Basics of Applied Rheology

Oregon State University

Corvallis, OR

August 10, 2016

Gina Paroline

Manager of Technical and Professional Development

Anton Paar USA

Agenda

- Rheology
  - The Language of Rheology
  - Viscosity and Flow Properties
  - Modulus, Elasticity, and Viscoelasticity
- Rheometry
  - Rheometer Basics
  - Rheometer Important Considerations
- Getting Started
  - Experimental Considerations
  - Which Test When

Rheology

The Language of Rheology

Rheology and Rheometry Defined

Rheology

- Study of deformation and flow behavior of all kinds of materials
- From Greek ῥέω rhéō, "flow" and -λογία, -logia, "study of"
- Term coined by Prof. Bingham and Prof. Reiner in 1920
- πάντα ῥεῖ (*panta rhei*), meaning "everything flows/is in a state of flux"

Rheometry

- Experimental techniques and tools used to determine the rheological properties of materials

Rheology - Flow and Deformation Properties of ALL KINDS OF MATERIALS

Anton Paar

Viscous ← **Viscoelastic** → **Elastic**

Ideally viscous liquids [water, oil, solvents] Newton's Law	Viscoelastic liquids [milk, shampoo, paint]	Viscoelastic solids [pastes, gels, films]	Ideally elastic (rigid) solids [steel, wood] Hooke's Law

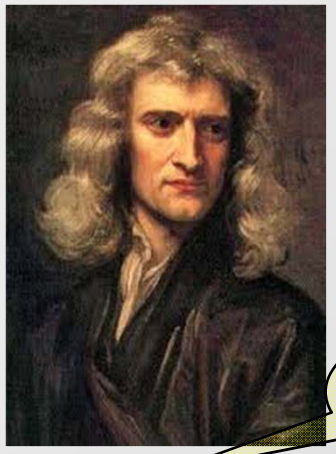
Flow behavior describes samples which flow.

Deformation behavior describes samples which deform.

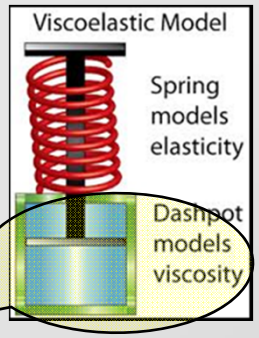
Which Materials Flow? Which Deform?

- **Flow properties** are used to characterize fluids.
  - When a force is applied to a **fluid**, it **flows**.
  - When the force is removed, the fluid does not regain its original shape. **Fluids lose**, or dissipate, energy as flow and heat.
- **Response to deformation** is used to characterize solids.
  - When a force is applied to a **solid**, it **deforms**.
  - When the force is removed, the solid returns to its original shape. **Solids store** energy and use it to recover or maintain shape.
- Most materials exhibit both **fluid (viscous)** and **solid (elastic) behavior**. They are **viscoelastic**.
- Rheology describes how **all kinds of materials** respond to an applied force.

Fluid Flow – Newton's Law



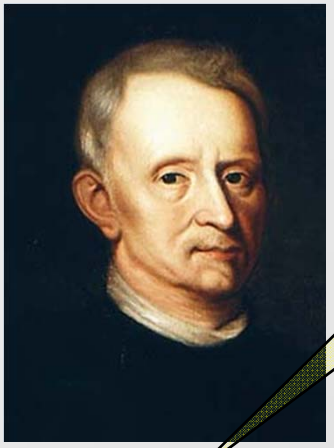
Sir Isaac Newton
1643-1727



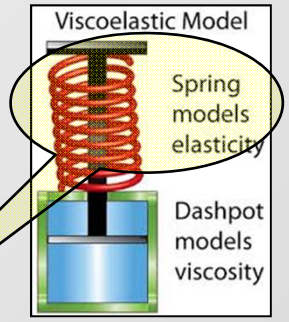
Viscosity was first described by Newton who found that the velocity at which a liquid moved was proportional to the force applied to it.

- Newton discovered that a force applied to a liquid, it moved at a certain speed.
- If more force was applied, the liquid moved faster. Less force applied, the liquid moved slower.
- If the same force was applied to a thick liquid, it moved slower than a thin sample.
- The proportionality constant between applied force and resulting speed is viscosity.
- Viscosity describes the flow behavior of

Solid Deformation – Hooke's Law



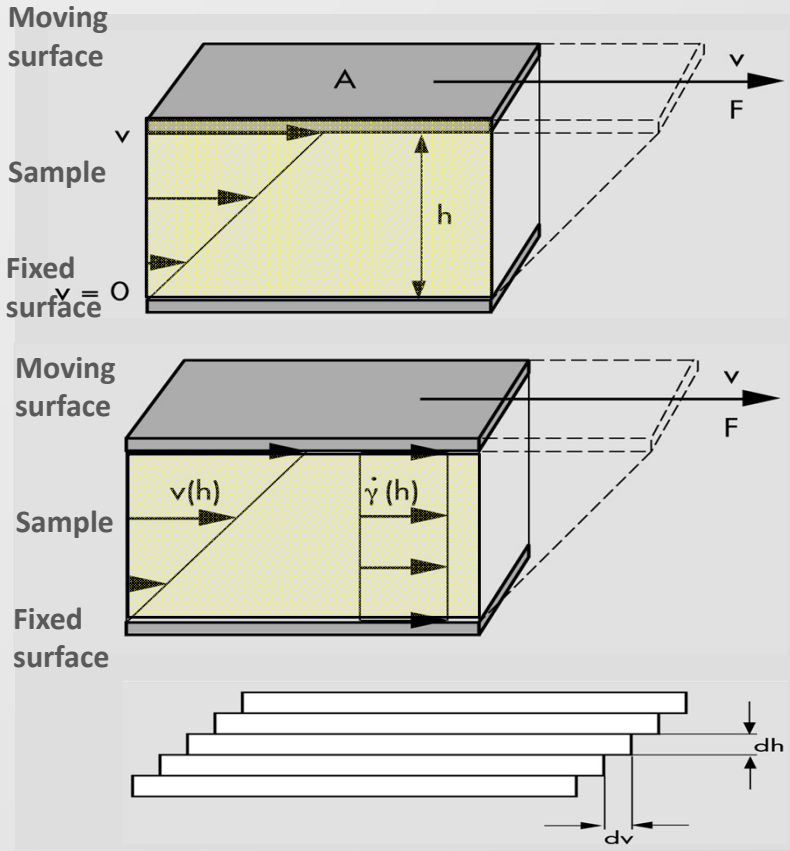
Robert Hooke
1635 - 1703



Elasticity was first described by Hooke who found that a spring deformed proportionally to the force applied to it.

- Hooke discovered that if a mass was attached to a spring, it deformed a certain amount.
- A light mass attached to a given spring deformed it less than a heavy mass.
- A given mass attached to a soft spring resulted in more deformation than when attached to a stiff spring.
- The proportionality constant between applied force (mass) and resulting deformation is modulus.
- Modulus describes the deformation behavior of elastic (solid) materials.

From Forces and Velocities to Rheological Parameters – Two Plate Model



Shear stress = τ (”tau”)

$$\tau = \frac{F}{A} = \frac{\text{shear (force)}}{\text{(shear) area}} = \frac{\text{N}}{\text{m}^2} = Pa$$

Force applied divided by the surface area of sample.

Shear rate = $\dot{\gamma}$ (”gamma dot”)

$$\dot{\gamma} = \frac{v}{h} = \frac{\text{velocity}}{\text{gap}} = \frac{\text{m/s}}{\text{m}} = \frac{1}{s}$$

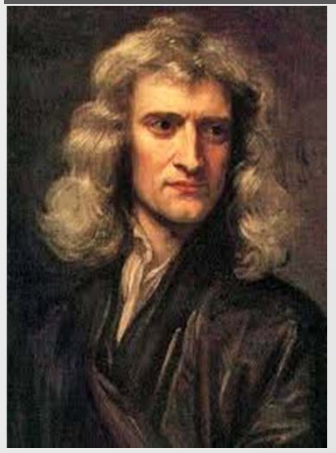
Velocity (speed) divided by the sample thickness (gap).

Strain = γ (” gamma”)

$$\gamma = \frac{\text{v}}{h} = \frac{\text{displacement}}{gap} = \frac{m}{m} = 1(\text{dimensionless})$$

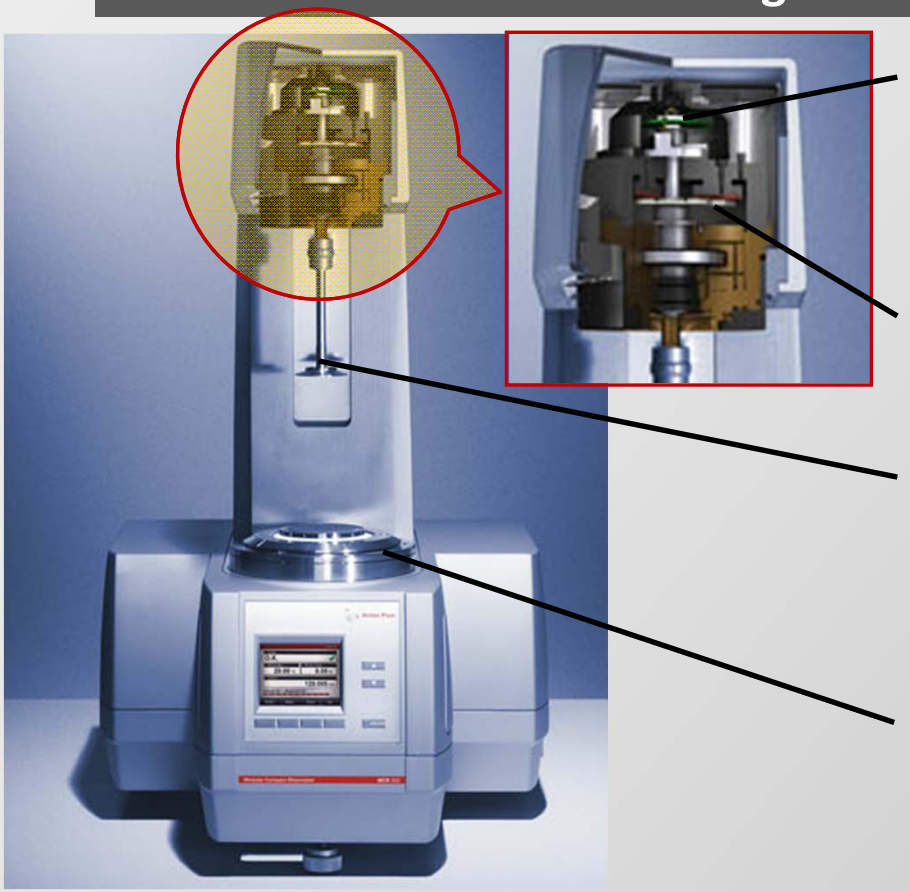
Displacement divided by the thickness.

From Rheological Parameters to Material Properties



- Viscosity = $\frac{Shear\ Stress}{Shear\ Rate} = \frac{\tau}{\dot{\gamma}} = \frac{Pa}{\frac{1}{s}}$ = Pa·s ("Pascal second")
  - The Greek symbol η ("eta") is used to denote viscosity.
  - The SI unit for viscosity is Pa·s.
  - In the U.S., cP (centiPoise) is more commonly used.
  - 1 cP = 1 mPa·s
  - Viscosity is usually used to describe liquids and viscoelastic liquids.
- Shear Modulus = $\frac{Shear\ Stress}{Strain} = \frac{\tau}{\gamma} = \frac{Pa}{Unitless}$ = Pa ("Pascal")
  - G is used to denote shear modulus.
  - The SI unit for shear modulus is Pa.
  - Modulus is usually used to describe solids and viscoelastic solids.

Refresher on Rheometer Design



Optical Encoder
Measures or controls **speed** → **shear rate**
Measures or controls **displacement** → **strain**

Electronically Commutated Motor
Measures or controls torque → shear stress

Measuring System
Sample holder → **defined flow field** (sample shape) → CP, PP, CC, SRF

Chamber
Temperature control, additional settings, accessories

CP=cone-plate; PP=parallel plate; CC=concentric cylinder; SRF=solid rectangular fixture

How are Rheological Measurements Made?

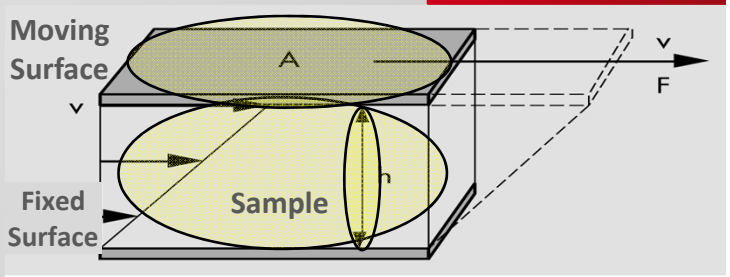
- Viscosity and Modulus are calculated from Shear Stress and Shear Rate (Viscosity) or Strain (Modulus).
- When Measuring Viscosity:
  - Control Shear Stress → Measure Shear Rate
    - Hit the sample with a force and see how fast it moves
  - Control Shear Rate → Measure Shear Stress
    - Move the sample so fast and see how much force is required
- When Measuring Shear Modulus:
  - Control Shear Stress → Measure Strain
    - Hit the sample with a force and see how far it moves
  - Control Strain → Measure Shear Stress
    - Move the sample so far and see how much force is required
- When measuring Viscosity or Modulus, then, one rheological parameter is controlled while the other is the measured sample response.

