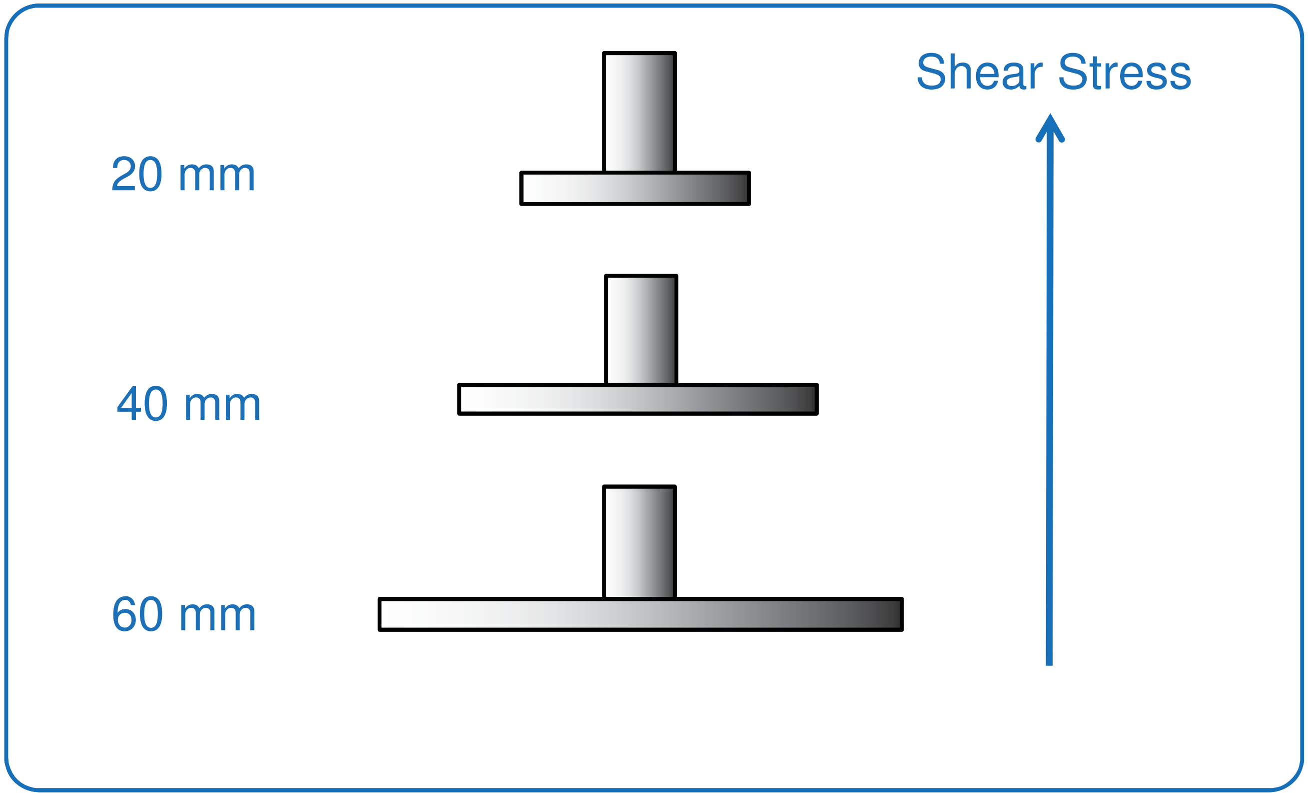


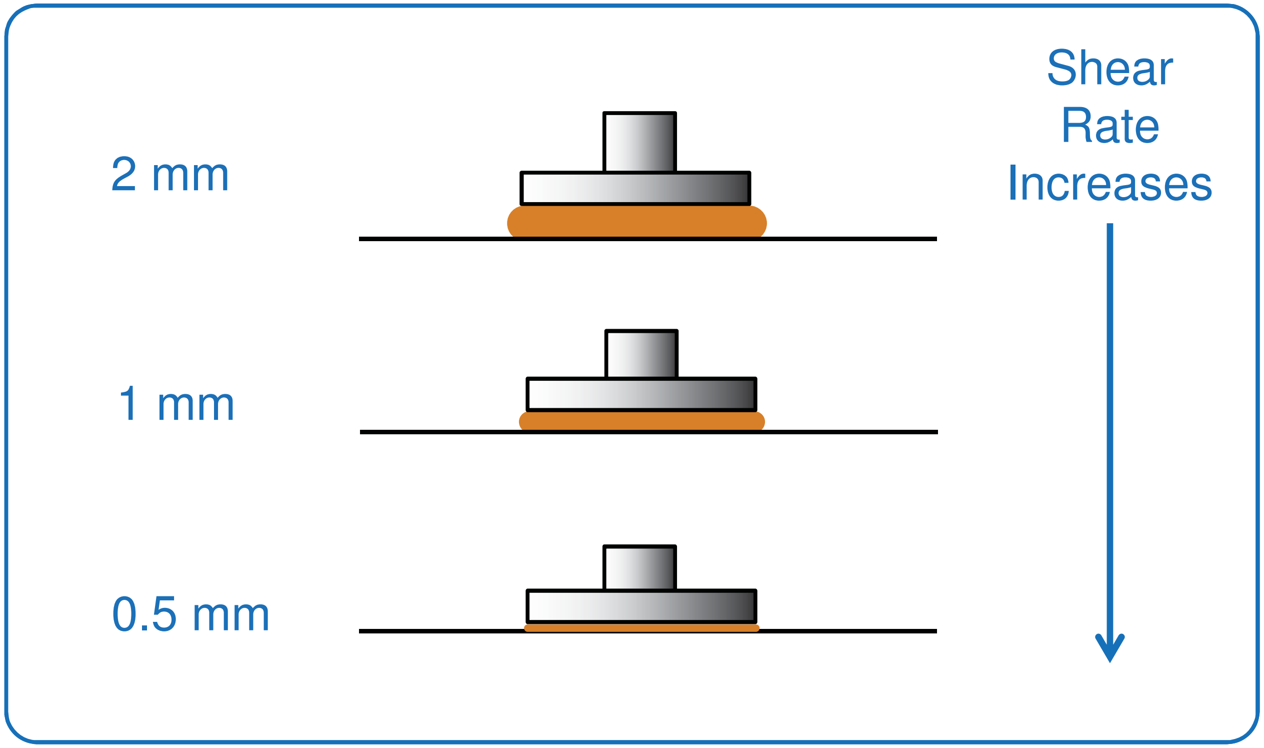
Plate Diameters



As diameter decreases, shear stress increases

$$\sigma = M\frac{2}{\pi r^2}$$

Plate Gaps

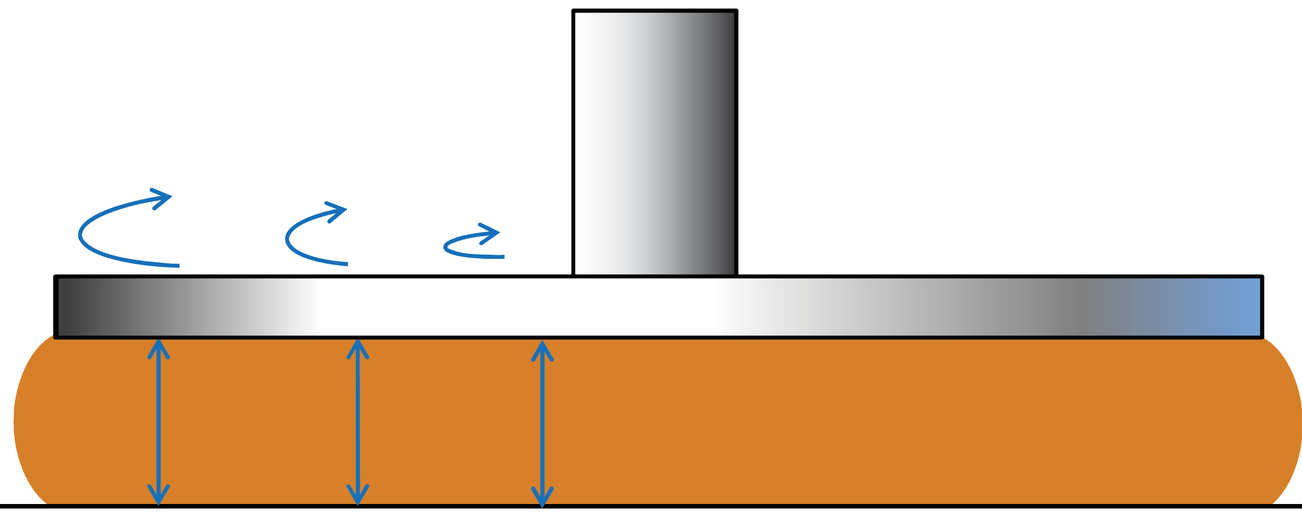


As gap height decreases, shear rate increases

$$\dot{\gamma} = \Omega \frac{r}{h}$$

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

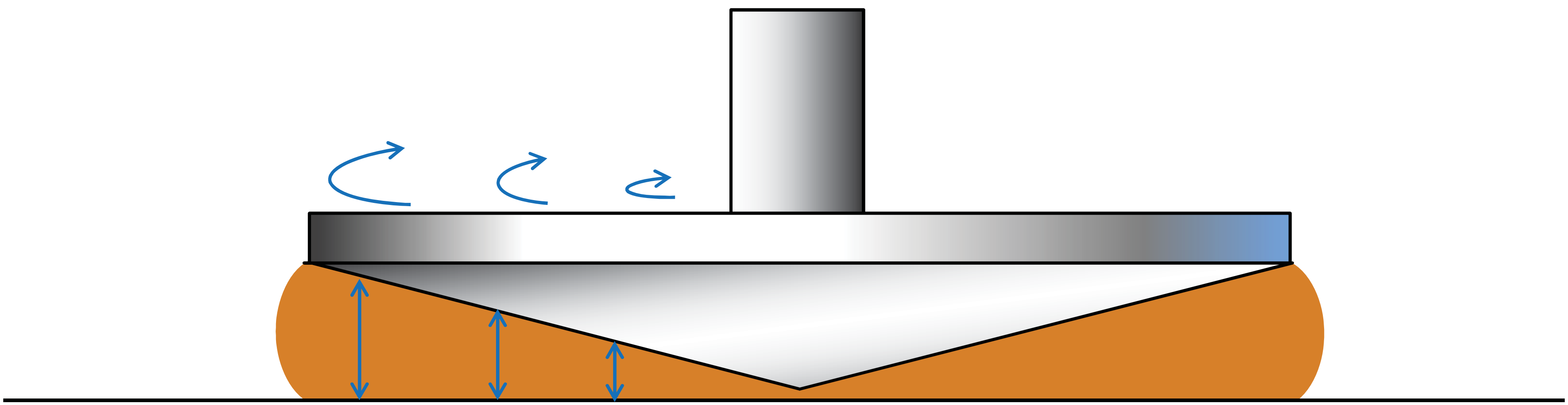


$$\gamma = \frac{dx}{h}$$

dx increases further from the center,
h stays constant

Shear Rate is Normalized across a Cone

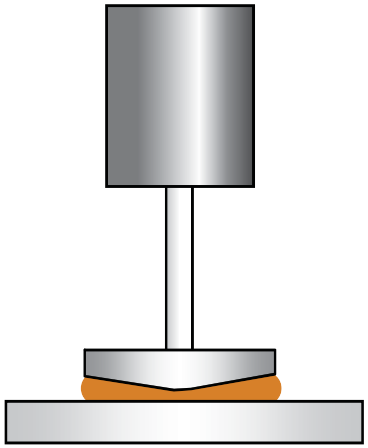
- The cone shape produces a smaller gap height closer to inside, so the shear on the sample is constant



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

h increases proportionally to *dx*, γ is uniform

Cone and Plate

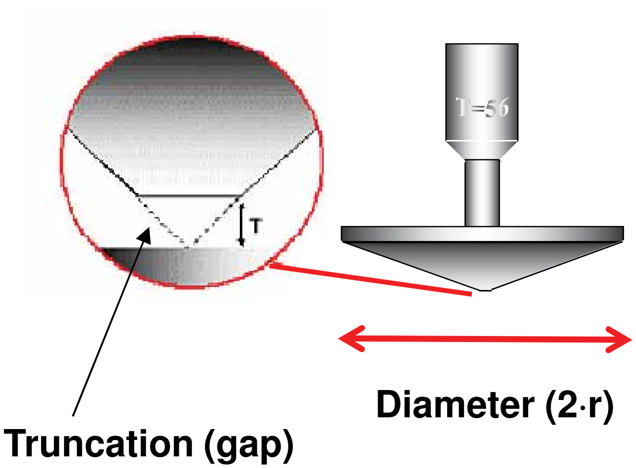


Strain Constant: $K_\gamma = \frac{1}{\beta}$

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

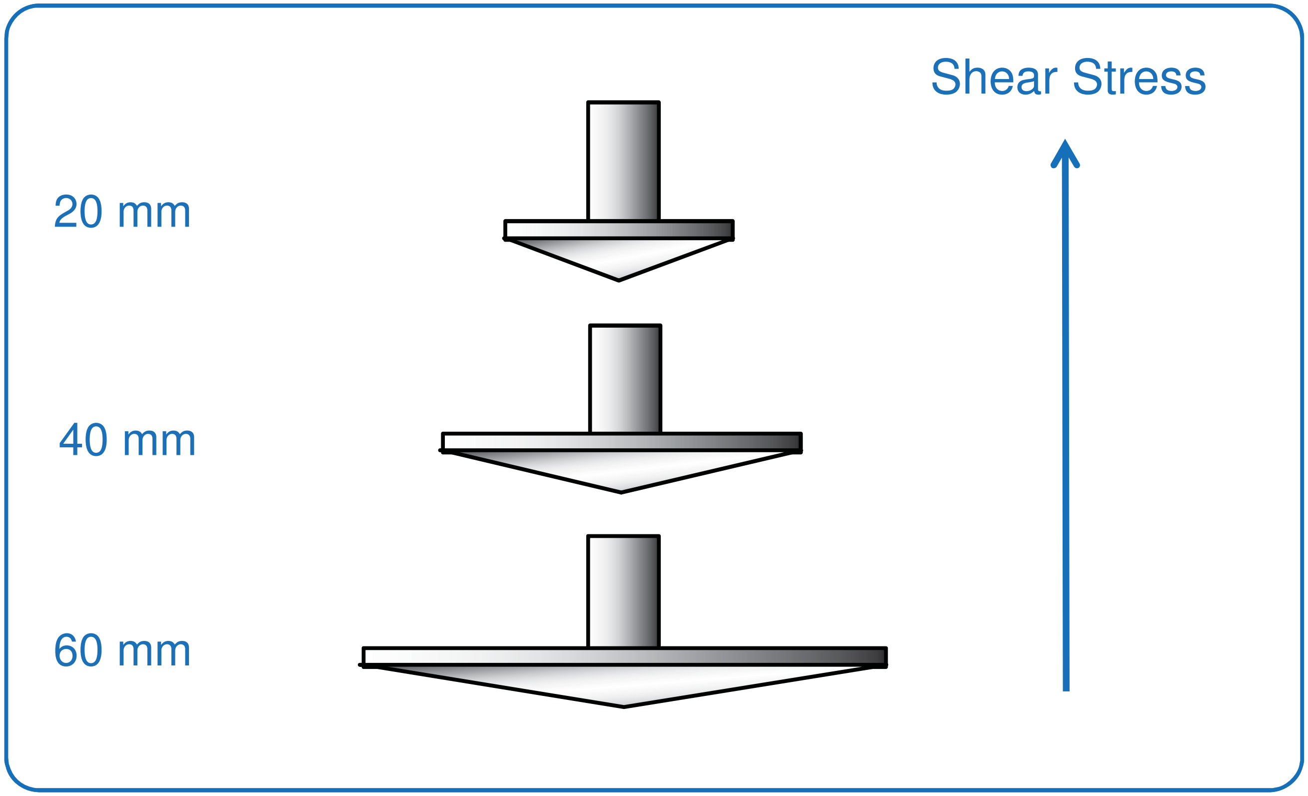
(to convert torque, N·m, to shear stress, Pa. The radius, r, is expressed in meters)



When to use Cone and Plate

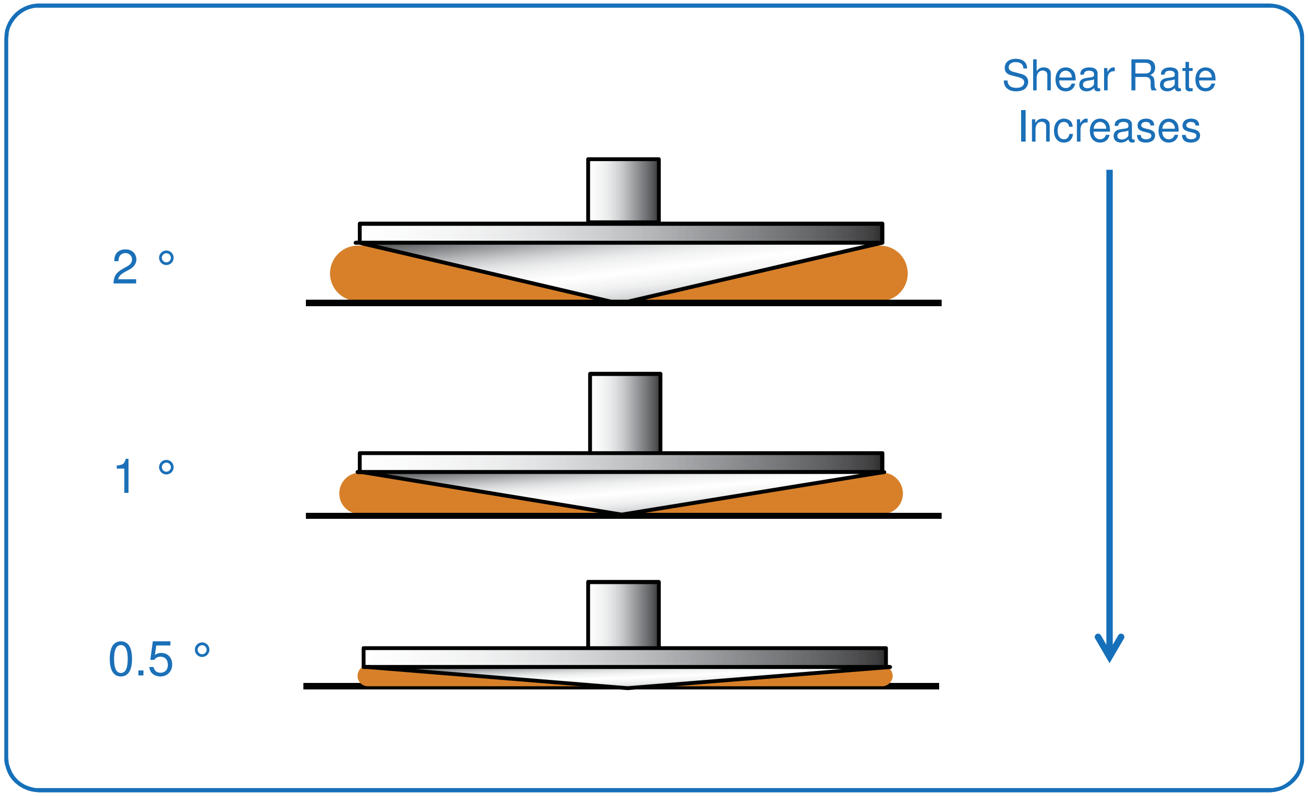
- Very Low to High Viscosity Liquids
- High Shear Rate measurements
- Normal Stress Growth
- Unfilled Samples
- Isothermal Tests
- Small Sample Volume

Cone Diameters



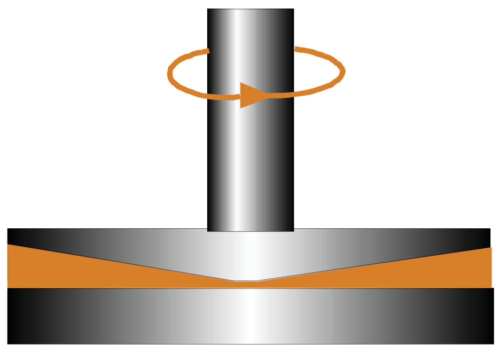
As diameter decreases, shear stress increases $\sigma = M \frac{3}{2\pi r^3}$

Cone Angles



As cone angle decreases, shear rate increases $\dot{\gamma} = \Omega \frac{1}{\beta}$

Limitations of Cone and Plate



Cone & Plate

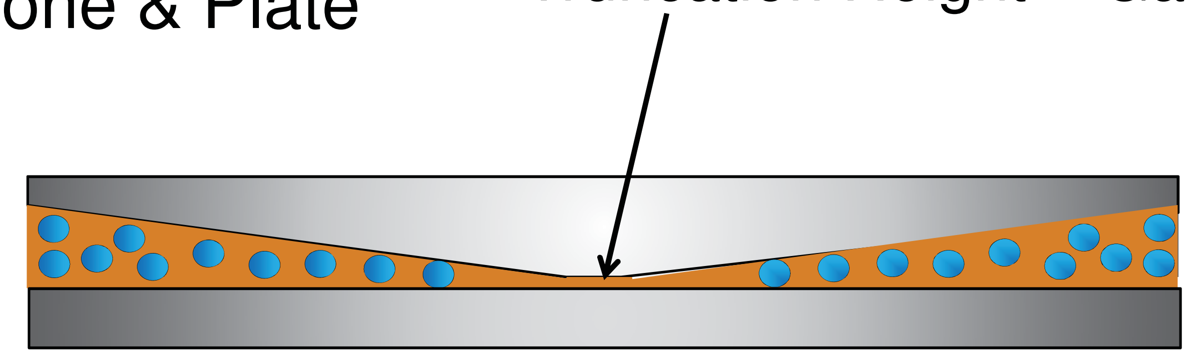
Typical Truncation Heights:

1° degree ~ 20 - 30 microns

2° degrees ~ 60 microns

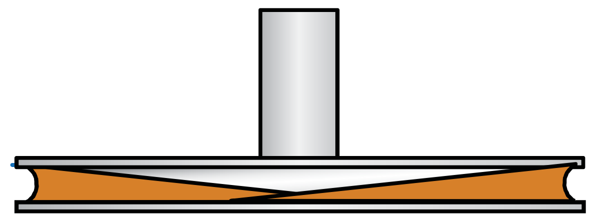
4° degrees ~ 120 microns

Truncation Height = Gap

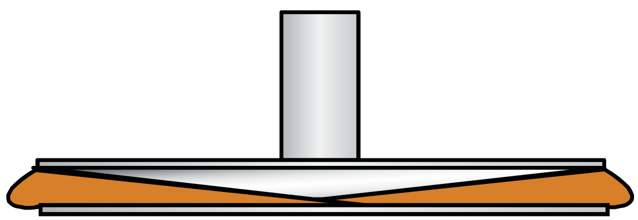


Gap must be > or = 10 [particle size]!!

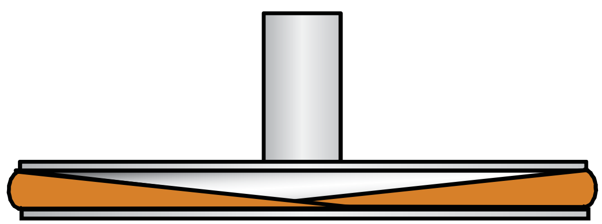
Correct Sample Loading



× Under Filled sample:
Lower torque contribution

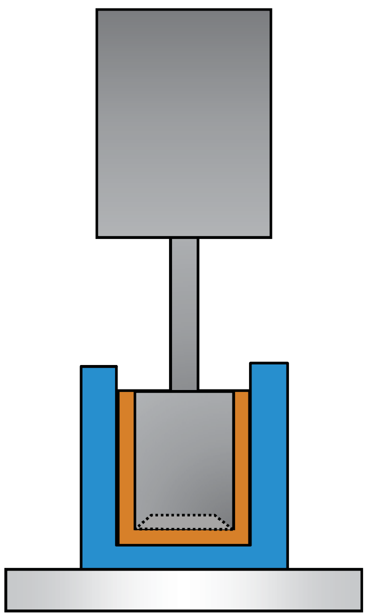


× Over Filled sample:
Additional stress from drag along the edges



✓ **Correct Filling**

Concentric Cylinder



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

(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)

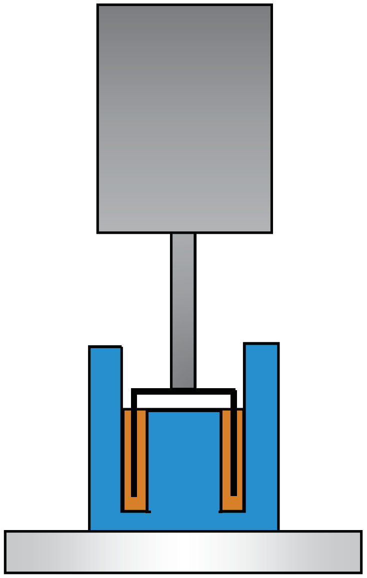
Stress Constant: $$K_\sigma = \frac{1}{4\pi l}\left[\frac{{r_1}^2 + {r_2}^2}{{r_2}^2 {r_1}^2}\right]^*$$

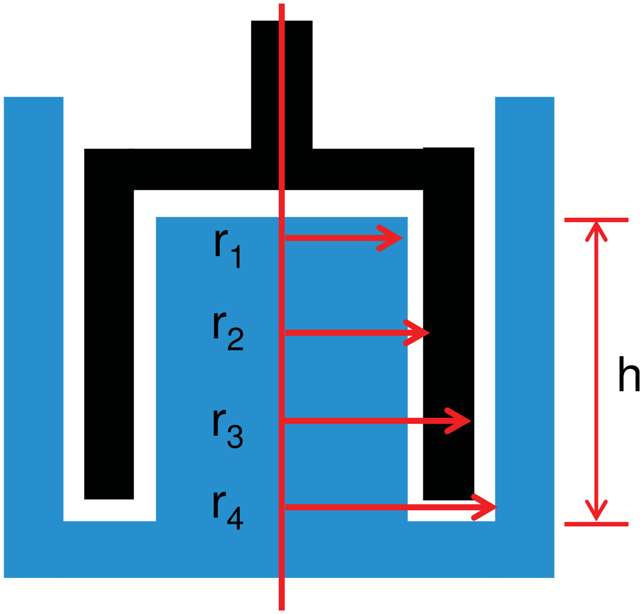
(to convert torque, N·m, to shear stress, Pa. The bob length, l, and the radius, r, are expressed in meters)

*Note including end correction factor. See TRIOS Help

Double Wall

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





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

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

ARES Gap Settings: standard operating gap DW = 3.4 mm
narrow operating gap DW = 2.0 mm
Use equation Gap > 3 × (R_2 –R_1)

When to Use Concentric Cylinders

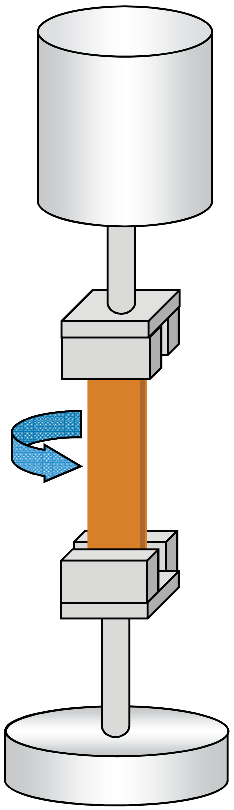
- Low to Medium Viscosity Liquids
- Unstable Dispersions and Slurries
- Minimize Effects of Evaporation
- Weakly Structured Samples (Vane)
- High Shear Rates

Peltier Concentric Cylinders

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



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

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

w = Width

l = Length

t = Thickness

Advantages:

- High modulus samples
- Small temperature gradient
- Simple to prepare

Disadvantages:

- No pure Torsion mode for high strains

Torsion cylindrical also available

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)

Rectangular and cylindrical torsion

DMA 3-point bending and tension (cantilever not shown)

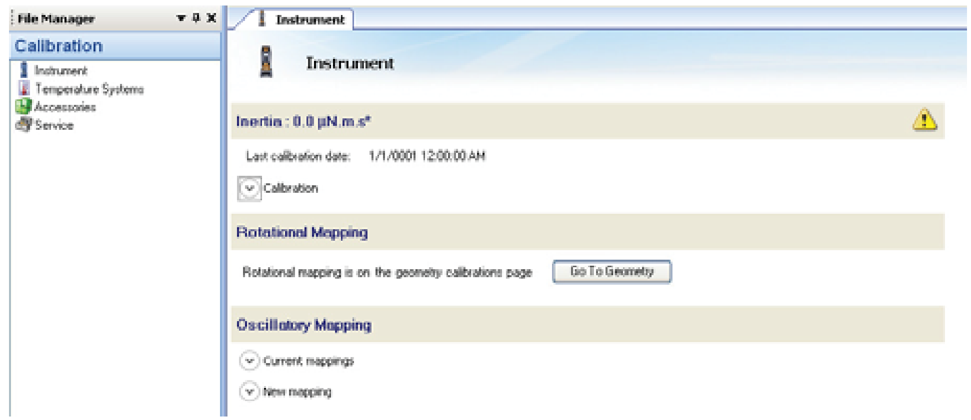
Geometry Overview

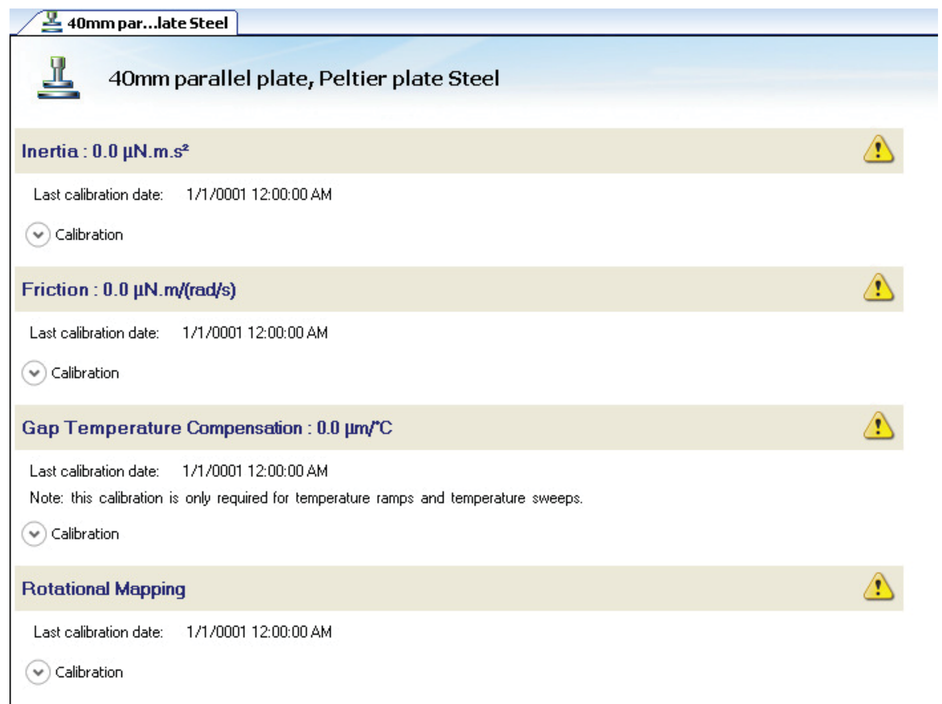
Geometry	Application	Advantage	Disadvantage
Cone/plate	fluids, melts viscosity > 10mPas	true viscosities	temperature ramp difficult
Parallel Plate	fluids, melts viscosity > 10mPas	easy handling, temperature ramp	shear gradient across sample
Couette	low viscosity samples < 10 mPas	high shear rate	large sample volume
Double Wall Couette	very low viscosity samples < 1mPas	high shear rate	cleaning difficult
Torsion Rectangular	solid polymers, composites	glassy to rubbery state	Limited by sample stiffness
DMA	Solid polymers, films, Composites	Glassy to rubbery state	Limited by sample stiffness (Oscillation and stress/strain)

Rheometer Calibrations and Performance Verification

DHR – Calibration Options

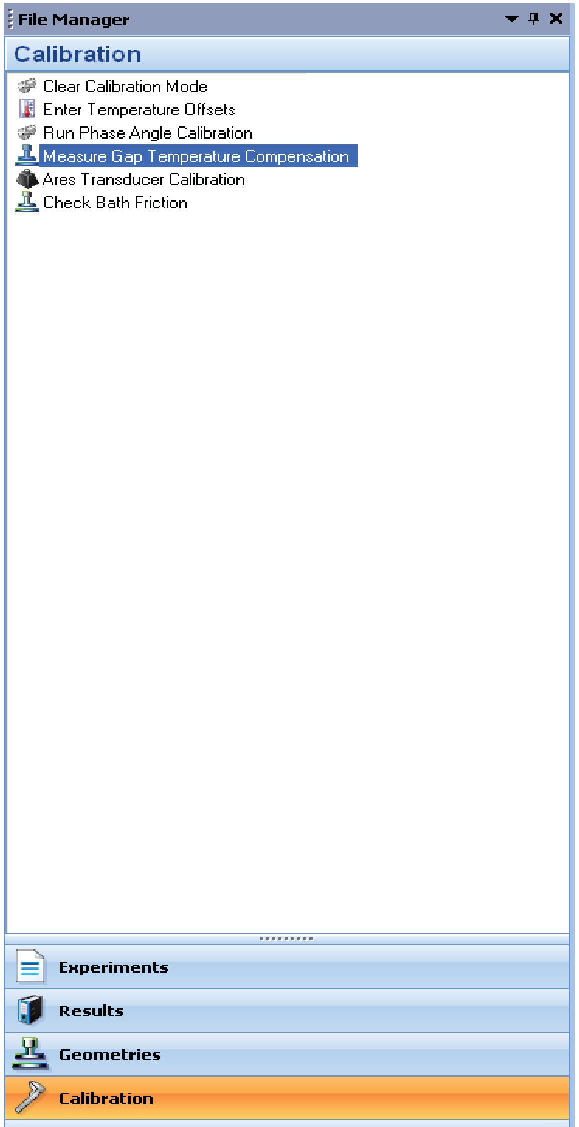
- Instrument Calibrations
  - Inertia (Service)
  - Rotational Mapping
- Geometry Calibrations:
  - Inertia
  - Friction
  - Gap Temperature Compensation
  - Rotational Mapping
- Details in Appendix #4





ARES-G2 – Calibration Options

- Instrument Calibrations
  - Transducer
  - Temperature Offsets
  - Phase Angle (Service)
  - Measure Gap Temperature Compensation
- Geometry Calibrations:
  - Compliance and Inertia (from table)
  - Gap Temperature Compensation
- Details in Appendix #4



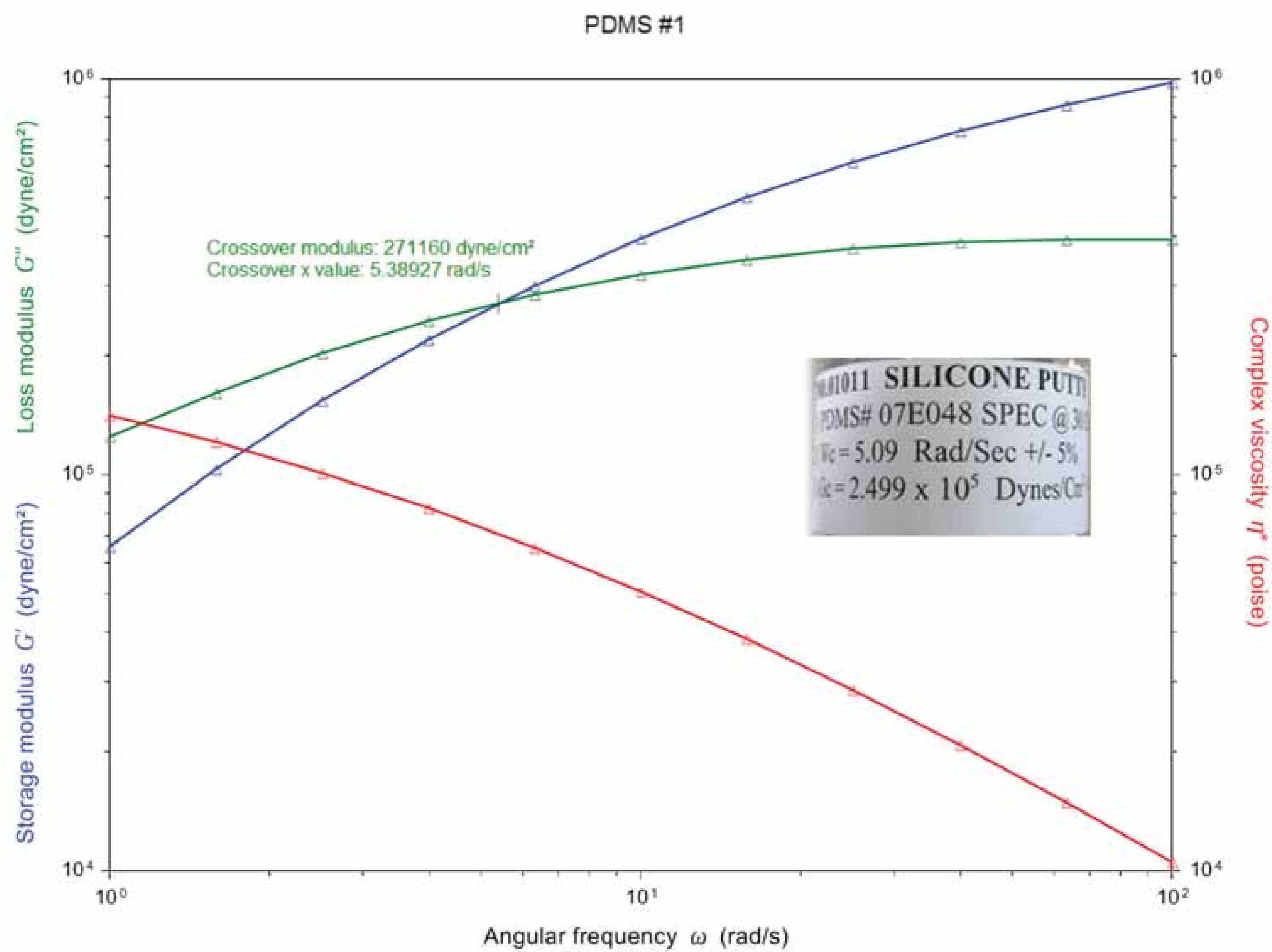
Verify Rheometer Performance

- Rheometers are calibrated from the factory and again at installation.
- TA recommends routine validation or confidence checks using standard oils or Polydimethylsiloxane (PDMS).

- PDMS is verified using a 25 mm parallel plate.
  - Oscillation - Frequency Sweep: 1 to 100 rad/s with 5% strain at 30°C
  - Verify modulus and frequency values at crossover

- Standard silicone oils can be verified using cone, plate or concentric cylinder configurations.
  - Flow – Ramp: 0 to 88 Pa at 25°C using a 60 mm 2° cone
    - Service performs this test at installation

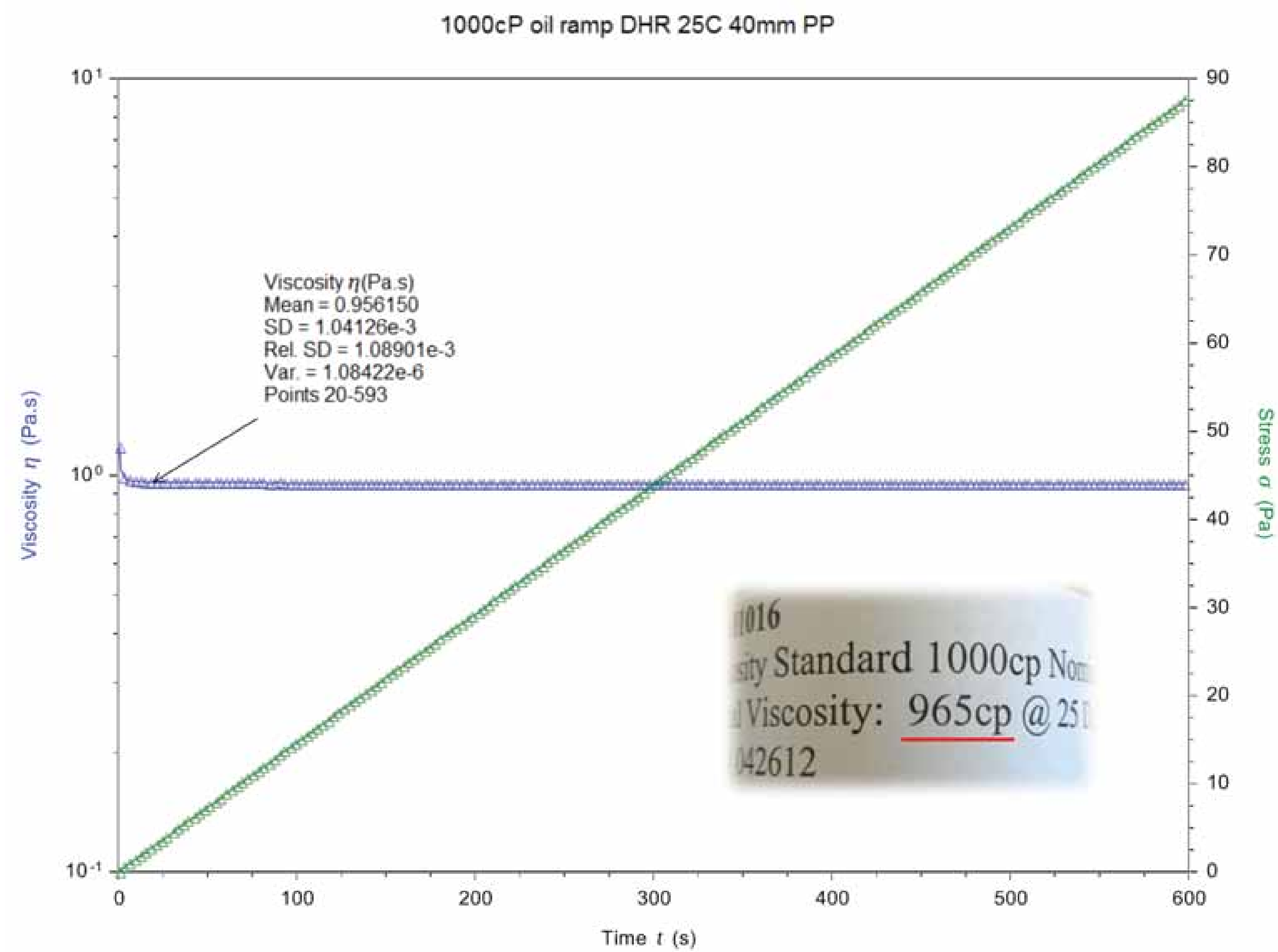
PDMS Frequency Sweep Results



Load Standard Oil

- Set Peltier temperature to 25°C and equilibrate.
  - Zero the geometry gap
- Load sample
  - Be careful not to introduce air bubbles!
- Set the gap to the trim gap
- Lock the head and trim with non-absorbent tool
  - Important to allow time for temperature equilibration.
- Go to geometry gap and initiate the experiment.

Flow Ramp – Standard Oil (Service Test)



Setting up Rheological Experiments

Flow Tests

Viscosity: Definition

- Viscosity is…
  - "lack of slipperiness"
  - synonymous with internal friction
  - resistance to flow

- The Units of Viscosity are …
  - SI unit is the Pascal·second (Pa·s)
  - cgs unit is the Poise
  - 10 Poise = 1 Pa·s
    - 1 cP (centipoise) = 1 mPa·s (millipascal second)

Equation for Viscosity

In Spec

Describe Correctly

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

Rheological Parameter

Constitutive Equation

Raw rheometer Specifications

Geometric Shape Constants

Typical Viscosity Values (Pa-s)

Asphalt Binder --------------	100,000
Polymer Melt ----------------	1,000
Molasses --------------------	100
Liquid Honey ----------------	10
Glycerol --------------------	1
Olive Oil -------------------	0.01
Water -----------------------	0.001
Air -------------------------	0.00001

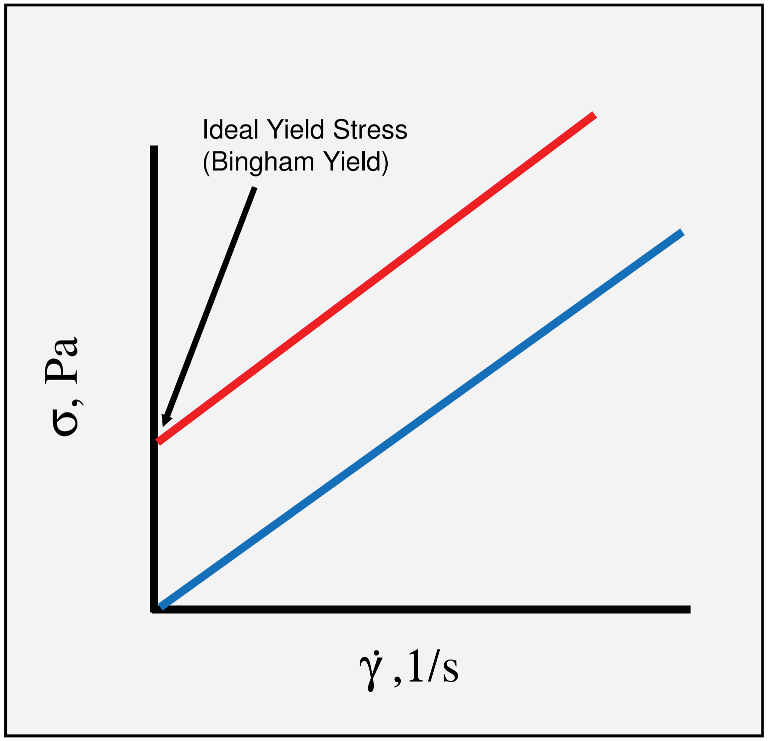
Need for Log scale

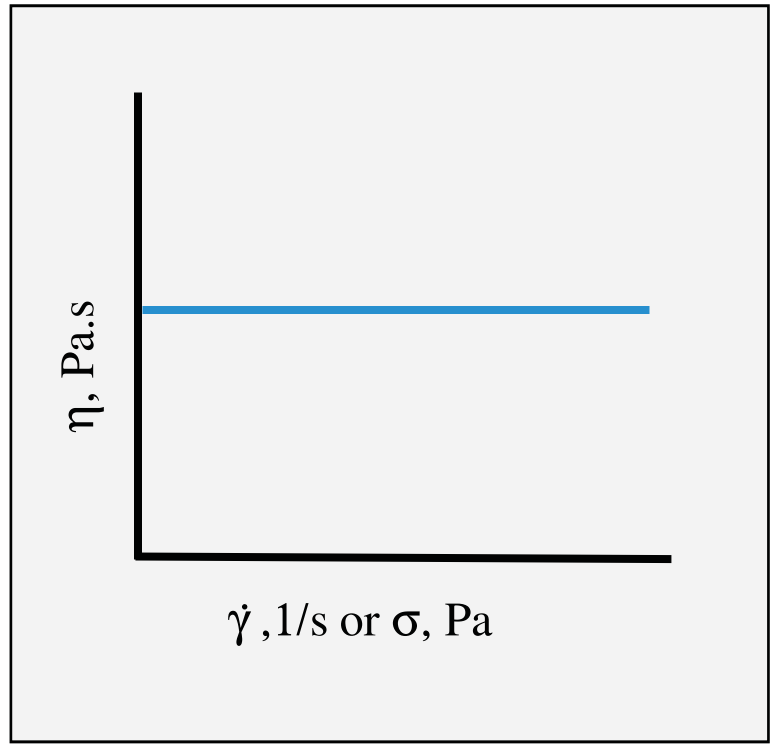
Newtonian and Non-Newtonian Fluids

- Newtonian Fluids - constant proportionality between shear stress and shear-rate

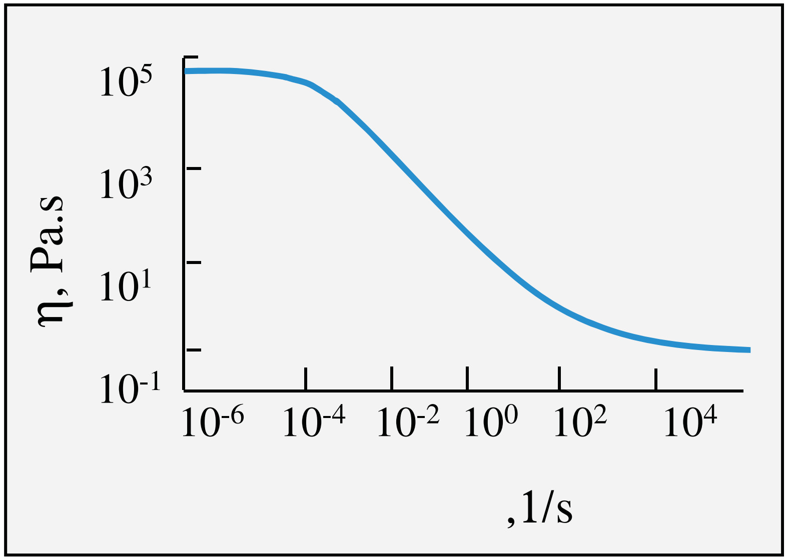
- Non-Newtonian Fluids - Viscosity is time or shear rate dependent
  - Time:
    - At constant shear-rate, if viscosity
    - Decreases with time – Thixotropy
    - Increases with time - Rheopexy
  - Shear-rate:
    - Shear - thinning
    - Shear - thickening

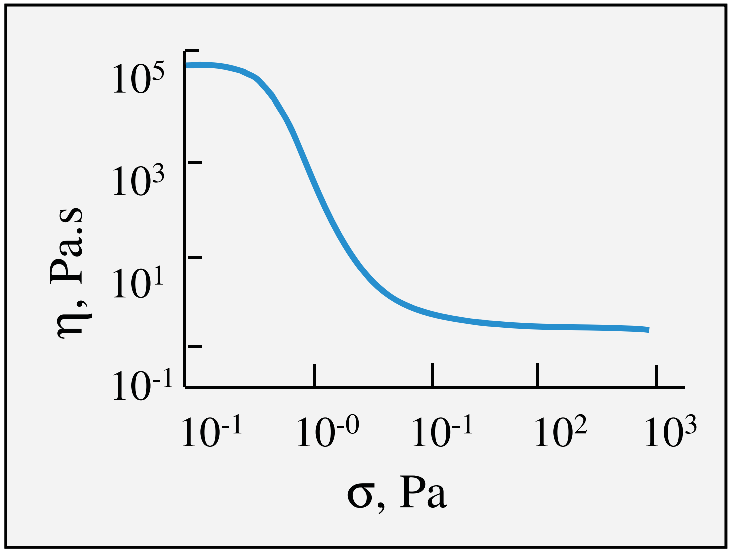
Characteristic Diagrams for Newtonian Fluids

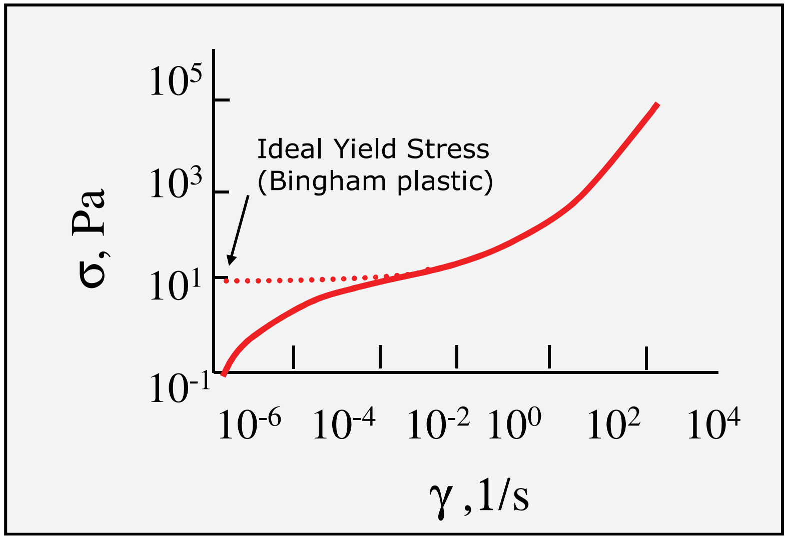




Characteristic Diagrams for Shear Thinning Fluids

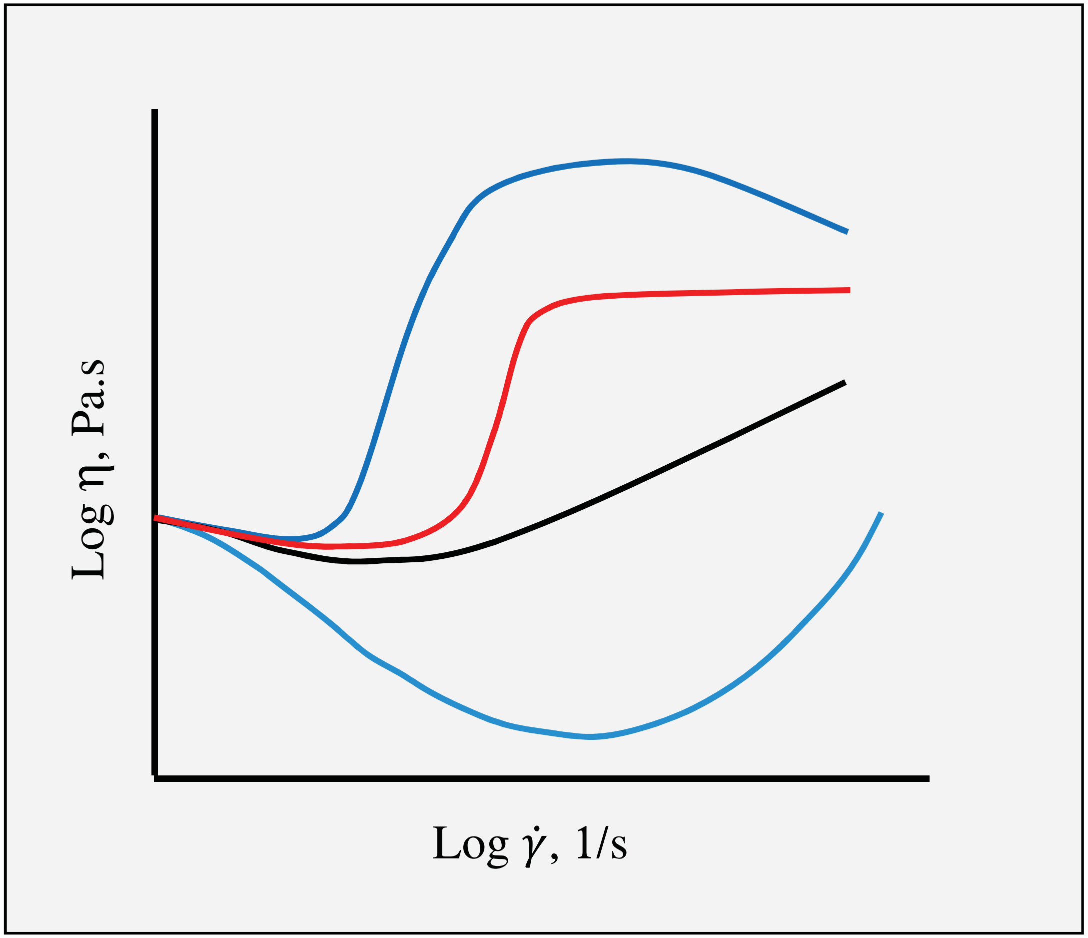






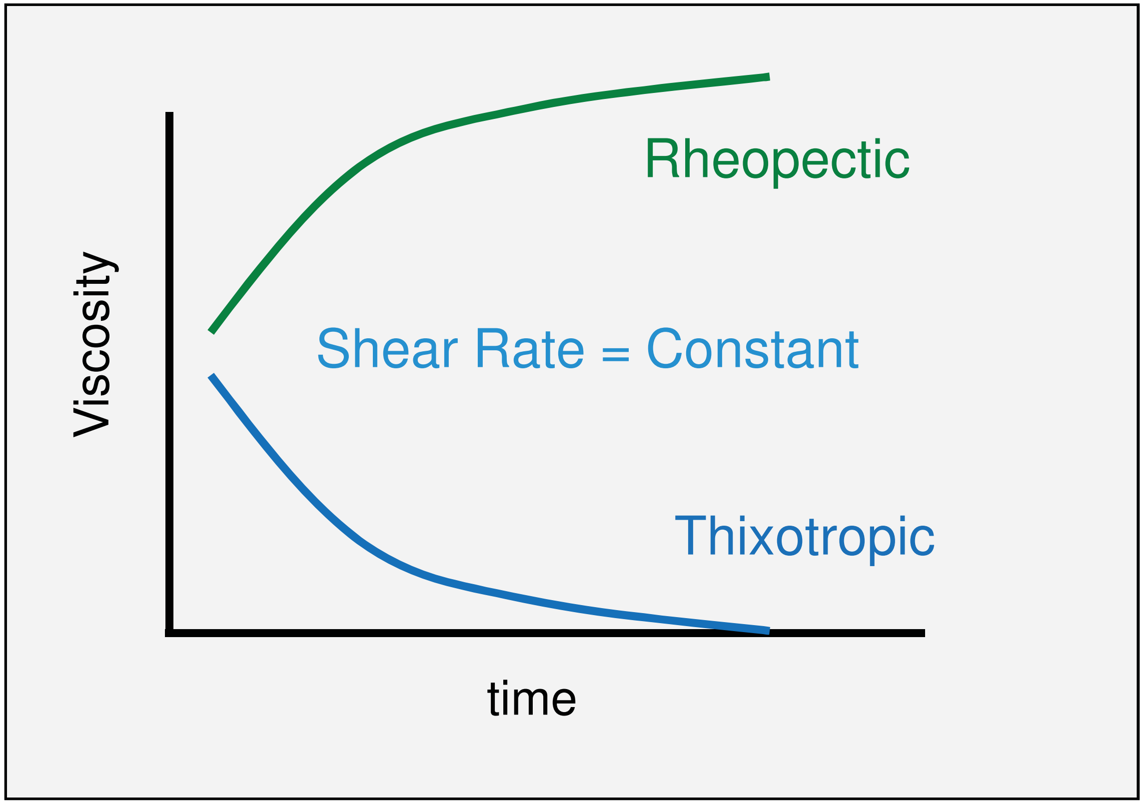
- Another name for a shear thinning fluid is a pseudo-plastic

Characteristic Diagrams for Shear Thickening Fluids



- Dilatant material resists deformation more than in proportion to the applied force (shear-thickening)
- Cornstarch in water or sand on the beach are actually dilatant fluids, since they do not show the time-dependent, shear-induced change required in order to be labeled rheopectic

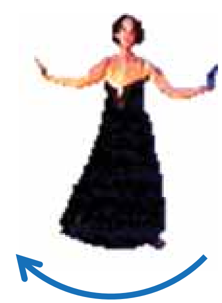
Non-Newtonian, Time Dependent Fluids



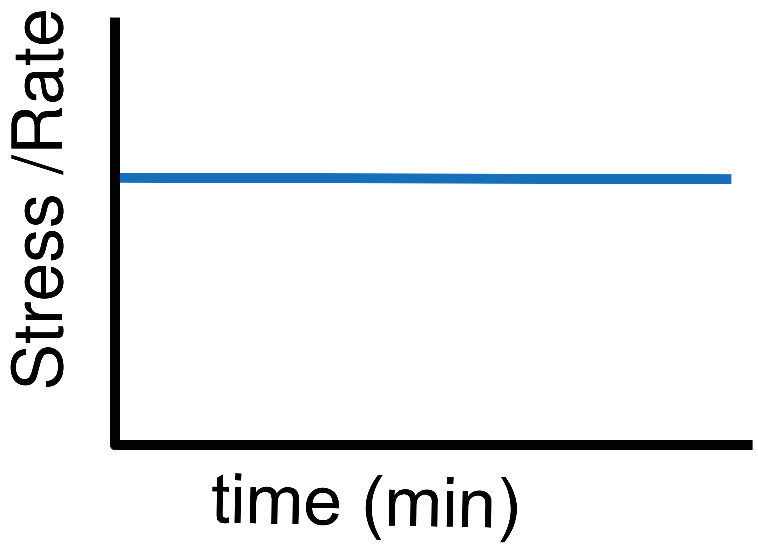
- Rheopectic materials become more viscous with increasing time of applied force
- Higher concentration latex dispersions and plastisol paste materials exhibit rheopectic behavior
- Thixotropic materials become more fluid with increasing time of applied force
- Coatings and inks can display thixotropy when sheared due to structure breakdown

Flow Experiments

- Flow Experiments
  - Constant shear rate/stress (or Peak hold)
  - Continuous stress/rate ramp and down
  - Stepped flow (or Flow sweep)
  - Steady state flow
  - Flow temperature ramp



Constant Shear Rate/Stress

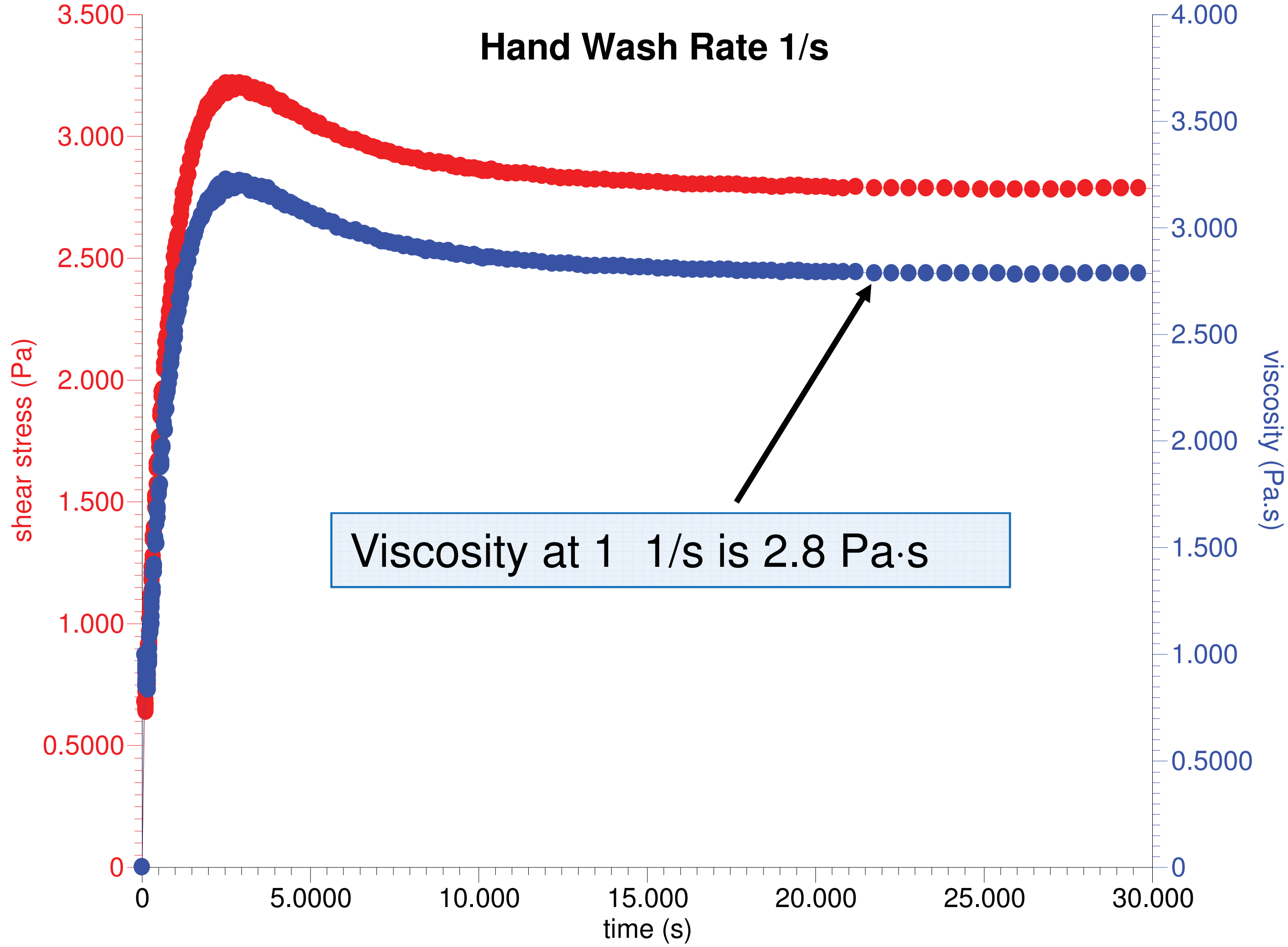


- Constant rate vs. time
- Constant stress vs. time

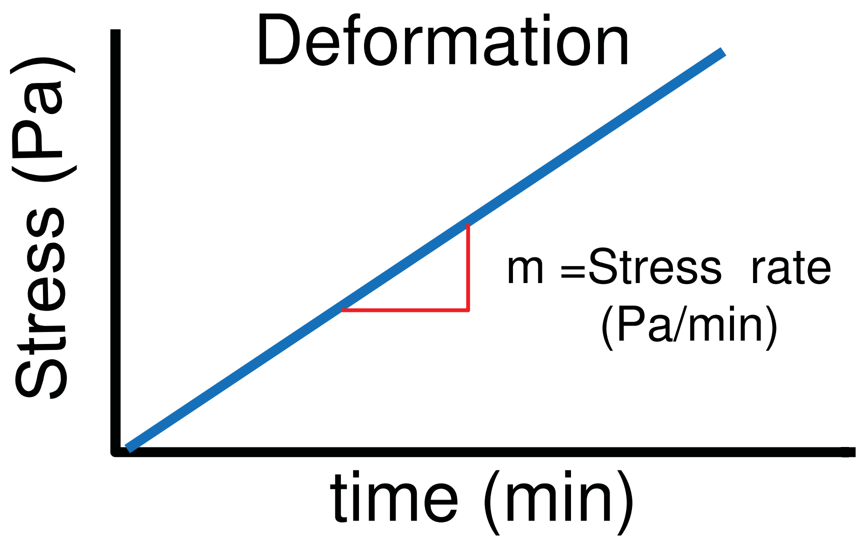
USES

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

Constant Shear Rate/Stress



Continuous Ramp

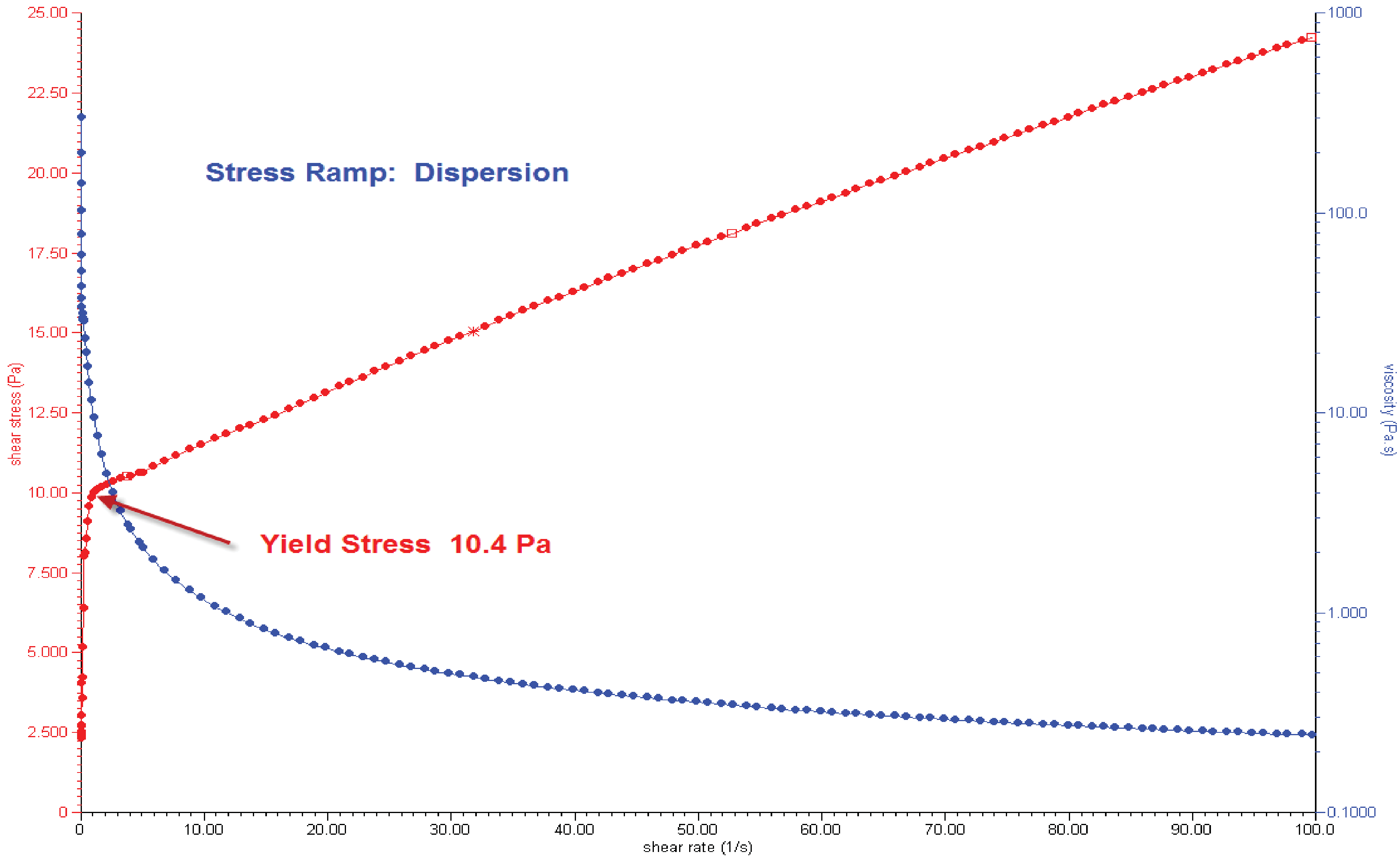


- Stress is applied to material at a constant rate. Resultant strain is monitored with time.

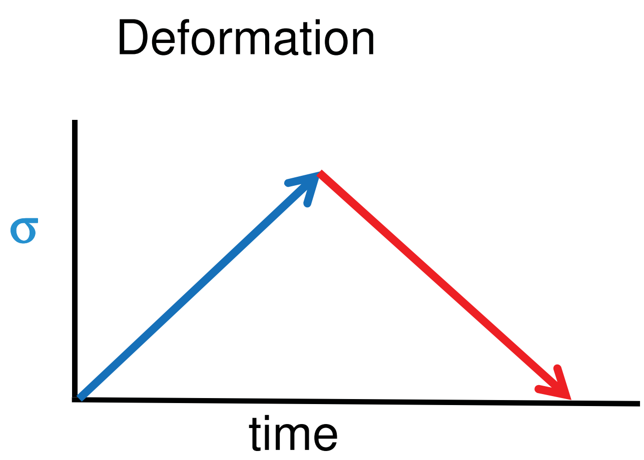
USES

- Yield stress
- Scouting Viscosity Run

Stress Ramp: Flow Media Dispersion



Thixotropic Loop - Continuous Ramp Up and Down



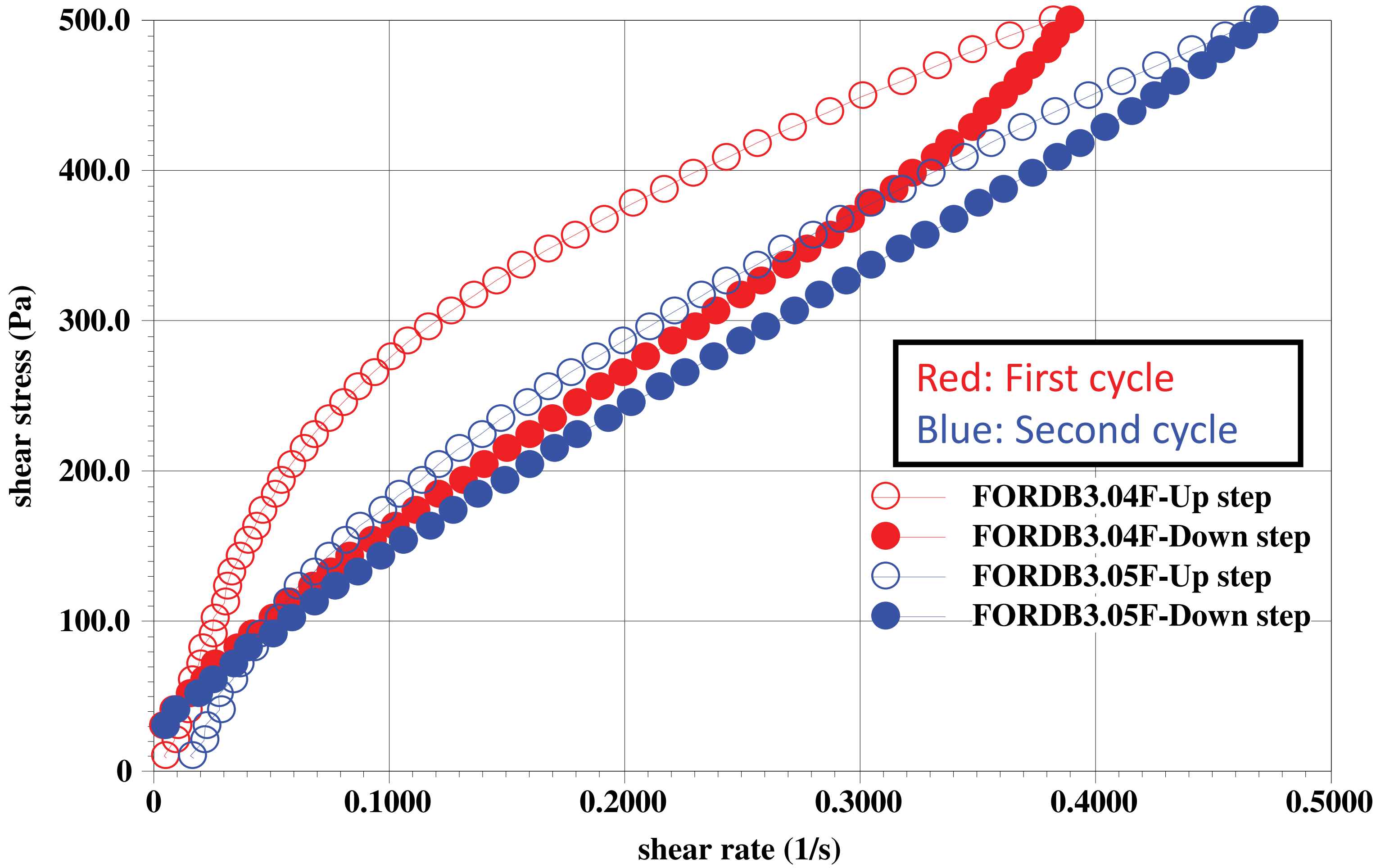
- Stress is first increased, then decreased, at a constant rate. Resultant strain is monitored with time.

USES

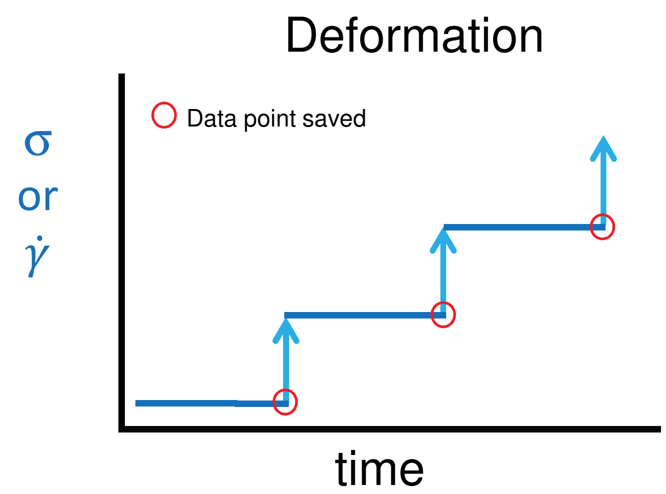
- "Pseudo-thixotropy" from Hysteresis loop

Up & Down Flow Curves - 2 Repeats

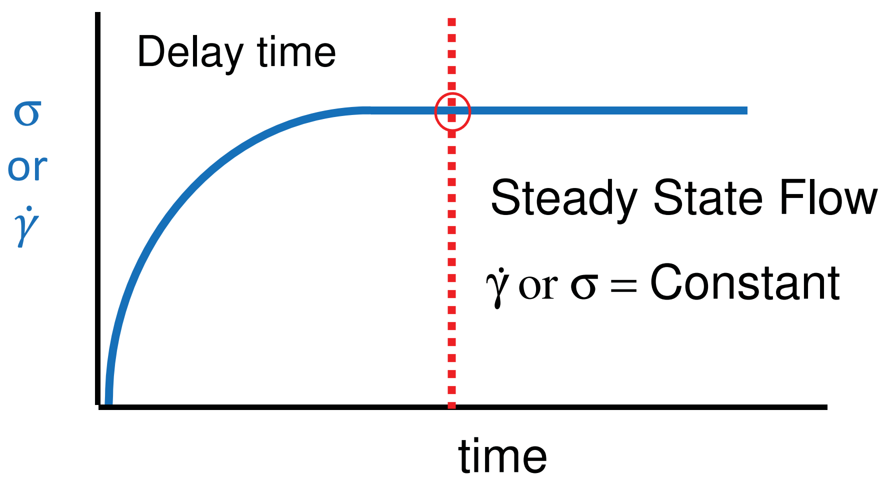
Run in Stress Control



Stepped or Steady-State Flow



- Stress is applied to sample. Viscosity measurement is taken when material has reached steady state flow. The stress is increased(logarithmically) and the process is repeated yielding a viscosity flow curve.

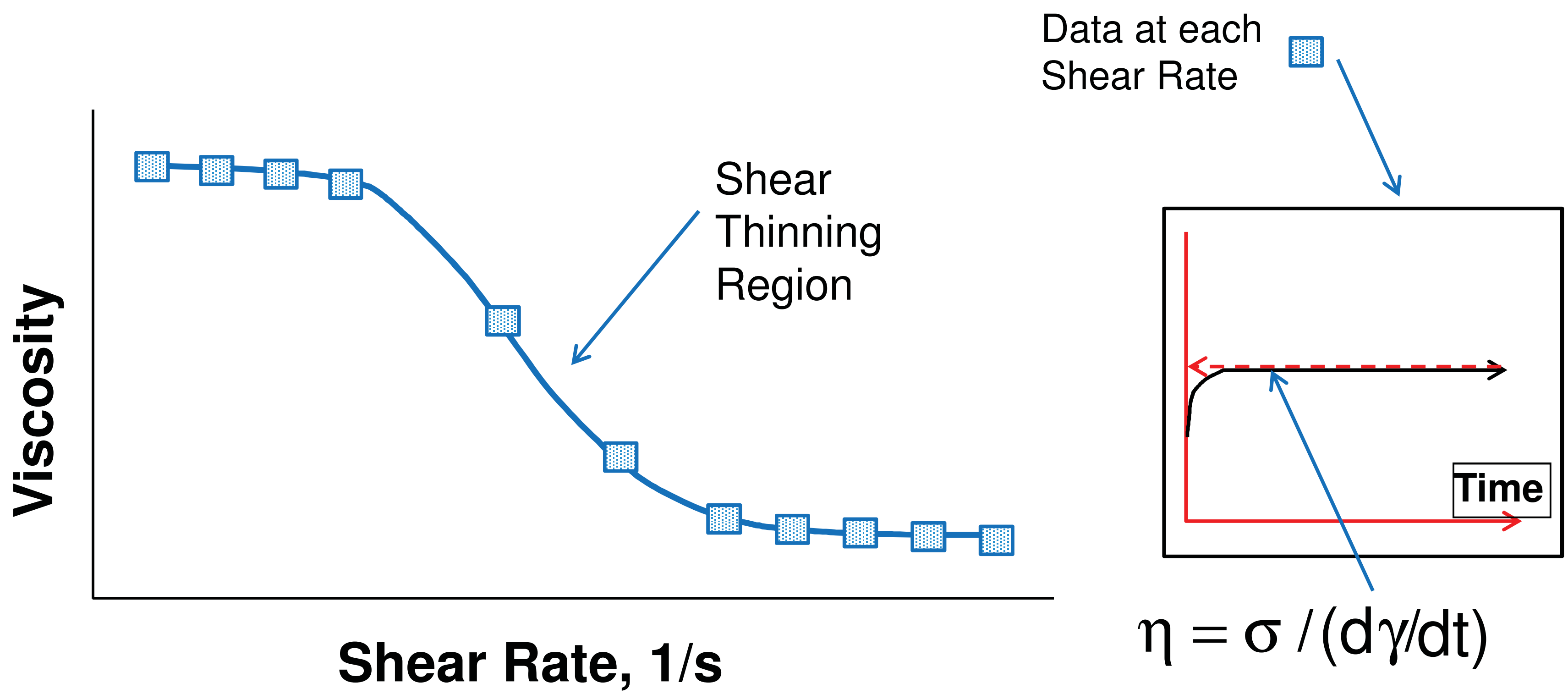


USES

- Viscosity Flow Curves
- Yield Stress Measurements

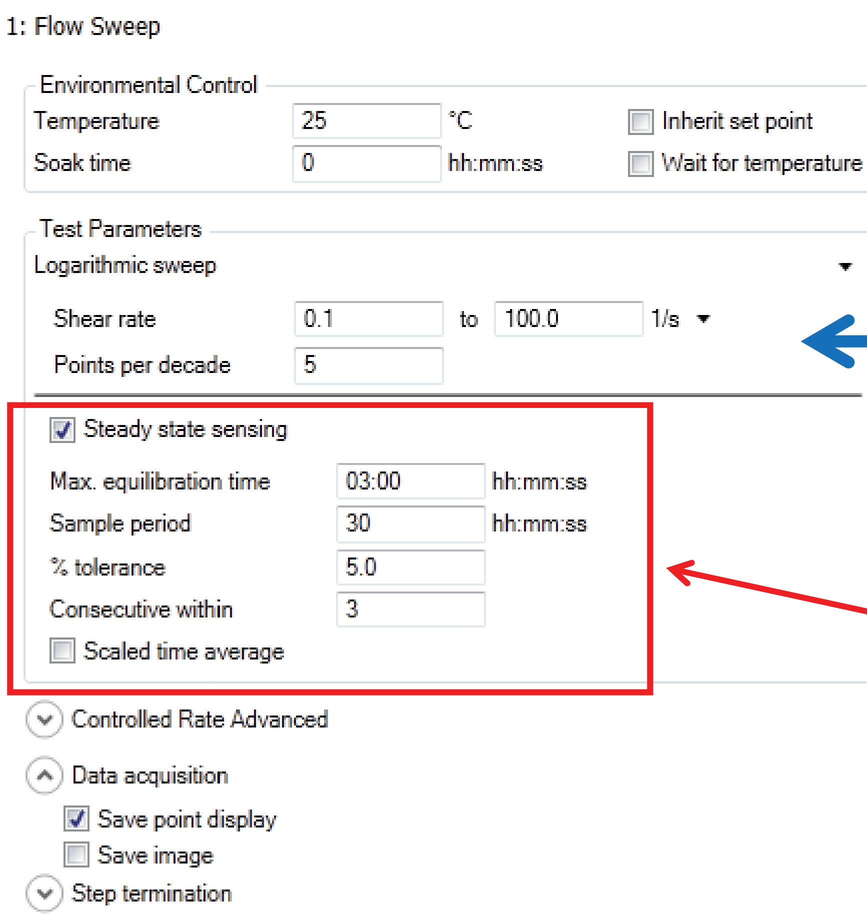
Stepped or Steady-State Flow

- A series of logarithmic stress steps allowed to reach steady state, each one giving a single viscosity data point:



$$\eta = \sigma / (d\gamma/dt)$$

DHR and ARES G2: Steady State Flow

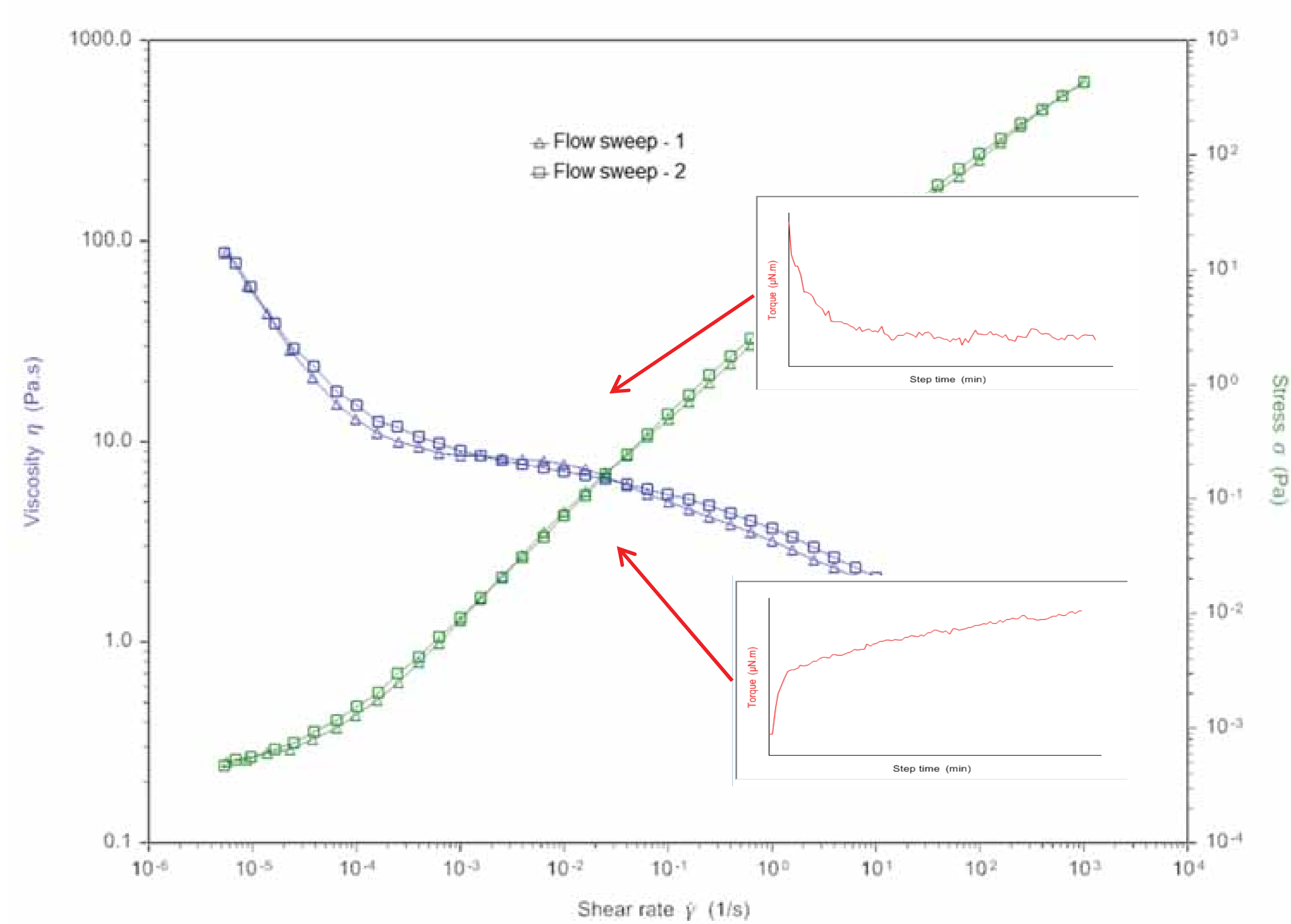


Control variables:

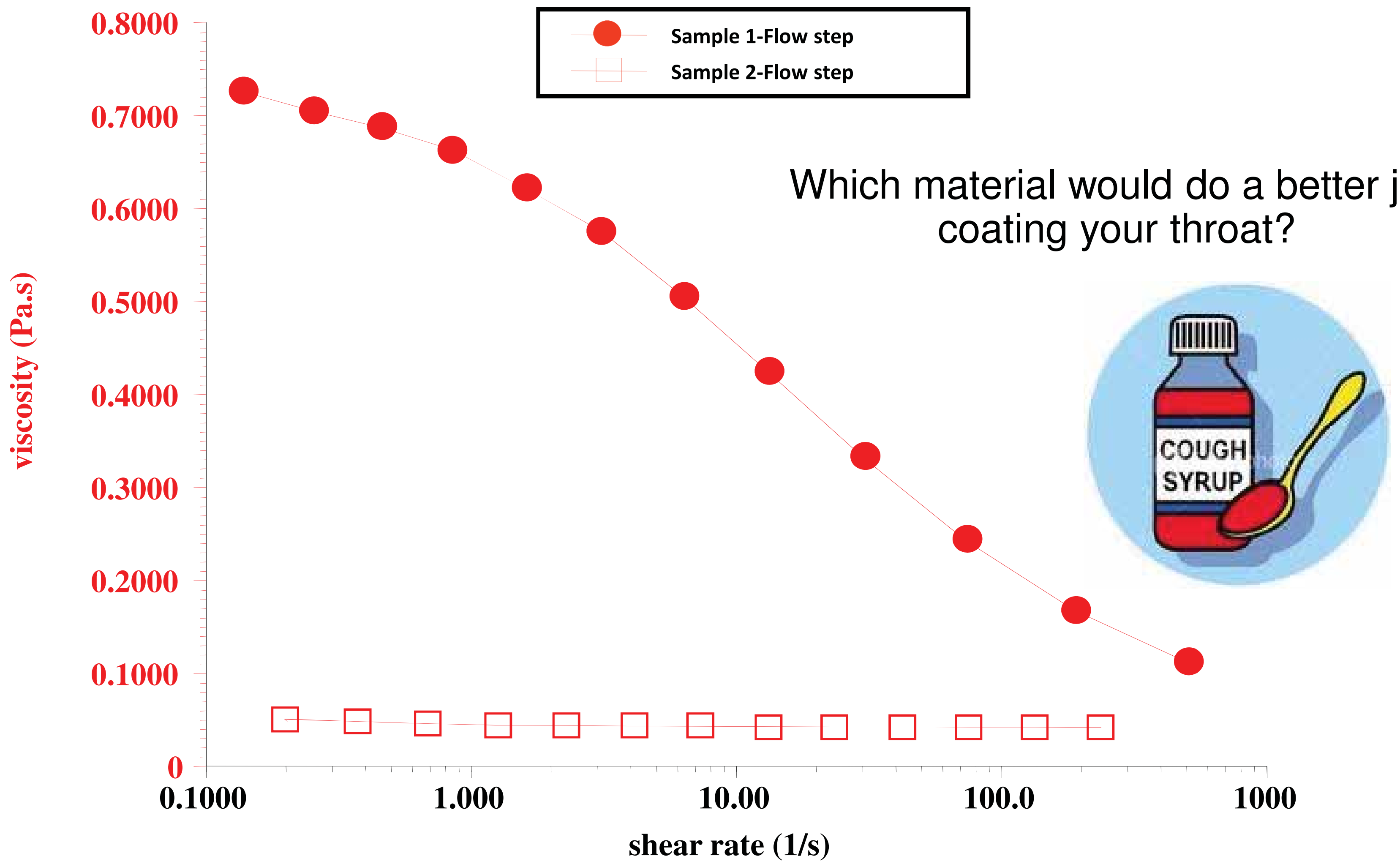
- Shear rate
- Velocity
- Torque
- Shear stress

Steady state algorithm

Flow Sweeps- Water-Based Paint with Solvent Trap

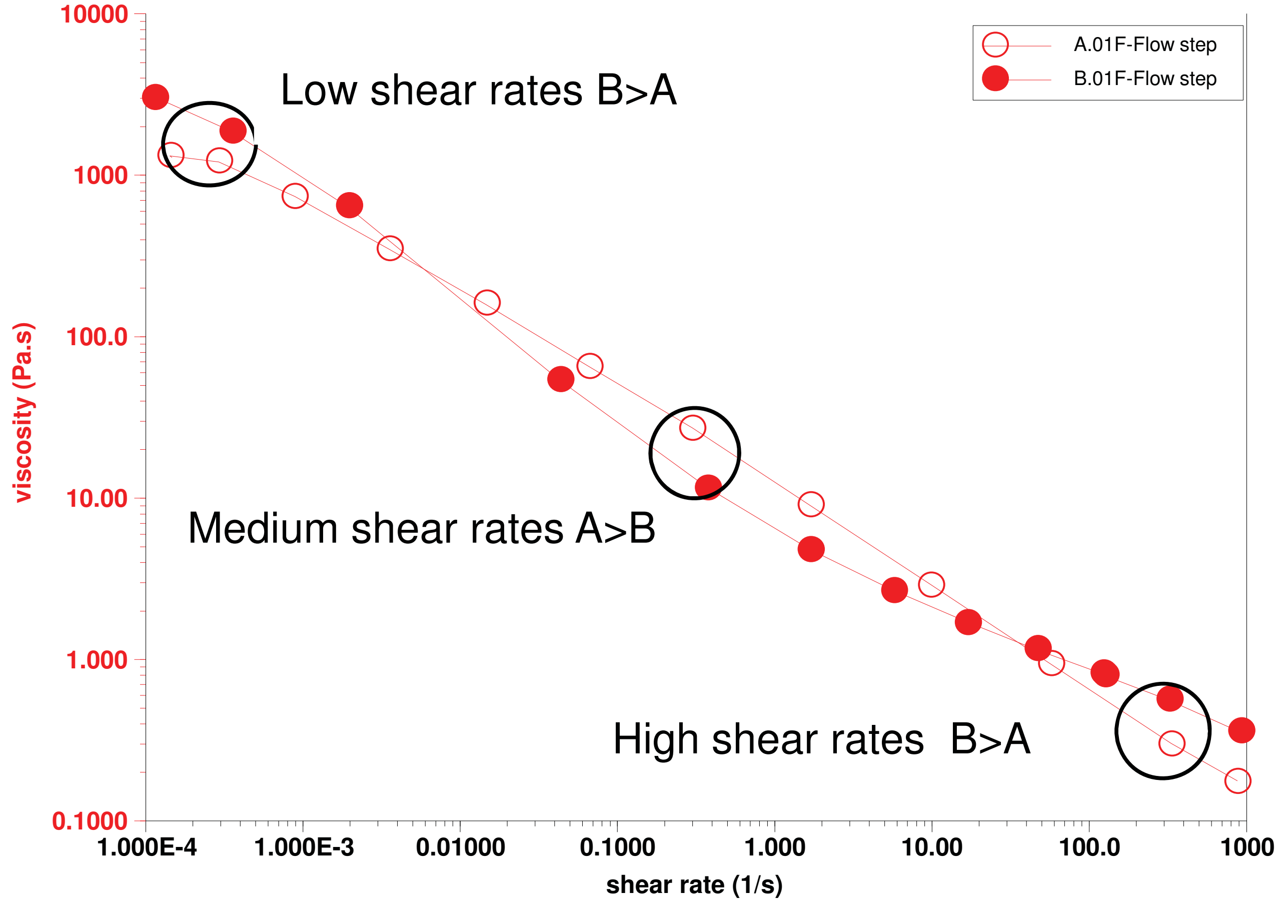


Comparison of Cough Syrups

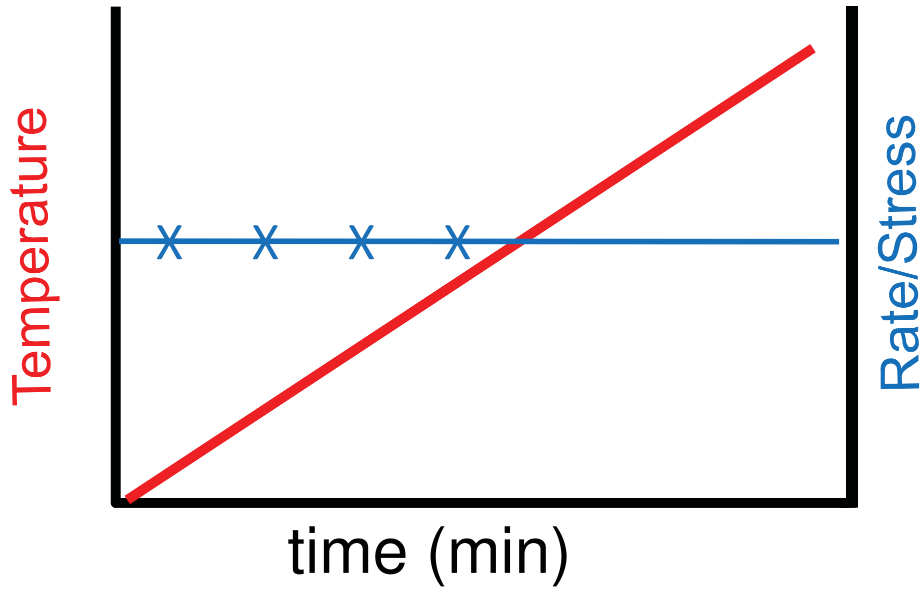


Which material would do a better job coating your throat?