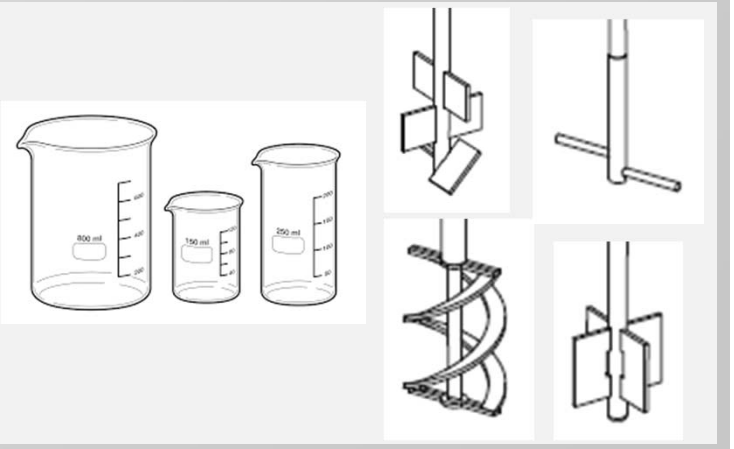
$$\text{Viscosity} = \frac{\text{Shear Stress}}{\text{Shear Rate}} = \frac{\tau}{\dot{\gamma}}$$

$$\text{Shear Modulus} = \frac{\text{Shear Stress}}{\text{Strain}} = \frac{\tau}{\gamma}$$

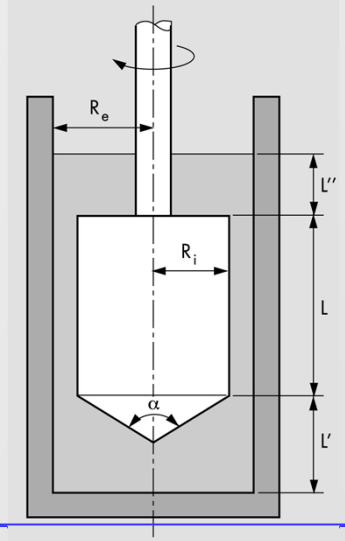
Basics of Absolute and Empirical Measurements

- Absolute measurements require that the flow field, or sample shape, is well defined
- The two plate model is used to define the geometry of the flow field and absolute viscosity
  - Sample is shear between a fixed and moving surface
  - Sample shape, i.e. flow field, is well defined
  - Absolute shear rate requires narrow gap, h
  - Absolute shear stress requires well defined sample area, A (shear field)
- Tests made in a beaker with a spindle are relative to the beaker size, spindle size, and fill volume. The sample shape cannot be defined so the measurements are empirical, not absolute
- Absolute measuring systems include concentric cylinder, cone-plate, and parallel plate

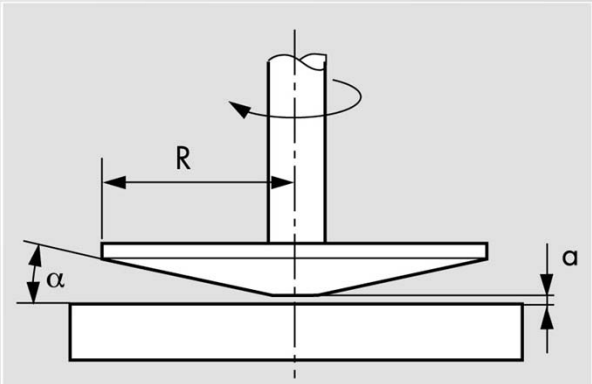




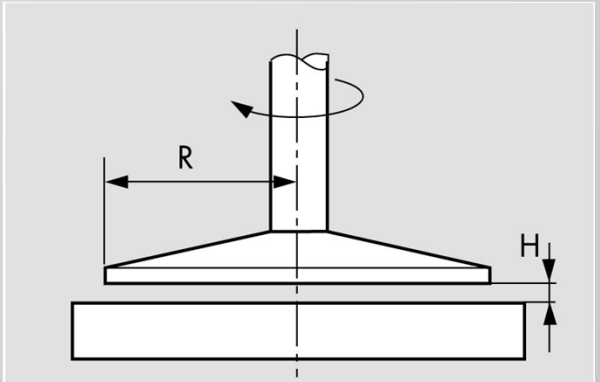
Absolute Measuring Systems



Concentric Cylinder, CC
For flowable samples
Sample must be able to flow and fill the gap upon loading with no entrapped air



Cone & Plate, CP
For flowable samples (dispersions with a limited particle size)
Cone gap a = 50 µm thus max. particle size ≤ (h/10) = 5 µm
Sample must be able to flow and fill the gap upon loading



Parallel Plate, PP
For liquids, gels, pastes, soft solids, polymer melts

☞ **The keys to absolute measurements are a well defined sample shape (flow field) and a small gap.**

The Language of Rheology Summary

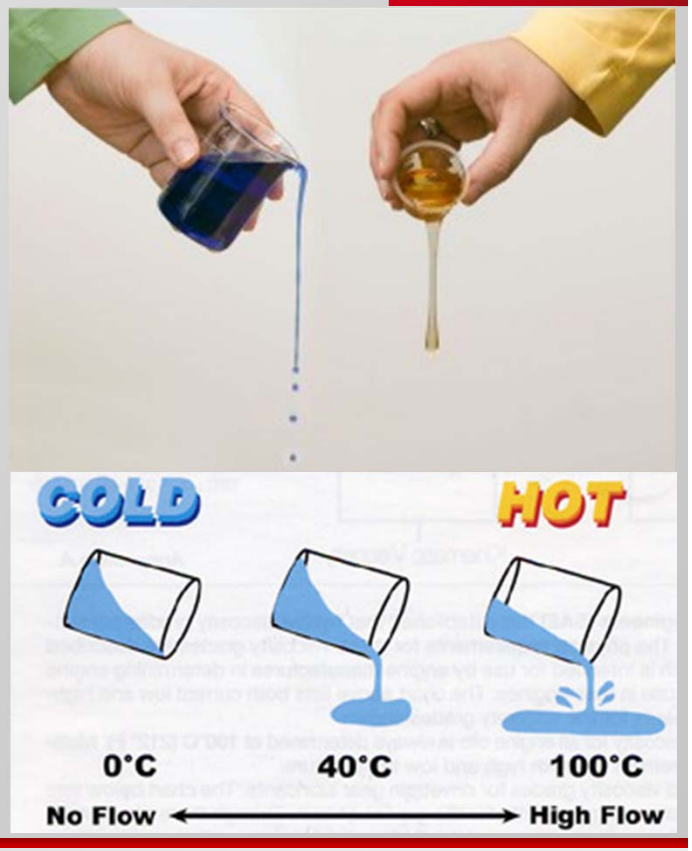
- Rheology studies the **flow** and **deformation** behavior of **all kinds of materials**.
- **Viscosity** is used to describe the **flow** properties of **liquids**.
- **Shear modulus** is used to describe the **deformation** properties of **solids**.
- **Viscoelastic** materials exhibit both **liquid** (viscous) and **solid** (elastic) behavior.
- **Rheometer** parameters are **speed** (velocity), **displacement**, and **torque**.
- **Rheological** parameters are **shear rate**, **strain**, and **shear stress** which require a known "flow field" or well defined sample shape (geometry).
- **Material** properties are described using the rheological properties of **viscosity** and **shear modulus**.
- **Absolute measurements** require a well **defined flow field**.
- The three main **absolute** measuring systems are **concentric cylinder**, **cone-plate**, and **parallel plate**.

Rheology

Viscosity and Flow Properties

What is Viscosity?

- "Property of a fluid that tends to prevent it from flowing when subjected to an applied force".
- Requires that the material be flowing to be measured.
- Describes the flow properties of fluids and viscoelastic fluids, i.e. the sample must able to flow.
- In structured material, viscosity is dependent on temperature, shear rate, shear history and sometimes pressure.
- **Unless the material is an unstructured fluid (water, pure oil), then viscosity is a CURVE not a POINT.**



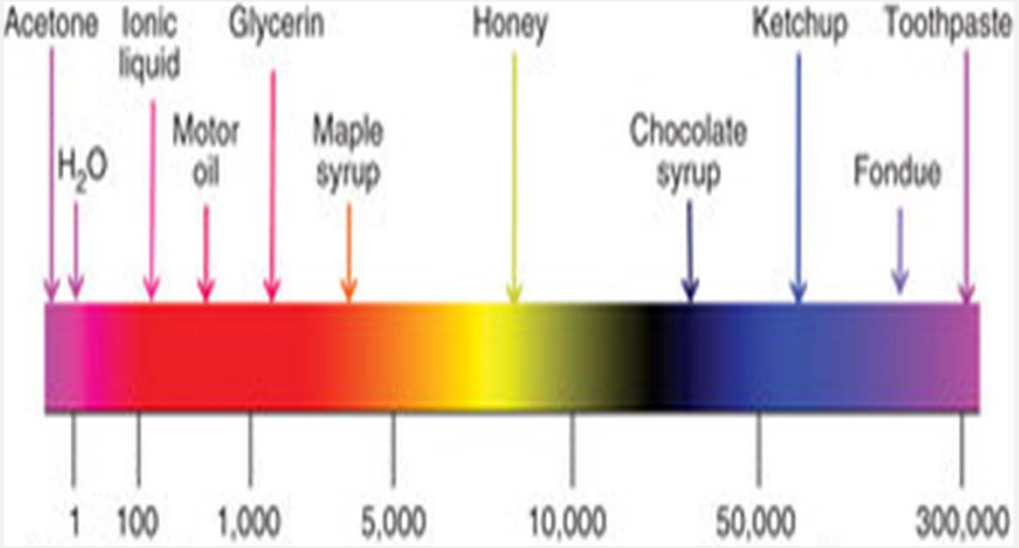
How is Viscosity Measured with a Rotational Viscometer or Rheometer?

- Viscosity is determined by shearing a sample and measuring its resistance to that shear.
- The sample is placed in a stationary container and a moving spindle (bob, cone, plate), which is attached to the rheometer's motor, is lowered into or onto the sample.
- The spindle is moved at a fixed speed (shear rate) and the force (shear stress) required to move that speed is measured.
- Viscosity is the ratio of shear stress to shear rate $\eta = \tau \div \dot{\gamma}$.

$$\text{Viscosity} = \frac{\text{Shear Stress}}{\text{Shear Rate}} = \frac{\tau}{\dot{\gamma}}$$

Viscosity of Everyday Materials

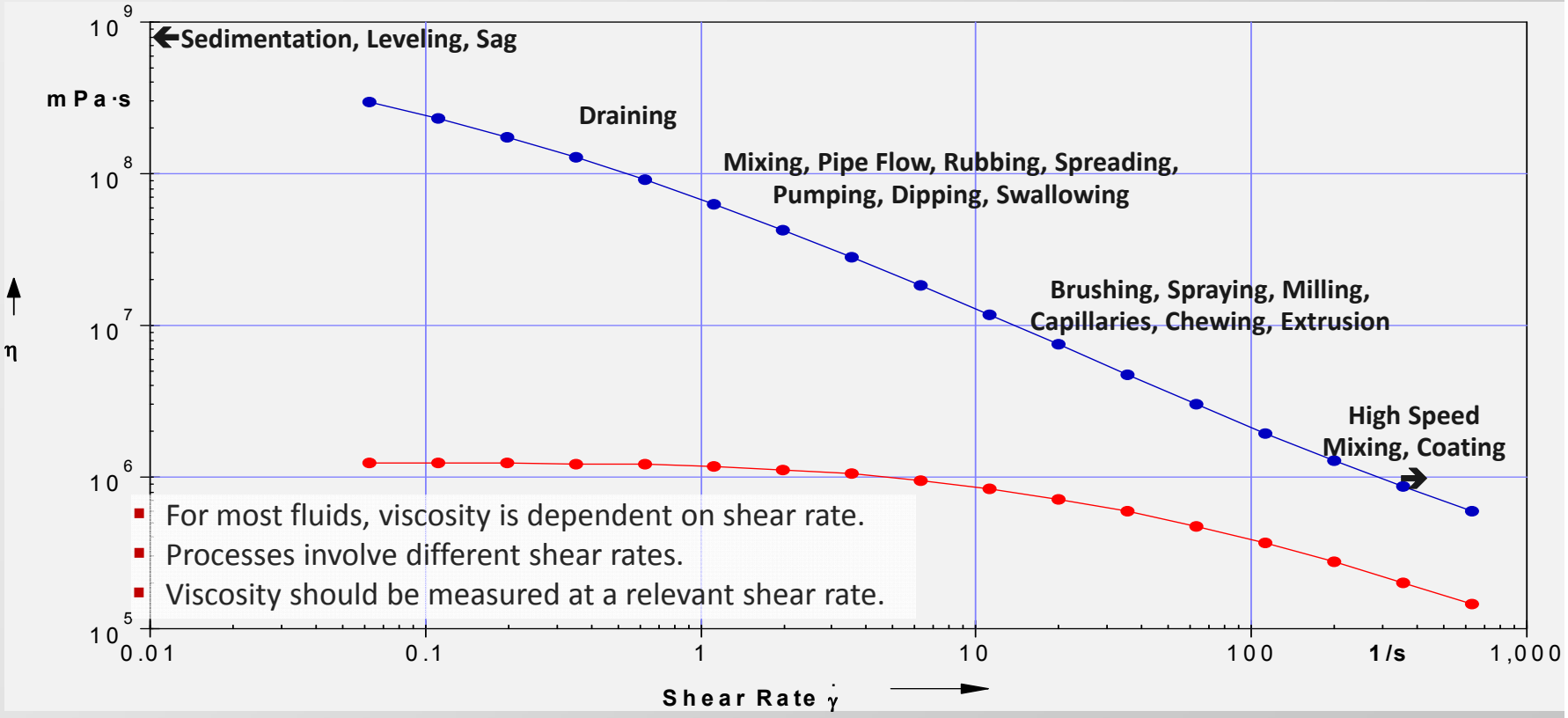
- **Gasoline at 20°C** — **0.5 cP**
- **Water at 25°C** — **1 cP**
- **Whole cream at 25°C** — **10 cP**
- **Olive oil at 25°C** — **100 cP**
- **Pancake Syrup at 25°C** — **1,000 cP**
- **Honey at 20°C** — **10,000 cP**
- **(η_0) Polyethylene at 200°C** — **100,000 cP**



Q. What's wrong with this picture?

(A. For structured materials like chocolate syrup, ketchup, etc… viscosity is not a single point and thus the shear rate should be noted. Also, temperature should be noted.)

Why is Shear Rate Important?



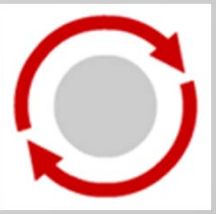
- For most fluids, viscosity is dependent on shear rate.
- Processes involve different shear rates.
- Viscosity should be measured at a relevant shear rate.

What are Flow Properties?

- Flow properties are the response of a sample to applied shear.
- Viscosity is the property used to describe flow behaviors.
- Does the sample flow?
- Does the sample get thinner? Thicker? Not change?
- When shear is applied, does the sample's response change with time, temperature, pressure?
- When the shear is removed, does the sample return to its pre-shear condition?
- **Flow properties measure the response of the sample to the test conditions, i.e. applied shear.**
- Flow properties are measured via rotational (steady shear) test types.

Rotational (Steady Shear) Test Methods

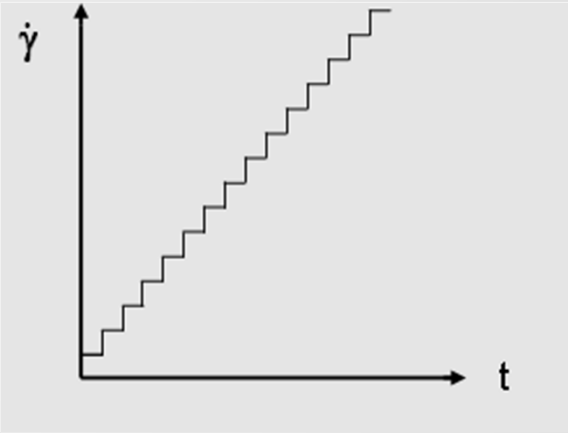
- Single Point Measurement - viscosity measured at a single shear rate or shear stress and one temperature
- Flow Curve – viscosity measured over range of shear rates or shear stresses under isothermal conditions
- Thixotropy – viscosity is measured prior to, during, and after shear as a means to characterize recovery after shear
- Time Test – viscosity measured at a constant shear rate or shear stress at one temperature for a fixed length of time
- Temperature Ramp - viscosity is measured at a fixed shear rate or a fixed shear stress while ramping temperature up or down

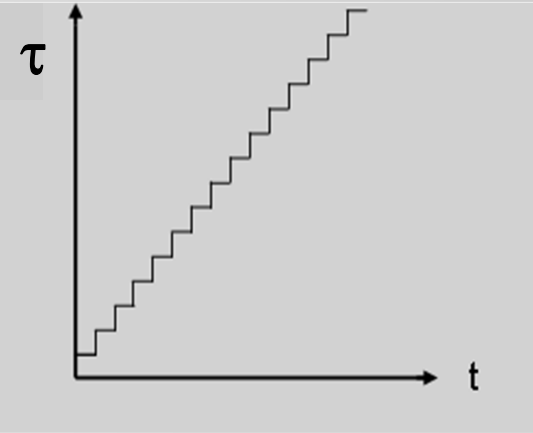


Flow Curve Setup

Flow curves are of two varieties.