Comparison of Two Latex Paints



Flow Temperature Ramp

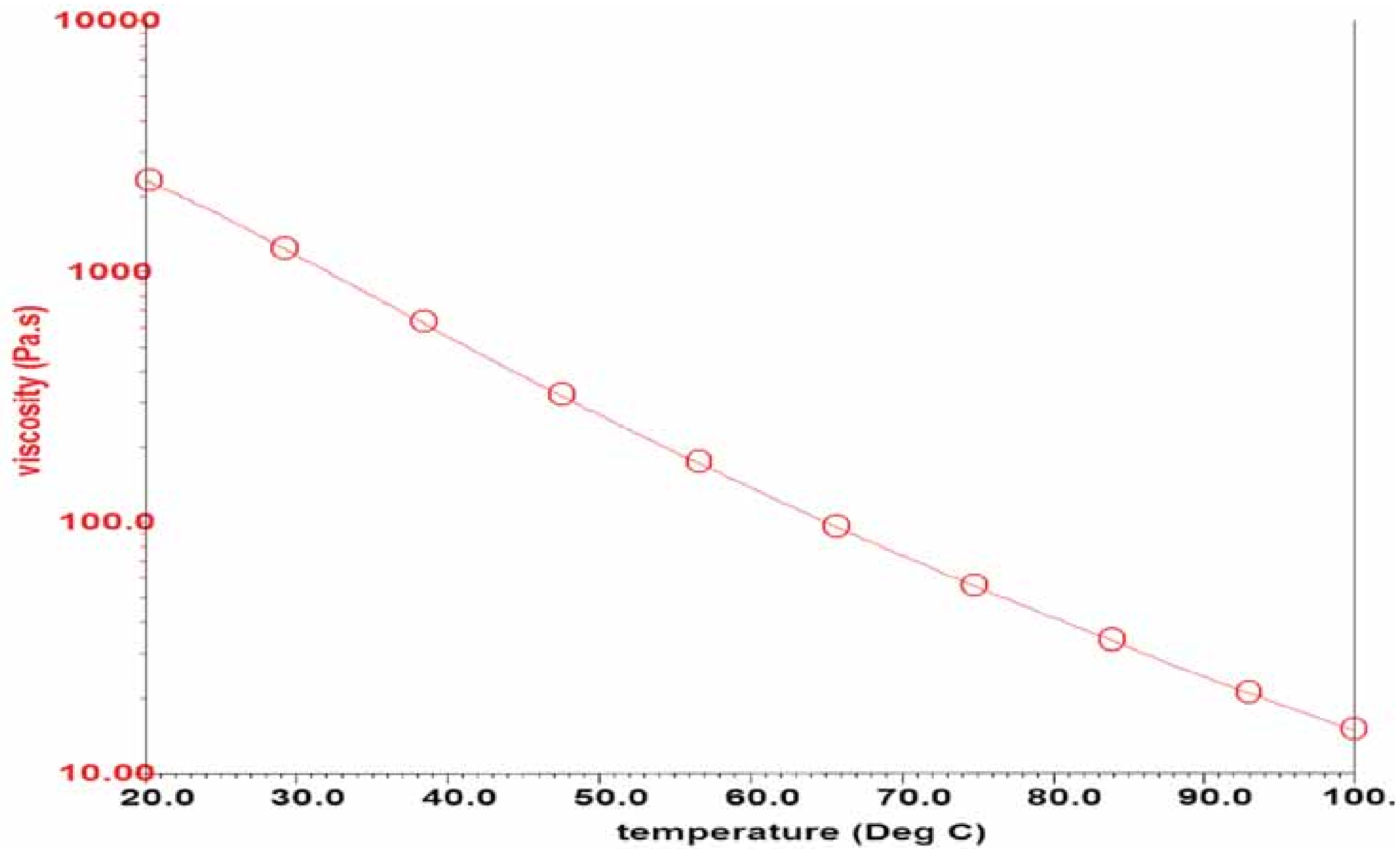


- Hold the rate or stress constant whilst ramping the temperature.

USES

- Measure the viscosity change vs. temperature

Viscosity: Temperature Dependence



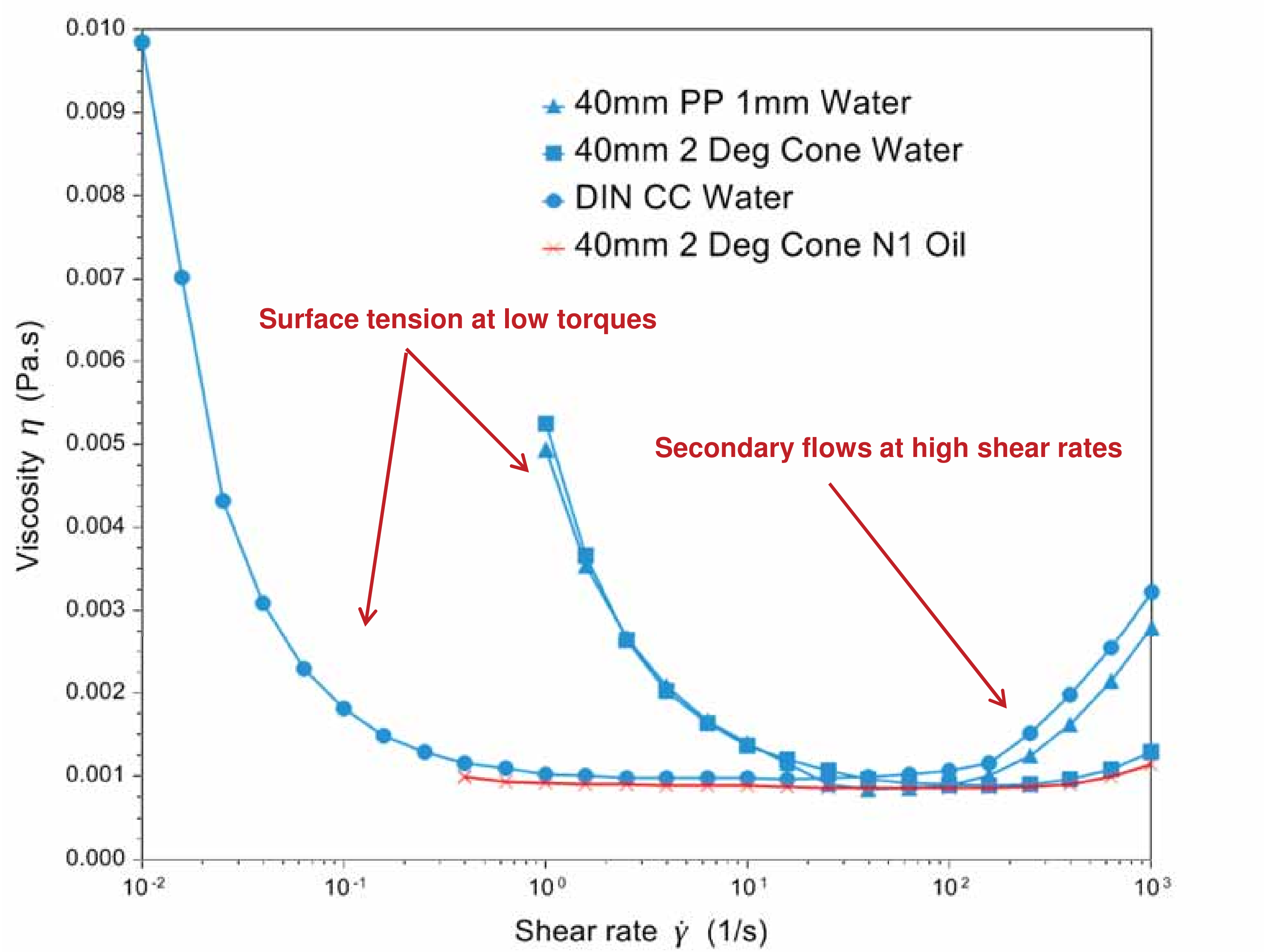
Notice a nearly 2 decade decrease in viscosity.   This displays the importance of thermal equilibration of the sample prior to testing.

i.e. Conditioning Step or equilibration time for 3 to 5 min

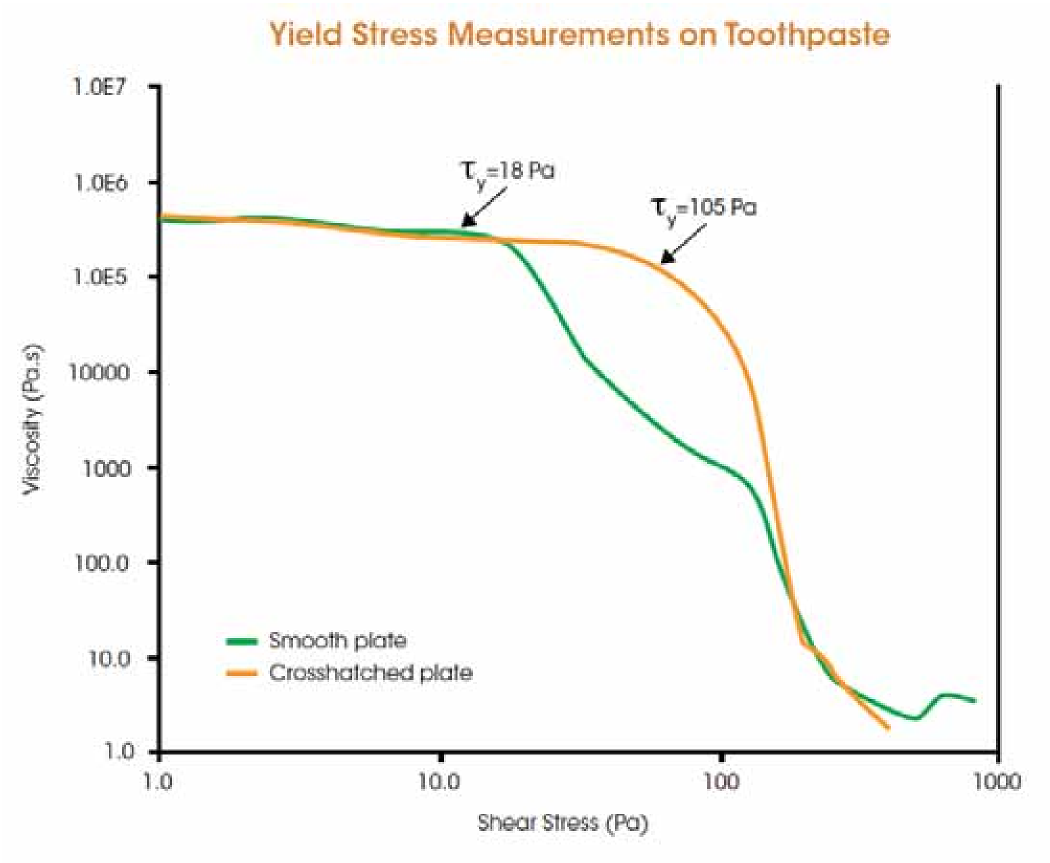
Flow Testing Considerations

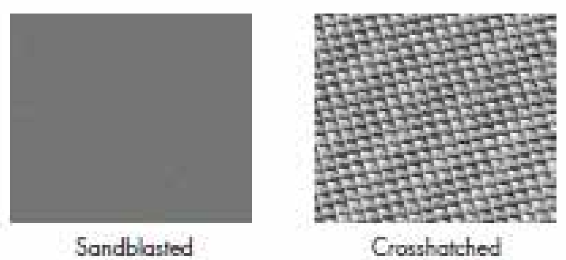
- Small gaps give high shear rates
  - Be careful with small gaps:
    - Gap errors (gap temperature compensation) and shear heating can cause large errors in data.
    - Recommended gap is between 0.5 to 2.0 mm.
    - Secondary flows can cause increase in viscosity curve
- Be careful with data interpretation at low shear rates
  - Surface tension can affect measured viscosity, especially with aqueous materials

Water at 25°C – Secondary Flow



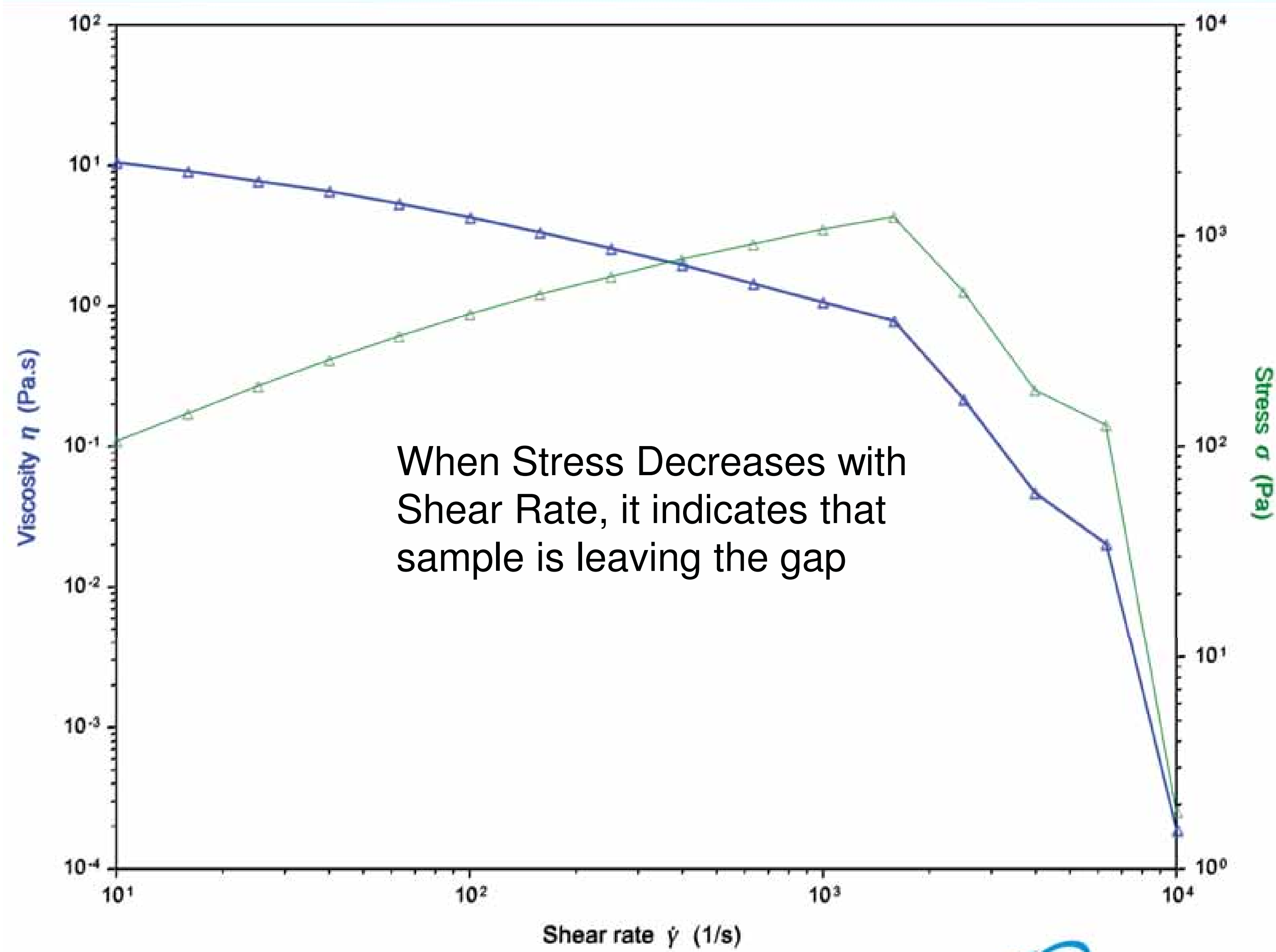
Wall Slip





- Wall slip can manifest as “apparent double yielding”
- Can be tested by running the same test at different gaps
- For samples that don’t slip, the results will be independent of the gap

Shear Thinning or Sample Instability?



Flow Testing Considerations

- Edge Failure – Sample leaves gap because of normal forces
  - Look at stress vs. shear rate curve – stress should not decrease with increasing shear rate – this indicates sample is leaving gap
- Possible Solutions:
  - use a smaller gap or smaller angle so that you get the same shear rate at a lower angular velocity
  - if appropriate (i.e. Polymer melts) make use of Cox Merz Rule

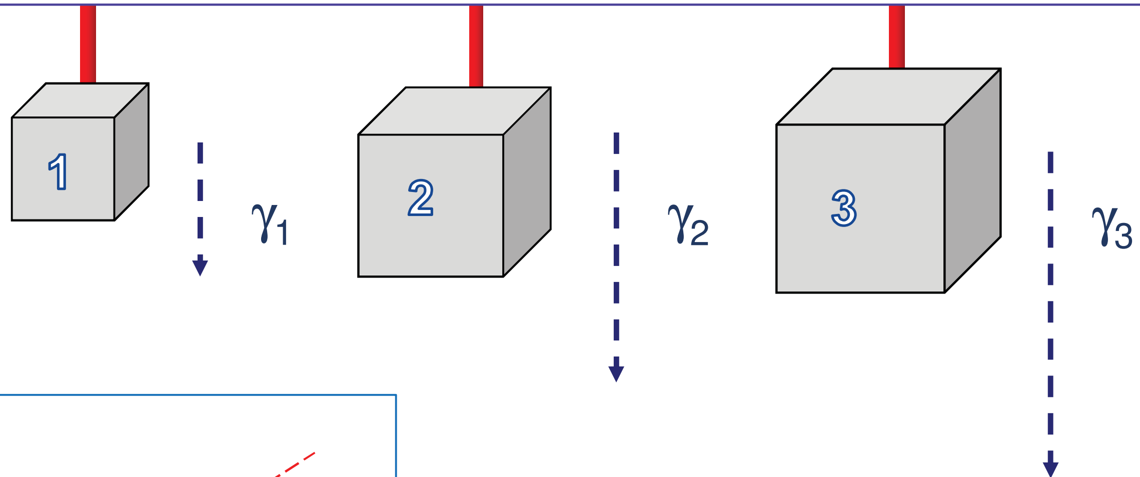
$$\eta(\dot{\gamma}) \equiv \eta^{*}(\omega)$$

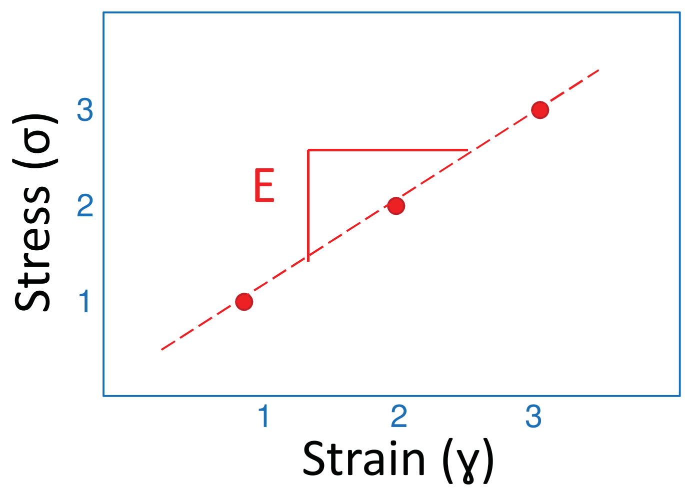
Viscoelasticity

Elastic Behavior of an Ideal Solid

Hooke's Law of Elasticity: Stress = Modulus · Strain

$$\sigma = E \cdot \gamma$$



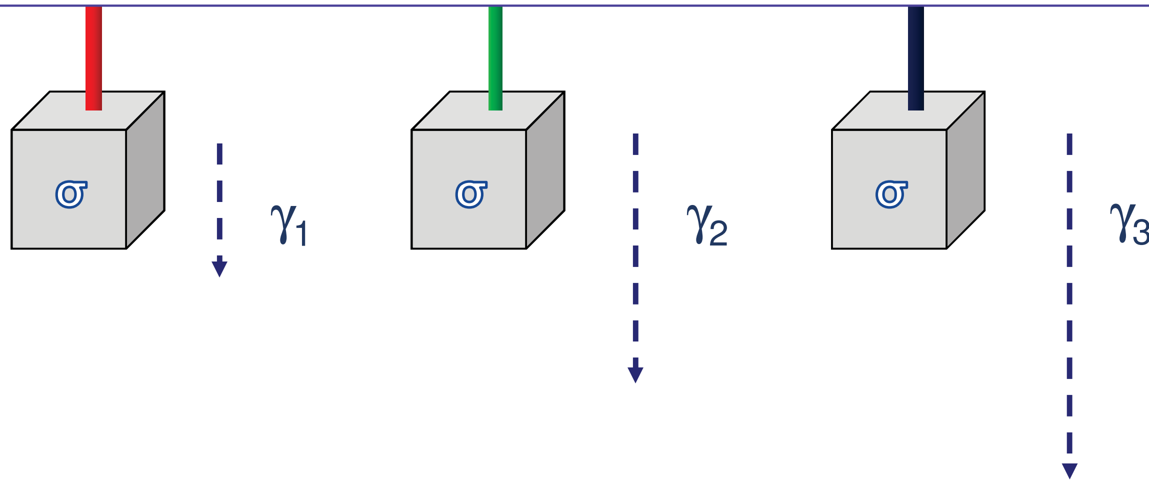


Elastic Behavior of an Ideal Solid

Hooke's Law of Elasticity: Stress = Modulus · Strain

E > E > E

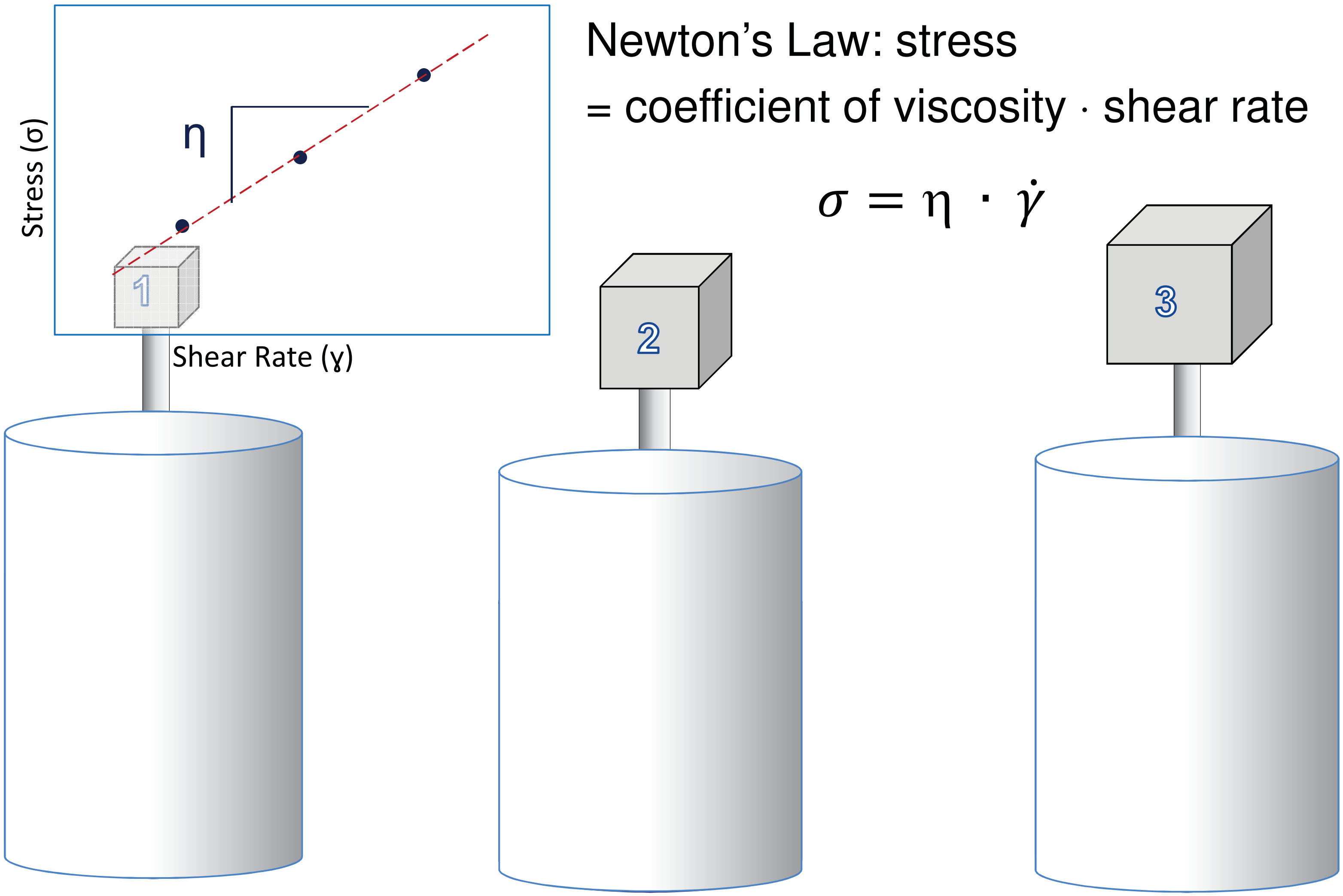
$$E = \frac{\sigma}{\gamma}$$



Viscous Behavior of an Ideal Liquid

Newton's Law: stress
= coefficient of viscosity · shear rate

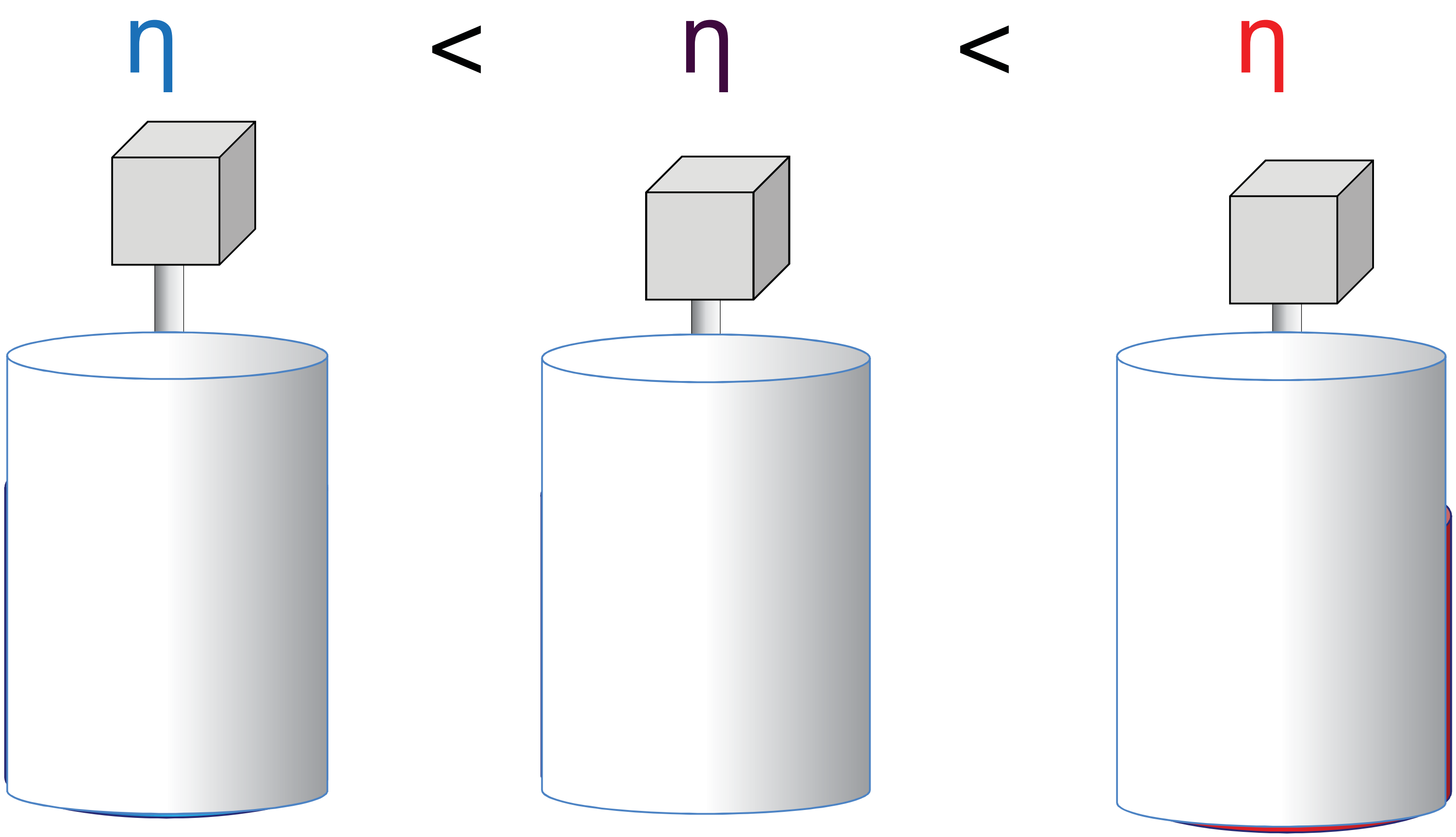
$$\sigma = \eta \cdot \dot{\gamma}$$



Viscous Behavior of an Ideal Liquid

Newton's Law: stress= coefficient of viscosity · shear rate

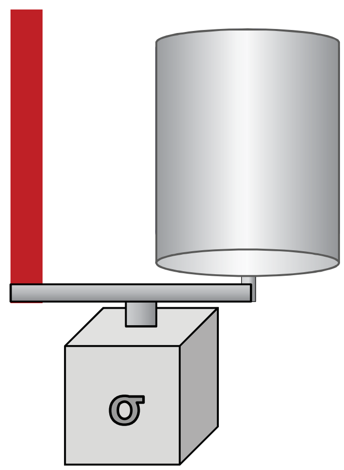
$$\eta = \frac{\sigma}{\dot{\gamma}}$$



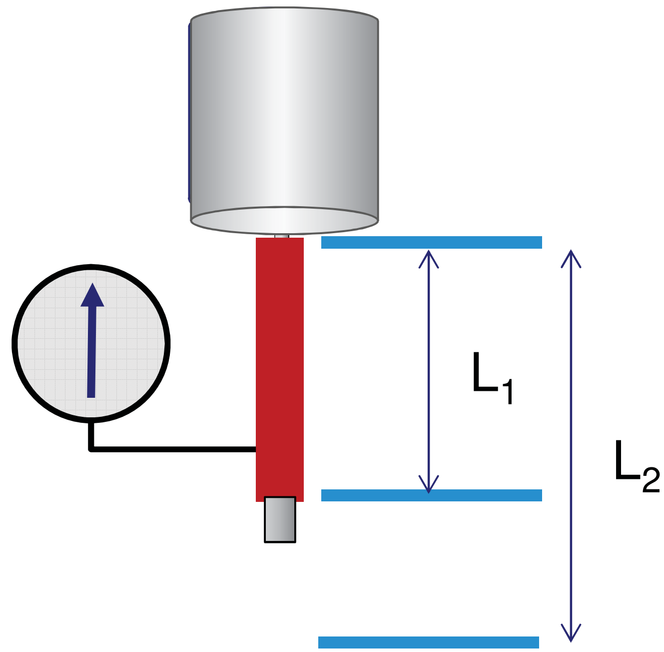
Viscoelastic Behavior

$$\sigma = E^*\varepsilon + \eta^* d\varepsilon/dt$$

Kelvin-Voigt Model (Creep)



Maxwell Model (Stress Relaxation)



Viscoelastic Materials: Force depends on both Deformation and Rate of Deformation and vice versa.

Viscoelasticity Defined

<u>Range of Material Behavior</u>

Liquid Like----------- Solid Like

Ideal Fluid ----- Most Materials -----Ideal Solid

Purely Viscous ----- *Visco*elastic ----- Purely Elastic

Viscoelasticity: Having both viscous and elastic properties

- Materials behave in the linear manner, as described by Hooke and Newton, only on a small scale in stress or deformation.

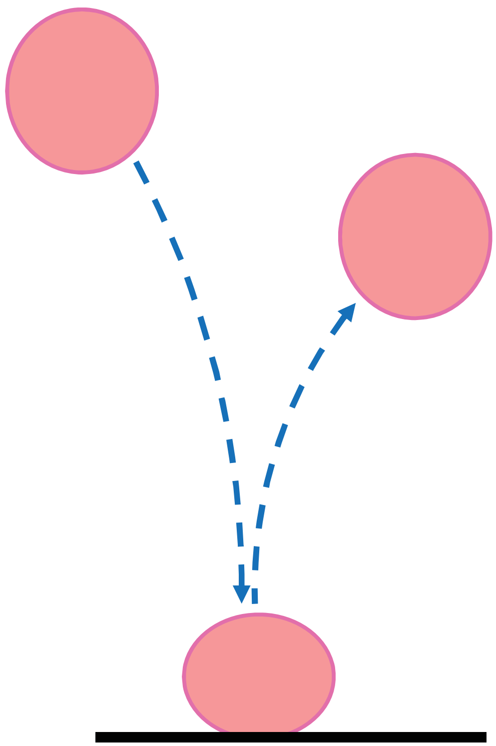
Pitch Drop Experiment

- Long deformation time: pitch behaves like a highly viscous liquid
  - 9th drop fell July 2013
- Short deformation time: pitch behaves like a solid

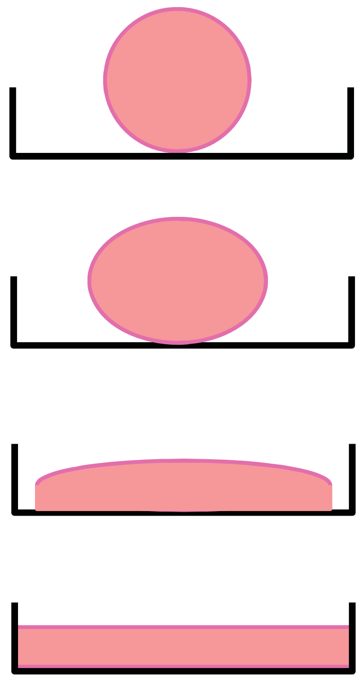
Started in 1927 by Thomas Parnell in Queensland, Australia

http://www.theatlantic.com/technology/archive/2013/07/the-3-most-exciting-words-in-science-right-now-the-pitch-dropped/277919/

Time-Dependent Viscoelastic Behavior



T is short [< 1s]



T is long [24 hours]

Time-Dependent Viscoelastic Behavior

- Silly Putties have different characteristic relaxation times
- Dynamic (oscillatory) testing can measure time-dependent viscoelastic properties more efficiently by varying frequency (deformation time)

Viscoelasticity, Deborah Number

- Old Testament Prophetess who said (Judges 5:5): "The Mountains 'Flowed' before the Lord"

- Everything Flows if you wait long enough!

- Deborah Number, De - The ratio of a characteristic relaxation time of a material (τ) to a characteristic time of the relevant deformation process (T).

$$De = \tau/T$$

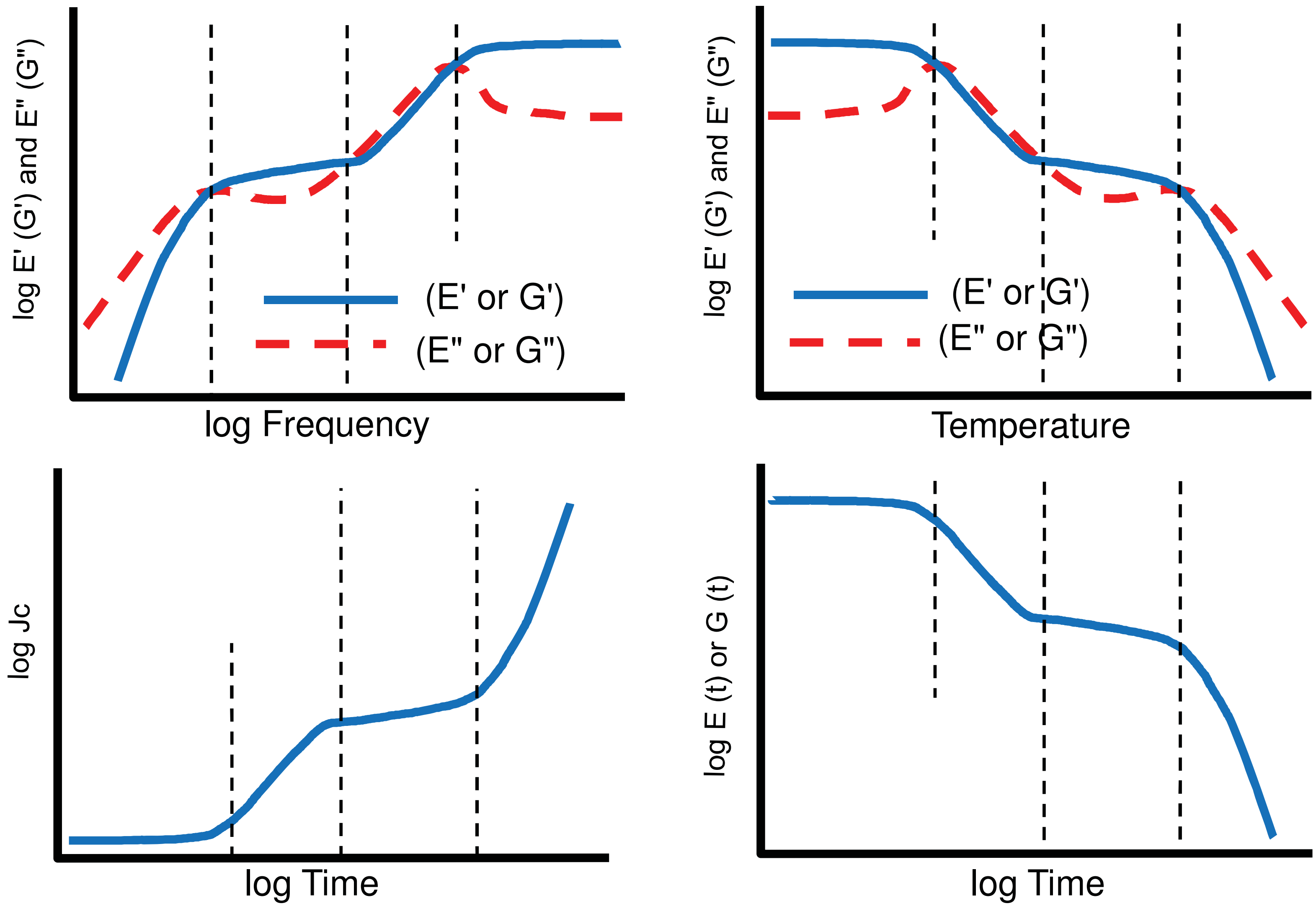
Deborah Number

- Hookean elastic solid - τ is infinite
- Newtonian Viscous Liquid - τ is zero
- Polymer melts processing - τ may be a few seconds

High De	→	Solid-like behavior
Low De	→	Liquid-like behavior

IMPLICATION: Material can appear solid-like because
1) it has a very long characteristic relaxation time or
2) the relevant deformation process is very fast

Time and Temperature Relationship



Linear Viscoelasticity Region (LVR) Defined

"If the deformation is small, or applied sufficiently slowly, the molecular arrangements are never far from equilibrium.

The mechanical response is then just a reflection of dynamic processes at the molecular level which go on constantly, even for a system at equilibrium.

This is the domain of LINEAR VISCOELASTICITY.

The magnitudes of stress and strain are related linearly, and the behavior for any liquid is completely described by a single function of time."

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

Importance of LVR

Linear Viscoelastic Properties

E’ (or G’), E” (or G”), tan δ, η^*

Measuring linear viscoelastic properties helps us bridge the gap between molecular structure and product performance

Setting up Rheological Experiments

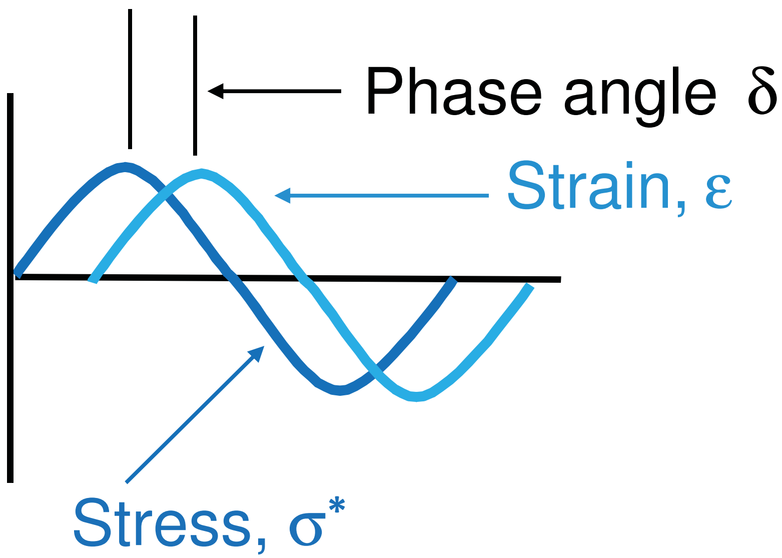
Oscillatory Tests

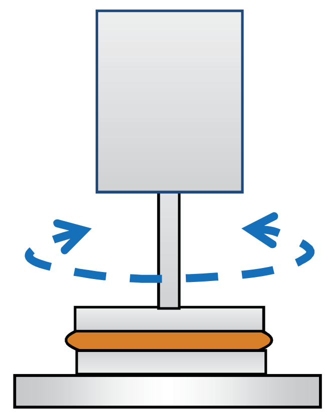
Understanding Oscillation Experiments

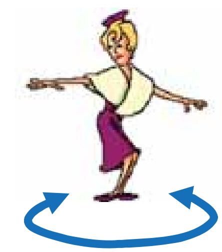
- Define Oscillation Testing

- Approach to Oscillation Experimentation
  - Stress and Strain Sweep
  - Time Sweep
  - Frequency Sweep
  - Temperature Ramp
  - Temperature Sweep (TTS)

What is Oscillation?







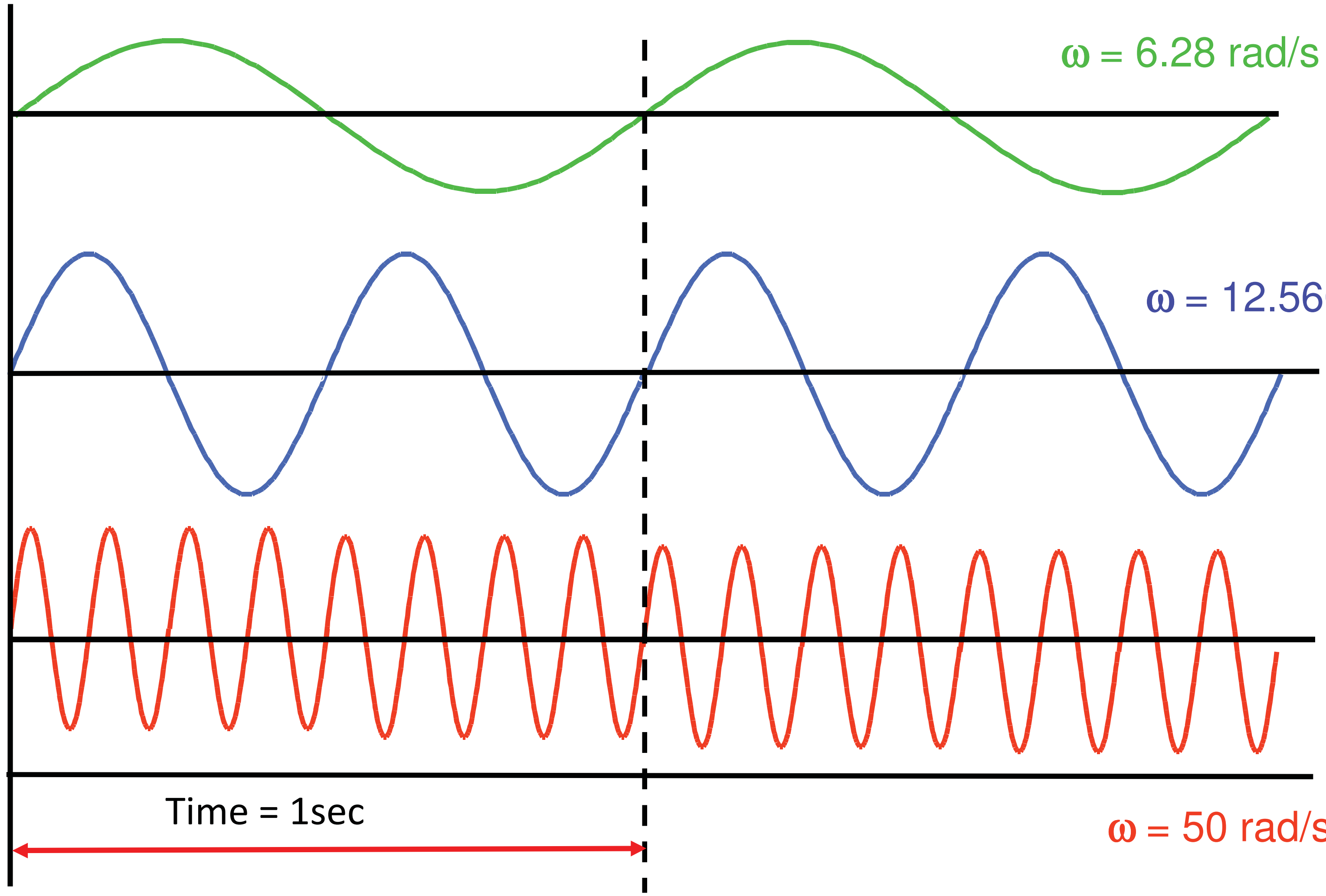
Dynamic stress applied sinusoidally

User-defined Stress or Strain amplitude and frequency

Frequency Defined

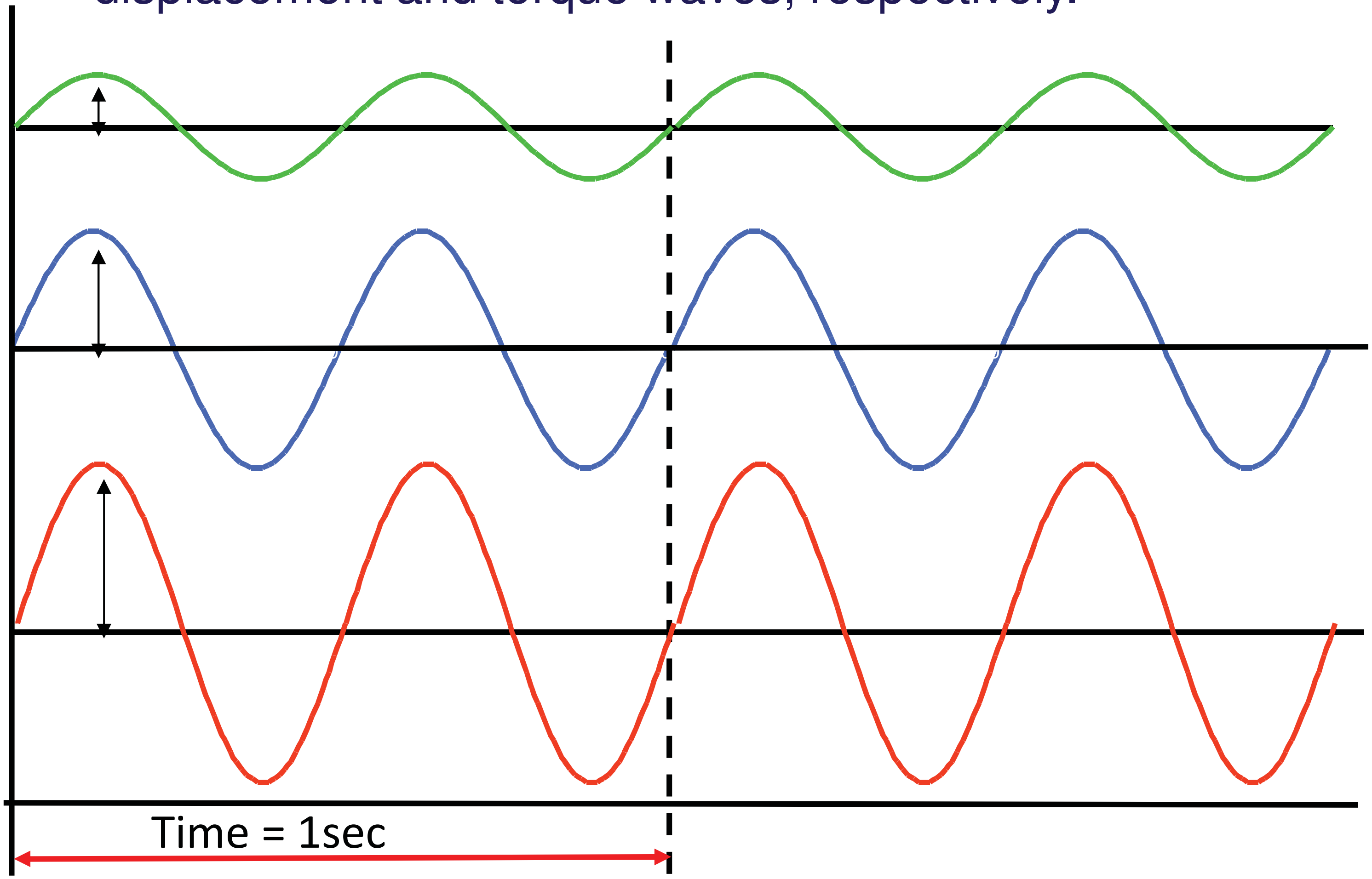
- Time to complete one oscillation
- Frequency is the inverse of time
- Units
  - Angular Frequency = radians/second
  - Frequency = cycles/second (Hz)
- Rheologist must think in terms of rad/s.
  - 1 Hz = 6.28 rad/s

Frequency



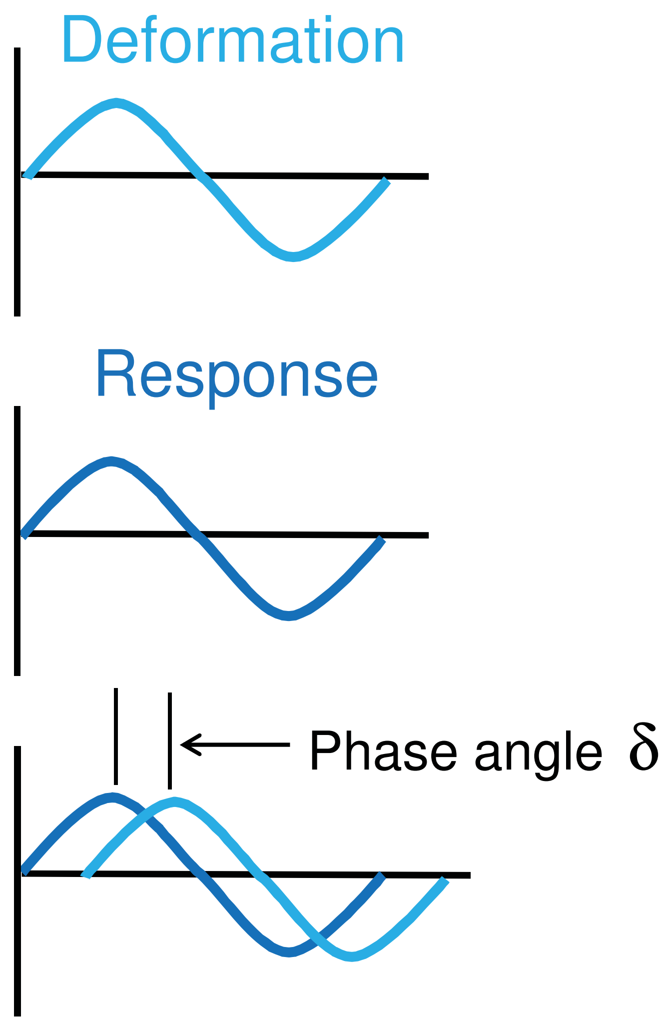
Amplitude: Strain or Stress

- Strain and stress are calculated from peak amplitude in the displacement and torque waves, respectively.



Dynamic Mechanical Testing

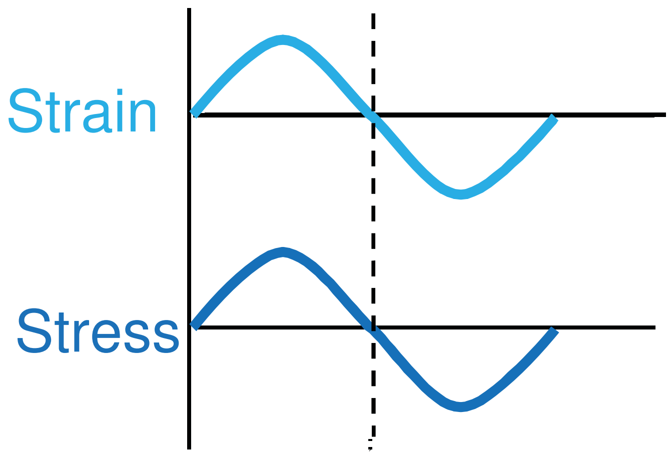
- An oscillatory (sinusoidal) deformation (stress or strain) is applied to a sample.
- The material response (strain or stress) is measured.
- The phase angle δ, or phase shift, between the deformation and response is measured.



Dynamic Testing: Response for Classical Extremes

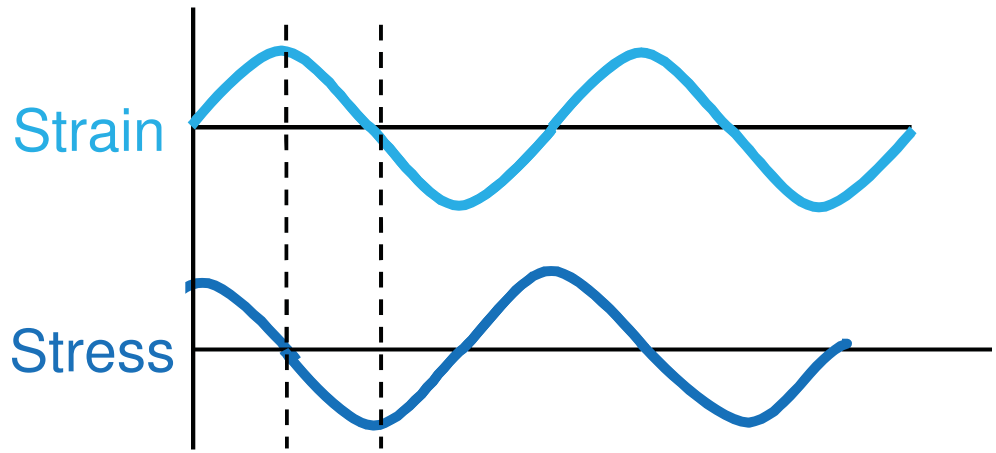
Purely Elastic Response (Hookean Solid)

$\delta = 0°$

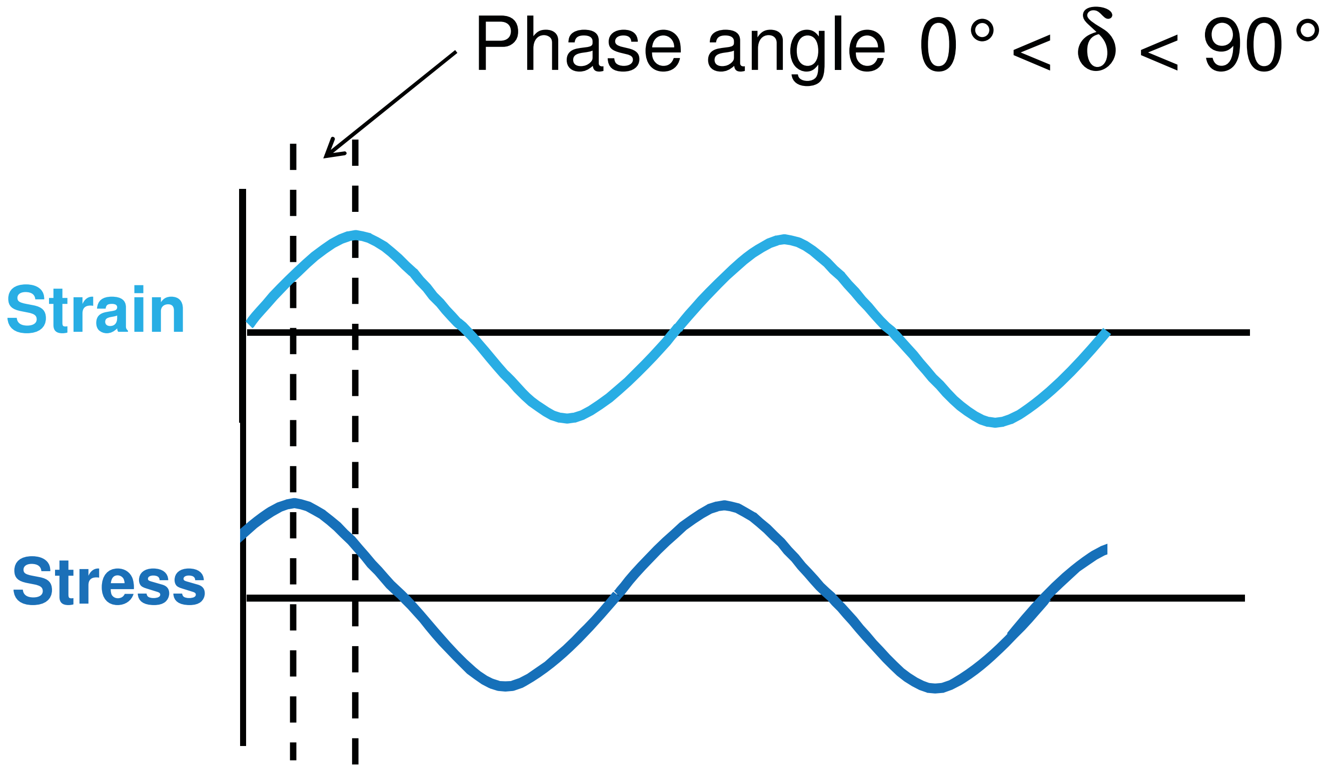


Purely Viscous Response (Newtonian Liquid)

$\delta = 90°$



Dynamic Testing: Viscoelastic Material Response



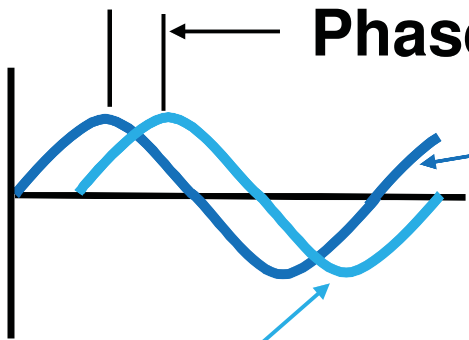
Viscoelastic Parameters: Complex, Elastic, & Viscous Stress

- The stress in a dynamic experiment is referred to as the complex stress σ^*
- The complex stress can be separated into two components:
  1) An elastic stress in phase with the strain. $\sigma' = \sigma^*\cos\delta$

  σ' is the degree to which material behaves like an elastic solid.

  2) A viscous stress in phase with the strain rate. $\sigma'' = \sigma^*\sin\delta$

  σ'' is the degree to which material behaves like an ideal liquid.



$$\sigma^* = \sigma' + i\sigma''$$

Complex number: $|x + iy| = \sqrt{x^2 + y^2}$

The material functions can be described in terms of complex variables having both real and imaginary parts. Thus, using the relationship:

$$\mathrm{Cos}\,x + j\,\mathrm{Sin}\,x = e^{jx}$$

where $j = \sqrt{-1}$

Viscoelastic Parameters

The Modulus: Measure of materials overall resistance to deformation.

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

The Elastic (Storage) Modulus: Measure of elasticity of material. The ability of the material to store energy.

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

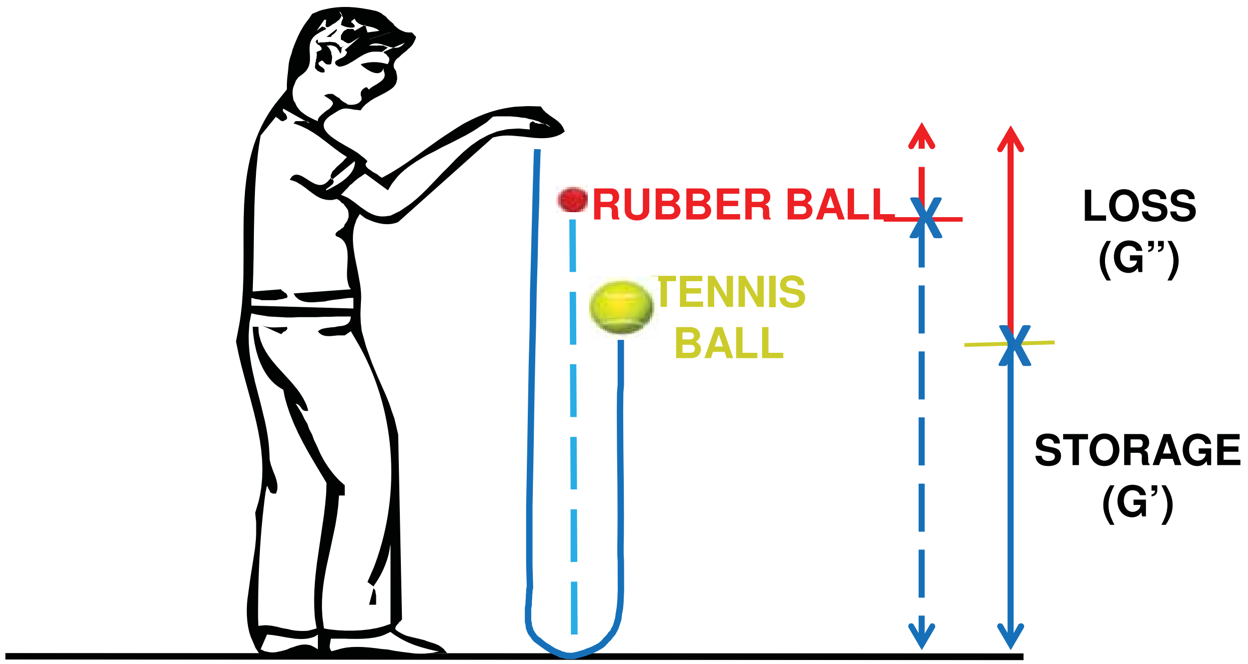
The Viscous (loss) Modulus: The ability of the material to dissipate energy. Energy lost as heat.

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

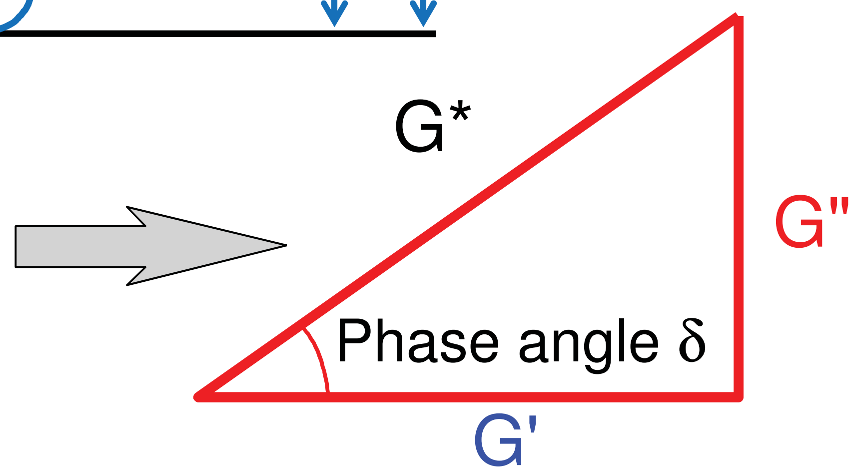
Tan Delta: Measure of material damping - such as vibration or sound damping.

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

Storage and Loss of a Viscoelastic Material



Dynamic measurement
represented as a vector



Complex Viscosity

- The viscosity measured in an oscillatory experiment is a Complex Viscosity much the way the modulus can be expressed as the complex modulus. The complex viscosity contains an elastic component and a term similar to the steady state viscosity.

- The Complex viscosity is defined as:

$$\eta^* = \eta' + i\,\eta''$$

or

$$\eta^* = G^*/\omega$$

Note: frequency must be in rad/sec!

Dynamic Rheological Parameters

Parameter	Shear	Elongation	Units
Strain	$\gamma = \gamma_0 \sin(\omega t)$	$\varepsilon = \varepsilon_0 \sin(\omega t)$	---
Stress	$\sigma = \sigma_0 \sin(\omega t + \delta)$	$\tau = \tau_0 \sin(\omega t + \delta)$	Pa
Storage Modulus (Elasticity)	$G' = (\sigma_0/\gamma_0)\cos\delta$	$E' = (\tau_0/\varepsilon_0)\cos\delta$	Pa
Loss Modulus (Viscous Nature)	$G'' = (\sigma_0/\gamma_0)\sin\delta$	$E'' = (\tau_0/\varepsilon_0)\sin\delta$	Pa
Tan δ	G''/G'	E''/E'	---
Complex Modulus	$G^* = (G'^2+G''^2)^{0.5}$	$E^* = (E'^2+E''^2)^{0.5}$	Pa
Complex Viscosity	$\eta^* = G^*/\omega$	$\eta_E^* = E^*/\omega$	Pa·sec

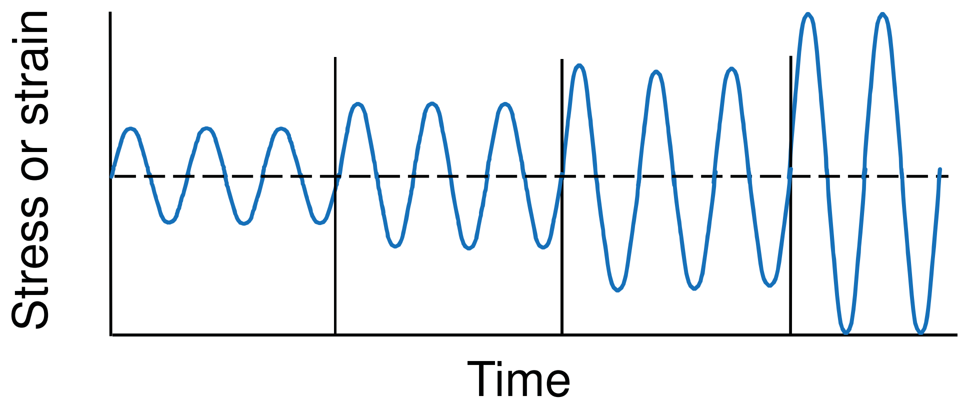
Cox-Merz Rule for Linear Polymers: $\eta^*(\omega) = \eta(\dot{\gamma})$ @ $\dot{\gamma} = \omega$

Understanding Oscillation Experiments

- Define Oscillation Testing

- Approach to Oscillation Experimentation
  1. Stress and Strain Sweep
  2. Time Sweep
  3. Frequency Sweep
  4. Temperature Ramp
  5. Temperature Sweep (TTS)

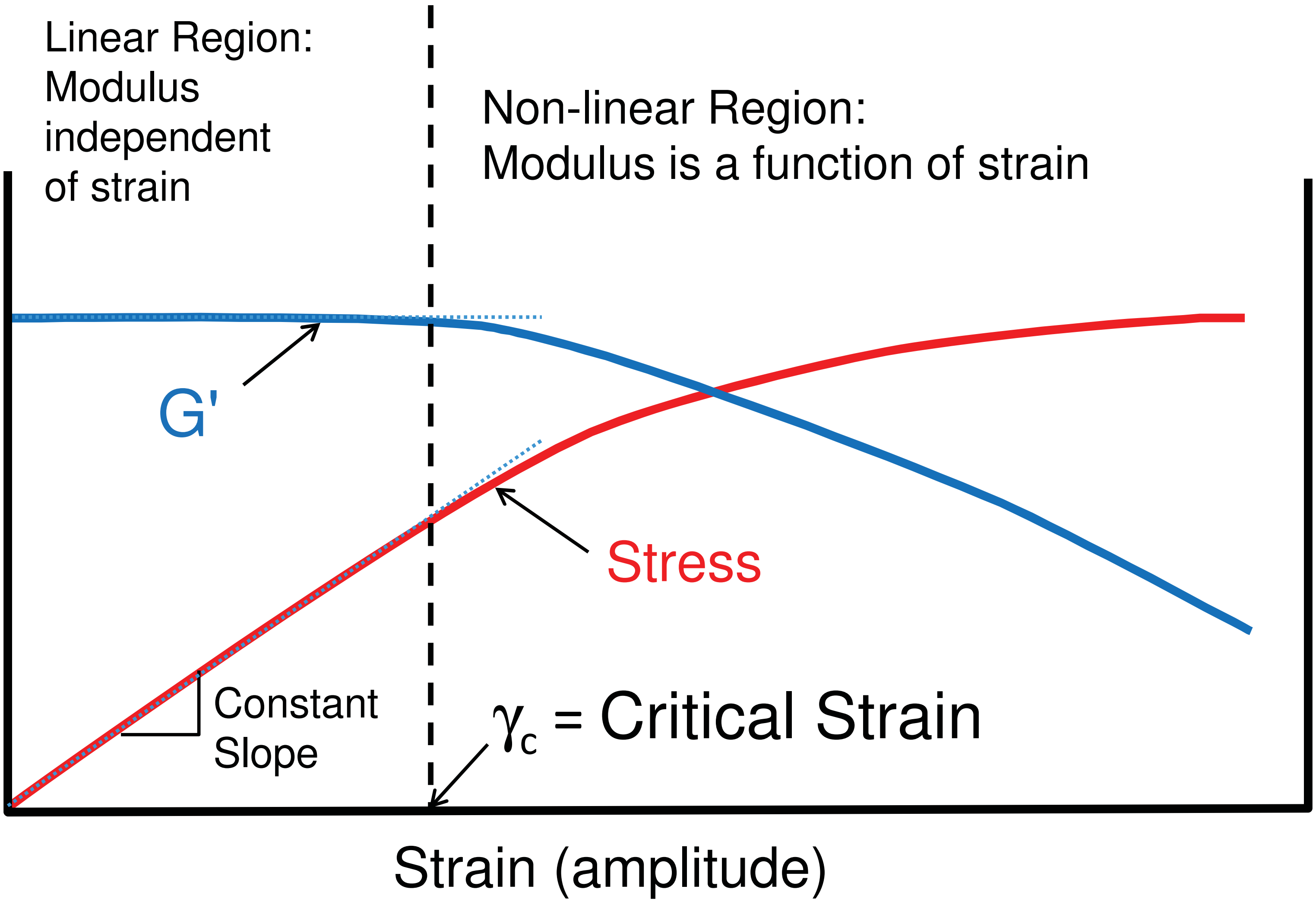
Dynamic Strain or Stress Sweep



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

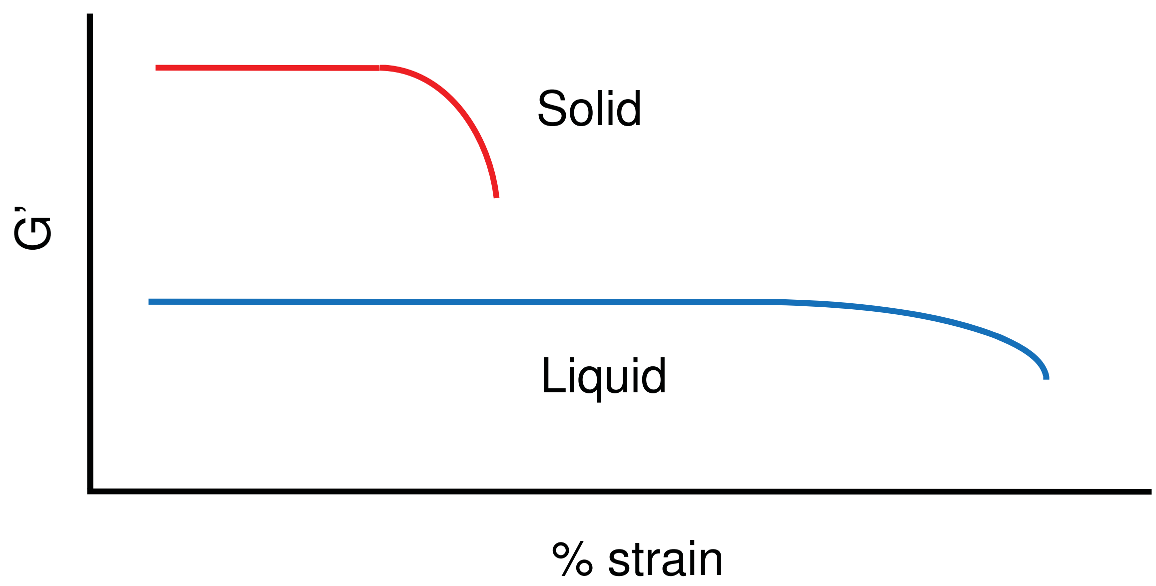
- Main use is to determine LVR
  - All subsequent tests require an amplitude found in the LVR
- Tests assumes sample is stable
- If not stable use Time Sweep to determine stability

Dynamic Strain Sweep: Material Response

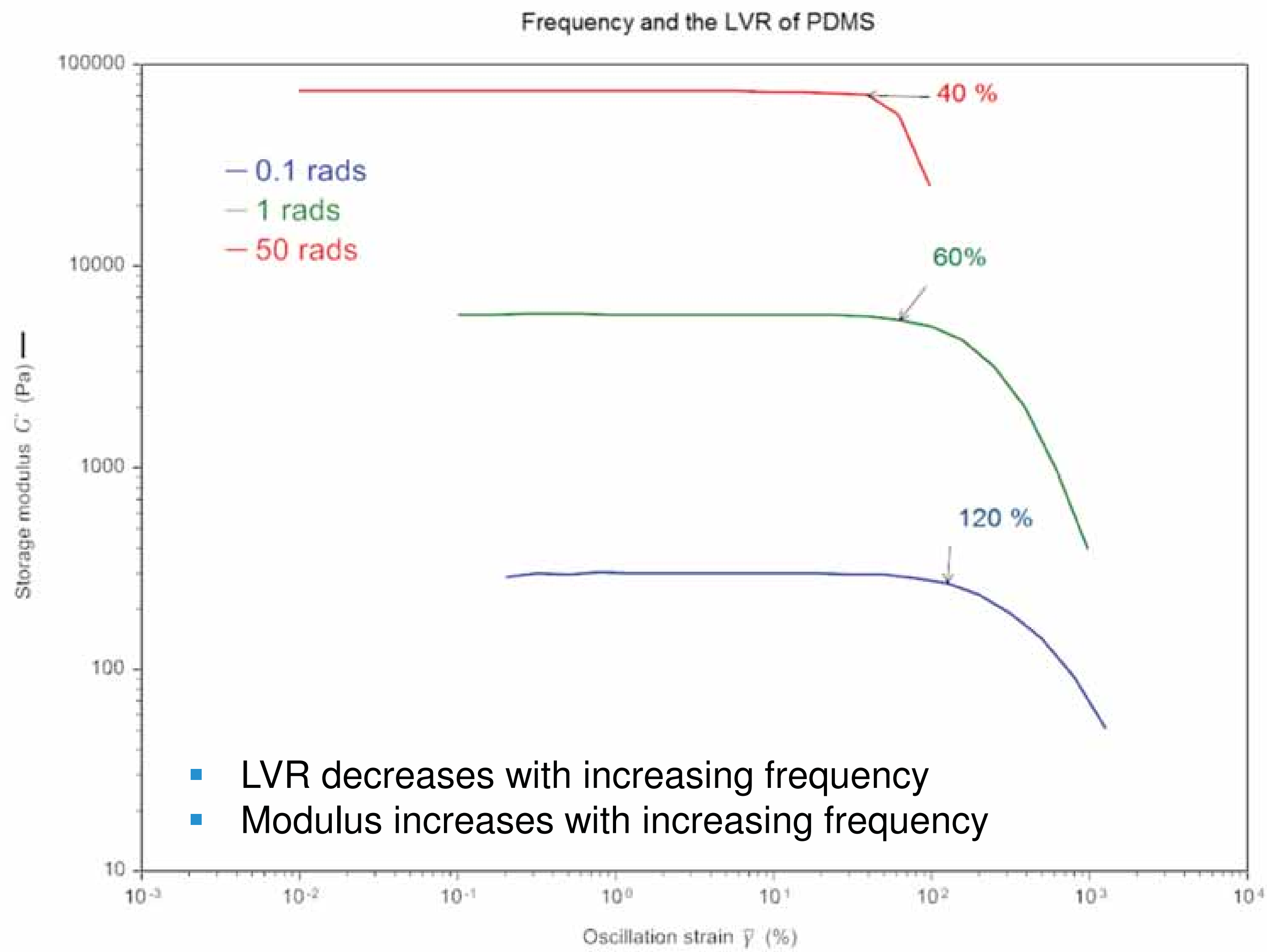


Temperature Dependence of LVR

- In general, the LVR is shortest when the sample is in its most solid form.

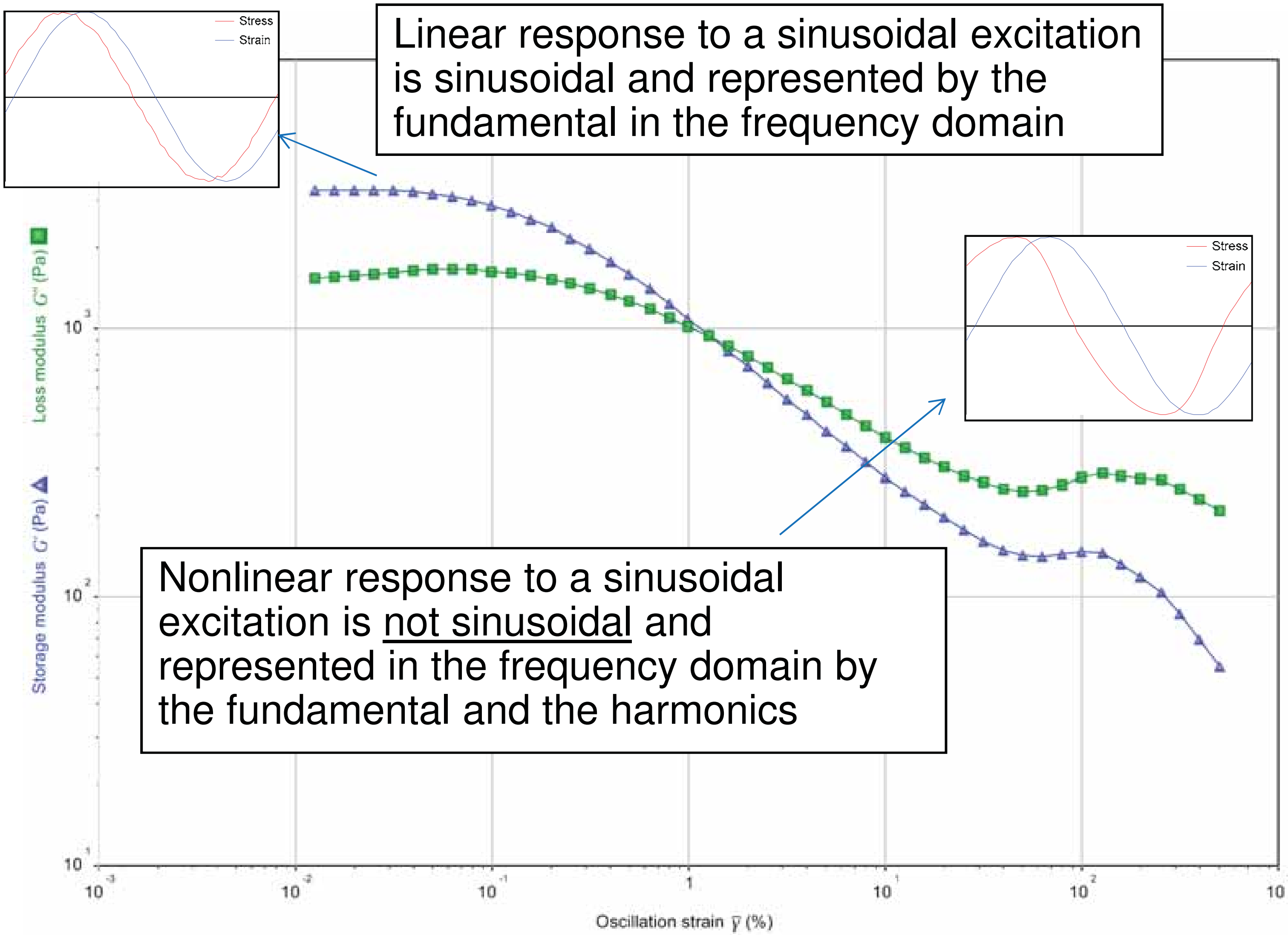


Frequency Dependence of LVR



- LVR decreases with increasing frequency
- Modulus increases with increasing frequency

SAOS versus LAOS Waveforms

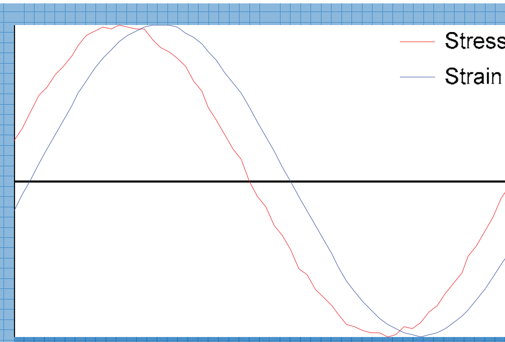


LAOS: Analysis of Higher Harmonics

SAOS

$$\gamma(t) = \gamma_0 \sin(\omega t)$$

$$\tau(t) = \tau_0 \sin(\omega t + \delta)$$



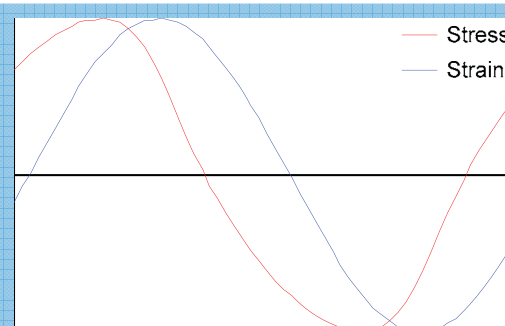
LAOS

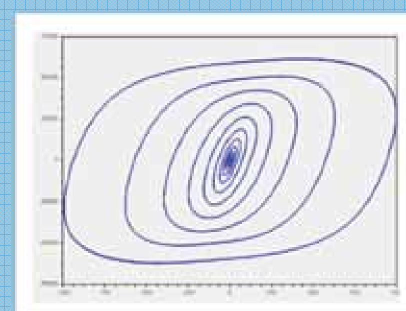
$$\gamma(t) = \gamma_0 \sin(\omega t)$$

Fourier Series expansion:

$$\tau(t) = \tau_1 \sin(\omega_1 t + \varphi_1) + \tau_3 \sin(3\omega_1 t + \varphi_3) + \tau_5 \sin(5\omega_1 t + \varphi_5) + \ldots$$

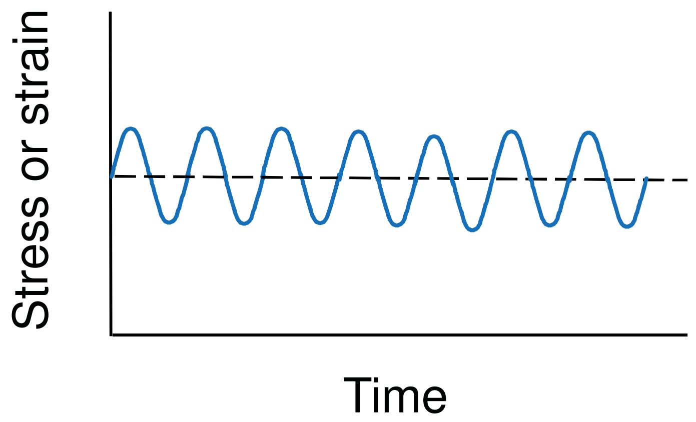
$$= \sum_{\substack{n=1 \\ \text{odd}}}^{\infty} \tau_n \sin(n\omega_1 + \varphi_n)$$





Lissajous plot: Stress vs. Strain (shown) or stress vs. Shear rate

Dynamic Time Sweep



- The material response is monitored at a constant frequency, amplitude and temperature.