Controlled shear rate (CSR) or Controlled shear stress (CSS)



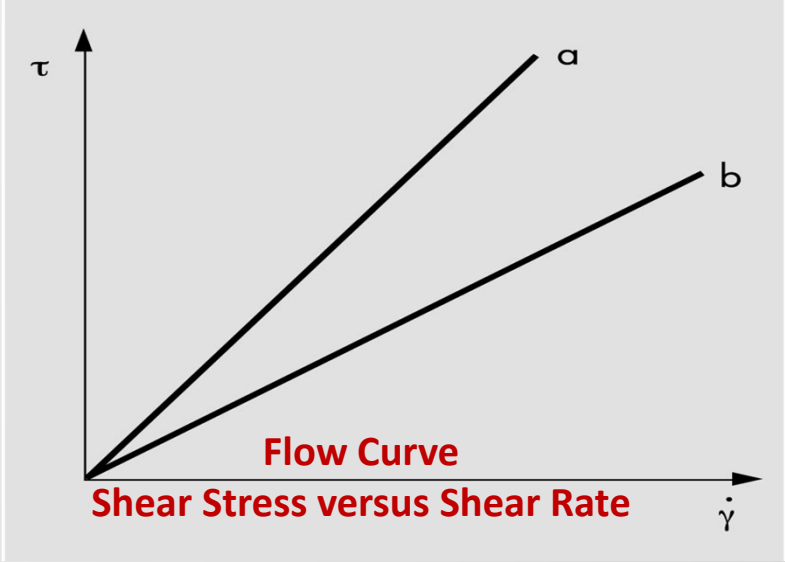


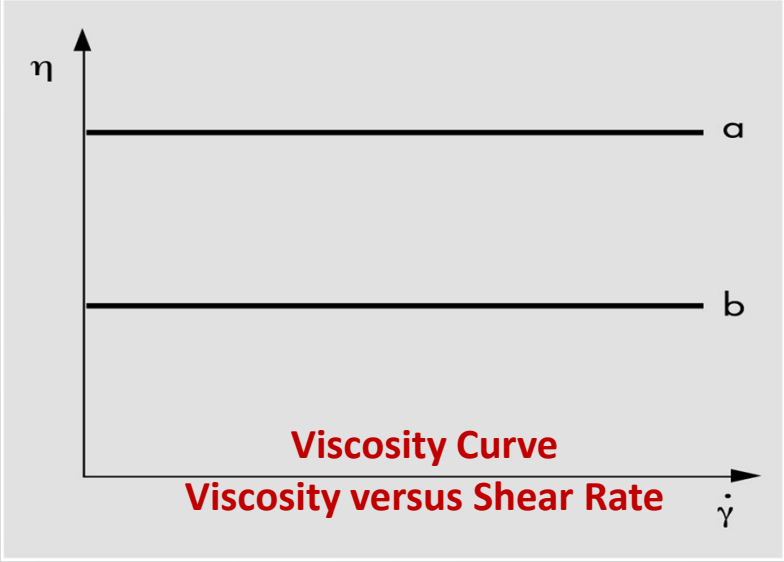
Controlled Shear Rate Flow Curve
The shear rate is ramped up or down.
The shear stresses required to obtain the shear rates are measured.

Controlled Shear Stress Flow Curve
The shear stress is ramped up or down.
The shear rates obtained from the applied shear stresses are measured.

Flow Curve Data Reporting

Flow curve data may be presented in two ways.



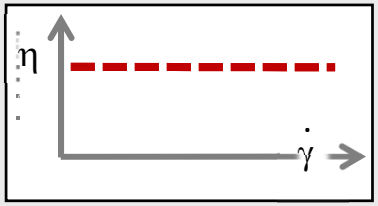


These data show two ideal viscous fluids or Newtonian fluids meaning their viscosity is not dependent upon the applied shear rate.

Flow Curve: The Four Flow Behaviors

Increasing Shear Rate -> Increasing Shear Forces

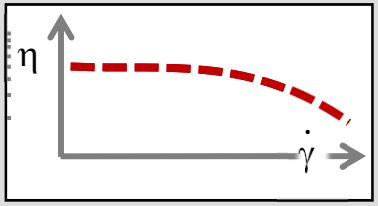
Ideally Viscous



Newtonian

- Viscosity is a material constant
- Solvents, water, oils, honey

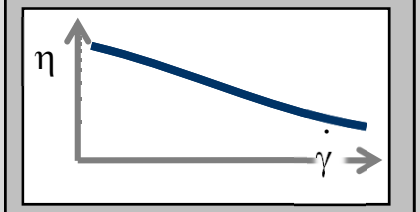
Shear Thinning



Visco-elastic liquid

- Constant at low shear
- Shear thinning at high shear rates
- Polymer solutions, melts

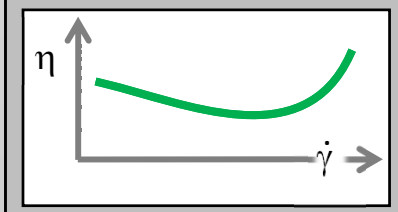
Shear Thinning



Visco-elastic gel

- Infinite viscosity at low shear
- Shear thinning
- Emulsions, suspensions, gels

Shear Thickening

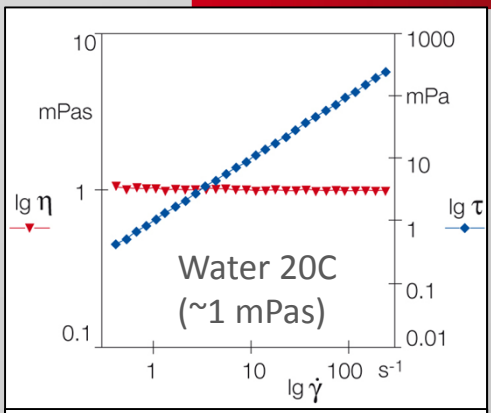


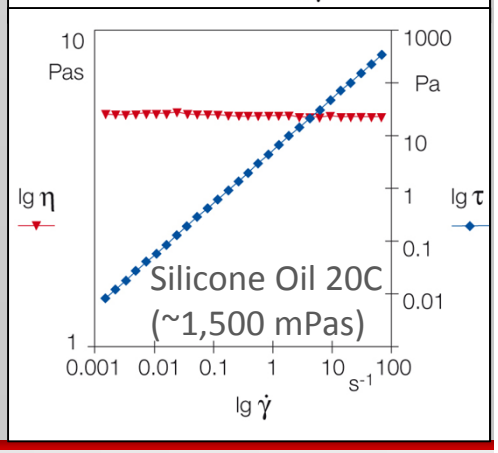
Visco-elastic paste

- Shear thinning at low shear but shear thickening at high shear
- Dispersions

Newtonian Fluids

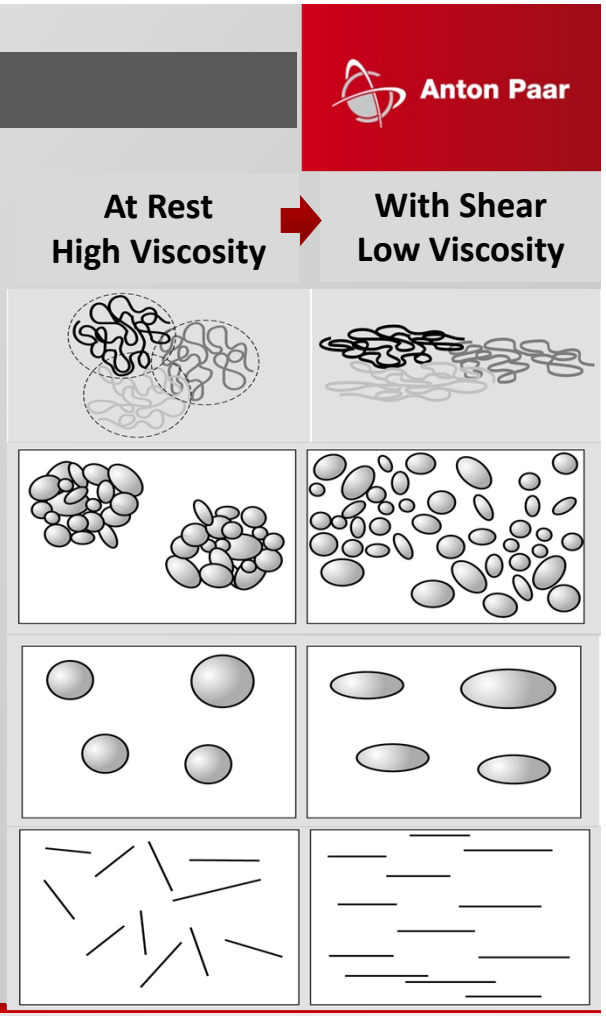
- Simple, non-structured fluids exhibit ideally (purely) viscous flow behavior.
- Their viscosity is not dependent upon the amount of shear applied (shear rate) at some temperatures.
  - Viscosity unchanging over shear rate
  - Slope of shear stress to shear rate linear
- Rheologically speaking, Newtonian fluids are not too interesting, i.e. they are not viscoelastic.
- At some temperatures, many simple fluids will begin to grow structures (crystallize) which then gives them non-Newtonian behavior.





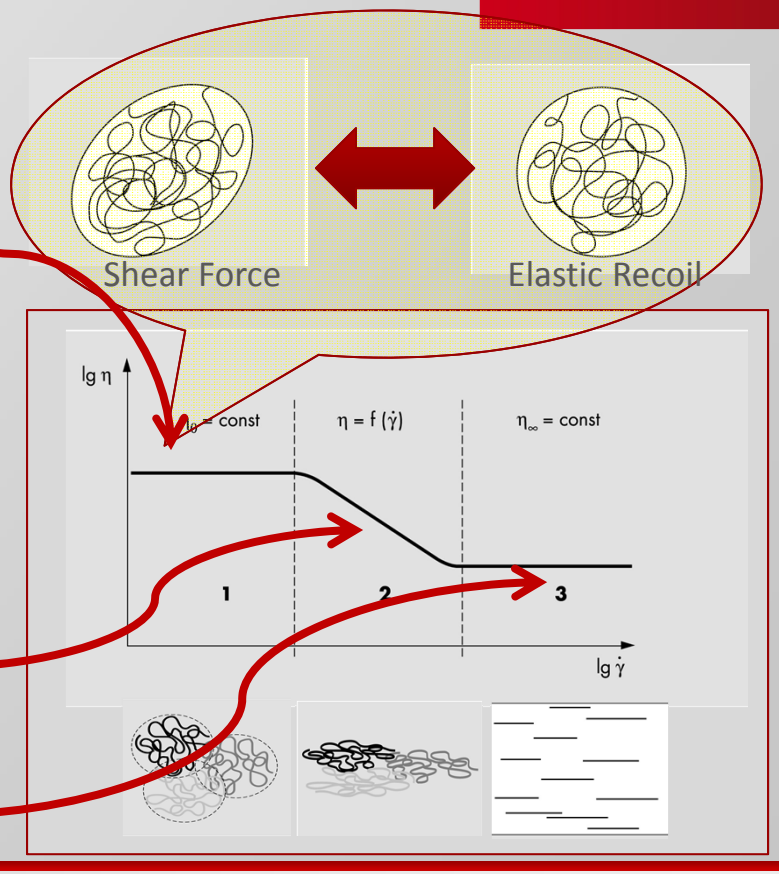
Shear Thinning – What is the Cause?

- Shear thinning occurs in non-Newtonian fluids due to changes in particle/molecular orientations and/or alignment in the direction of flow.
  - Polymer solutions/melts – entanglements/coils at rest unfold and align with the applied shear
  - Suspensions – agglomerates at rest break up with applied shear
  - Emulsions – droplets spherical at rest elongate with the applied shear
  - Dispersions – solid particles randomly oriented at rest align with the applied shear
- In all cases, disorder (high viscosity) at rest to order (low viscosity) with applied shear causes shear thinning.



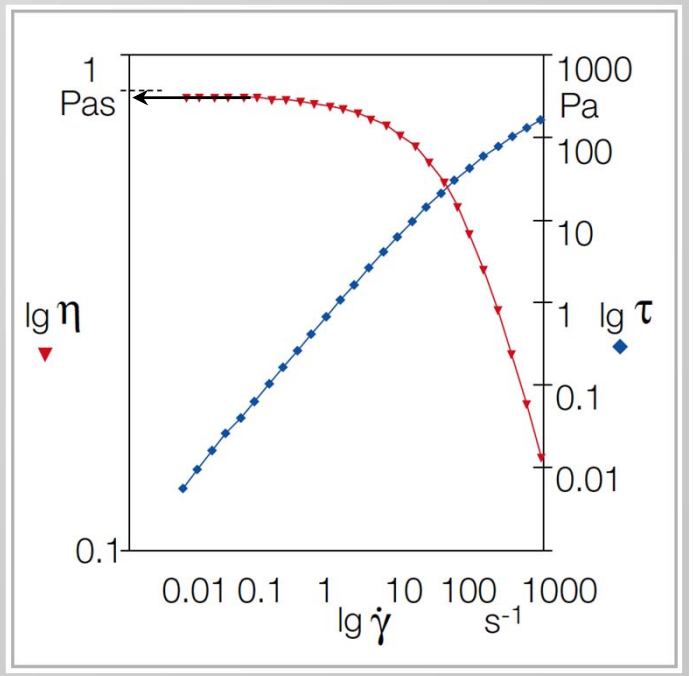
Shear Thinning Behavior - Zero Shear Viscosity Fluid

- Amorphous polymers in the low shear range exhibit a zero shear viscosity (η_0)
- Stems from the superposition of two processes
  - Orientation of the macro-molecules under shear leads to disentanglement and thusly decreasing viscosity (viscous flow - dashpot)
  - Recoil due to elastic behavior of the molecular interactions leads to re-entanglement and thusly increasing viscosity (elastic recoil - spring)
  - Two processes balance each other and there is no net change in viscosity
- Once the shear imparted overpowers the molecular interactions (spring behavior), shear thinning is seen
- Once the polymer structure is completely torn up, a 2nd plateau in viscosity is reached (η_∞)



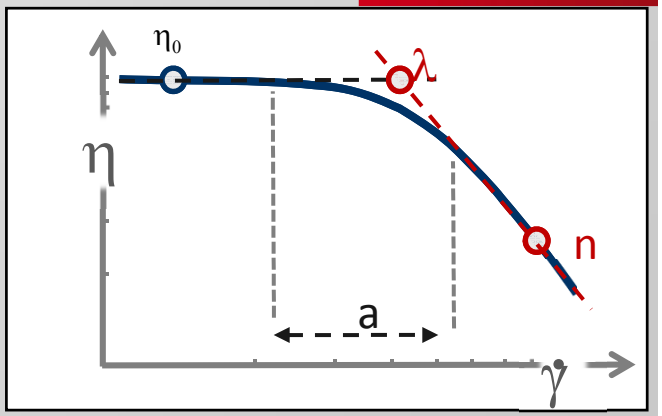
What About the Zero Shear Viscosity?