USES

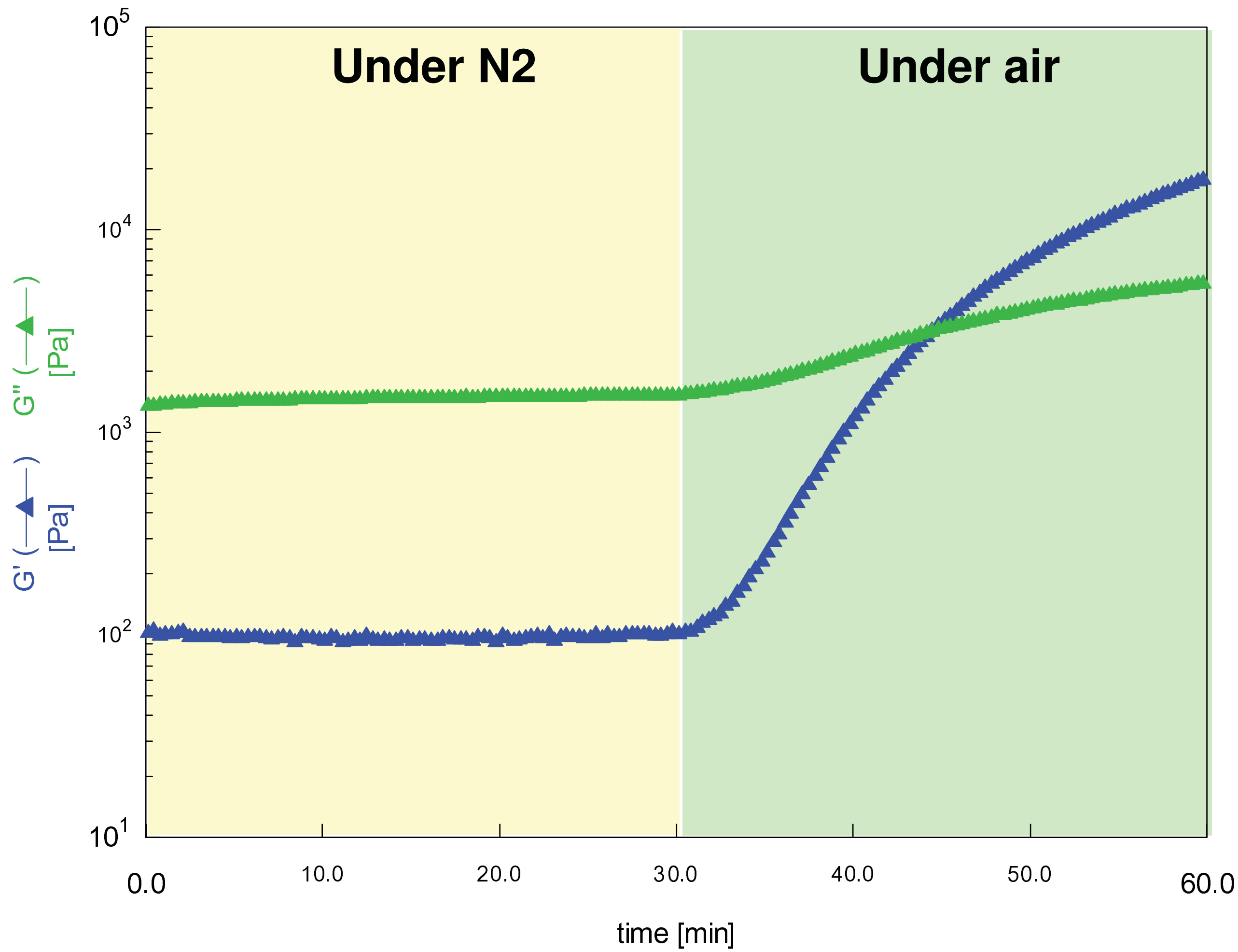
- Time dependent Thixotropy
- Cure Studies
- Stability against thermal degradation
- Solvent evaporation/drying

Importance of Time Sweep

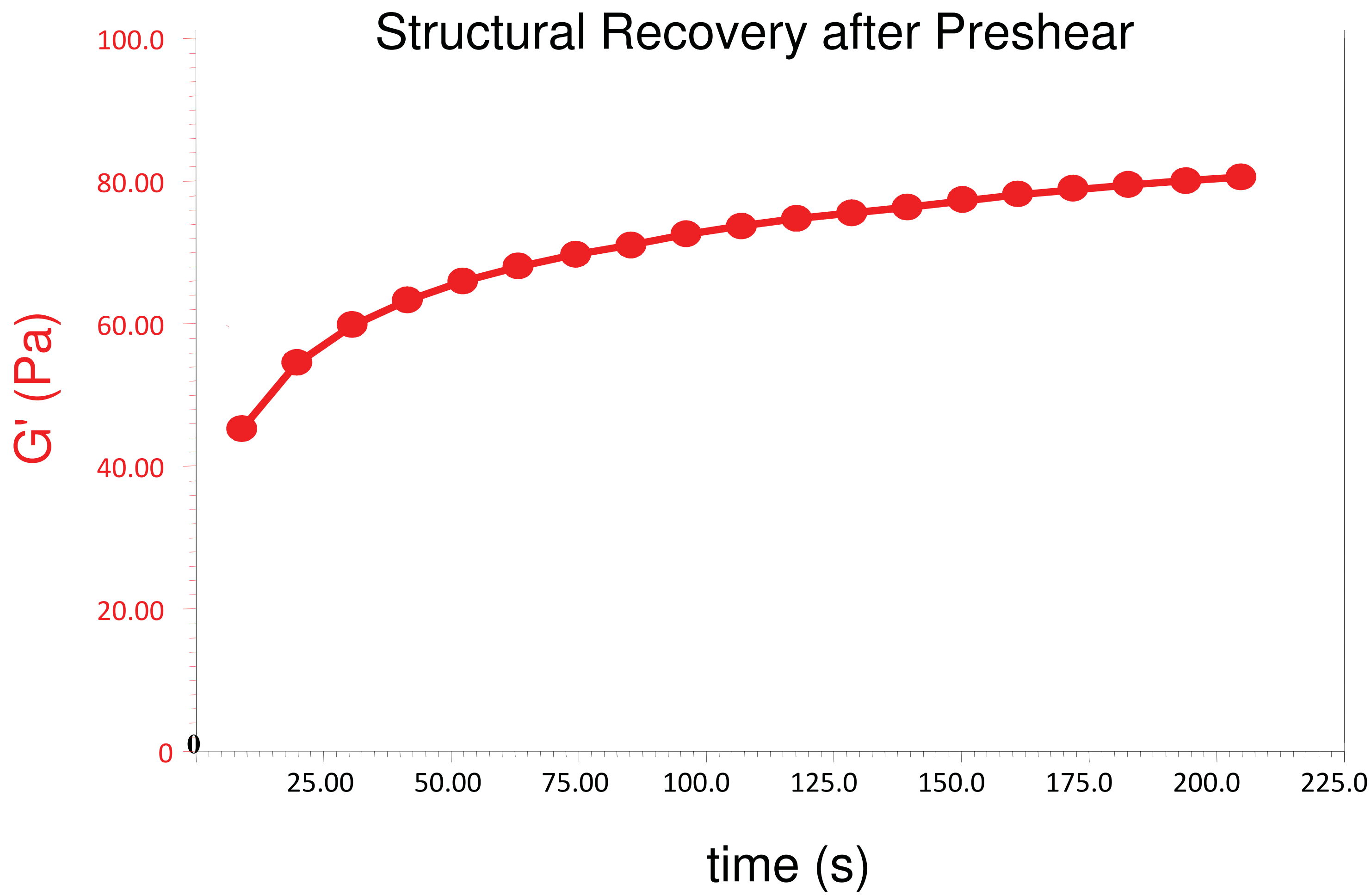
- Important, but often overlooked
  - Visually observe the sample
- Determines if properties are changing over the time of testing
  - Complex Fluids or Dispersions
    - Preshear or effects of loading
    - Drying or volatilization (use solvent trap)
    - Thixotropic or Rheopectic
  - Polymers
    - Degradation (inert purge)
    - Crosslinking

Time Sweep on PEEK Melt - Thermal Stability

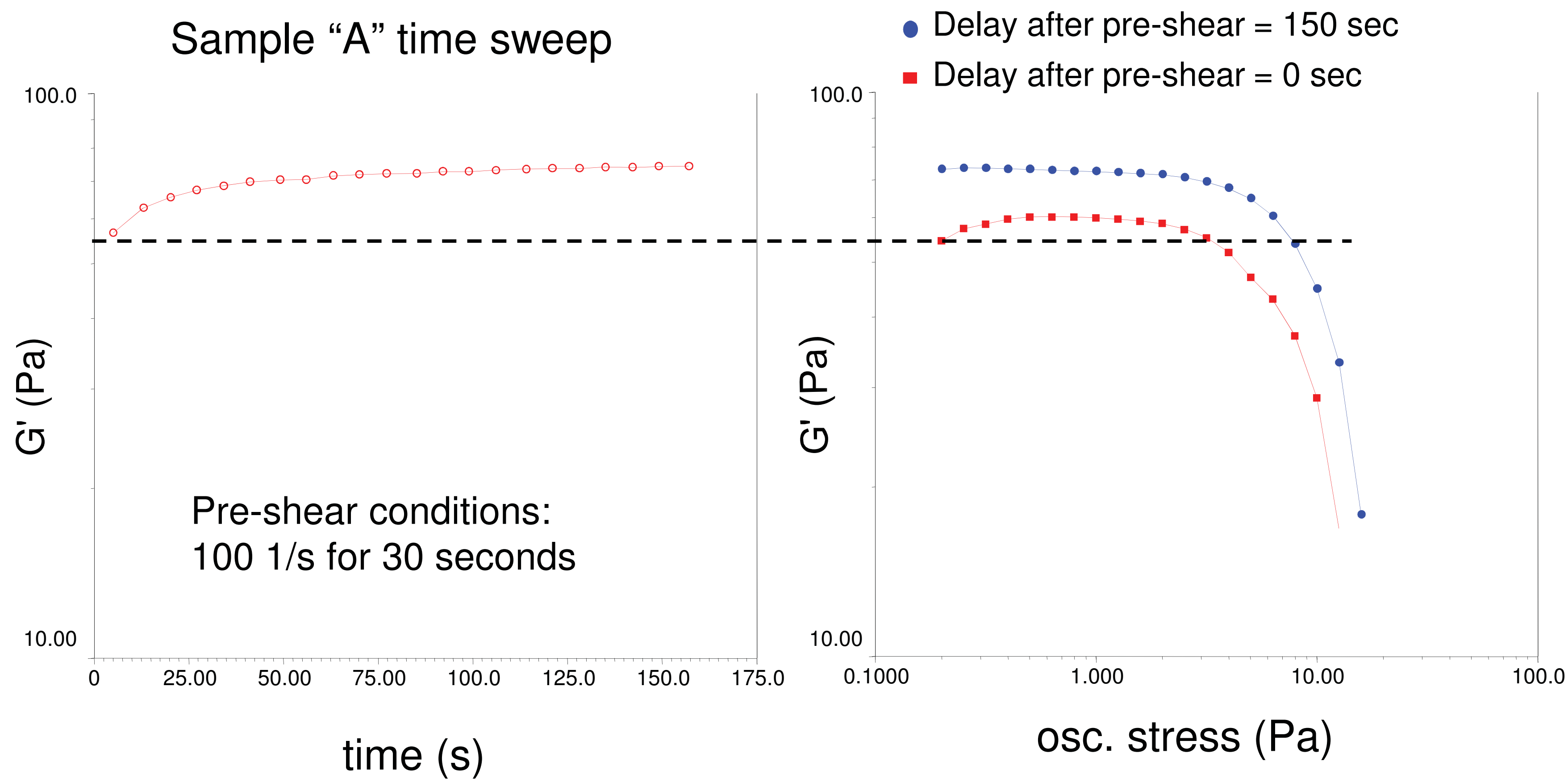
2000G time sweep at 400°C



Time Sweep on Latex



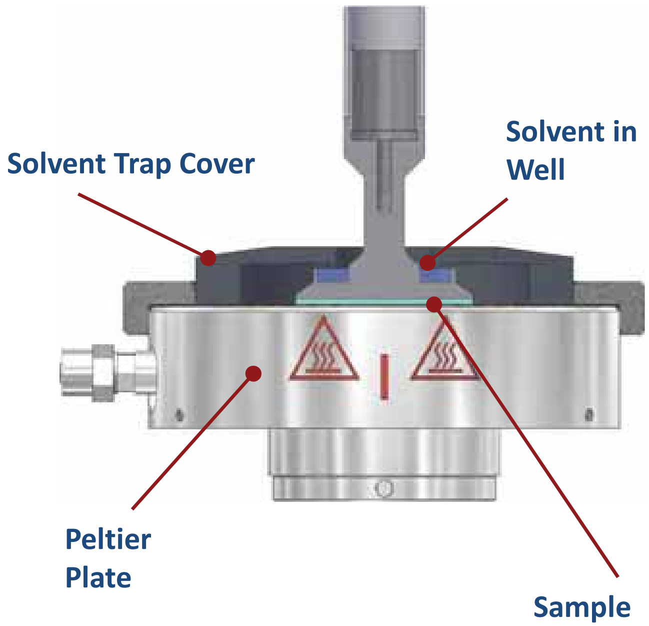
Importance of Waiting for Structure Rebuild

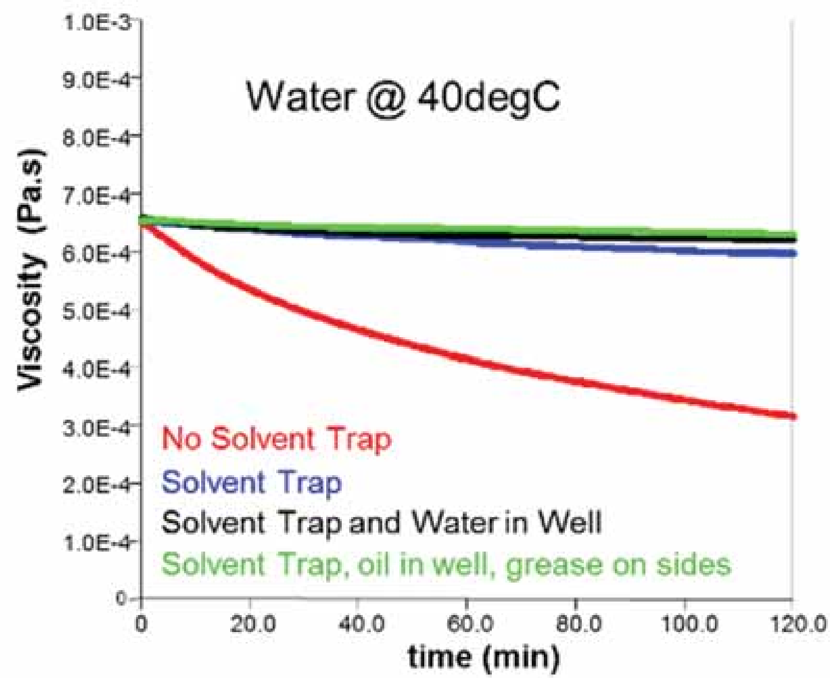


- End of LVR is indicative of "Yield" or "Strength of Structure"
- Useful for Stability predictions (stability as defined by yield)

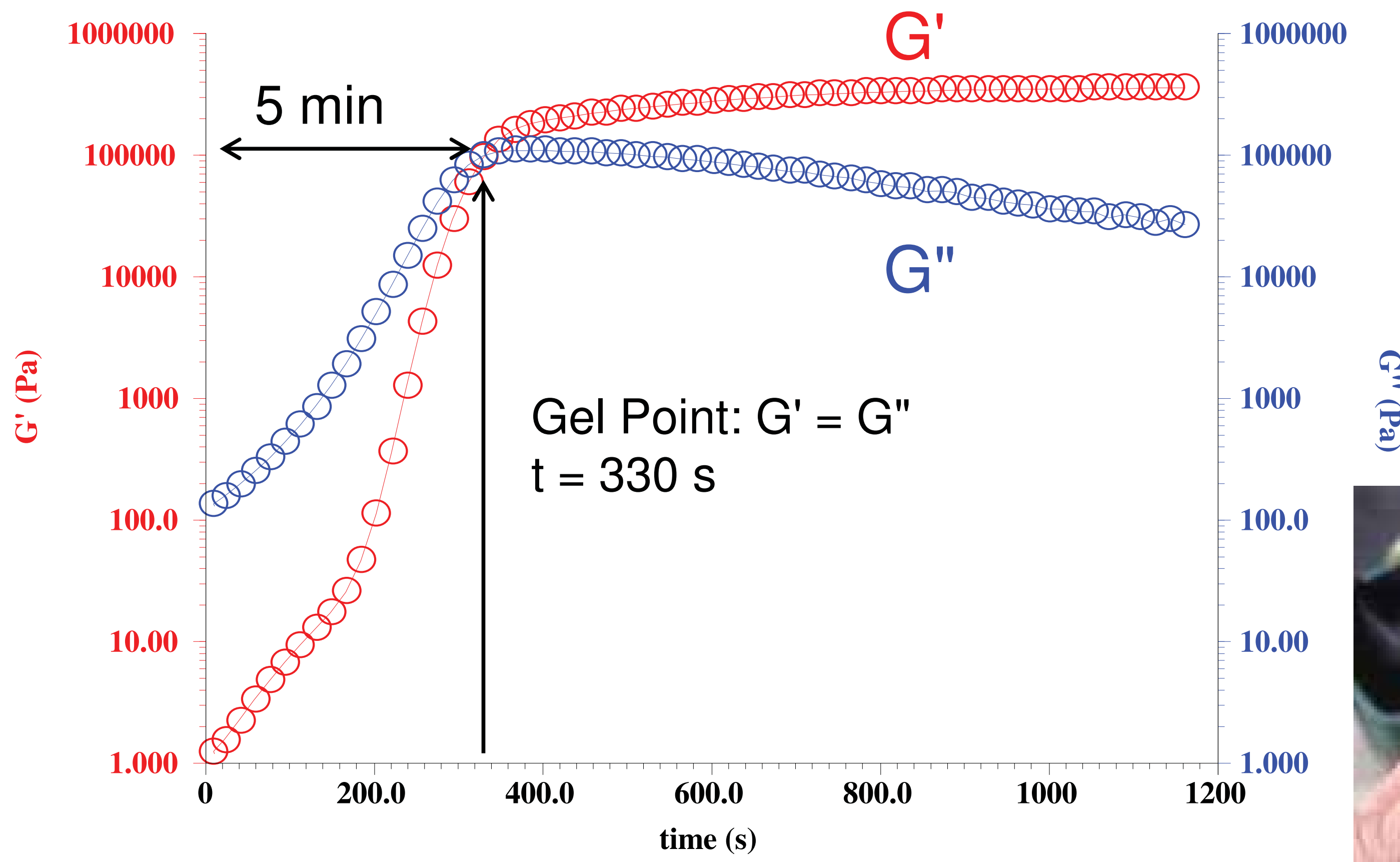
Solvent Trap System for Effective Evaporation Control

Solvent trap cover picks up heat from Peltier Plate to insure uniform temperature





Cure of a "5 Minute" Epoxy



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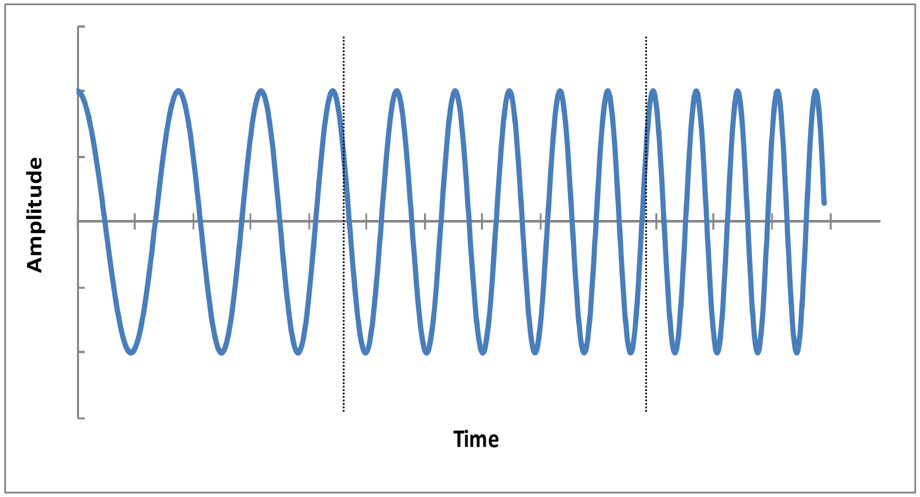
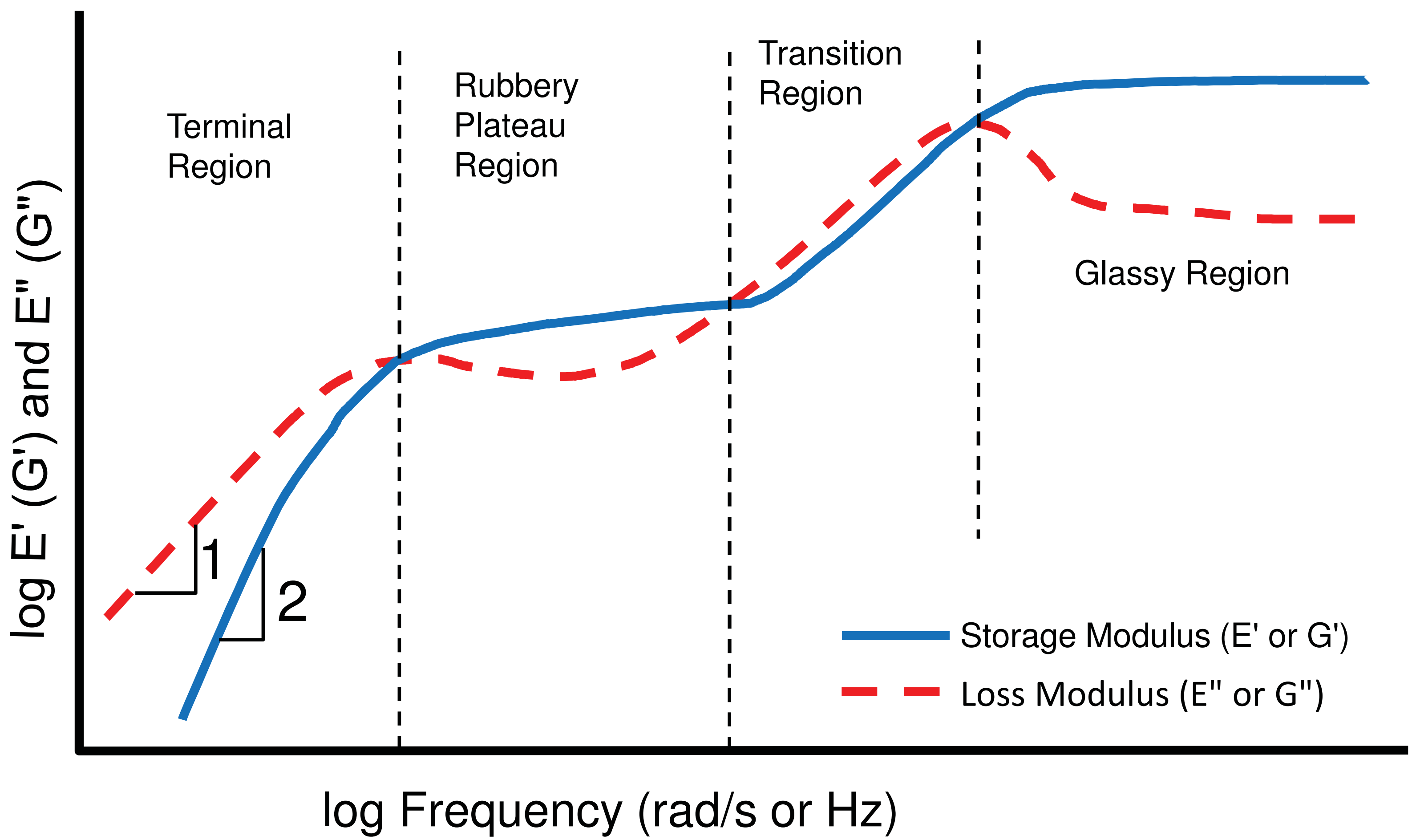
Frequency Sweep



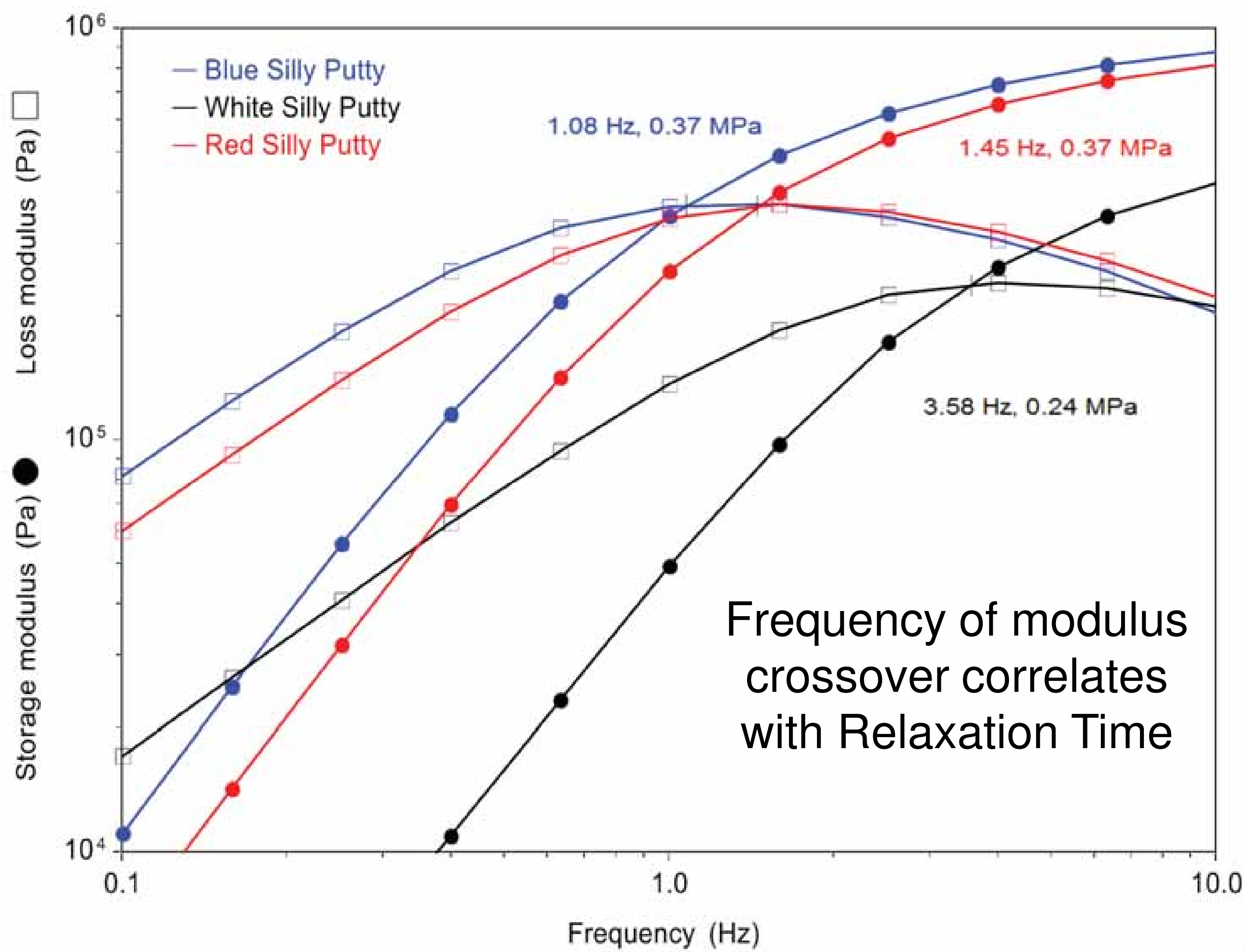
- The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude (strain or stress) and temperature.

- Strain should be in LVR
- Sample should be stable
- Remember – Frequency is 1/time so low frequencies will take a long time to collect data – i.e. 0.001Hz is 1000 sec (over 16 min)

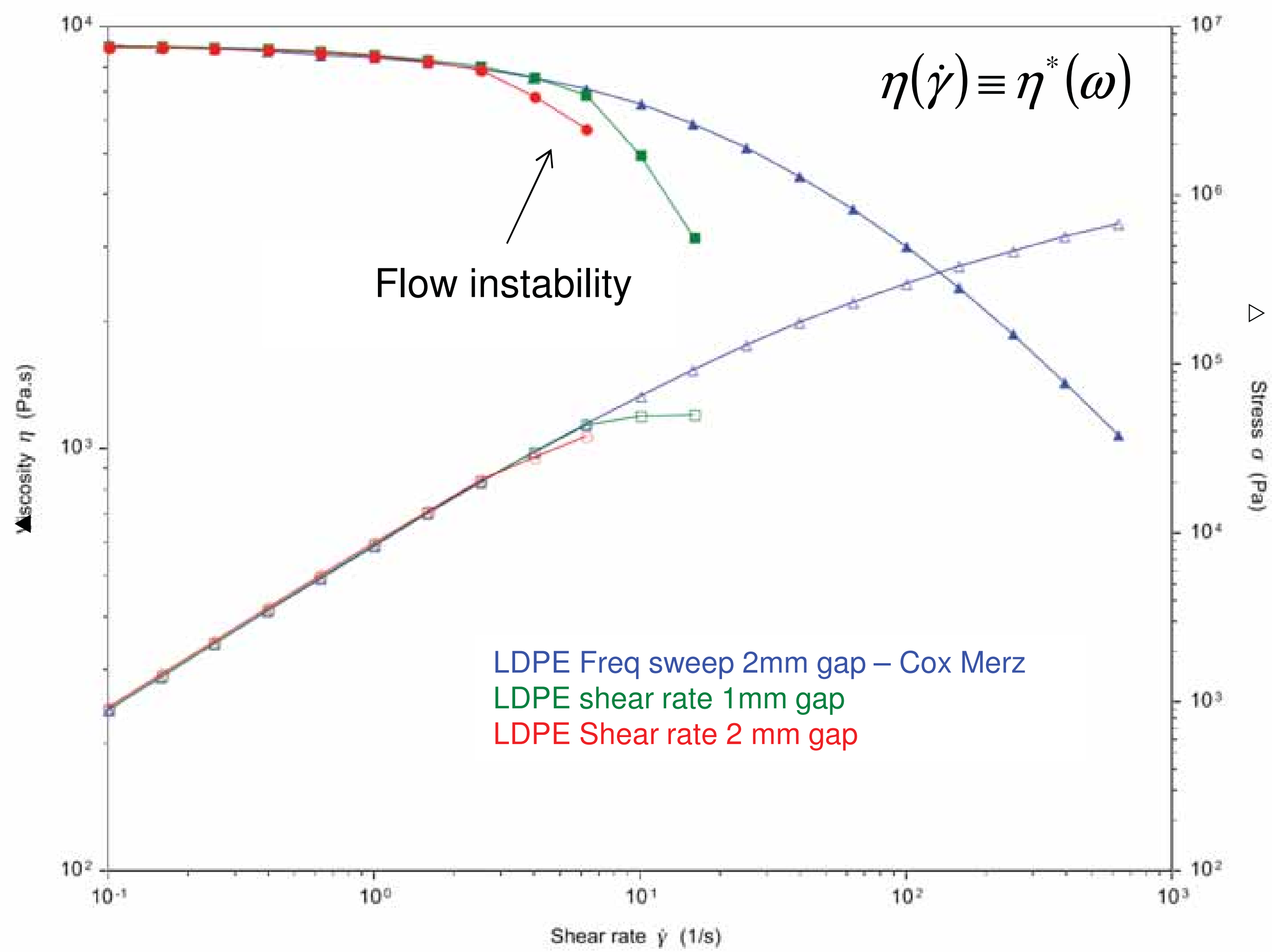
Frequency Sweep: Material Response



Frequency Sweep- Time Dependent Viscoelastic Properties



Cox-Merz Example - LDPE at 190°C



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Importance of Frequency Sweeps

- High and low rate (short and long time) properties
- Viscosity Information - Zero Shear Viscosity, shear thinning
- Elasticity (reversible deformation) in materials
- MW & MWD differences polymer melts and solutions
- Finding yield in gelled dispersions
- Can extend time or frequency range with TTS

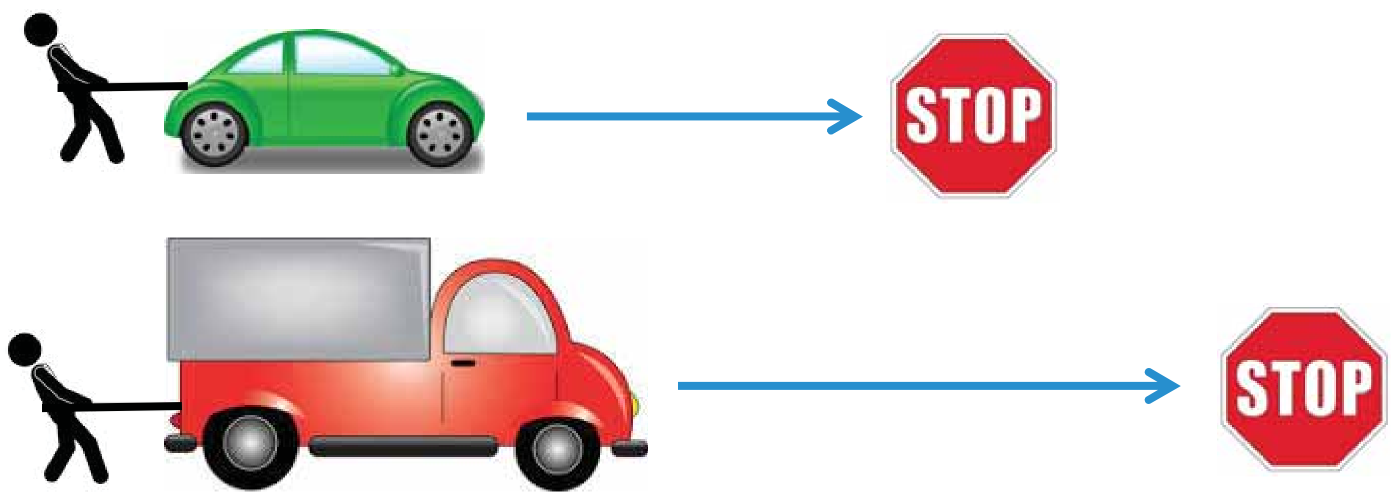
$$\eta_0 \approx M_w^{3.4} \text{ and } J_e = \frac{G'}{(G'')^2} \approx \left(\frac{M_w}{M_z}\right)^{3.4}$$

Frequency in DHR Rheometer

- DHR has a combined motor and transducer design.
  - In an DHR rheometer, the applied motor torque and the measured amplitude are coupled.
  - The moment of inertia required to move the motor and geometry (system inertia) is coupled with the angular displacement measurements.
  - This means that ***BOTH*** the system inertia and the sample contributes to the measured signal.

Inertial Effects

- What is Inertia?
  - <u>Definition</u>: That property of matter which manifests itself as a resistance to any change in momentum of a body
  - Instrument has inertia
  - Sample has inertia



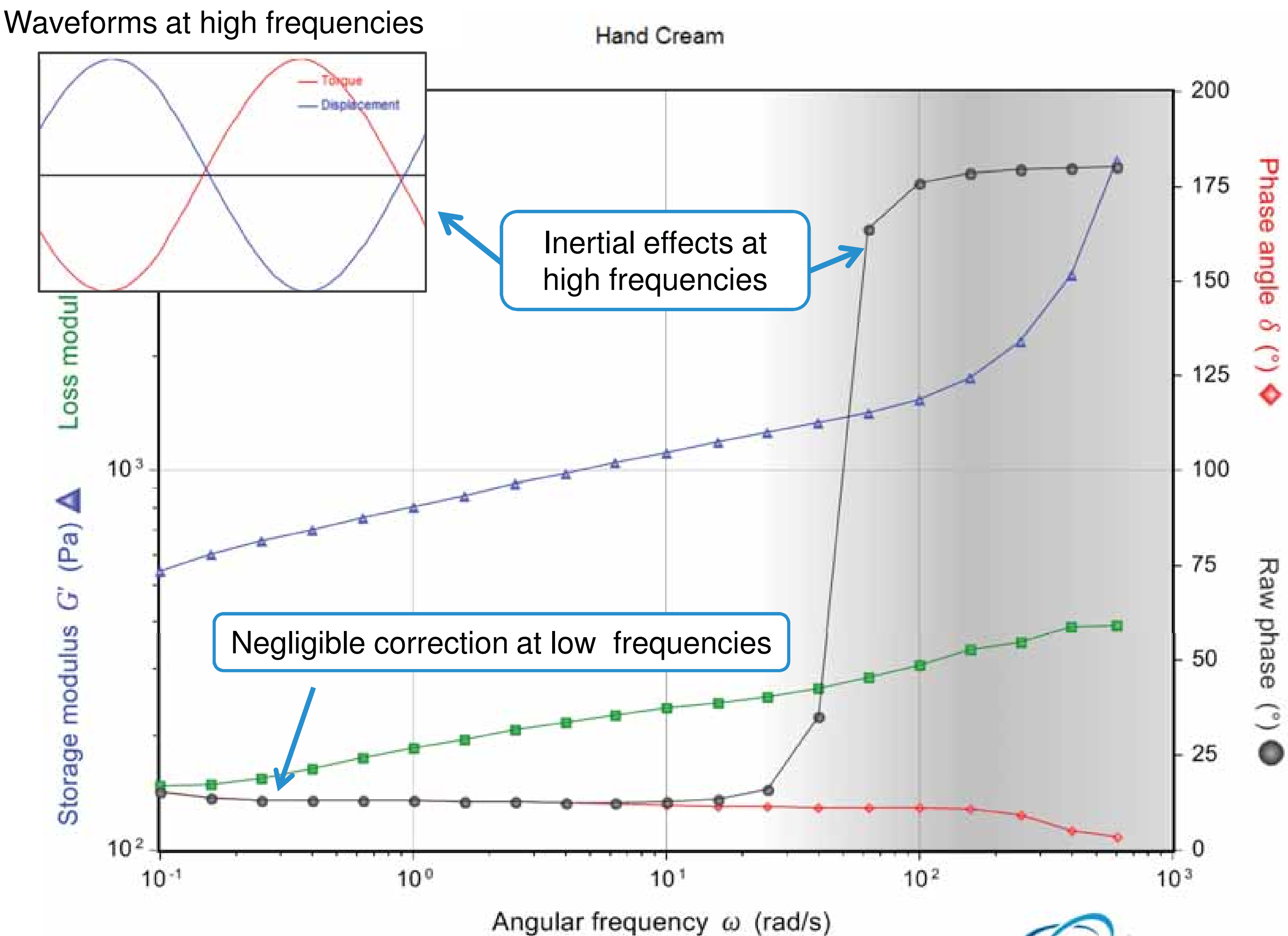
Inertial Effects in Oscillation for DHR

- Inertia consideration
  - Viscosity limitations with frequency
  - Minimize inertia by using low mass geometries
  - Monitor inertia using Raw Phase in degree
  - When Raw Phase is greater than:
    - **150° degrees for AR series**
    - **175° degrees for DHR series**
    - This indicates that the system inertia is dominating the measurement signal. Data may not be valid

Raw Phase × Inertia Correction = delta

DHR Correction for Inertia

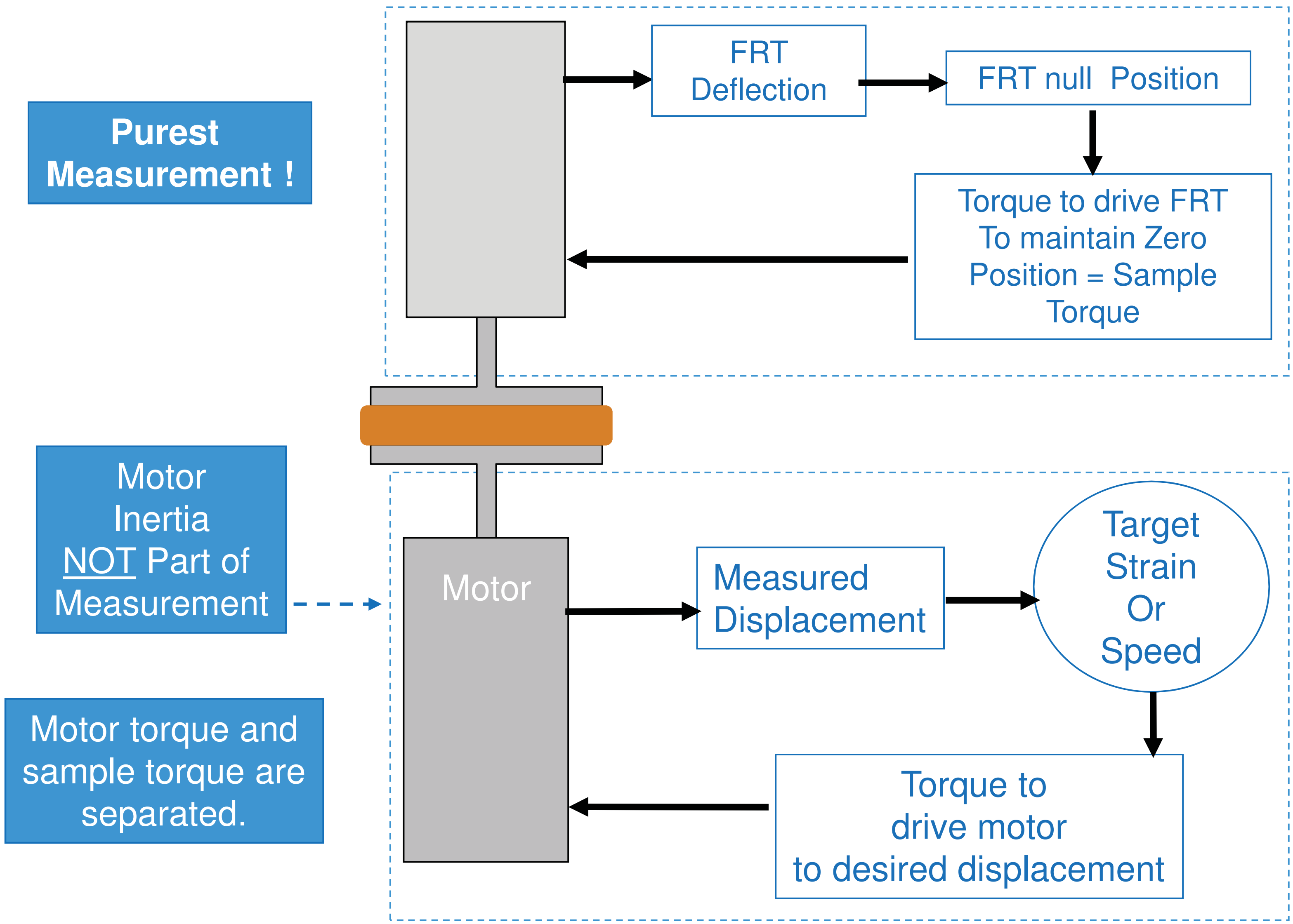
Access to raw phase angle only available with TA Instruments Rheometers!



Frequency Sweeps in ARES-G2

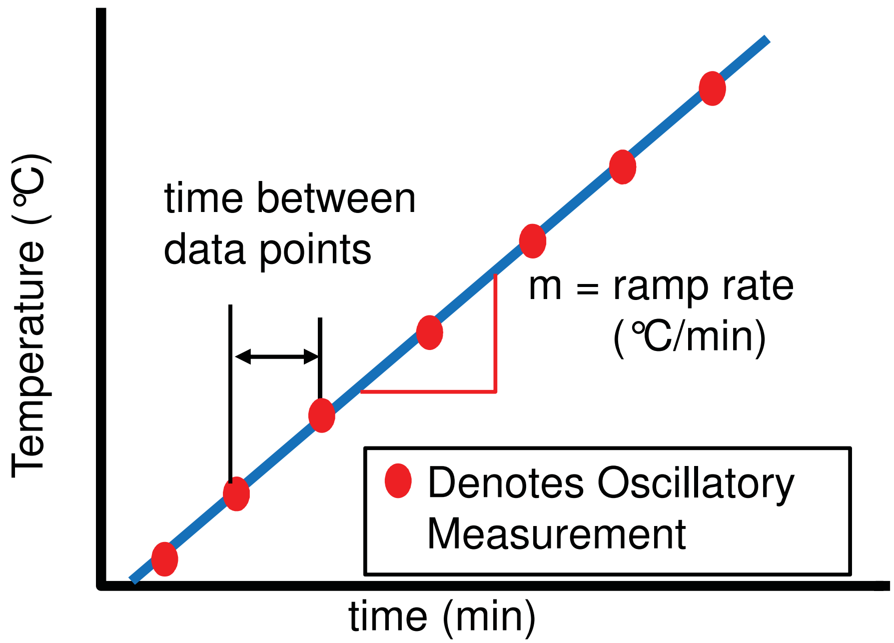
- ARES-G2 has a separate motor and transducer design.
  - In an ARES-G2, the motor applies the deformation independent of the torque measurement on the transducer.
  - The moment of inertia required to move the motor is decoupled from the torque measurements.
  - This means the motor inertia does not contribute to the test results.
- Benefits of ARES-G2:
  - System inertia free
  - Capable of running low viscosity samples up to high frequency

ARES-G2 Closed-Loop Control



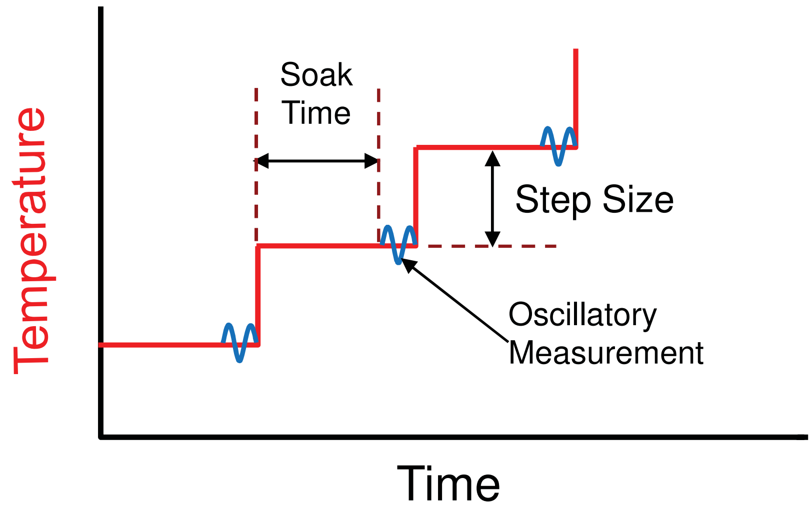
Dynamic Temperature Ramp

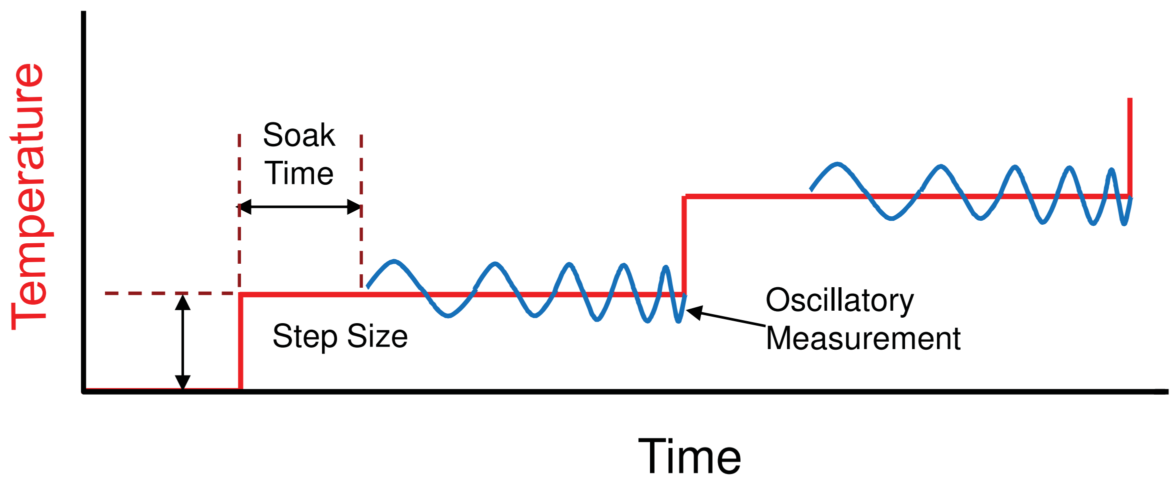
- A linear heating rate is applied. The material response is monitored at a constant frequency and constant amplitude of deformation. Data is taken at user defined time intervals.



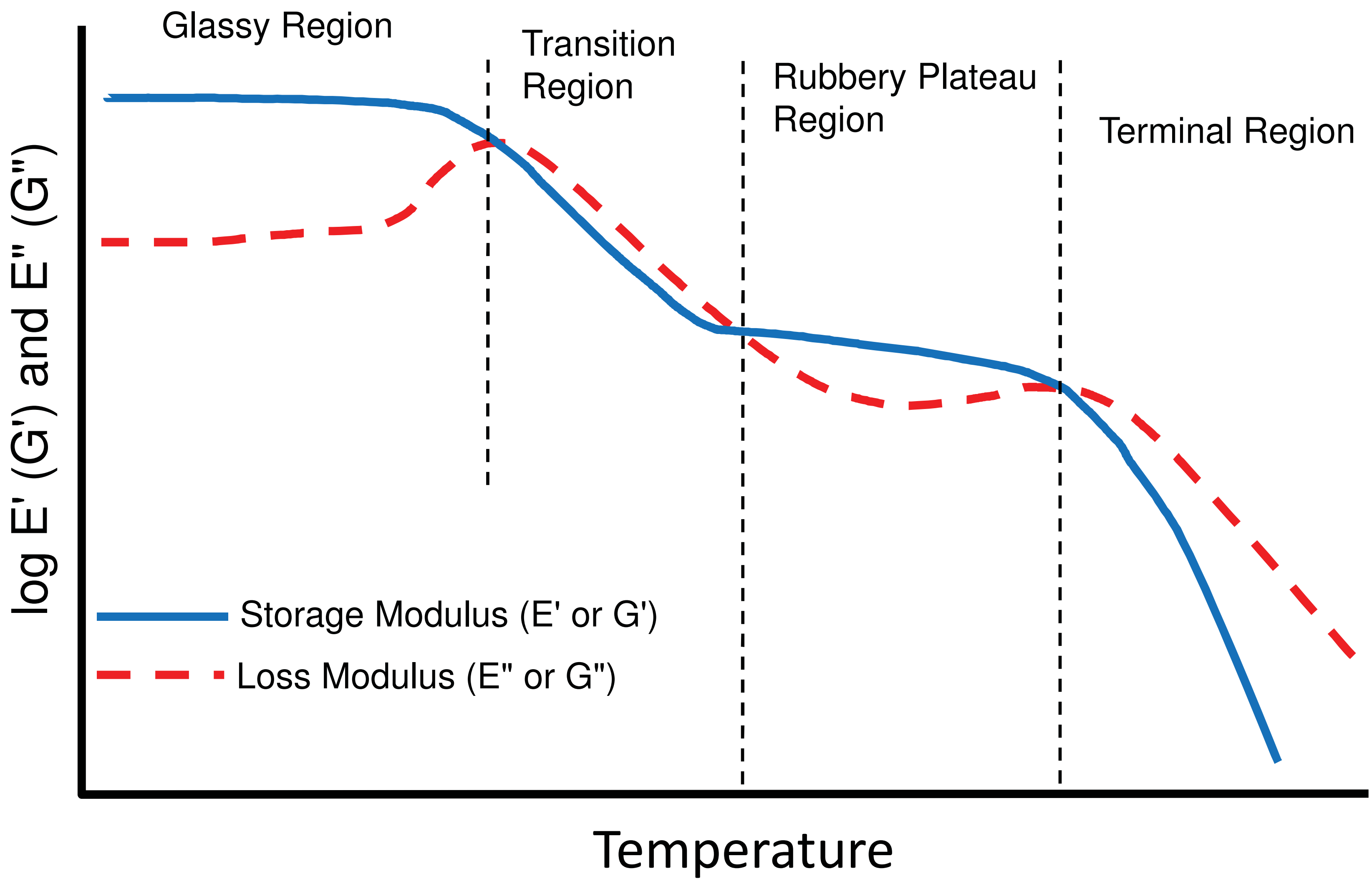
Temperature Sweep (or Step) - Single /Multi-Frequency

- A step and hold temperature profile is applied. The material response is monitored at one, or over a range of frequencies, at constant amplitude of deformation.
  - No thermal lag





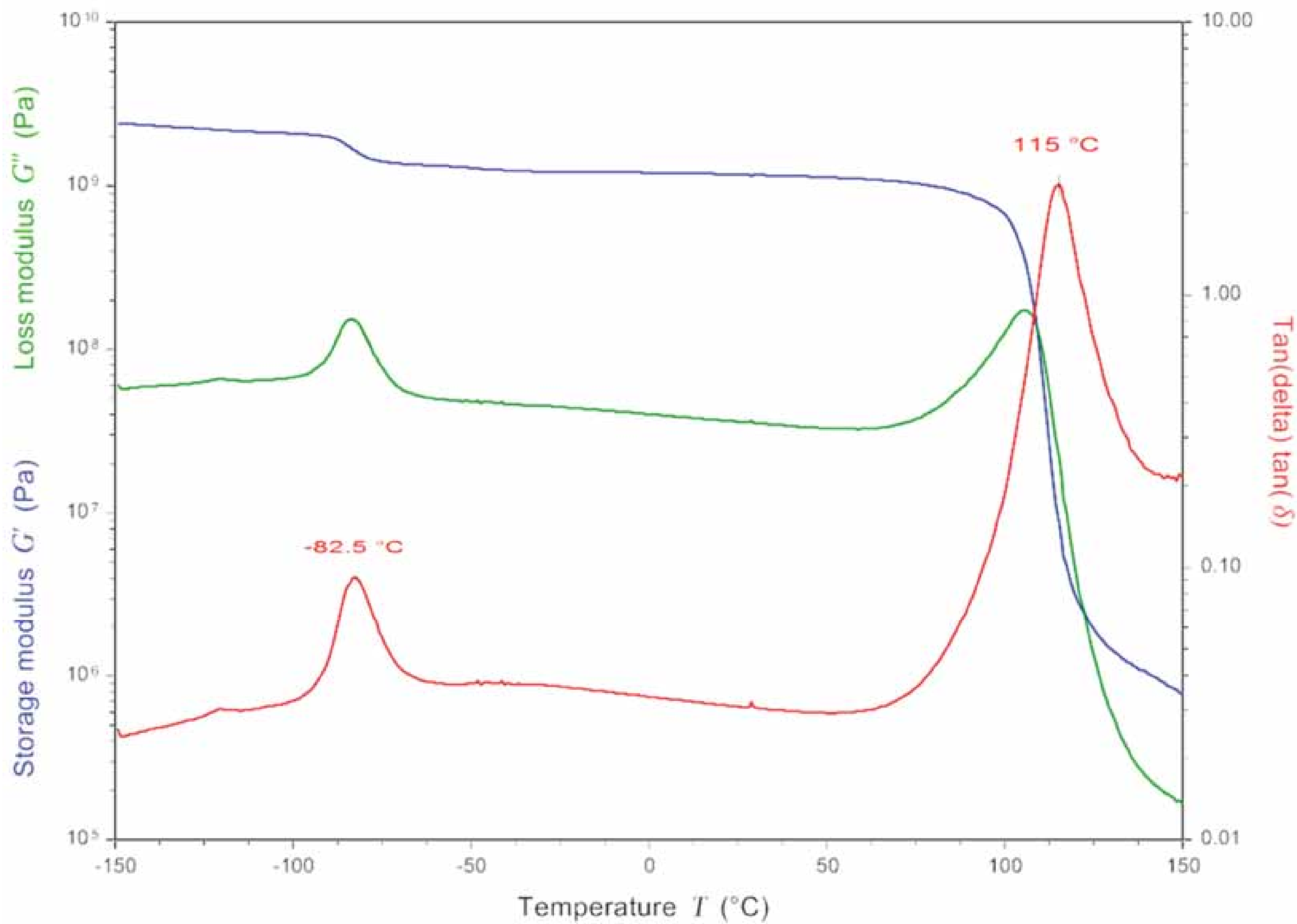
Dynamic Temperature Ramp or Sweep: Material Response



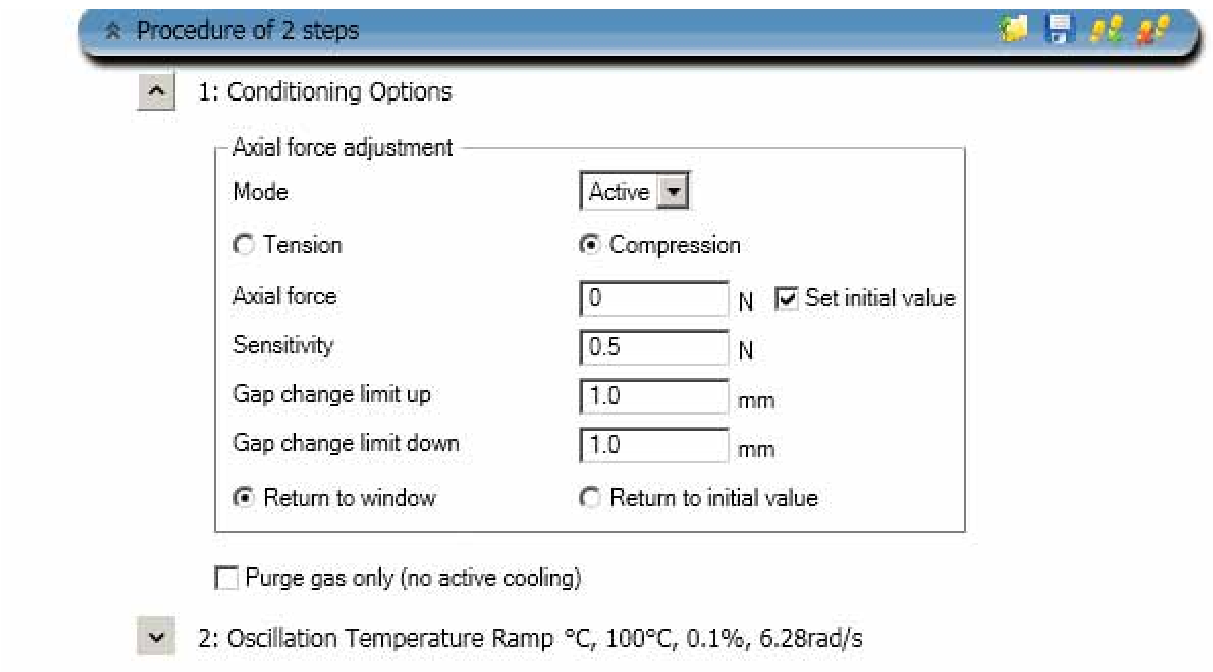
Why look at temperature dependence?

- Solid in torsion rectangular
  - Look at T_g, secondary transitions and study structure-property relationships of finished product.
- Themosetting polymers
  - Follow curing reactions
- Polymer melts and other liquids
  - Measure temperature dependence of viscoelastic properties

Acrylonitrile Butadiene Styrene (ABS)

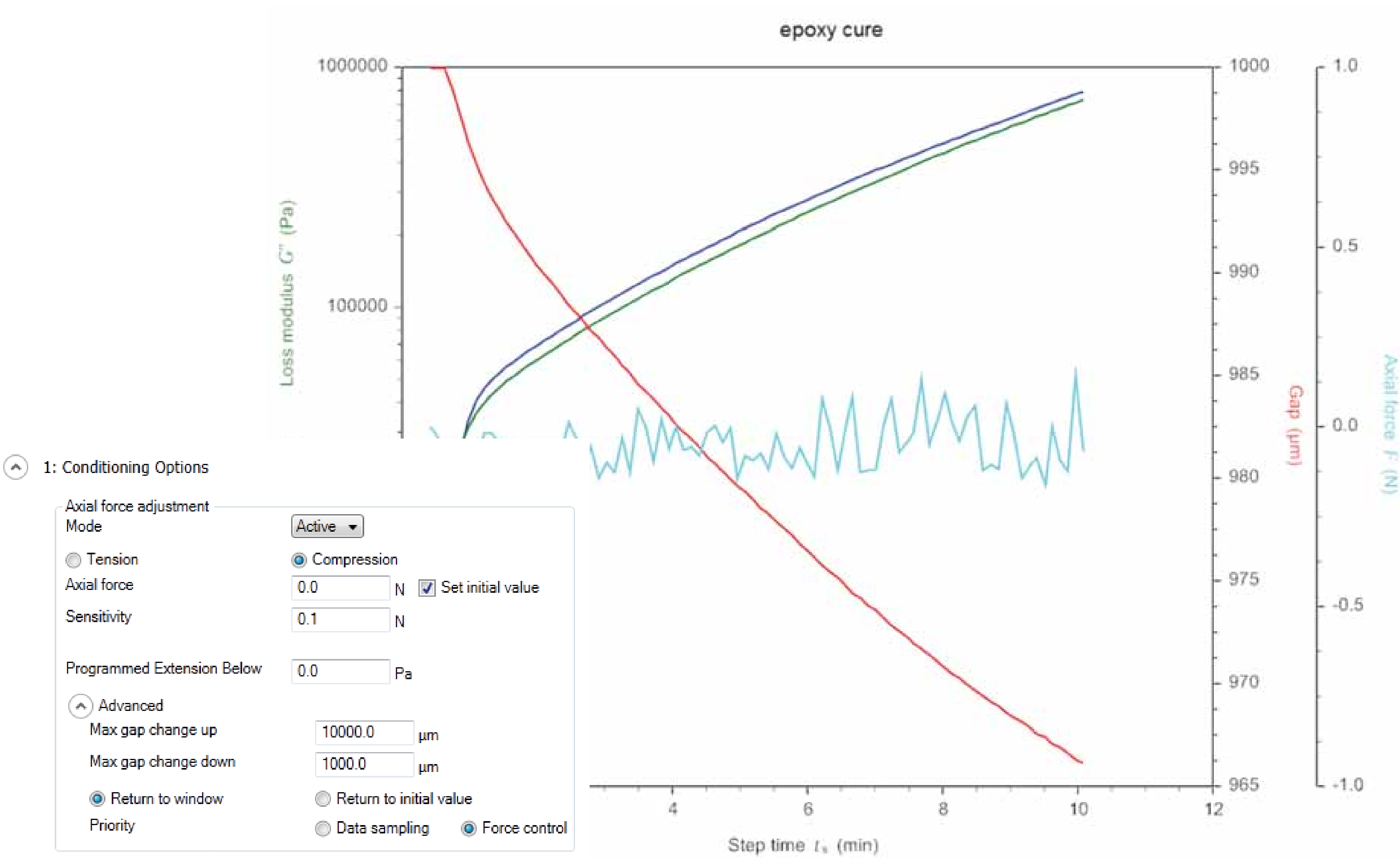


DHR: Axial Force Control

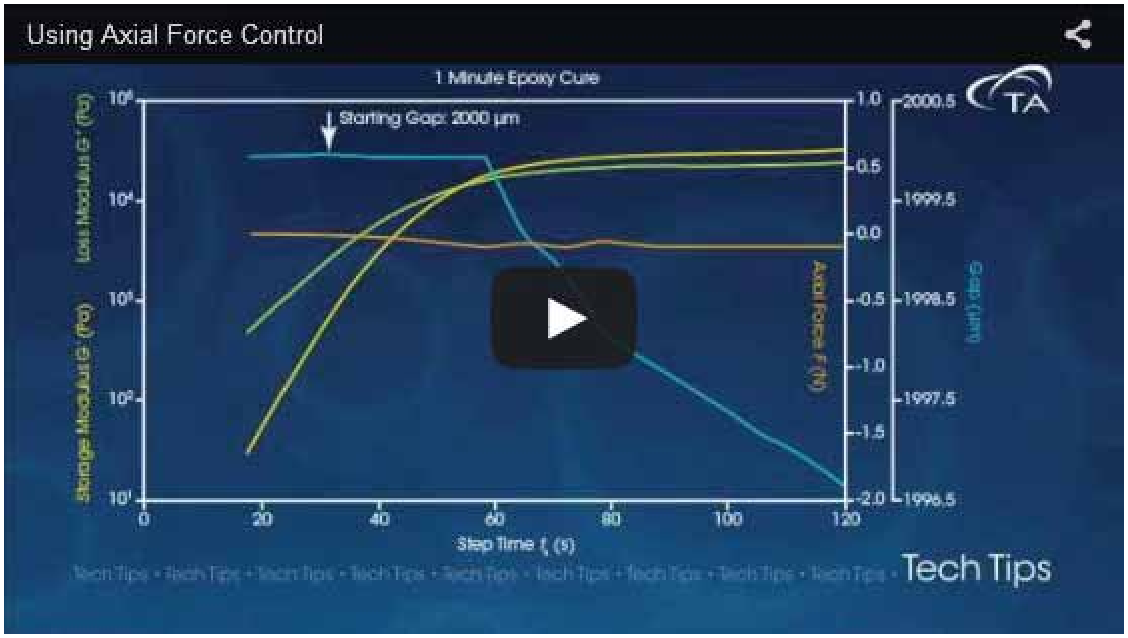


- It is important to setup normal force control during any temperature change testing or curing testing
- Some general suggestions for normal force control
  - For torsion testing, set normal force in tension: 1-2N ± 0.5-1.0N
  - For curing or any parallel plate testing, set normal force in compression: 0 ± 0.5N

Using Axial Force Control in a Thermosetting Material



TA Tech Tip – Axial Force Control

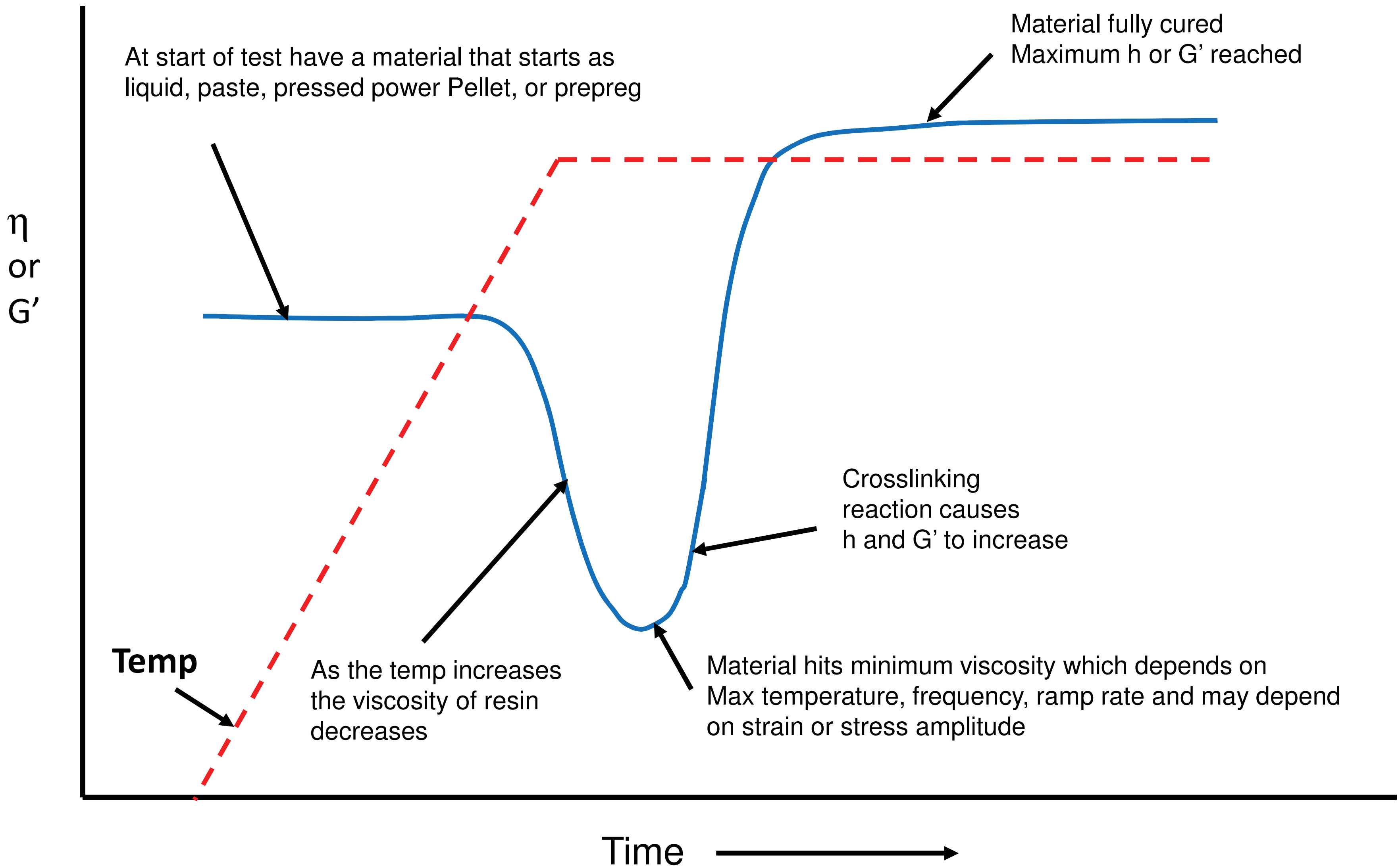


- Videos available at www.tainstruments.com under the Videos tab or on the TA tech tip channel of YouTube™ (https://www.youtube.com/user/TATechTips)

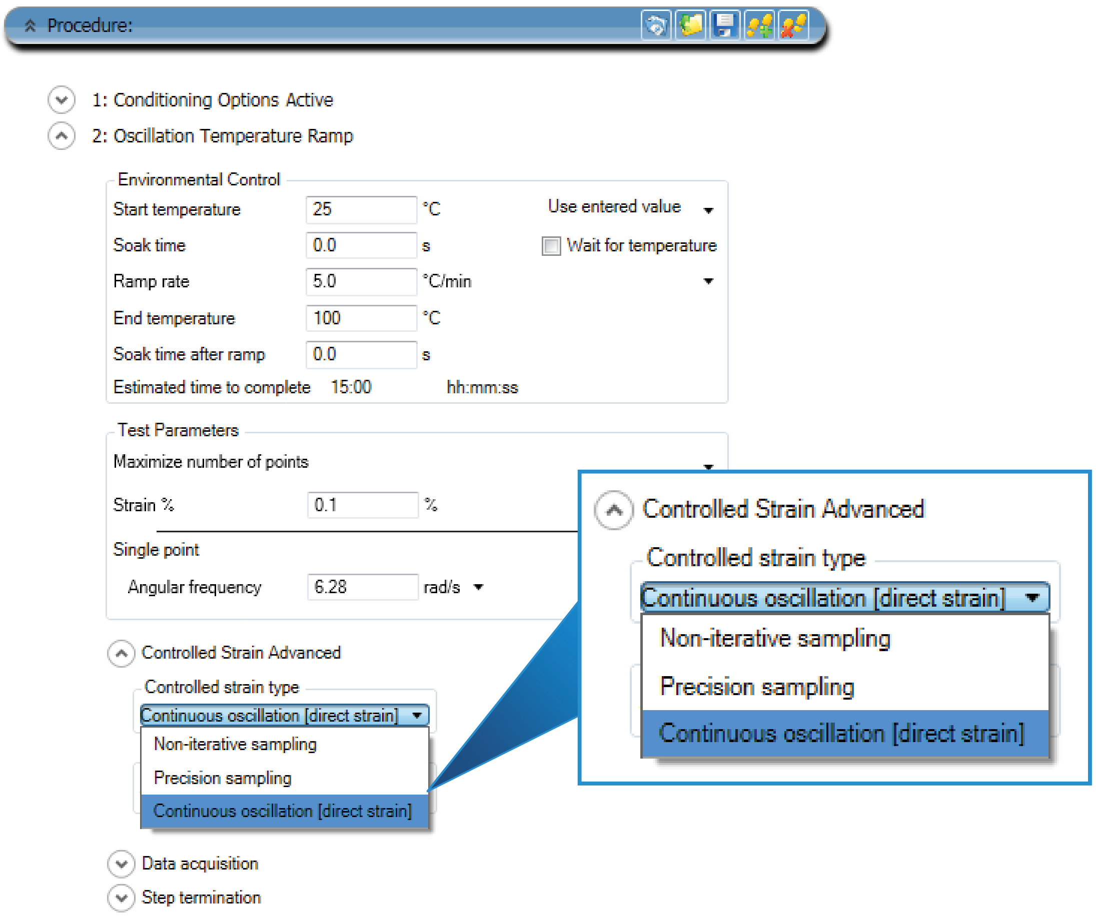
Cure or Thermoset Materials

- Cures are perhaps the most challenging experiments to conduct on rheometers as they challenge all instrument specifications both high and low.
- The change in modulus as a sample cures can be as large as 7-8 decades and change can occur very rapidly.
- **AR, DHR, and ARES** instruments have ways of trying to cope with such large swings in modulus
  - AR: **Non-iterative sampling** (w/ Axial force control)
  - DHR: **Non-iterative sampling** (w/ Axial force control) and **Auto-strain** (w/ Axial force active) in TRIOS v3.2 or higher
  - ARES: **Auto-strain** (w/ Axial force or auto-tension active)

Thermosetting Polymers



DHR and AR: Data Collection Options

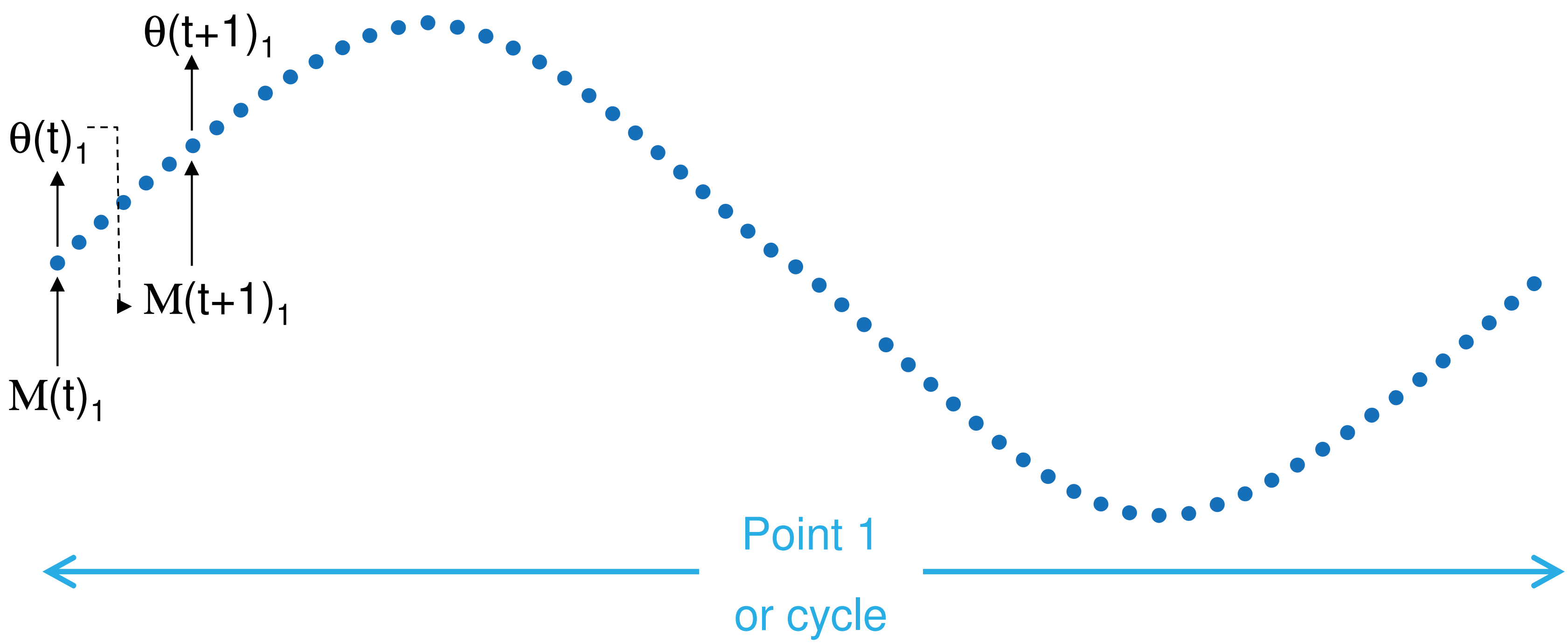


- Non-Iterative Sampling – motor torque is adjusted based on previous stress value and predicts new value required to obtain the target strain (good for rapid measurements)
- Precision Sampling – motor torque is adjusted at the end of an oscillation cycle in order to reach commanded strain
- Continuous Oscillation (direct strain)* – motor torque is adjusted during the oscillation cycle to apply the commanded strain

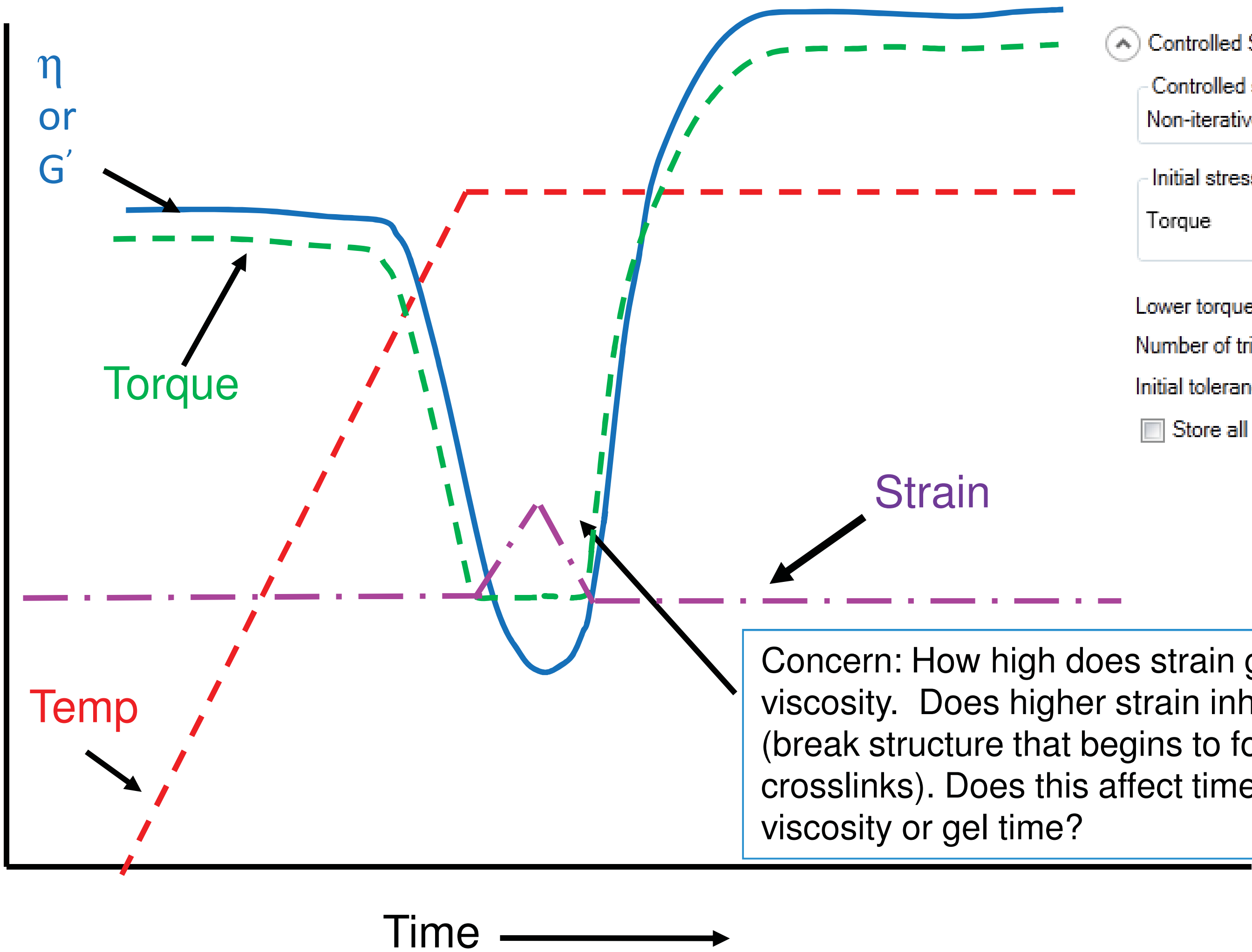
*Continuous oscillation only available with DHR-2 and DHR-3

Continuous Oscillation on Single Head Rheometer

Continuous oscillation (or direct strain control): incremental approach controls the strain and hits the target during a single cycle
Non-iterative: uses the settings entered for the first data point and then uses previous cycle
Precision: iterates using the initial settings entered for each data point



DHR and AR: Non-iterative Sampling



Controlled Strain Advanced

Controlled strain type	
Non-iterative sampling	

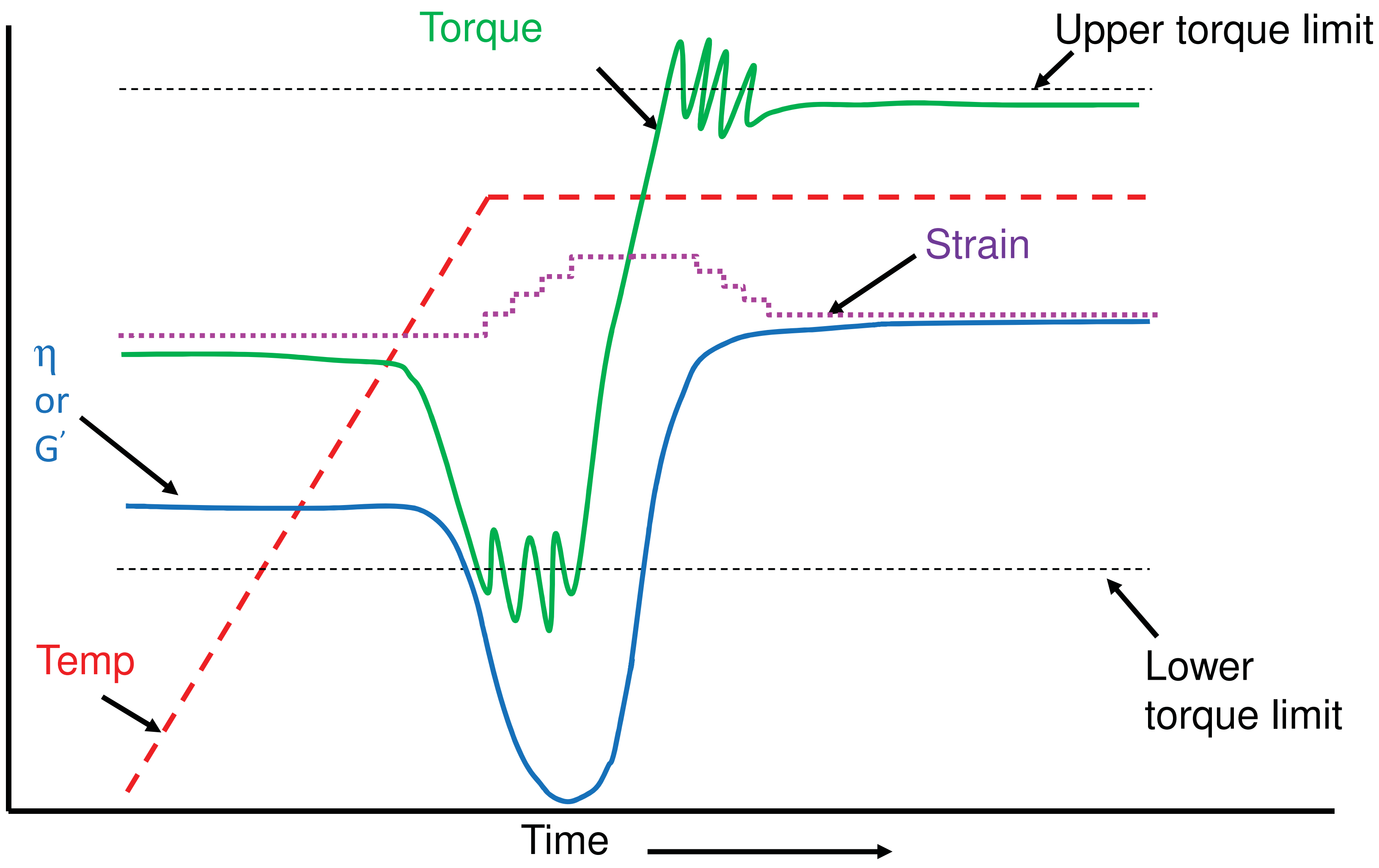
Initial stress		
Torque	10.0	µN.m

Lower torque limit	0.1	µN.m
Number of tries	4	
Initial tolerance	0.5	%

☐ Store all tries as data points

Concern: How high does strain go at minimum viscosity. Does higher strain inhibit the cure (break structure that begins to form as material crosslinks). Does this affect time to minimum viscosity or gel time?

ARES, ARES-G2 and DHR: Auto-Strain



Axial Force Control and Auto-strain

ARES-G2

1: Conditioning Options

Axial force adjustment

Mode	Active		
Tension	Compression (selected)		
Axial force	2.0	N	Set initial value (checked)
Sensitivity	0.1	N	
	Compensate for stiffness changes (unchecked)		

Advanced

Max gap change up	2.0	mm
Max gap change down	0.5	mm
Return to window (selected)	Return to initial value	
Priority	Data sampling (selected)	Force control
Adjustment time out	2.0	s

Auto strain adjustment

Mode	Enabled	
Strain adjust	20.0	%
Minimum strain	0.01	%
Maximum strain	5.0	%
Minimum torque	1.0	µN.m
Maximum torque	500.0	µN.m

DHR

1: Conditioning Options

Axial force adjustment

Mode	Active		
Tension	Compression (selected)		
Axial force	0.0	g	Set initial value (checked)
Sensitivity	20.0	g	

Advanced

Gap change limit up	1000.0	µm
Gap change limit down	1000.0	µm
Return to window (selected)	Return to initial value	

Purge gas only (no active cooling) (unchecked)

Auto strain adjustment

Mode	Enabled	
Strain adjust	20.0	%
Displacement / Strain / % Strain (selected)		
Minimum % strain	0.0	%
Maximum % strain	0.0	%
Torque (selected) / Stress		
Minimum torque	0.0	µN.m
Maximum torque	0.0	µN.m

Using Auto Strain in a Temperature Ramp- Up

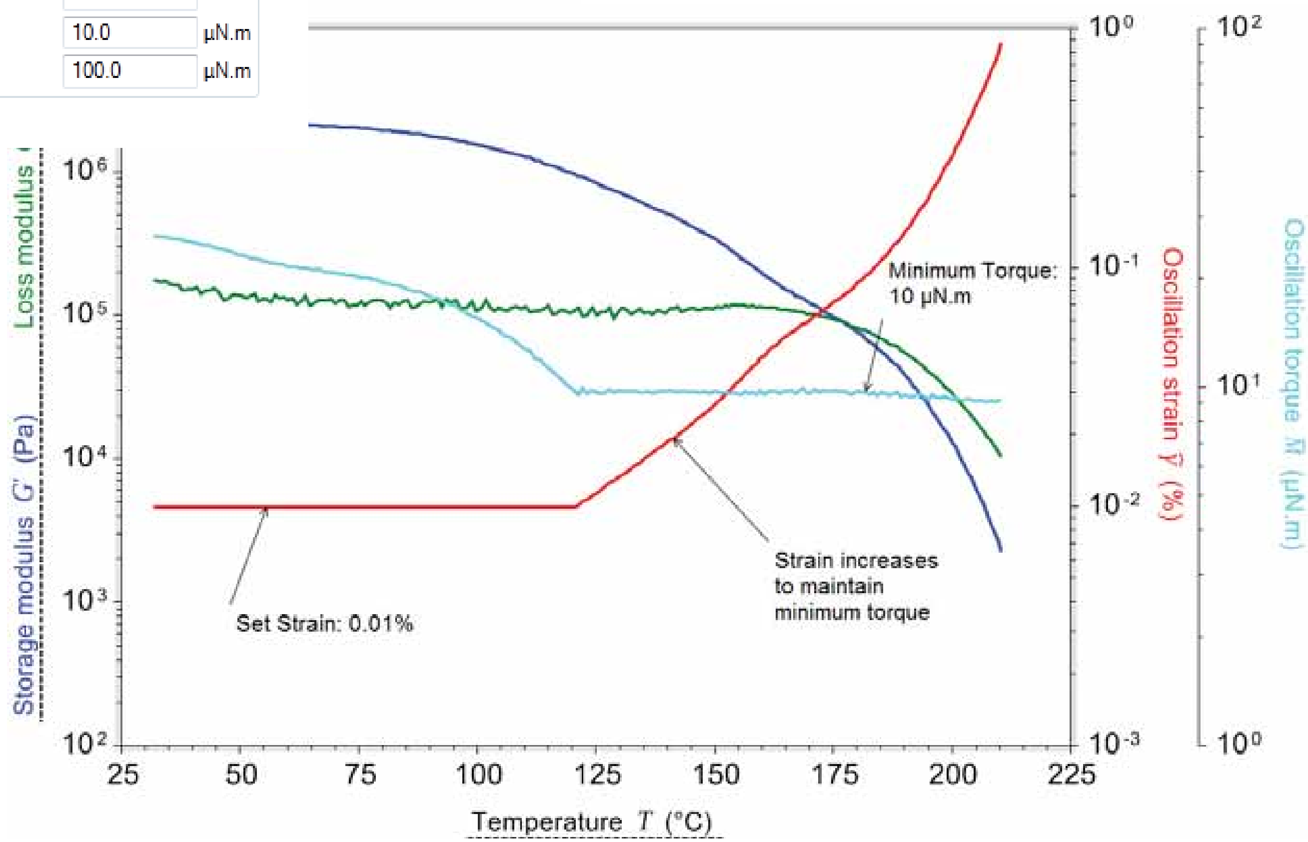
1: Conditioning Options

Auto strain adjustment

Mode	Enabled	
Strain adjust	20.0	%
Minimum strain	1.0e-3	%
Maximum strain	1.0	%
Minimum torque	10.0	µN.m
Maximum torque	100.0	µN.m

Test Parameters

Sampling rate	1.0	pts/s
Strain %	0.01	%
Single point		
Angular frequency	10.0	rad/s

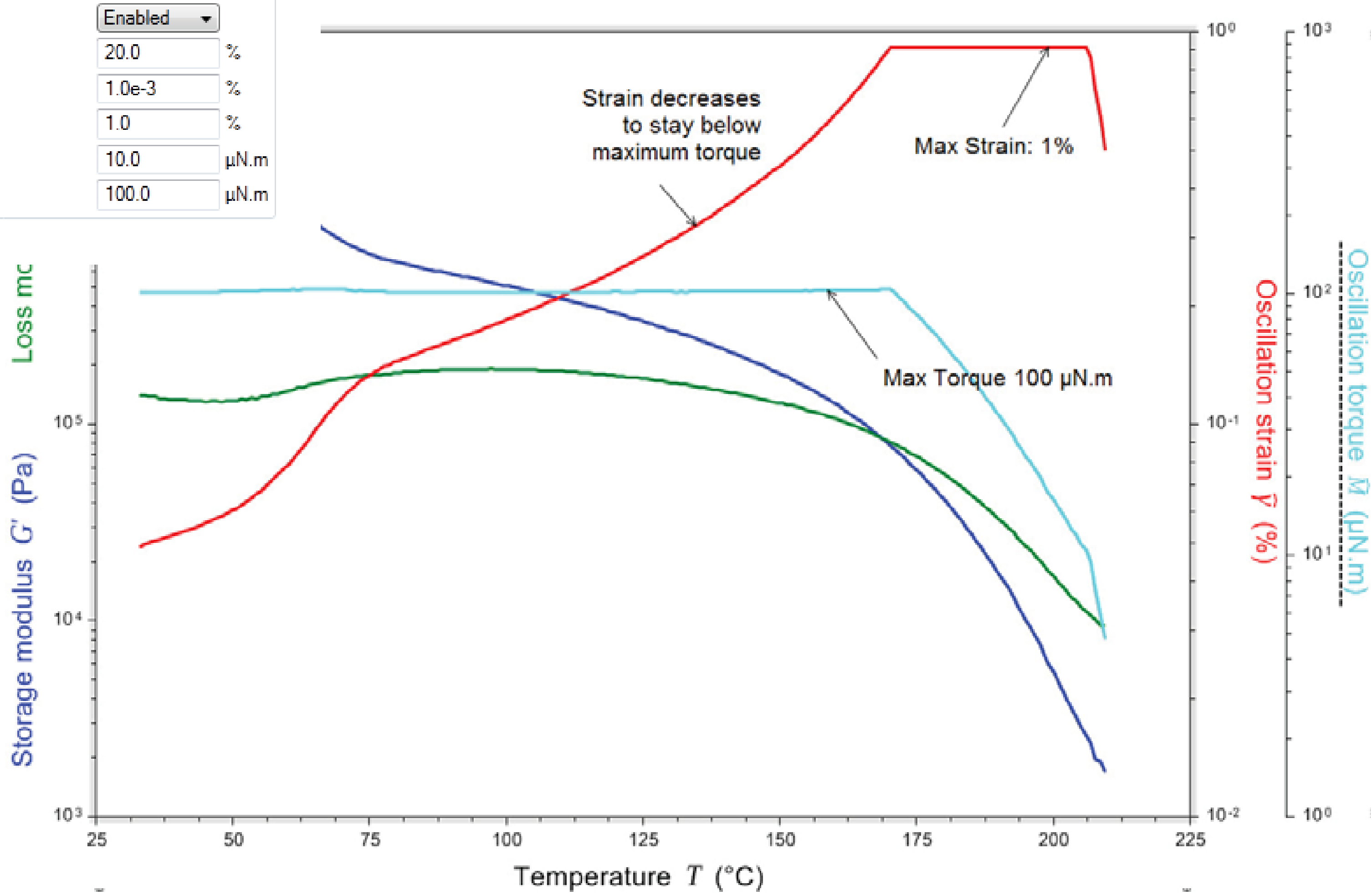


Using Auto Strain in a Temperature Ramp- Down

1: Conditioning Options

Auto strain adjustment

Mode	Enabled	
Strain adjust	20.0	%
Minimum strain	1.0e-3	%
Maximum strain	1.0	%
Minimum torque	10.0	µN.m
Maximum torque	100.0	µN.m



Thermoset Testing Considerations

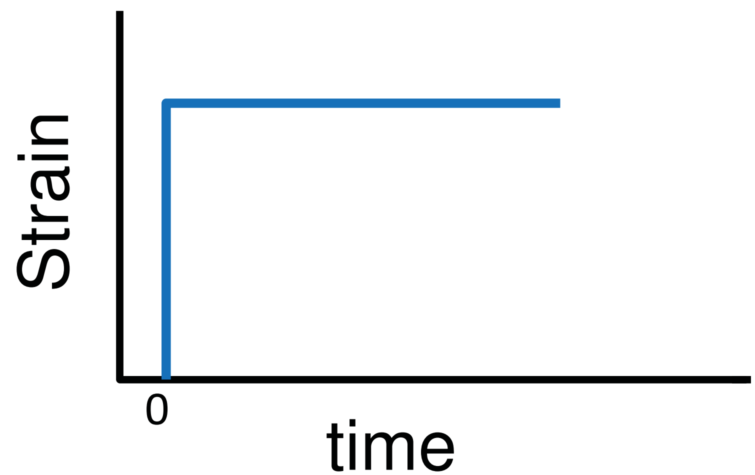
- Strain
  - Depends on sample
  - Verify the LVR **in the cured state (e.g. 0.05%)**
- Normal force control or auto-tension
  - Requires active to adjust for sample shrinkage and/or thermal expansion in parallel plates
- Temperature
  - Isothermal
  - Fast ramp + isotherm: the fastest ramp rate
  - Continuous ramp rate: 3 – 5 °C/min.
- Frequency
  - Typically 1Hz (6.28 rad/s), 10 rad/s or higher

Setting up Rheological Experiments

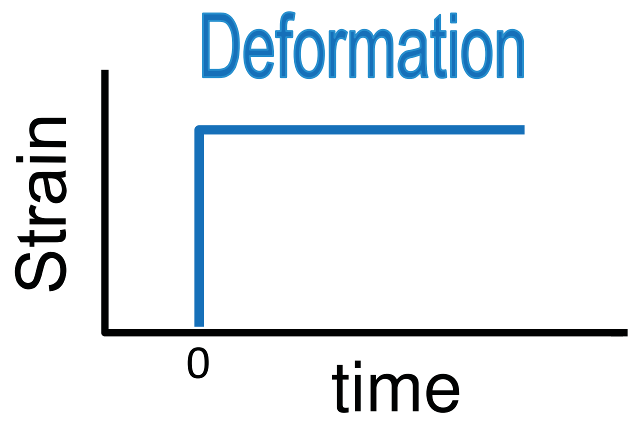
Transient Tests

Stress Relaxation Experiment

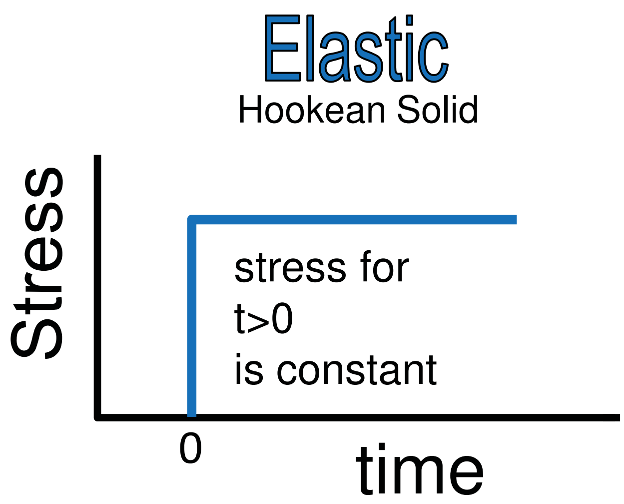
- Strain is applied to sample instantaneously (in principle) and held constant with time.
- Stress is monitored as a function of time $\sigma(t)$.
- DHR and AR
  - Response time dependent on feedback loop

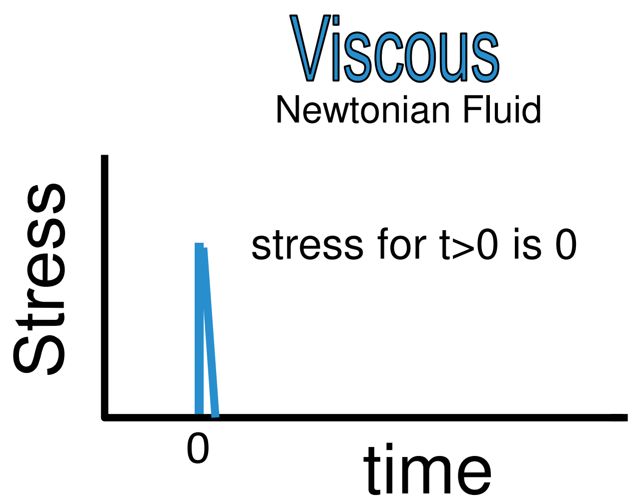


Stress Relaxation Experiment



Response of Classical Extremes

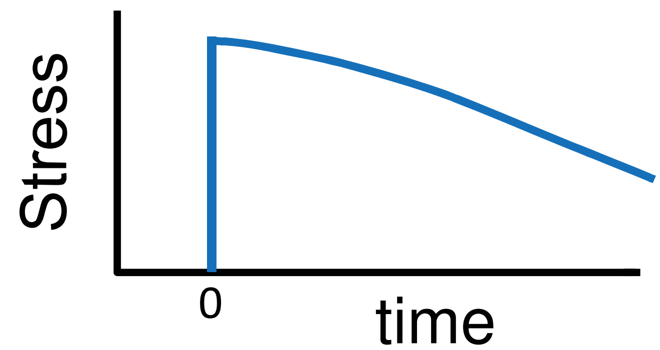




Stress Relaxation Experiment

Response of **ViscoElastic** Material

Stress decreases with time starting at some high value and decreasing to zero.

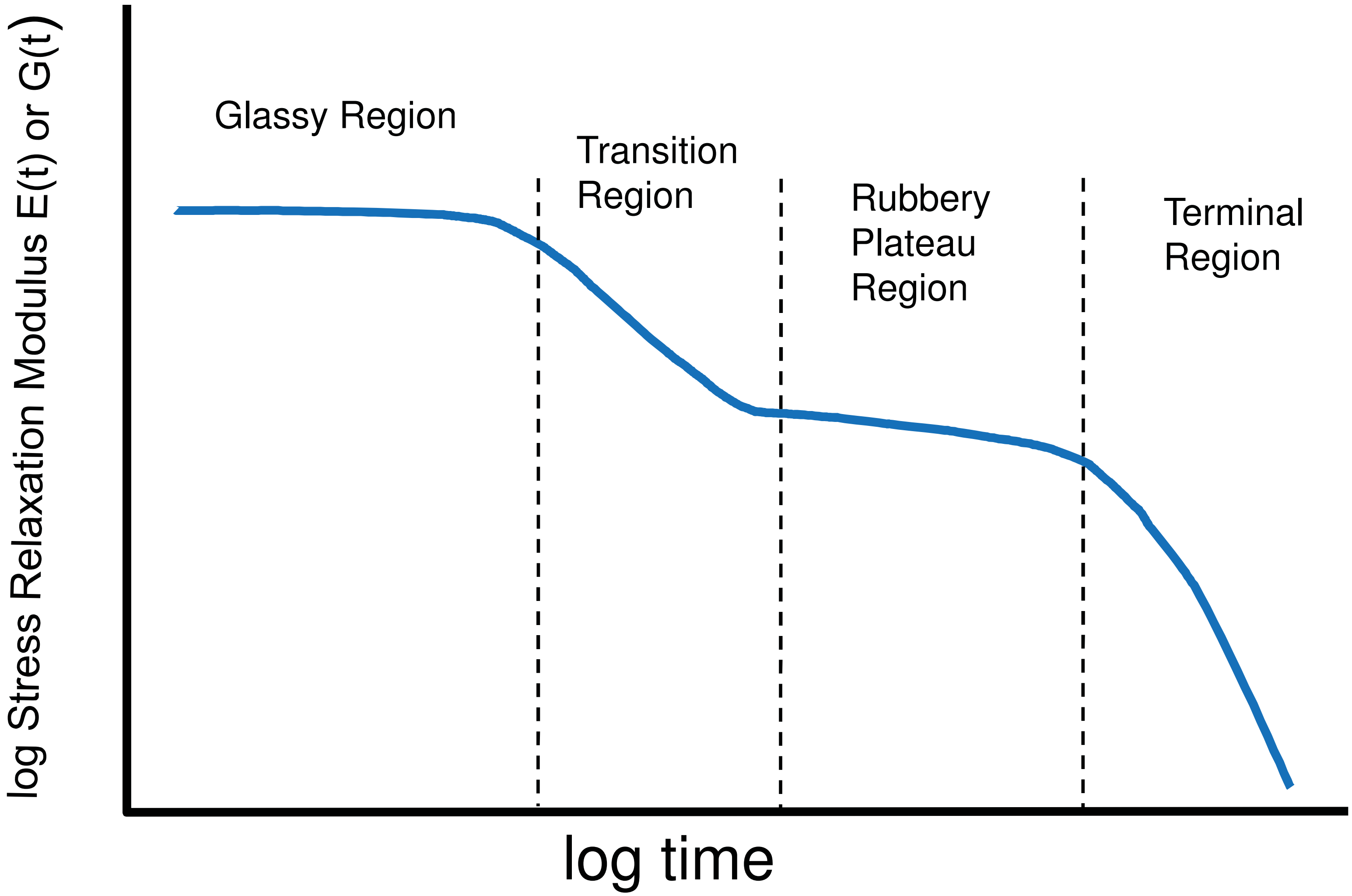


- For small deformations (strains within the linear region) the ratio of stress to strain is a function of time only.

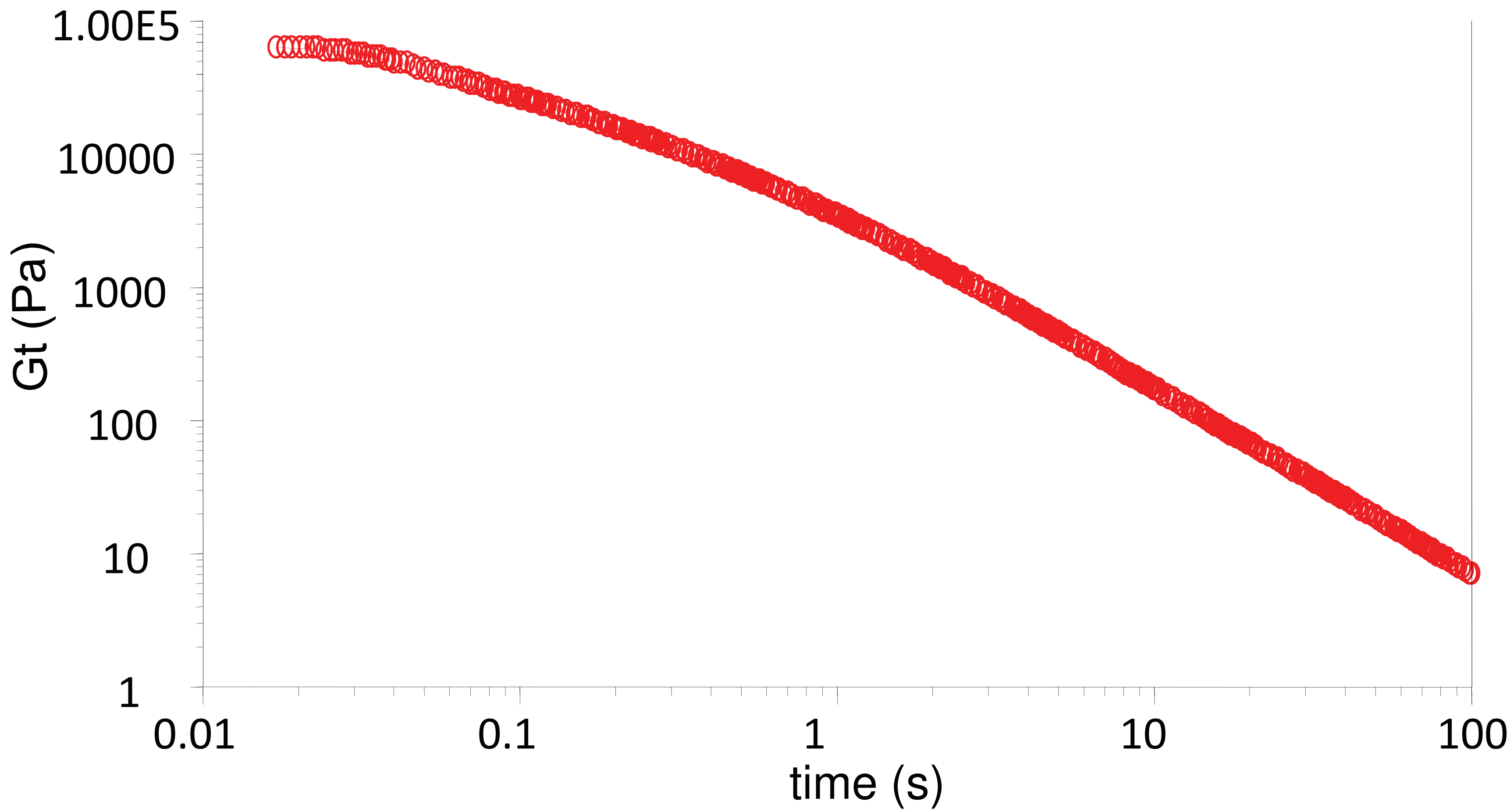
- This function is a material property known as the STRESS RELAXATION MODULUS, G(t)

$$G(t) = \sigma(t)/\gamma$$

Stress Relaxation: Material Response



Stress Relaxation on PDMS



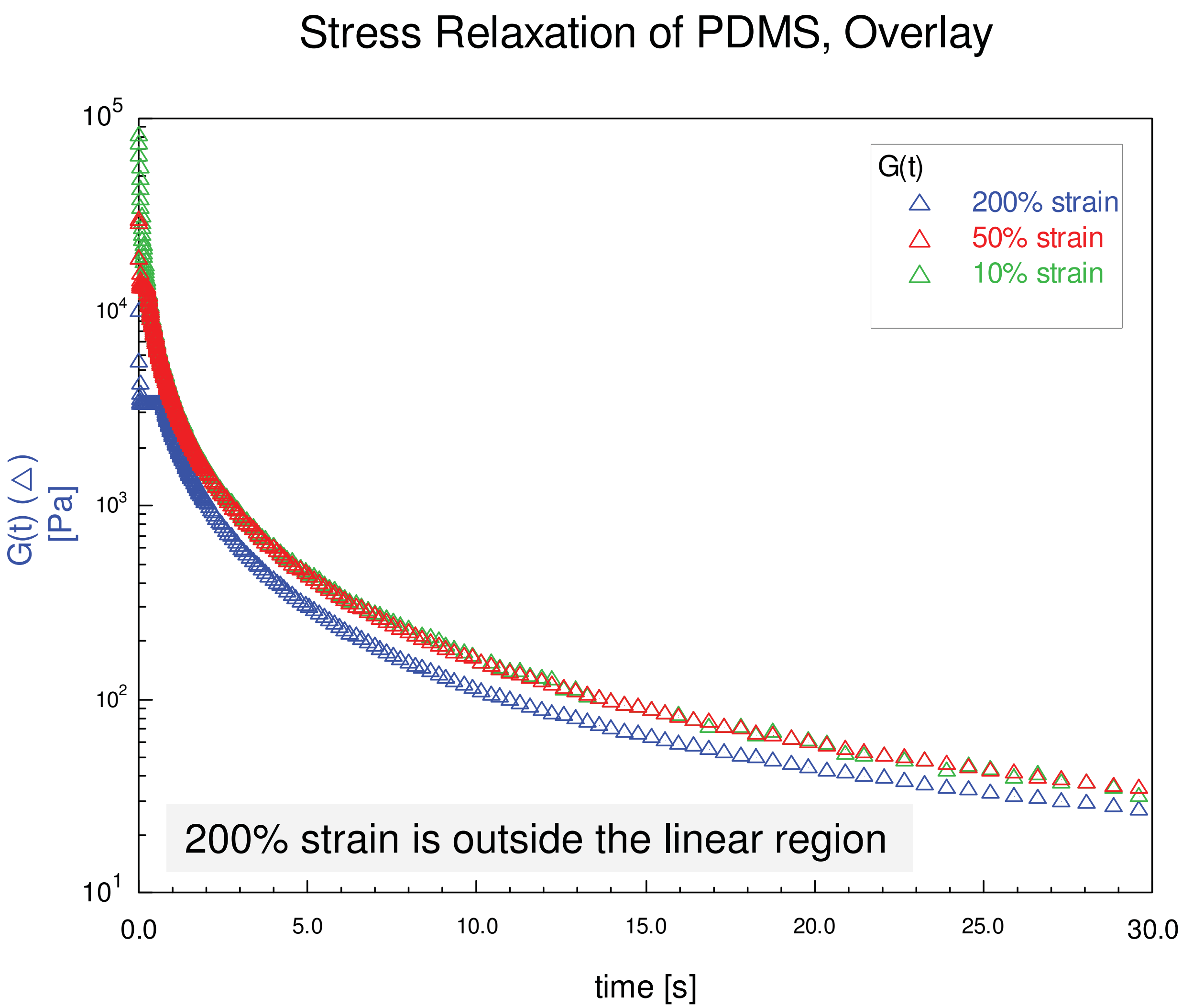
Determining Strain For Stress Relaxation

- **Research Approach**, such as generation of a family of curves for TTS, then the strain should be in the linear viscoelastic region. The stress relaxation modulus will be independent of applied strain (or will superimpose) in the linear region.

- **Application Approach**, mimic real application. Then the question is "what is the range of strain that I can apply on the sample?" This is found by knowing the Strain range the geometry can apply.
  - The software will calculated this for you.

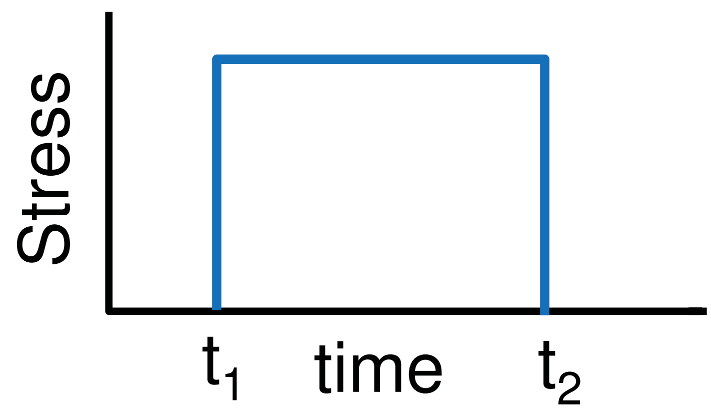
$$\gamma = K_\gamma \times \theta \quad (\%\gamma = \gamma \times 100)$$

Stress Relaxation and Linear Region



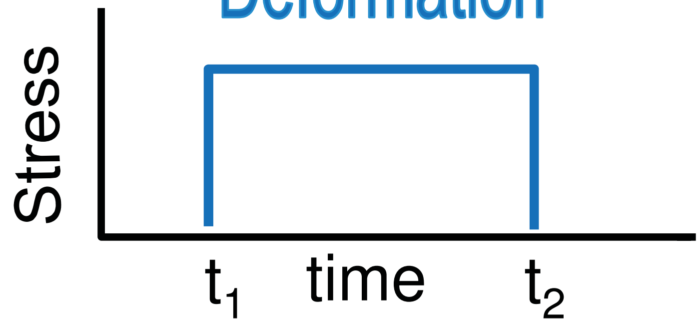
Creep Recovery Experiment

- Stress is applied to sample instantaneously, t_1, and held constant for a specific period of time. The strain is monitored as a function of time ($\gamma(t)$ or $\varepsilon(t)$)
- The stress is reduced to zero, t_2, and the strain is monitored as a function of time ($\gamma(t)$ or $\varepsilon(t)$)
- Native mode on AR (<1 msec)



Creep Recovery Experiment

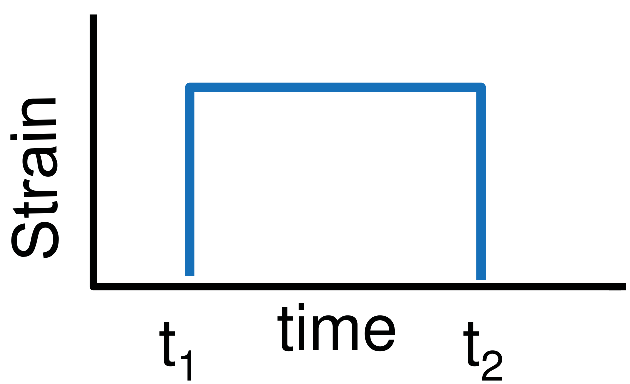
Deformation



Response of Classical Extremes

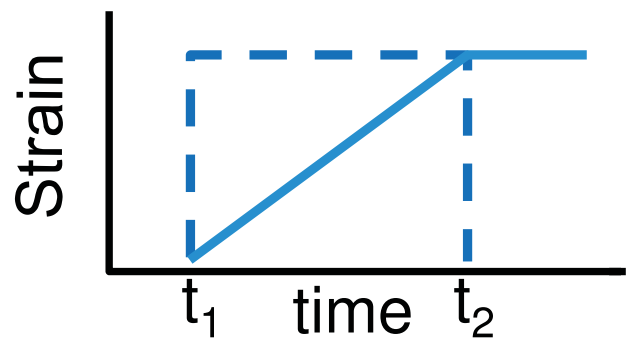
Elastic

- Stain for t>t1 is constant
- Strain for t >t2 is 0

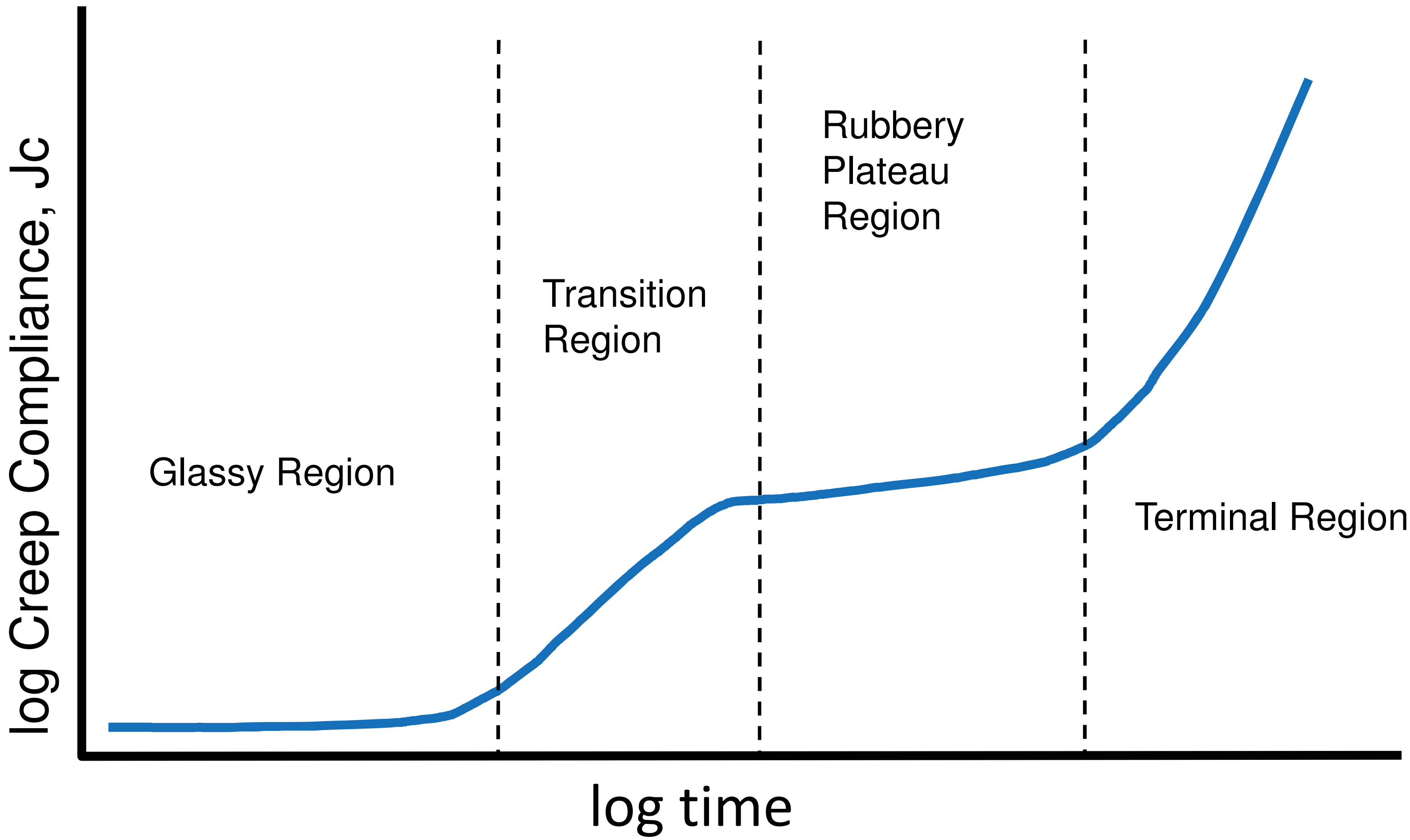


Viscous

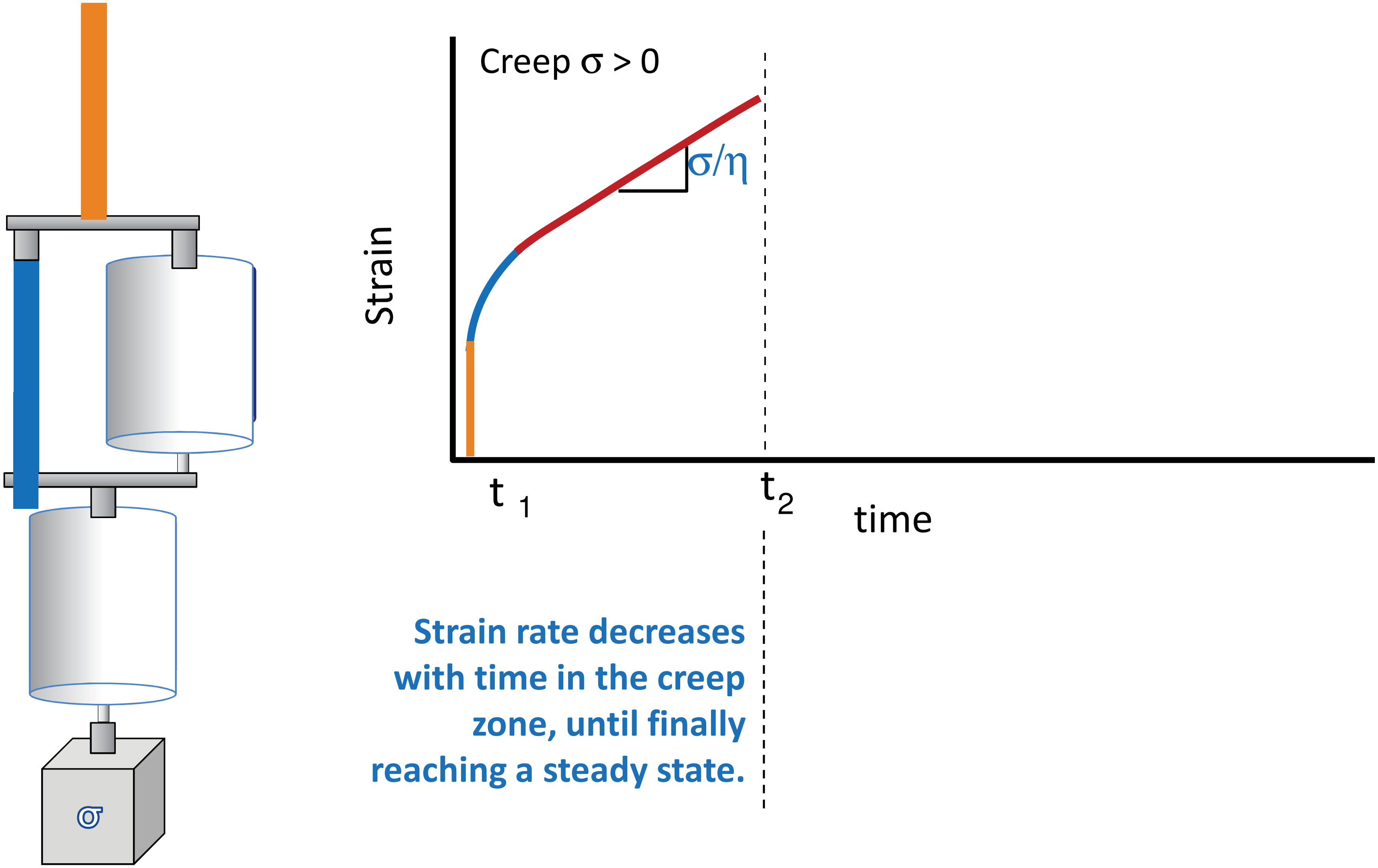
- Stain rate for t>t1 is constant
- Strain for t>t1 increase with time
- Strain rate for t >t2 is 0



Creep: Material Response



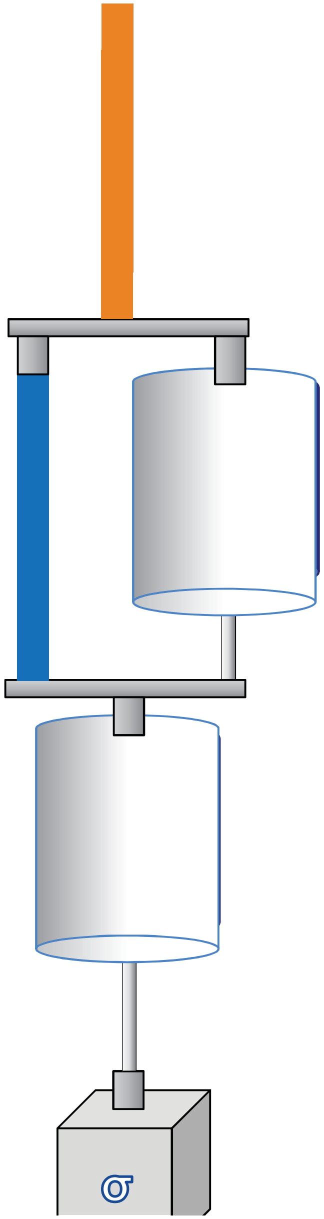
Creep Recovery: Response of Viscoelastic Material

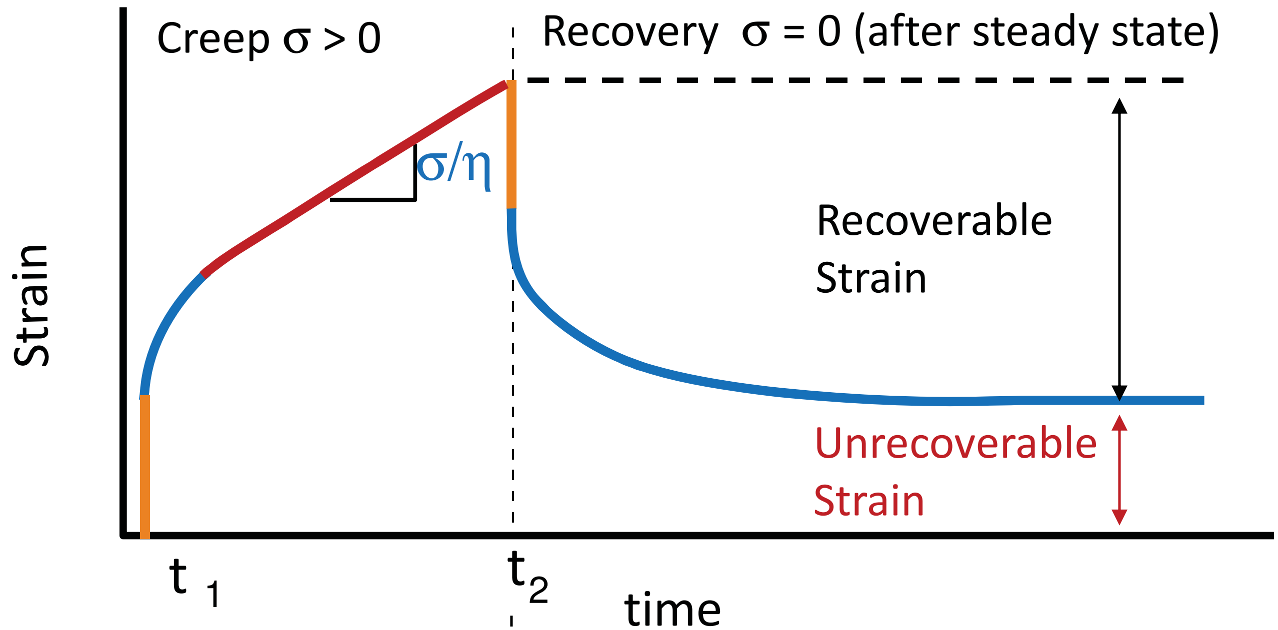


Strain rate decreases with time in the creep zone, until finally reaching a steady state.

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

Creep Recovery: Response of Viscoelastic Material



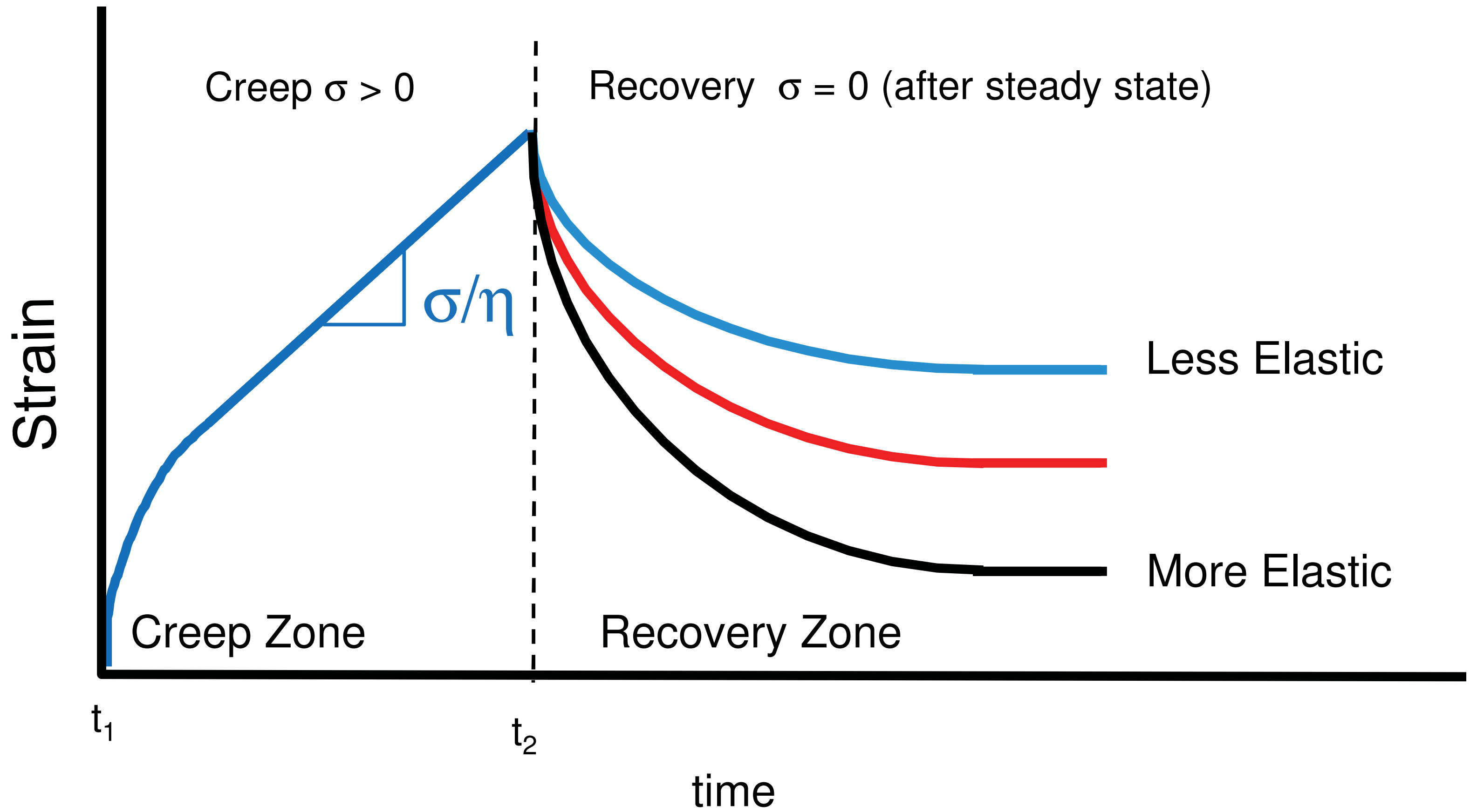


Strain rate decreases with time in the creep zone, until finally reaching a steady state.

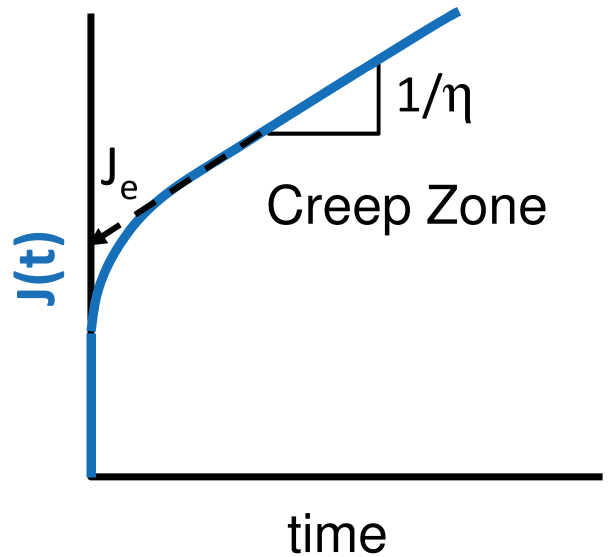
In the recovery zone, the viscoelastic fluid recoils, eventually reaching a equilibrium at some small total strain relative to the strain at unloading.

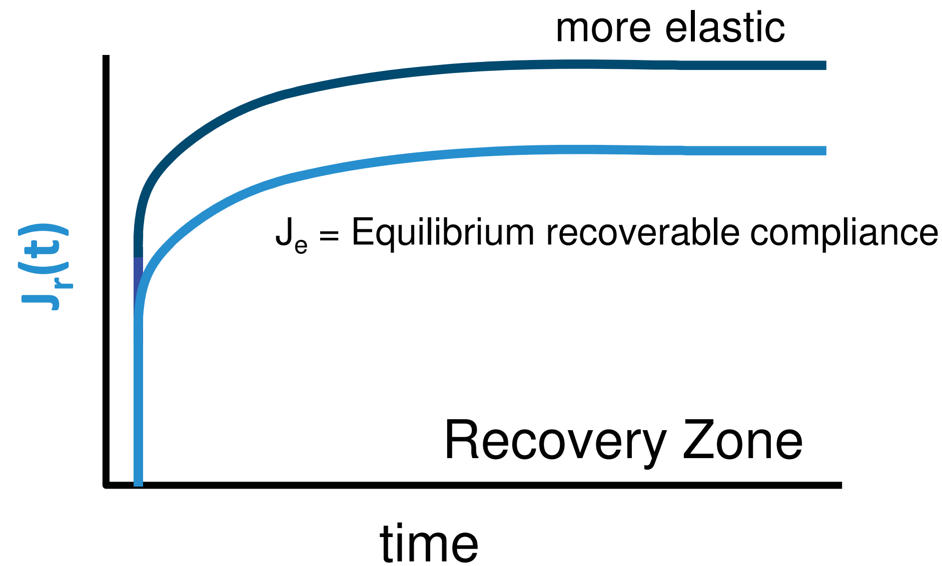
Mark, J., et. al., Physical Properties of Polymers, American Chemical Society, 1984, p. 102.

Creep Recovery Experiment



Creep Recovery : Creep and Recoverable Compliance





Creep Compliance

$$J(t) = \frac{\gamma(t)}{\sigma}$$

The material property obtained from Creep experiments:
Compliance = 1/Modulus (in a sense)

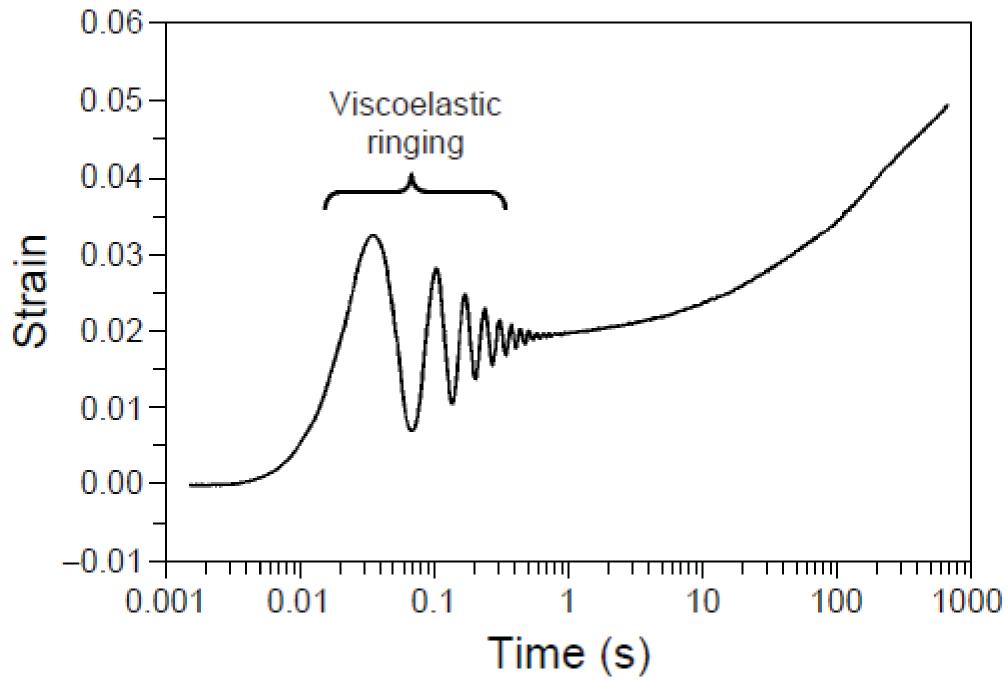
Recoverable Compliance

$$J_r(t) = \frac{[\gamma_u - \gamma(t)]}{\sigma}$$

Where γ_u = Strain at unloading
$\gamma(t)$ = time dependent recoverable strain

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

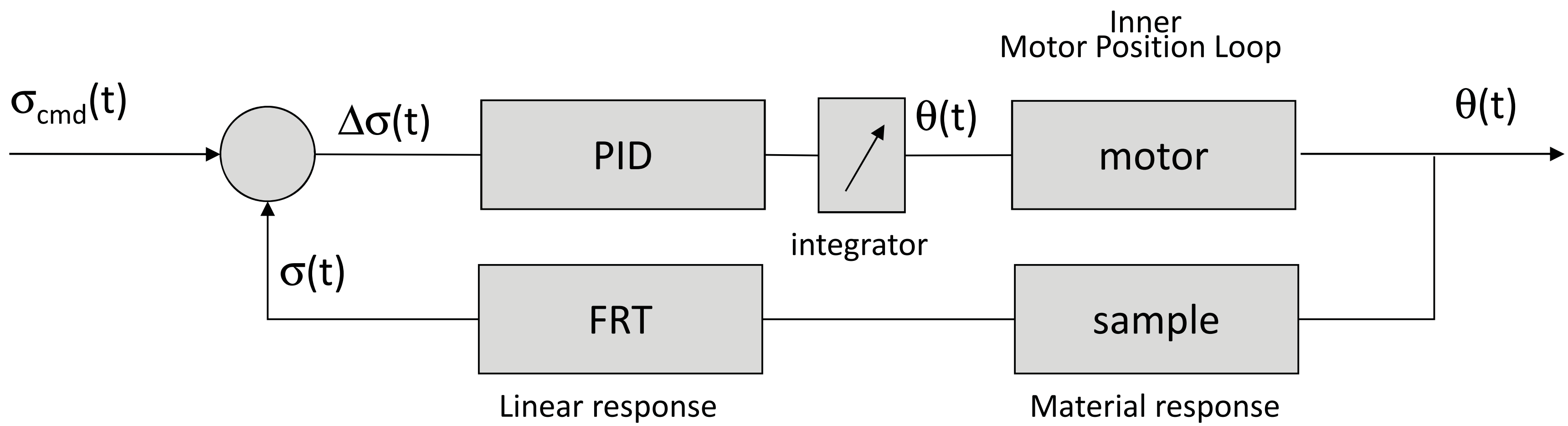
Viscoelastic Ringing – DHR or AR



- The ringing oscillations can be rather short-lived and may not be apparent unless using log time scale.
- The sudden acceleration, together with the measurement system's inertia, causes a strain overshoot. For viscoelastic materials, this can result in viscoelastic ringing, where the material undergoes a damped oscillation just like a bowl of Jell-o when bumped.

Creep ringing in rheometry or how to deal with oft-discarded data in step stress tests!
RH Ewoldt, GH McKinley - Rheol. Bull, 2007

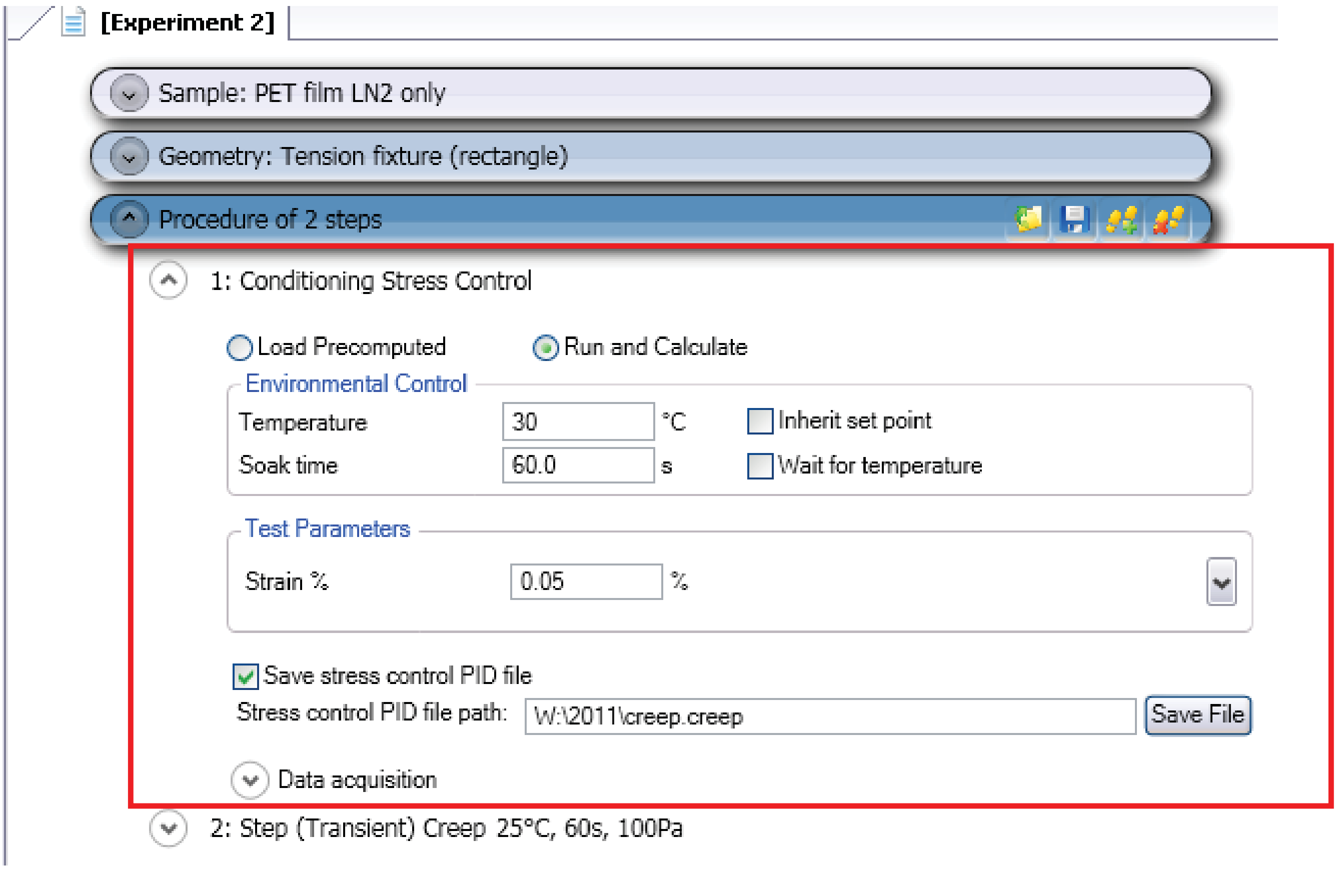
ARES-G2 Stress Control Loop



- Stress is controlled by closing the loop around the sample → requires optimization of control PID parameters
- Pretest to determine material's response and PID Constants

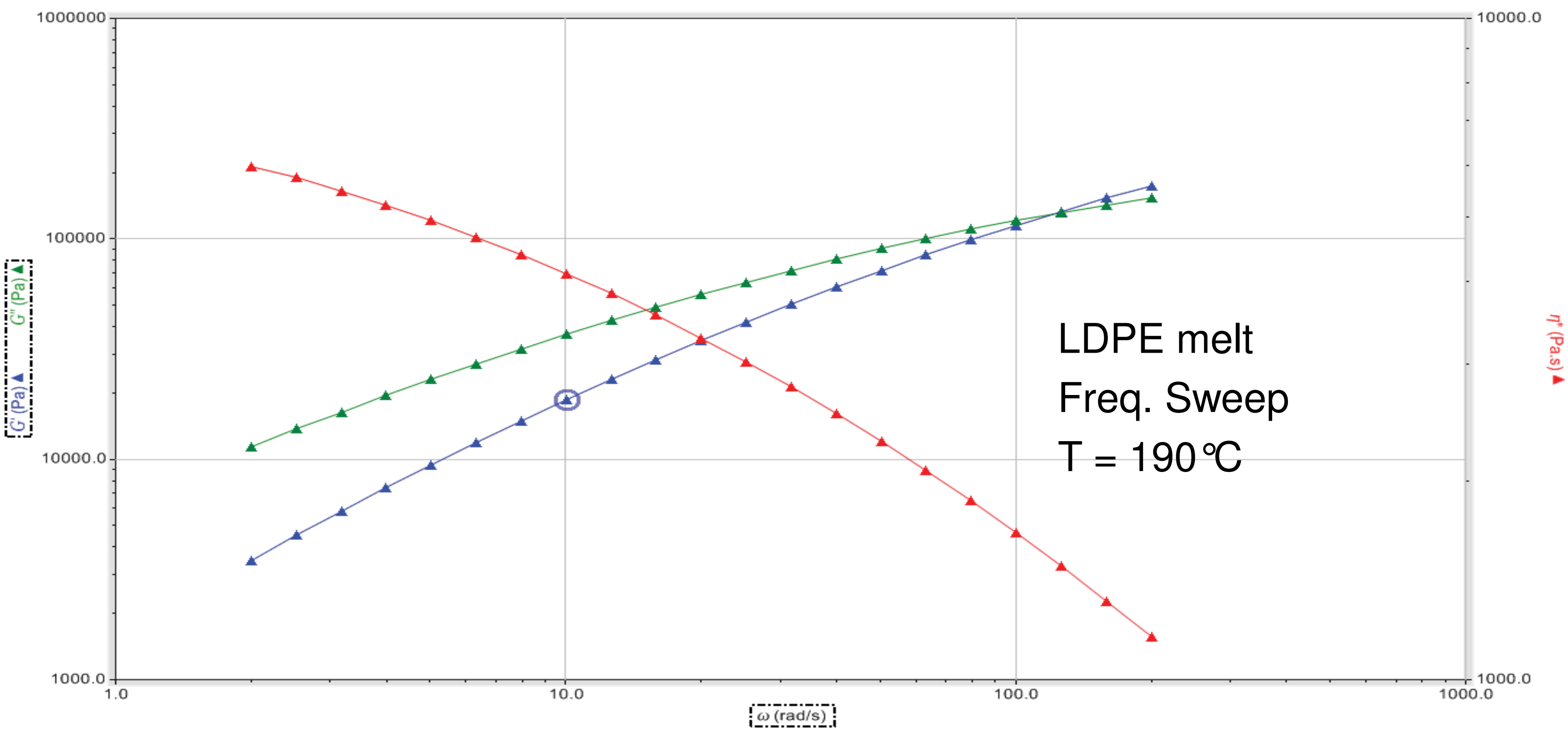
Programming Creep on an ARES-G2

- Set up a pre-test and get the sample information into the loop
- Stress Control Pre-test: frequency sweep within LVR

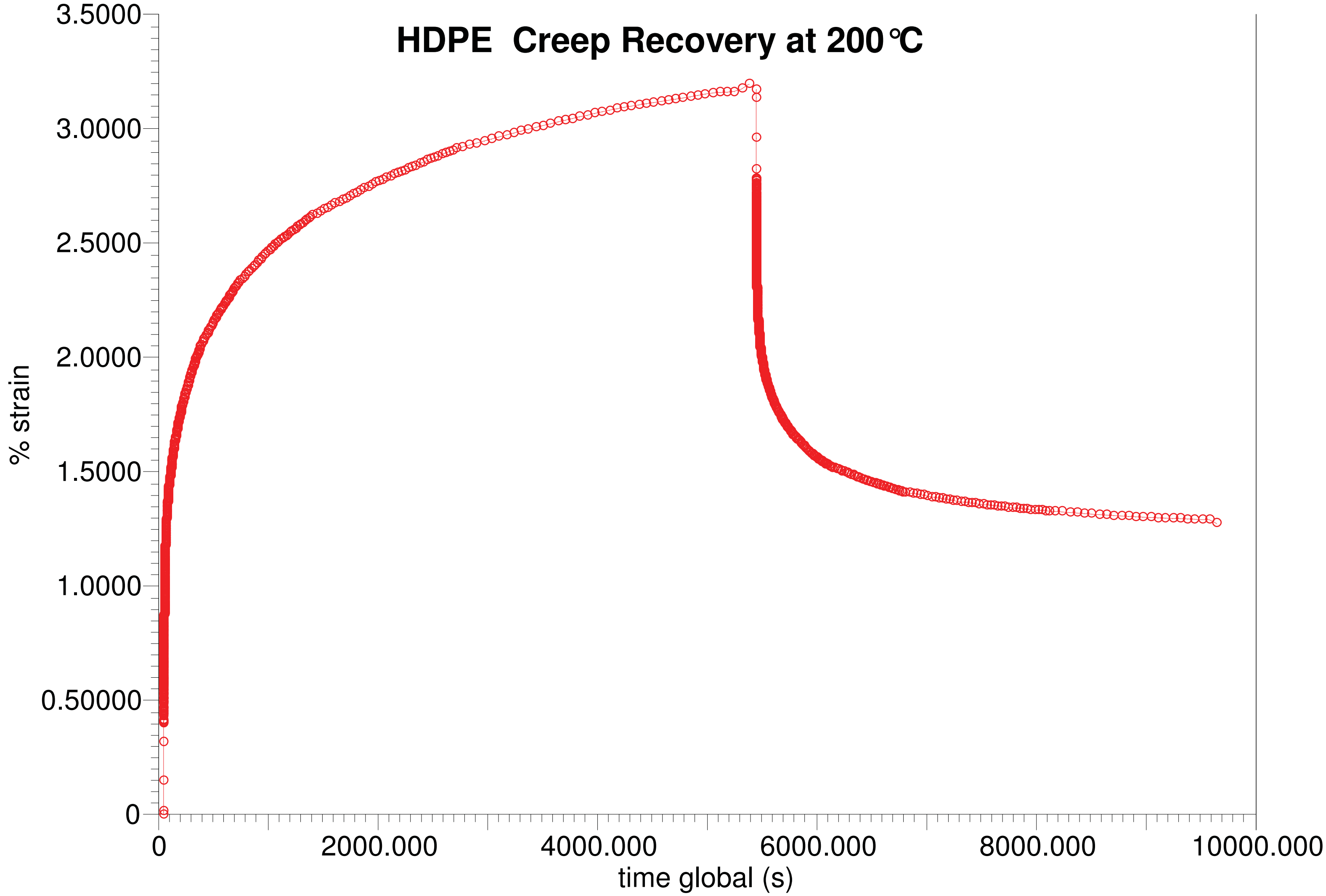


ARES-G2 Stress Control Pretest

Pretest → Frequency Sweep from 2 to 200 rad/s → data analyzed in software to optimize Motor loop control PID constants



Creep on HDPE Melt



Determining Stress For Creep Experiment

- **Research Approach** - If you are doing creep on a polymer melt, and are interested in viscoelastic information (creep and recoverable compliance), then you need to conduct the test at a stress within the linear viscoelastic region of the material.
- **Application Approach** - If you are doing creep on a solid, you want to know the dimension change with time under a specified stress and temperature, then the questions is "what is the max/min stress that I can apply to the sample?". This is found by knowing the Stress range the geometry can apply.
  - The software will calculated this for you.

$$\sigma = K_\sigma \text{ x } M$$

Applications of Rheology

Polymers

Purpose of a Rheological Measurement

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 Testing and Rheology

Molecular Structure

↑↓
- MW and MWD
- Chain Branching and Cross-linking
- Interaction of Fillers with Matrix Polymer
- Single or Multi-Phase Structure

Viscoelastic Properties

As a function of:

↑↓
- Strain Rate(frequency)
- Strain Amplitude
- Temperature

Processability & Product Performance

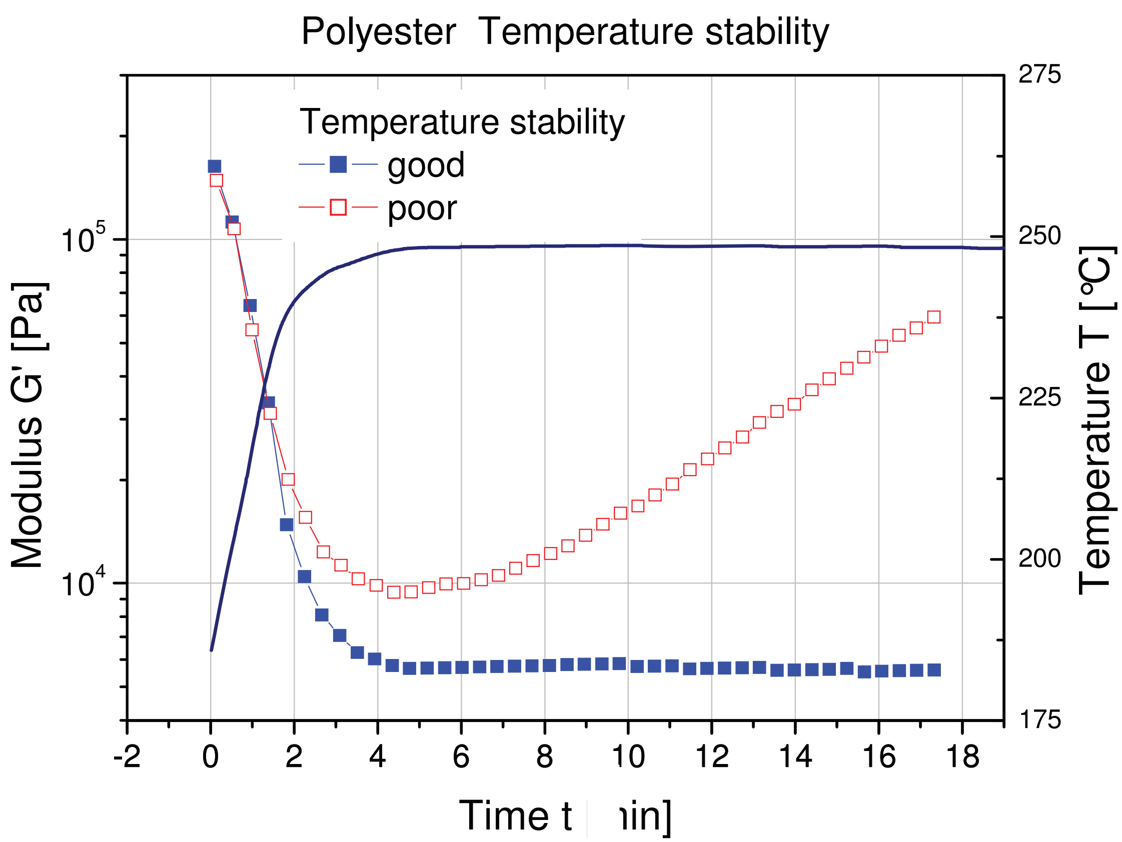
Rheology Applications in Polymers

Material	Property
Composites, Thermosets	Viscosity, Gelation, Rate of Cure, Effect of Fillers and Additives
Cured Laminates	Glass Transition, Modulus Damping, impact resistance, Creep, Stress Relaxation, Fiber orientation, Thermal Stability
Thermoplastics	Blends, Processing effects, stability of molded parts, chemical effects
Elastomers	Curing Characteristics, effect of fillers, recovery after deformation
Coating, Adhesives	Damping, correlations, rate of degree of cure, glass transition temperature, modulus

Most Common Experiments on Polymers

- **Oscillation/Dynamic**
  - Time Sweep
    - Degradation studies, stability for subsequent testing
  - Strain Sweep – Find LVER
  - Frequency Sweep – G', G", η^*
    - Sensitive to MW/MWD differences melt flow can not see
  - Temperature Ramp/Temperature Step
    - Transitions, viscosity changes
  - TTS Studies
- **Flow/Steady Shear**
  - Viscosity vs. Shear Rate Plots
  - Find Zero Shear Viscosity
  - Low shear information is sensitive to MW/MWD differences melt flow can not see
- **Creep and Recovery**
  - Creep Compliance/Recoverable Compliance
  - Very sensitive to long chain tails

Polymer Melt Thermal Stability

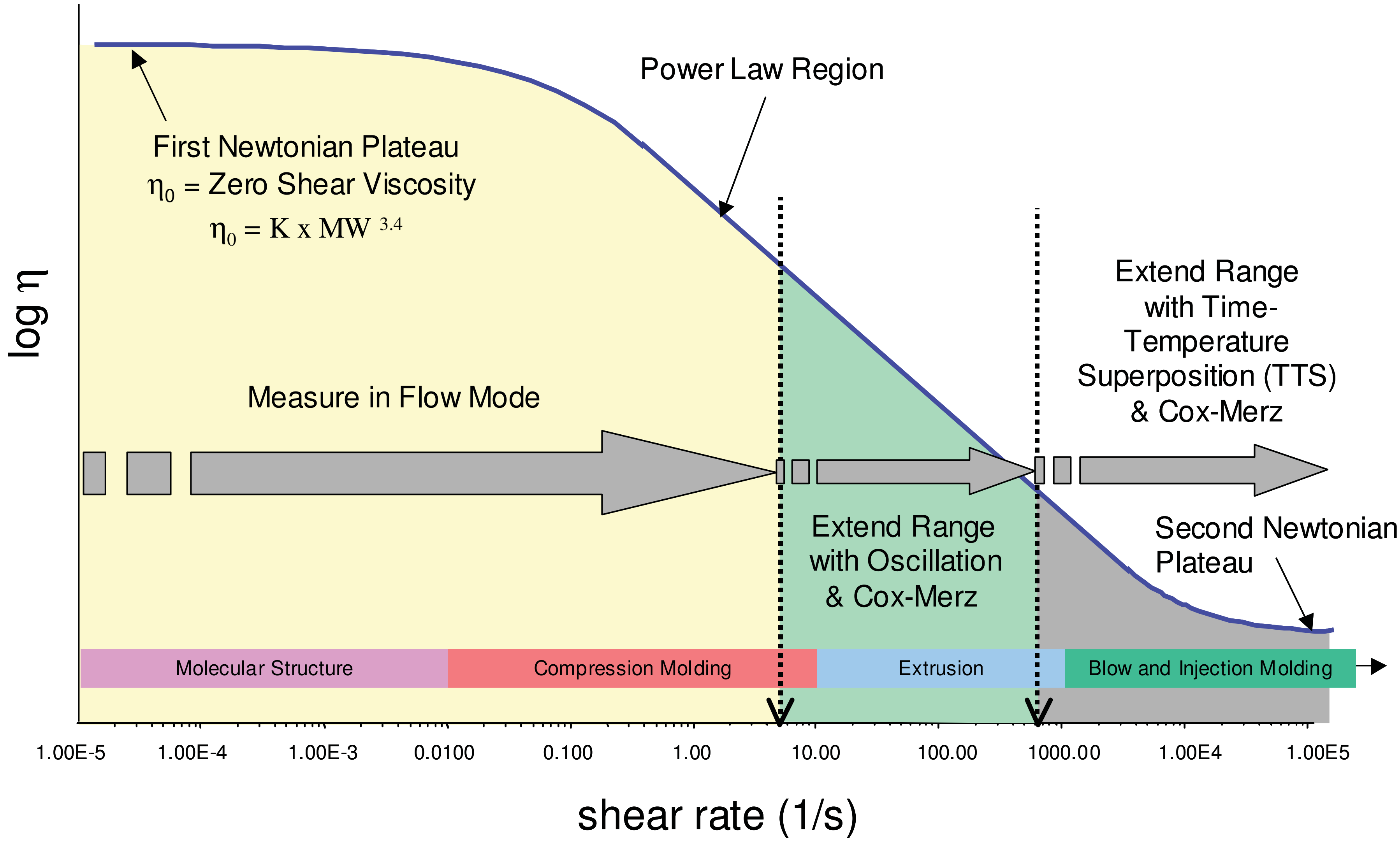


Determines if properties are changing over the time of testing

- Degradation
- Molecular weight building
- Crosslinking

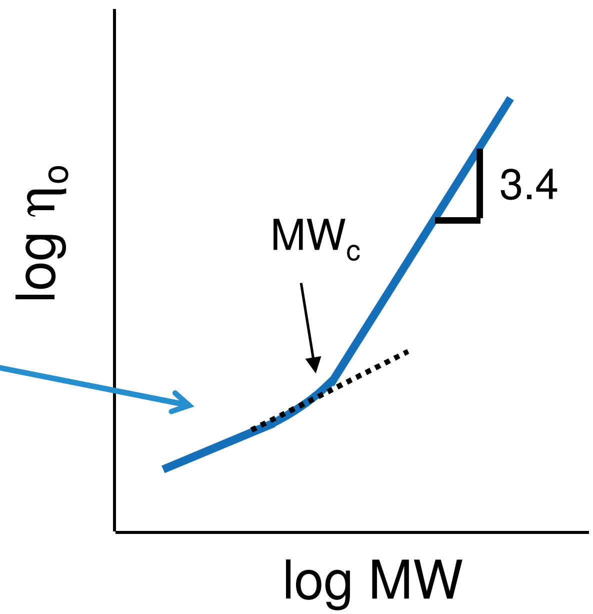
Important, but often overlooked!

Idealized Flow Curve – Polymer Melts



Melt Rheology: MW Effect on Zero Shear Viscosity

- 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 $MW^{3.4}$



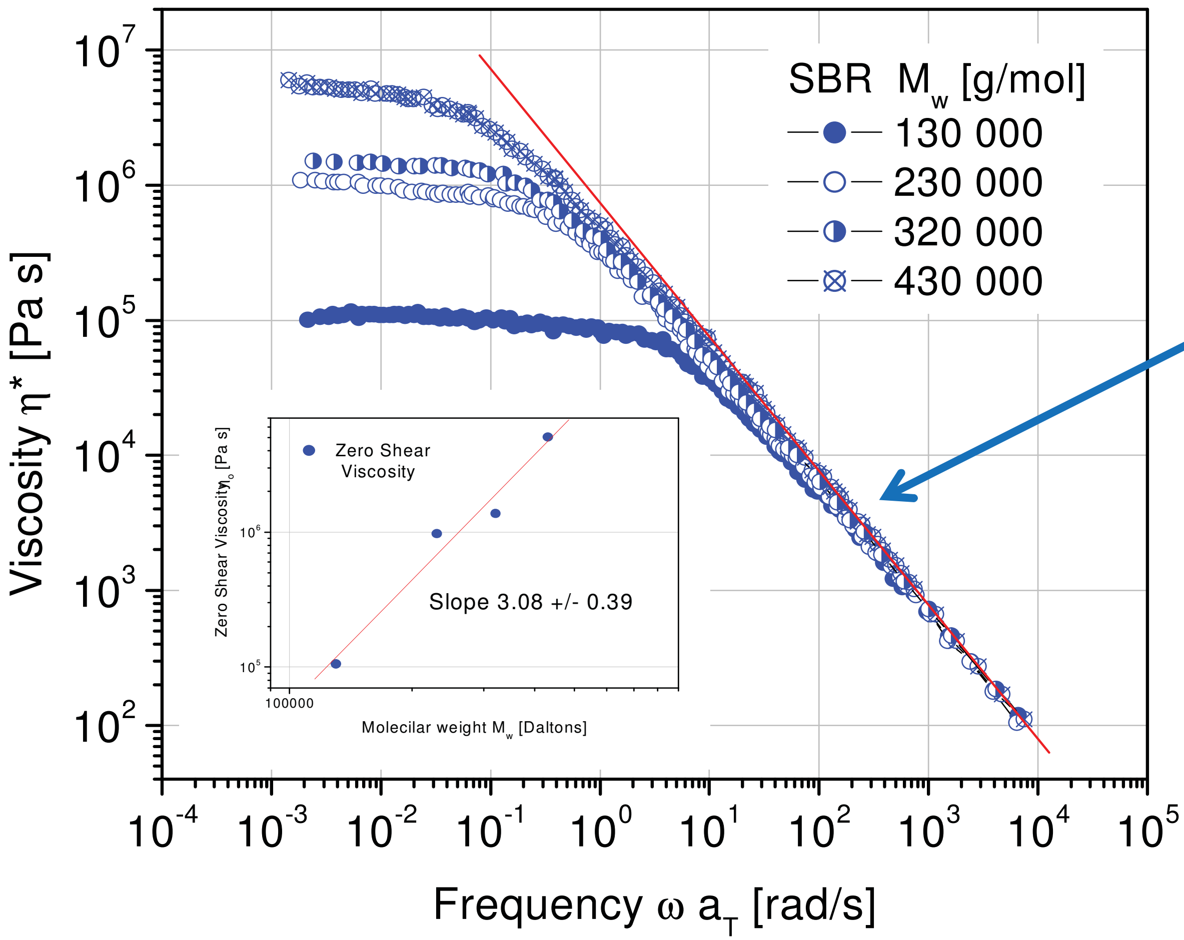
$\eta_0 = K \cdot Mw$

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

Ref. Graessley, Physical Properties of Polymers, ACS, c 1984.

Influence of MW on Viscosity

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

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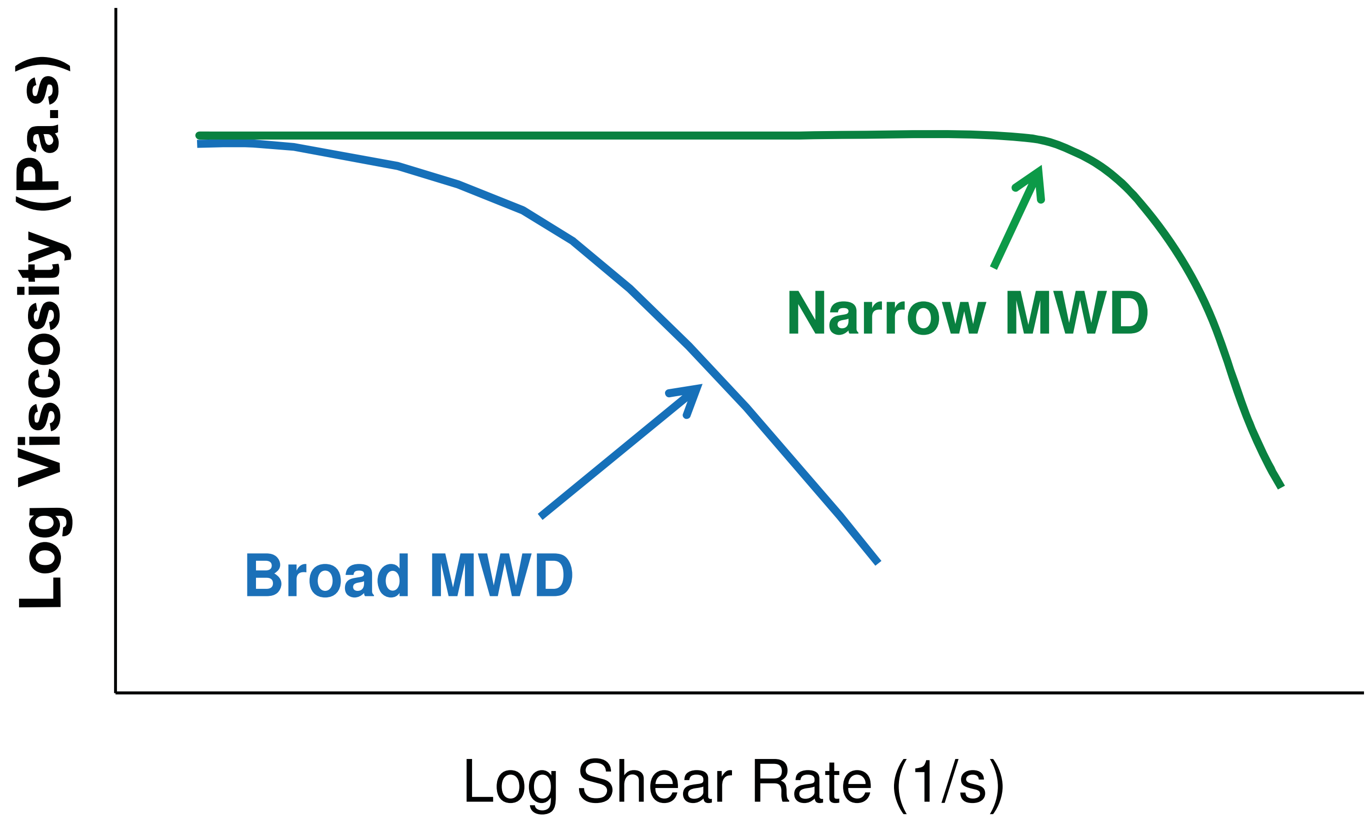
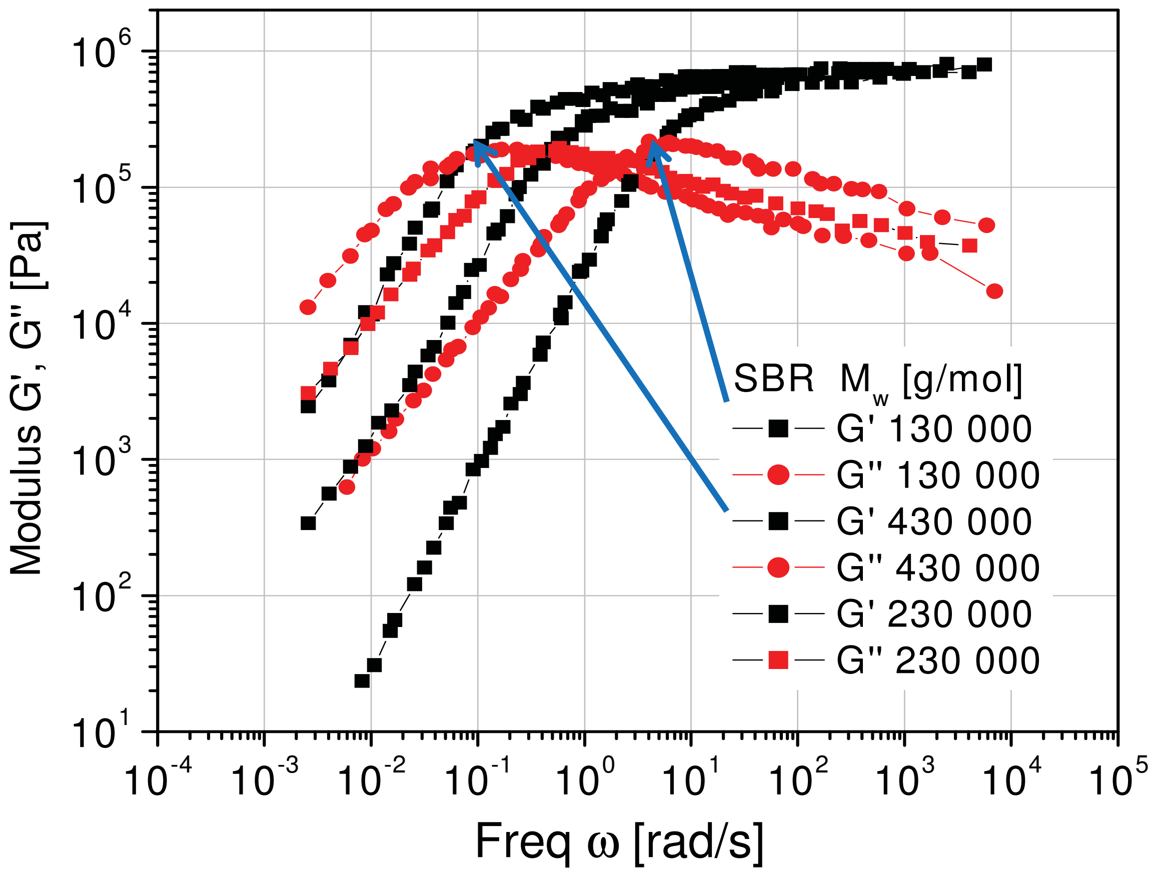
Influence of MWD on Viscosity

- 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.

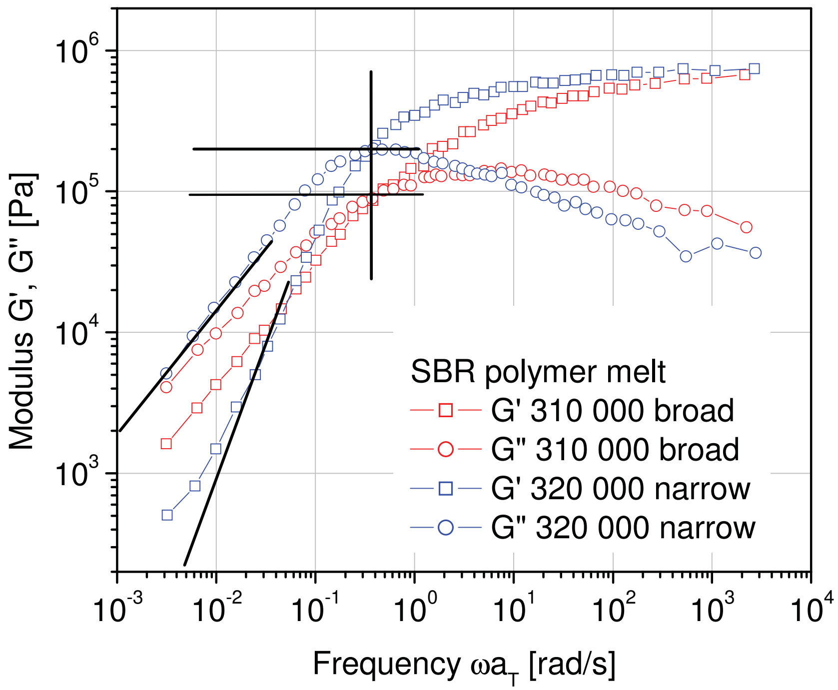


Influence of MW on G‘ and G“

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



Influence of MWD on G' and G"

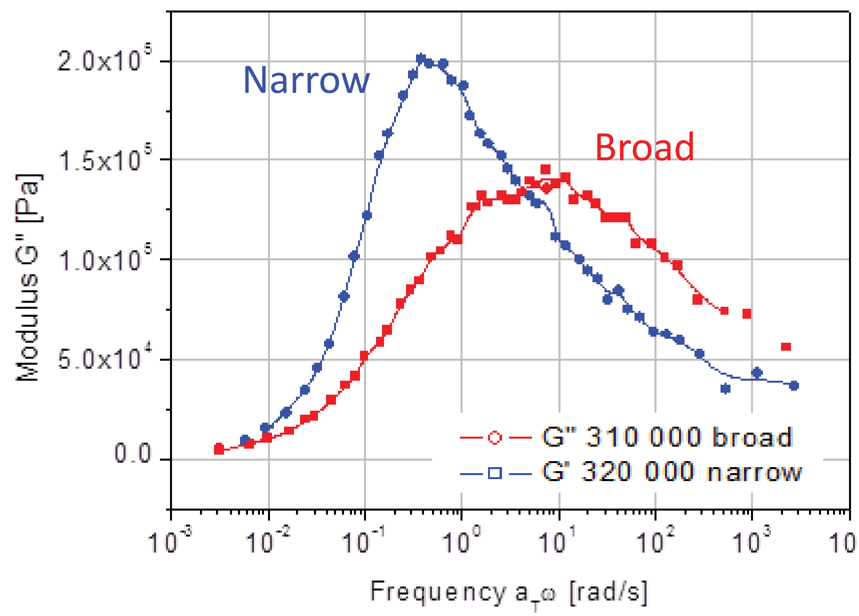


Higher crossover frequency : lower M_w

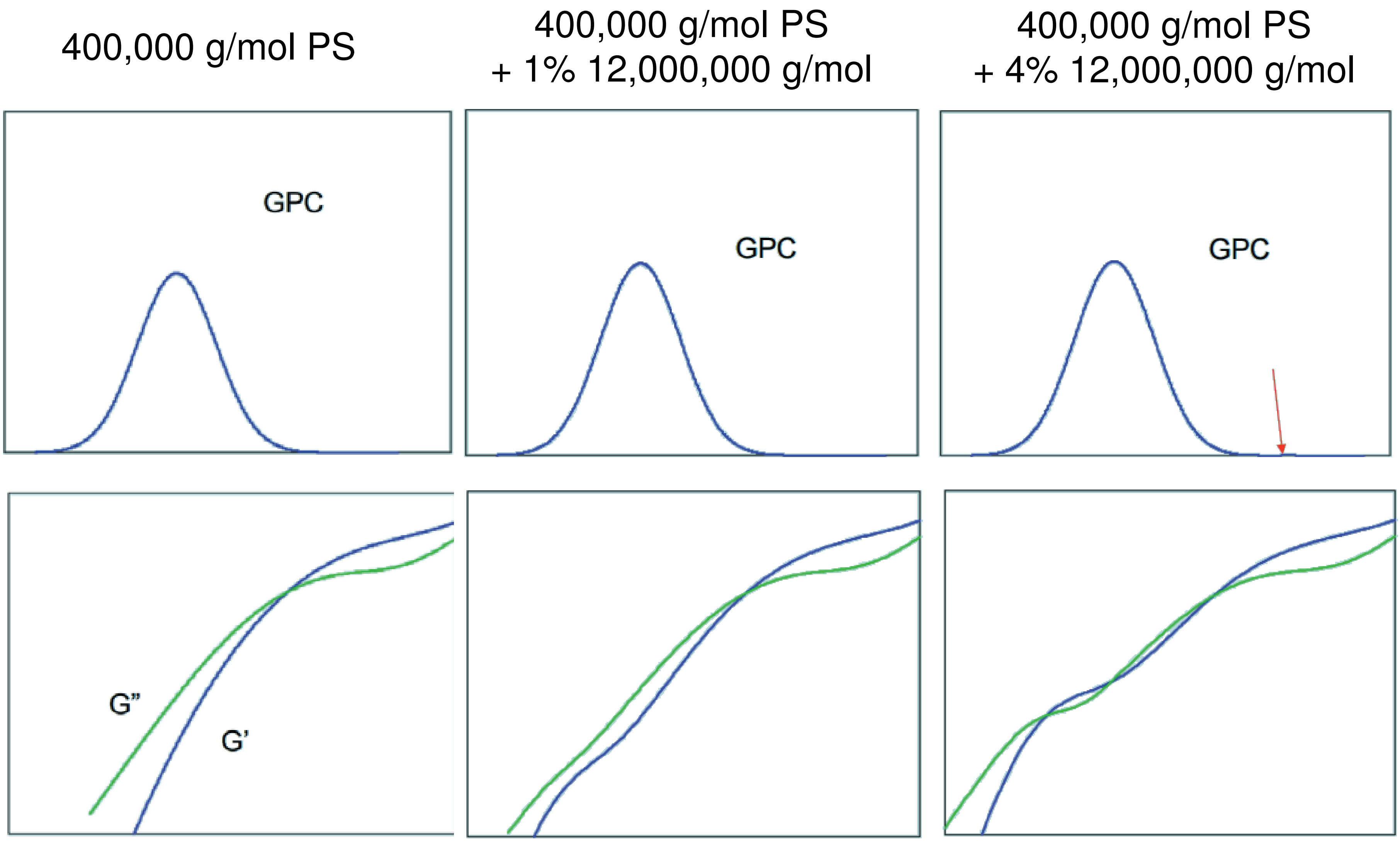
Higher crossover Modulus: narrower MWD

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

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

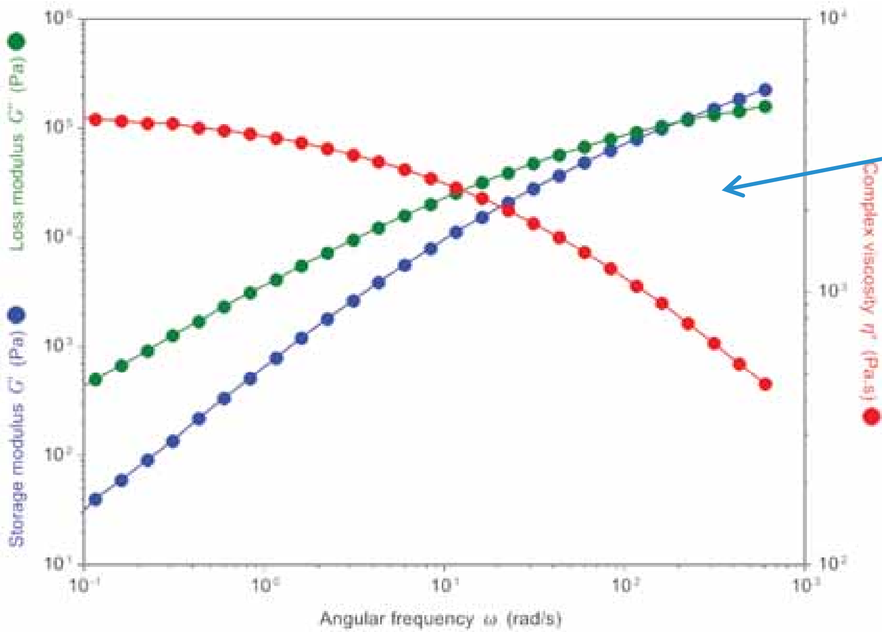


High MW Contributions



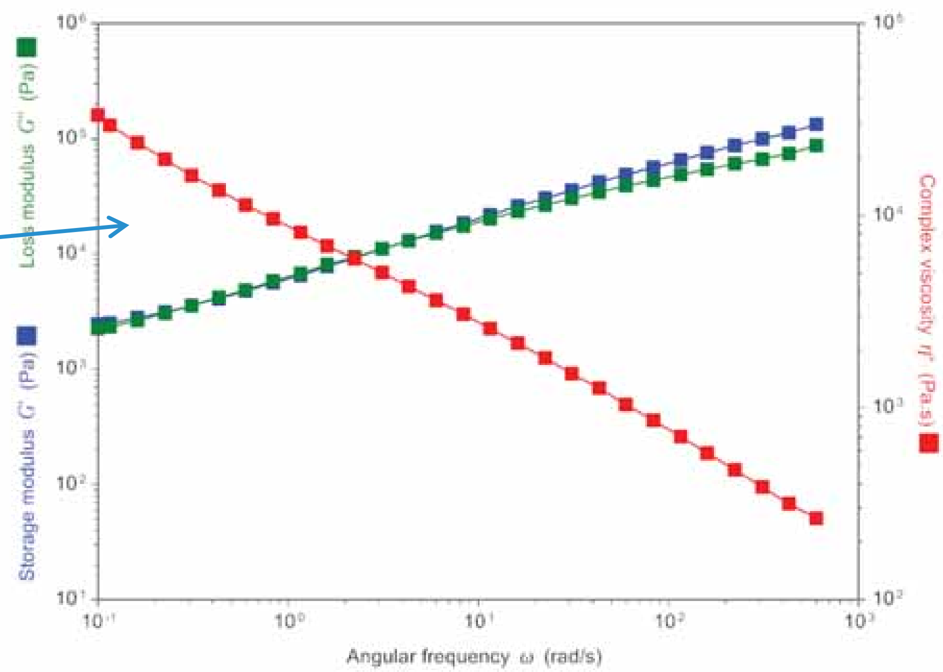
Macosko, TA Instruments Users' Meeting, 2015

Importance of Verifying Thermal Stability

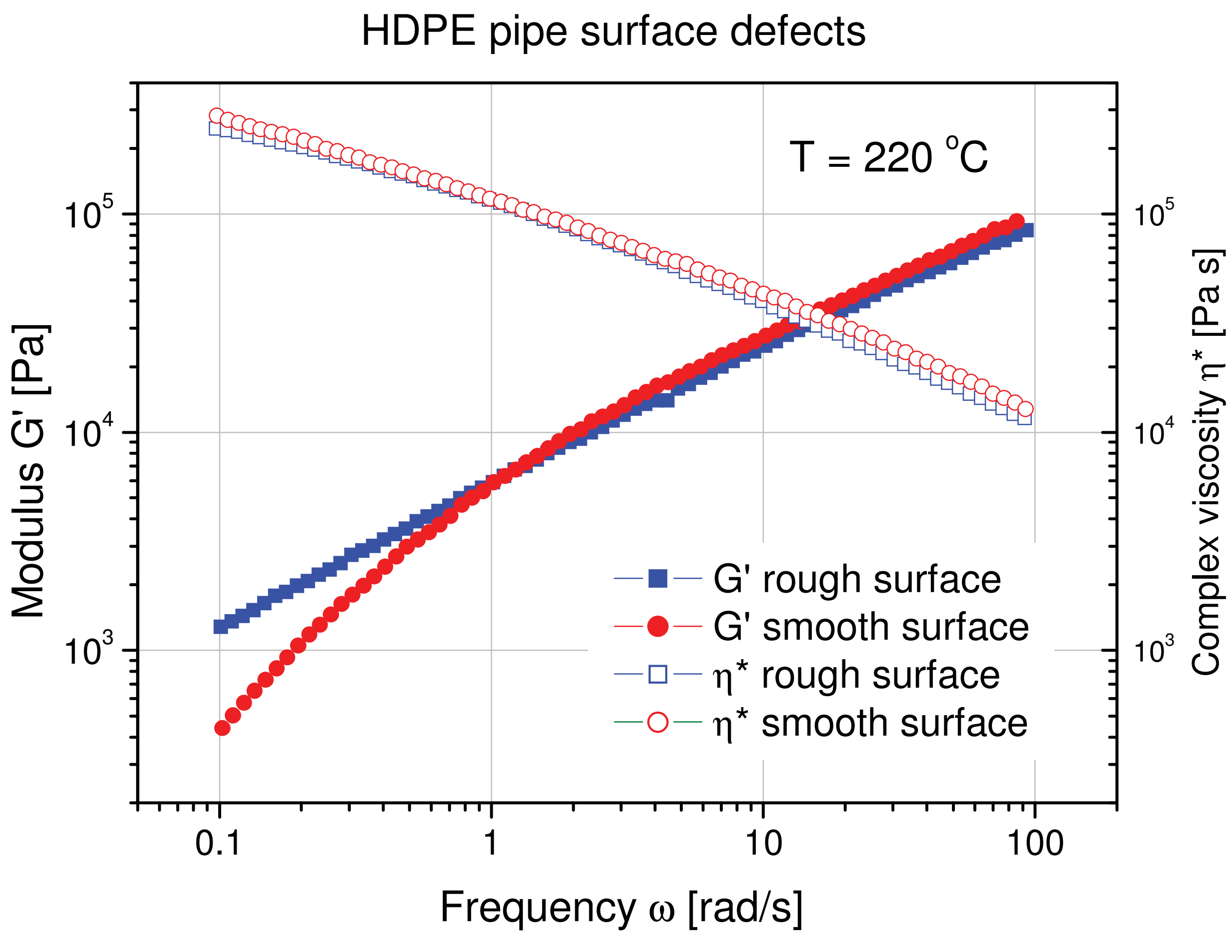


- Good thermal stability
  - one crossover point,
  - η^* plateaus at low ω

- Poor thermal stability
  - multiple crossover points
  - η^* continues to increase over time
  - Time Sweep can verify if the sample is unstable



Surface Defects during Pipe Extrusion



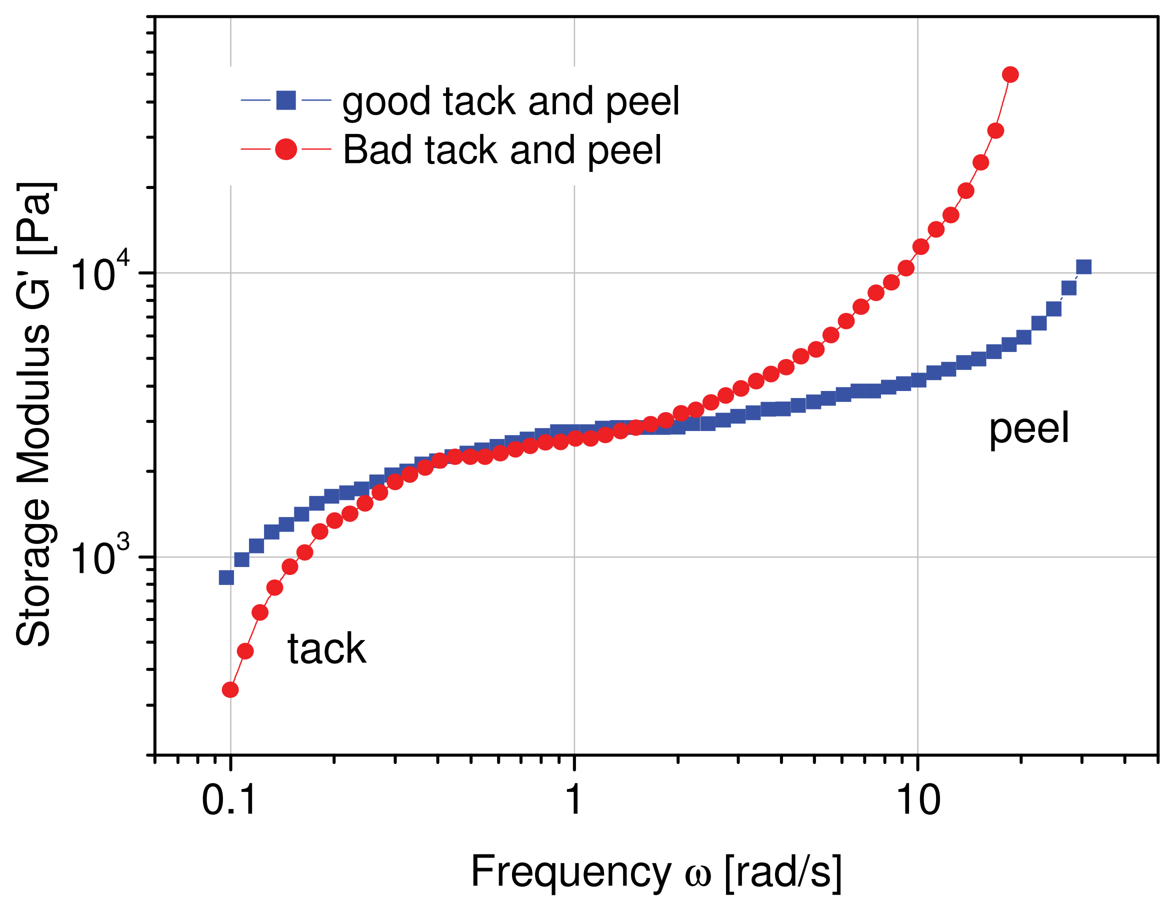
- Surface roughness correlates with G‘ or elasticity → broader MWD or tiny amounts of a high MW component

Blue-labled sample shows a rough surface after extrusion

Tack and Peel of Adhesives

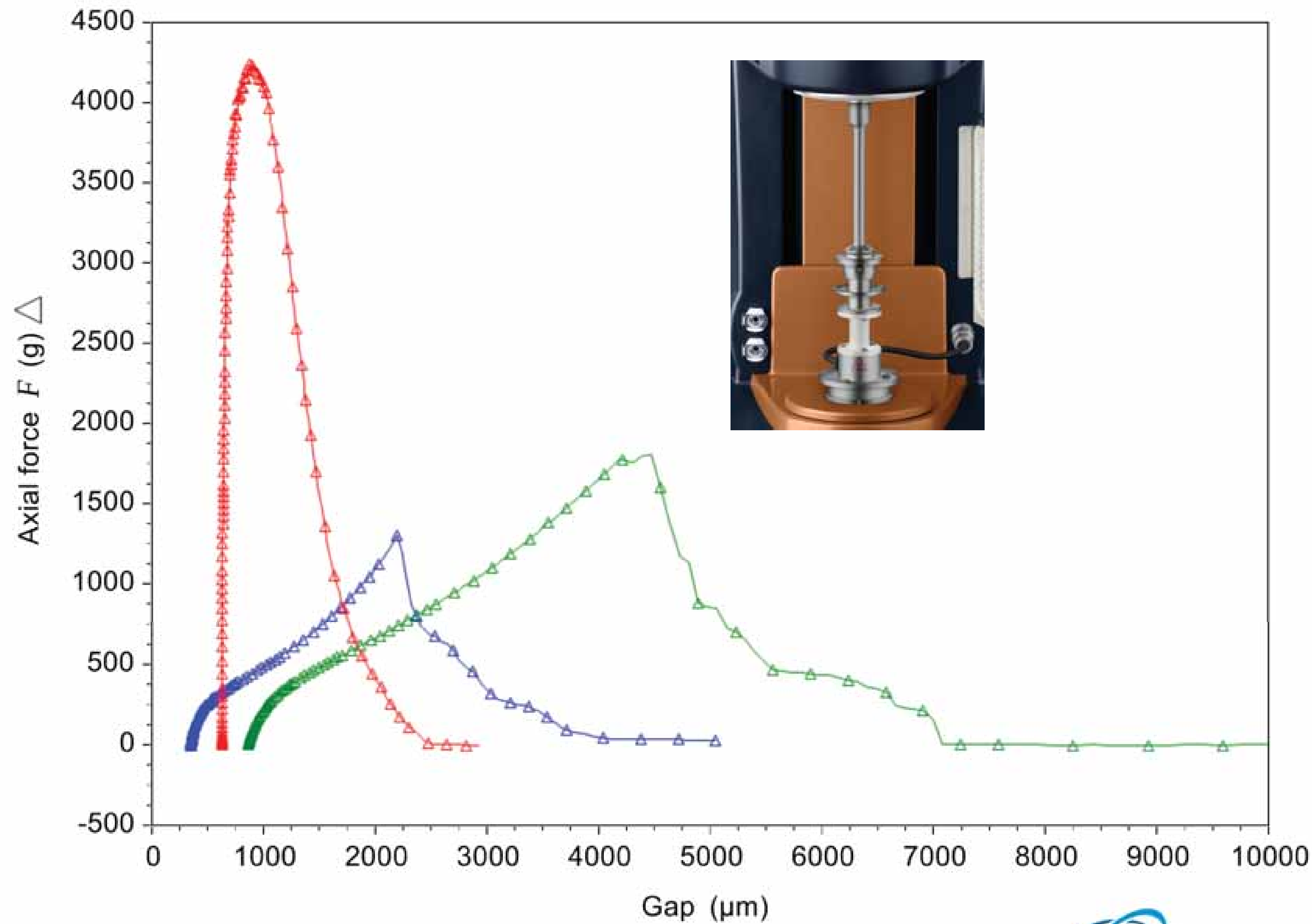
- Bond strength is obained from peel (fast) and tack (slow) tests
- It can be related to the viscoelastic properties at different frequencies

Tack and Peel performance of a PSA

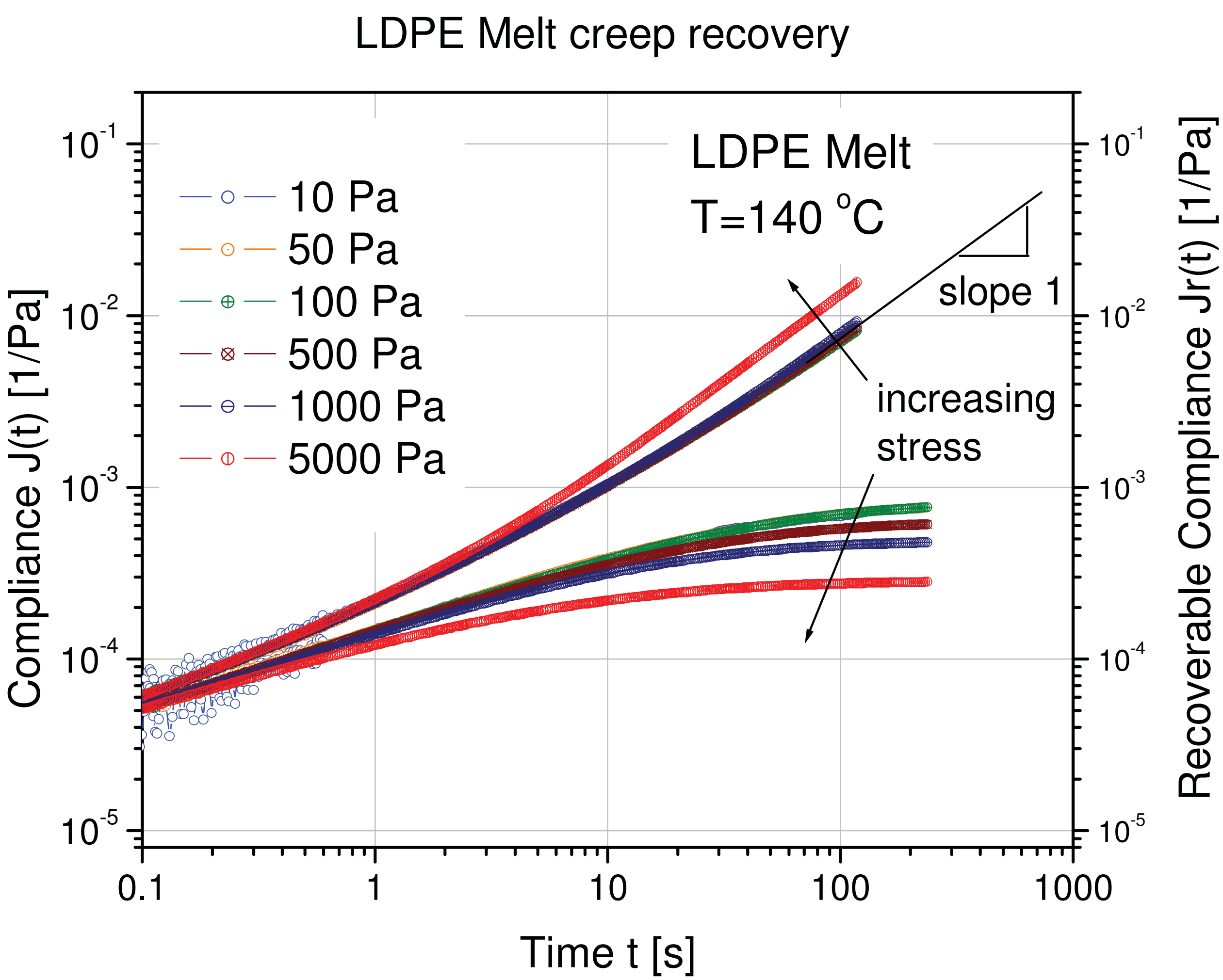


Tack and peel have to be balanced for an ideal adhesive

Dried Adhesives- Tack Test

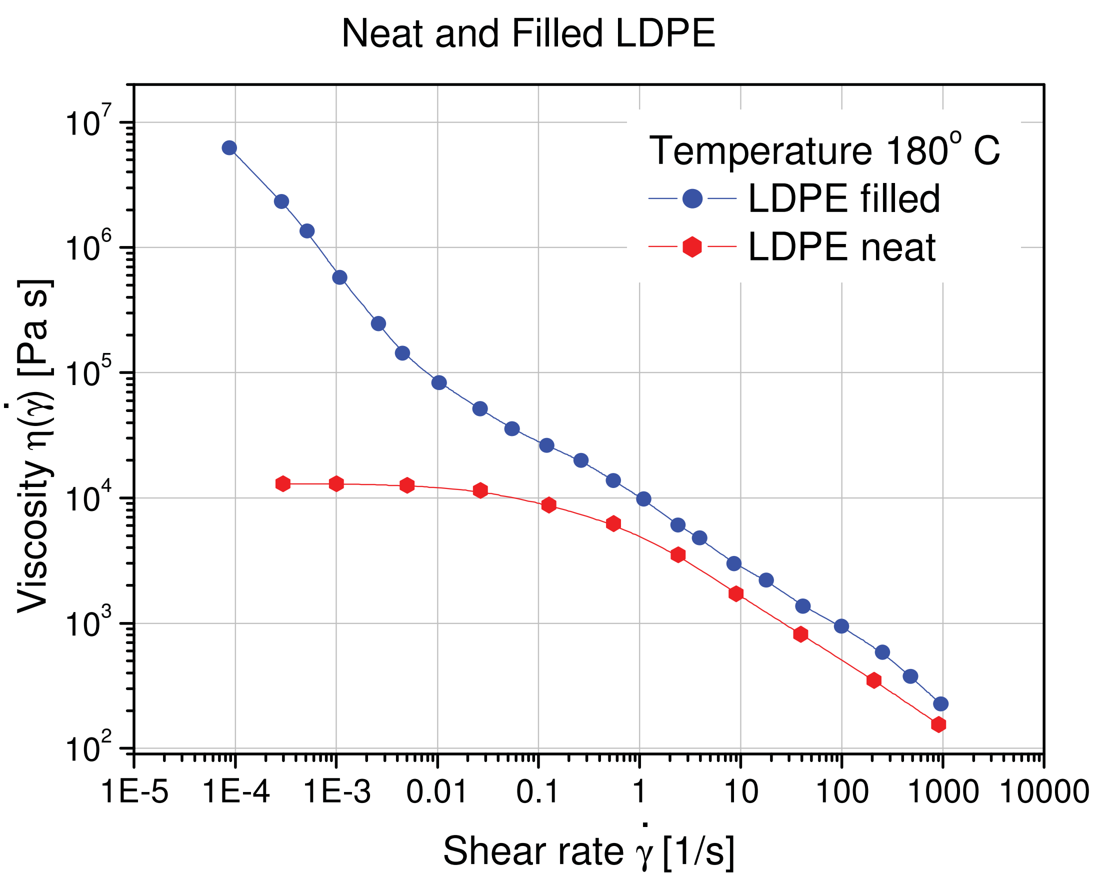


Creep and Recovery with Increasing Stress



- Non linear effects can be detected in recovery before they are seen in the creep (viscosity dominates)

Effect of Filler on Melt Viscosity



- Fillers increase the melt viscosity
- Due to inter-particle interactions, the non-Newtonian range is extended to low shear rates and the zero shear viscosity increases dramatically

The material has a yield, when rate and viscosity are inverse proportional at low rate.