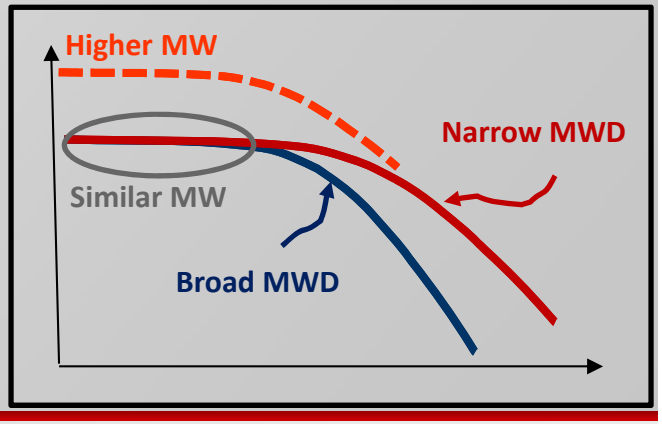
- Zero shear viscosity indicates that a sample's flow curve has a flat plateau at low shear rates where it appears Newtonian.
- From this plateau, the viscosity at zero shear rate can be extrapolated (remember, viscosity cannot be measured at zero shear rate because viscosity measurement requires the sample to be flowing, i.e. shear rate greated than zero)
- Fluids exhibiting a zero shear viscosity region are "viscoelastic liquids"
- The magnitude of η_0 is proportional to average molecular weight (higher η_0 , the higher the molecular weight)



Zero Shear Viscosity Summary

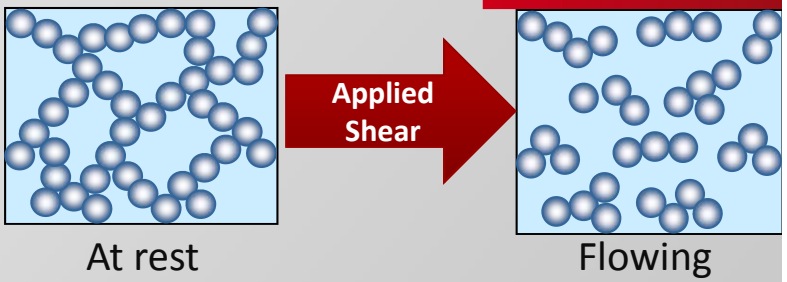
- Regression methods for zero shear viscosity fluids:
  - Carreau
  - Carreau-Gahleitner
  - Carreau-Yasuda
  - Cross
- η_0 analysis provides information on:
  - Molecular weight or concentration
    - Higher η_0 = higher MW / higher concentration
  - Molecular weight distribution (a)
    - Zero shear plateau ends sooner the broader the MWD
  - Relaxation time (λ)
    - Inverse of shear rate at end of zero shear plateau
  - Power law behavior (n)
    - Tendency towards shear thinning once η_0 is exceeded

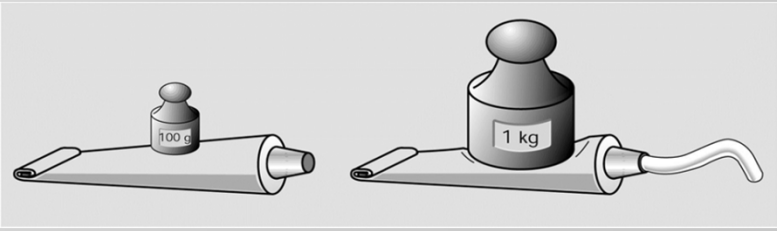


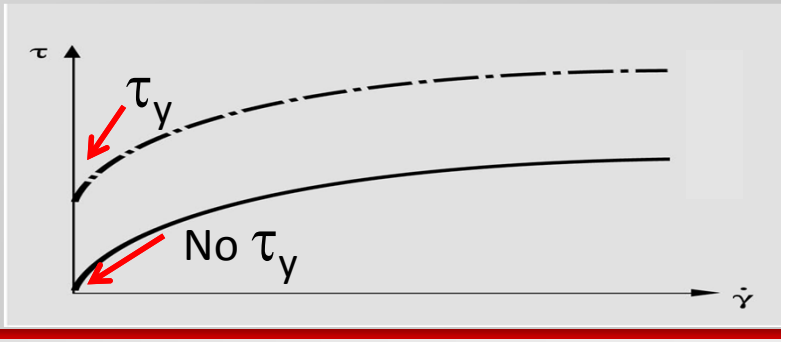


Shear Thinning Behavior - Yield Stress Fluid

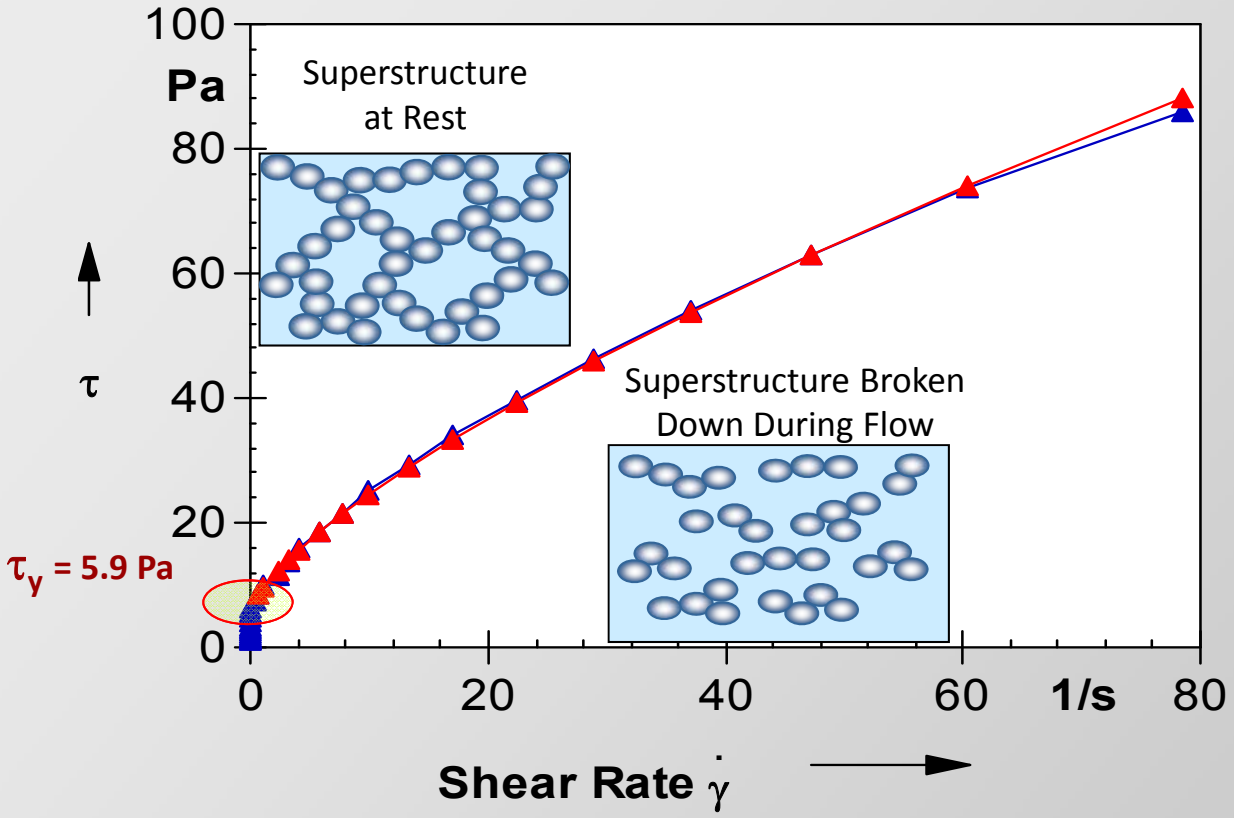
- Some minimum stress required to initiate flow
- Superstructure developed at rest must be overcome, i.e. broken down, by the applied shear before the sample yields then flows
- Must be accounted for in process design due to increased energy required to initiate movement, i.e. stirring, mixing, pumping
- Prior to the yield stress, the sample exhibits elastic deformation
- Beyond the yield stress, the sample exhibits viscous flow
- Influences velocity profile during pipe transport, sedimentation, and slump







Interpolated Yield Stress Determination via a Herschel-Bulkley Fit



Measured Data (Blue Symbols)

Analysis Data (Red)
Herschel-Bulkley:

Yield Stress τ_y = 5.9 Pa

Direct Yield Stress Determination Via A Strain Versus Stress Method

Anton Paar

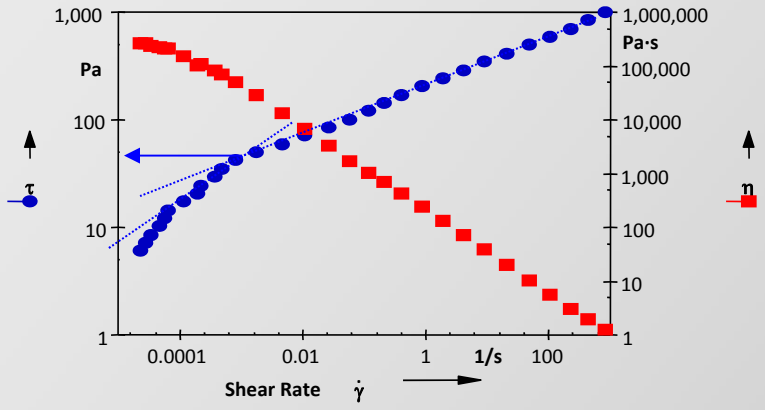
Controlled Shear Stress Test:

Logarithmic ramp from 5 Pa to 1000 Pa

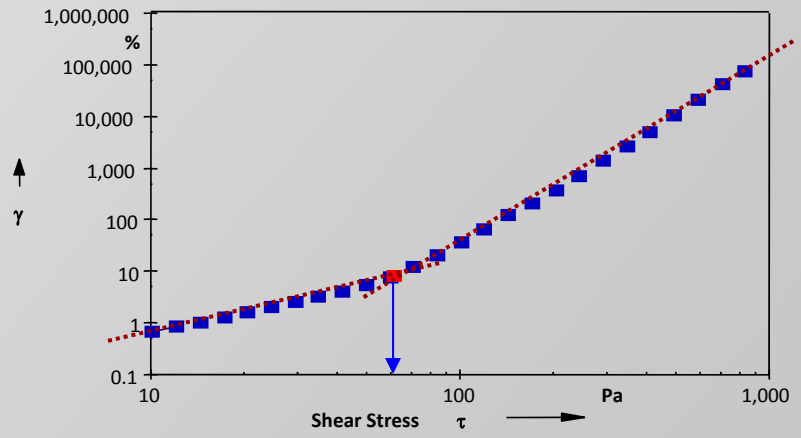
t_{MP} = 5 s (hand cream data shown)

Better method for the yield point characterization

Logarithmic presentation



Gamma-Tau Presentation



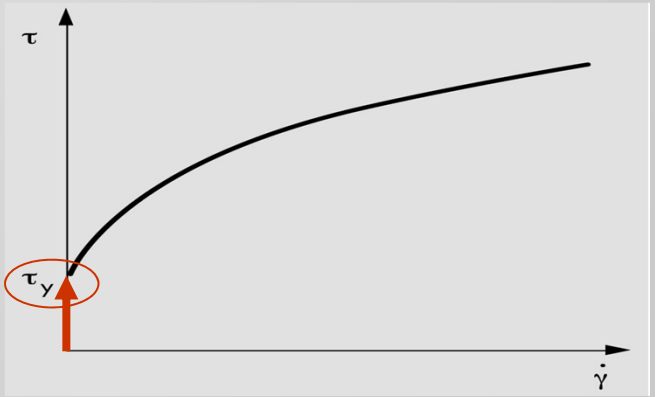
The change in slope of the strain versus shear stress curve is the yield stress.

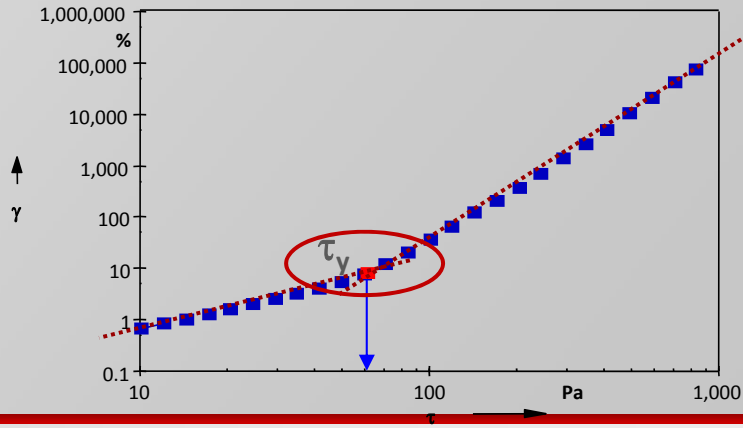
What about the Yield Stress?

- Consumers have expectations of good yield stresses even if they do not know that is what it is.
  - Ketchup
  - Toothpaste
  - Mayonnaise
  - Caulk
- In processes, a yield stress can be a very bad thing if it is not recognized and taken into consideration during process design.
- Packaging must take into consideration the yield stress.
- Is a yield stress a good or bad thing? It depends!

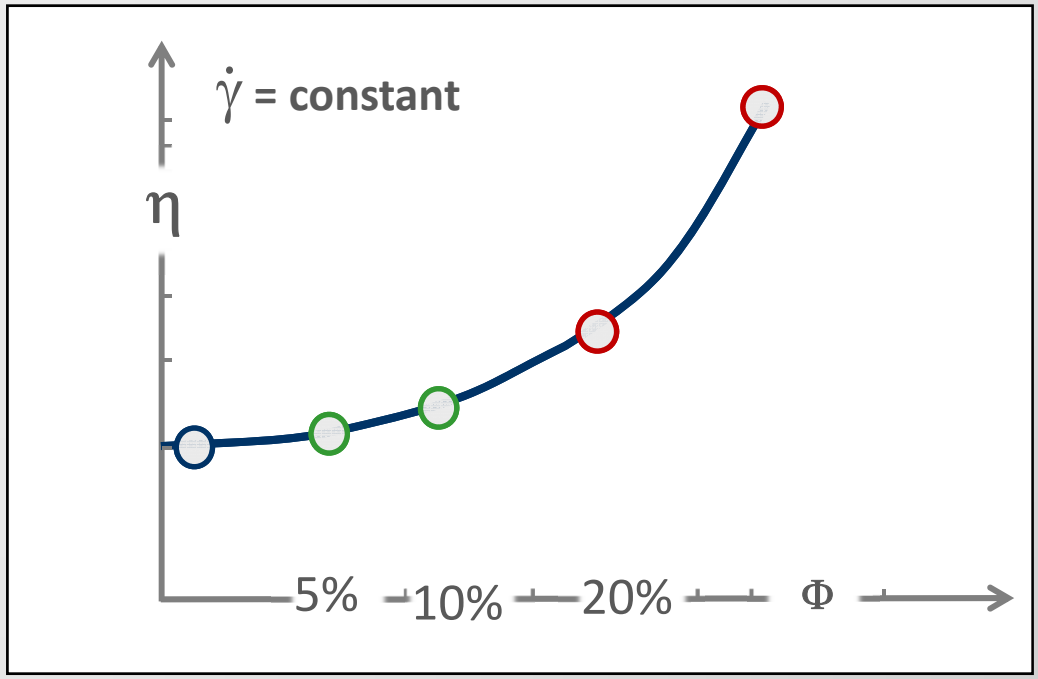
Apparent Yield Stress Summary

- Regression methods for yield stress fluids include:
  - Bingham
  - Herschel-Bulkley
  - Casson
  - Windhab
  - Upward inflection γ
- Larger yield stress indicates:
  - More stable structure
  - Better sedimentation stability
  - Higher layer thickness
  - More paste or gel like character
- Be aware that apparent yield stress is dependent upon:
  - Instrument resolution
  - Test duration
  - Measuring conditions
  - Presentation
  - Analysis method





Shear Thickening – What is the Cause?