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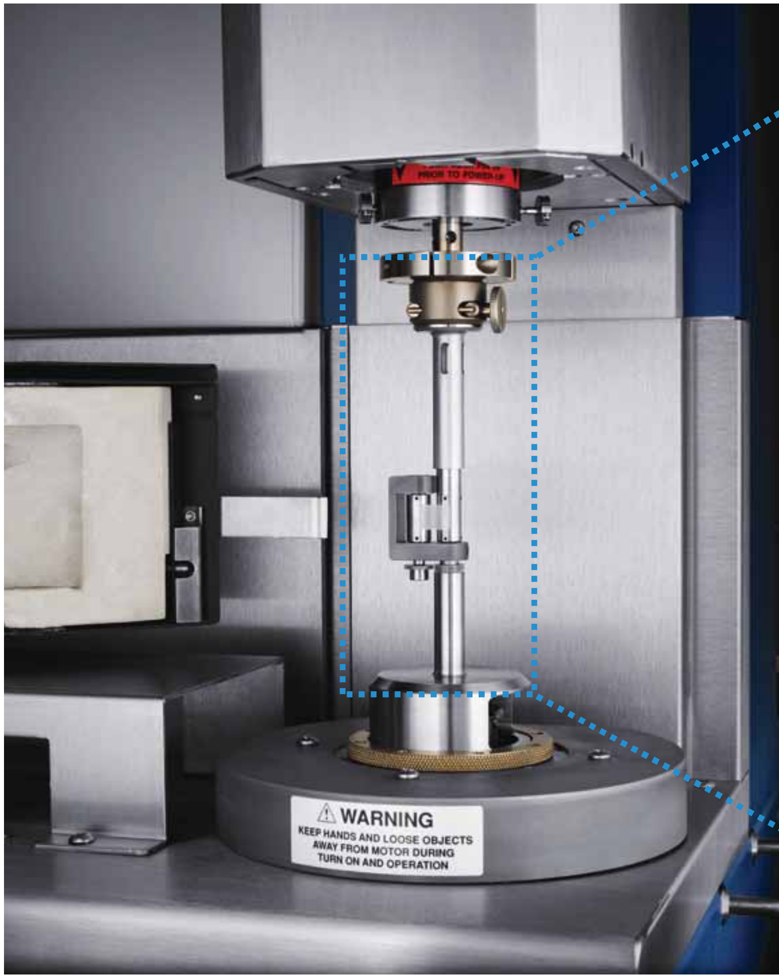
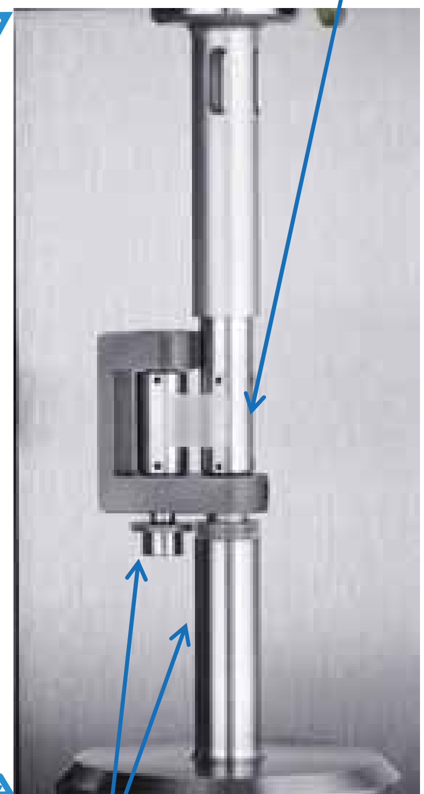
Extensional Viscosity Measurements



Fix drum connected to transducer



Rotating drum connected to the motor:

- rotates around its axis
- rotates around axis of fixed drum

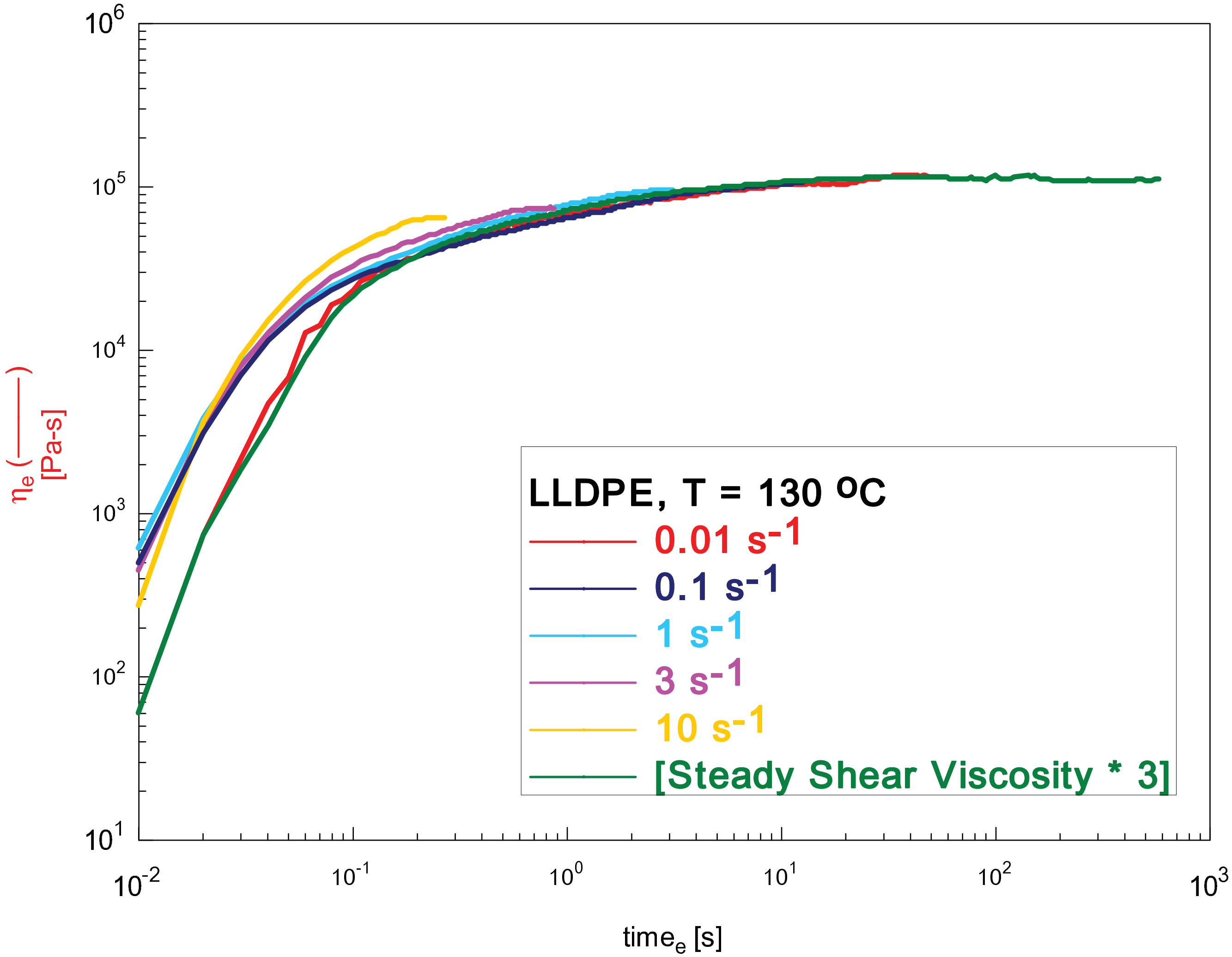
Why is Elongation Viscosity Important?

- Application to processing: many processing flows are elongation flows - testing as close as possible to processing conditions (spinning, coating, spraying)

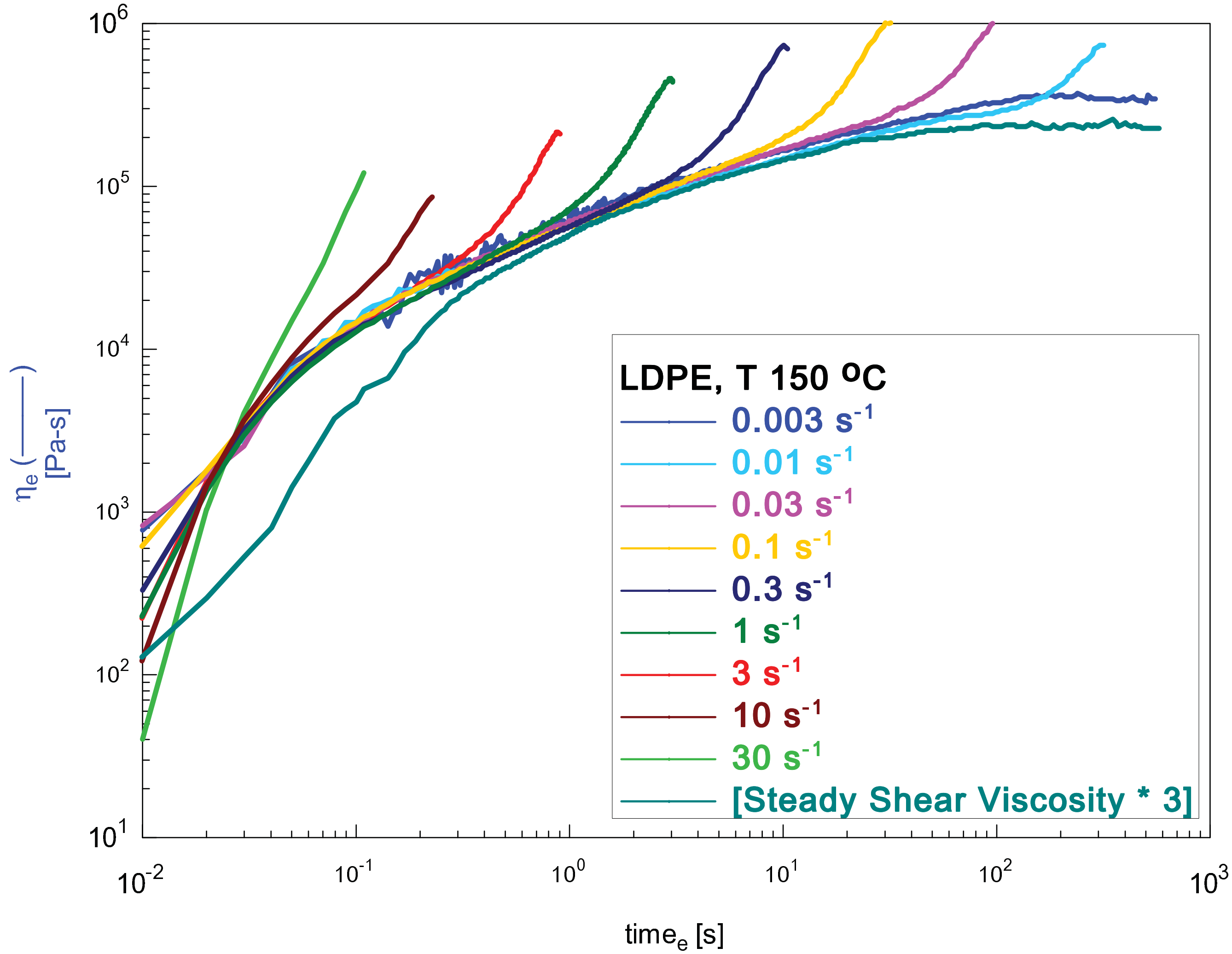
- Relation to material structure: non linear elongation flow is more sensitive for some structure elements than shear flows (branching, polymer architecture)

- Testing of constitutive equations: elongation results in addition to shear data provide a more general picture for developing material equations

LLDPE (Low branching)



LDPE (High branching)



Thermosetting Polymers

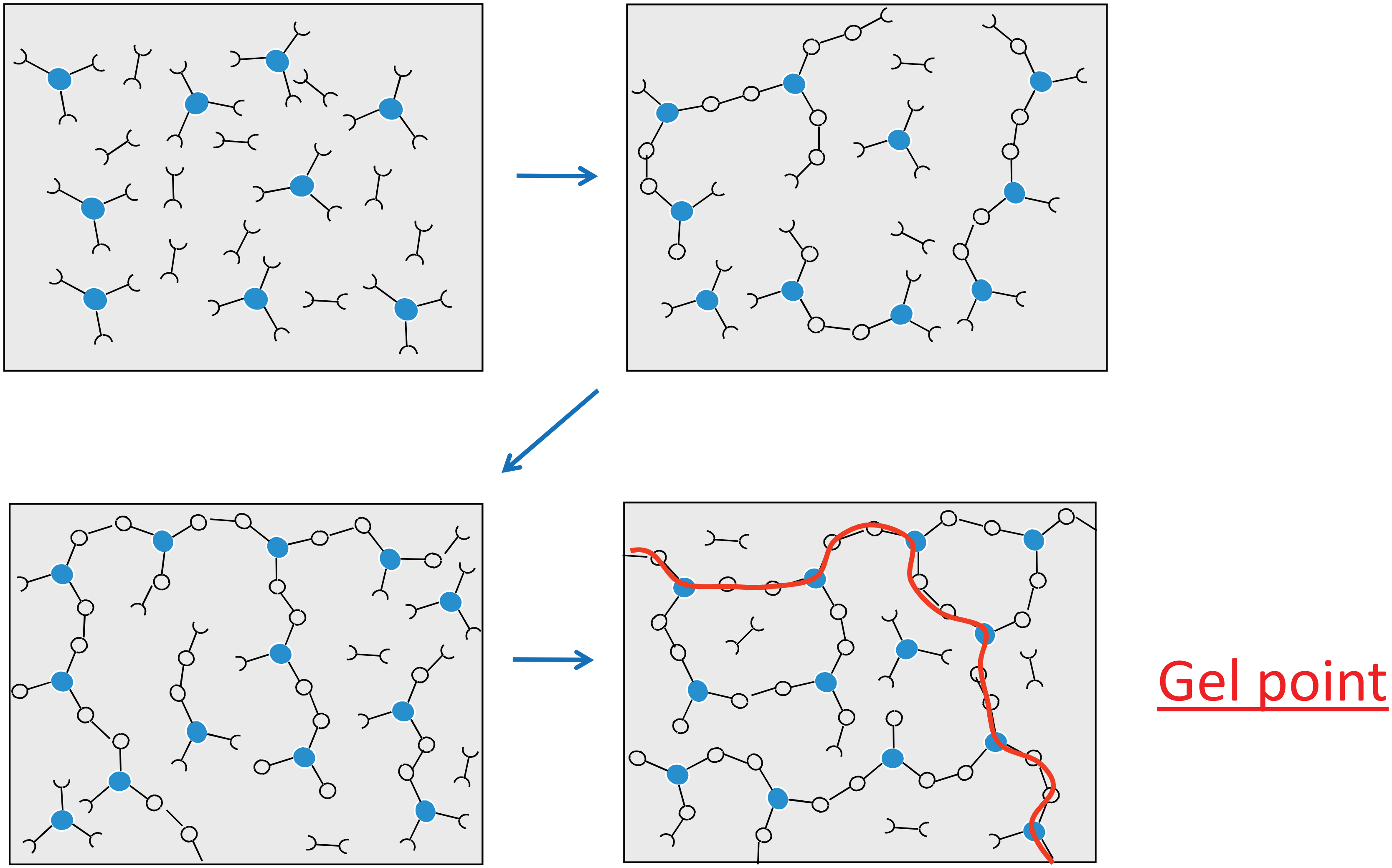
- Thermosetting polymers are perhaps the most challenging samples to analyze on rheometers as they challenge all instrument specifications both high and low.

- The change in modulus as a sample cures can be as large as 7-8 decades and change can occur very rapidly.

Thermosets Analysis

- Monitor the curing process
  - Viscosity change as function of time or temperature
  - Gel time or temperature
- Test methods for monitoring curing
  - Temperature ramp
  - Isothermal time sweep
  - Combination profile to mimic process
- Analyze cured material's mechanical properties (G', G", tan δ , T_g etc.)

Structural Development During Curing

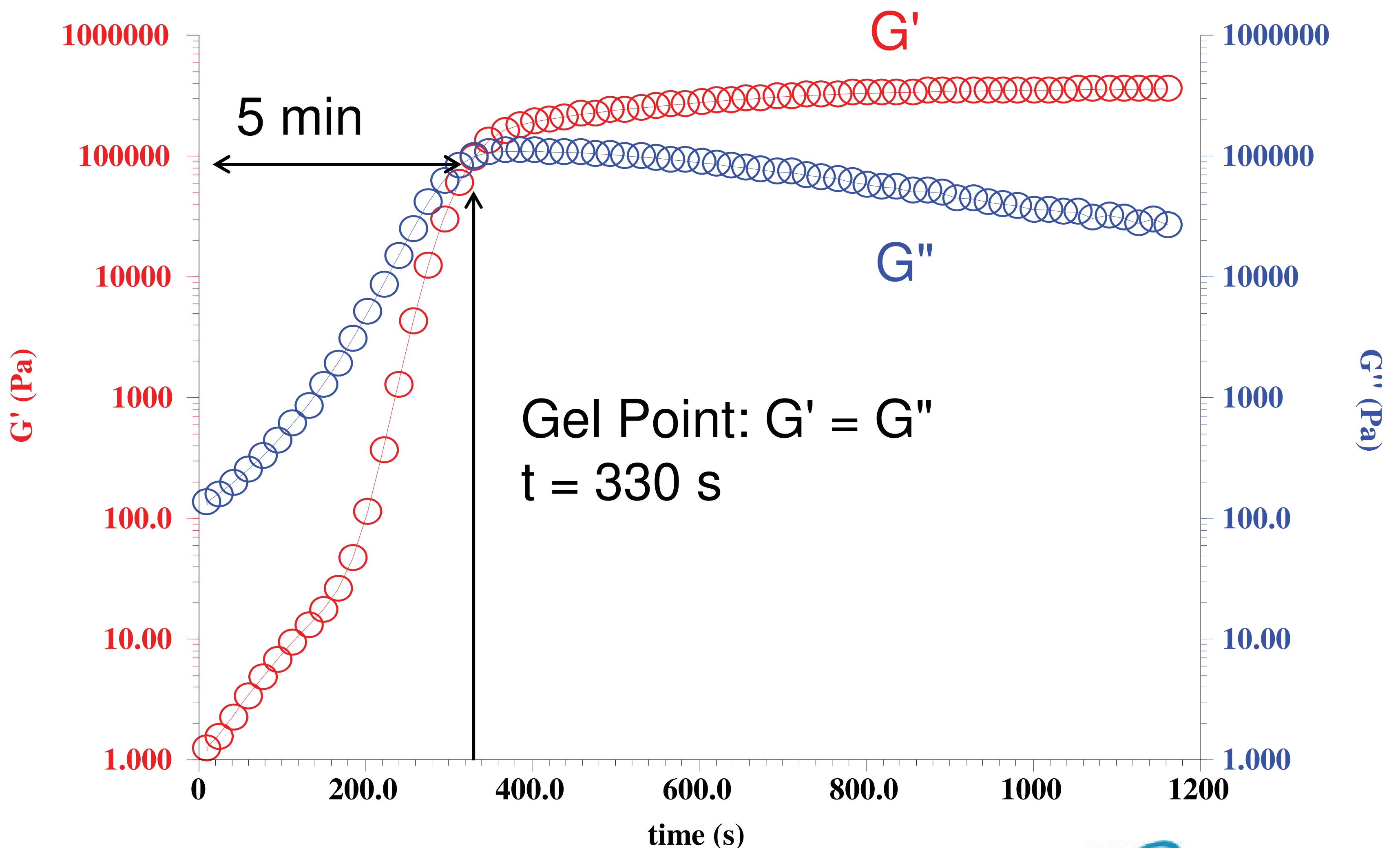


At the Gel Point

- Molecular weight M_w goes to infinity
- System loses solubility
- Zero shear viscosity goes to infinity
- Equilibrium Modulus is zero and starts to rise to a finite number beyond the gel point

Note: For most applications, gel point can be considered as when G' = G" and tan δ = 1

Curing Analysis: Isothermal Curing



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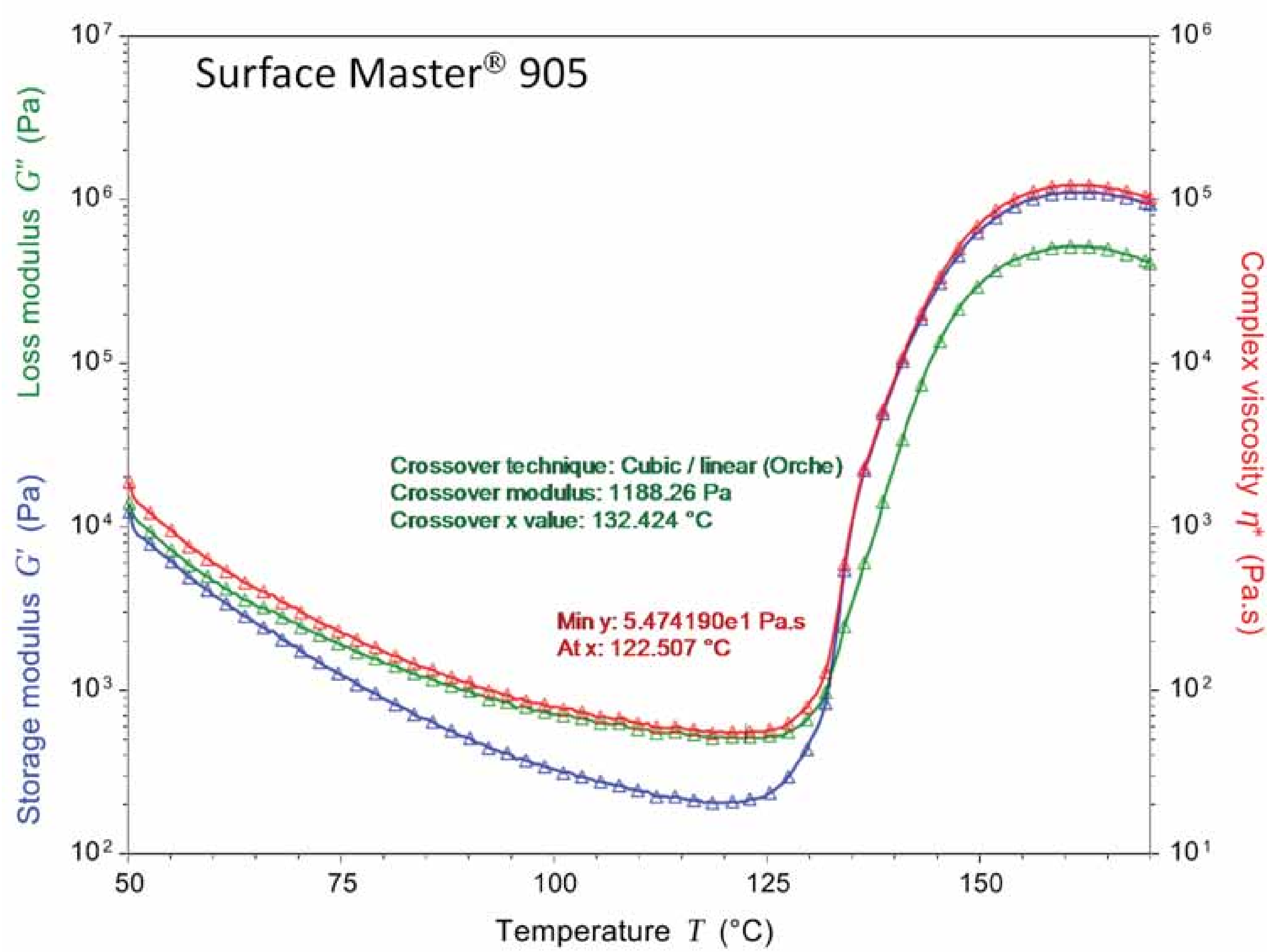
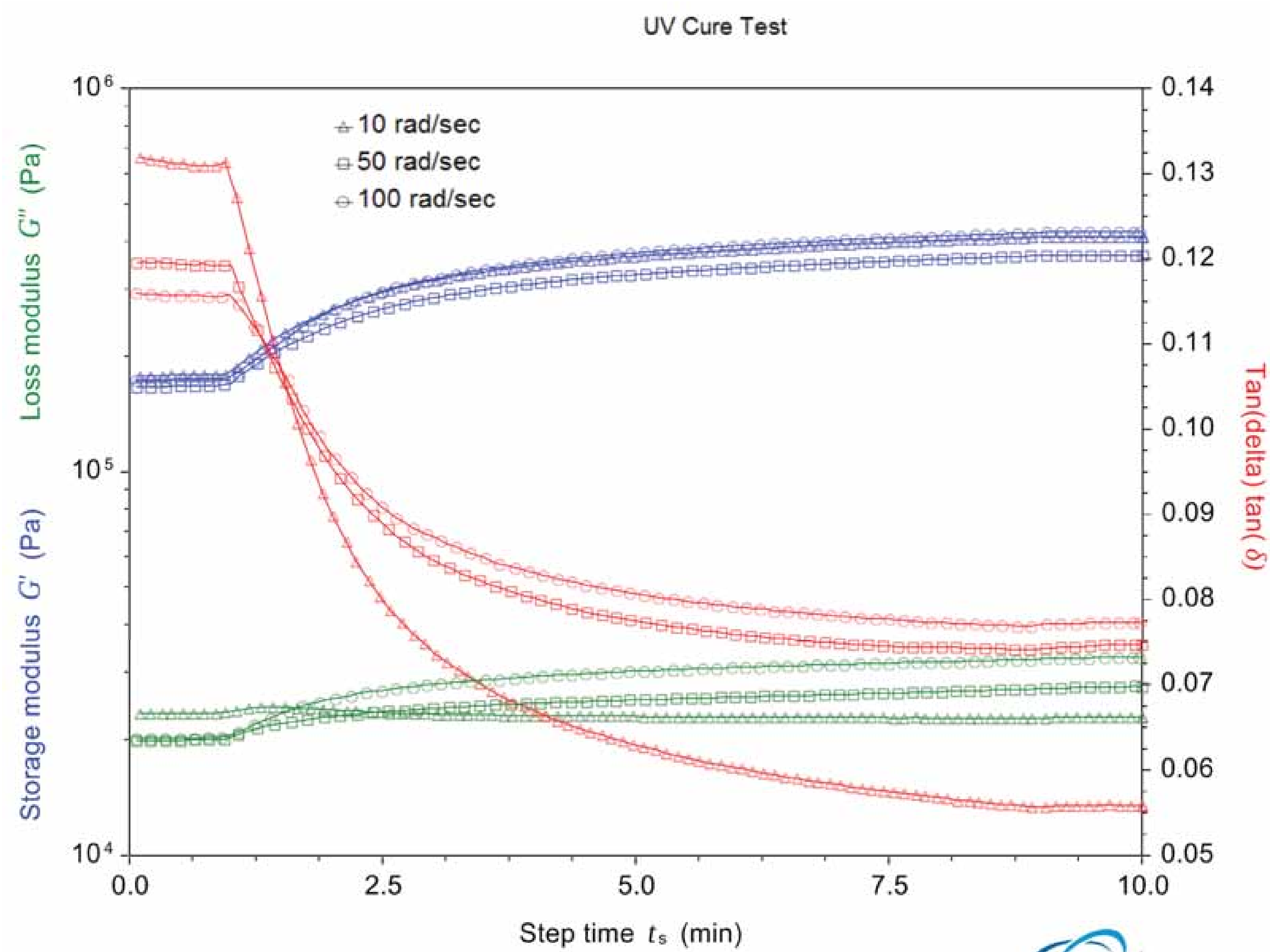
Thermoset Using a Temperature Ramp



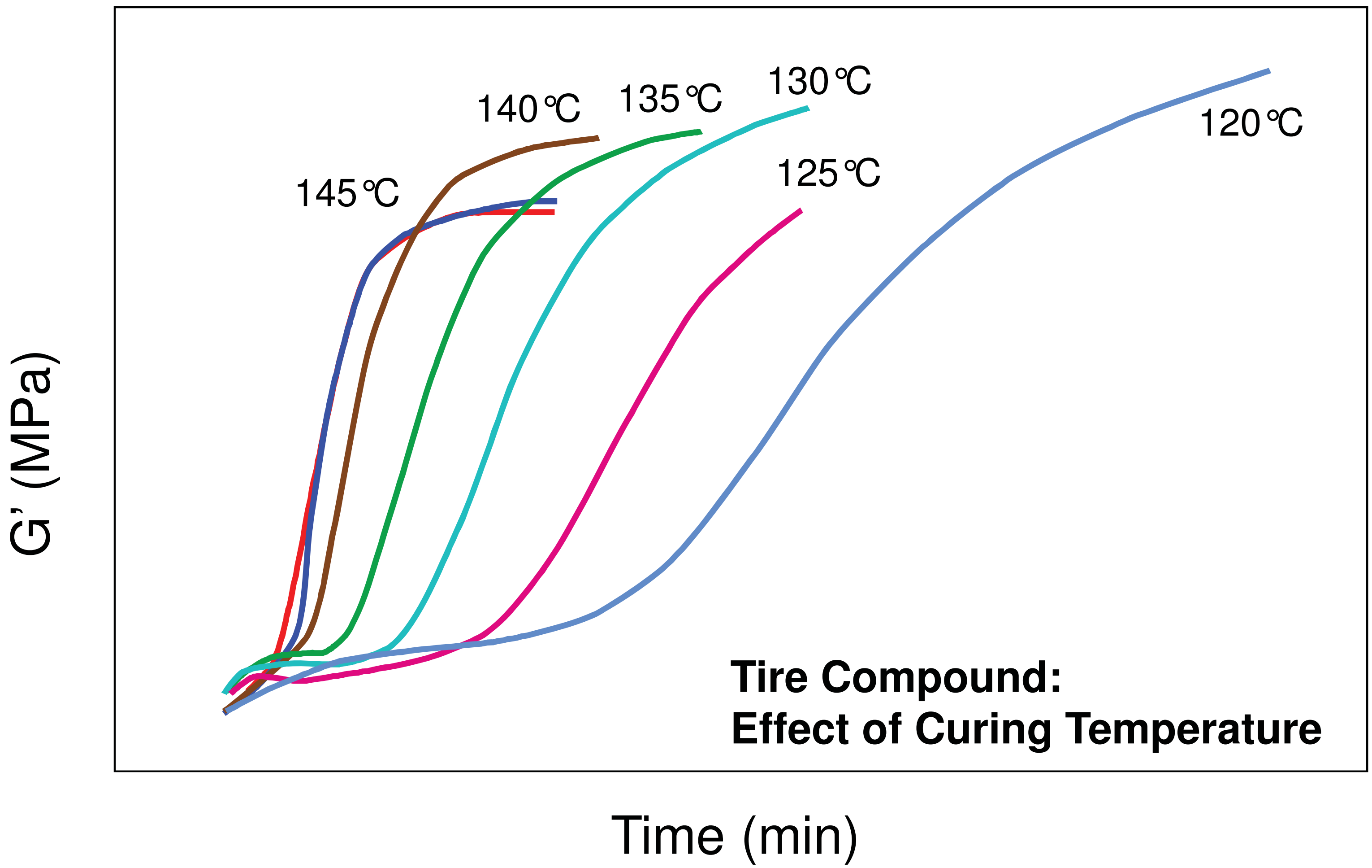
At the Gel Point Continued…

- The process of viscosity increasing takes place in two stages: the gelation process (frequency independent) and vitrification (related to the network Tg relative to cure temperature and is frequency dependent).
- When you look at an isothermal cure at a constant frequency the modulus crossover point has both the information of gelation and vitrification.
  - To avoid this, run multiple isothermal runs at different frequencies and plot the cross over in tan delta. This is the frequency independent gel point.
    - Alternatively, use a single mutliwave test

Gel Point using Tan Delta



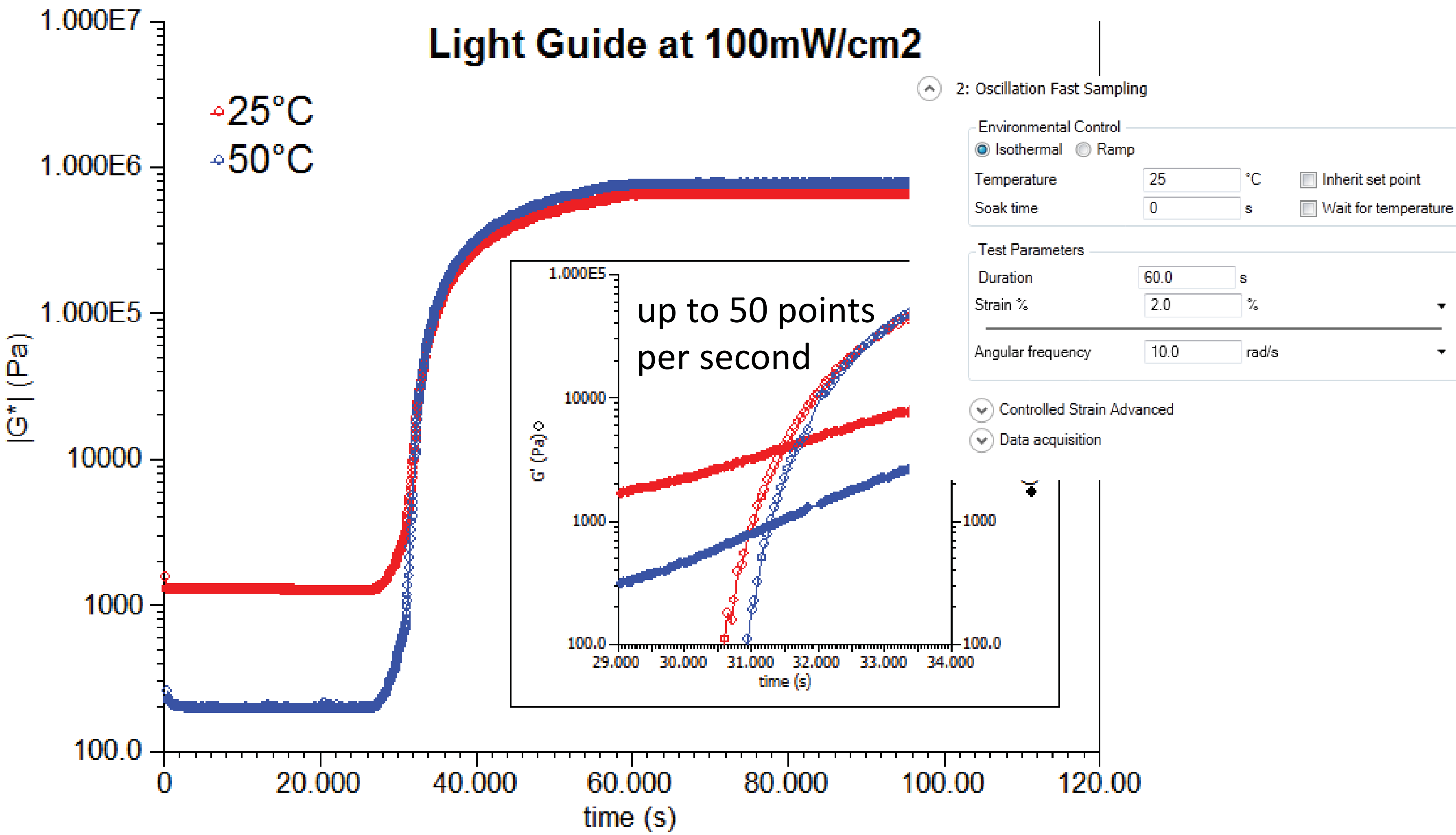
Isothermal Curing



UV Light Guide Curing Accessory

- Collimated light and mirror assembly insure uniform irradiance
- Maximum intensity at plate 300 mW/cm^2
- Broad range spectrum with main peak at 365 nm
- Cover with nitrogen purge ports
- Optional disposable acrylic plates

UV Cure Profile Changes with Temperature



Polymer Structure-Property Characterization

- Glass transition
- Secondary transitions
- Crystallinity
- Molecular weight/cross-linking
- Phase separation (polymer blends, copolymers,...)
- Composites
- Aging (physical and chemical)
- Curing of networks
- Orientation
- Effect of additives

Reference: Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 489.

How to Measure Glass Transition

G' Onset: Occurs at lowest temperature - Relates to mechanical failure

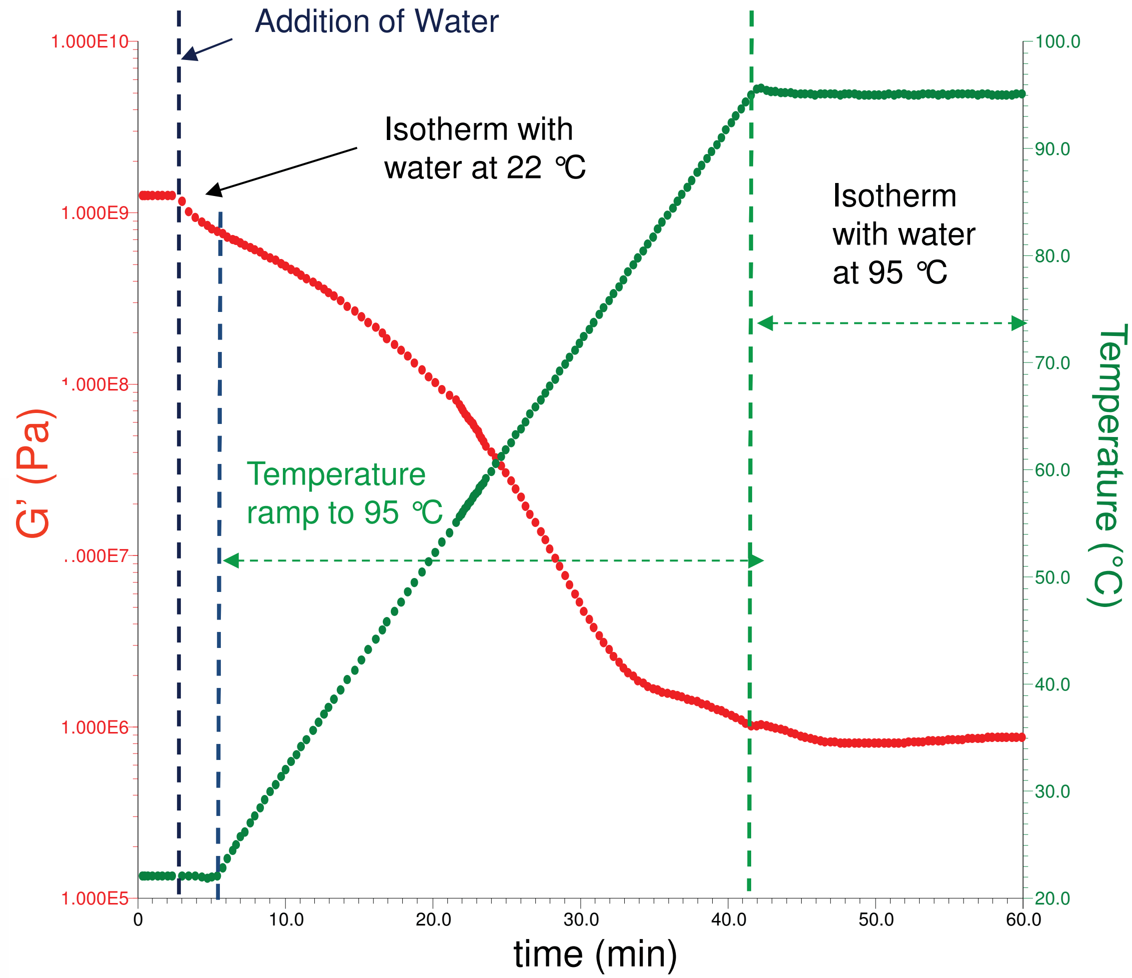
G" Peak: Occurs at middle temperature - more closely related to the physical property changes attributed to the glass transition in plastics. It reflects molecular processes - agrees with the idea of T_g as the temperature at the onset of segmental motion.

tan δ Peak: Occurs at highest temperature - used historically in literature - a good measure of the "leatherlike" midpoint between the glassy and rubbery states - height and shape change systematically with amorphous content.

Reference: Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 980.

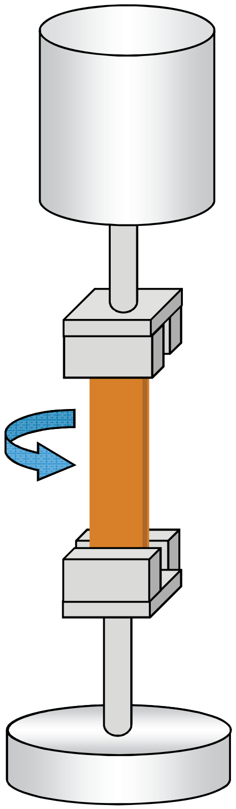
Pasta Cooked in Torsion Immersion

- Allows samples to be characterized while fully immersed in a temperature controlled fluid using Peltier Concentric Cylinder Jacket
- Track changes in mechanical properties such as swelling or plasticizing



Testing Solids on a Rheometer

- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment
  - DMA functionality is standard with ARES G2 and optional DHR



$$E = 2G(1 + \nu) \qquad \nu : \text{Poisson's ratio}$$

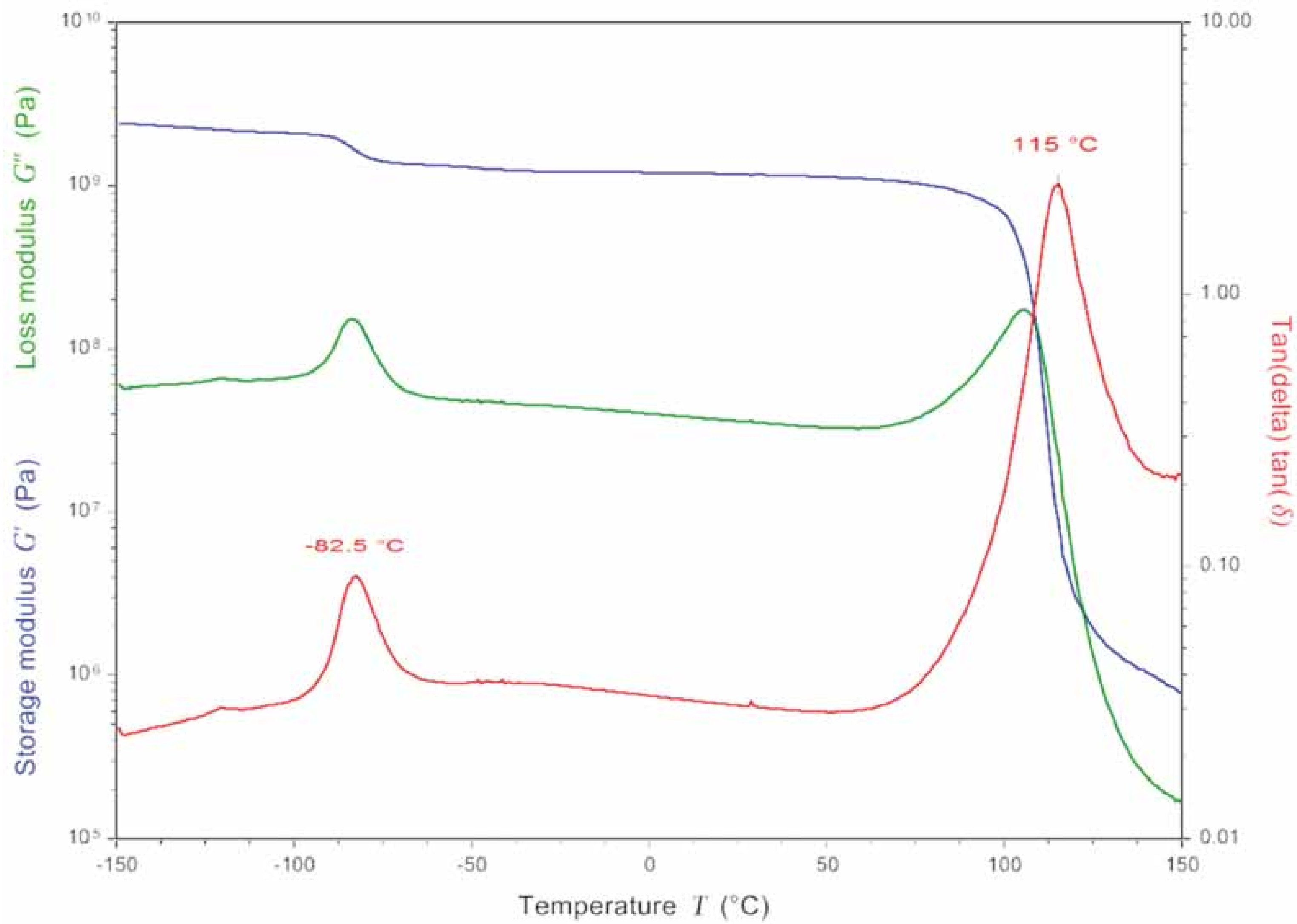
Modulus: G', G'', G^*

Rectangular and cylindrical torsion

Modulus: E', E'', E^*

DMA 3-point bending and tension (Cantilever not shown)

Glass Transition- ABS



The Glass & Secondary Transitions

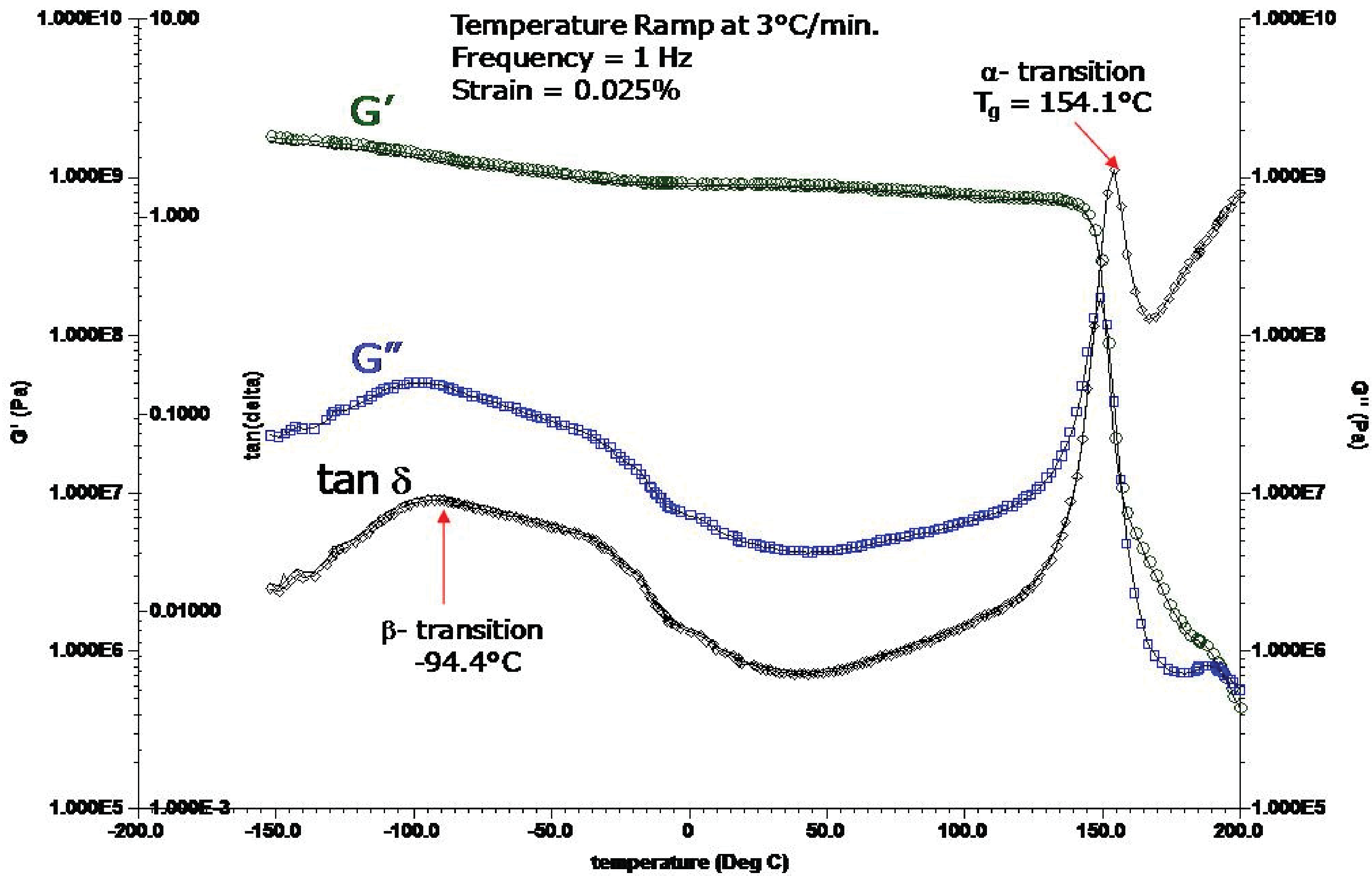
Glass Transition - Cooperative motion among a large number of chain segments, including those from neighboring polymer chains

Secondary Transitions

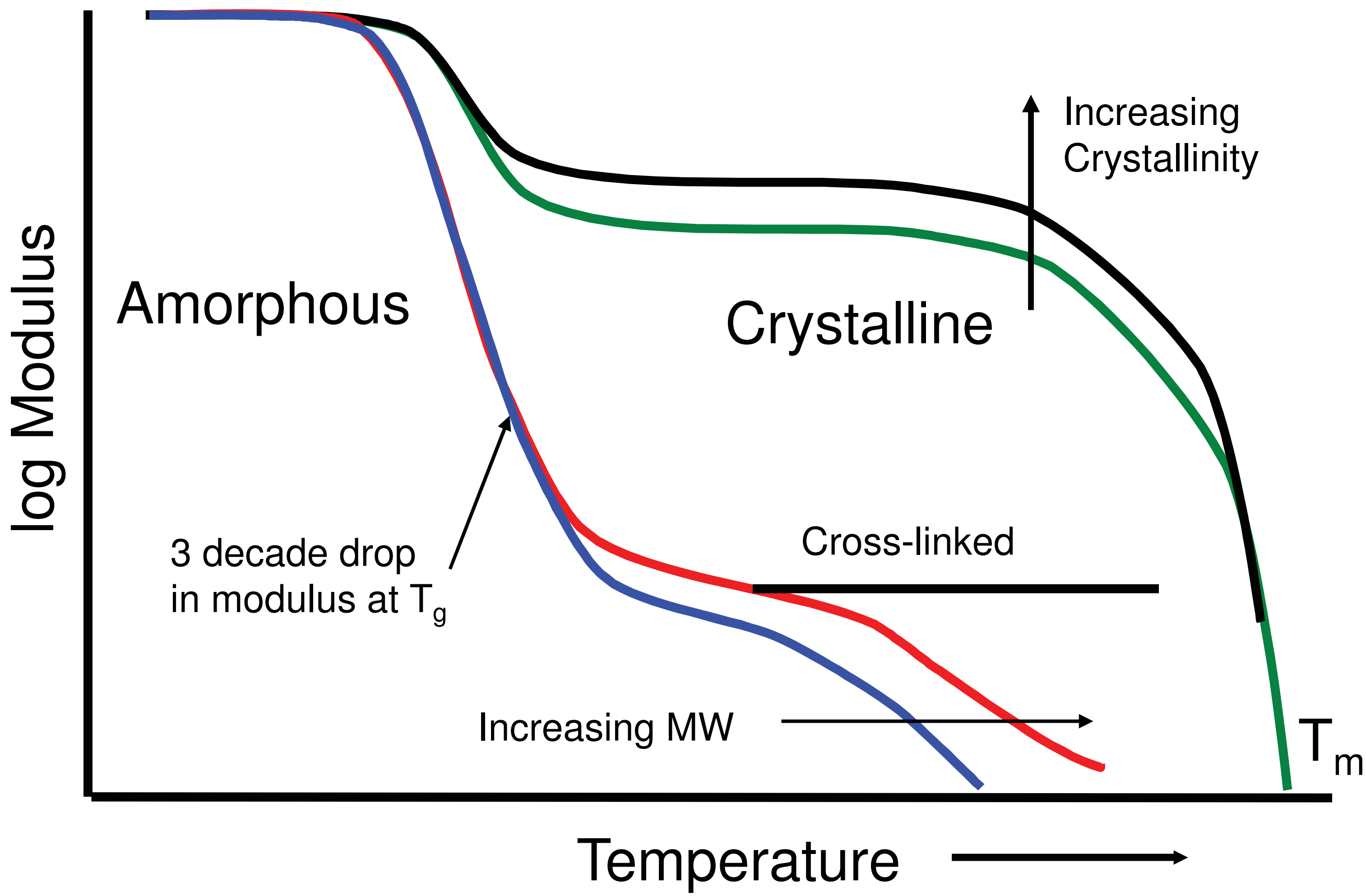
- Local main-chain motion - intramolecular rotational motion of main chain segments four to six atoms in length
- Side group motion with some cooperative motion from the main chain
- Internal motion within a side group without interference from side group
- Motion of or within a small molecule or diluent dissolved in the polymer (e.g. plasticizer)

Reference: Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 487.

Polycarbonate in Torsion



Crystallinity, Molecular Weight, and Crosslinking



Applications of Rheology

Structured Fluids

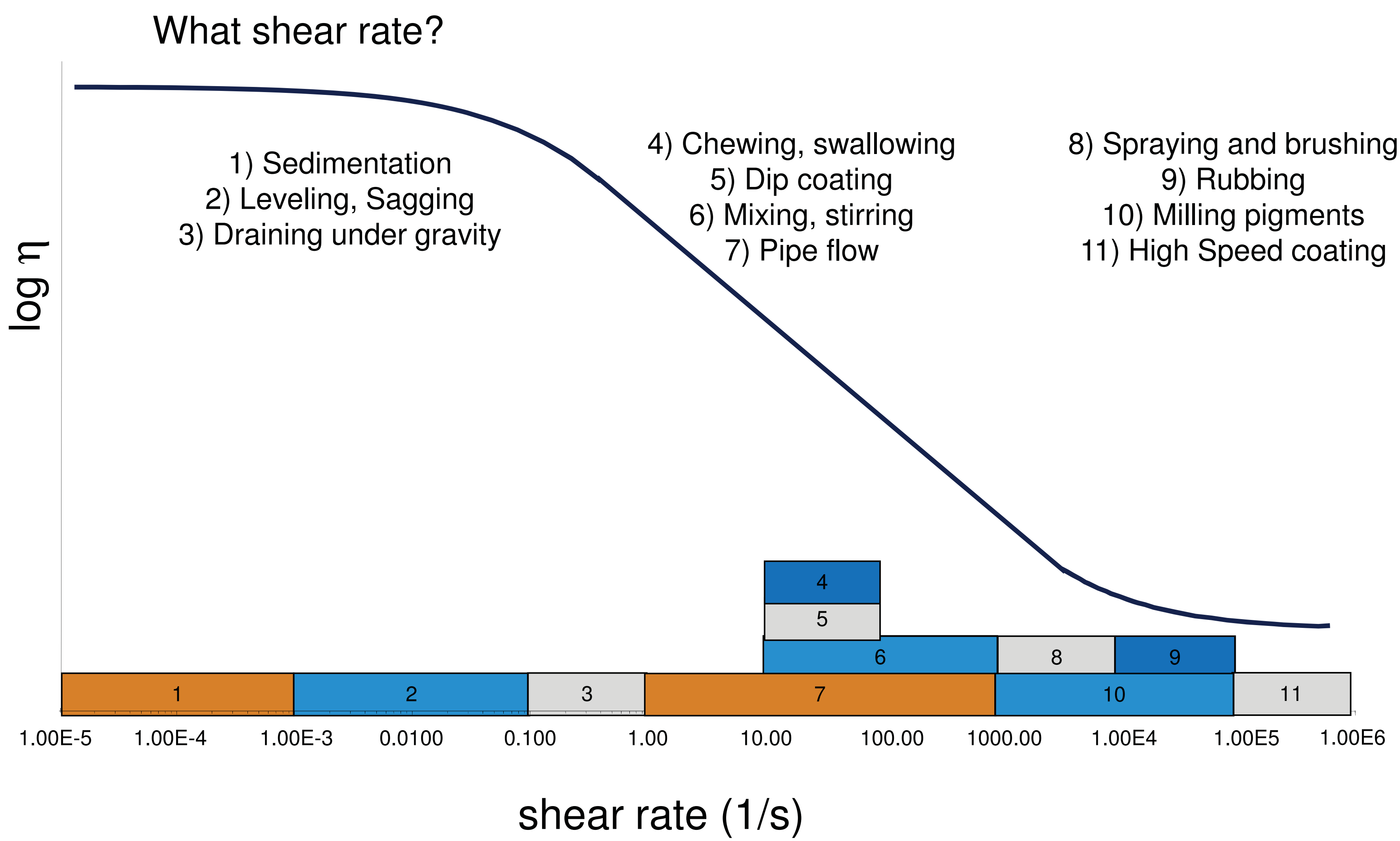
Structured Fluids

- Multiphase systems consisting of a dispersed phase (solid, fluid, gas) in surrounding fluid phase

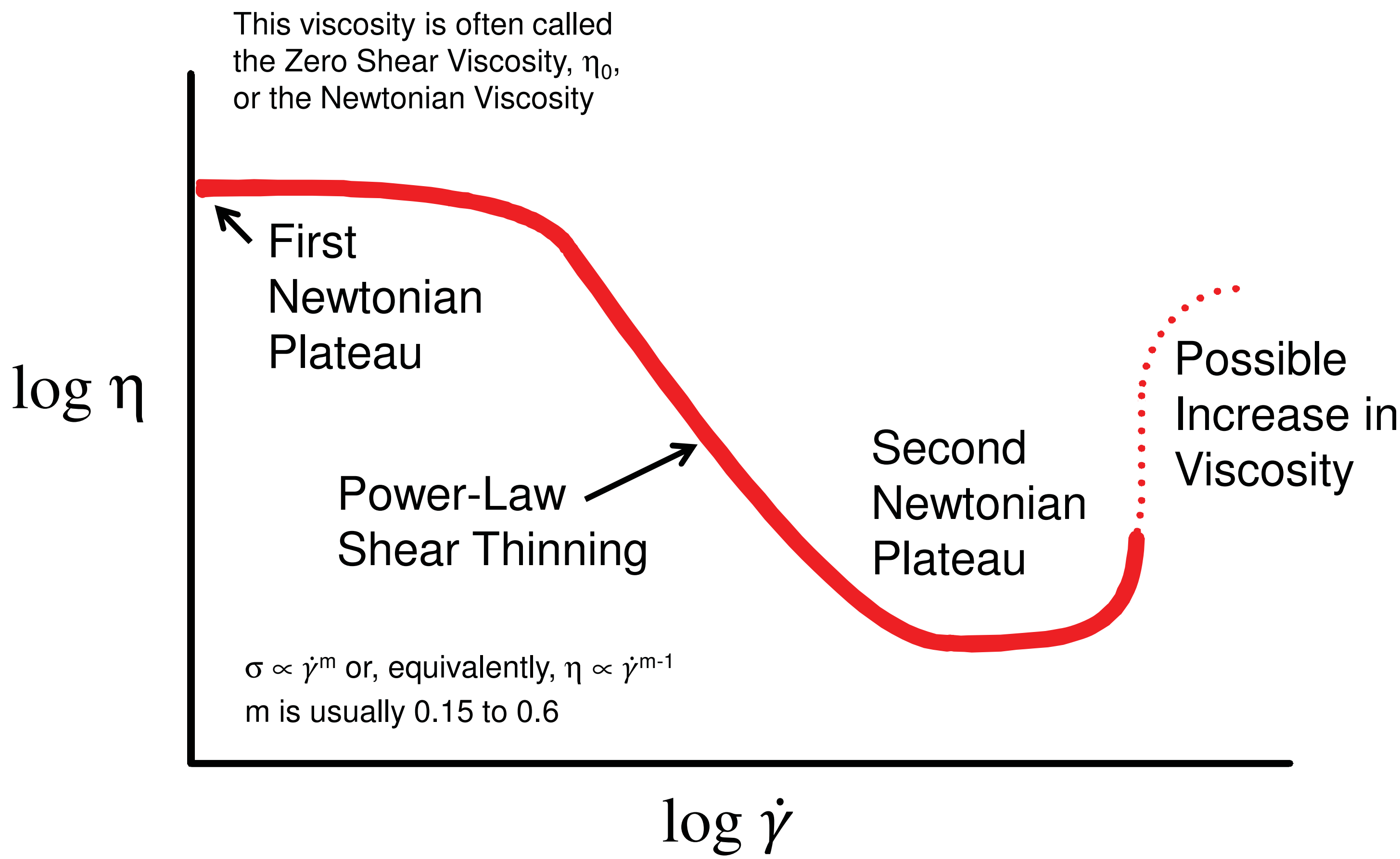
- Examples are:
  - Paints
  - Coatings
  - Inks
  - Personal Care Products
  - Cosmetics
  - Foods

- Properties:
  - Yield Stress
  - Non-Newtonian Viscous Behavior
  - Thixotropy
  - Elasticity

Idealized Flow Curve

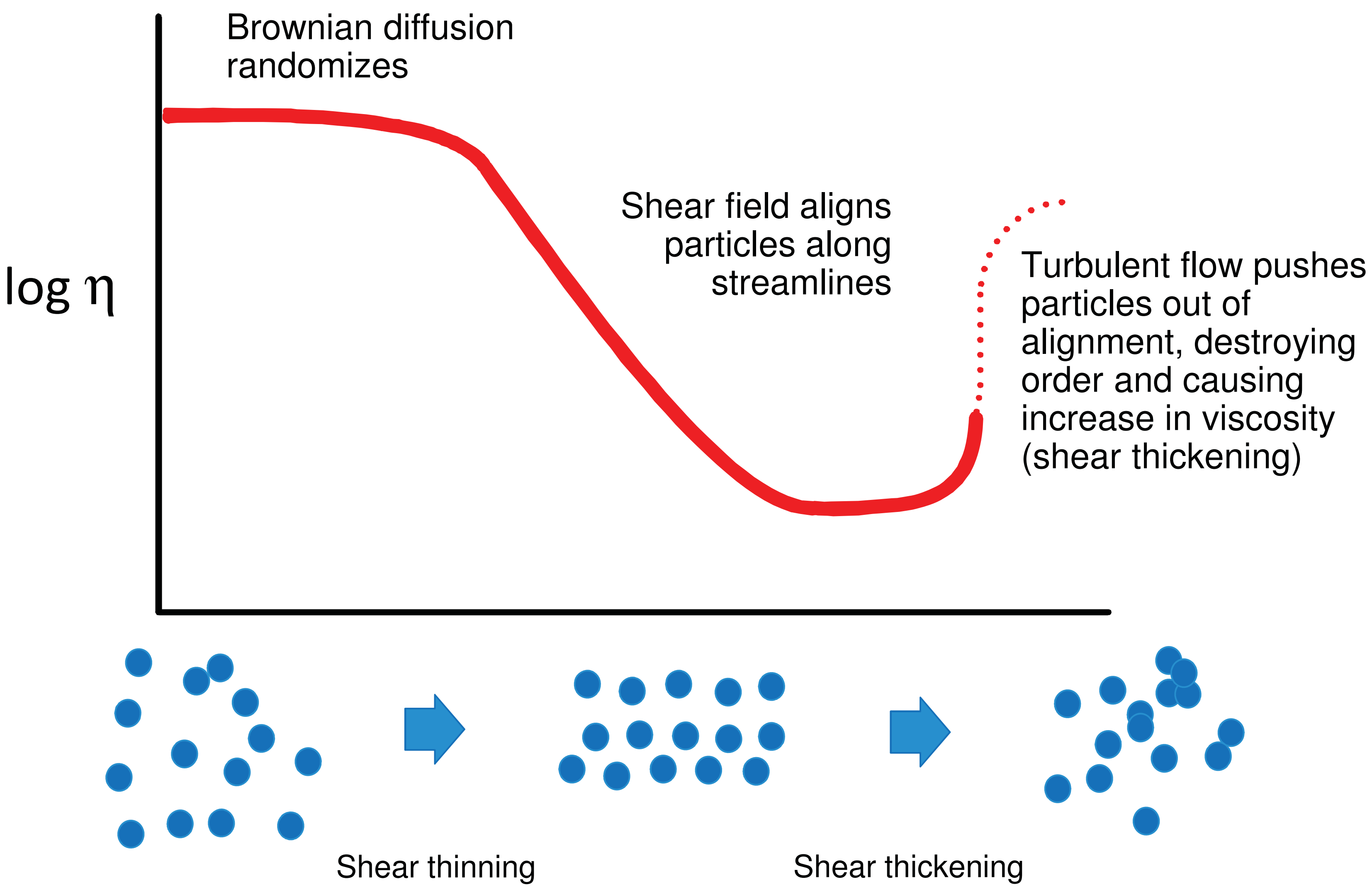


General Viscosity Curve for Suspensions

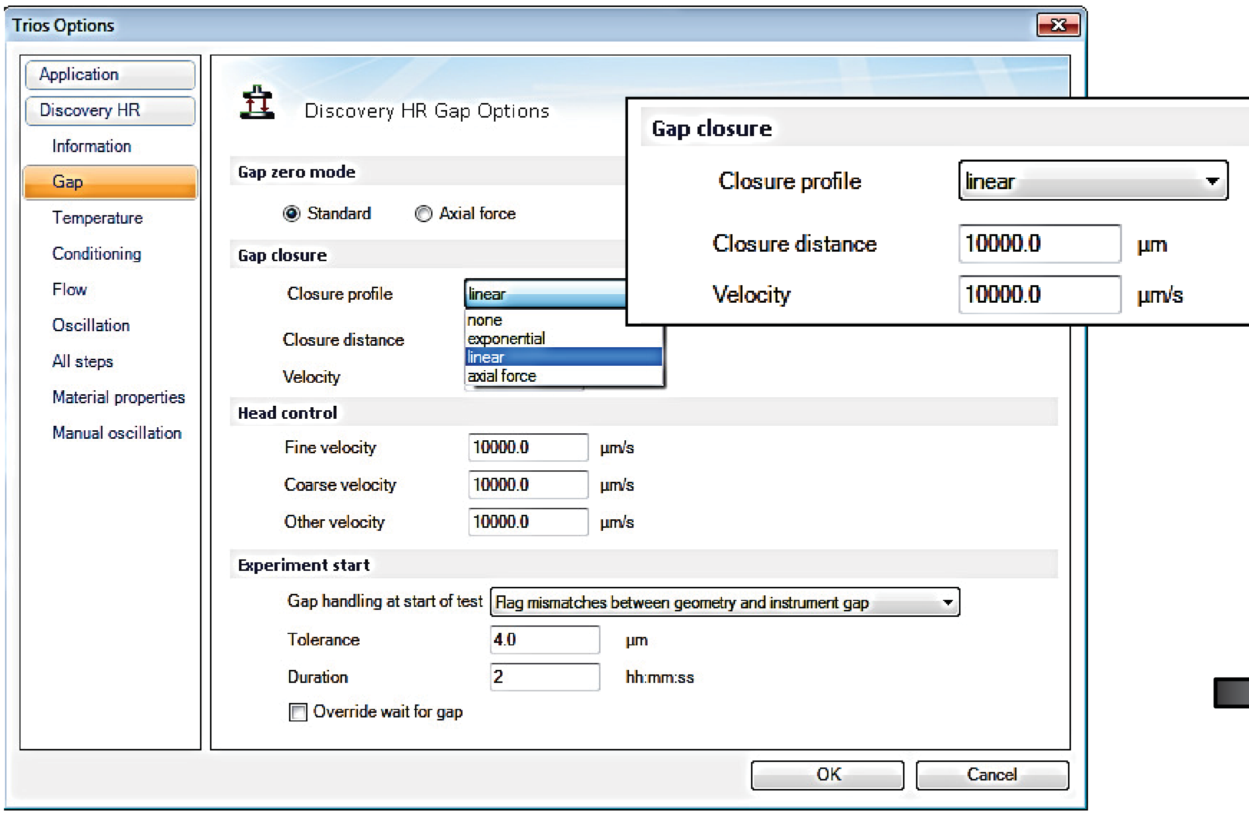


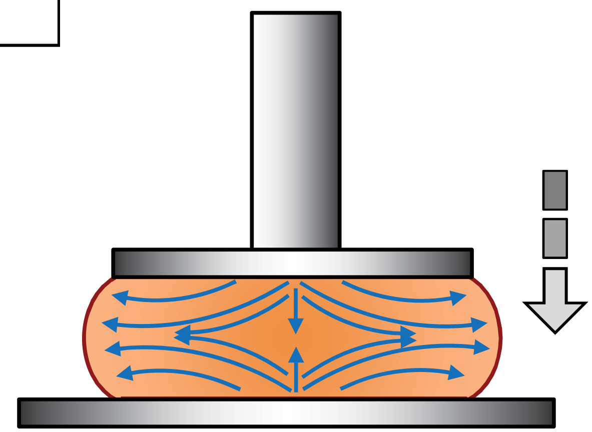
Reference:Barnes, H.A., Hutton, J.F., and Walters, K., An Introduction to Rheology, Elsevier Science B.V., 1989. ISBN 0-444-87469-0

Reason for Shape of General Flow Curve



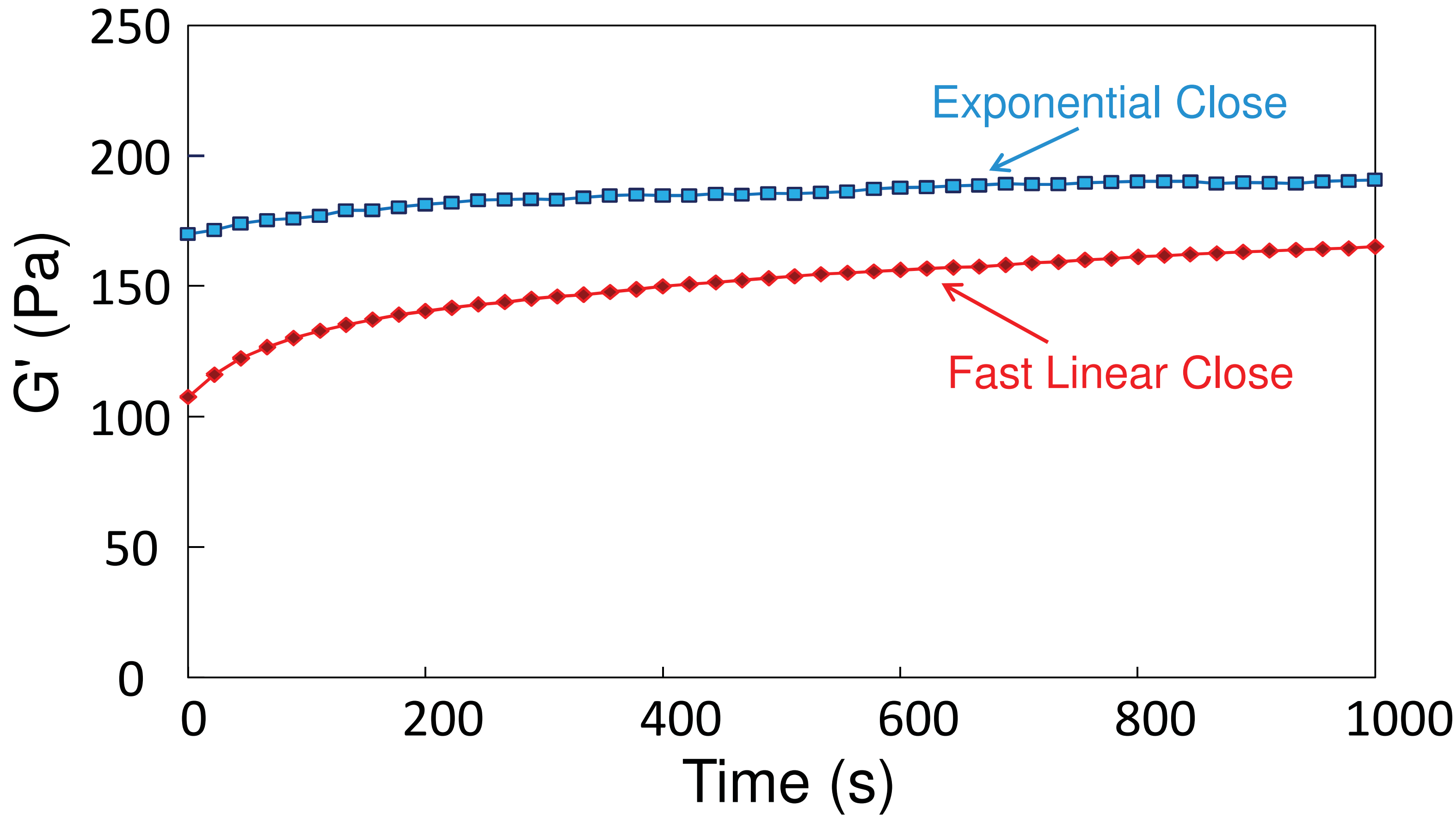
Closing the Gap





- Linear or Exponential speed profile after reaching 'Closure Distance'
- Normal Force set not to exceed a certain value after reaching the user defined 'Closure Distance'

Comparison of Linear and Exponential Closing

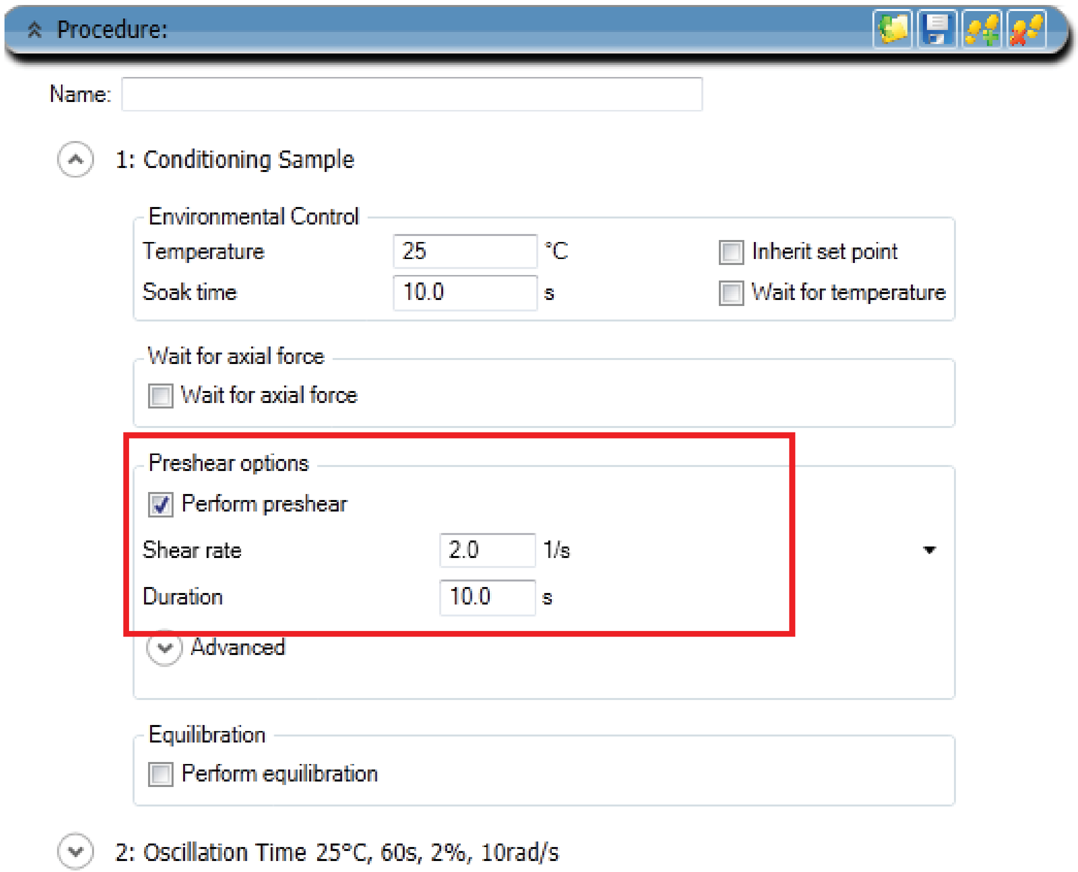


Lowering the gap can introduce shear, breaking down weakly structured samples
Reducing the gap closure speed can minimize this effect

Using Pre-Shearing

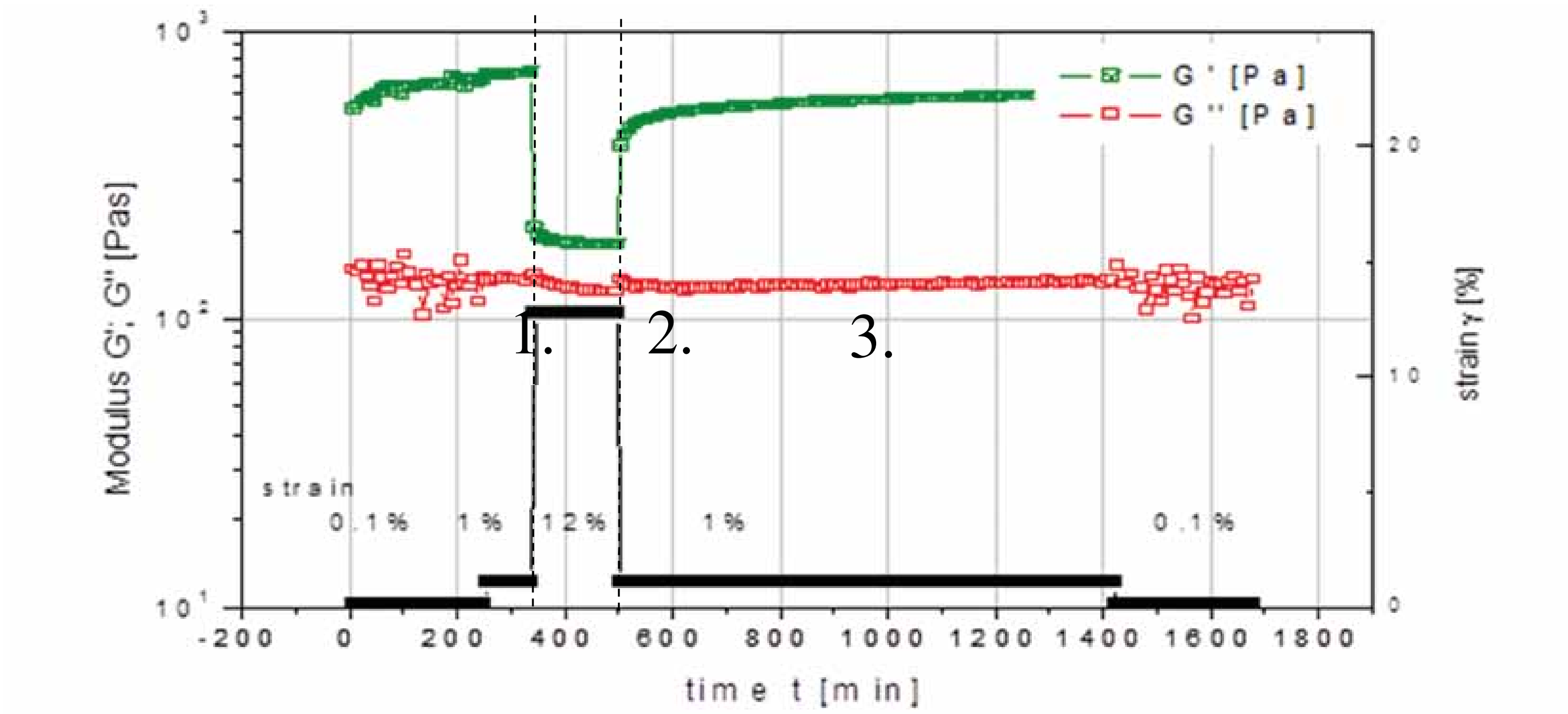
- Monitor the viscosity signal during the pre-shear to determine if the rate and duration are appropriate
  - If the viscosity is increasing during the pre-shear, the sample is rebuilding. The pre-shear should be higher than the shear introduced during loading to erase sample loading history
  - The viscosity should decrease and then level off
  - Typical Pre-Shear: 1- 100 sec^{-1}, 30-60 seconds
- Use an amplitude sweep to determine what strain to use for time sweep
  - A high strain will break down the sample, and not allow rebuilding
  - A low strain will give a weak signal
- Based on the Time Sweep, determine an appropriate equilibration time for that sample

Pre-shear Conditions



- The goal for pre-shear is to remove the sample history at loading
- For high viscosity sample, use low rate (10 1/s) and long time (2 min.)
- For low viscosity sample, use high rate (100 1/s) and short time (1 min.)

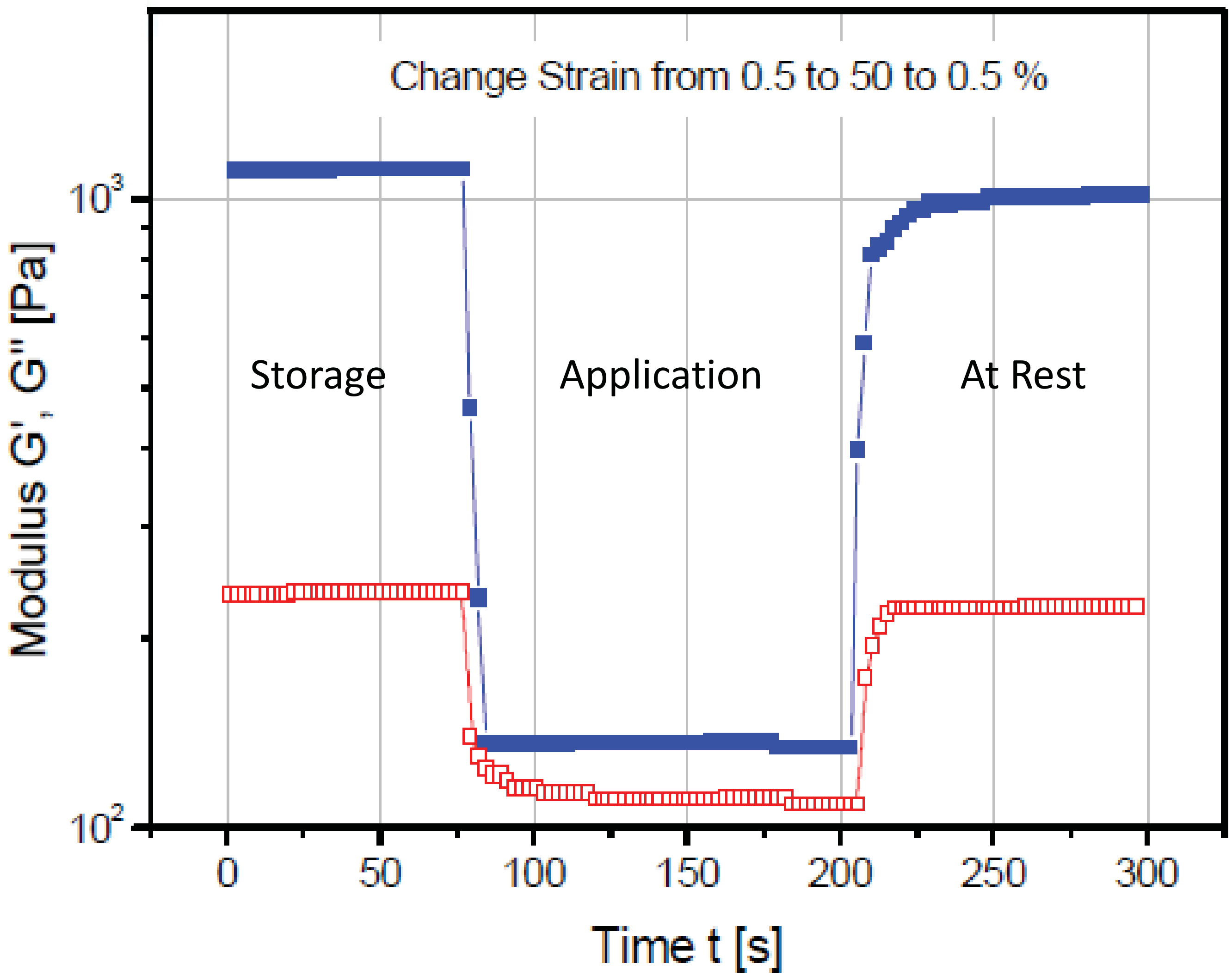
Structured Fluid: Pre-testing



Three consecutive time sweeps:

- Time sweep within LVR (check if loading destroyed structure)
- Time sweep at large strain
- Time sweep back to LVR (check structure rebuild)

Time Sweeps- Hand Cream



Yield Stress

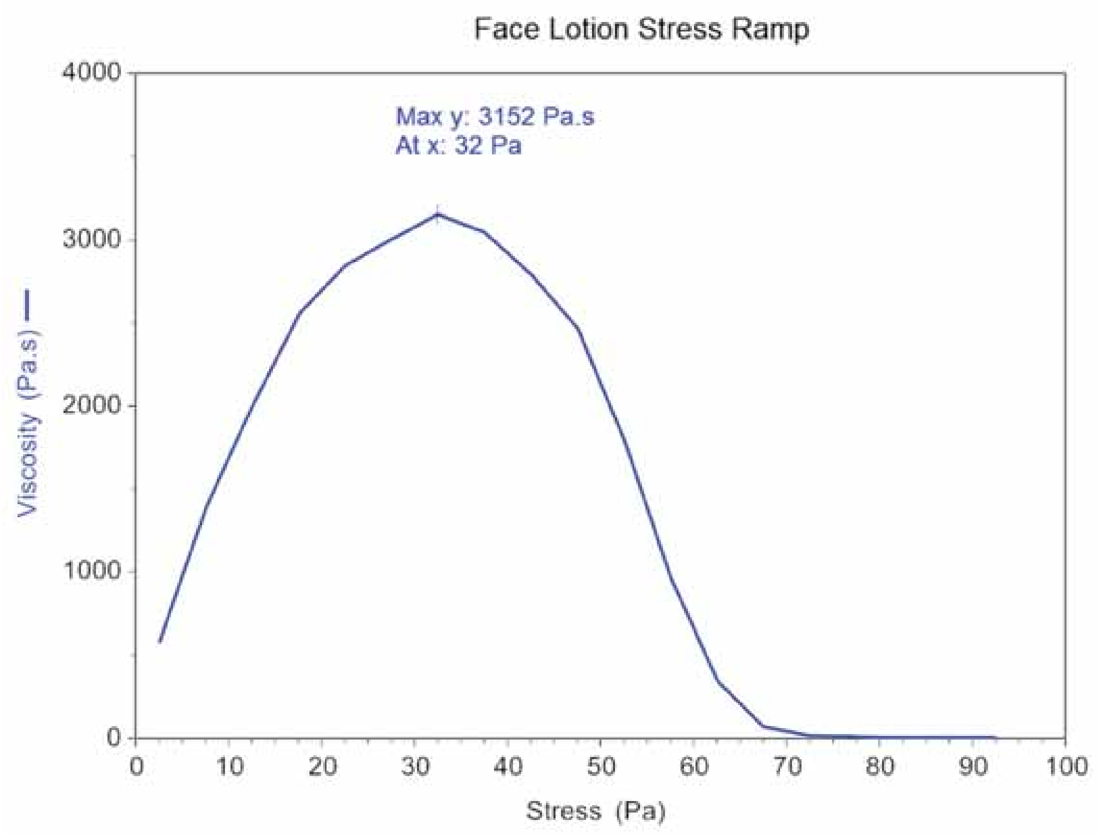
- Structured fluids exhibit yield-like behavior, changing from ‘solid-like’ to readily flowing fluid when a critical stress is exceeded. Rheological modifiers are often used to control the yield behavior of fluids.

- There are multiple methods to measure Yield stress. The apparent yield stress measured is not a single value, as it will vary depending on experimental conditions.

Why modify the yield behavior?

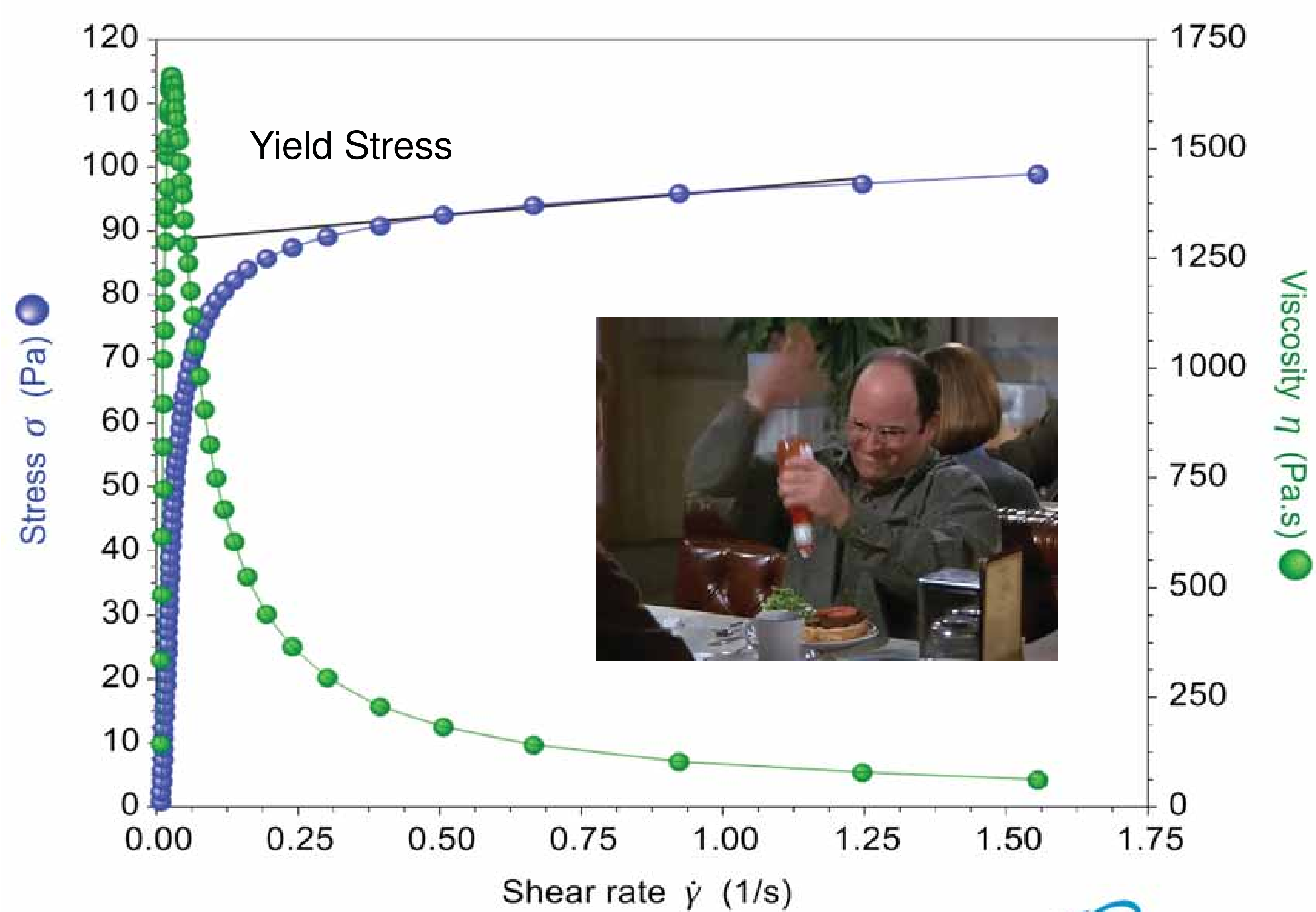
- to avoid sedimentation and increase the shelf live
- to reduce flow under gravity
- to stabilize a fluid against vibration

Yield Stress in a Flow Stress Ramp



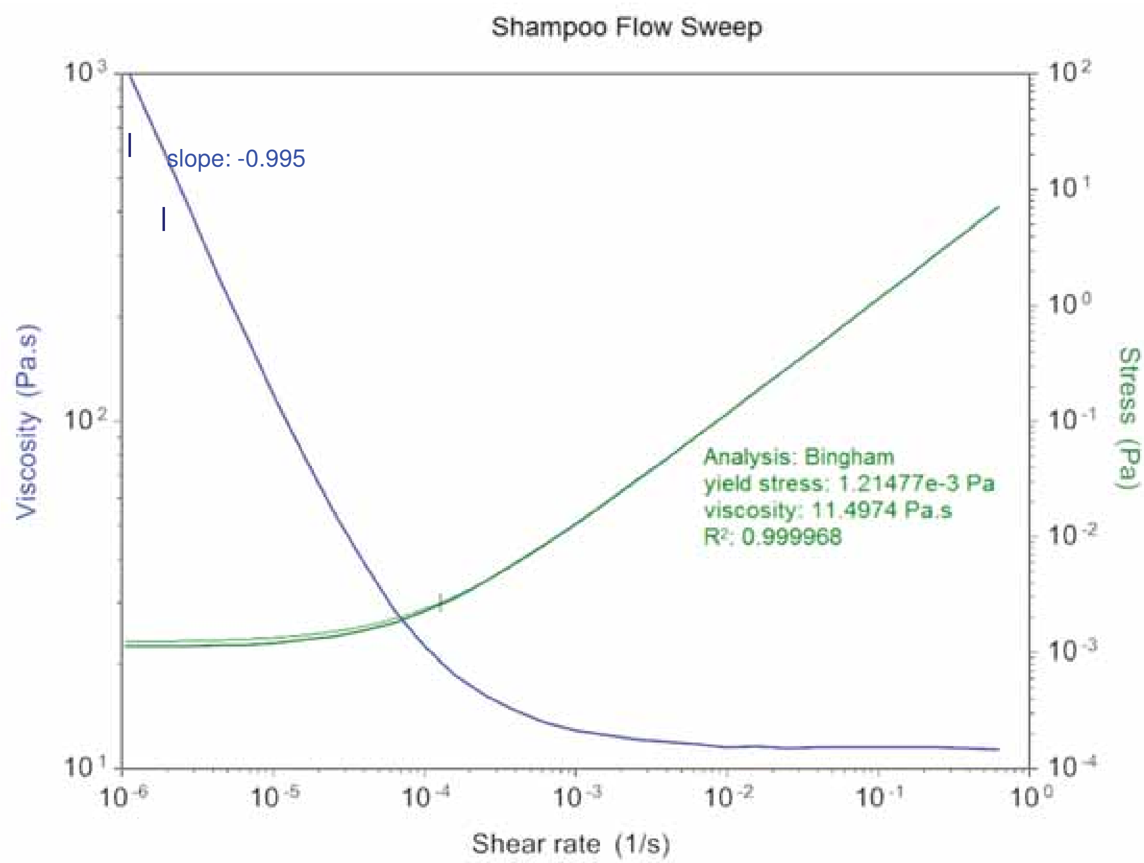
- Stress is ramped **linearly** from 0 to a value above Yield Stress and the stress at viscosity maximum can be recorded as Yield Stress
- The measured yield value will depend on the rate at which the stress is increased. The faster the rate of stress increase, the higher the measured yield value

Yield Stress in a Flow Stress Ramp



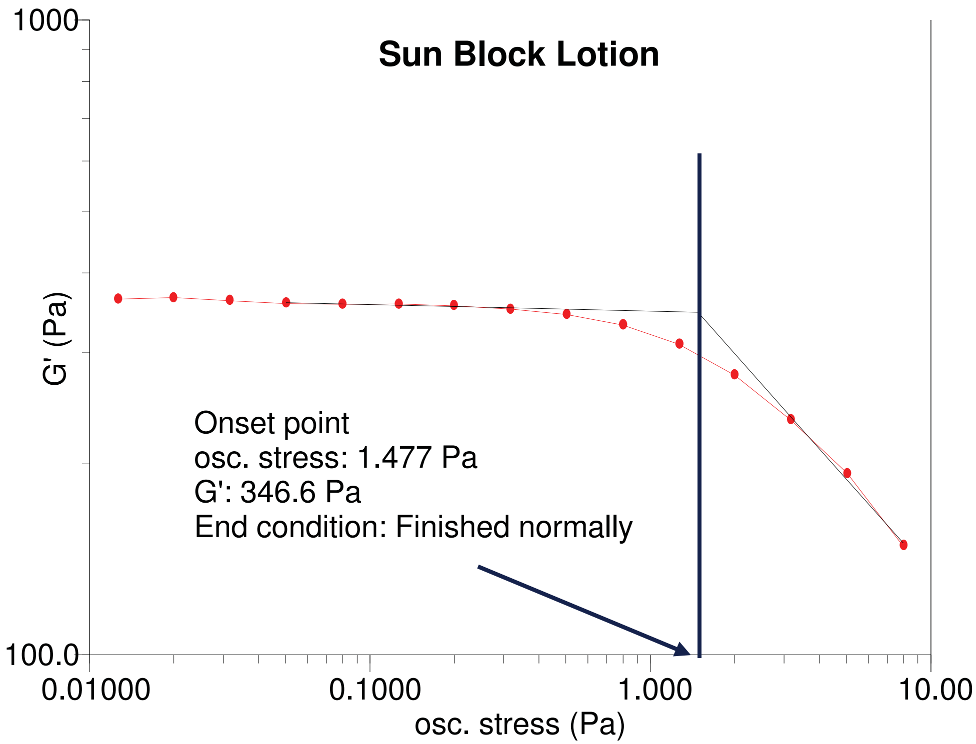
Yield Stress: Flow Sweep Down - Rate Control

When the Yield Stress is small, a flow rate sweep from high to low shear rate is preferred



- Eliminates start-up effects for more accurate measurements
- Initial high shear rate acts as a pre-shear, erasing loading effects
- Steady State sensing allows the sample time to rebuild
- The plateau in shear stress is a measure of the yield stress.
- At the plateau, Viscosity vs. Shear Rate will have a slope of -1

Yield: Stress/Strain Sweep Method

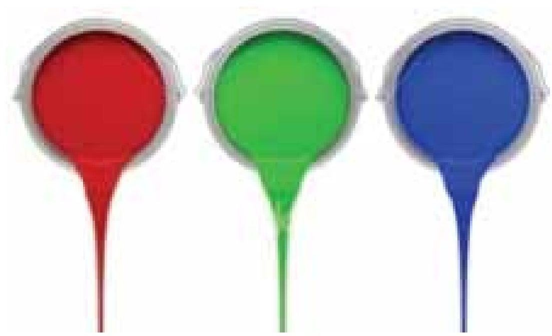


Yield stress of a sun block lotion

- Perform strain or stress sweep in oscillation
- Yield stress is the on set of G' curve. It is the critical stress at which irreversible plastic deformation occurs.

Viscosity Ranges of Paints/Coatings

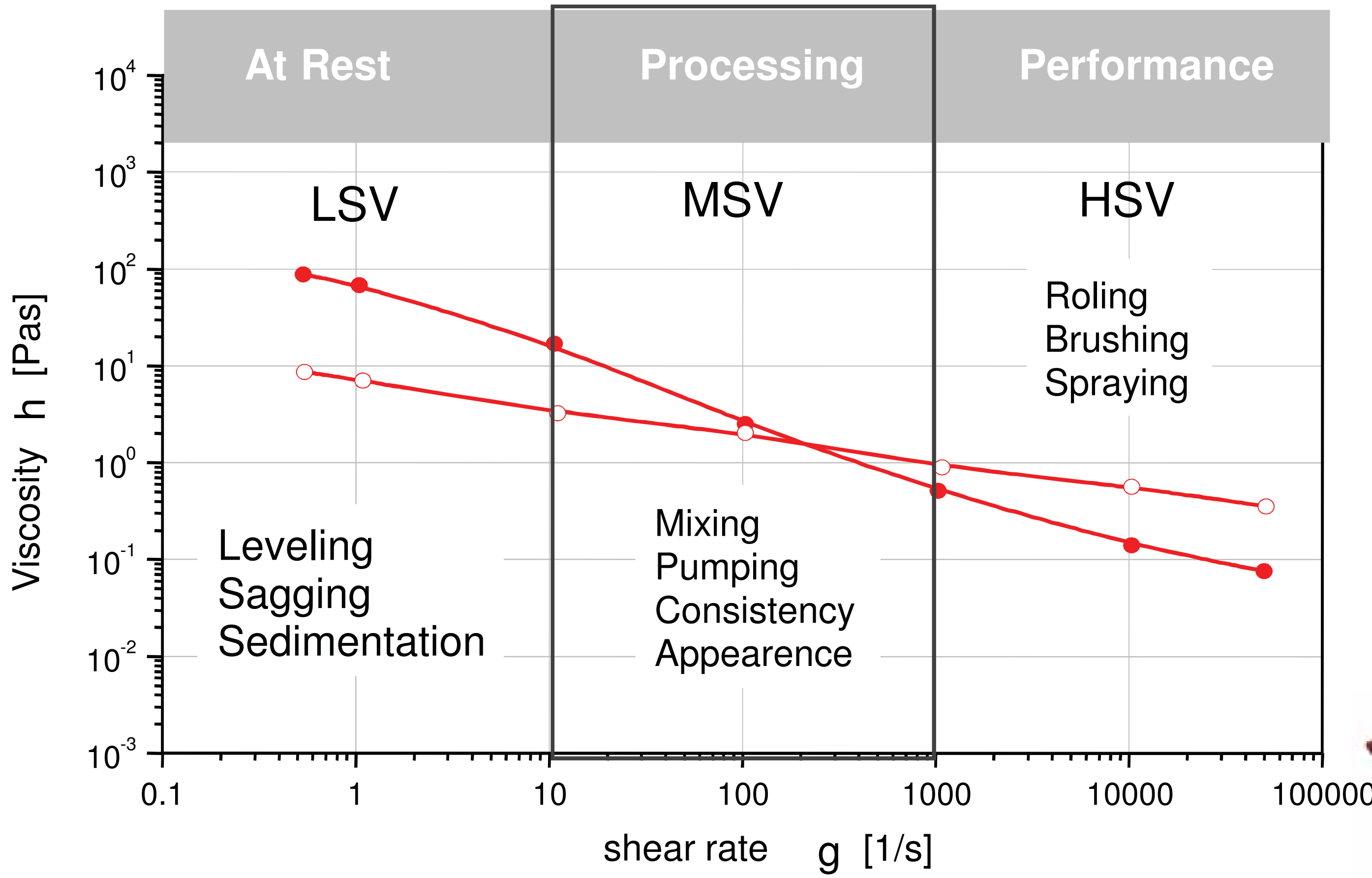
- Low shear viscosity 10^{-3} to 1 s^{-1}
  - leveling, sagging, sedimentation



- Medium shear viscosity $10-10^{3}$ s^{-1}
  - mixing, pumping and pouring

- High shear viscosity 10^{3} - 10^{6} s^{-1}
  - brushing, rolling spraying

Viscosity Ranges of Paints/Coatings



The two coatings show the same consistency after formulation, but they exhibit very different application performance

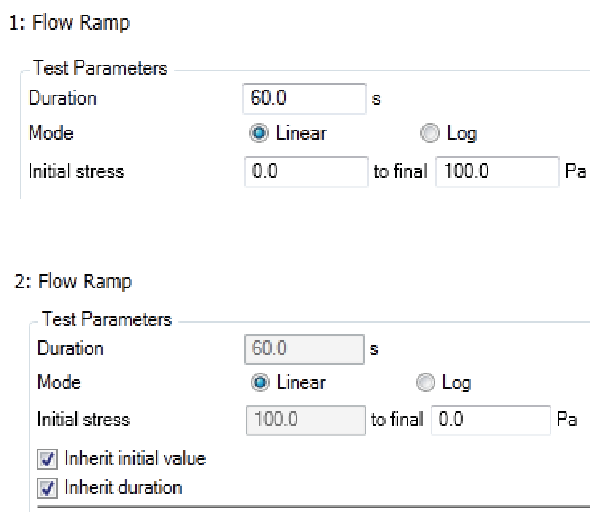
Thixotropy

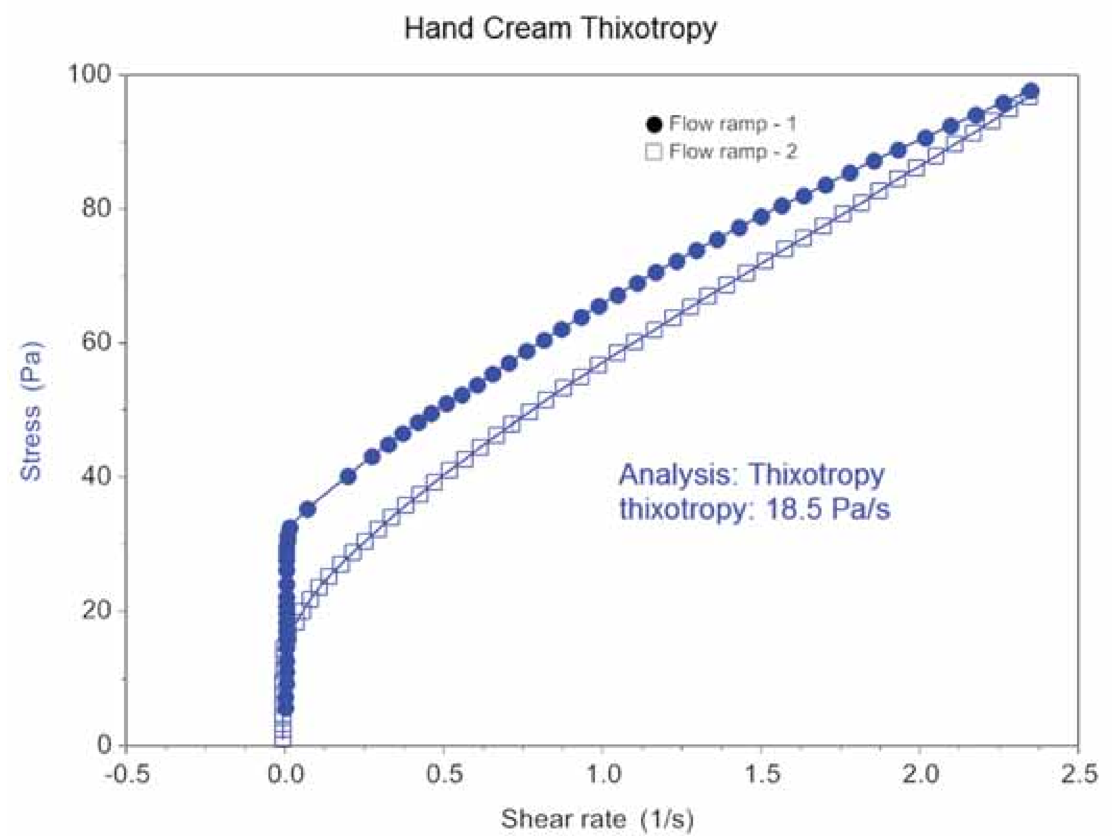
The thixotropy characterizes the time dependence of reversible structure changes in complex fluids. The control of thixotropy is important to control:

- process conditions for example to avoid structure build up in pipes at low pumping rates i.e. rest periods, etc....
- sagging and leveling and the related gloss of paints and coatings, etc..

Thixotropic Loop Test

Stress is ramped up linearly, and then back down, over the same duration





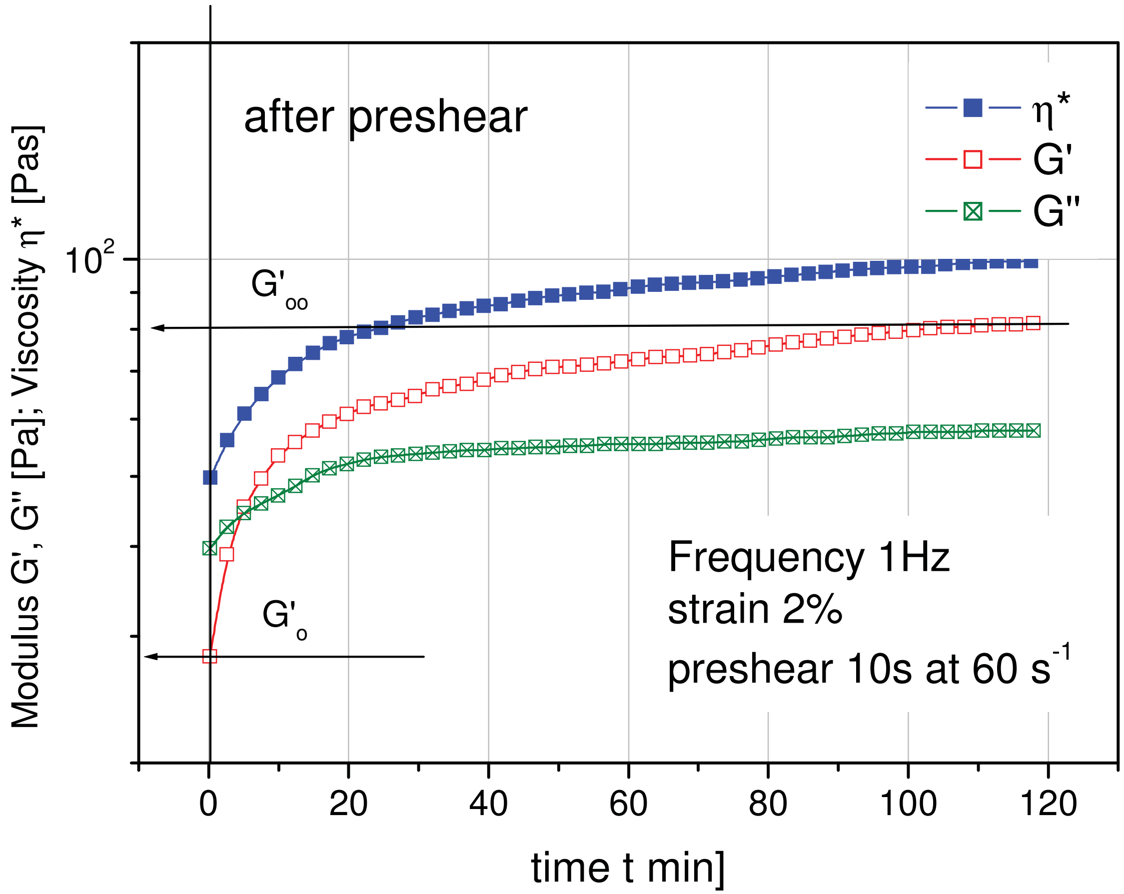
In a thixotropic material, there will be a hysterisis between the two curves

The further the up ramp and down ramp curves differ, the larger the area between the curves, the higher the thixotropy of the material.
See also AAN 016 – Structured Fluids

Structure Recovery

Structure build up

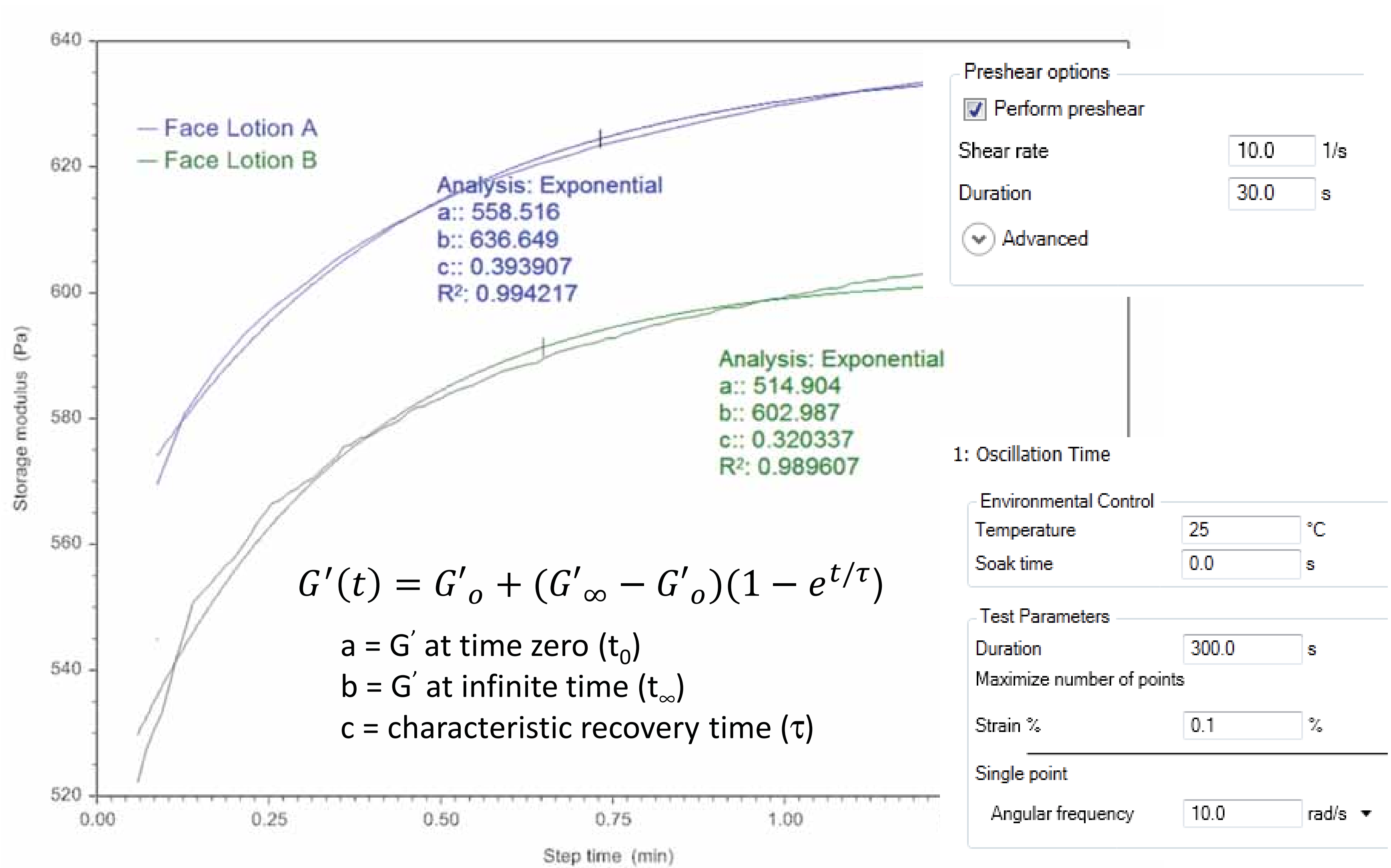
Pre-shear the sample to break down structure. Then monitor the increase of the modulus or complex viscosity as function of time.



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

τ = characteristic recovery time

Time Sweep after Pre-Shearing



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

a = G′ at time zero (t_0)
b = G′ at infinite time (t_∞)
c = characteristic recovery time (τ)

Thixotropic Index & Recovery Time

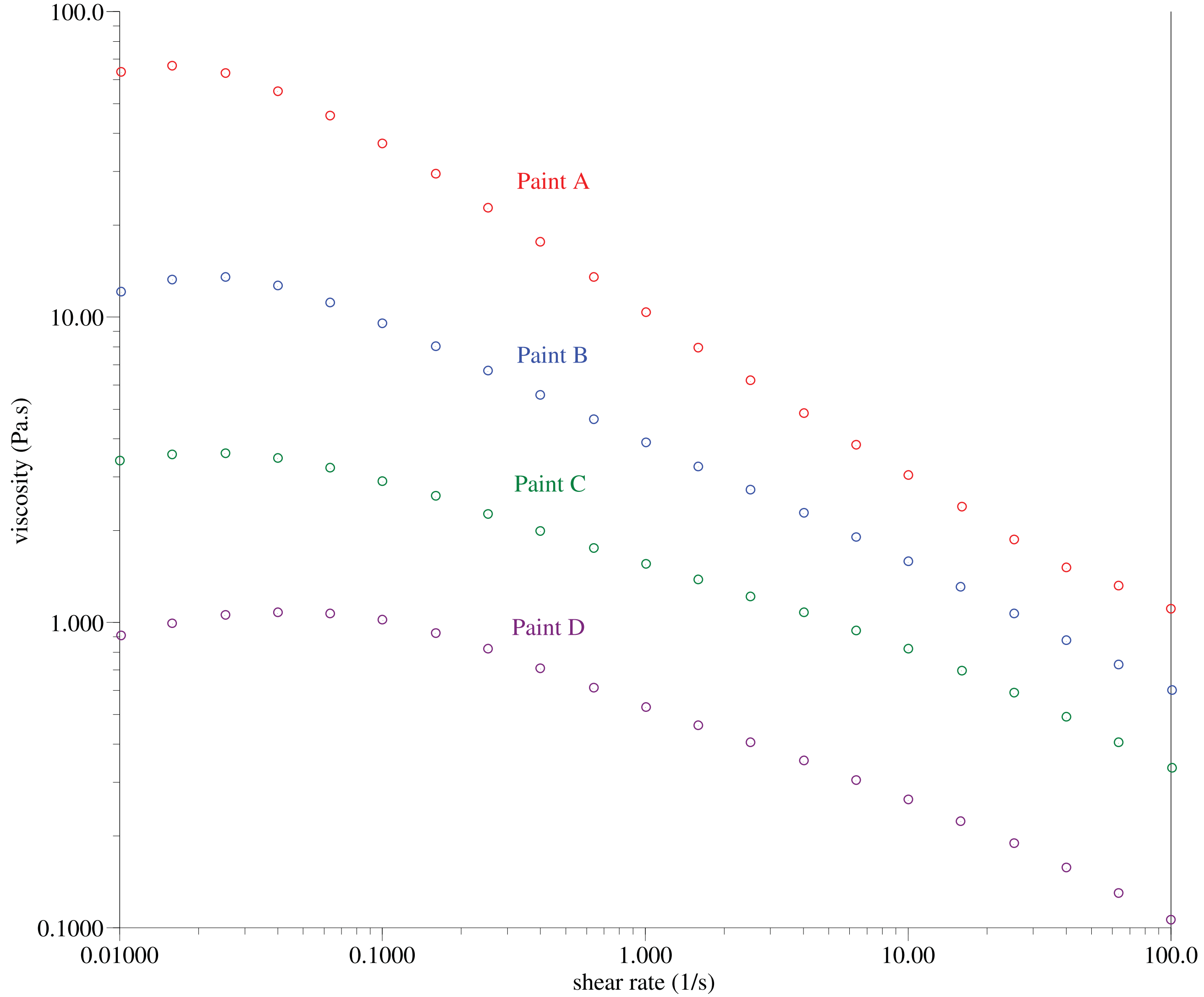
- The non-sagging formula (with additive) has both a shorter recovery time and a higher final recovered viscosity (or storage modulus), and the recovery parameter takes both of these into account to predict significantly better sag resistance.

- The ratio η(∞) /t, is the recovery parameter (a true thixotropic index), and has been found to correlate well to thixotropy-related properties such as sag resistance and air entrainment.

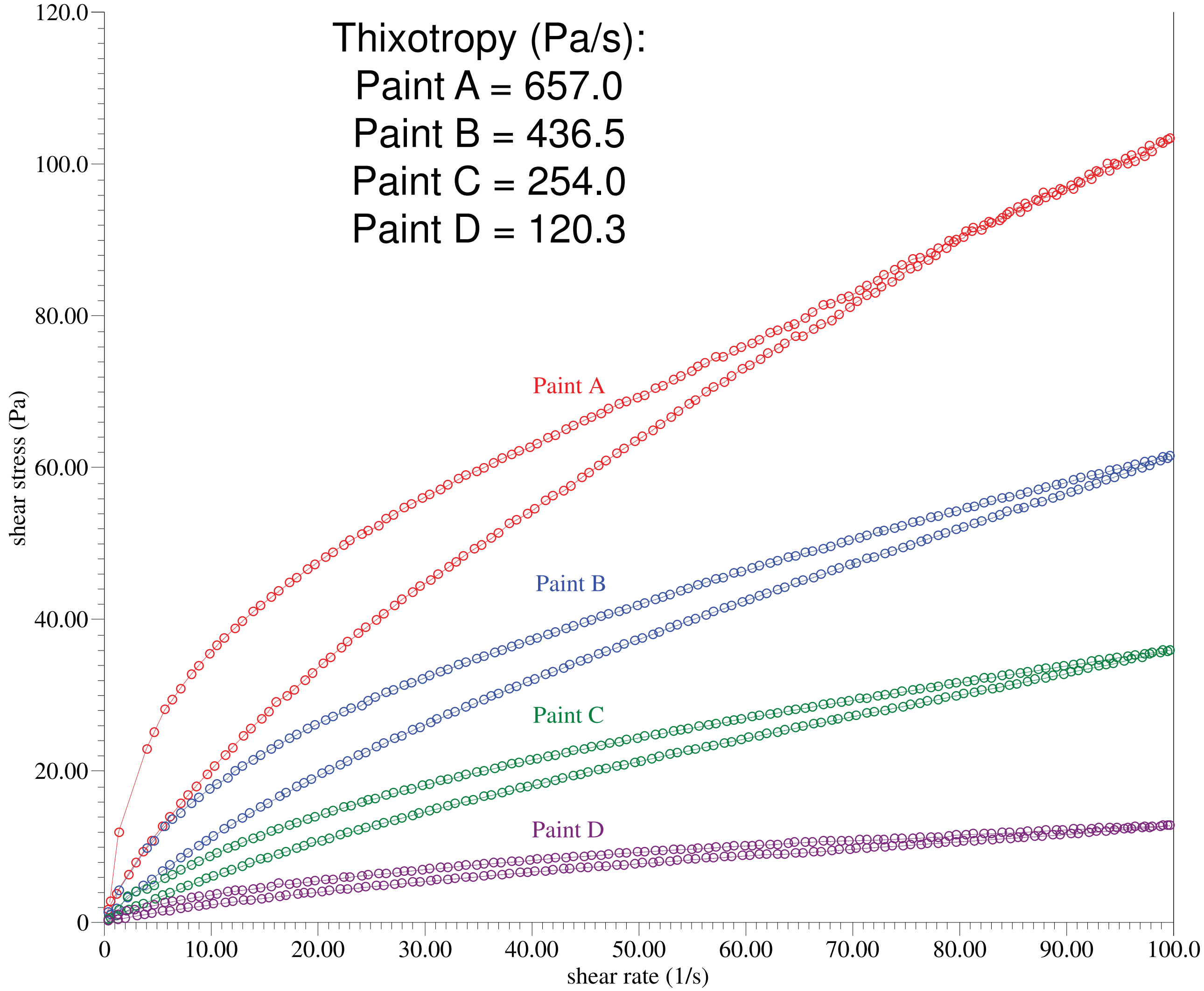
Composition	τ (s)	$\eta(\infty)$ (P)	$\eta(\infty)/\tau$ (P s^{-1})	Thix index	Sag?
With additive	8.9	226	13	4.04	no
Without additive	18.2	97.3	5.4	5.24	yes

Rheology in coatings, principles and methods
RR Eley - Encyclopedia of Analytical Chemistry, 2000 - Wiley Online Library

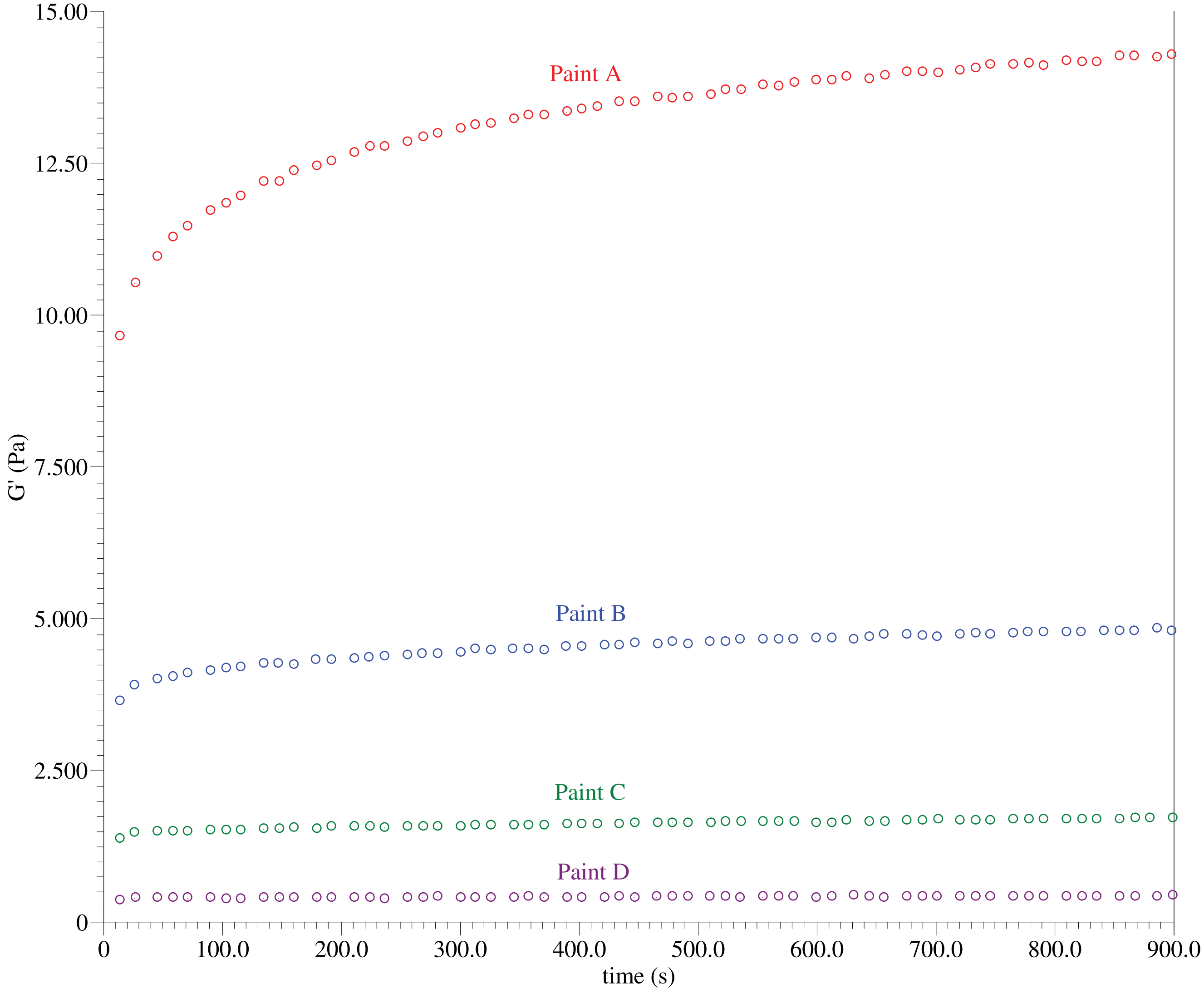
Case Study of 4 Paints



Case Study of 4 Paints



Case Study of 4 Paints



Case Study of 4 Paints

Paint A

Paint B

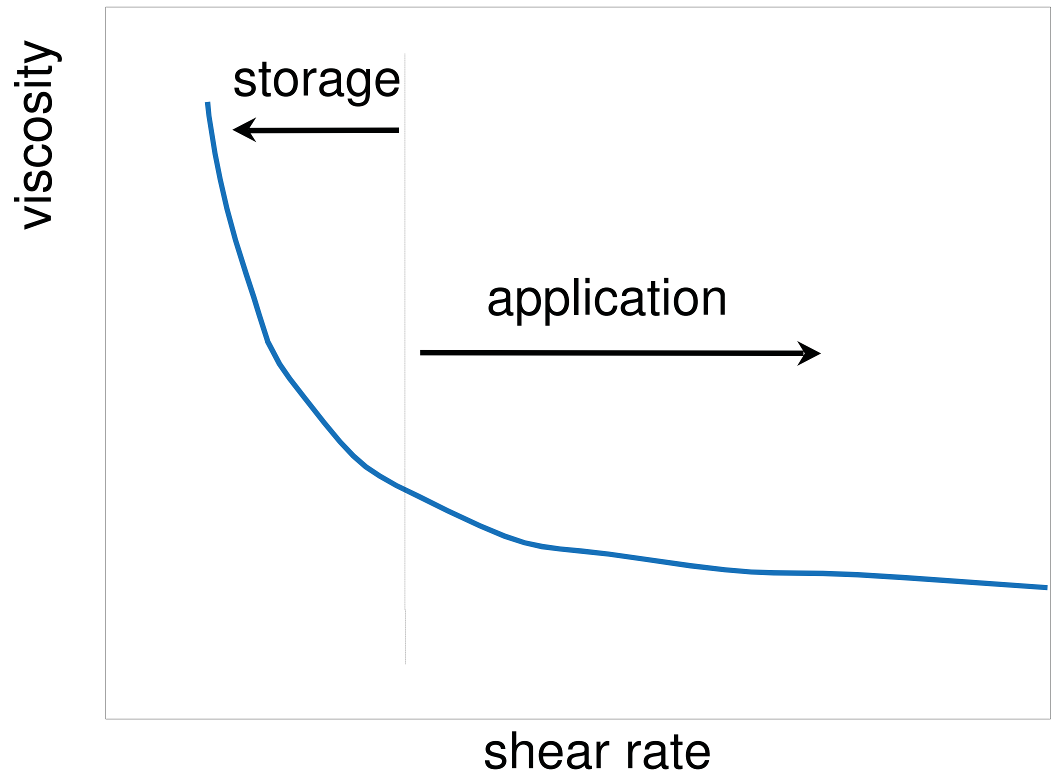
Paint C

Paint D

Antiperspirant/Deodorant

<u>*Roll-ons: Rheology and end-use performance*</u>

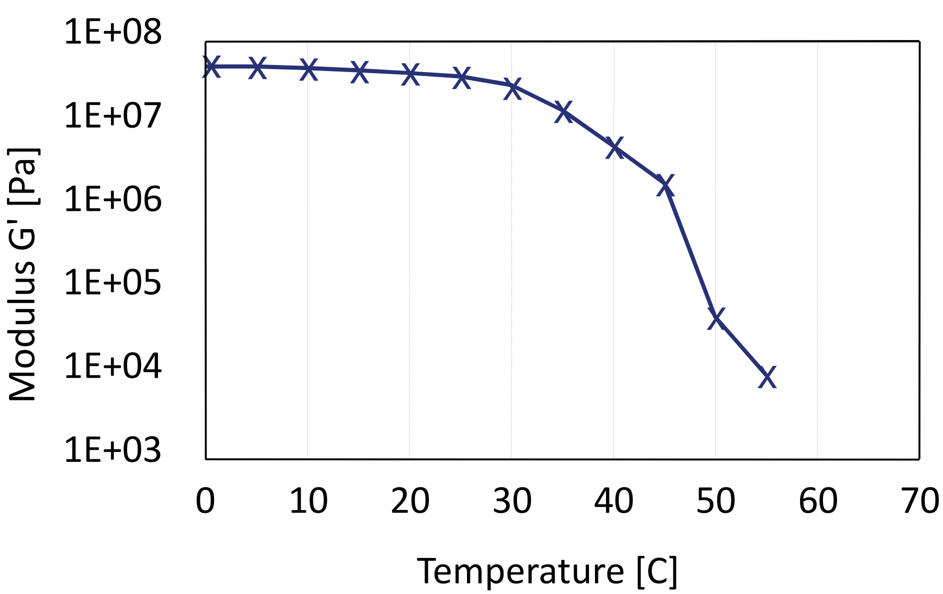
The viscosity has to be balanced to provide the correct viscosity at a given shear rate



Antiperspirant/Deodorant

Sticks: Rheology and process performance

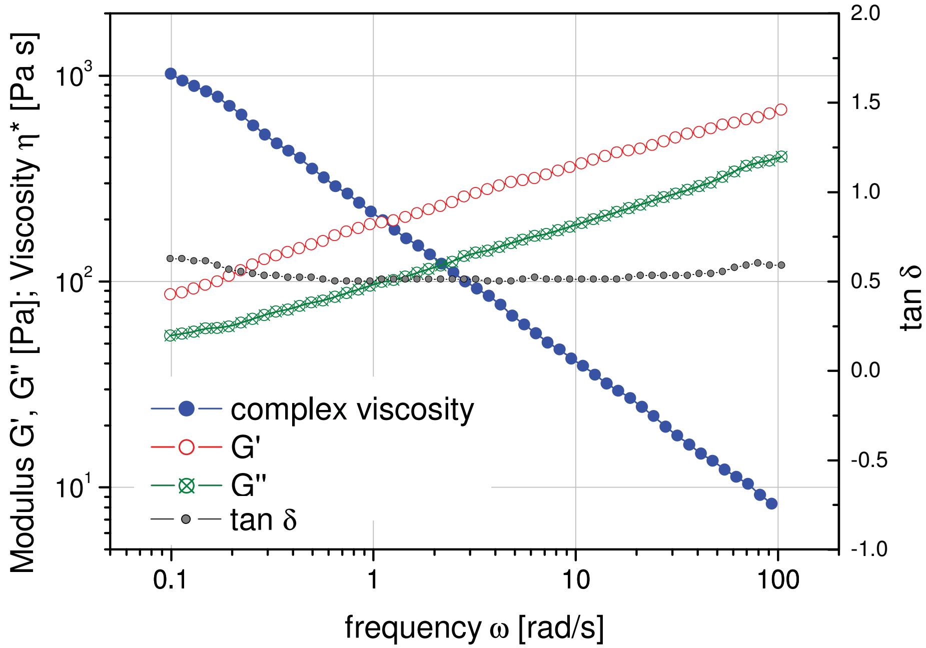
- use **small particles** to reduce sedimentation speed
- add **rheological modifier** like clay to stabilize the suspension and keep the particles in suspension



The temperature dependence of the modulus governs the behavior during the application to the skin

Elasticity: Oscillation Frequency Sweep

Cosmetic lotion



- Many dispersion exhibit solid like behavior at rest
- The frequency dependence and the absolute value of tan δ correlate with long time stability

- Note: strain amplitude has to be in the linear region

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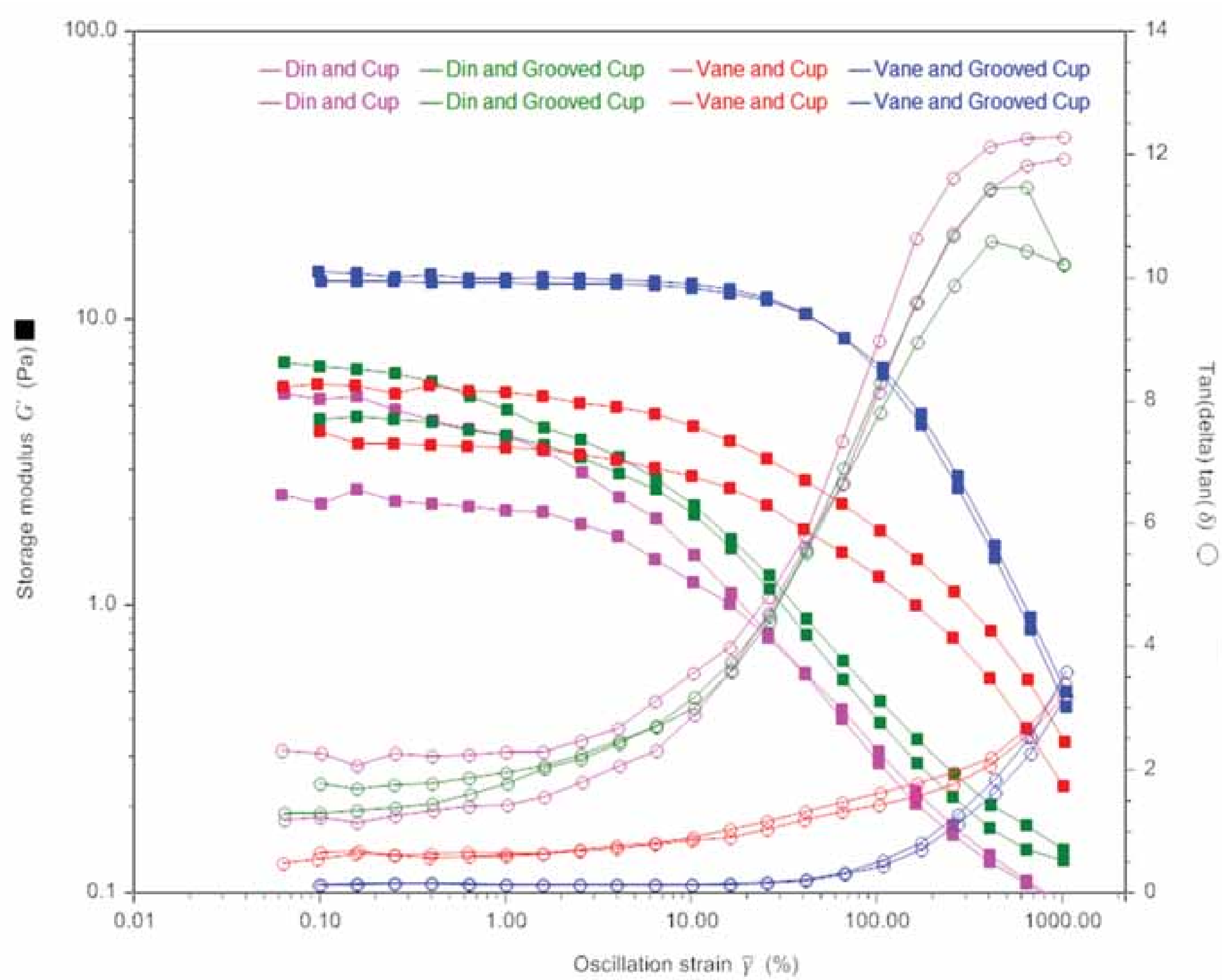
Foam Handwash Strain Sweep: Din vs Vane Rotor

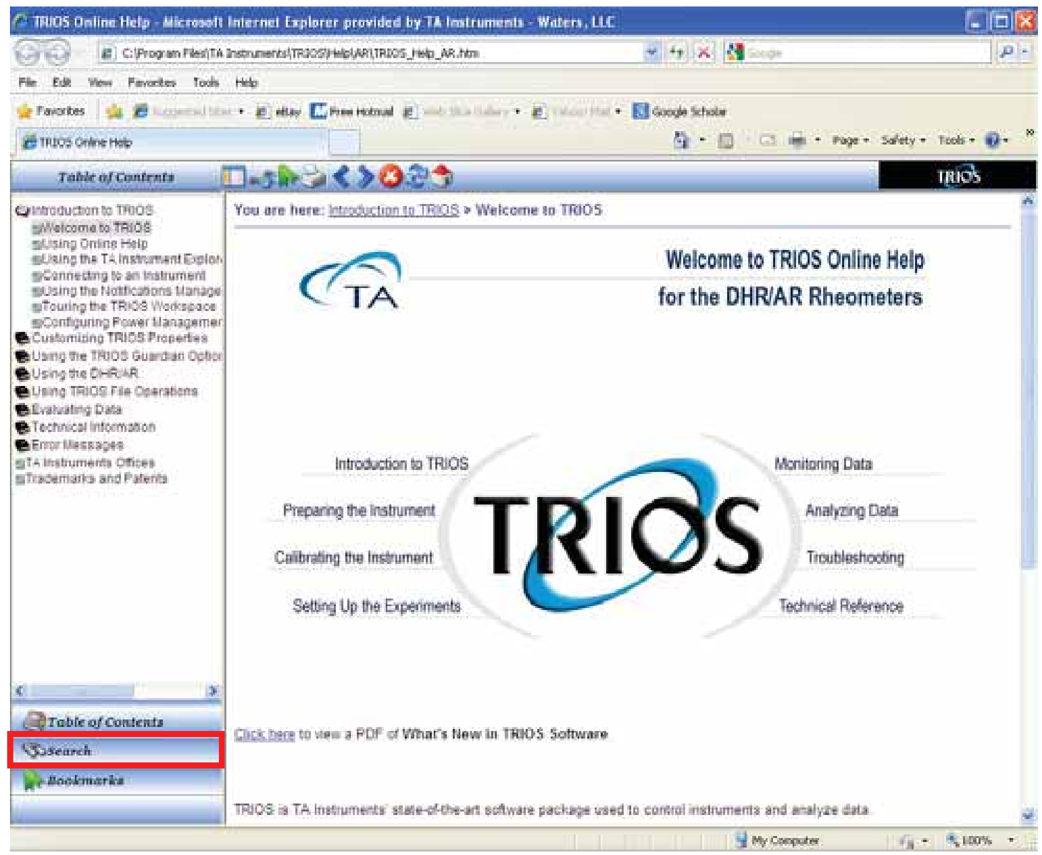
DIN



Vane

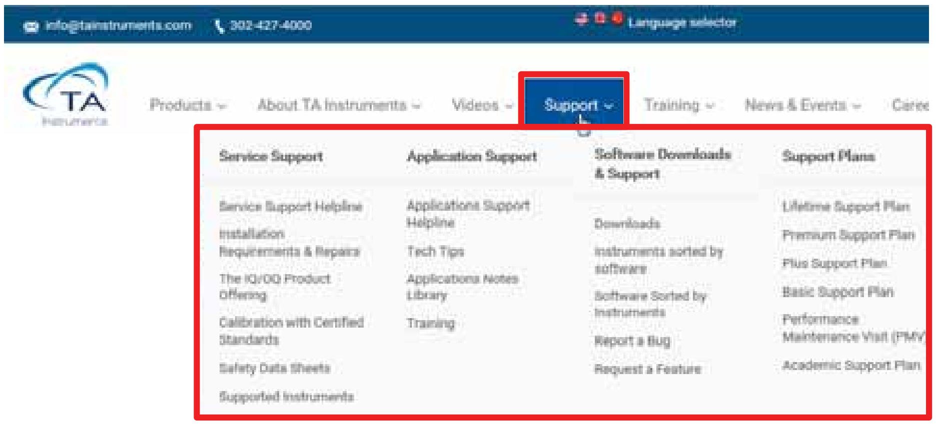
TRIOS Help Menu

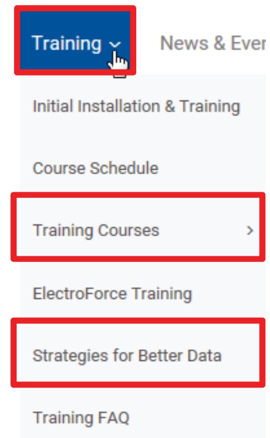
- Browse the contents list or search using the search tab.
- Access to <u>Getting Started Guides</u> also found through the help menu.



Instructional Videos

- From www.tainstruments.com click on Videos, Support or Training



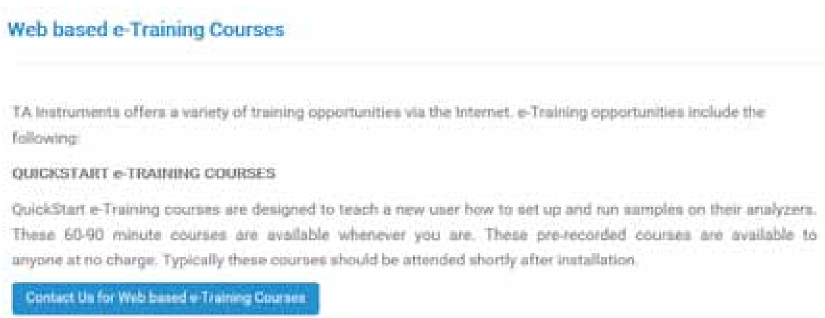


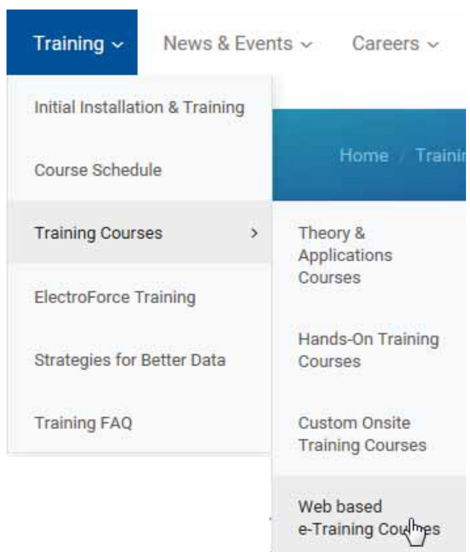
- Select Videos for TA Tech Tips, Webinars and Quick Start Courses

See also: https://www.youtube.com/user/TATechTips

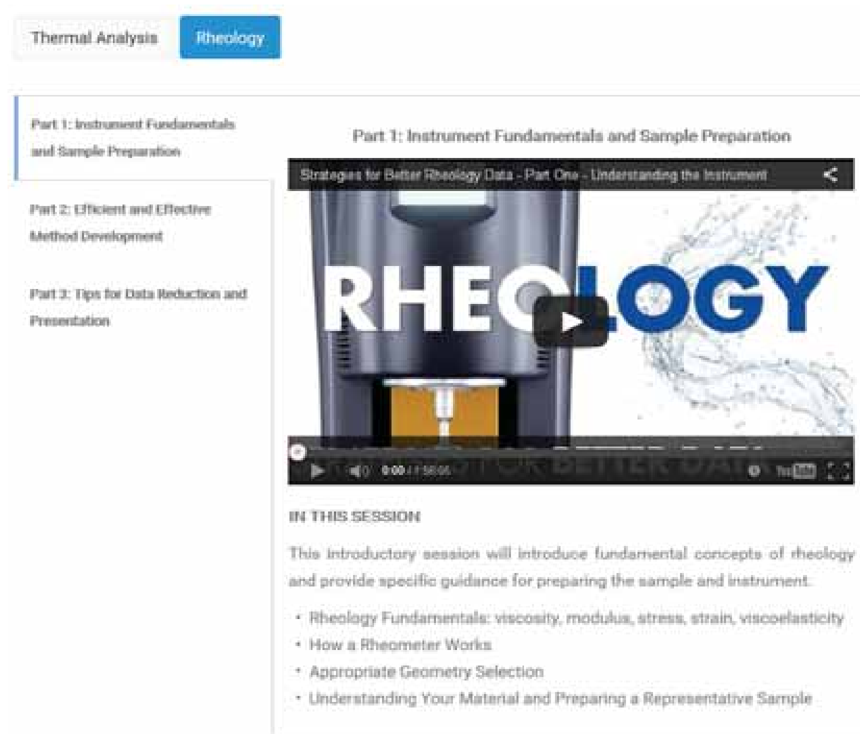
Instructional Video Resources

Quickstart e-Training Courses





Strategies for Better Data - Rheology



Need Assistance?

- Check the online manuals and error help.
- Contact the TA Instruments Hotline
  - Phone: **302-427-4070** M-F 8-4:30 EST
    - *Select Thermal , Rheology or Microcalorimetry Support*
  - Email: thermalsupport@tainstruments.com or rheologysupport@tainstruments.com or microcalorimetersupport@tainstruments.com
- Call your local Technical or Service Representative
- Call TA Instruments
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- Check out our Website: www.tainstruments.com
- For instructional videos go to: www.youtube.com/user/TATechTips

Thank You

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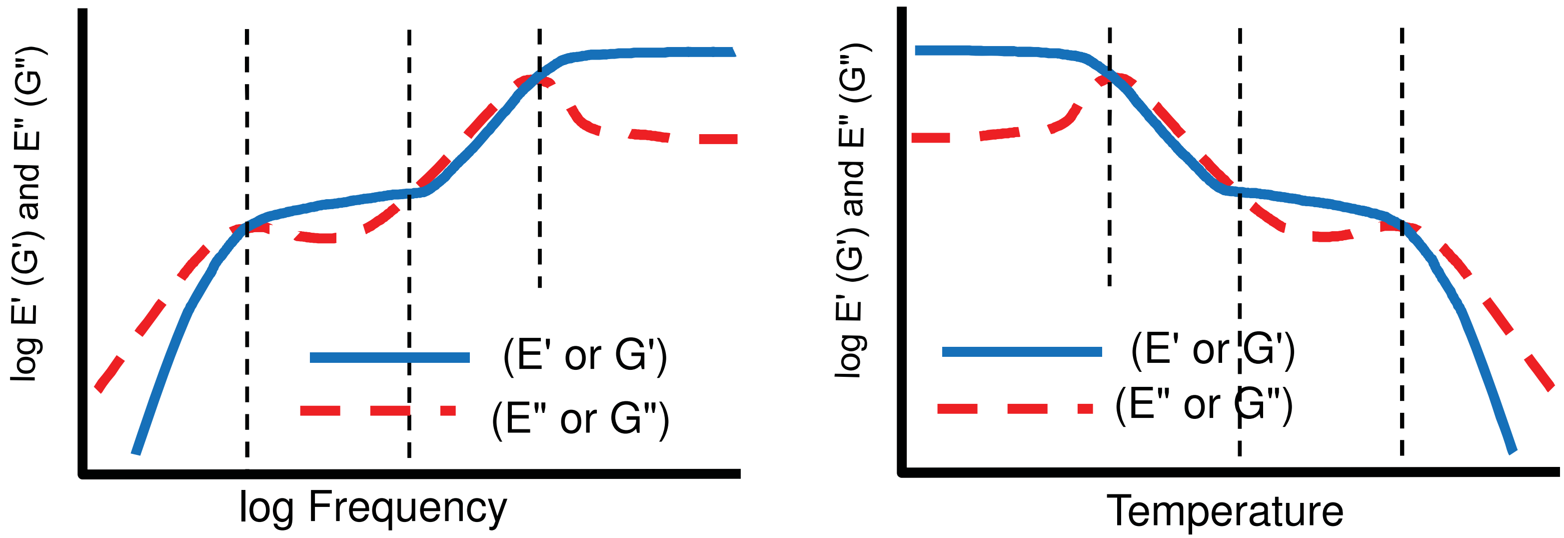
Appendix 1: Time Temperature Superposition (TTS)

Time and Temperature Relationship



- Linear viscoelastic properties are both time-dependent and temperature-dependent
- Some materials show a time dependence that is proportional to the temperature dependence
  - Decreasing temperature has the same effect on viscoelastic properties as increasing the frequency
- For such materials, changes in temperature can be used to “re-scale” time, and predict behavior over time scales not easily measured

Time Temperature Superpositioning Benefits

- TTS can be used to extend the frequency beyond the instrument's range
- Creep TTS or Stress Relaxation TTS can predict behavior over longer times than can be practically measured
- Can be applied to amorphous, non modified polymers
- Material must be thermo-rheological simple
  - One in which all relaxations times shift with the same shift factor a_T

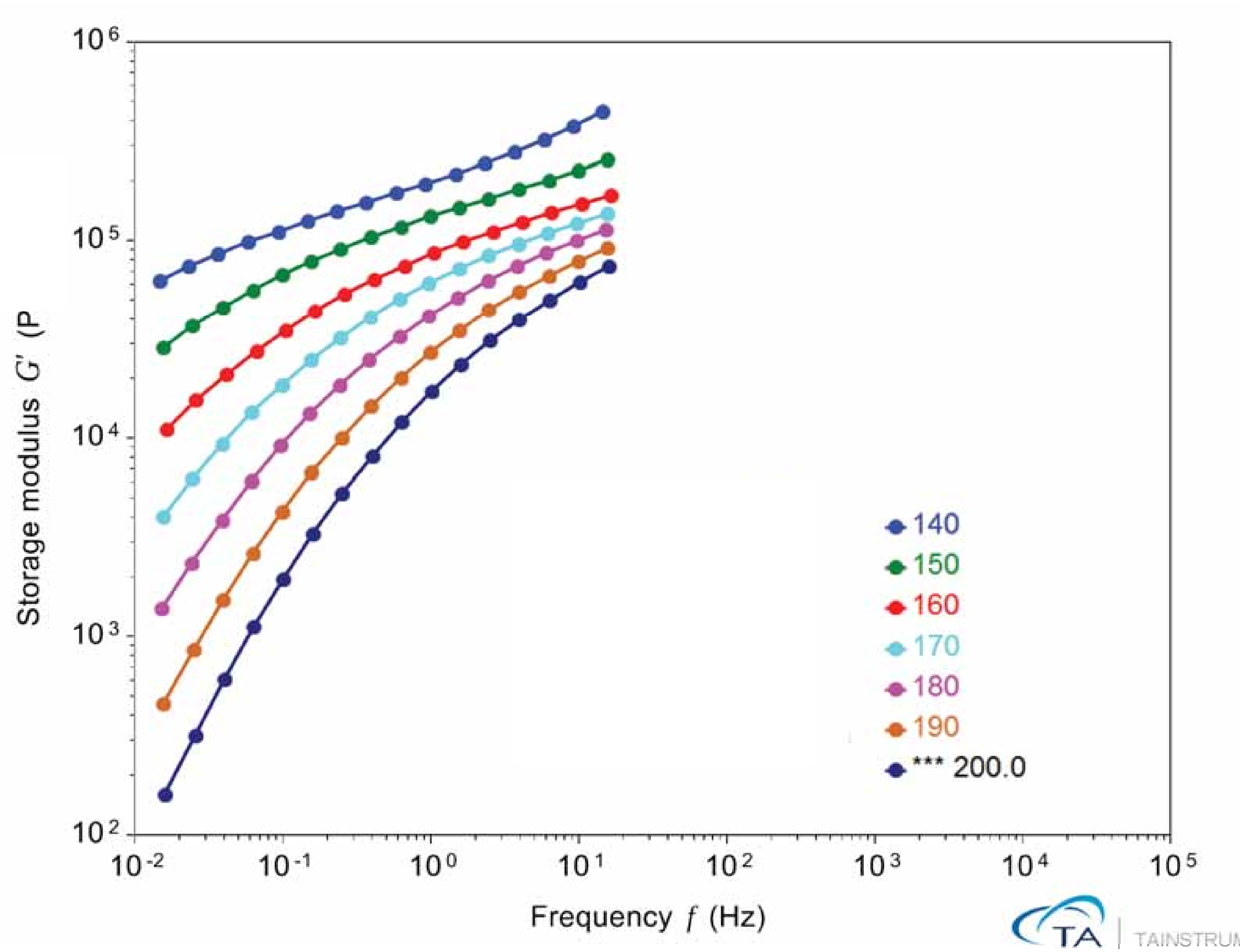
When Not to Use TTS

- If crystallinity is present, especially if any melting occurs in the temperature range of interest
- The structure changes with temperature
  - Cross linking, decomposition, etc.
  - Material is a block copolymer (TTS may work within a limited temperature range)
  - Material is a composite of different polymers
  - Viscoelastic mechanisms other than configuration changes of the polymer backbone
    - e.g. side-group motions, especially near the Tg
    - Dilute polymer solutions
    - Dispersions (wide frequency range)
    - Sol-gel transition

Guidelines for TTS

- Decide first on the Reference Temperature: T_0. What is the use temperature?
- If you want to obtain information at higher frequencies or shorter times, you will need to conduct frequency (stress relaxation or creep) scans at temperatures lower than T_0.
- If you want to obtain information at lower frequencies or longer times, you will need to test at temperatures higher than T_0.
- Good idea to scan material over temperature range at single frequency to get an idea of modulus-temperature and transition behavior.

TTS Shifting



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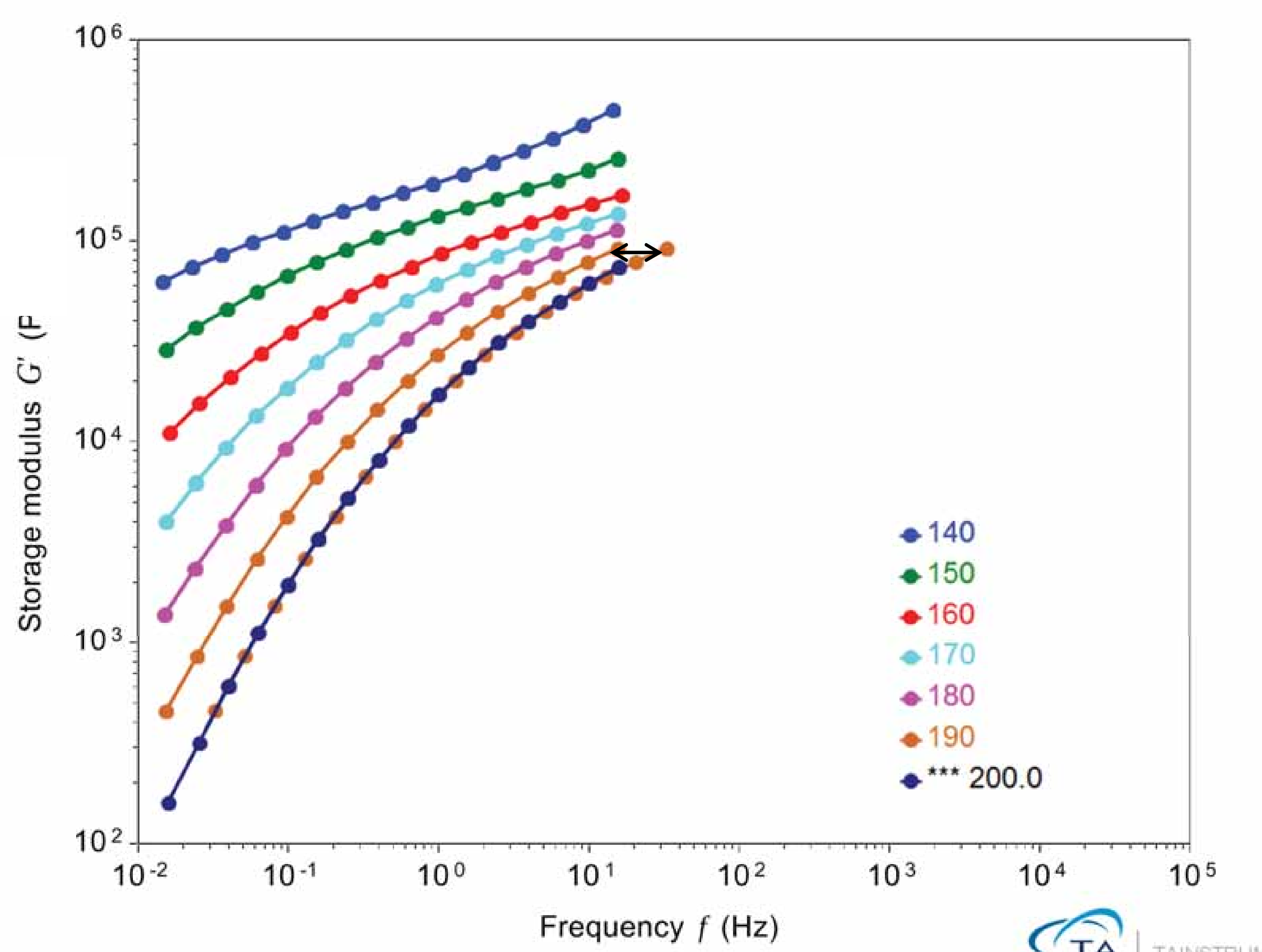
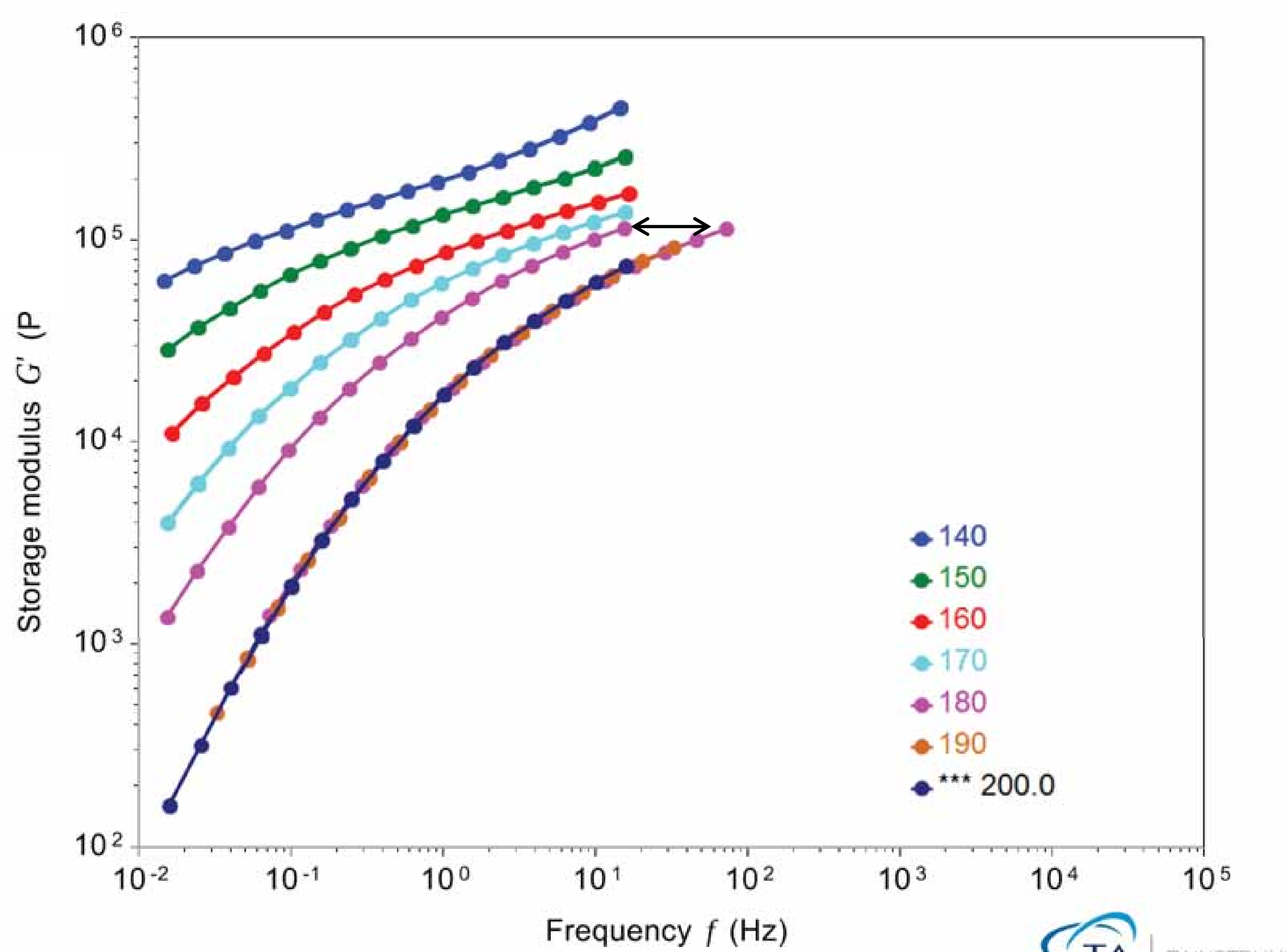
TTS Shifting



TTS Shifting



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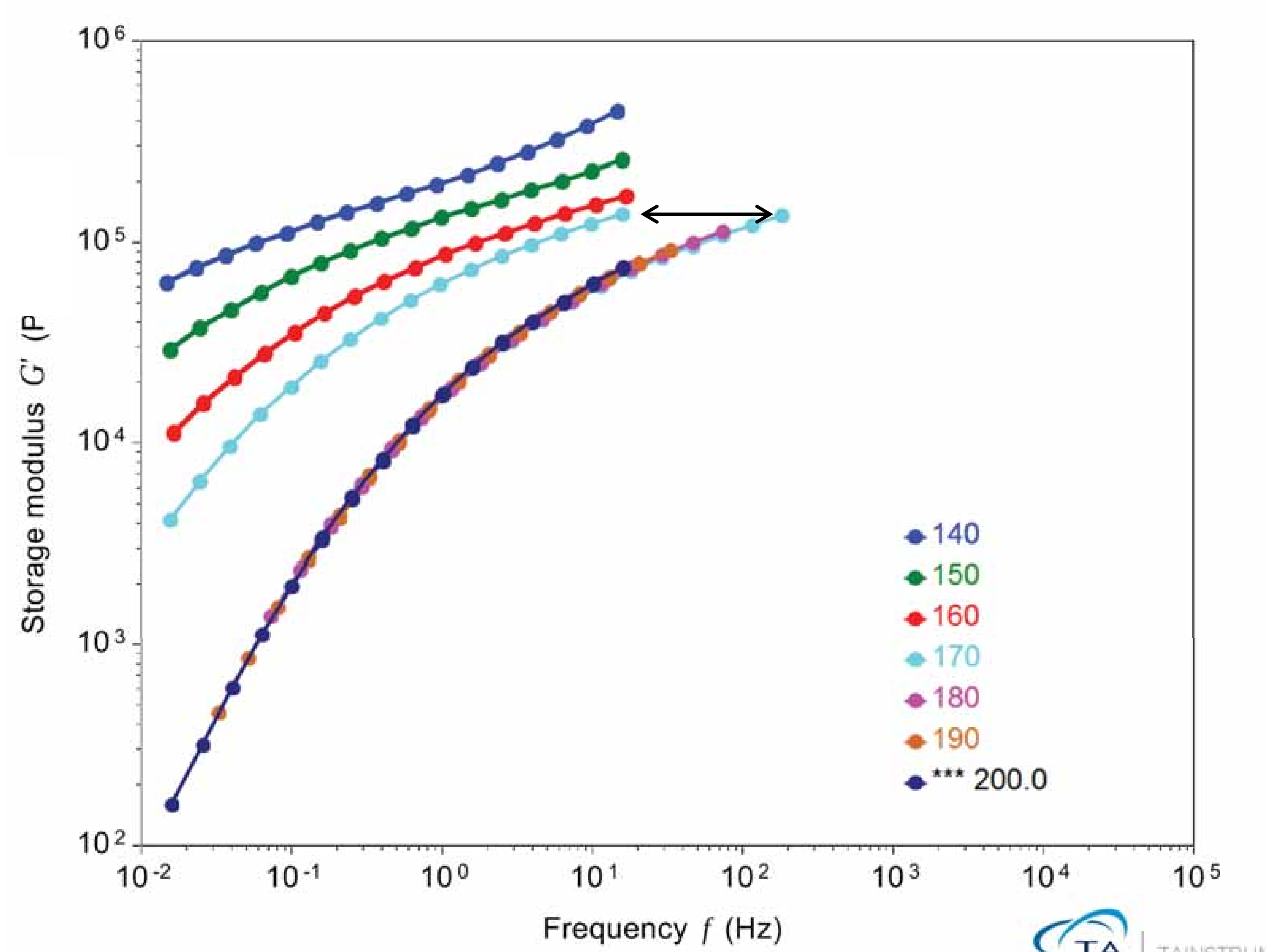
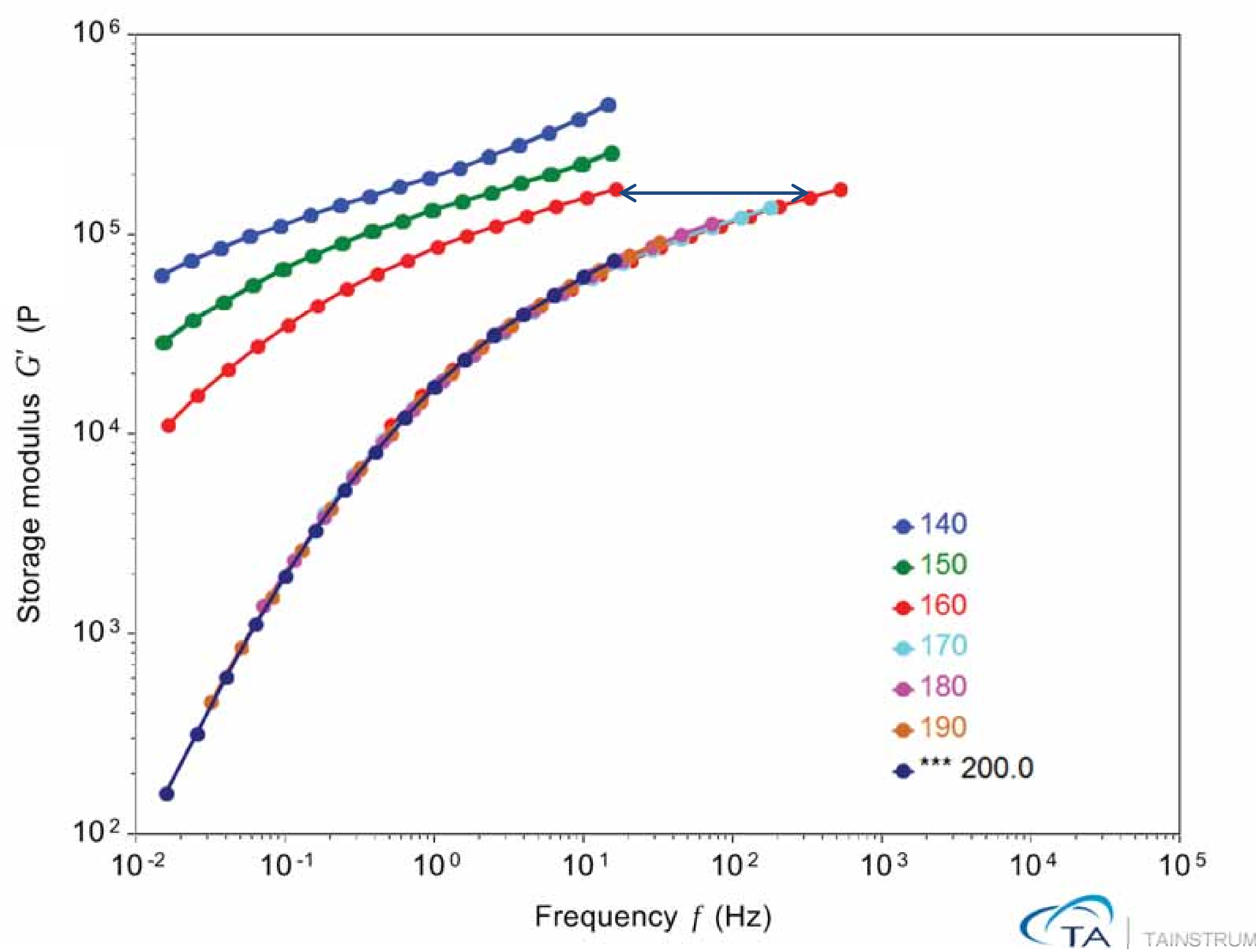
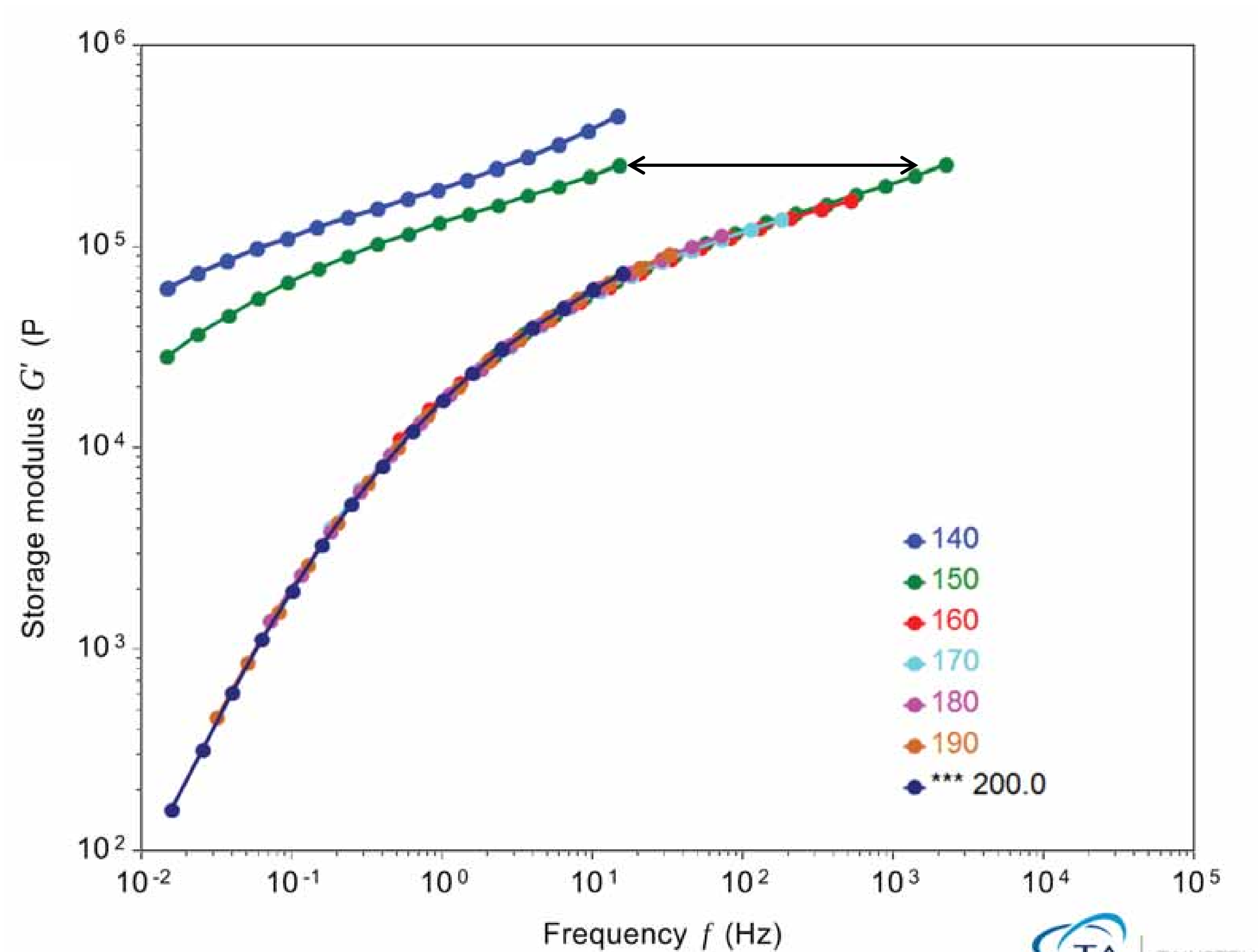
TTS Shifting



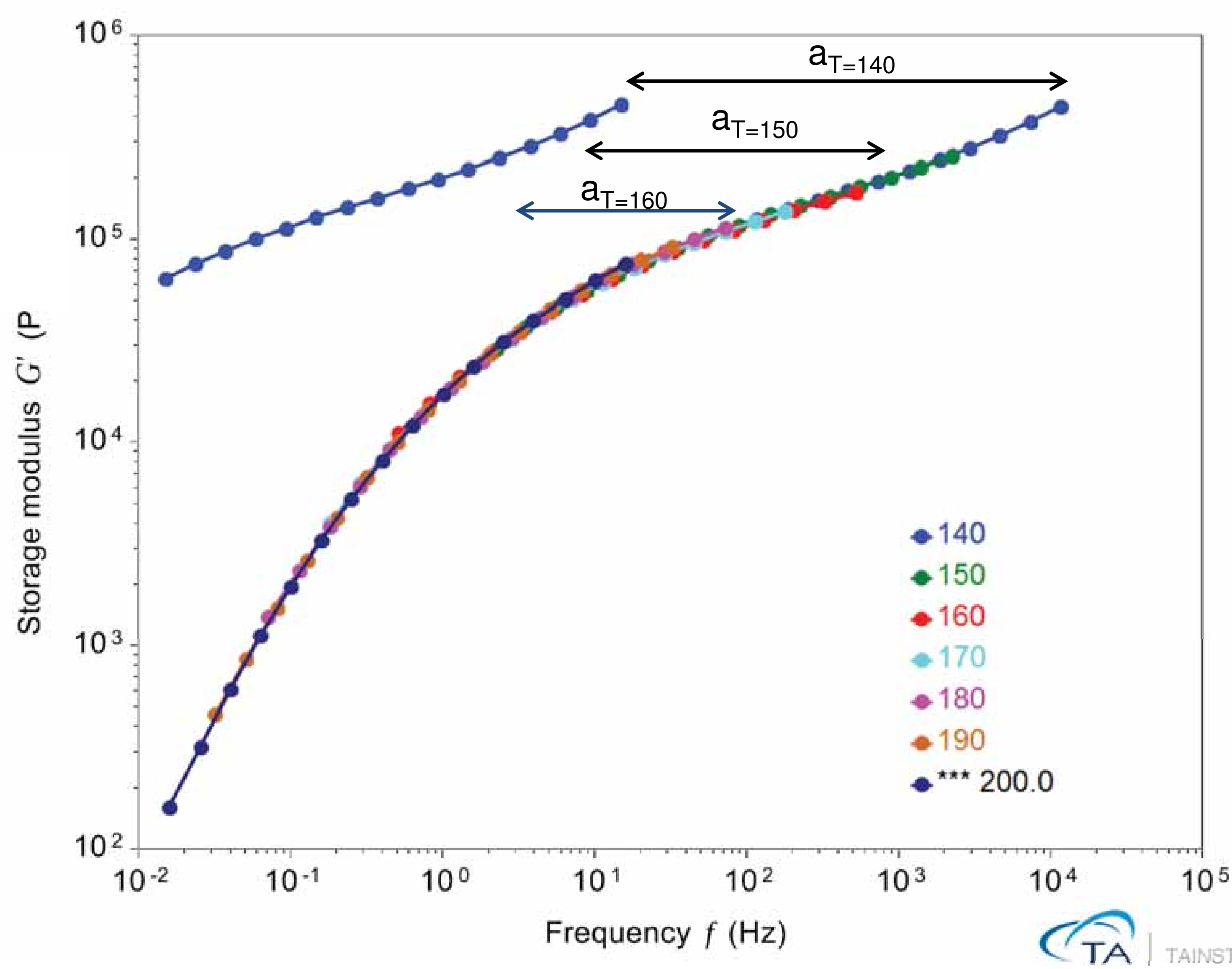
TTS Shifting



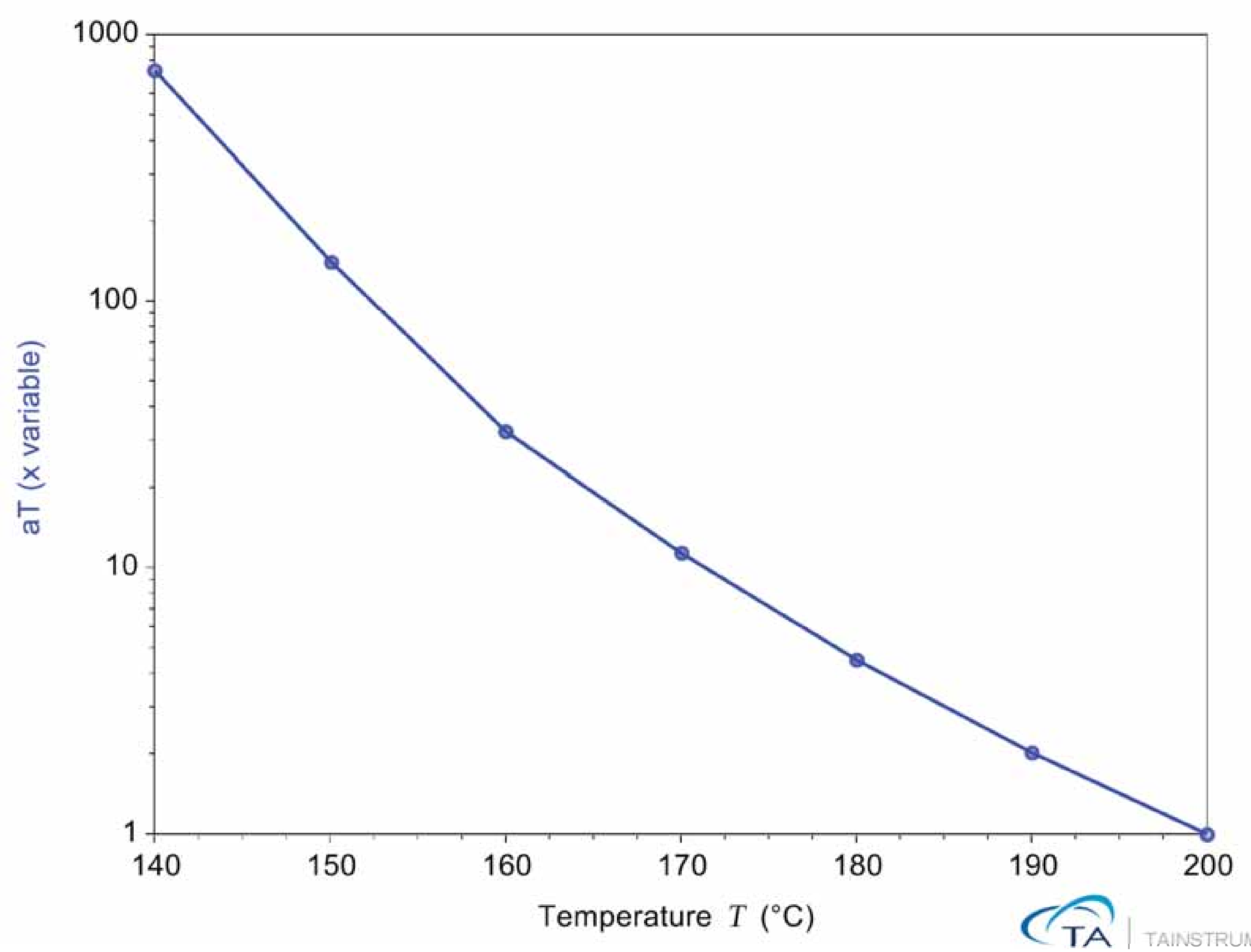
TTS Shifting



TTS Shifting



Shift Factors a_T vs Temperature



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Shift Factors: WLF Equation

- Master Curves can be generated using shift factors derived from the Williams, Landel, Ferry (WLF) equation

$$\log a_T = -c_1(T-T_0)/c_2+(T-T_0)$$

  - a_T = temperature shift factor
  - T_0 = reference temperature
  - c_1 and c_2 = constants from curve fitting
    - Generally, c_1=17.44 & c_2=51.6 when $T_0 = T_g$

When not to use the WLF Equation

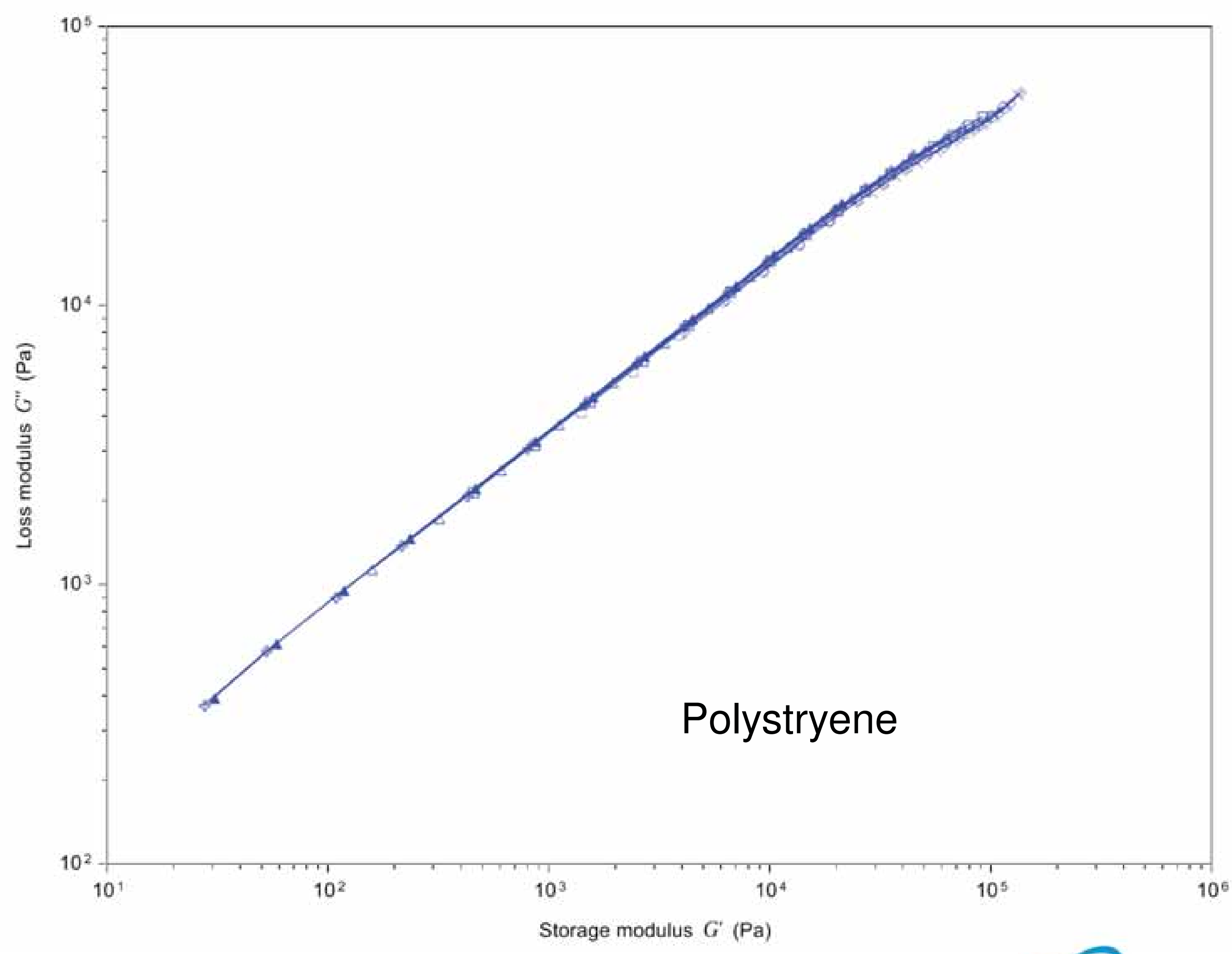
- Sometimes you shouldn't use the WLF equation (even if it appears to work)
- If $T > T_g + 100°C$
- If $T < T_g$ and polymer is not elastomeric
- If temperature range is small, then c_1 & c_2 cannot be calculated precisely

- In these cases, the Arrhenius form is usually better

$$\ln a_T = (E_a/R)(1/T - 1/T_0)$$

  - a_T = temperature shift factor
  - E_a = Apparent activation energy
  - T_0 = reference temperature
  - T = absolute temperature
  - R = gas constant
  - E_a = activation energy

Verify Data for TTS



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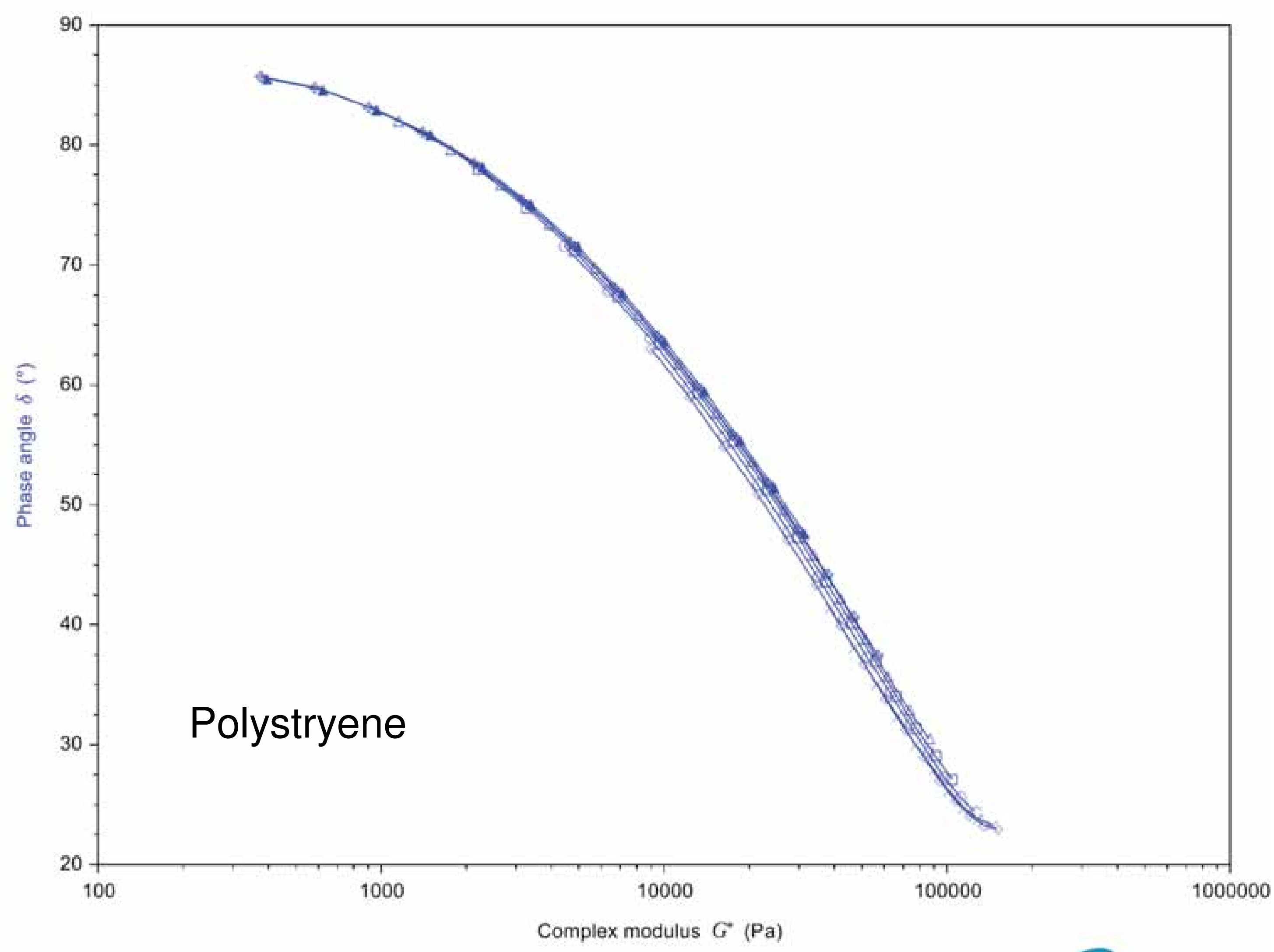


References for TTS

1) Ward, I.M. and Hadley, D.W., "*Mechanical Properties of Solid Polymers*", Wiley, 1993, Chapter 6.

2) Ferry, J.D., "*Viscoelastic Properties of Polymers*", Wiley, 1970, Chapter 11.