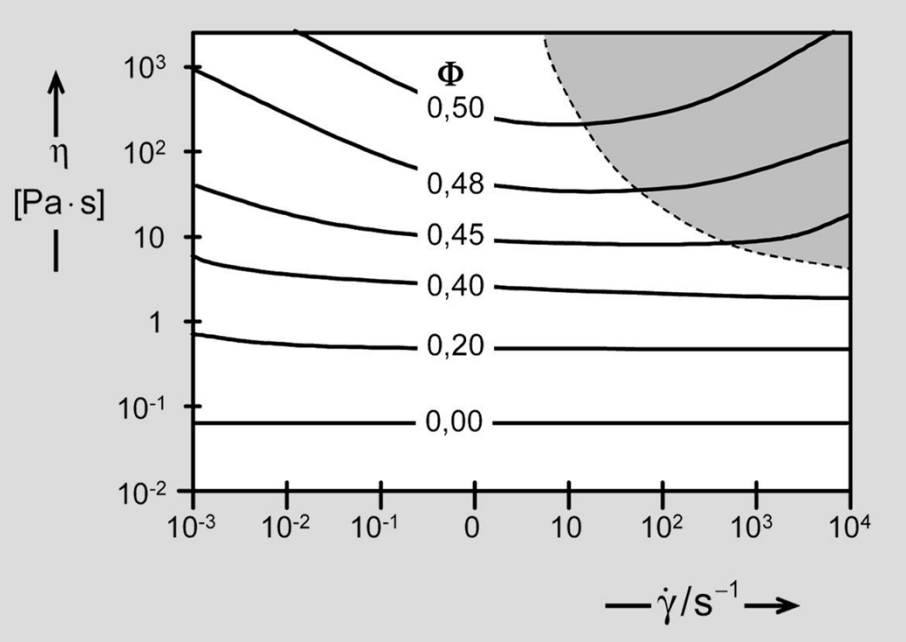


Φ = solid volume fraction (% of entire volume of suspension)

- Particles are "free" to move within the matrix liquid
- Particle-Particle Interactions -> Friction due to high concentration

- Shear thickening occurs in fluids with high concentration of solids
- Initially, shear thinning is seen as the solids align with the shear
- At some critical shear rate, the solids cannot readily flow past each other and begin to jam causing a rise in viscosity
- The critical shear rate differs with solid volume fraction

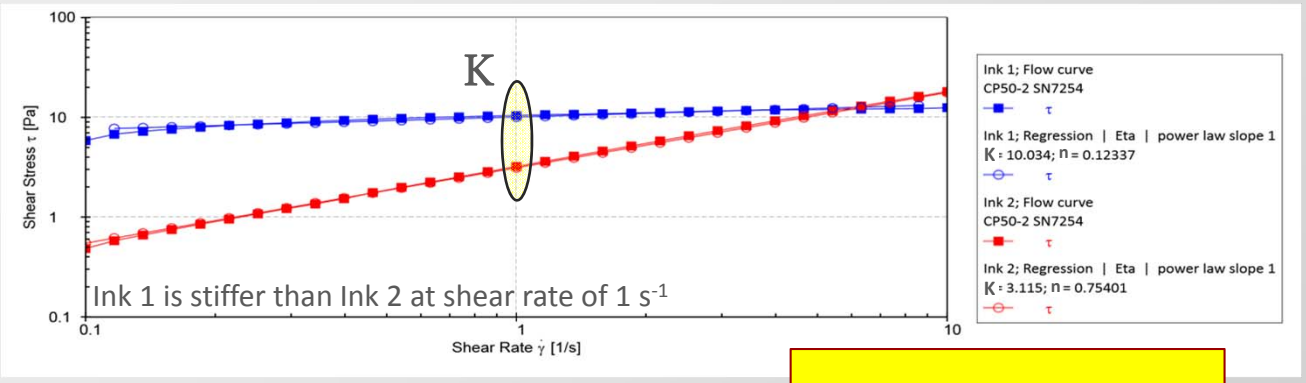
Summary of Shear Thickening Fluids



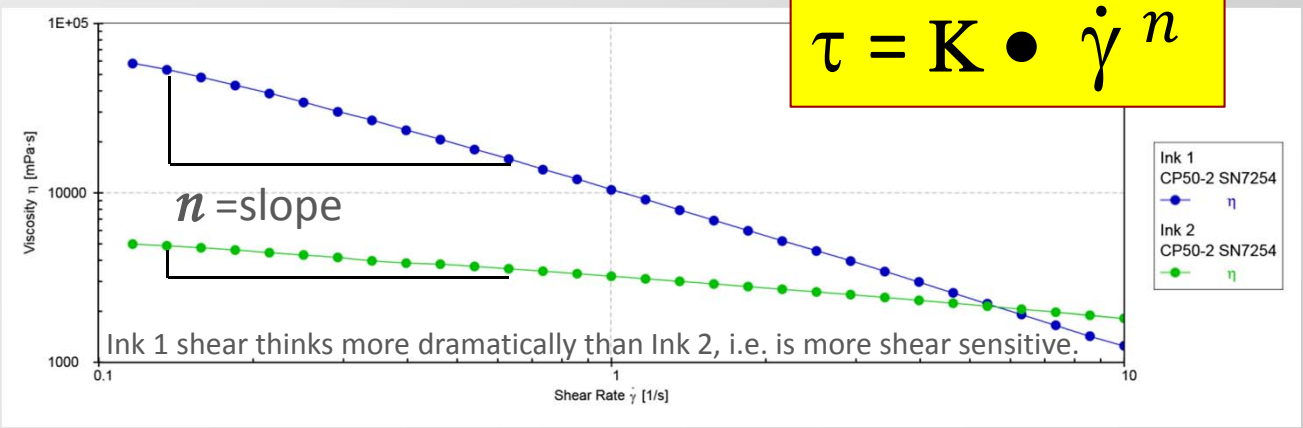
Φ = solid volume fraction (% of entire volume of suspension)

- Higher solid volume fraction results in:
  - Higher viscosity at low shear
  - More dramatic initial shear thinning
  - Lower critical shear rate at which thickening begins
- Particle size, shape, concentration, and polydispersity index influence shear thickening
  - Increasing the PDI, or particle size distribution, helps maintain viscosity when increasing concentration
  - Narrowing the particle size distribution increases viscosity
- Unexpected shear thickening during processing or use is usually undesirable

Power Law Modeling for Consistency and Flow Behavior



$$\tau = K \bullet \dot{\gamma}^{n}$$



- K = consistency index (shear stress at $\dot{\gamma}$ = 1 s-1)
- *n* = flow behavior index
  - *n = 1 for Newtonian liquids*
  - *n < 1 for shear thinning liquids*
  - *n > 1 for shear thickening liquids*
- Describes flow behavior of many process shear rates
- Does not describe flow behavior at low or high shear rates

Recap – Audience Participation!

- Why is it important to know the shear rate at which a viscosity measurement is made?

A. For most fluids, viscosity is very dependent in shear rate, i.e. changes as shear rate changes.

- What information is required to get from the rheometer parameters to the rheological parameters?

A. Shape of the sample, i.e. flow field

- Would a single point viscosity measurement be adequate for any of the 3 samples shown in the flow curve at the right?

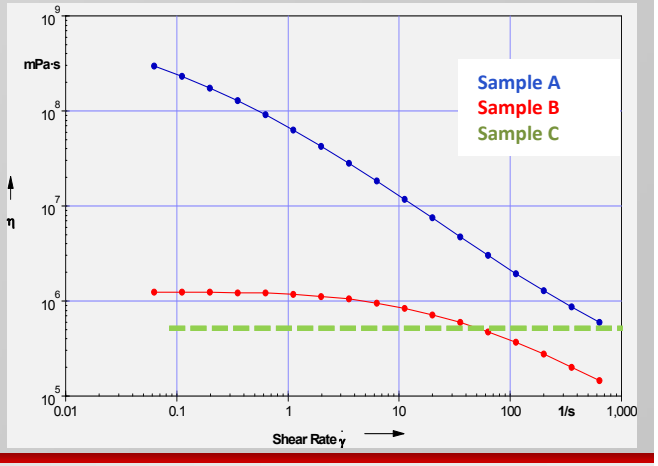
A. Yes, the green sample which is Newtonian.

- What shear rate range would one measure at if concerned about sedimentation?

A. As low as possible, i.e. <0.1 1/s)

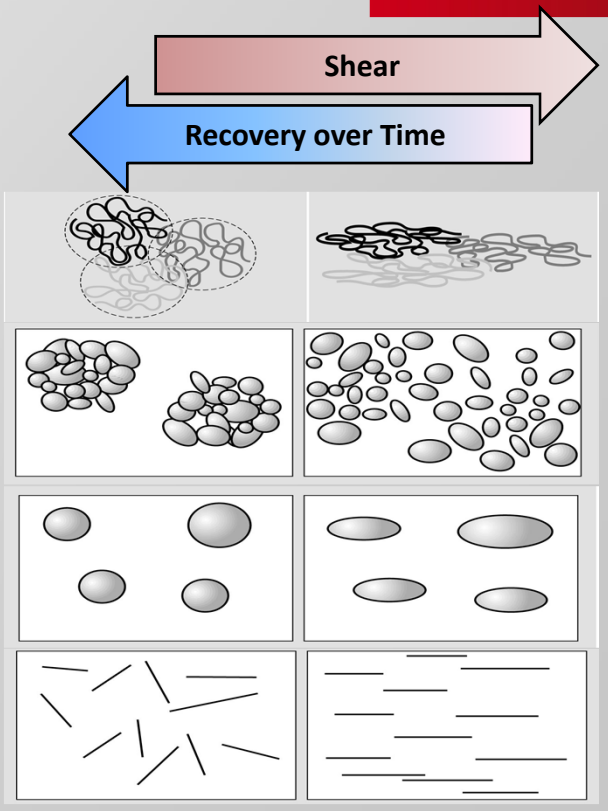
- Is yield stress a good or bad thing?

A. Both.



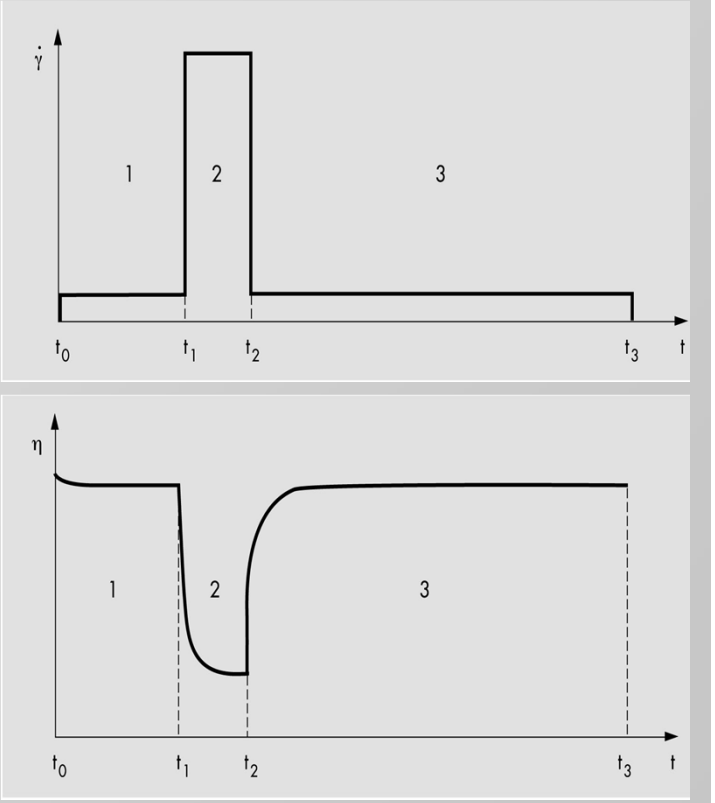
Thixotropic Behavior

- Thixotropy refers to the recovery of structure following shear
- The speed of structural recovery and the thoroughness define a materials thixotropic behavior
- Thixotropy is important for:
  - Coating quality
    - Leveling
    - Sag
    - Wet layer thickness
  - Component homogeneity following shear during processing
    - Components staying where you want them
- Thixotropy can be measured via rotational and oscillatory measurements



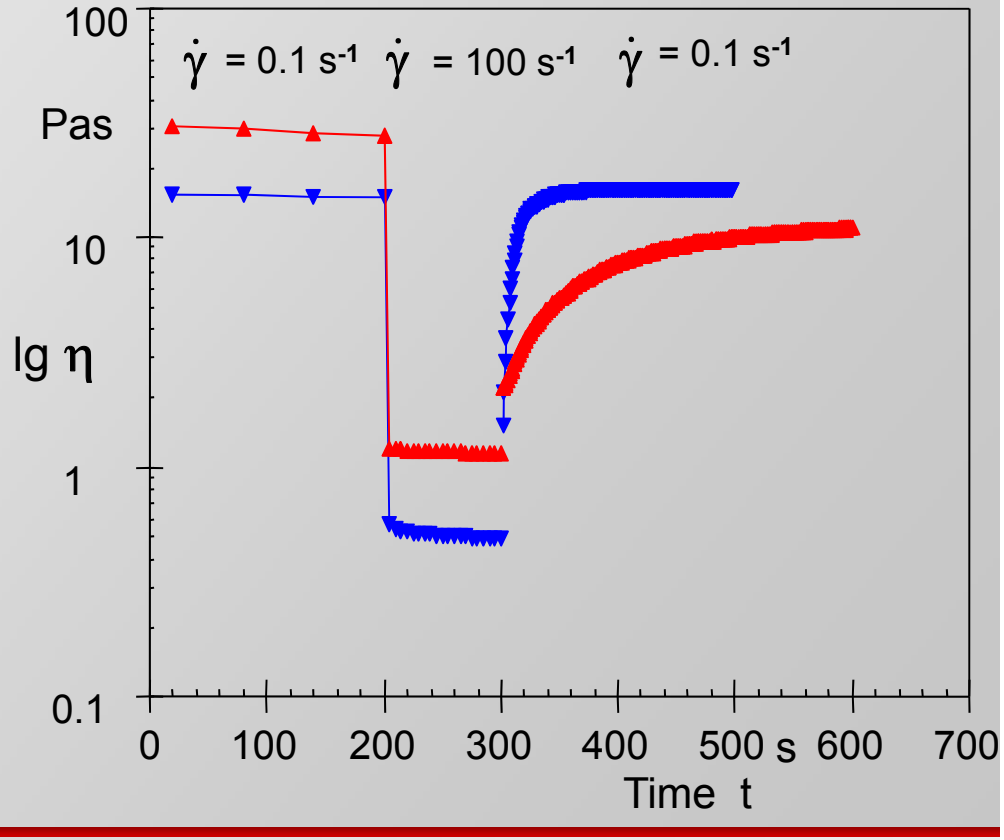
Rotational Three Interval Thixotropy Test – Recovery after Shear

- Interval 1 establishes “at rest, unperturbed” properties with a very low shear rate measurement.
- Interval 2 destroys structure by applying high shear rate.
- Interval 3 monitors structural recovery with a very low shear rate measurement.
- Data is presented as viscosity as a function of time.
- This test determines absolute structural recovery:
  - After a finite length of time
  - To a certain % of recovery



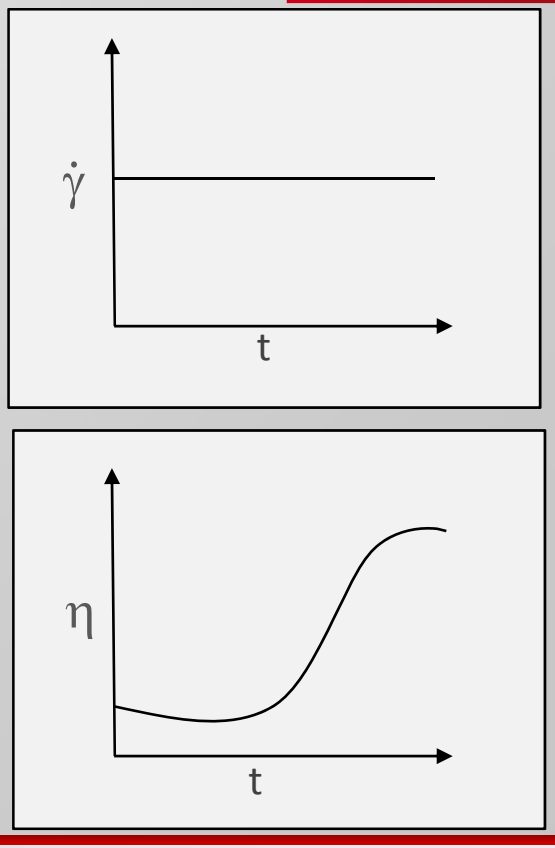
Thixotropy: Recovery after Shear – Balancing Leveling and Sag

- **Problem:**
  - Coating Blue contained a gellant for thickening. Coating Red contained a viscosifier for thickening.
  - The two coatings did not provide similar surface quality.
- **Solution:**
  - Measure recovery after shear to fine tune formulation to have desired surface quality.
  - Coating Blue is thinner but recovered fully and very rapidly insuring sag is not an issue.
  - Coating Red, while thicker, recovered slowly, incompletely and did not maintain the desired coating thickness, i.e. leveled too much.