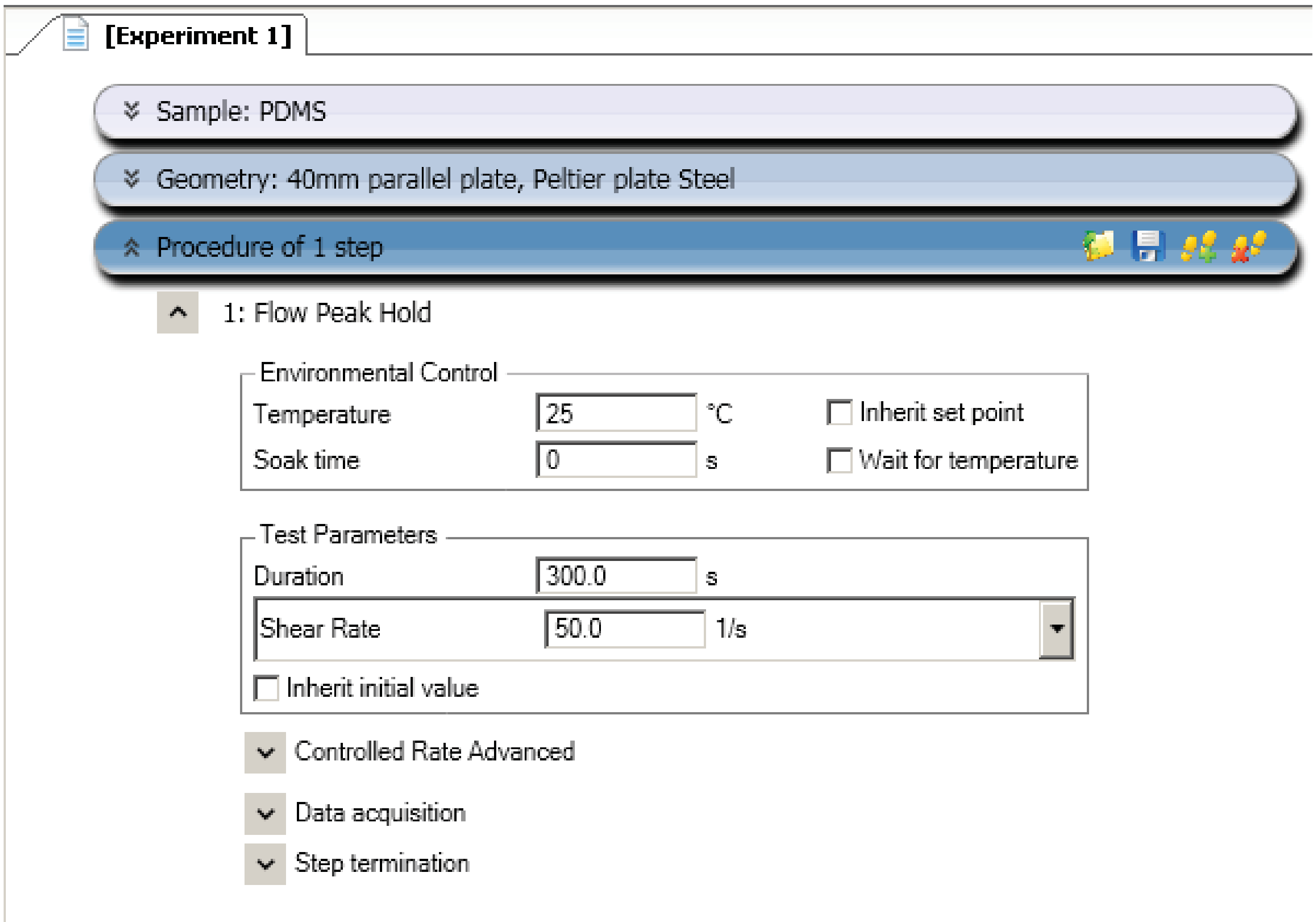
3) Plazek, D.J., "*Oh, Thermorheological Simplicity, wherefore art thou?*" Journal of Rheology, vol 40, 1996, p987.

4) Lesueur, D., Gerard, J-F., Claudy, P., Letoffe, J-M. and Planche, D., "*A structure related model to describe asphalt linear viscoelasticity*", Journal of Rheology, vol 40, 1996, p813.

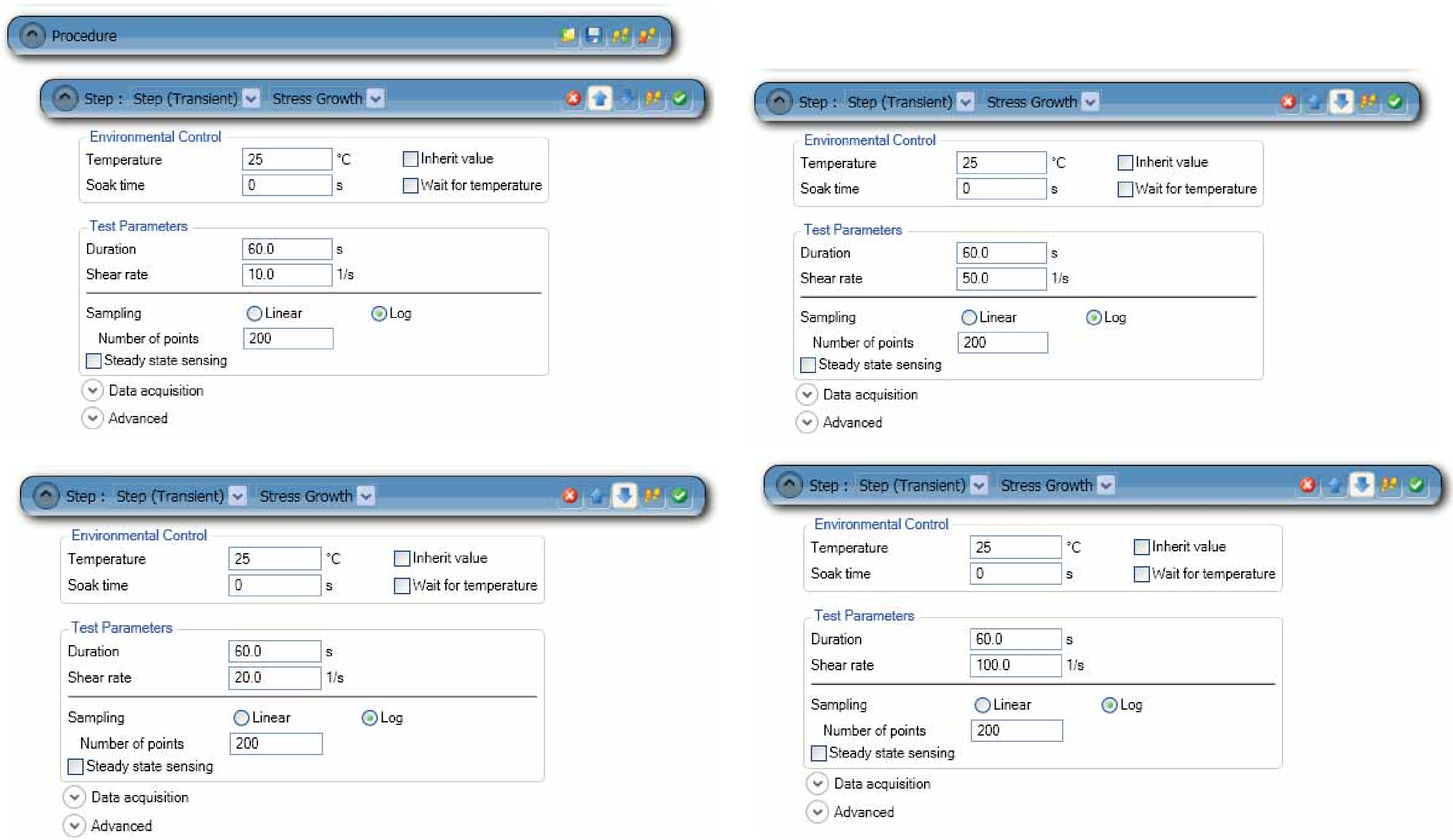
Appendix 2: Software Screen Shots

TRIOS

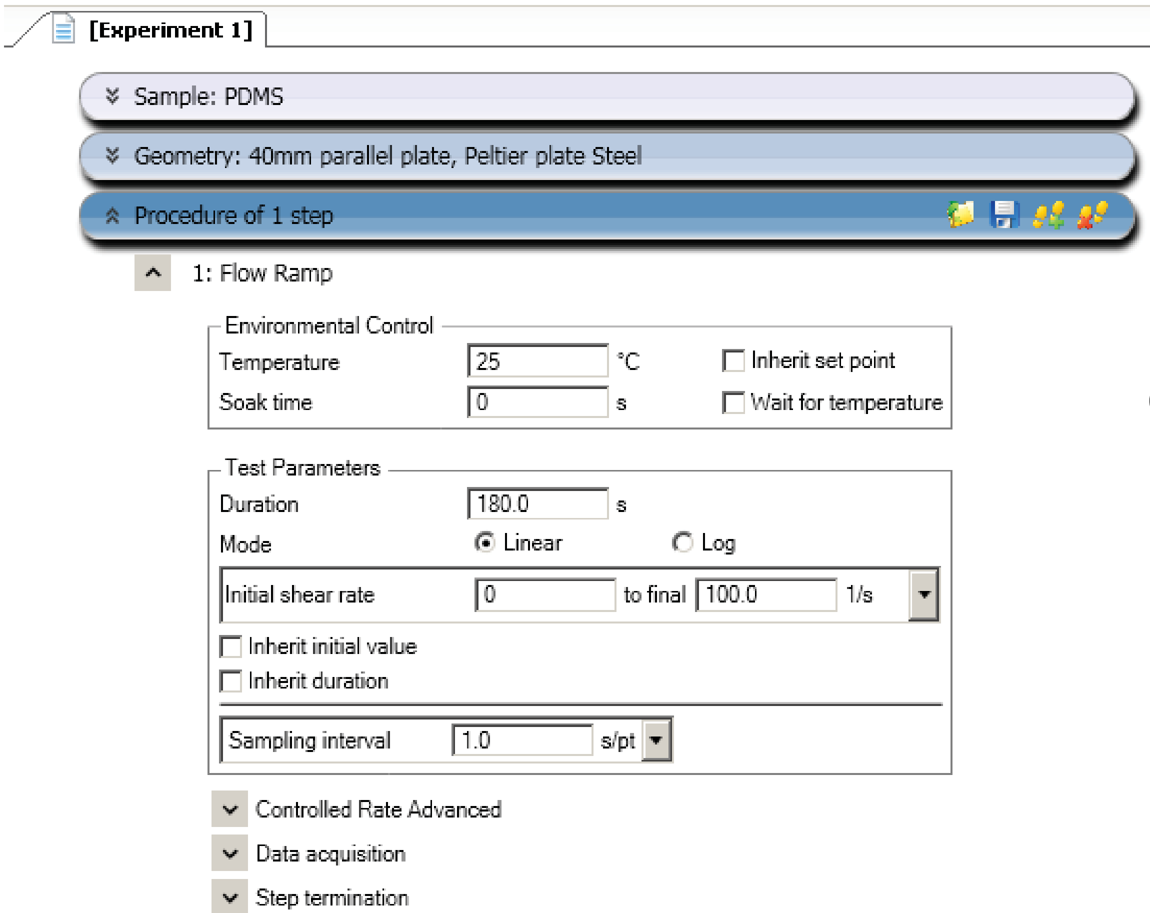
DHR Peak Hold: Constant Shear Rate vs. Time



ARES-G2: Stress Growth Test (Step Rate)



Continuous Ramp

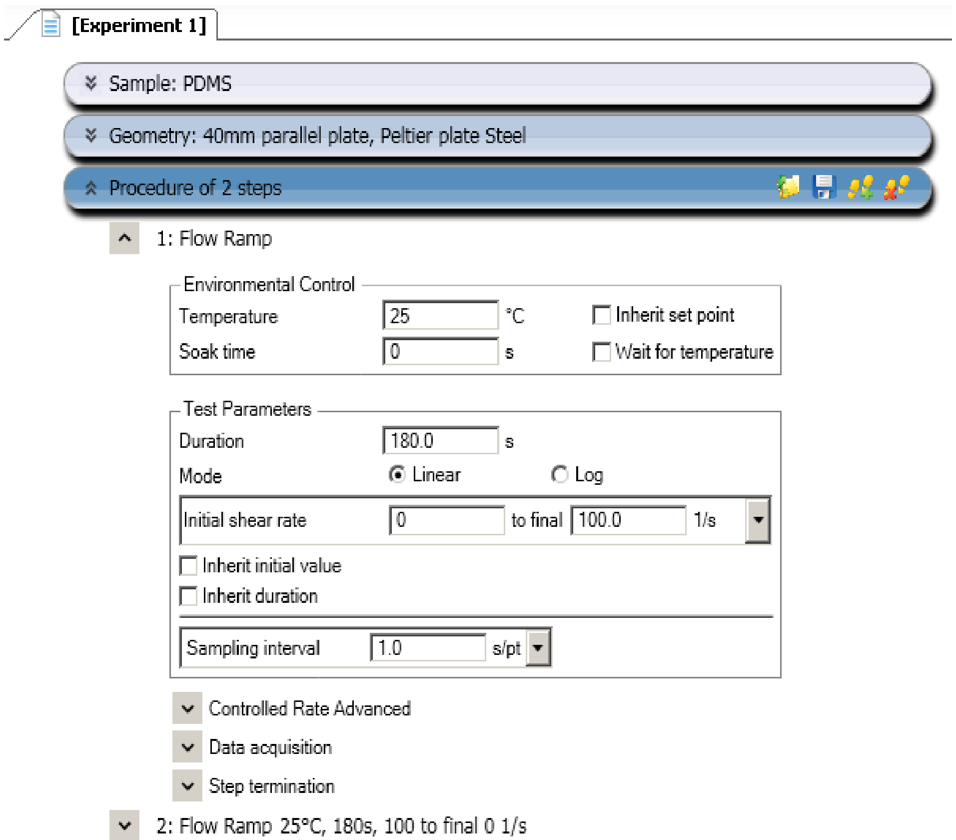


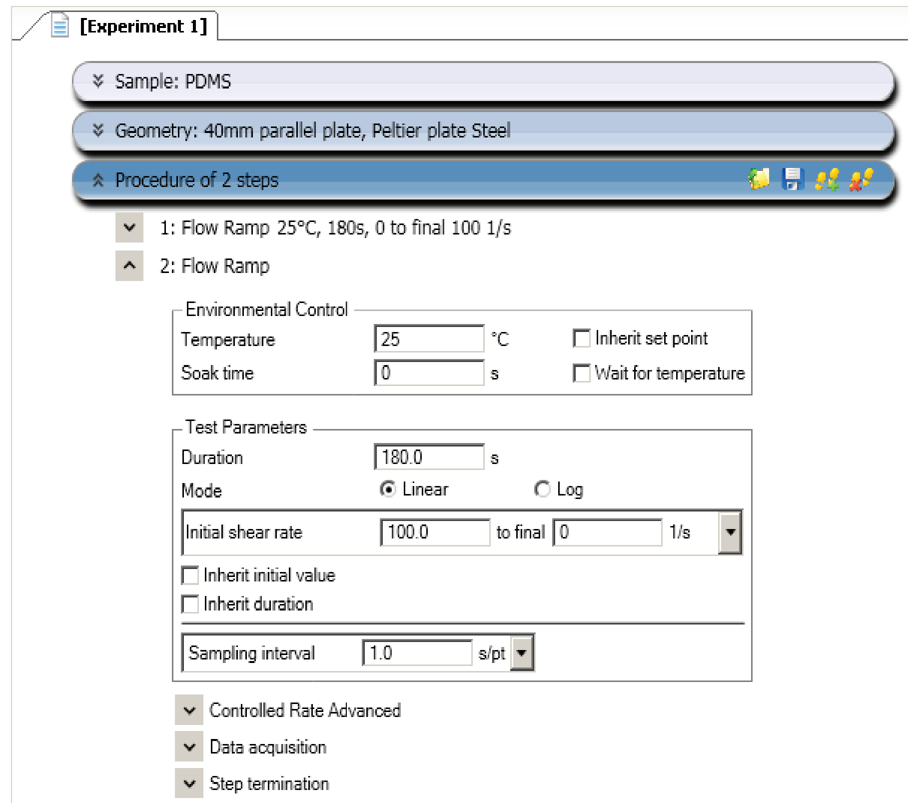
Control variables:

- Shear rate
- Velocity
- Torque
- Shear stress

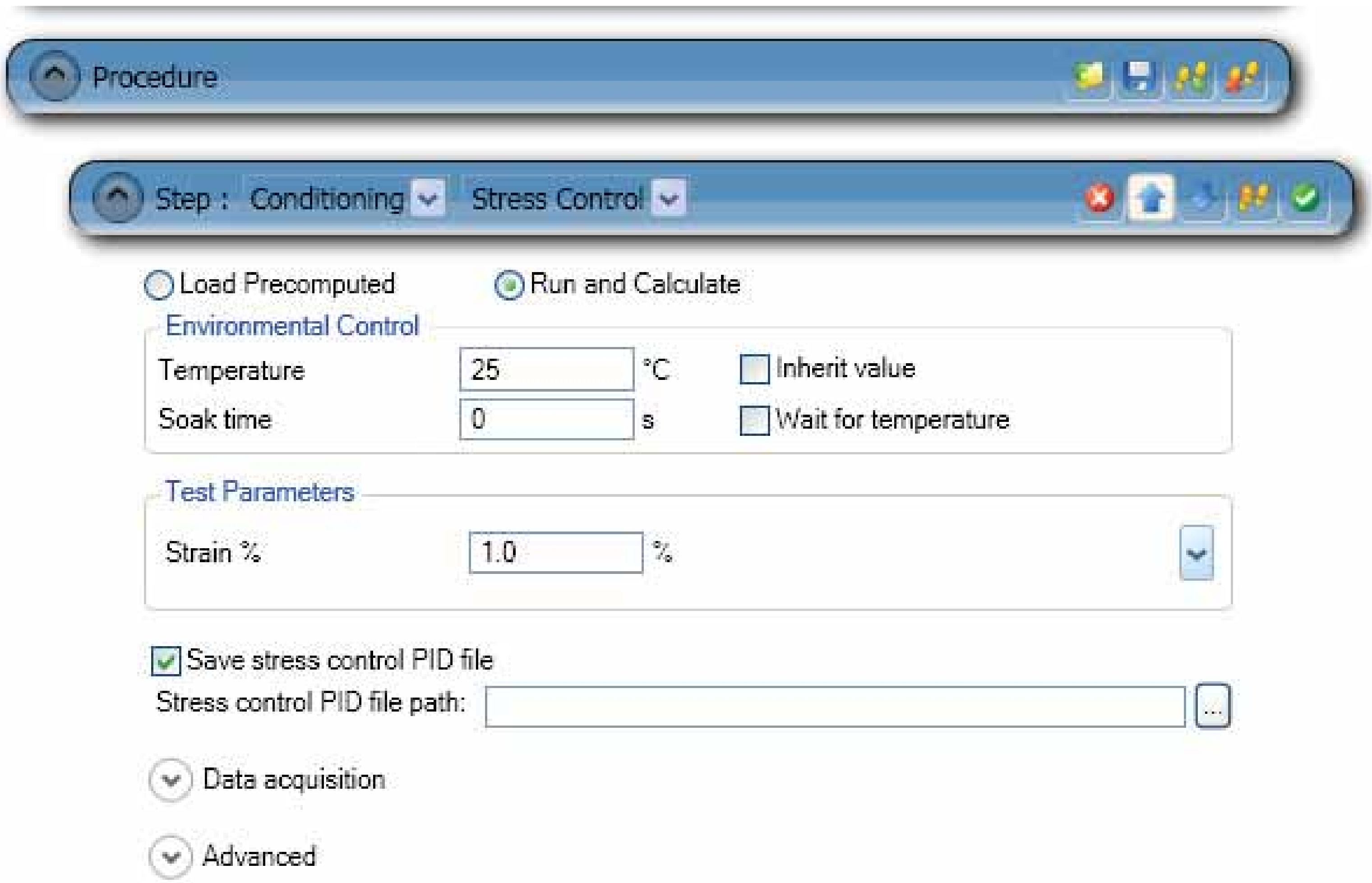
- Thixotropic loop be done by adding another ramp step

Thixotropic loop

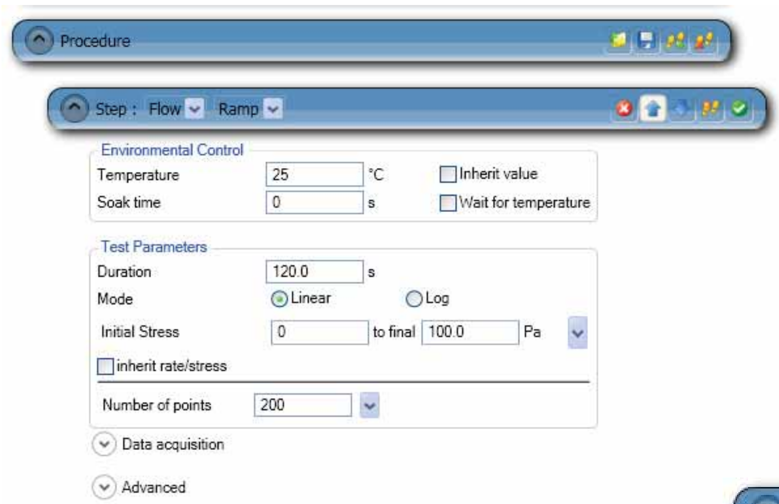


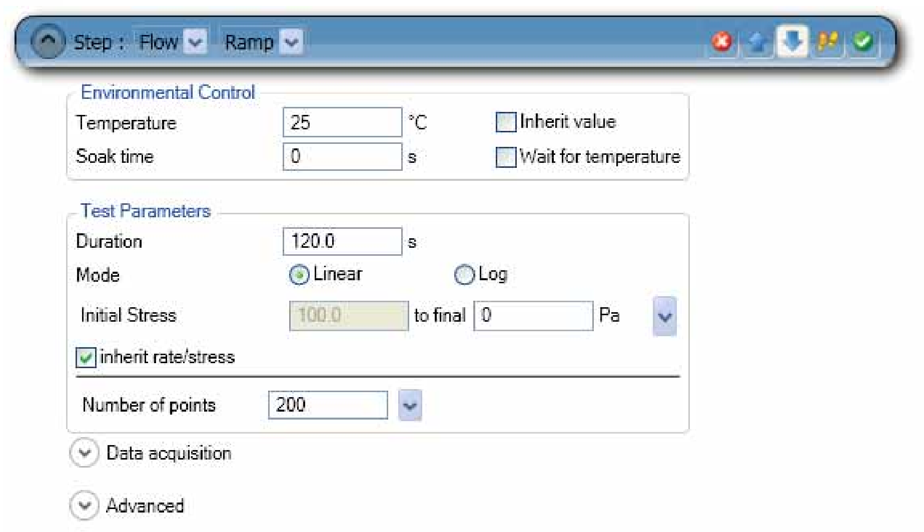


ARES G2: Stress Ramp: Stress Control Pre-test

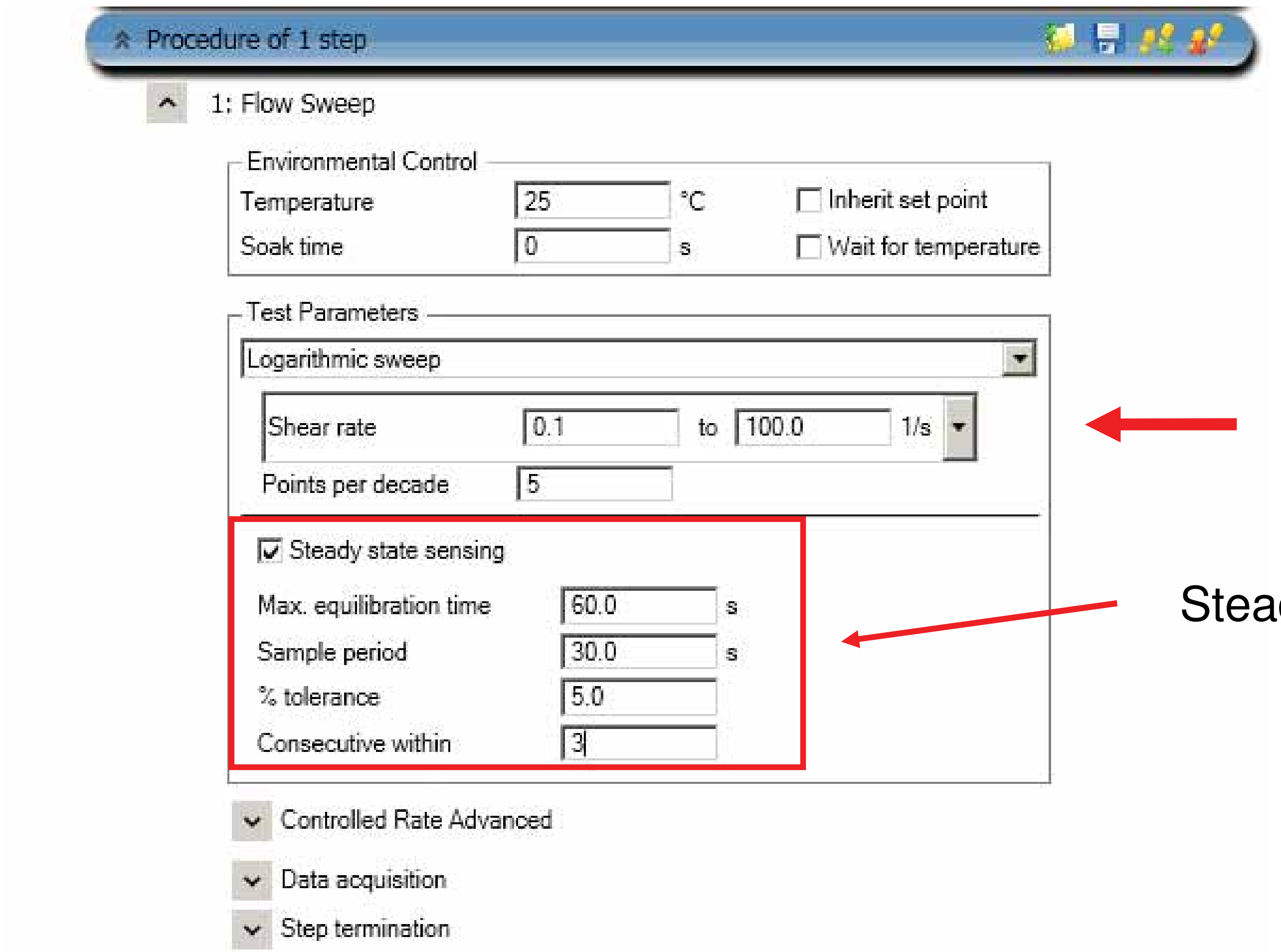


ARES G2: Stress Ramp (Thixotropic Loop)





DHR and ARES G2: Steady State Flow

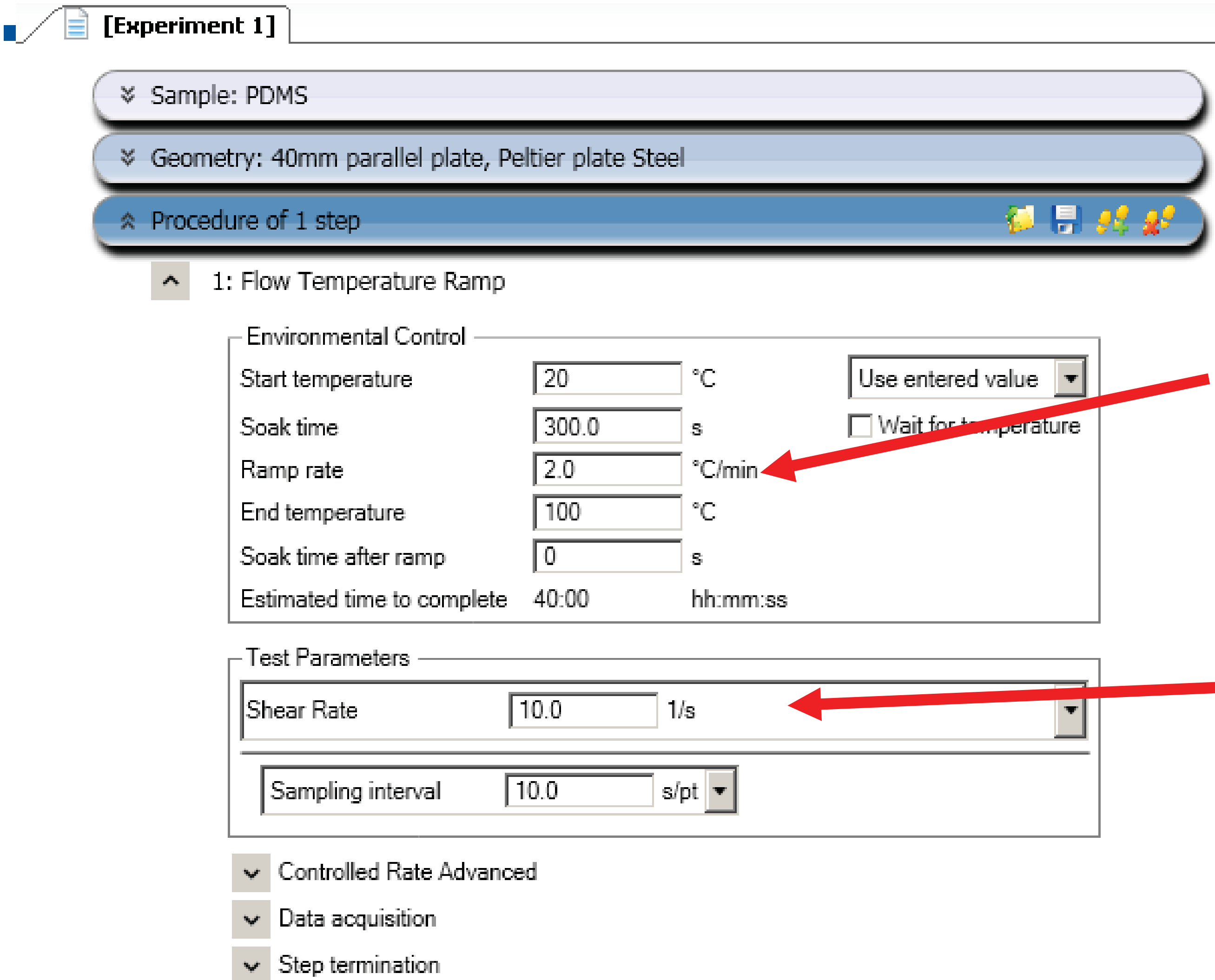


Control variables:

- Shear rate
- Velocity
- Torque
- Shear stress

Steady state algorithm

DHR and ARES G2: Flow Temp Ramp

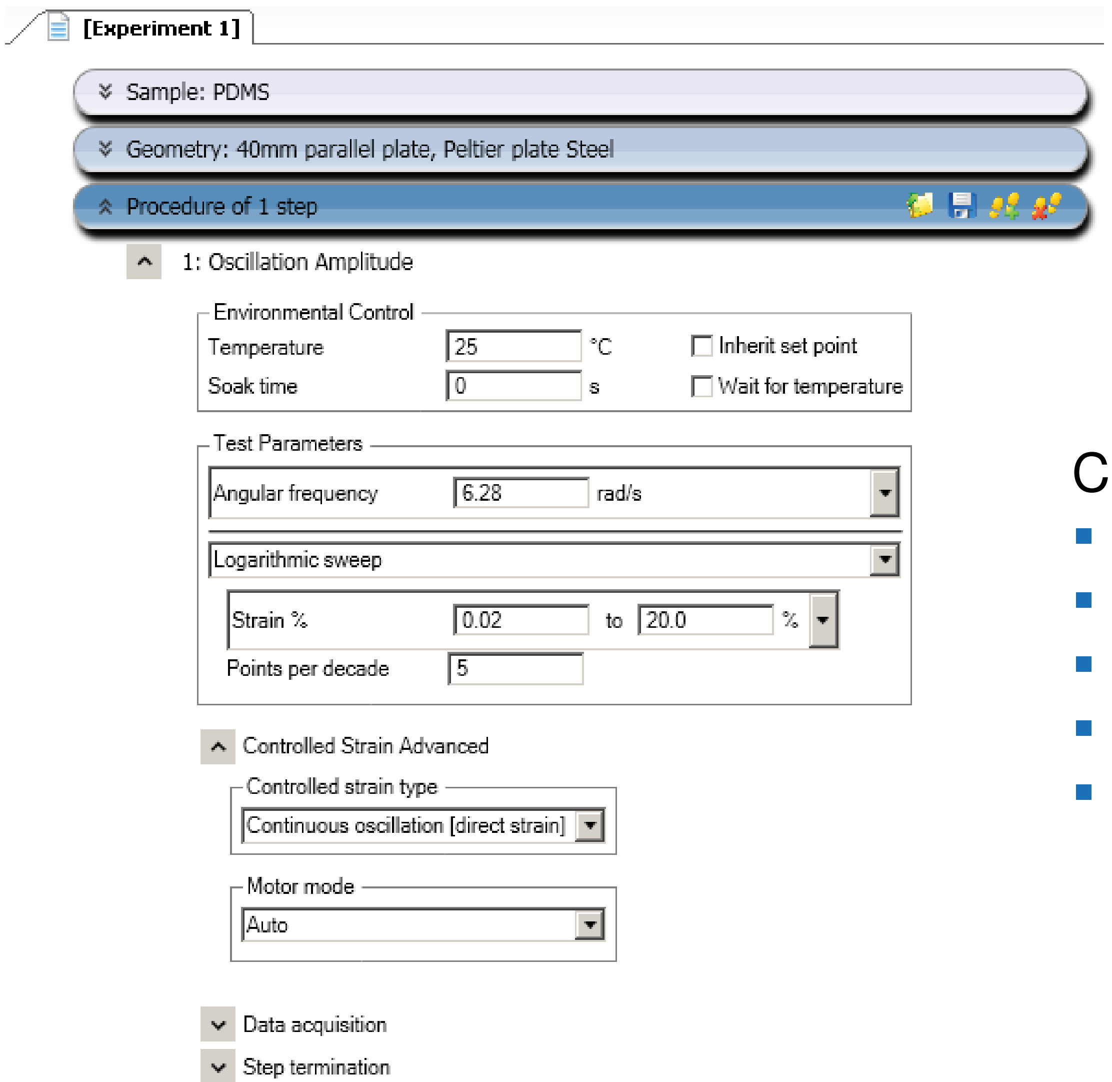


To minimize thermal lag, the ramp rate should be slow. 1-5℃/min.

Control variables:

- Shear rate
- Velocity
- Torque
- Shear stress

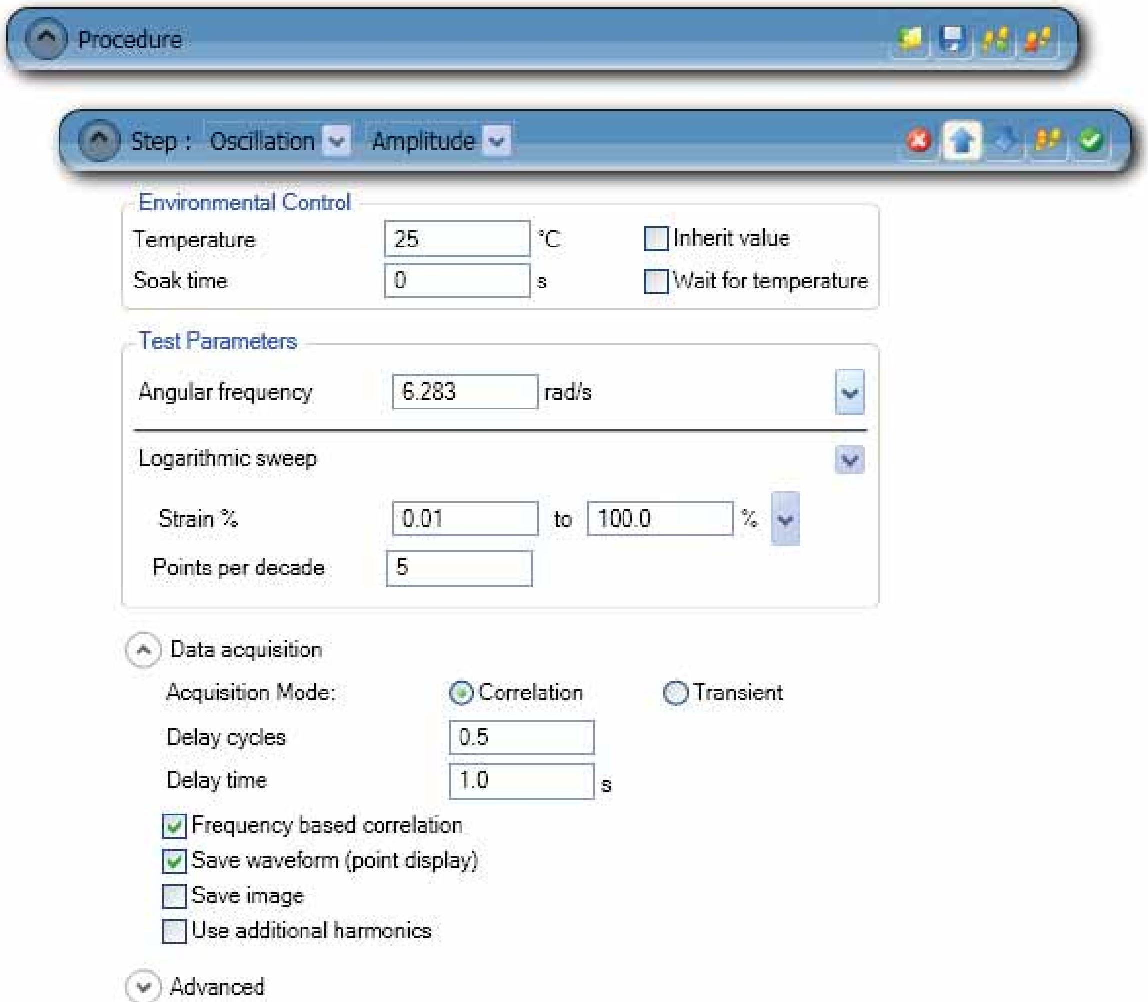
DHR: Strain/Stress Sweeps



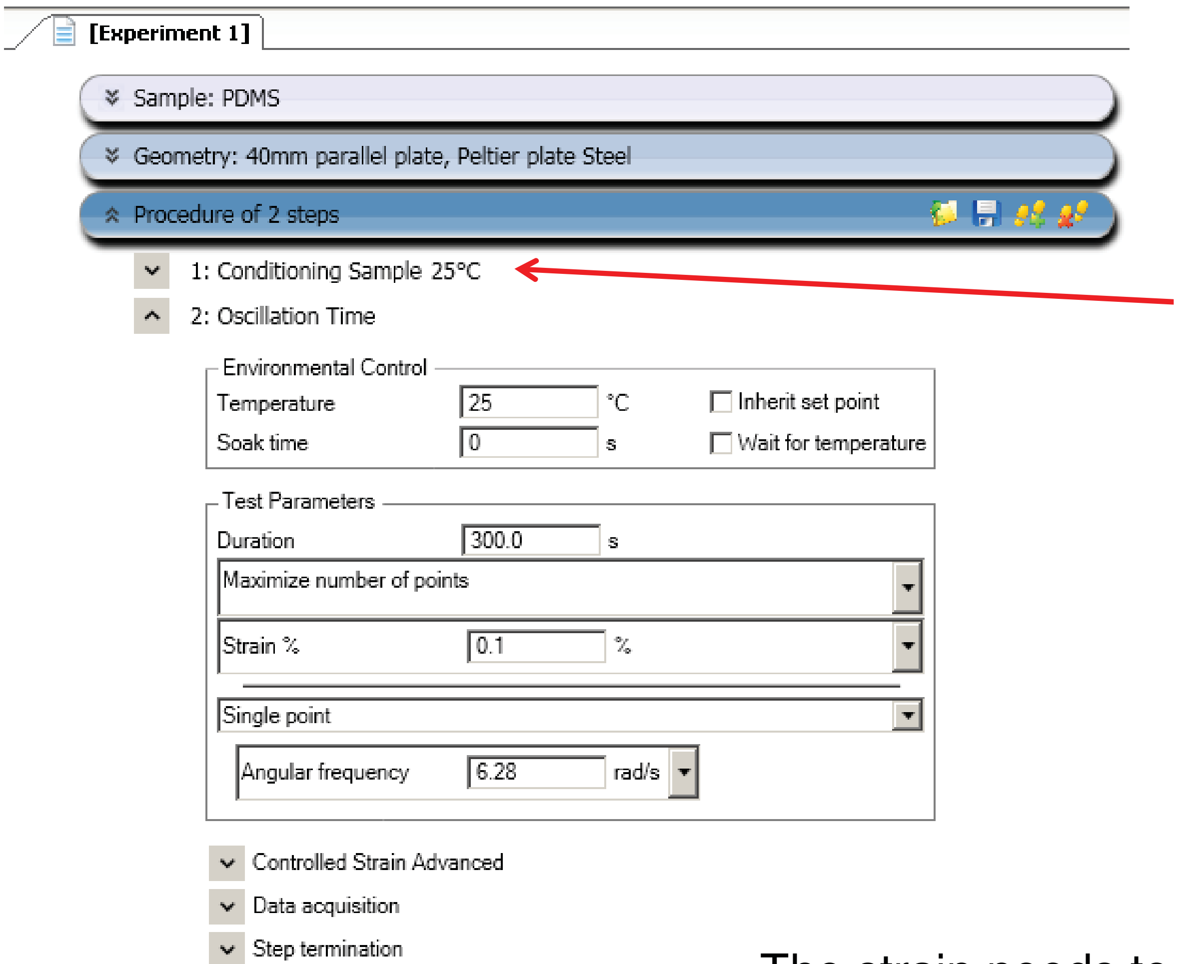
Control variables:

- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

ARES G2: Strain Sweep



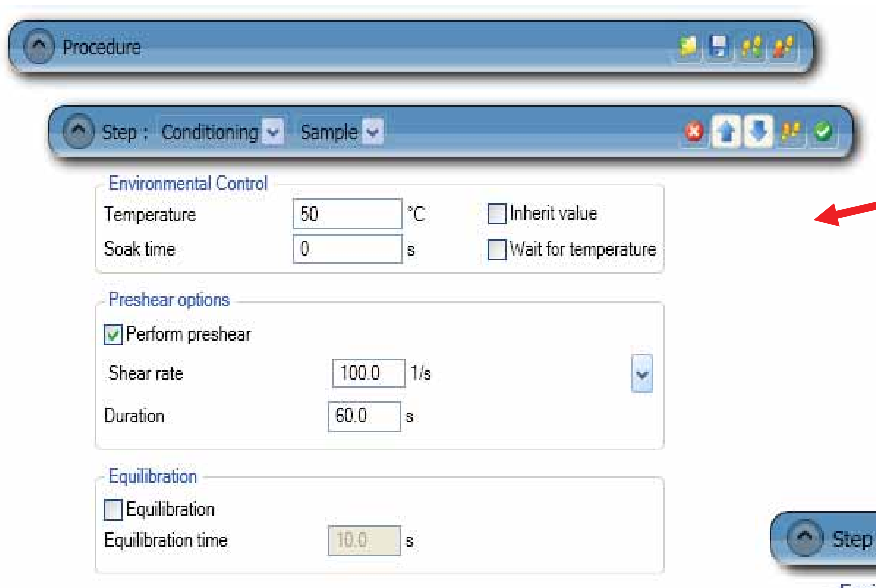
DHR: Time Sweep



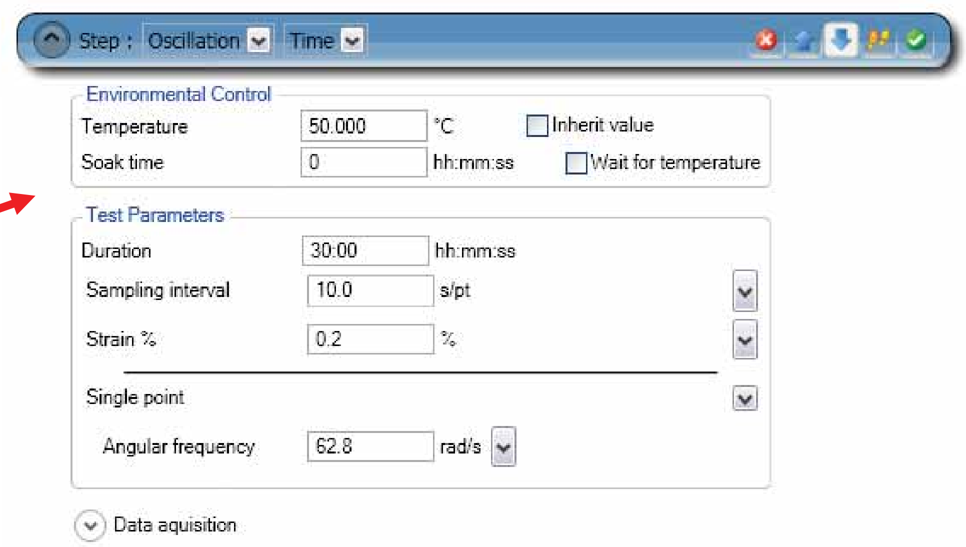
Pre-shear can be setup by adding a “conditioning” step before the time sweep.

- The strain needs to be in the LVR

ARES G2: Time Sweep

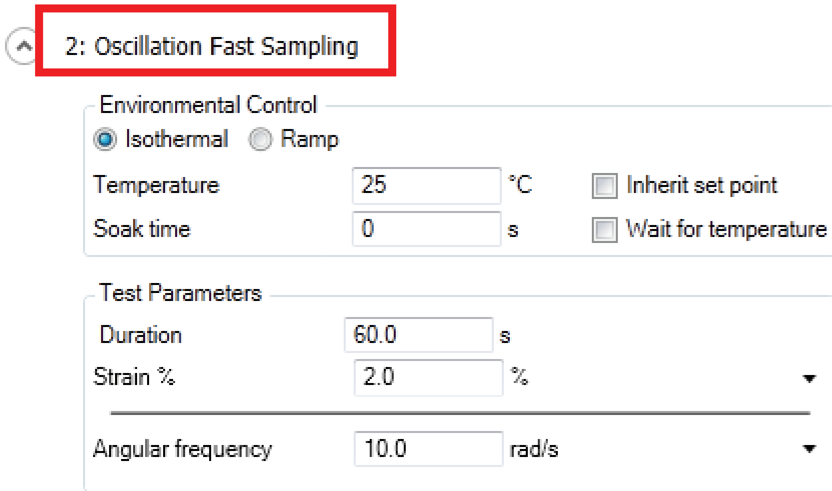


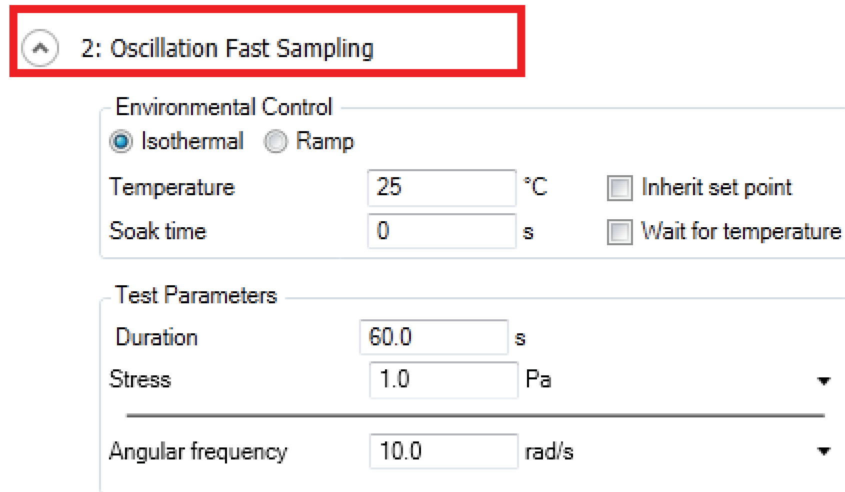
Pre-shear step



Structure Recovery

Fast Data Sampling Option in Time Sweep

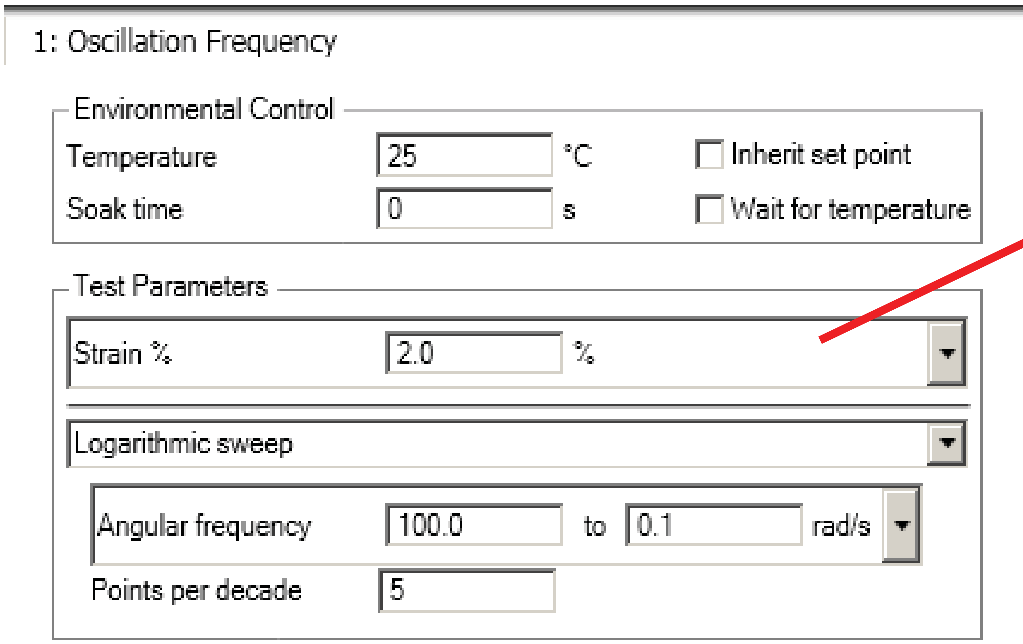




- Strain control mode
- Stress control mode

- Fast data acquisition is used for monitoring fast changing reactions such as UV initiated curing
- The sampling rate for this mode is twice the functional oscillation frequency up to 25Hz.
- The fastest sampling rate is 50 points /sec.

Frequency Sweep

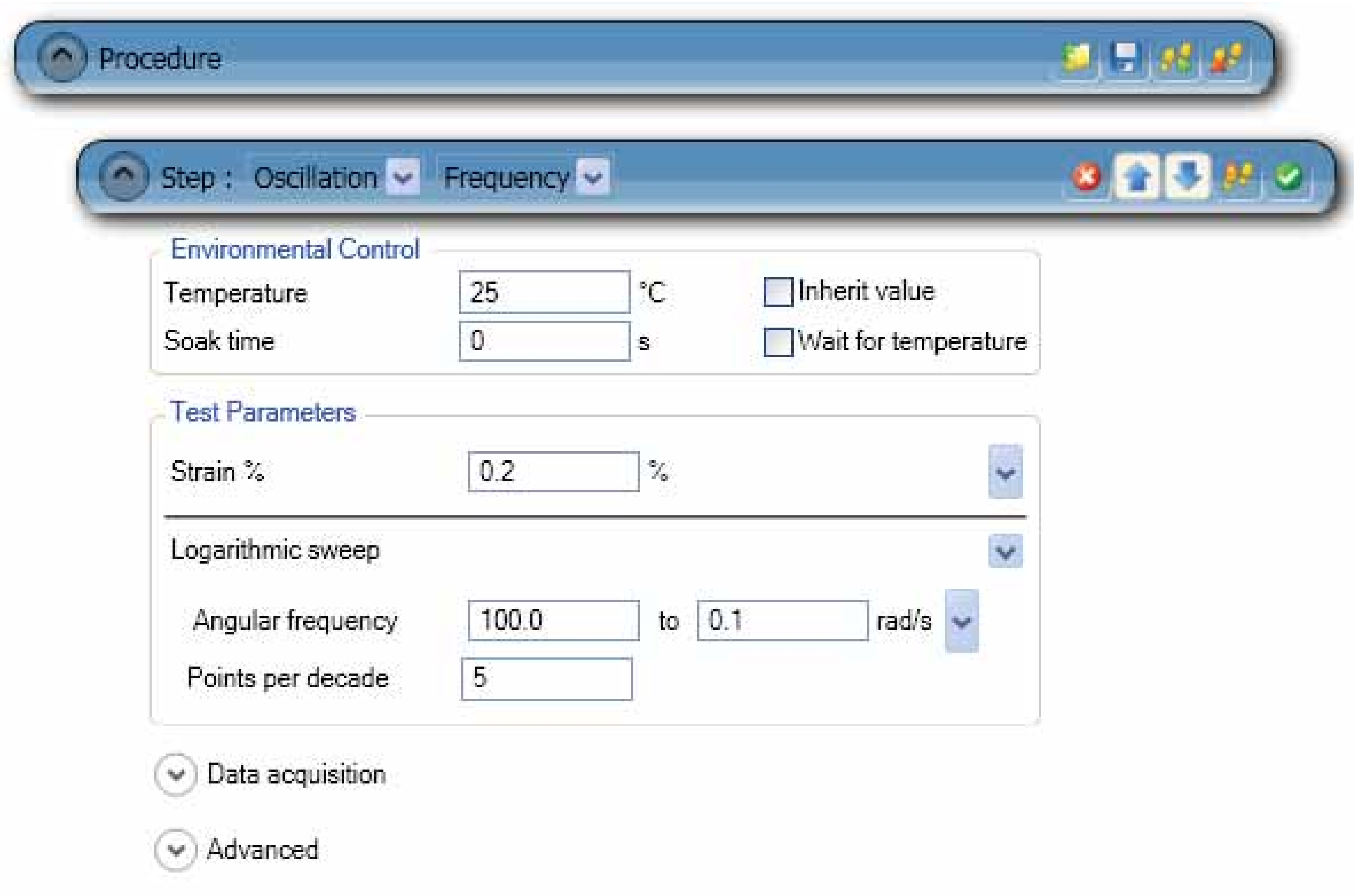


Control variables:

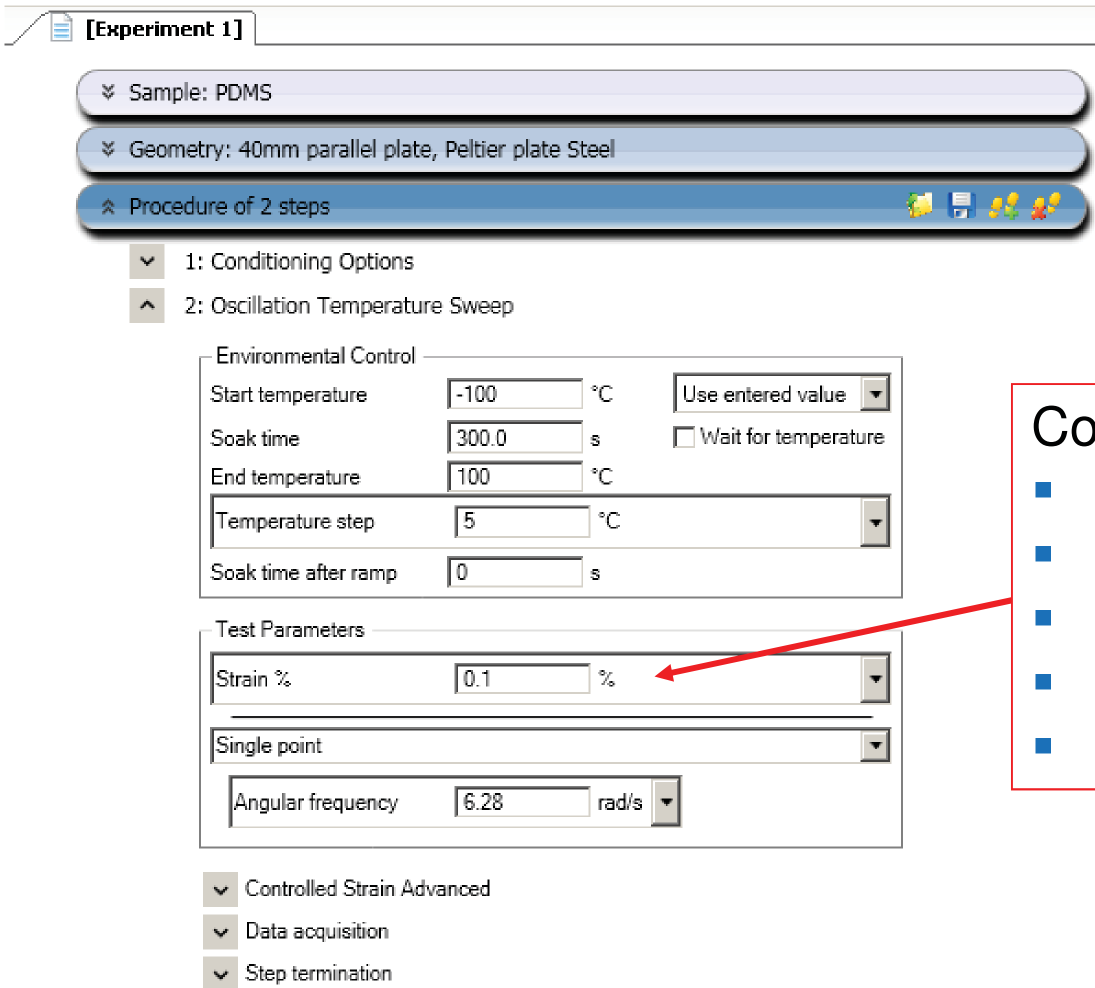
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

- Common frequency range: 0.1 – 100 rad/s.
- Low frequency takes long time
- As long as in the LVR, the test frequency can be set either from high to low, or low to high
- The benefit doing the test from high to low
  - Being able to see the initial data points earlier

ARES G2:Frequency Sweep (Strain Control)



DHR: Temperature Sweep

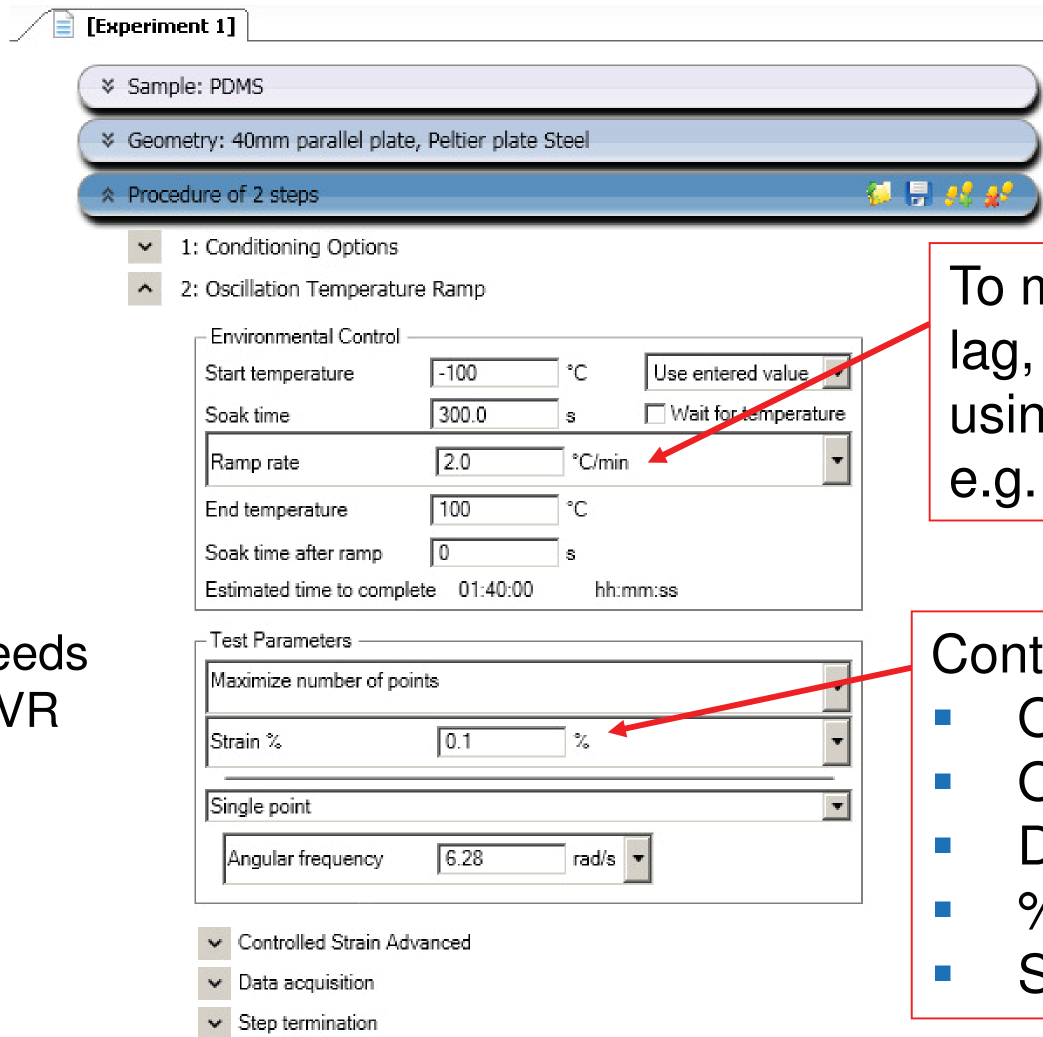


Control variables:

- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

- The strain needs to be in the LVR

DHR: Temperature Ramp



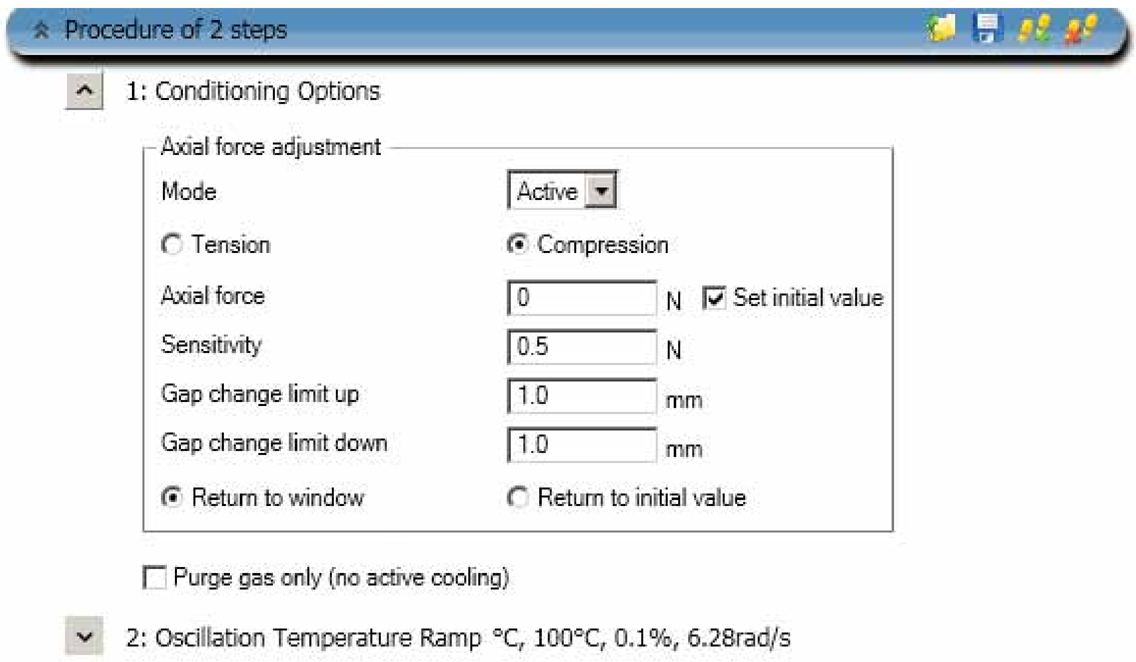
To minimize thermal lag, recommend using slow ramp rate e.g. 1-5 °C/min.

- The strain needs to be in the LVR

Control variables:

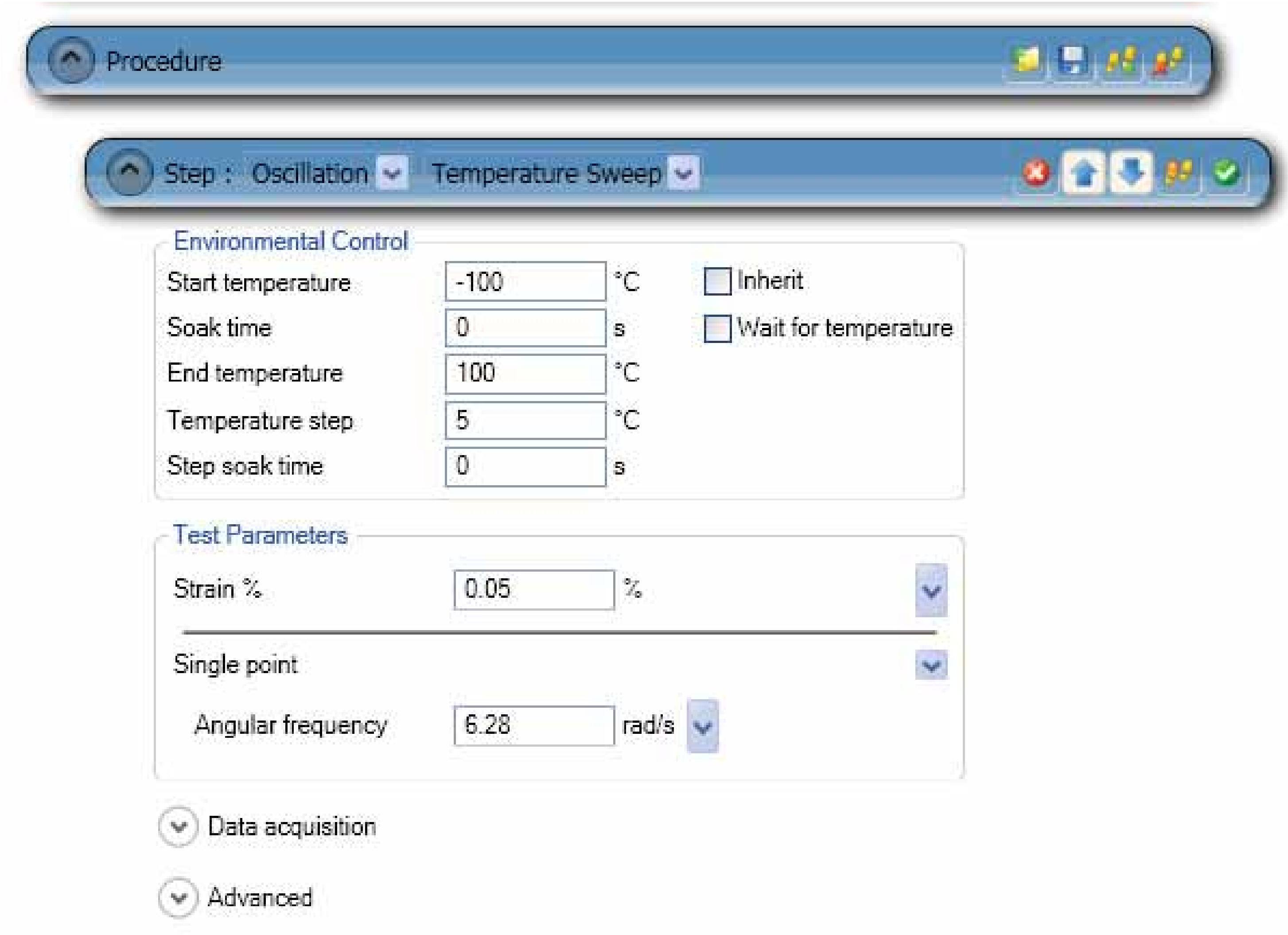
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

DHR: Axial Force Control

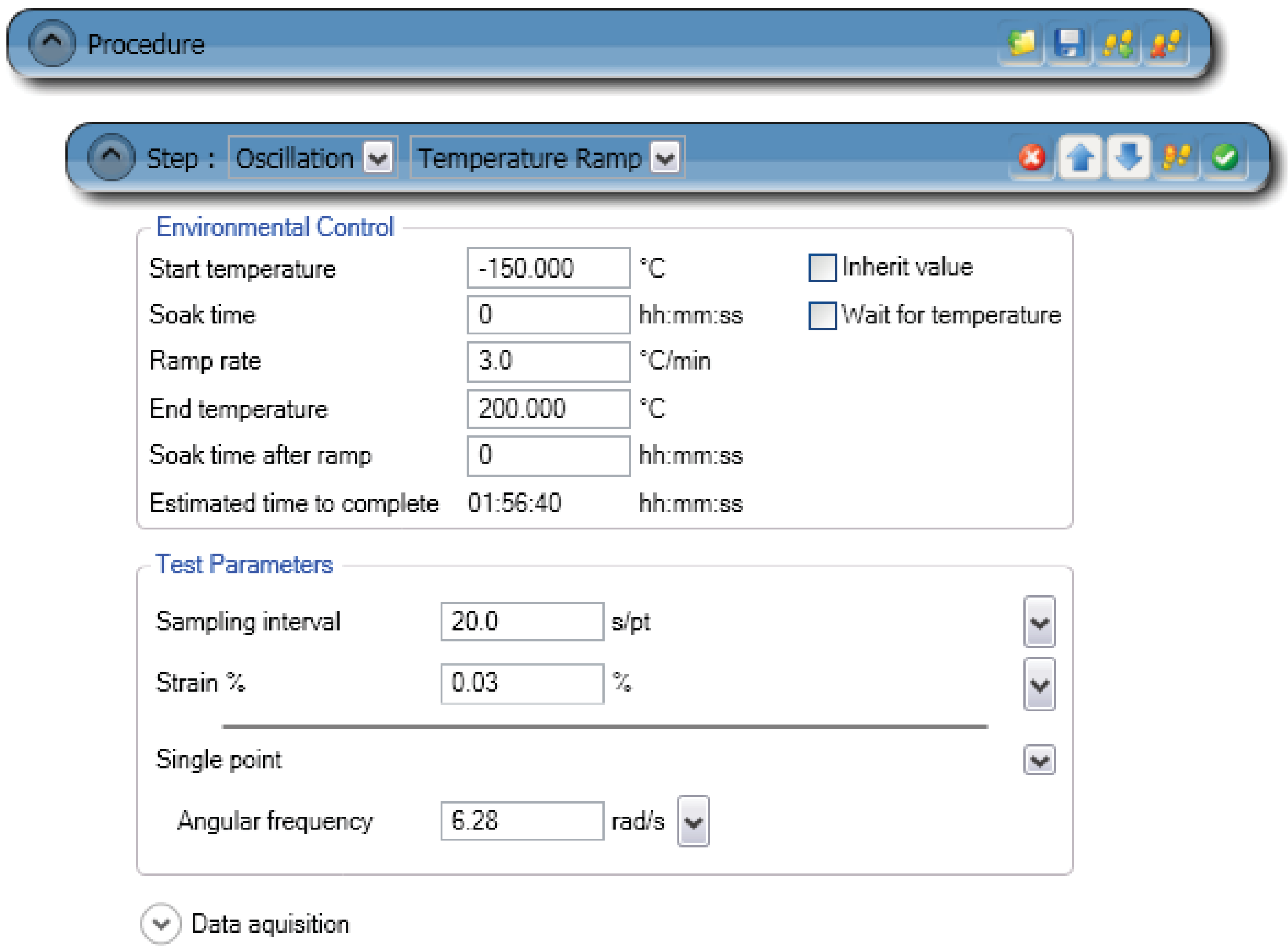


- It is important to setup normal force control during any temperature change testing or curing testing
- Some general suggestions for normal force control
  - For torsion testing, set normal force in tension: 1-2N ± 0.5-1.0N
  - For curing or any parallel plate testing, set normal force in compression: 0 ± 0.5N

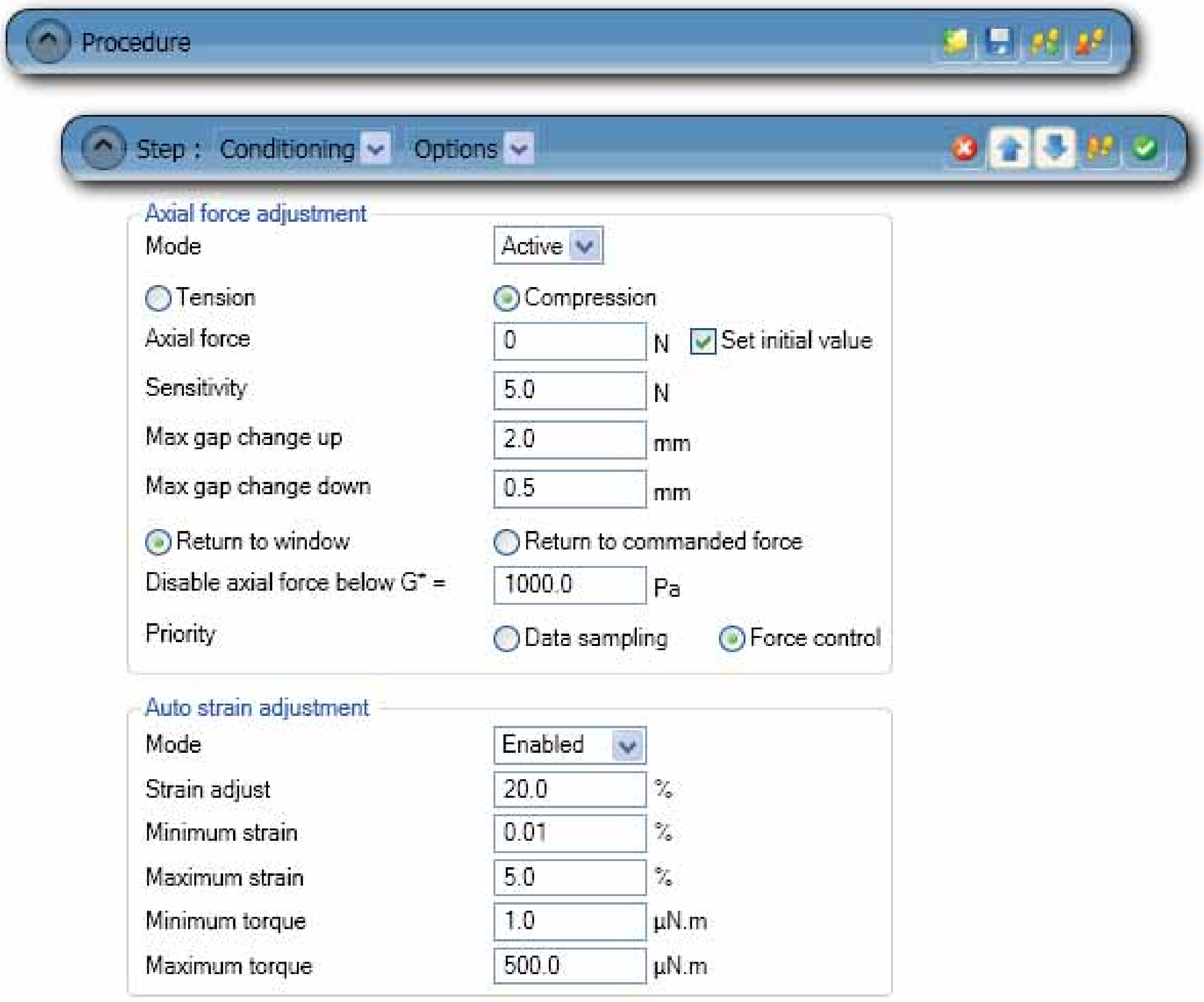
ARES G2: Temp Step



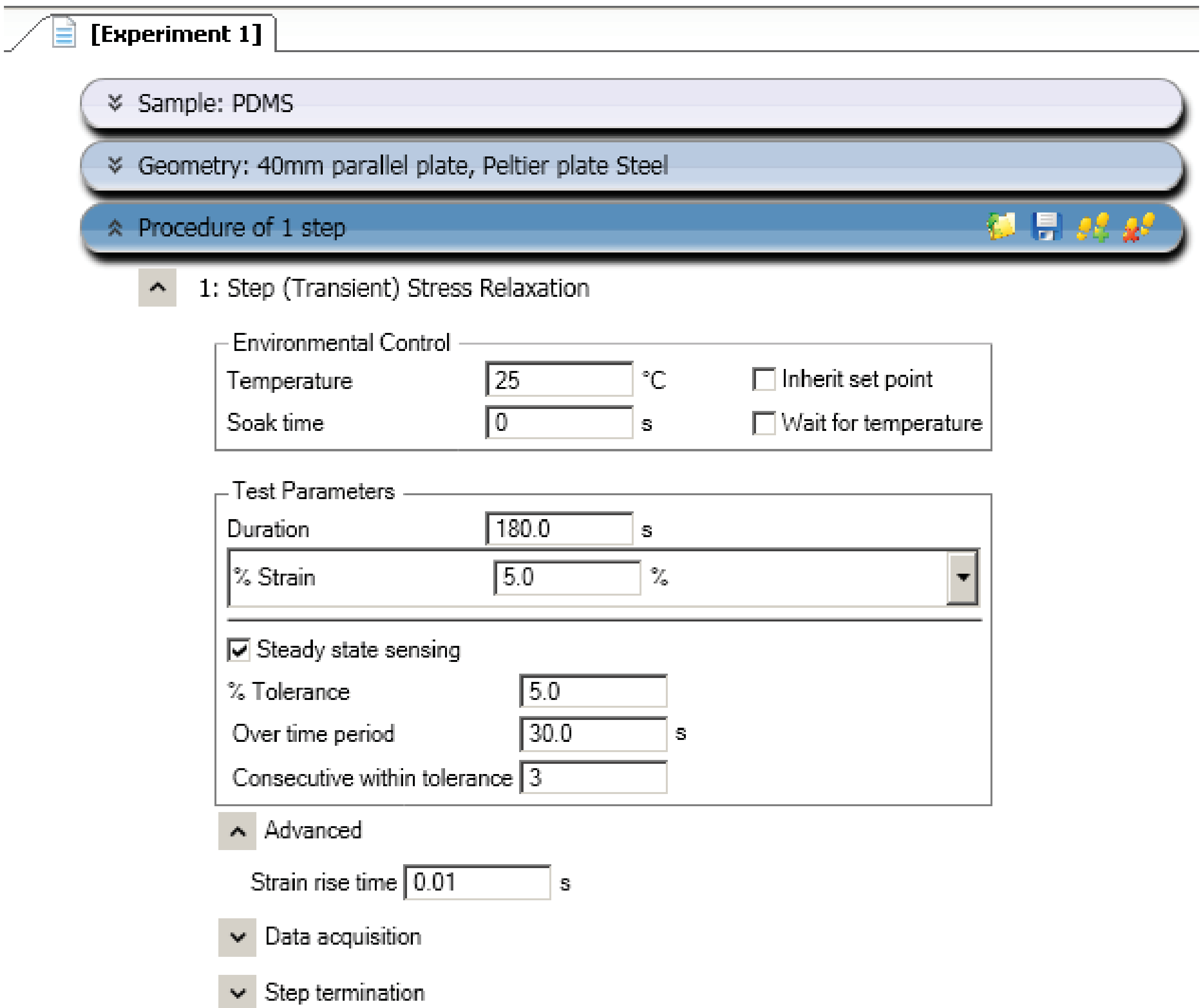
ARES G2: Temp Ramp



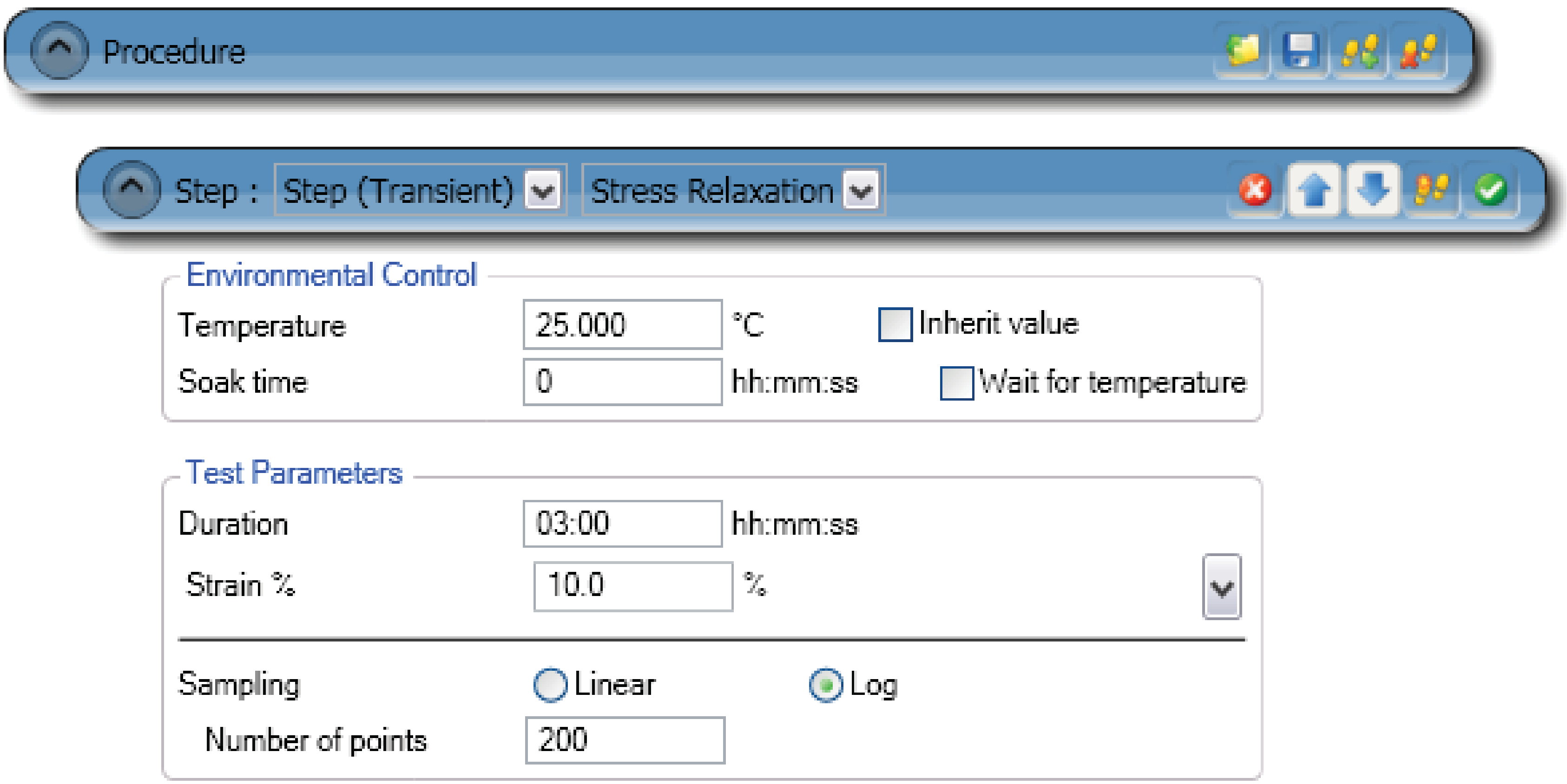
ARES G2: Axial force control and auto-strain



DHR: Stress Relaxation

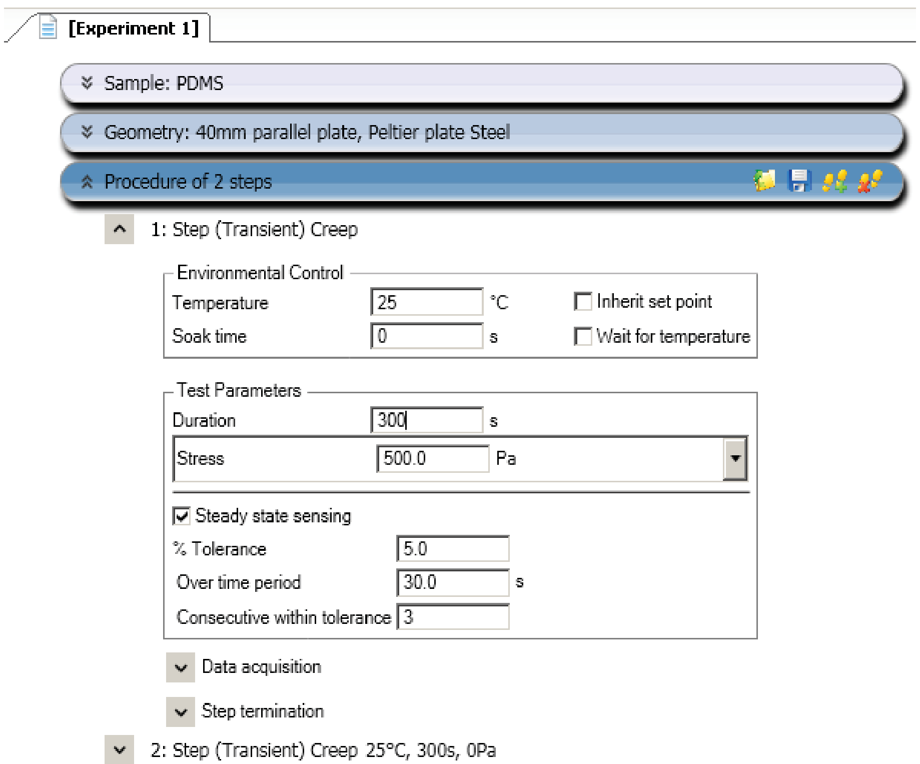


ARES G2: Stress Relaxation

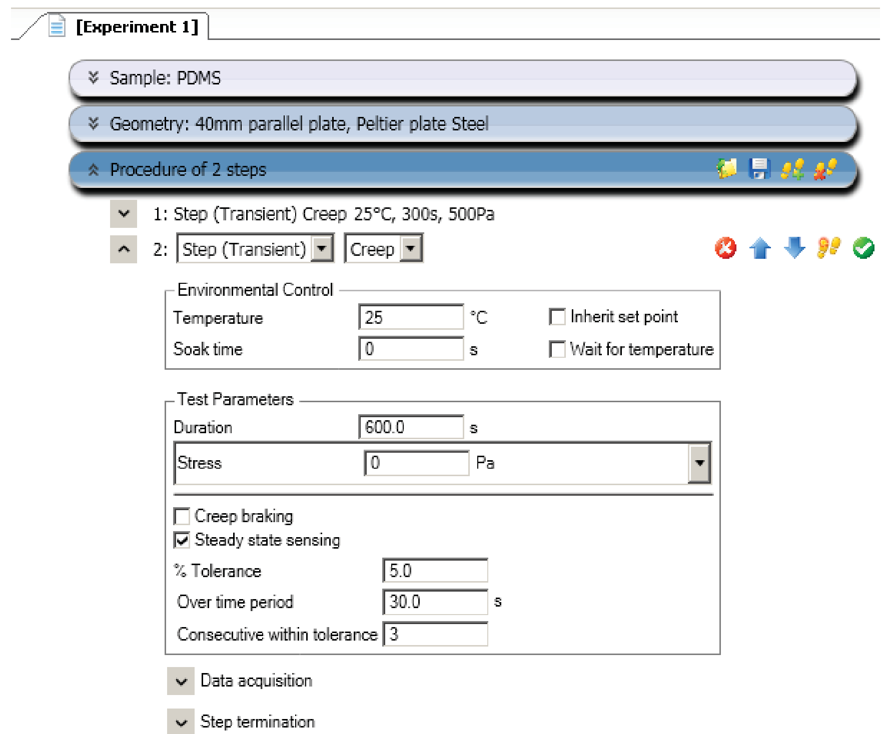


DHR: Creep Recovery

Creep

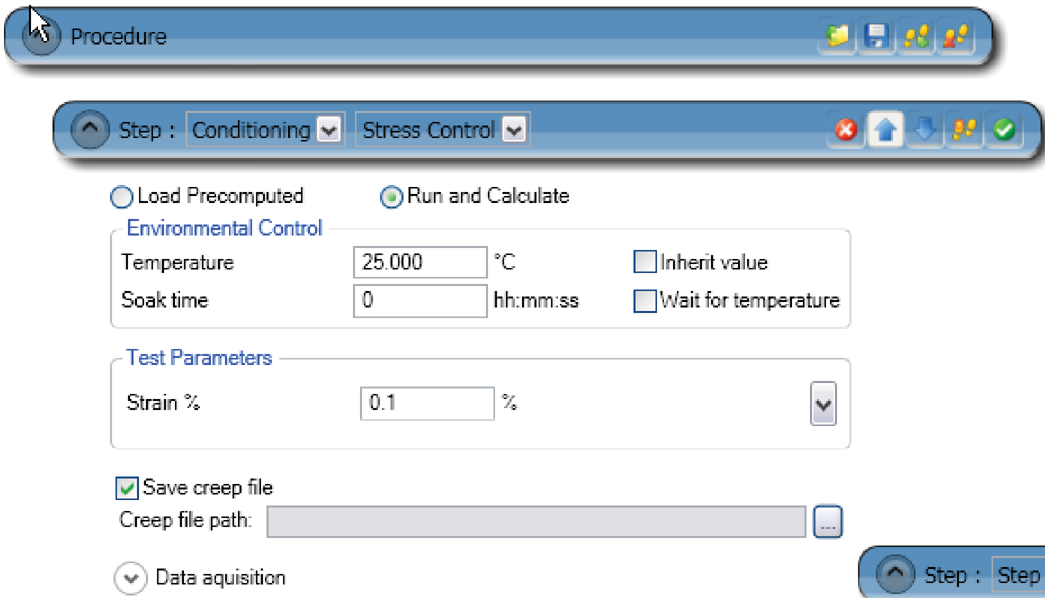


Recovery

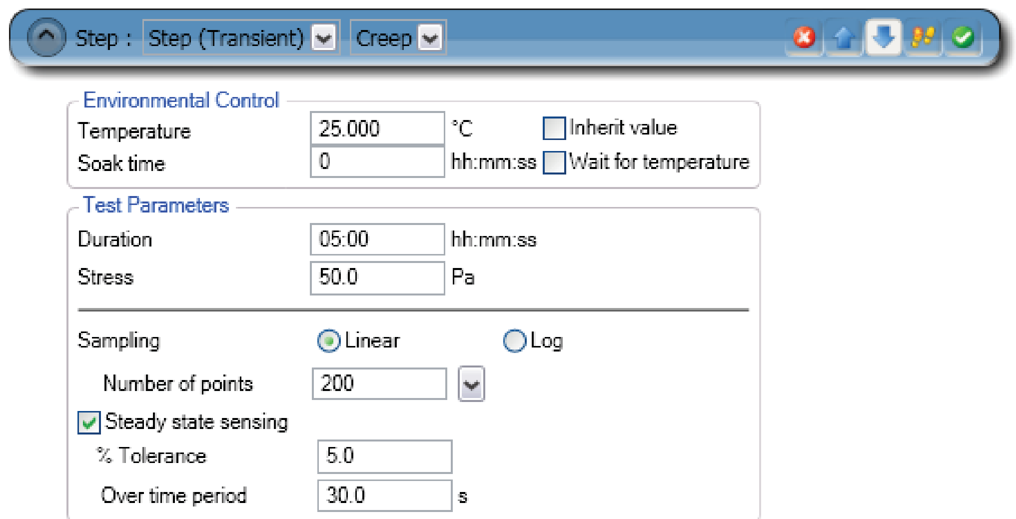


- **Rule of thumb: recovery time is 2-3 times longer than creep time**

ARES G2: Creep



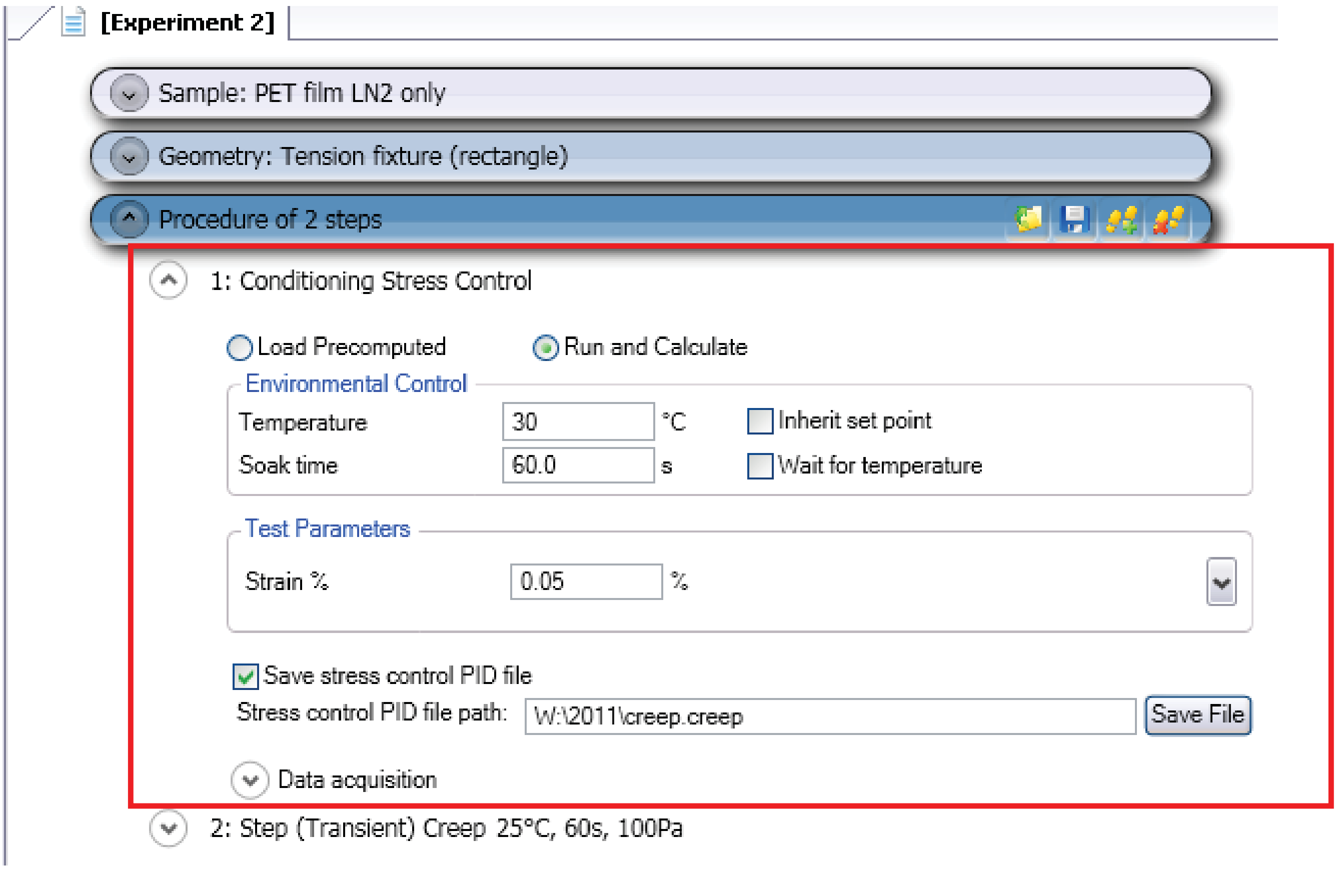
Requires measured modulus to start feed back loop



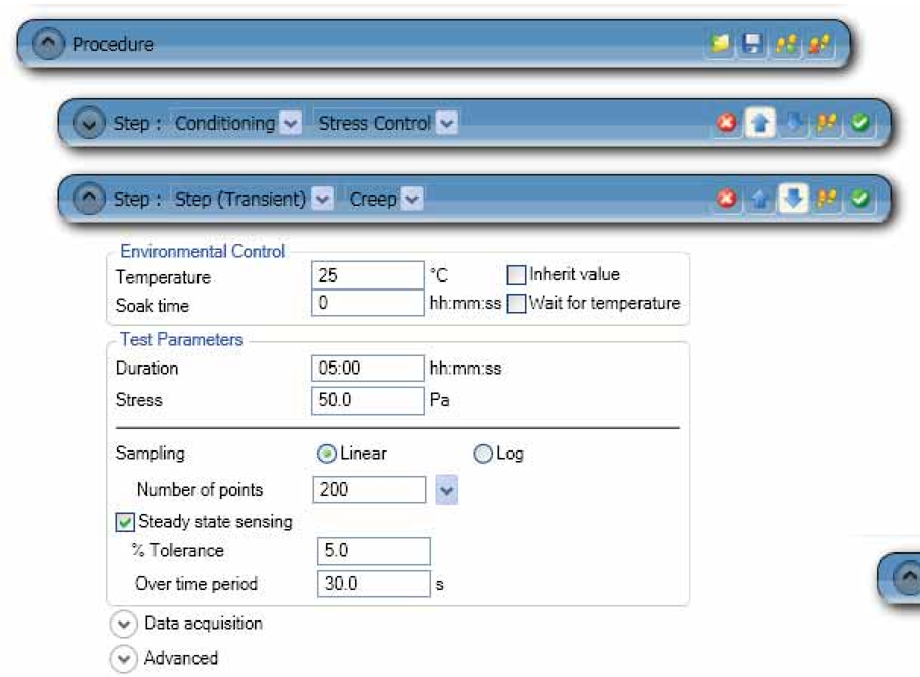
- Motor and transducer work in a feedback loop

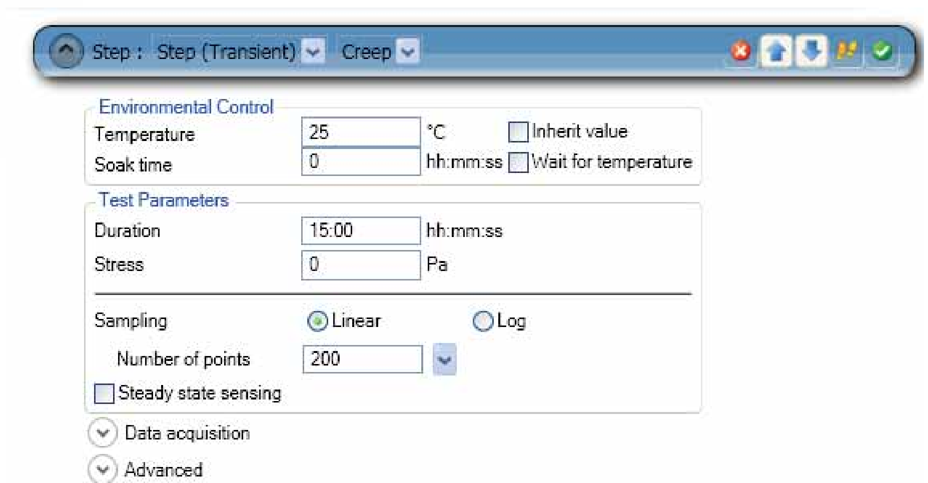
Programming Creep on a ARES G2

- Set up a pre-test and get the sample information into the loop
- Stress Control Pre-test: frequency sweep within LVR



ARES G2: Creep - Recovery

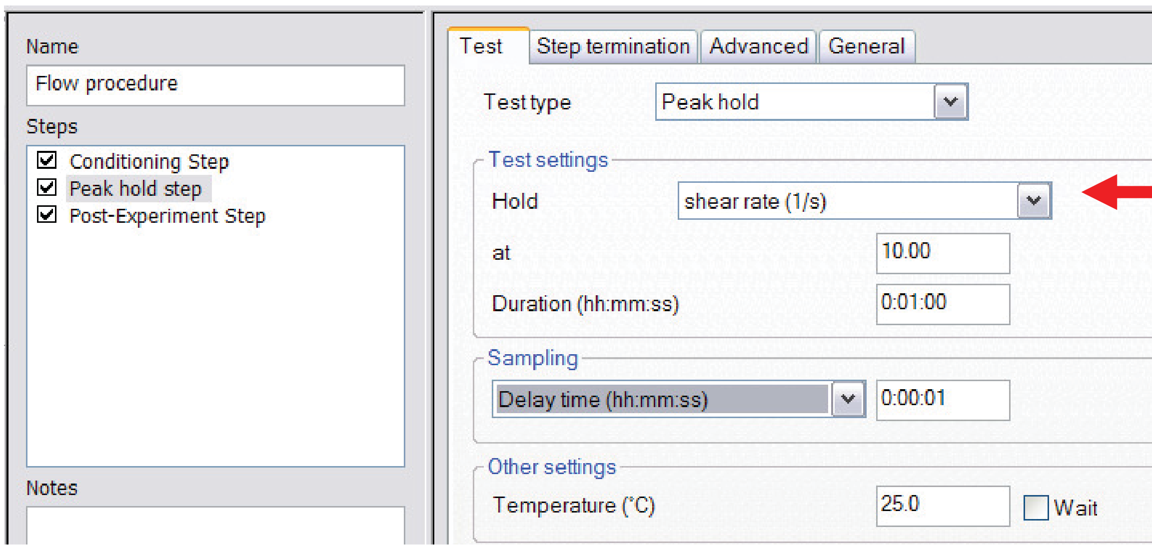




Appendix 3: Software Screen Shots

Rheology Advantage

AR: Peak Hold

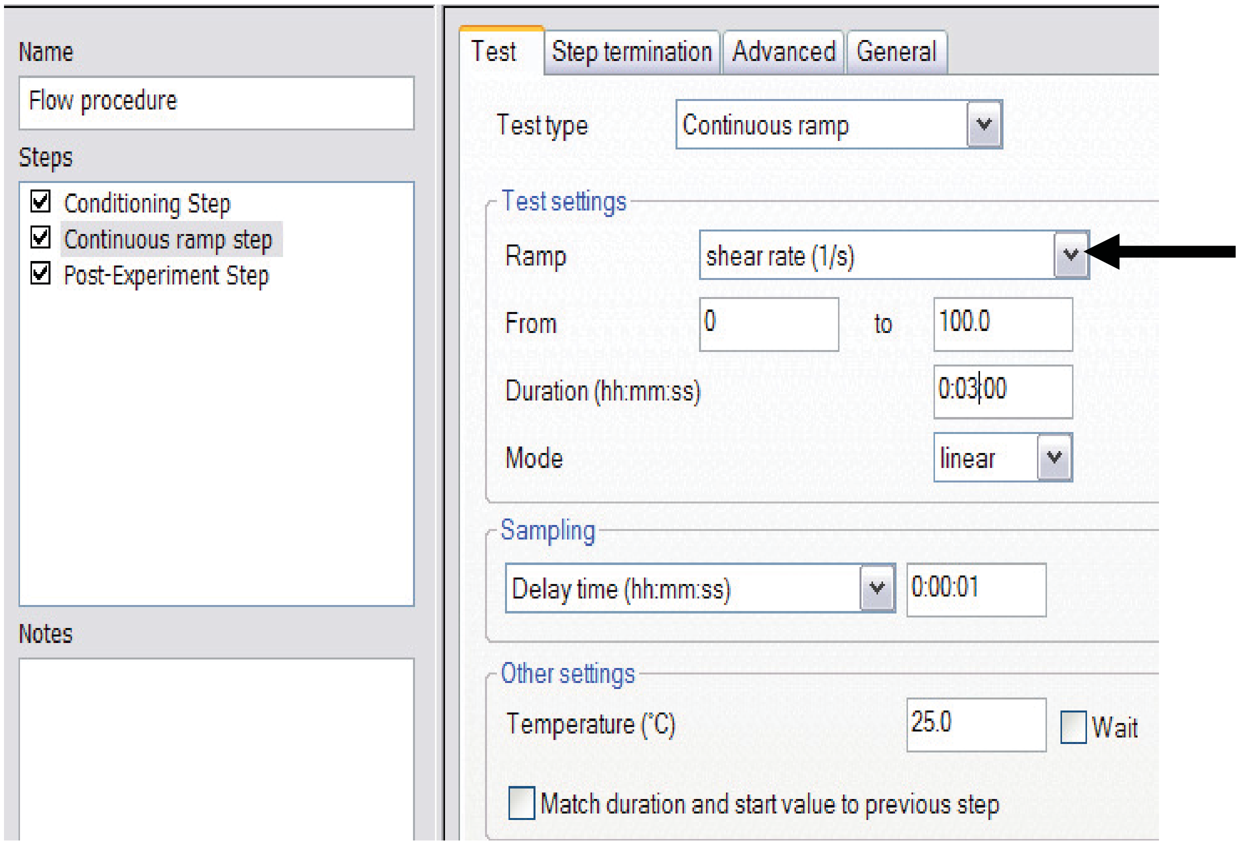


Control variables:

- Shear rate
- Velocity
- Torque
- Shear stress

- Multiple rate can be done by adding more peak hold steps

AR: Continuous Ramp

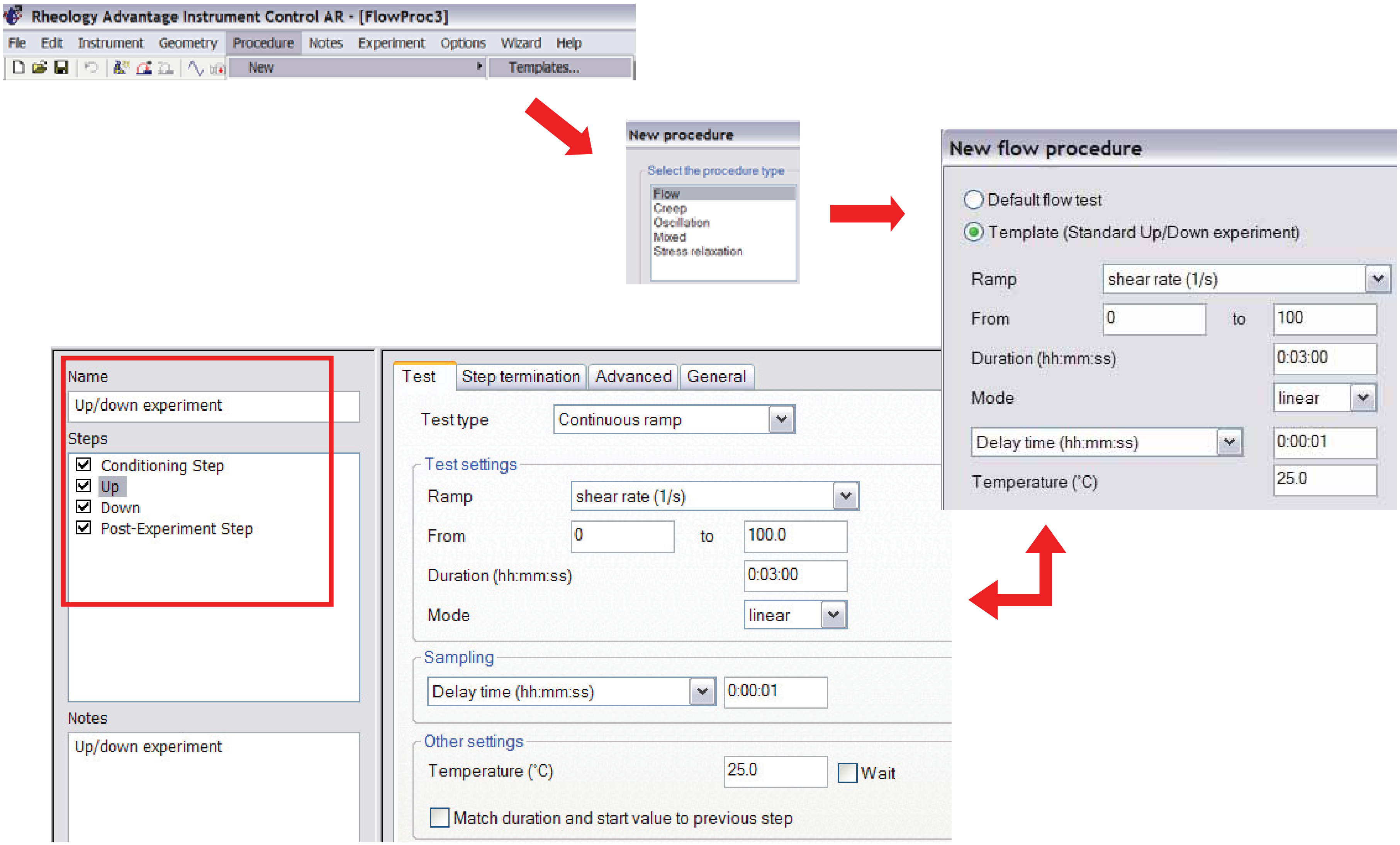


Control variables:

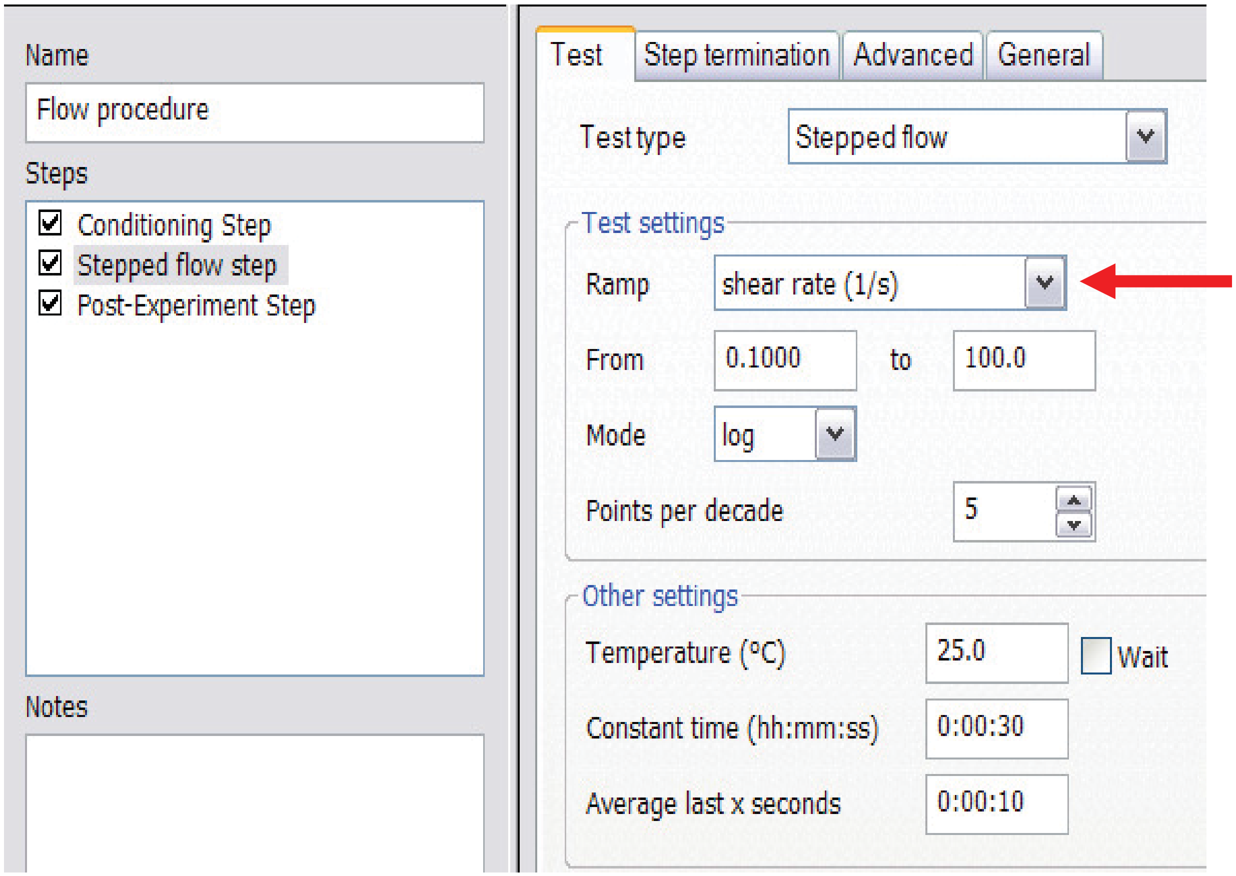
- Shear rate
- Velocity
- Torque
- Shear stress

- Thixotropic loop be done by adding another ramp step
- Or go through the template

AR: Continuous Ramp



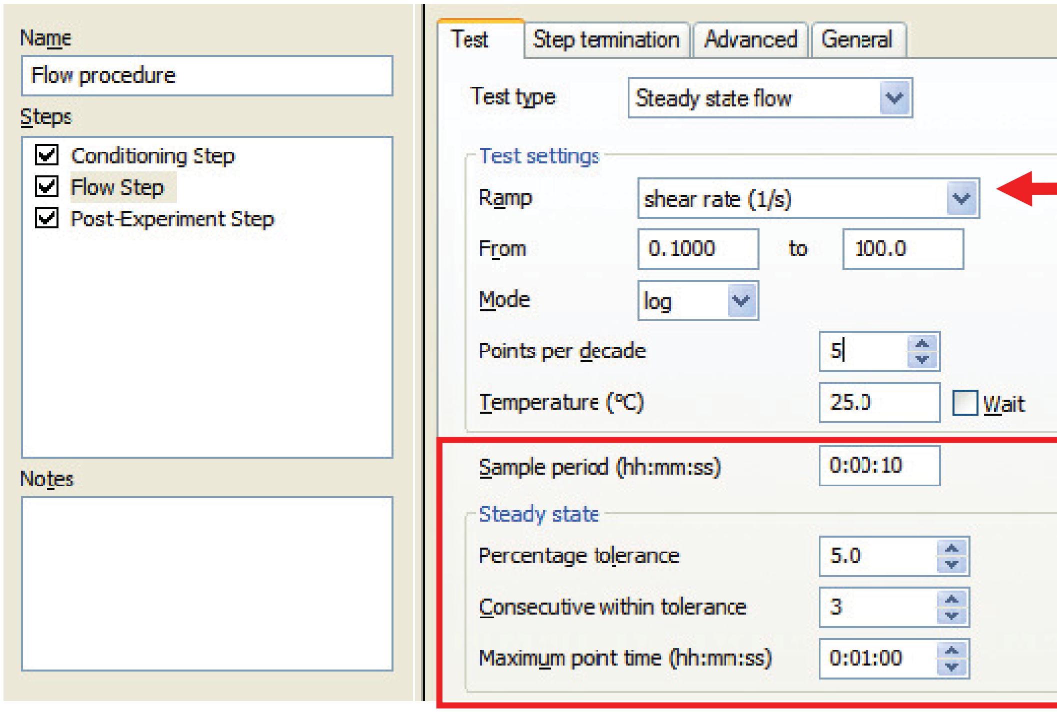
AR: Stepped Flow



Control variables:

- Shear rate
- Velocity
- Torque
- Shear stress

AR: Steady State Flow



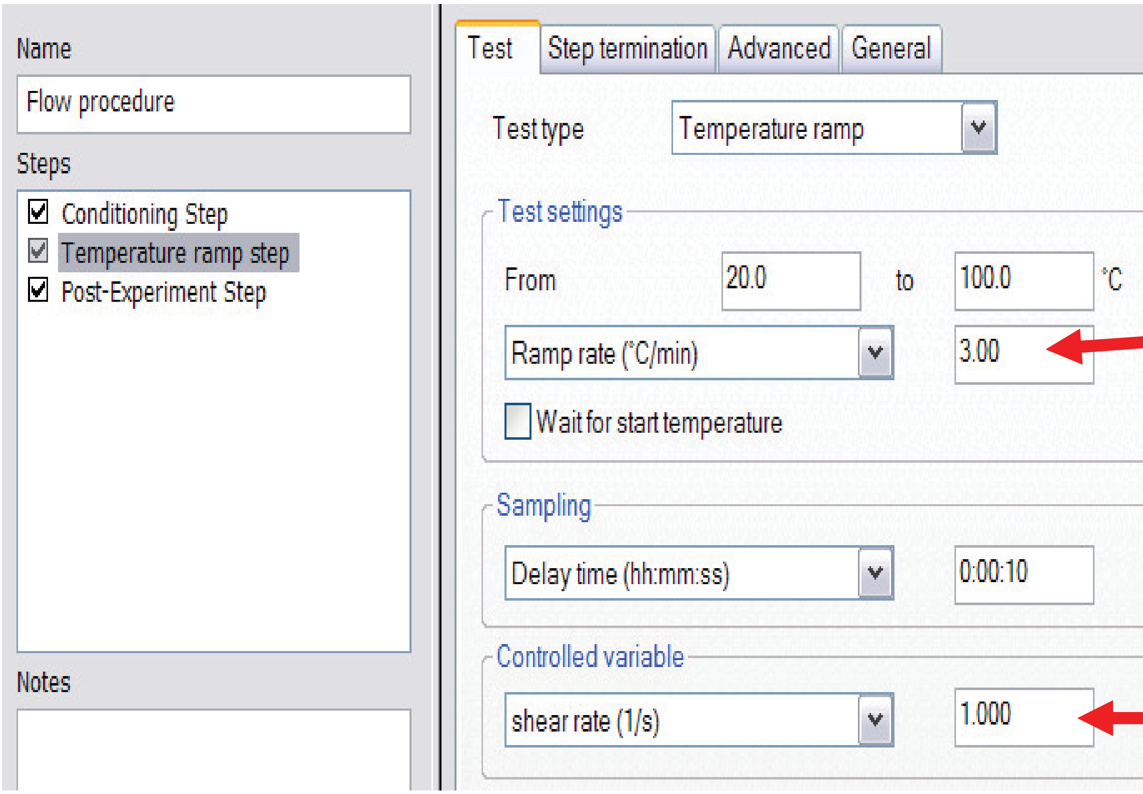
Control variables:

- Shear rate
- Velocity
- Torque
- Shear stress

Steady state algorithm

- During the test, the dependent variable (speed in controlled stress mode or torque in controlled shear rate mode) is monitored with time to determine when stability has been reached.
- An average value for the dependent variable is recorded over the *Sample period*.
- When consecutive average values *(Consecutive within tolerance)* are within the *Percentage tolerance* specified here, the data is accepted.
- The software will also accept the point at the end of the *Maximum point time*, should the data still not be at a steady state value.

AR: Flow Temp Ramp

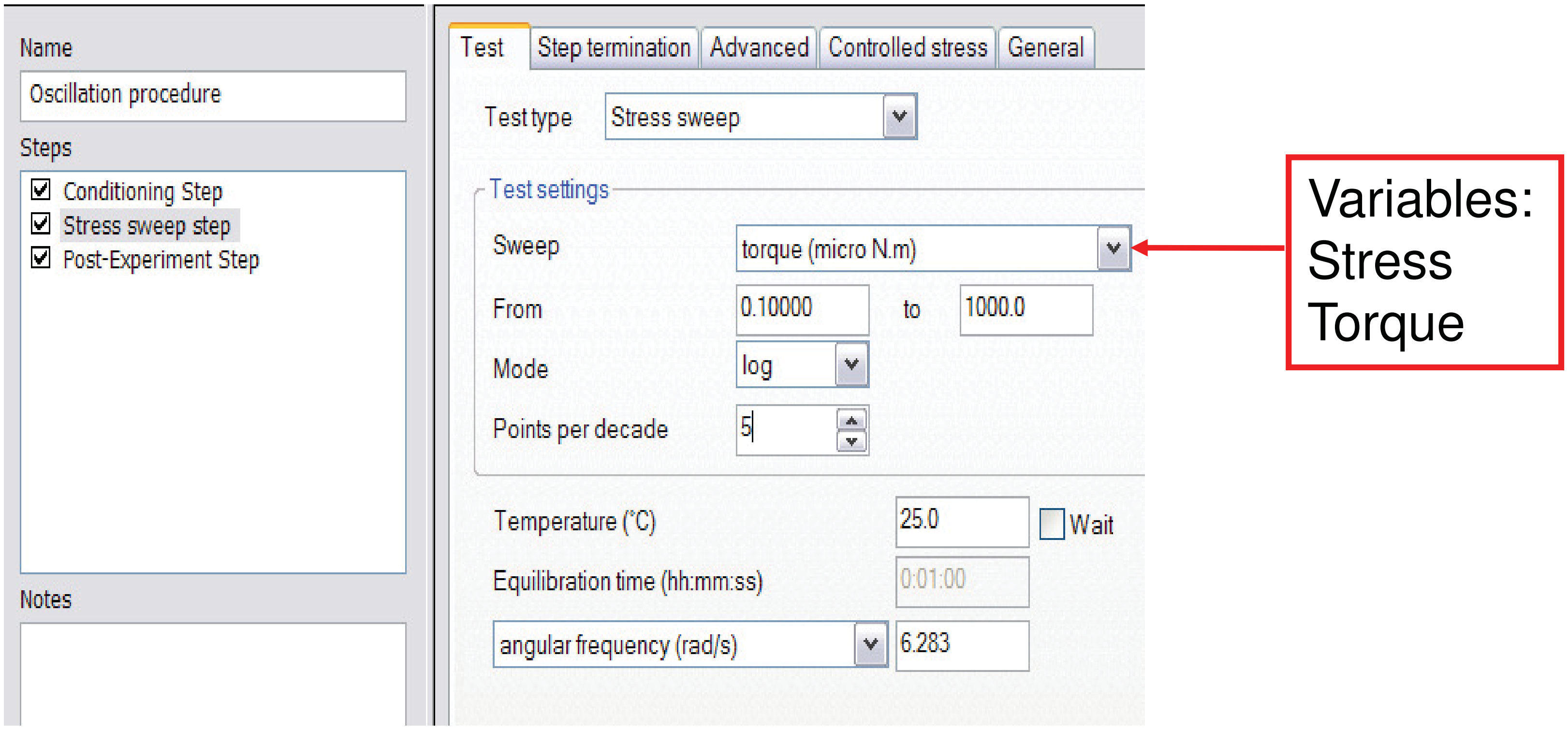


To minimize thermal lag, the ramp rate should be slow. 1-5 °C/min.

Control variables:

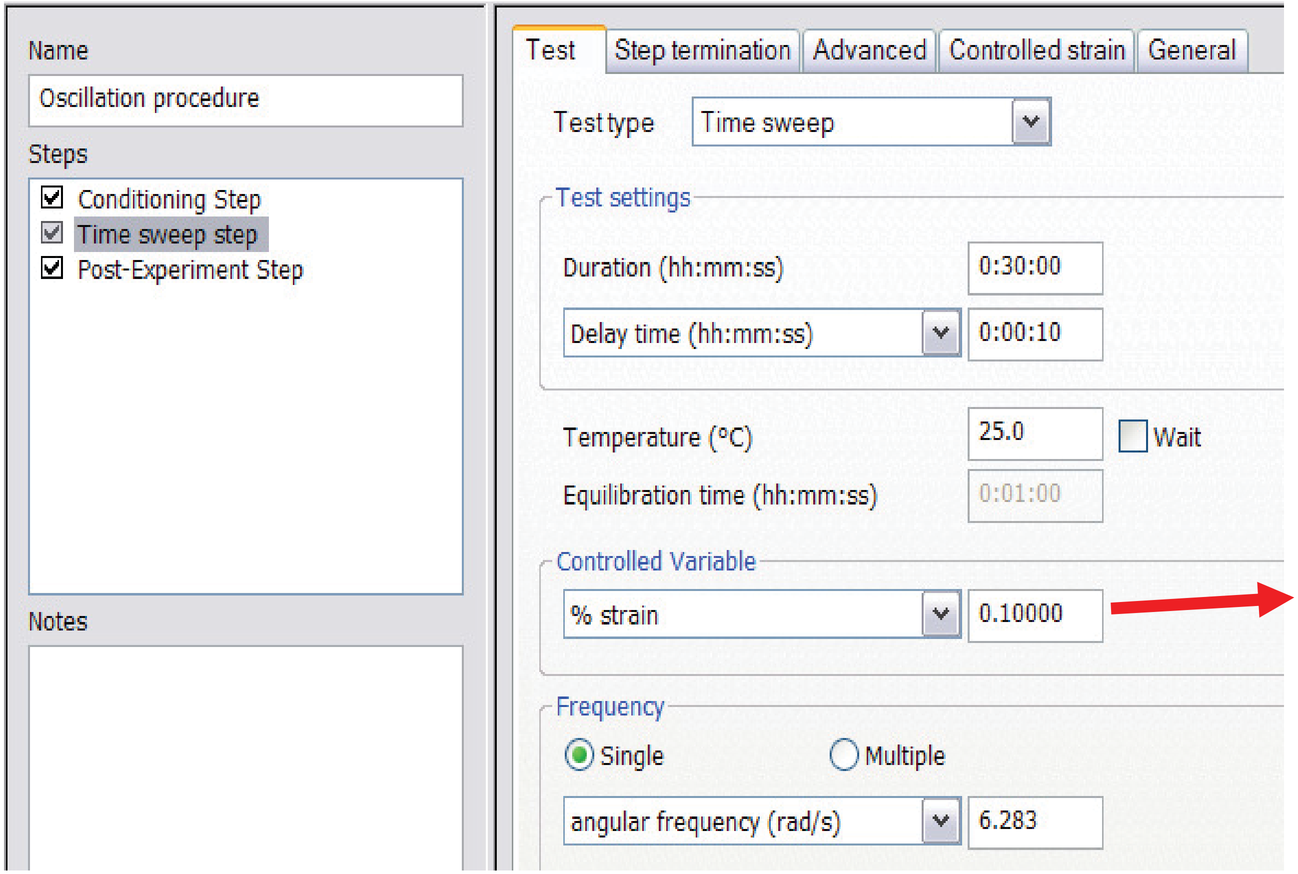
- Shear rate
- Velocity
- Torque
- Shear stress

AR: Stress Sweep



- For running an unknown sample, it is recommended to sweep torque instead of stress. Because stress is geometry dependent
- The starting torque can be from the lowest of the instrument specification
- The maximum torque is sample dependent. You can setup a high number and manually stop the test when it gets outside the LVR.

AR: Time Sweep

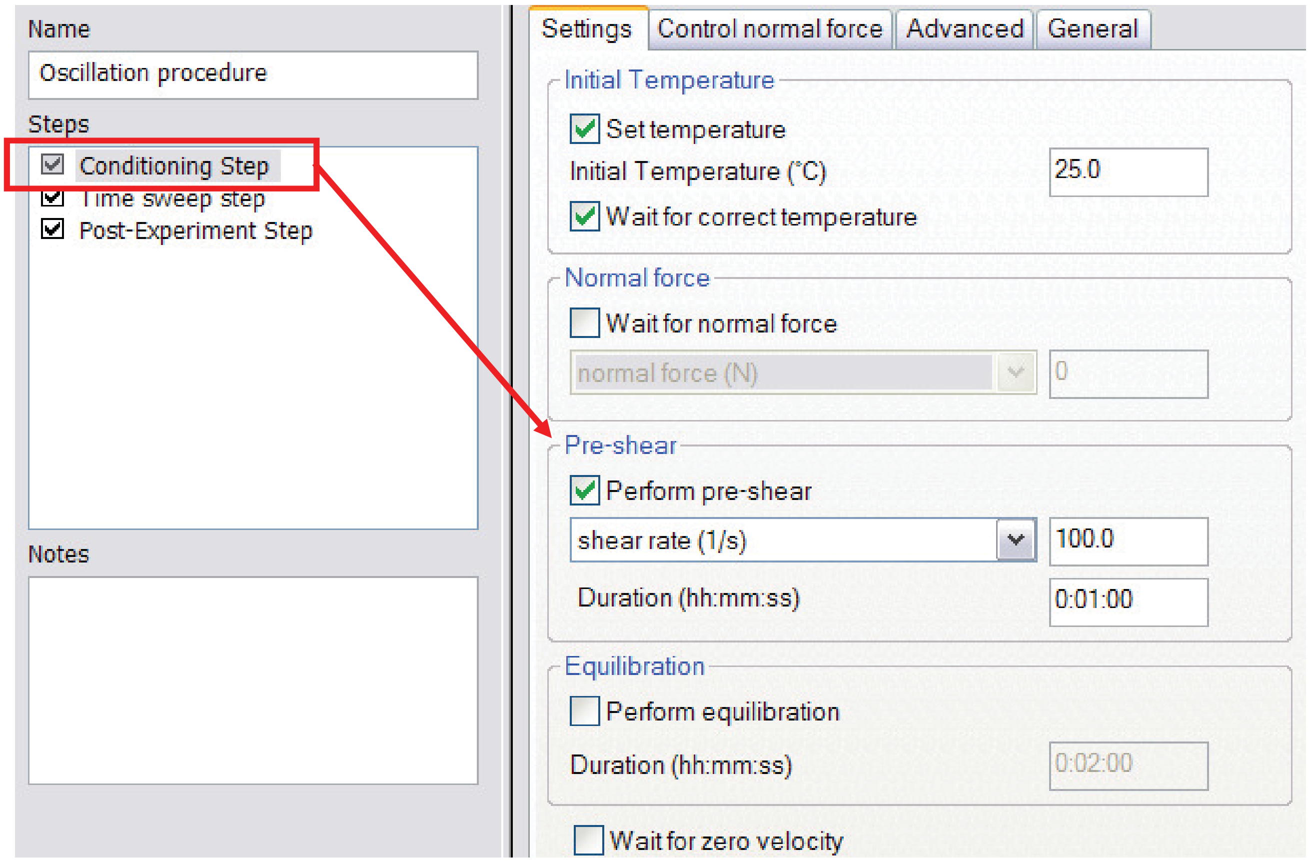


Control variables:

- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

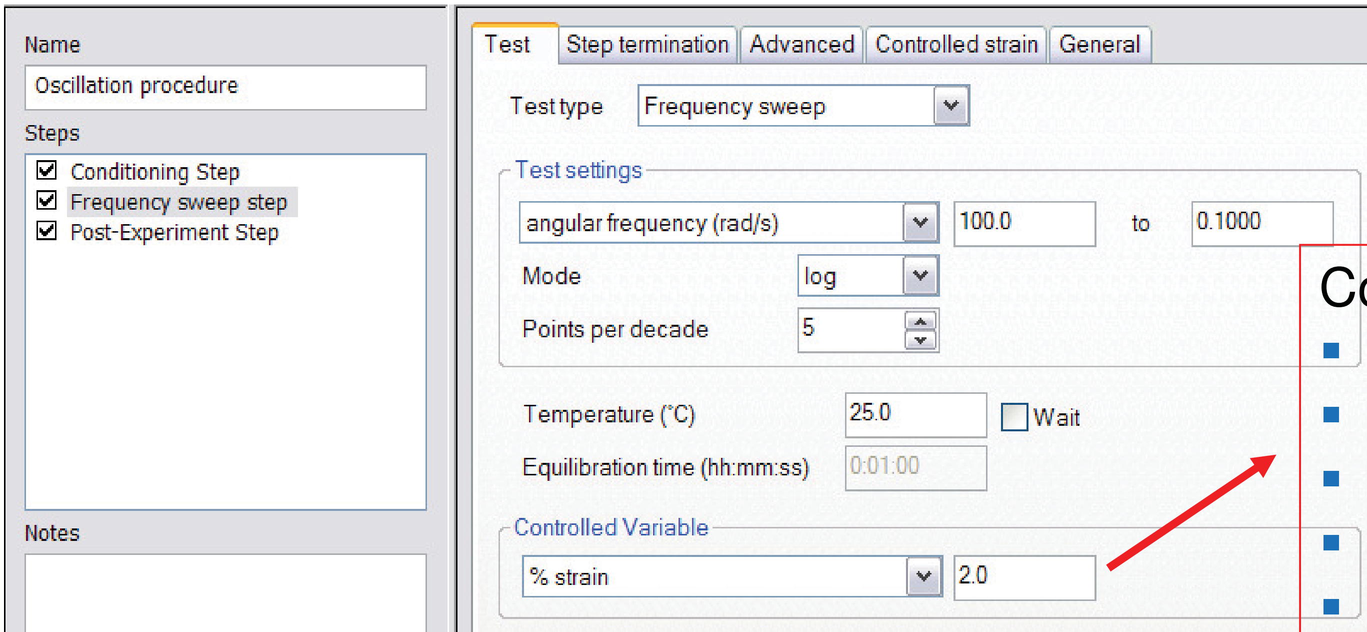
- The strain needs to be in the LVR

AR: Pre-shear Conditions



- The goal for pre-shear is to remove the sample history at loading
- For high viscosity sample, use low rate (10 1/s) and long time (2 min.)
- For low viscosity sample, use high rate (100 1/s) and short time (1 min.)

AR: Frequency Sweep

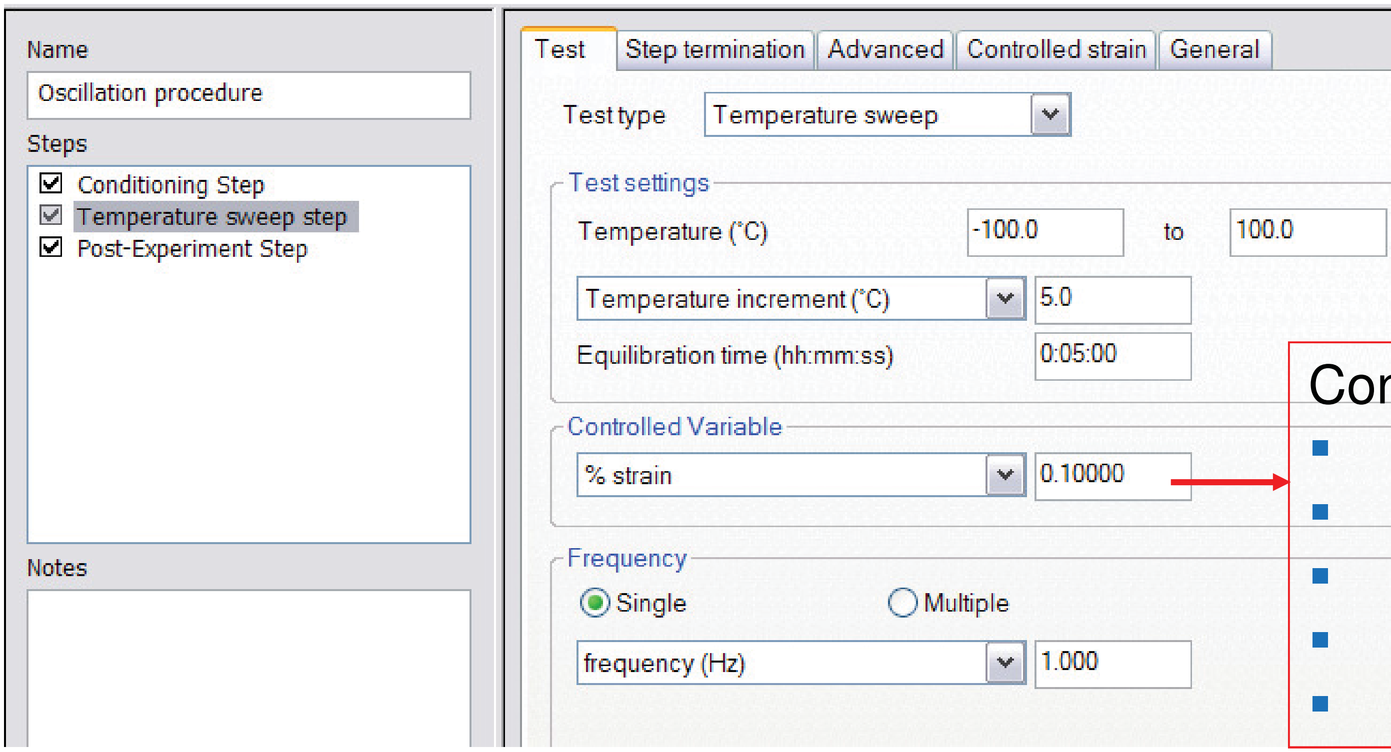


Control variables:

- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

- Common frequency range: 0.1 – 100 rad/s.
- Low frequency takes long time
- As long as in the LVR, the test frequency can be set either from high to low, or low to high
- The benefit doing the test from high to low
  - Being able to see the initial data points earlier

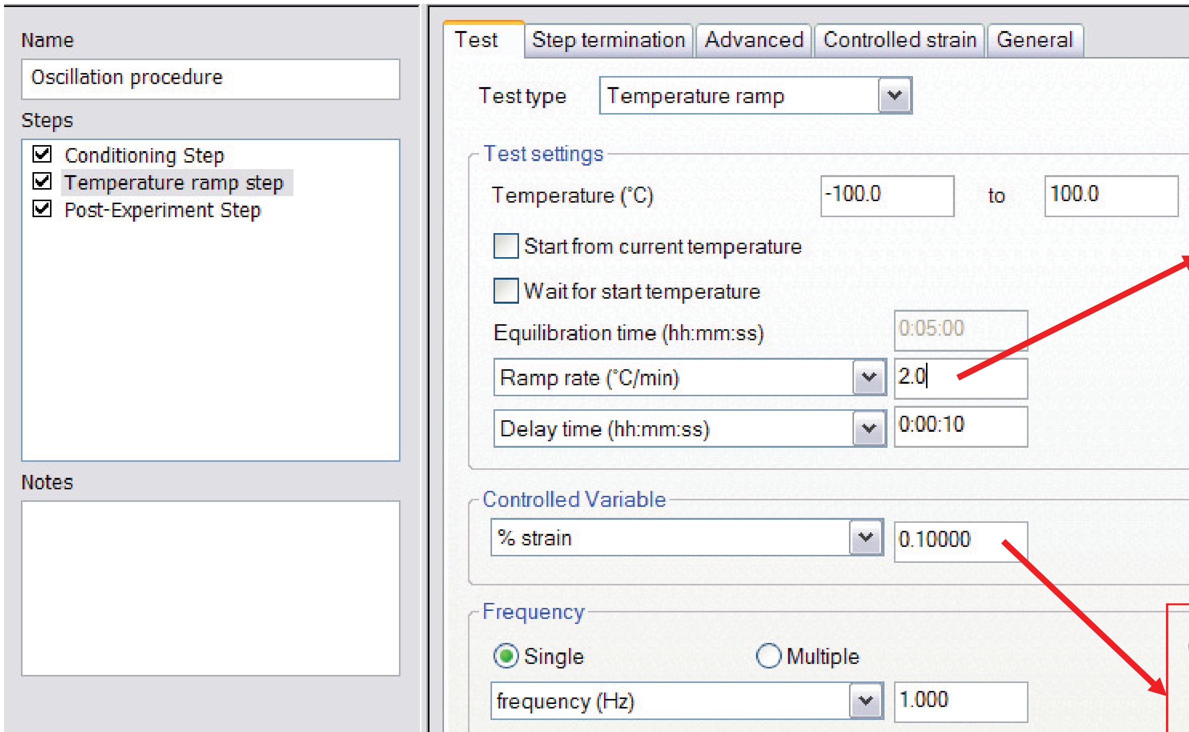
AR: Temp Sweep



Control variables:
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

- The strain needs to be in the LVR

AR: Temp Ramp

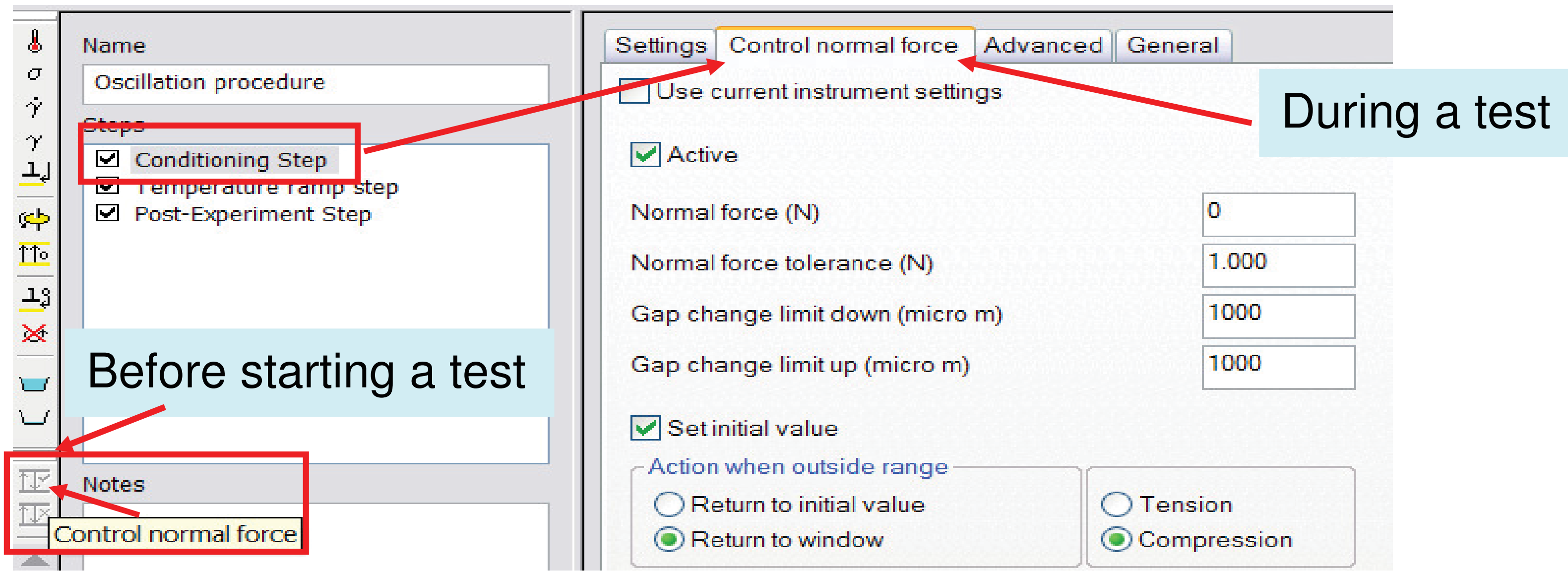


To minimize thermal lag, recommend using slow ramp rate e.g. 1-5℃/min.

Control variables:
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

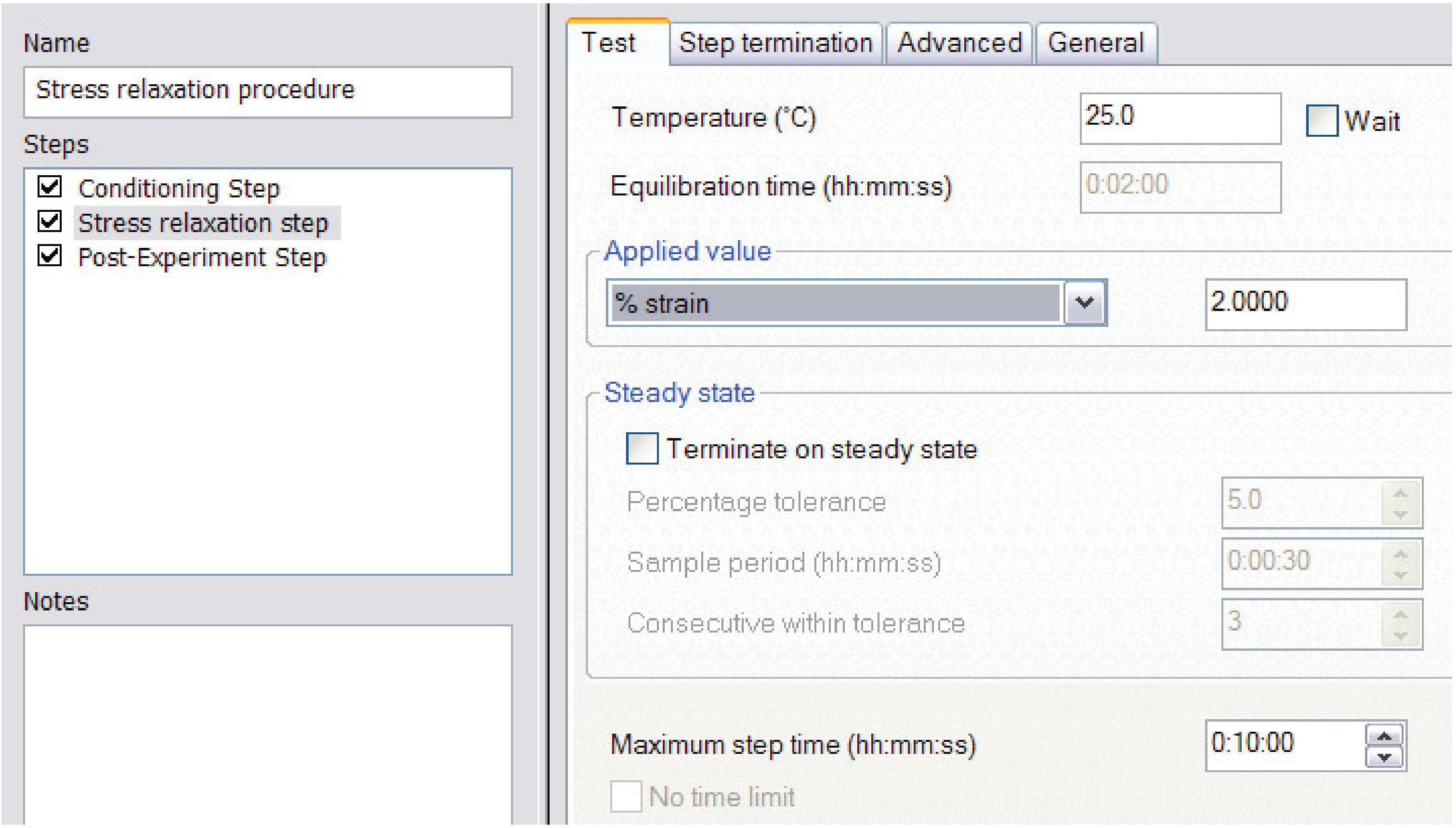
- The strain needs to be in the LVR

AR: Normal Force Control



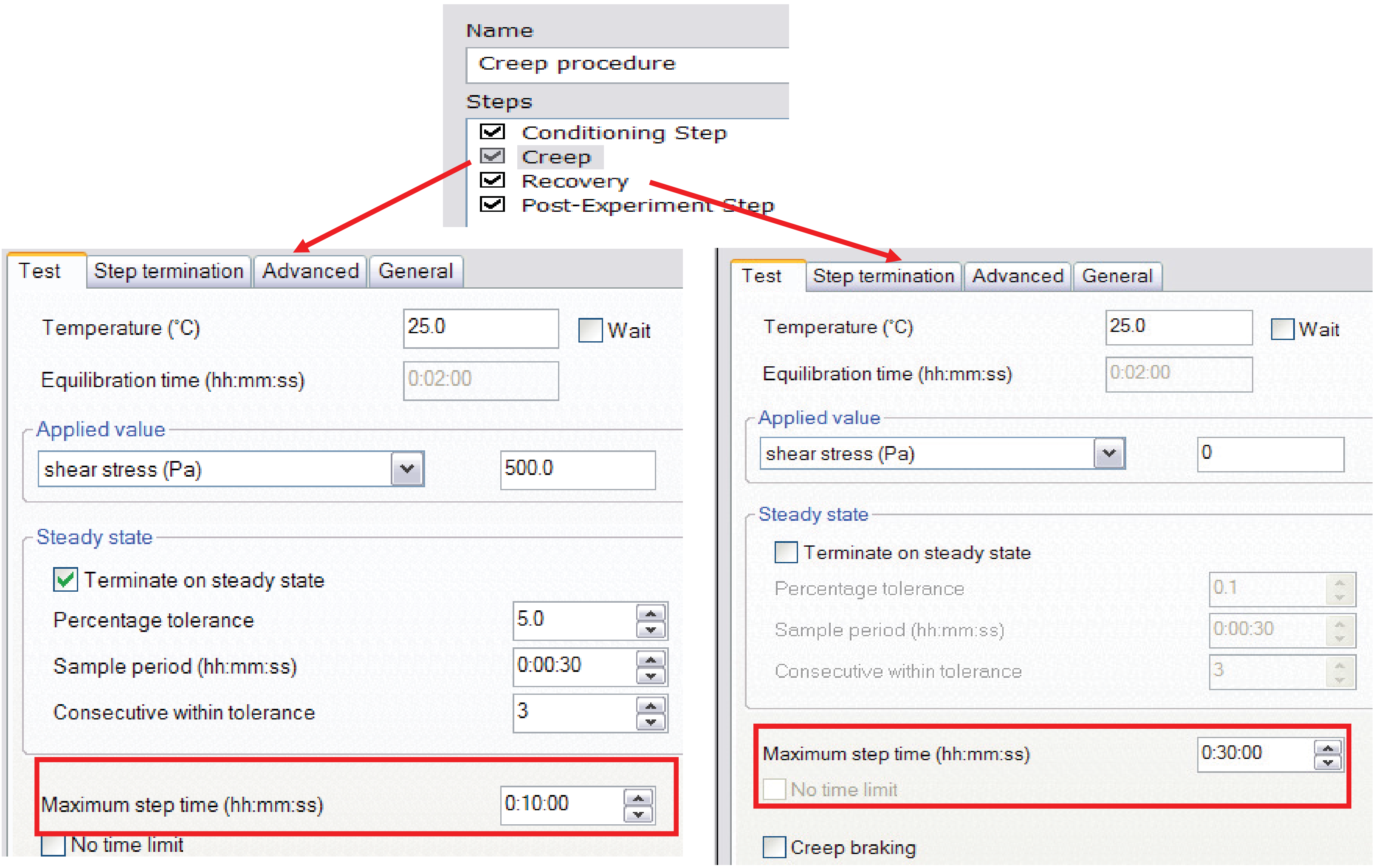
- It is important to setup normal force control during any temperature change testing or curing testing
- Some general suggestions for normal force control
  - For torsion testing, set normal force in tension: 1-2N ± 0.5-1.0N
  - For curing or any parallel plate testing, set normal force in compression: 0 ± 0.5N

AR: Stress Relaxation



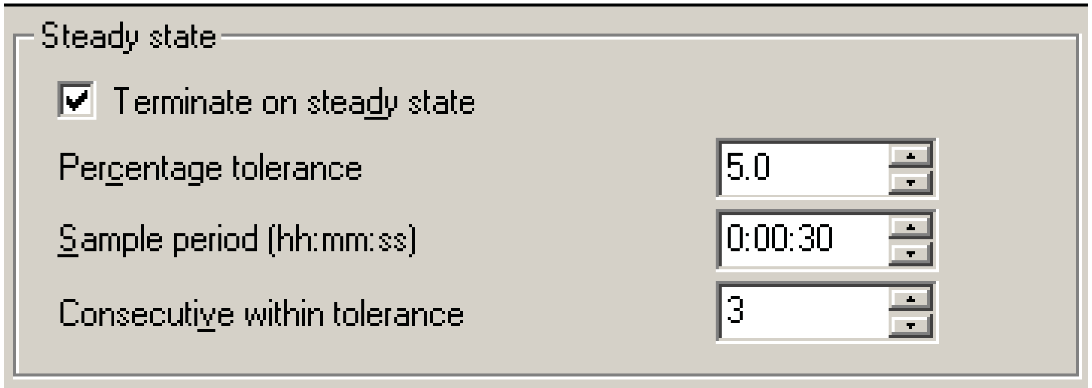
- Motor and transducer work in a feedback loop

AR: Creep Recovery



- Rule of thumb: recovery time is 2-3 times longer than creep time

AR : Steady State Algorithm Creep



Default values shown

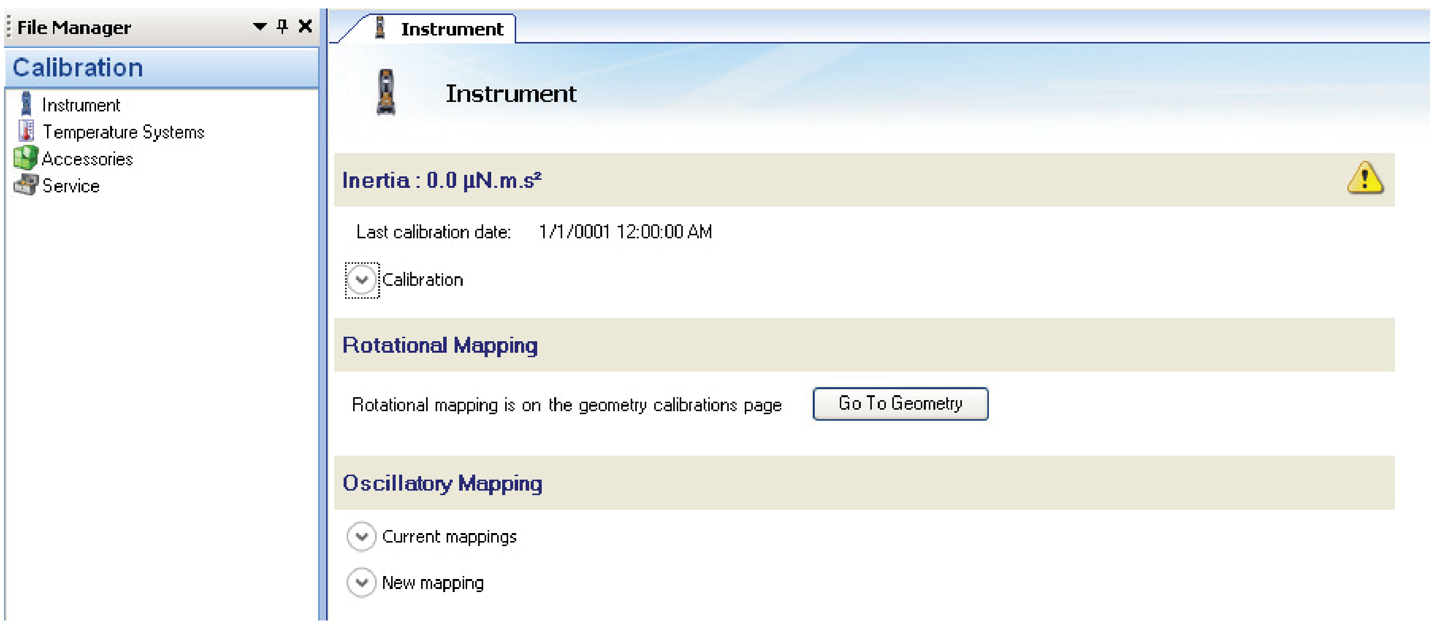
- During the test, the angular velocity is monitored with time to determine when stability has been reached.
- An average value for the angular velocity is recorded over the **Sample period**.
- When consecutive average values **(Consecutive within tolerance)** are within the **tolerance** specified here, the data is accepted.

Appendix 4: Rheometer Calibrations

DHR and AR

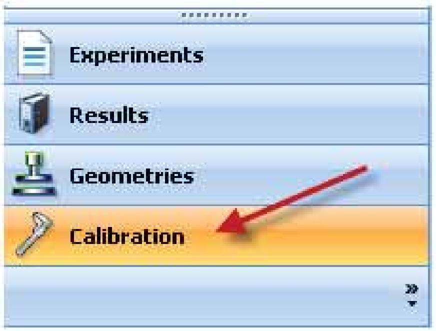
DHR – Calibration Options

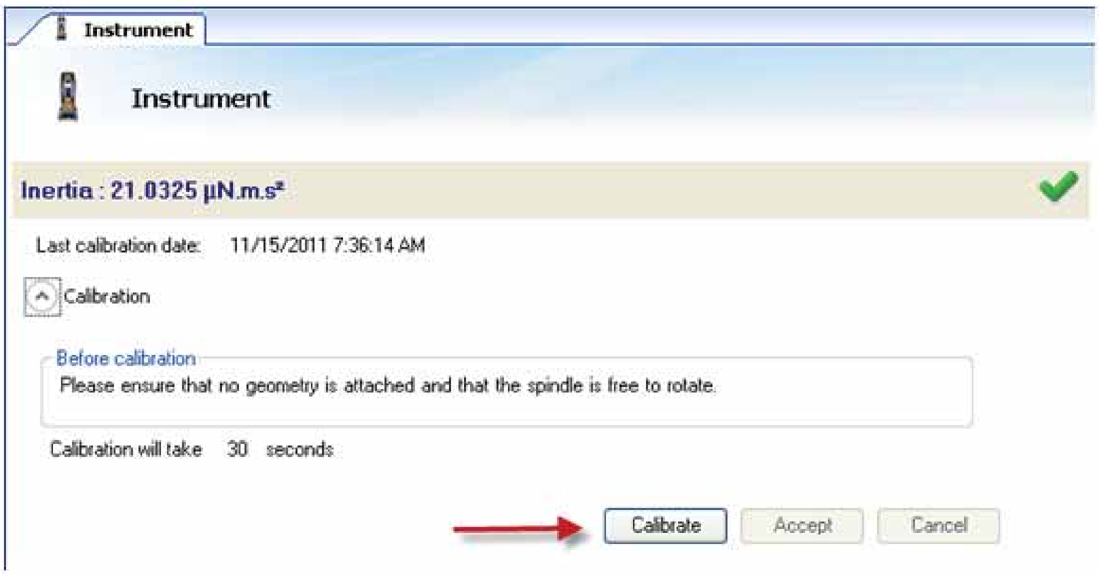
- Instrument Calibrations
  - Inertia (Service)
  - Rotational Mapping
  - Oscillation Mapping (recommended for interfacial measurements)



DHR – Inertia Calibration

- Go to the Calibration tab and select Instrument
  - Make sure there is no geometry installed and then click calibrate

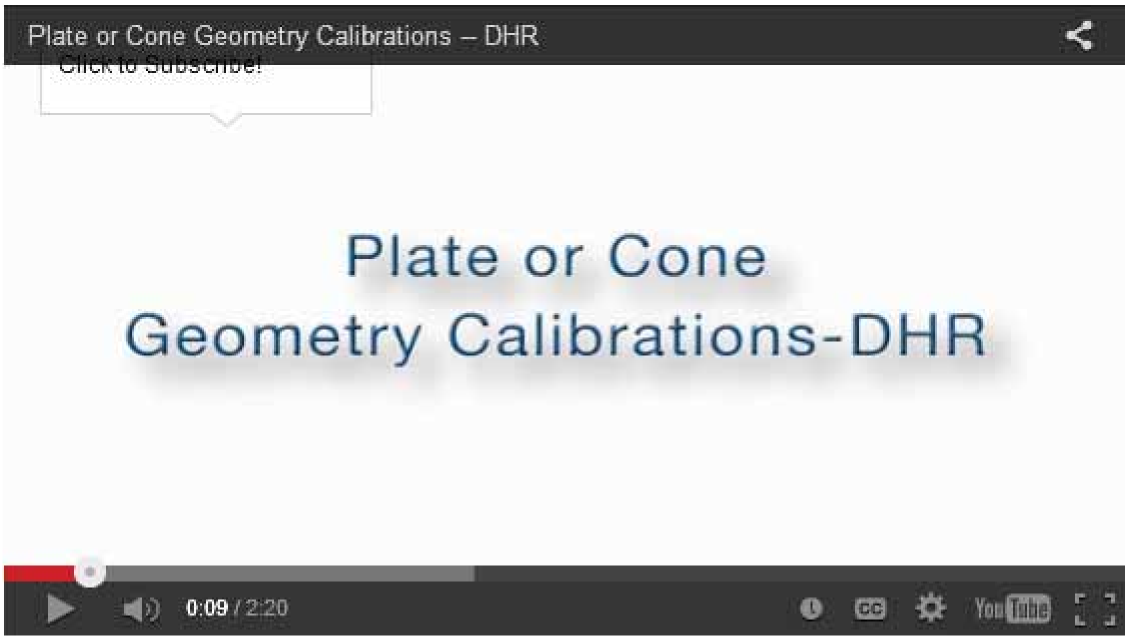




DHR – Geometry Calibration

- Geometry Calibrations:
  - Inertia
  - Friction
  - Gap Temperature Compensation
  - Rotational Mapping

TA Tech Tip – Geometry Calibrations



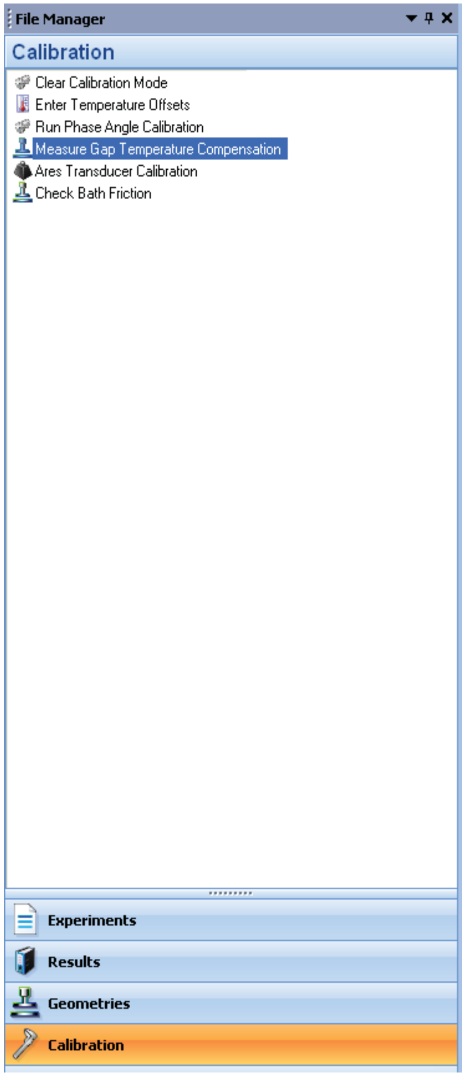
- Videos available at www.tainstruments.com under the Videos tab or on the TA tech tip channel of YouTube™ (http://www.youtube.com/user/TATechTips)

Rheometer Calibrations

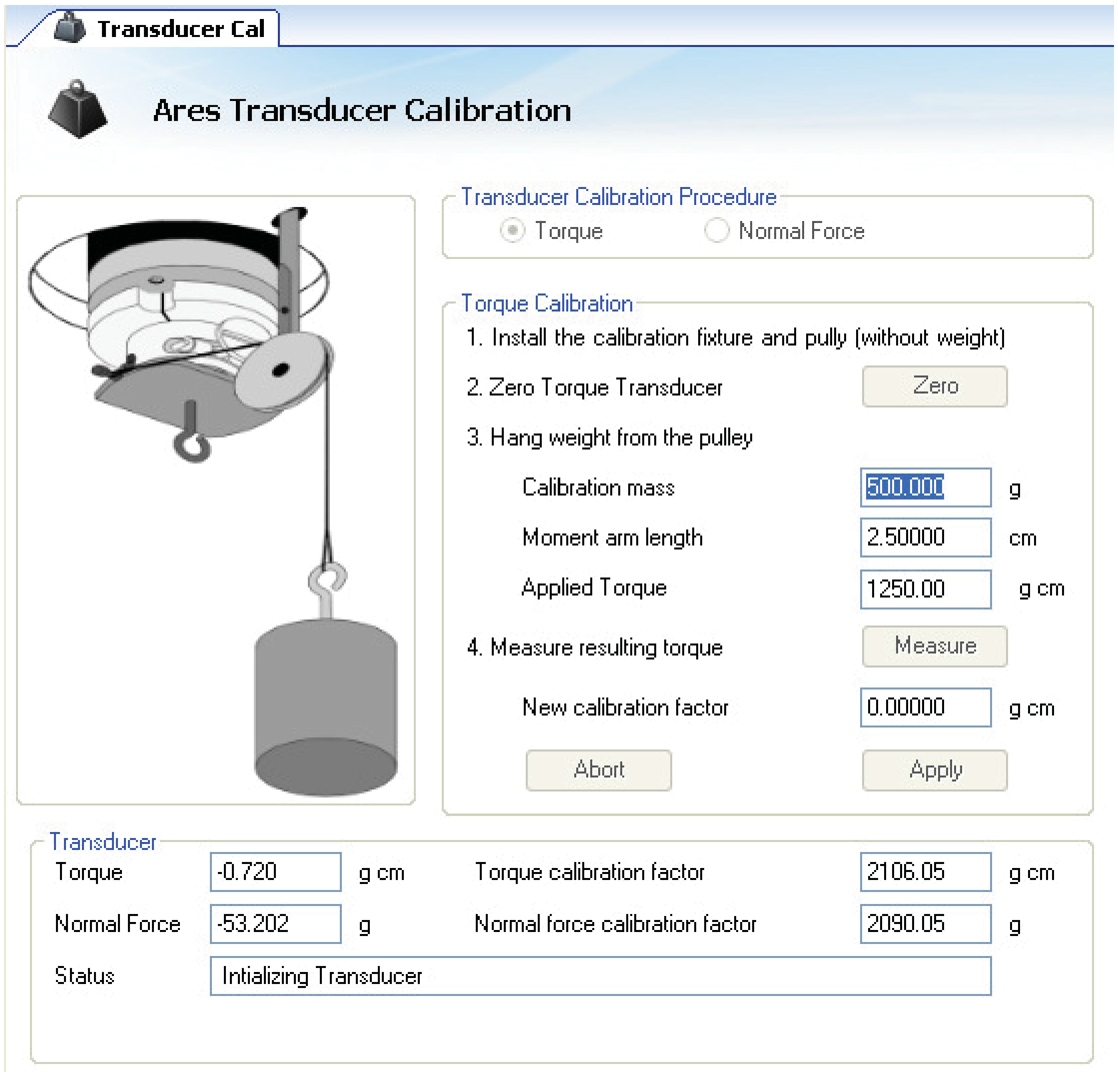
ARES-G2

ARES-G2 – Calibration Options

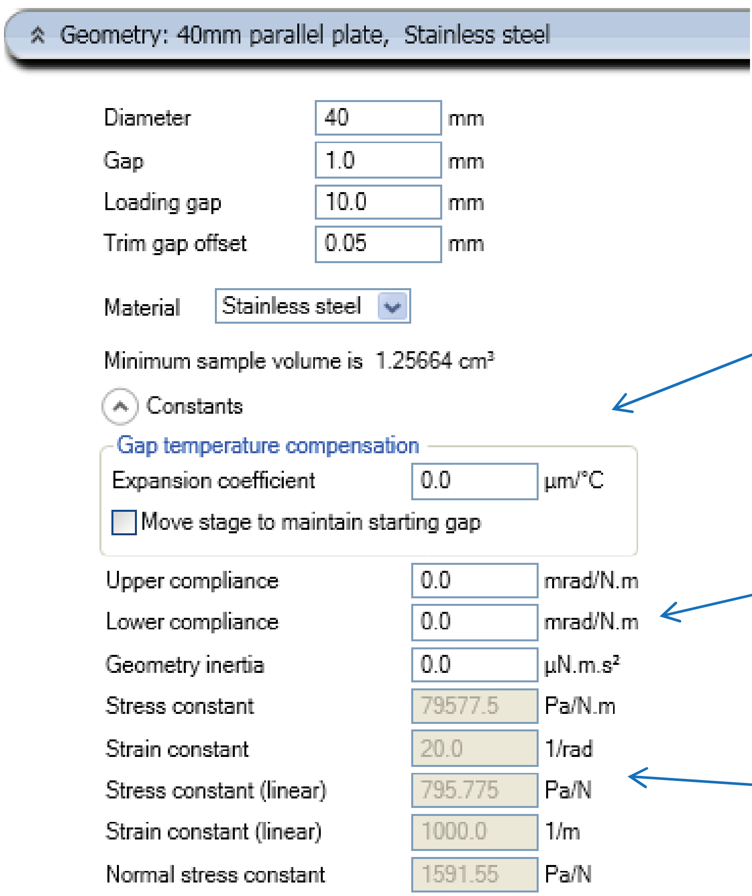
- Instrument Calibrations
  - Temperature Offsets
  - Phase Angle (Service)
  - Measure Gap Temperature Compensation
  - Transducer
- Geometry Calibrations:
  - Compliance and Inertia (from table)
  - Gap Temperature Compensation



ARES-G2 – Transducer Calibration



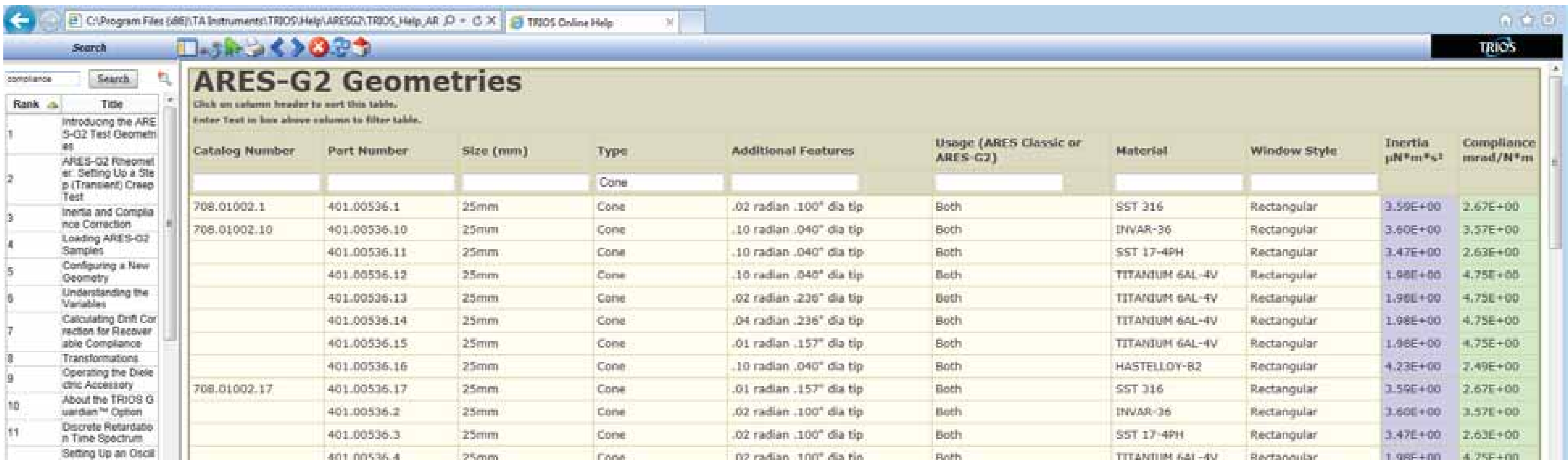
ARES-G2 – Geometry Calibration



- Gap Temperature Compensation
  - Enter manually or run calibration
- Compliance and Inertia
  - (from table in Help menu)
- Geometry Constants
  - Calculated based on dimensions

Geometry Inertia & Compliance- Help Menu

- Click here for a spreadsheet that contains the inertia, compliance, and gap compensation data for the majority of the ARES-G2/ARES tooling.



ARES-G2 Geometries

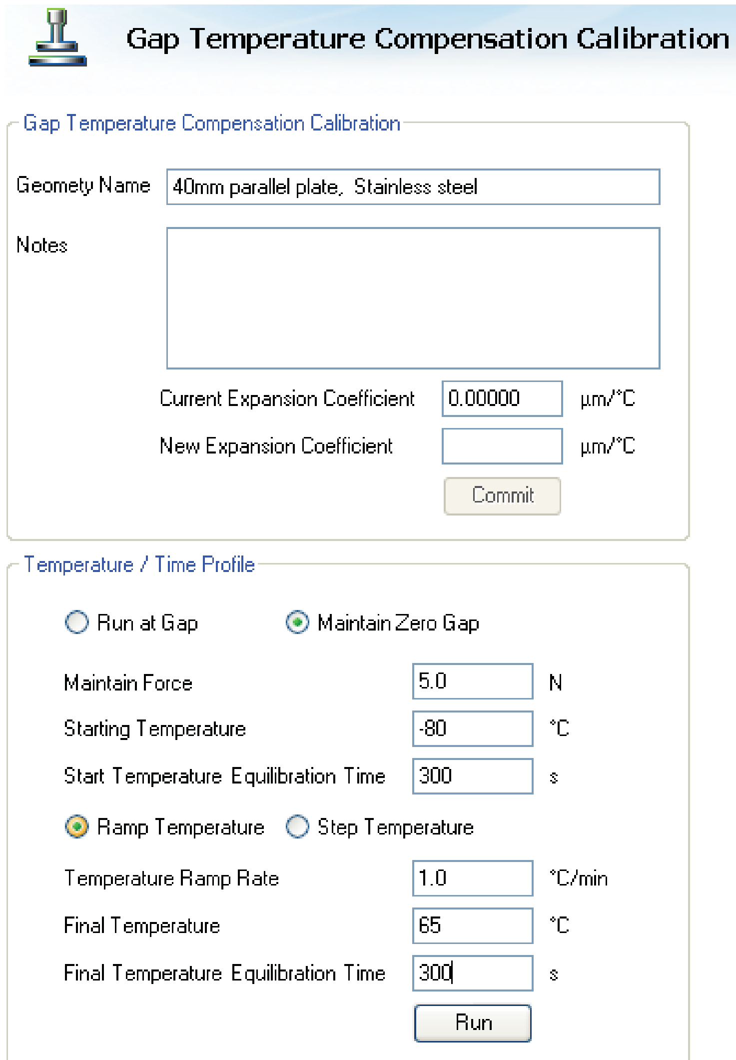
Click on column header to sort this table.
Enter Text in box above column to filter table.

Catalog Number	Part Number	Size (mm)	Type	Additional Features	Usage (ARES Classic or ARES-G2)	Material	Window Style	Inertia μN*m*s²	Compliance mrad/N*m
			Cone						
708.01002.1	401.00536.1	25mm	Cone	.02 radian .100" dia tip	Both	SST 316	Rectangular	3.59E+00	2.67E+00
708.01002.10	401.00536.10	25mm	Cone	.10 radian .040" dia tip	Both	INVAR-36	Rectangular	3.60E+00	3.57E+00
	401.00536.11	25mm	Cone	.10 radian .040" dia tip	Both	SST 17-4PH	Rectangular	3.47E+00	2.63E+00
	401.00536.12	25mm	Cone	.10 radian .040" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00
	401.00536.13	25mm	Cone	.02 radian .236" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00
	401.00536.14	25mm	Cone	.04 radian .236" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00
	401.00536.15	25mm	Cone	.01 radian .157" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00
	401.00536.16	25mm	Cone	.10 radian .040" dia tip	Both	HASTELLOY-B2	Rectangular	4.23E+00	2.49E+00
708.01002.17	401.00536.17	25mm	Cone	.01 radian .157" dia tip	Both	SST 316	Rectangular	3.59E+00	2.67E+00
	401.00536.2	25mm	Cone	.02 radian .100" dia tip	Both	INVAR-36	Rectangular	3.60E+00	3.57E+00
	401.00536.3	25mm	Cone	.02 radian .100" dia tip	Both	SST 17-4PH	Rectangular	3.47E+00	2.63E+00
	401.00536.4	25mm	Cone	.02 radian .100" dia tip	Both	TITANIUM 6AL-4V	Rectangular	1.98E+00	4.75E+00

What if the online table does not list a compliance value for my specific geometry?

Use the compliance value for a geometry of the same/similar dimension, type, and material.

ARES-G2 - Gap Temperature Compensation



General Rheometer Maintenance

- Air Supply
  - Dry particulate-free air (dew point -40 °C)
  - Check filters/regulators on a periodic basis to ensure proper pressure, free of moisture/oil/dirt buildup.
  - If air must be turned off, then make sure that the bearing lock is fastened
    - NOTE: Do not rotate drive-shaft if air supply is OFF!

- Location
  - Isolate the instrument from vibrations with a marble table or Sorbathane pads.
  - Drafts from fume hoods or HVAC systems and vibrations from adjacent equipment can contribute noise to measurements, particularly in the low torque regime. Use a Draft Shield to isolate instrument from drafts.

General Rheometer Maintenance - Peltier

- Circulator Maintenance
  - Proper operation of a fluid circulator is vital for correct and efficient operation of Peltier-based temperature control devices.
  - Check fluid levels and add anti-fungal additive regularly.
    - Note: if operating circulator below 5°C then it is recommended to fill the circulator with a mixture or material with a lower freezing point than water to prevent permanent circulator damage.
      - Example: add ~20% v/v ethanol to water

- Keep it clean!
  - Flush and clean circulator, Peltier system, and tubing at first sight of contamination.
  - When not in use, it is strongly recommended to deactivate the Peltier device and turn off the circulator.

Geometry Information – Estimated Min and Max Shear Rates

Geometry	Diameter (mm)	Degree	Gap (micron)	Sample Volume (mL)	**Max Shear Rate (approx) 1/s**	Min Shear Rate (approx) 1/s
Parallel Plate and Cone and Plate	8	0	1000	0.05	**1.20E+03**	4.00E-07
		0	500	0.03		
		0.5	18	1.17E-03		
		1	28	2.34E-03		
		2	52	4.68E-03		
		4	104	9.37E-03		
	20	0	1000	0.31	**3.00E+03**	1.00E-06
		0.5	18	0.02	**3.44E+04**	1.15E-05
		1	28	0.04	**1.72E+04**	5.73E-06
		2	52	0.07	**8.60E+03**	2.87E-06
		4	104	0.15	**4.30E+03**	1.43E-06
	25	0	1000	0.49	**3.75E+03**	1.25E-06
		0.5	18	0.04		
		1	28	0.07		
		2	52	0.14		
		4	104	0.29		
	40	0	1000	1.26	**6.00E+03**	2.00E-06
		0.5	18	0.15	**3.44E+04**	1.15E-05
		1	28	0.29	**1.72E+04**	5.73E-06
		2	52	0.59	**8.60E+03**	2.87E-06
		4	104	1.17	**4.30E+03**	1.43E-06
	60	0	1000	2.83	**9.00E+03**	3.00E-06
		0	500	1.41		
		0.5	18	0.49	**3.44E+04**	1.15E-05
		1	28	0.99	**1.72E+04**	5.73E-06
		2	52	1.97	**8.60E+03**	2.87E-06
		4	104	3.95	**4.30E+03**	1.43E-06
Concentric Cylinder	Conical Din Rotor			19.6	**4.36E+03**	1.45E-06
	Recessed End			6.65	**4.36E+03**	1.45E-06
	Double Wall			11.65	**1.59E+04**	5.31E-06
	Pressure Cell			9.5		
	Standard Vane			28.72		

Basic Parameters and Units

Stress = Force /Area [Pa, or dyne/cm^2]

σ = shear stress

Strain = Geometric Shape Change [no units]

γ = shear strain

Strain Rate or Shear Rate = Velocity Gradient [1/s]

$\dot{\gamma}$ = shear strain rate

Modulus = Stress / Strain [Pa or dyne/cm^2]

G = Shear Modulus

Compliance = Strain / Stress [1/Pa or cm^2/dyne]

Typically denoted by J

Viscosity = Stress /Strain Rate [Pa·s or Poise]

Denoted by η

S.I. units x 10 = *c.g.s. units*

Common Symbols used in Rheology

Greek

γ (gamma): Shear Strain
$\dot{\gamma}$ (gamma dot): Shear Rate
δ (delta): Phase Angle
ε (epsilon): Elongational Strain
$\dot{e}$ (epsilon dot): Elongational Strain Rate
η (eta): Shear Viscosity
η_E (eta E): Elongational Viscosity
η^* (eta star): Complex Viscosity
μ (mu): Microns
ν (nu): Frequency (Hz)
ρ (rho): Density
σ (sigma): Shear Stress
τ (tau): Elongational Stress
ω (omega): Angular Frequency (rad/sec)

Latin

a_T: Temperature shift factor
B: Bulk Creep Compliance
D: Tensile Compliance
E: Young's (Tensile) Modulus
E': Tensile Storage Modulus
E": Tensile Loss Modulus
G: Shear Modulus
G': Shear Storage Modulus
G": Shear Loss Modulus
E^* or G^*: Complex Modulus
J: Shear Compliance
K: Bulk Modulus (or also Stiffness)
N_1: Normal Force in Steady Flow
T: Temperature
T_g: Glass Transition Temperature

Sample Preparation

Polymers

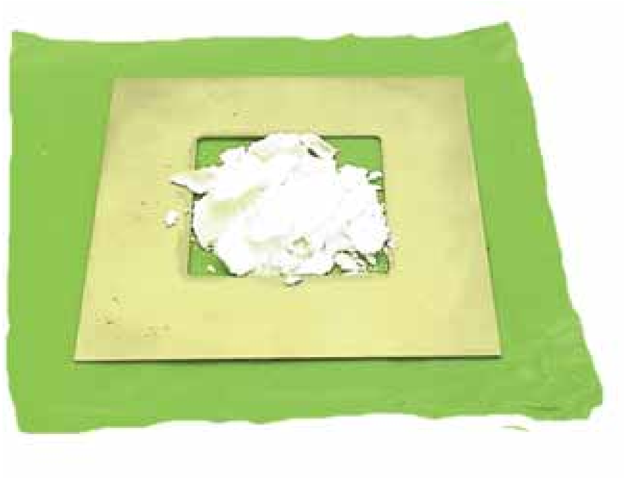
Know Your Sample – Polymers

- Polymer samples come in different forms (e.g. powder, flakes, pellets) and can be sensitive to environmental conditions
- Careful sample preparation techniques are required to prepare good test specimens for reproducible testing
  - Molding a sample
  - Handling powders, flakes
  - Controling the environment

Molding Polymer Pellets

- The best approach is to mold a sample plate (50x50 mm^2 or 100x100 mm^2)
- Molding temperature: 10 - 20℃ > than test temperature
  - Apply pressure: 8 – 12,000 lbs
  - Keep at elevated temperature long enough to let the sample relax
  - Cool down slowly under pressure to avoid orientations
- Punch out a sample disk (8 or 25 mm)

Molding Powders and Flakes



- Before molding at high temperature, the sample has to be compacted cold to reduce the volume
- The compacted samples are transferred to the mold
- Follow steps from the molding pellets procedure
- Note: Sample may need to be stabilized or dried to avoid degradation

Preparing Semi-solid Samples

- Cut rectangular sheets of prepreg or adhesive (30x30mm)
- Alternate direction of layer approx. 5 layer on top of each other (remove release paper from PSA)
- Compress the stack of sample layers in a press (4 – 5000 lbs)
- Punch out 25 mm disks

Controlling Environmental Conditions During Sample Prep

- Polypropylene and Polyolefines in general tend to degrade fast – need to be stabilized by adding antioxidents
- Moisture sensitive materials such as polyamides and polyester require drying in vacuum or at temperatures around 80℃.
- Materials such as Polystyrene or Polymethyl-methacrylate (PMMA) also absorb moisture. In the melt phase, the gas separates into bubbles and the sample foams
- Pre-drying in vacuum is essential prior to testing

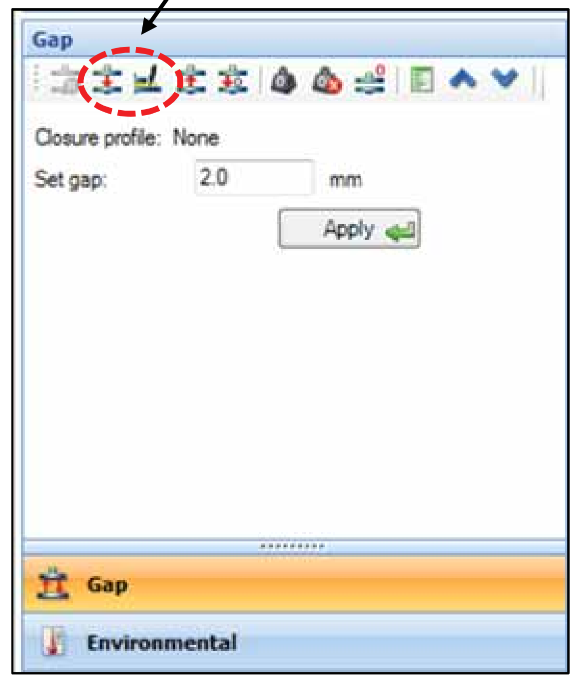
Vacuum oven

Loading a Molded Disk

Set Environmental System to test temperature

Load molded disk onto lower plate

Geometry gap and Trim gap icons



Close the oven and bring the upper plate to the trim gap position

Monitor Axial or Normal force during this period

After sample relaxes, open the oven and trim excess sample

Close the oven and adjust gap to geometry/test gap

Loading Polymer Pellet Samples

Set Environmental System to test temperature

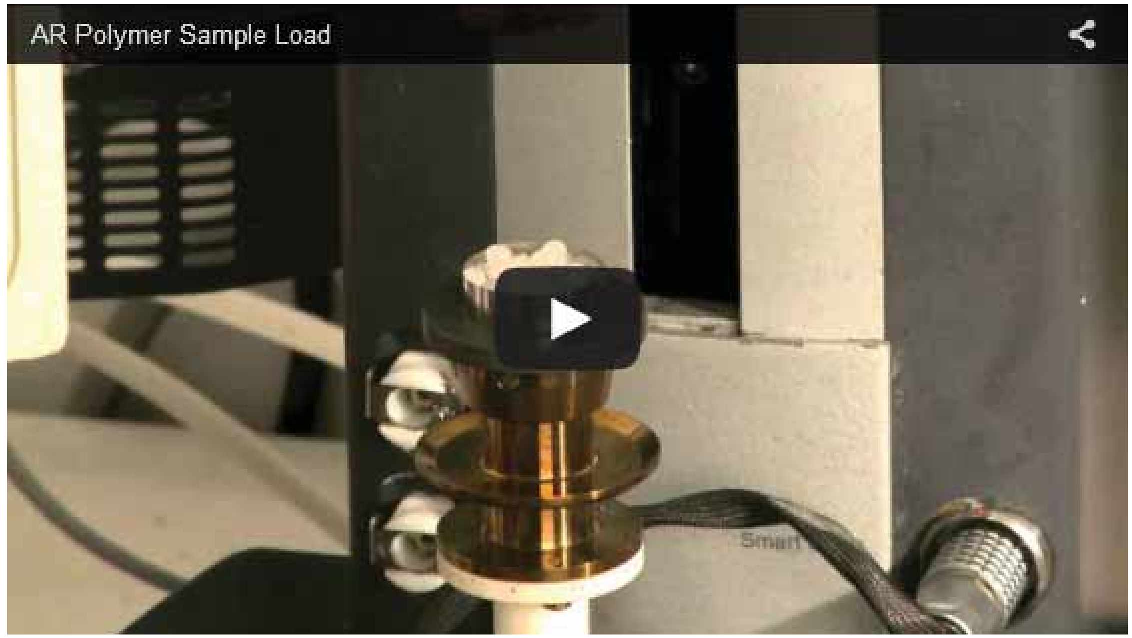
Mount melt ring onto the lower plate and load pellets

Bring the upper plate close to top of melt ring and close the oven

After few minutes, open the oven, remove melt ring and go to trim gap

After sample relaxes, open the oven and trim excess sample

Close the oven and adjust gap to geometry/test gap



Sample Preparation

Structured Fluids

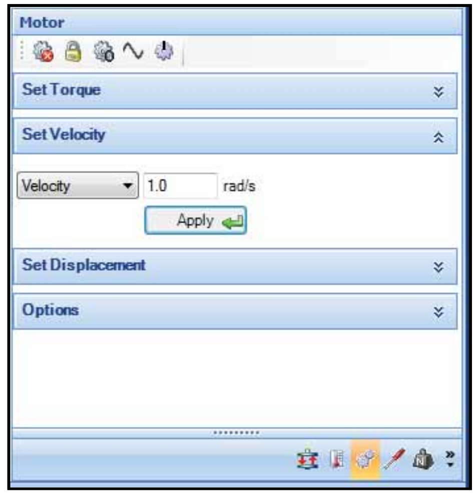
Know Your Sample – Structured Fluids

- Structured fluids can range in consistency from low viscosity (e.g. milk) to high viscosity, pasty materials (e.g. tooth paste)
- Structured materials are very sensitive to mechnical and environmental conditions
- Be aware of largest particle size in sample and choose the geometry appropriately (cone vs parallel plate vs vane geometry)
- Samples can also be time dependent – how you treat the sample (handling, loading, pre-conditioning) may affect test results!

Handling Low Viscosity Fluids

- Fluid samples which pour freely are relatively easy to handle prior to loading
- Keep the container closed to avoid evaporation of solvent or continuous phase
- Shake or stir sample to remove concentration gradients in suspensions
- Adequate shelf temperature may be necessary to avoid phase separation in emulsions
- Never return used sample into original flask to avoid contamination

Loading Low Viscosity Fluids

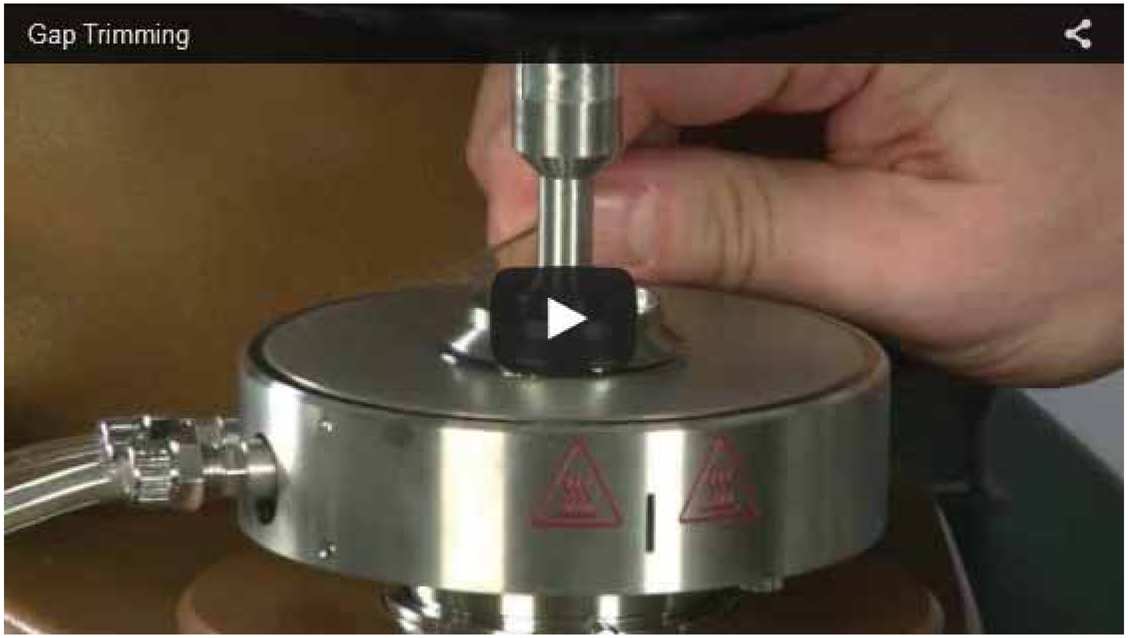


- Deposit fluid in the middle of the plate
- Set a motor velocity of ~ 1 rad/s and move to geometry gap
- Add additional material along the sides of the geometry – capillary forces will draw the sample between the gap
- When finished, click on the “Stop Motor” button
- NOTE: *If the sample is a structured fluid, setting a motor velocity will introduce shear history onto the sample and can destroy the sample structure!*

Handling Paste/Slurry & Gel Materials

- The structure of high viscosity pastes and slurries may change with time
- Food samples, like dough, can change continuously
- The test samples need to be prepared carefully and consistently for each experiment to obtain reproducibility
- Slurries that may settle can gradually build a cake – these samples have to be tested before sedimentation

Loading Pastes and Slurries



- Scoop up the paste with a spatula and deposit it at the center of the lower plate
- For less viscous materials, a syringe with a cut-off tip can be used
- Load ~ 10-20 excess material to ensure complete sample filling
- Set the gap to the trim gap and use exponential gap closure profile to minimize shear in the sample
- Lock the bearing, trim excess material and set final gap

Handling Gels

- Gels, especially chemical gels, may change irreversibly when large deformations are applied (for example, while loading)
- Prepare (formulate) the sample in the final shape required for the measurement so it can be loaded without deforming (cut, punch, …)
- Alternatively, prepare the sample in situ – on the rheometer → systemic rheology
- Take care to avoid introducing air bubbles!