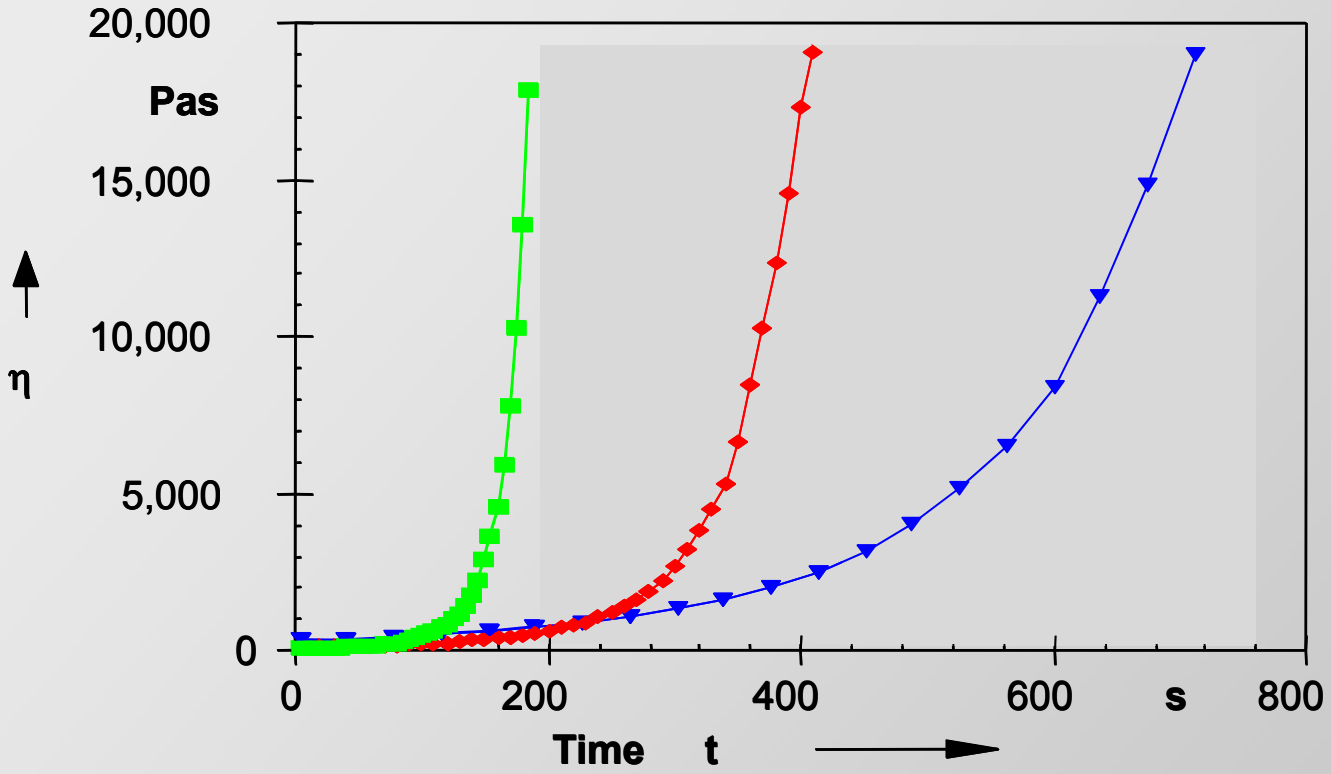


Rotational Time Test

- Shear rate and temperature are held constant
- Behaviors measured are:
  - Curing
  - Gelation
  - Degradation
  - Other reaction kinetics
- Change in viscosity over time is measured



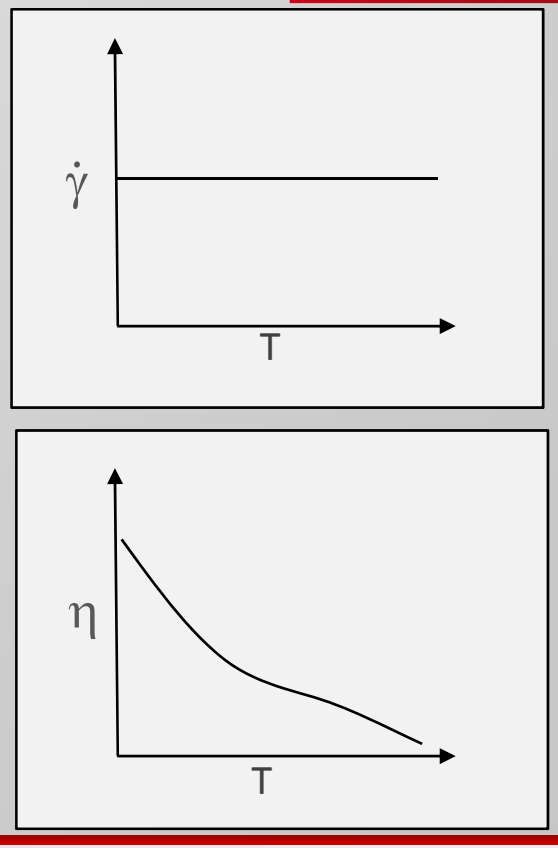
Rotational Time Test at Three Isothermal Conditions



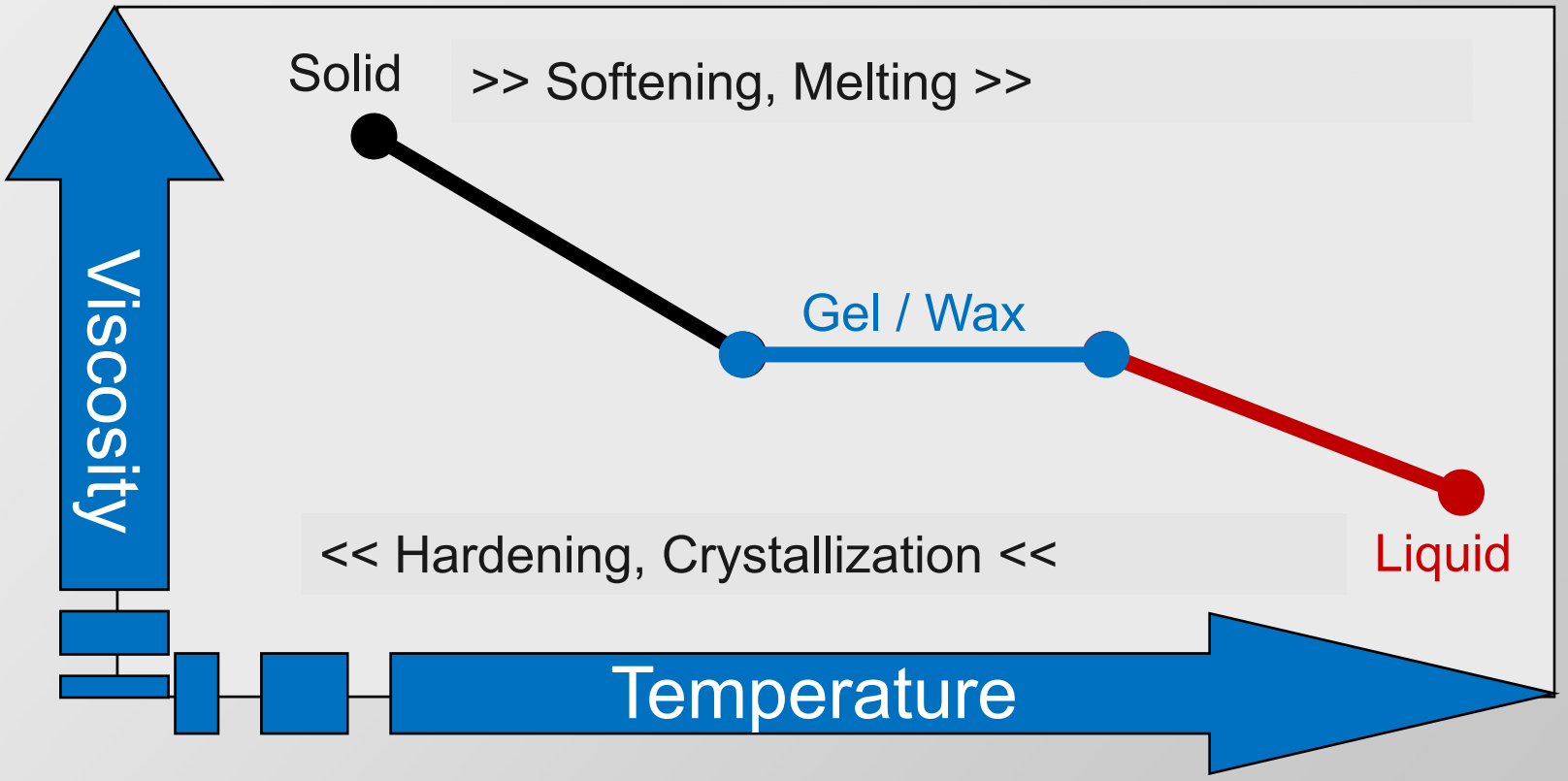
powder coating 120°C
η Viscosity
powder coating 140°C
η Viscosity
powder coating 160°C
η Viscosity

Rotational Temperature Test

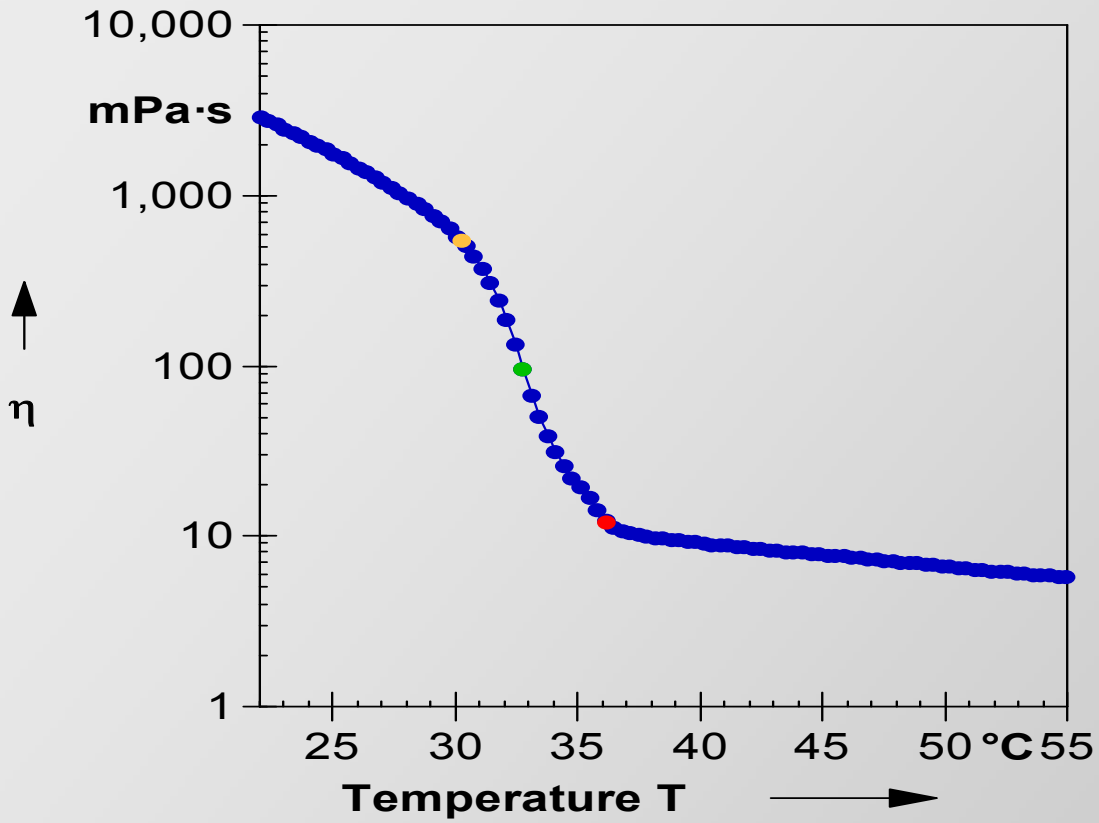
- Shear rate is held constant while temperature is ramped up or down
- Behaviors measured
  - Curing
  - Gelation
  - Melting
  - Freezing
  - Crystallization
  - Degradation
  - Other reaction kinetics
- Change in viscosity with changing temperature is measured



Rotational Testing Temperature Ramp - Result



Rotational Temperature Ramp Example – Pour and Cloud Point



Crude Oil

η Viscosity

Crude Oil [CLOUD-PT]

T = 36.22 °C; eta = 0.01199 Pa·s

η Viscosity

Crude Oil [POUR-PT,ETA]

T = 32.8 °C; eta = 0.09408 Pa·s

η Viscosity

Crude Oil [POUR-PT,HIGH]

T = 30.25 °C; eta = 0.5377 Pa·s

η Viscosity

Is Viscosity the Right Parameter for You?

- Does your sample flow at the temperature of interest?
- Are you interested in the sample's behavior when flowing, i.e. when it's moving?
- If either answer is no, then viscosity is not the right property for you.
  - **If your sample does not flow then viscosity is not the way to go.**
- If the answer is yes to both, then viscosity measurements can provide useful information for:
  - Processing - QC/QA of raw materials - evaluation of emulsifying agents, binders, thickeners, consistency agents, stabilizers, additives, thixotropy agents
  - Production - behavior at mixing, dispersing, homogenizing, degassing, stirring, no aggregation of particles
  - Transport and proportioning - behavior during pumping and filling
  - During use - squeezing out of a tube, squeezing out of a bottle, spreading on a substrate, pouring from a container

Summary of Viscosity and Flow Properties

- Newtonian fluids can be characterized using a single shear rate for viscosity measurement.
- All other fluids (non-Newtonian) must be characterized over a range of shear rates.
- The four flow behaviors are:
  - Newtonian
  - Shear thinning with yield point
  - Shear thinning with zero shear viscosity
  - Shear thickening
- For non-Newtonian fluids, viscosity is a CURVE not a POINT.
- Time dependent recovery in fluids is called thixotropy which is important for coating efficacy and sample homogeneity.
- Time, temperature, and pressure induced changes in viscosity can be measured at fixed shear conditions.
- Rotational tests measure the response of the sample to the test (shear) condition and the sample must be flowing

Recap – Audience Participation!

- What are the four types of flow behavior?
  Newtonian, shear thinning with zero shear viscosity, shear thinning with yield stress, shear thickening
- Name one process where thixotropy is important.
  Wall painting, spreading topical, dosing after mixing
- When would you need to control temperature during a rheological measurement?
  Always
- What influences the viscosity of a sample?
  Temperature, pressure, shear, concentration
- What parameters does the rheometer measure or control?
  Torque, speed, displacement
- What are the corresponding rheological parameters?
  Shear stress, shear rate, strain
- What causes shear thinning behavior?
  Break down of structure, alignment with flow field

Viscosity = $\frac{\textit{Shear Stress}}{\textit{Shear Rate}} = \frac{\tau}{\dot{\gamma}}$

Rheology

Viscoelastic Properties

Rheology - Flow and Deformation Properties of ALL KINDS OF MATERIALS

Anton Paar

Viscous ← **Viscoelastic** → **Elastic**

Ideally viscous liquids [water, oil, solvents] Newton's Law	Viscoelastic liquids [milk, shampoo, paint]	Viscoelastic solids [pastes, gels, films]	Ideally elastic (rigid) solids [steel, wood] Hooke's Law

Flow behavior describes samples which flow.

Deformation behavior describes samples which deform.

Recap - Hooke's Law

Robert Hooke
1635 - 1703

Elasticity was first described by Robert Hooke who found that a spring deformed proportionally to the force applied to it.

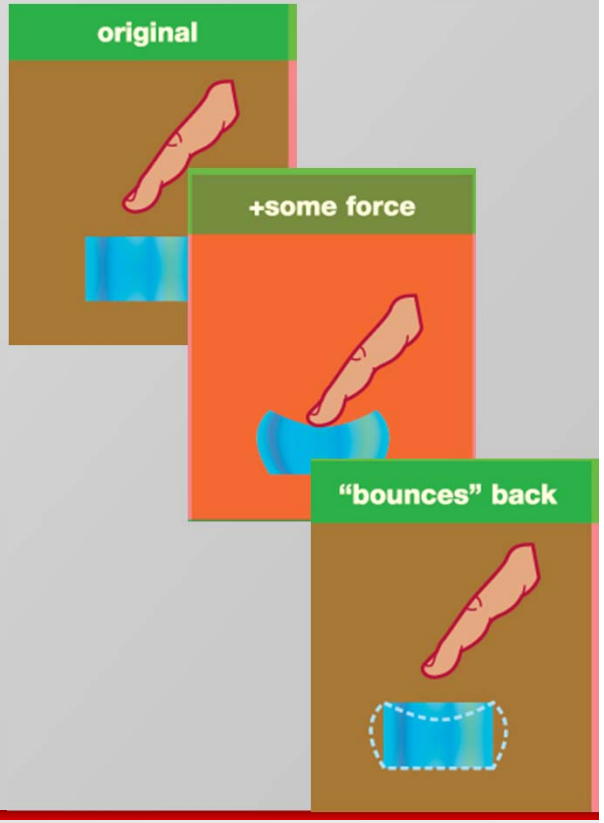
Shear Modulus G = shear stress / shear strain = $\tau \div \gamma$ = Pa/[1] = Pa

Shear Modulus G is usually used to describe viscoelastic behavior rather Viscosity η.

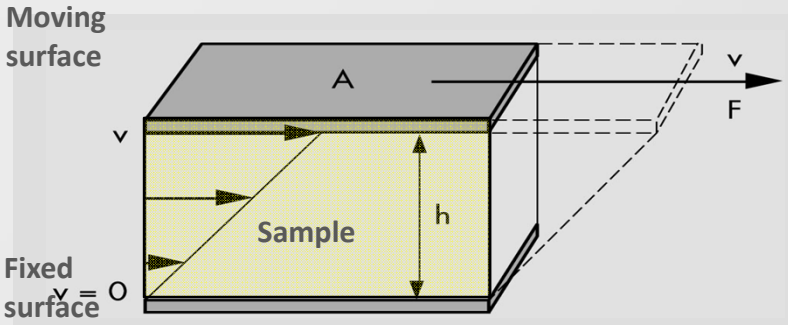
- Modulus is a calculated number.
- Shear stress and strain must be known.
- Modulus can be determined in two ways:
  - Controlling shear stress and measuring resulting strain
    - Rheometer applies a force (torque in mNm) to the sample and measures how far the sample moves
  - Controlling strain and measuring shear stress required to achieve that strain
    - Rheometer applies a fixed deformation to sample and measures torque required to achieve that deformation
- Most simple viscometers control the shear rate and measure the shear stress but most research rheometers can operate in either control mode.

What is Elasticity?

- Describes a material's ability to be deformed and how it responds after it is deformed.
- Refers to a material's ability to remember or store its shape.
- When a force is applied to an elastic material, it deforms. When the force is removed, the material recoils.
- Shear Modulus G is used to describe the deformation behavior instead of Viscosity η.
- Shear Modulus G is the stiffness of the sample.
- How much it bounces back is its elasticity.
- When a material does not flow, then stiffness (modulus) should be used to describe it rather than viscosity.



Shear Modulus and the Two Plate Model

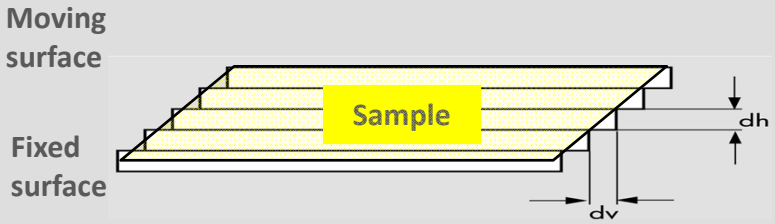


Shear stress = τ (”tau”)

$$\tau = \frac{F}{A} = \frac{\text{shear (force)}}{\text{(shear) area}} = \frac{\text{N}}{\text{m}^2} = Pa$$

Force applied divided by the surface area of sample.

$$\text{Shear Modulus} = \frac{\textit{Shear Stress}}{\textit{Strain}} = \frac{\tau}{\gamma}$$



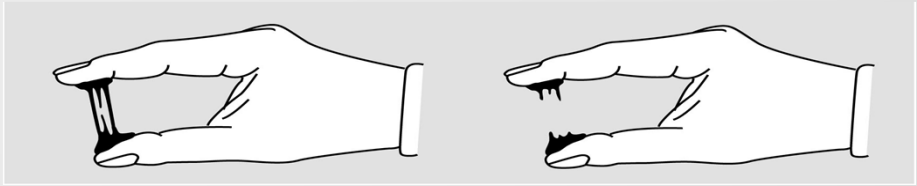
Strain = γ (” gamma”)

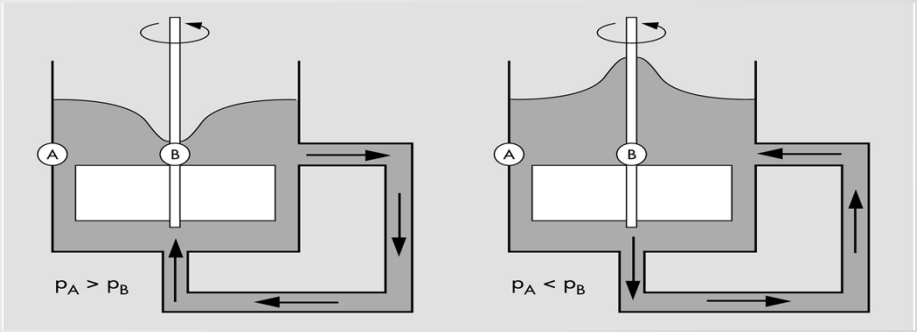
$$\gamma = \frac{\text{v}}{h} = \frac{\text{displacement}}{gap} = \frac{m}{m} = 1(\text{dimensionless})$$

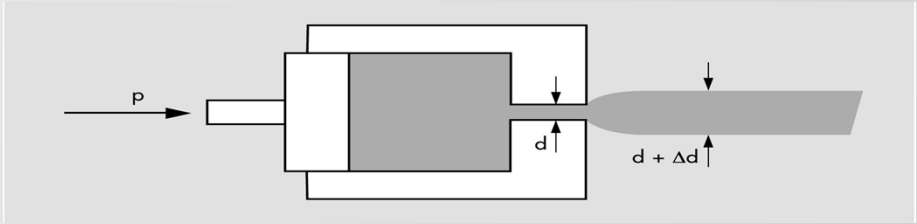
Displacement divided by the thickness.

Material Stiffness and Shear Moduli

Viscoelastic Behavior is Everywhere

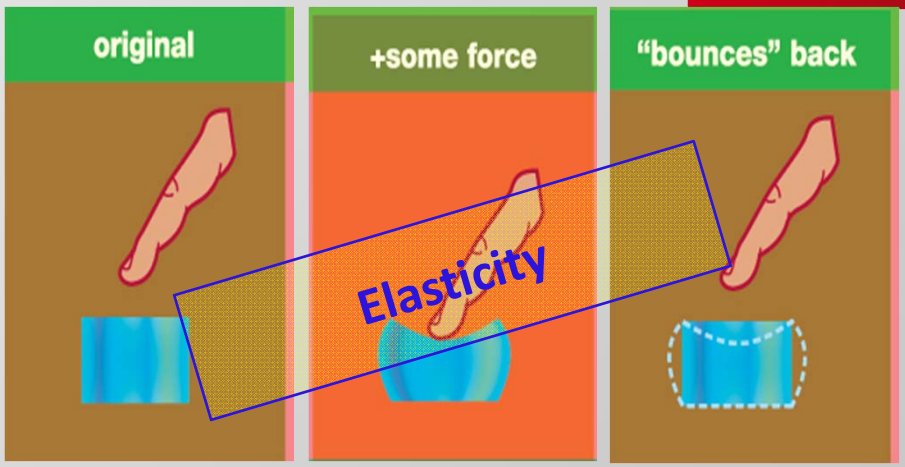






- Tack and stringiness
  - Adhesives
  - Printing inks
  - Food (mouthfeel)
- Stirring and mixing processes
  - Weissenberg effect (Karl Weissenberg, 1893 to 1976, rheologist)
  - Rod climbing
  - Poor mixing characterstics
- Extrusion
  - Extrudate swelling
  - Die swell
  - Poor dimensional (shape) stability

Why Bother with Oscillatory Measurements?



A material's ability to resist flow

When stress is applied, viscous materials flow

Fluids (viscous materials) dissipate (lose) the energy imparted upon them as stress through flow and heat

A material's ability to remember or store its shape

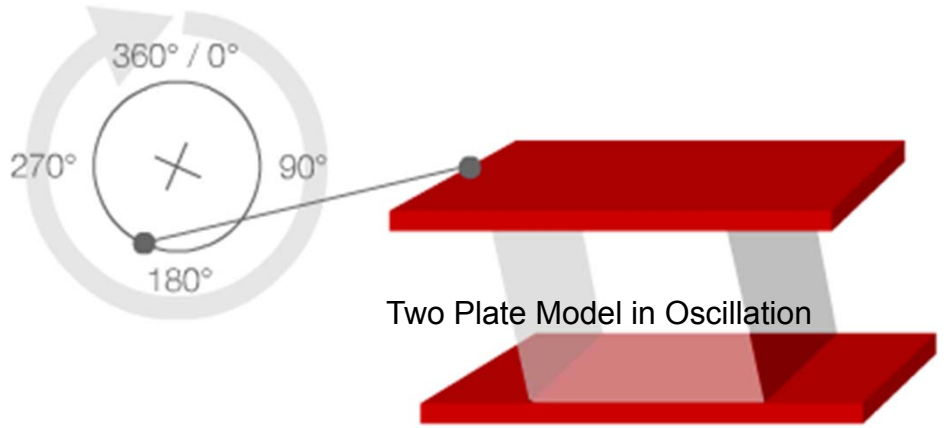
When stress is applied, elastic materials deform

Solids (elastic materials) store energy imparted into them as a stress and use it to restore their shape when the stress is removed

Viscoelastic materials exhibit both behaviors.
Oscillatory measurements identify just how viscous and just how elastic.

How is Viscoelasticity Measured?

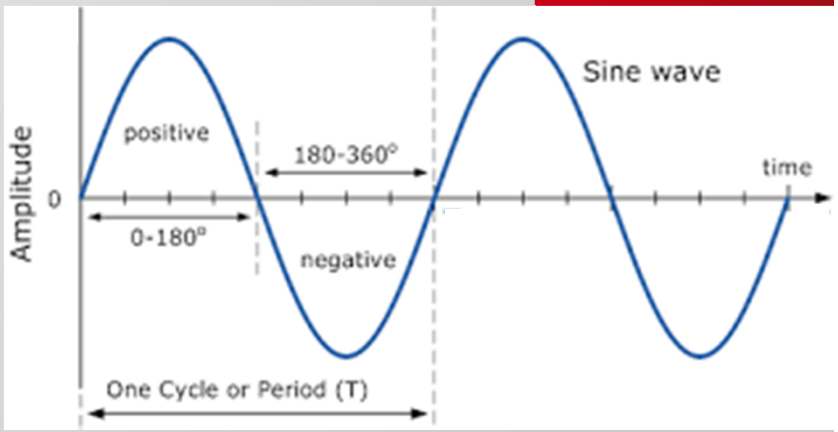
- The most effective way to measure viscoelastic properties is oscillatory testing.
- Oscillatory testing involves oscillating the sample around a fixed point, i.e. wiggling the sample.
- The oscillations are applied in a sinusoidal manner.
- The oscillations are so small that the inherent structures in a sample are measured without being perturbed.
- The test itself imparts no behavior in the sample.

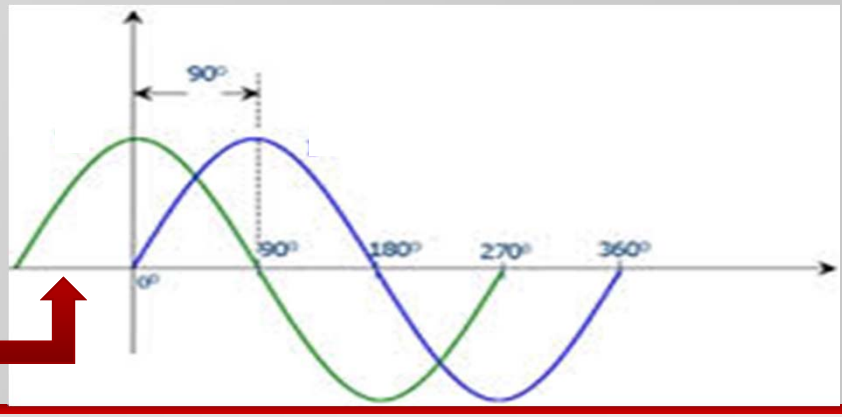


Two Plate Model in Oscillation

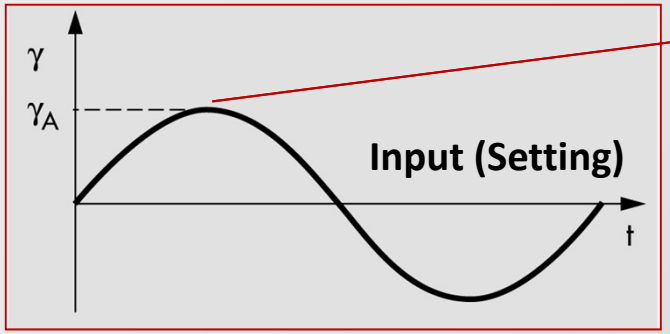
Sine Wave Basics

- Smooth, repetitive oscillation
- Amplitude = height of peaks (and valleys)
- Frequency = time for one full cycle (one peak and valley) to be completed
- The input sine wave starts at 0°
- The resultant sine wave, i.e. sample response, may lag behind the input sine wave and thus not start at 0°
- The phase angle is the time lag, or separation, between the input and resulting sine wave
- The phase angle holds the viscoelastic information

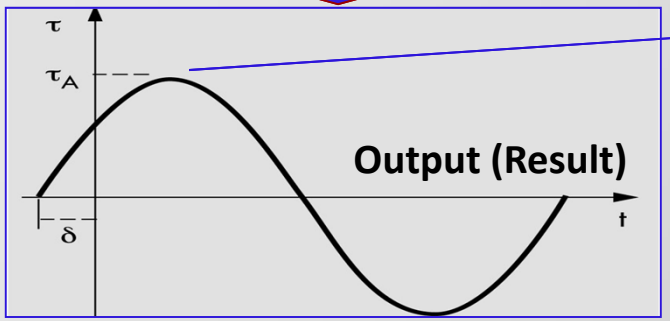




Complex Shear Modulus, G*: Ridigity, Stiffness



Sample Response



γ_A

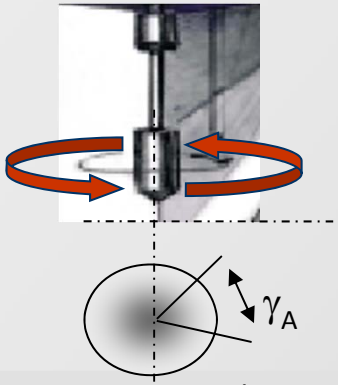
τ_A

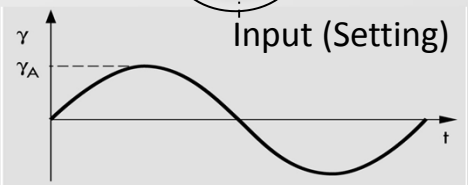
$$G^* = \frac{\tau_A}{\gamma_A}$$

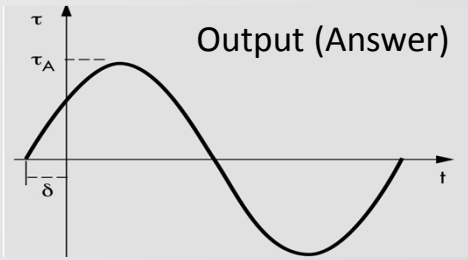
To achieve a given strain (displacement), a stiff sample will need more applied stress and thus, has a larger G*.

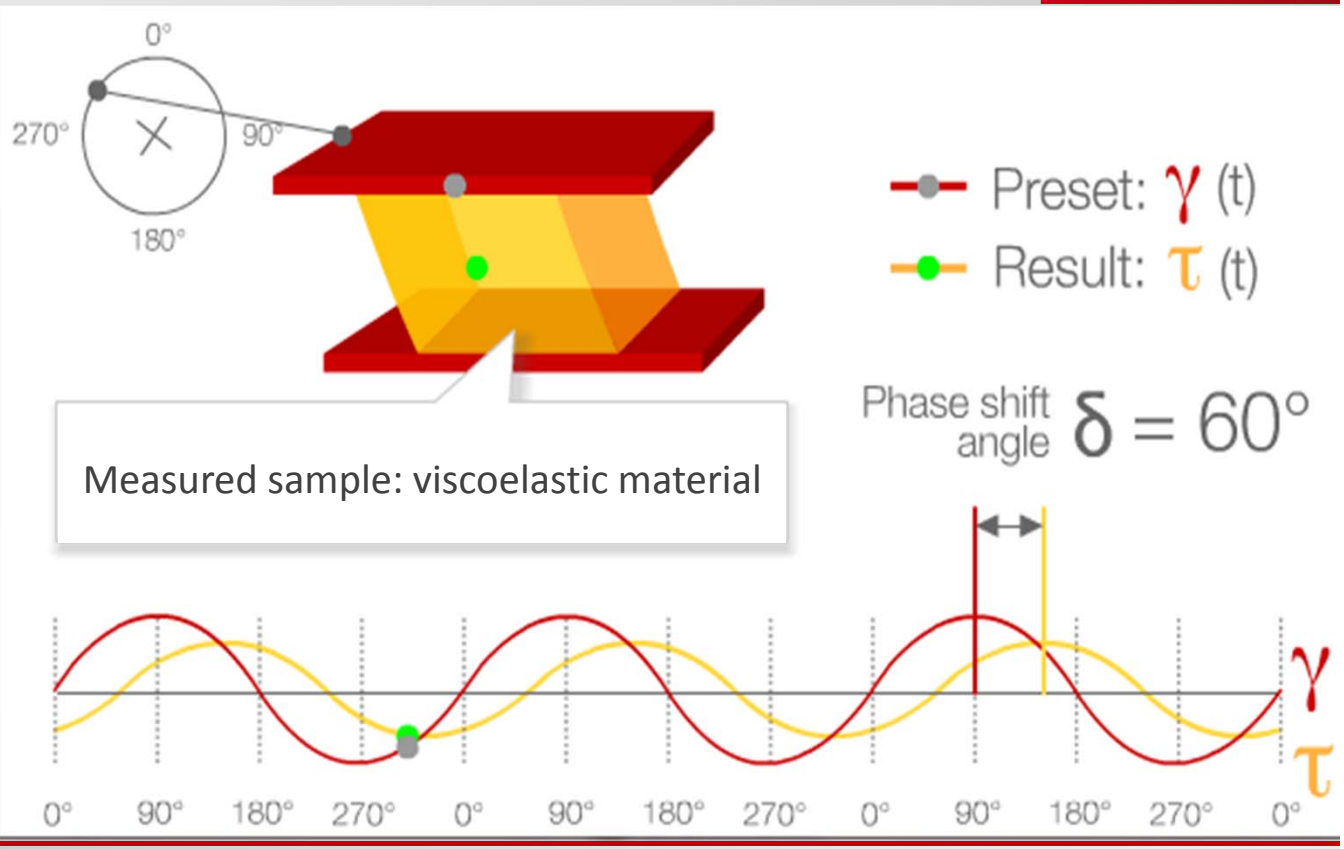
This example is for a controlled strain test, i.e. input is strain, output is stress.

Viscoelasticity: The Phase Angle is the Key



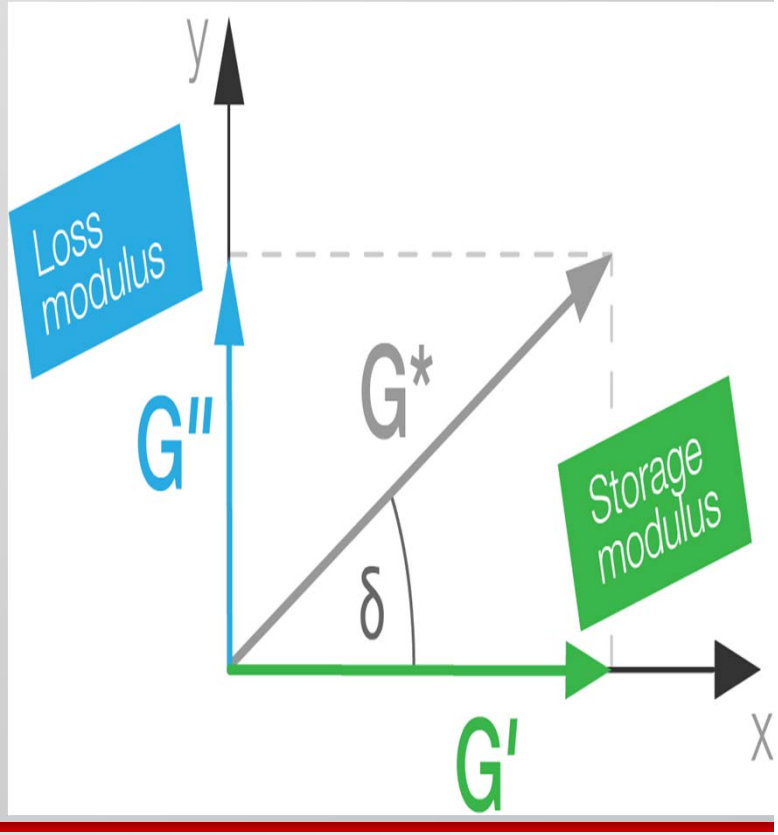






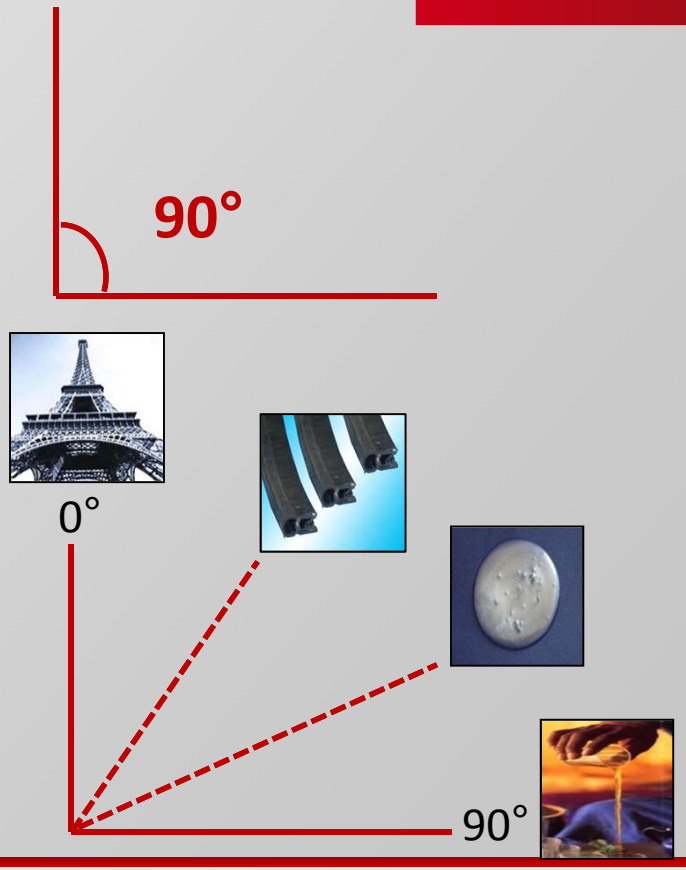
G*, G', G": What's Real, What's Not?

- G* is a complex number which can visualized using a complex plane or vector diagram.
- The phase angle allows separation of G* into a real part, G', and an imaginary part, G".
- A right triangle is always 90°.
- The real part, G' or G Prime, is the Storage Modulus = elastic modulus = tendency to recoil or retain shape. Its magnitude stems from the phase angle δ.
- The imaginary part, G" or G Double Prime, is the Loss Modulus = viscous modulus = tendency to flow. Its magnitude is what remains or 90° less the phase angle δ.
- G* (complex modulus) ÷ angulary frequency (rad/s) = complex viscosity η^*.

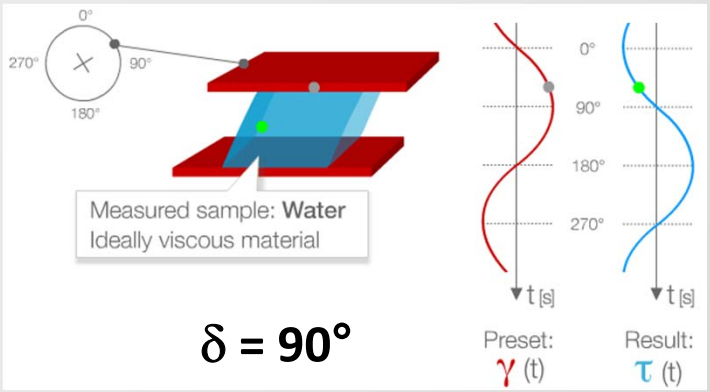


Getting to Know the Phase Angle

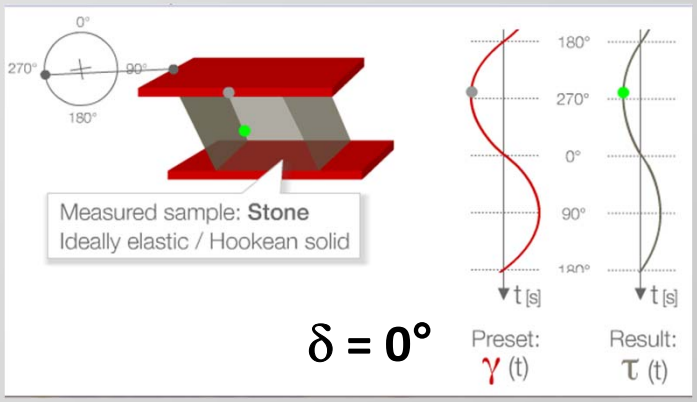
- Remember, a right angle has 90°
- So the phase angle, δ (delta) must lie between 0° and 90°
- δ = 0° → purely elastic (solid) behavior
- δ = 90° → purely viscous (liquid) behavior
- Viscoelastic materials have phase angles larger than 0° but smaller than 90°
- The tangent of the phase angle (tan δ) is the ratio G ″ / G’, describes the viscoelastic balance of the material, and is called the Damping Factor.



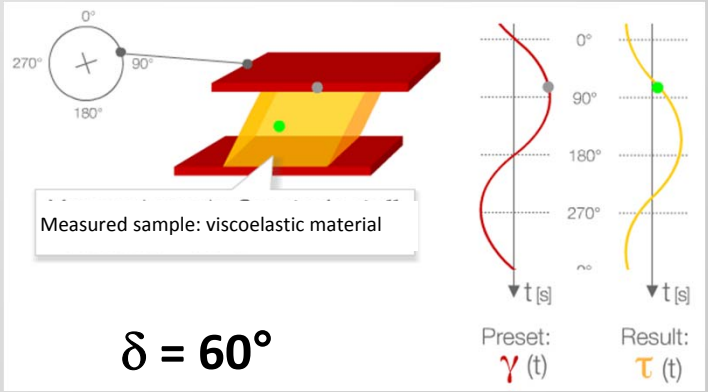
The Phase Angle in Action - Seeing is Believing



δ = 90°



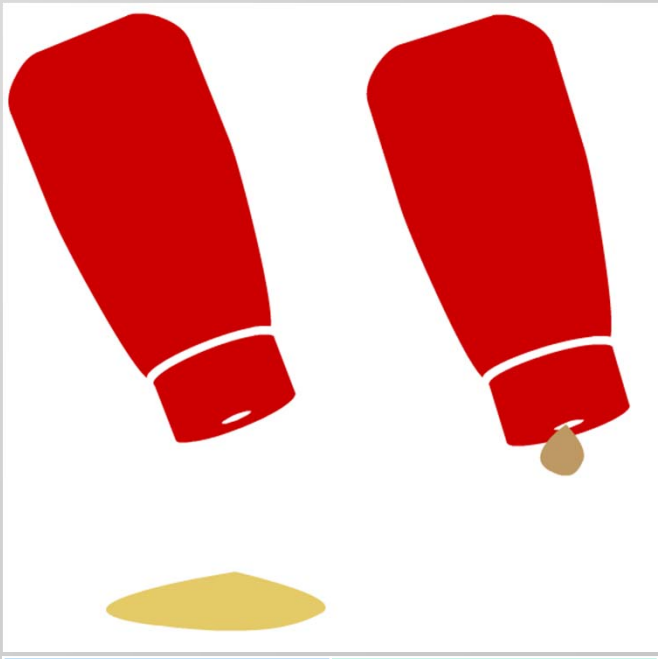
δ = 0°



δ = 60°

Getting a Feel for Viscoelastic Materials

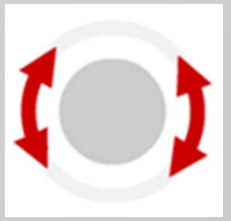
G" >> G'	G" > G'	G" = G'	G' > G"	G' >> G"
Liquid-like Structure		Gel Point	Gel-like Structure	
tanδ >> 1 → ∞	tanδ > 1	tan δ = 1	tanδ < 1	tanδ << 1 → 0

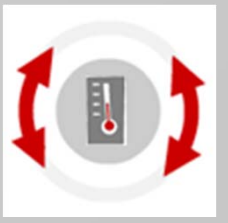


G" > G'	G' > G"
Viscoelastic Liquid	Viscoelastic Solid

Oscillatory (Dynamic)Test Methods

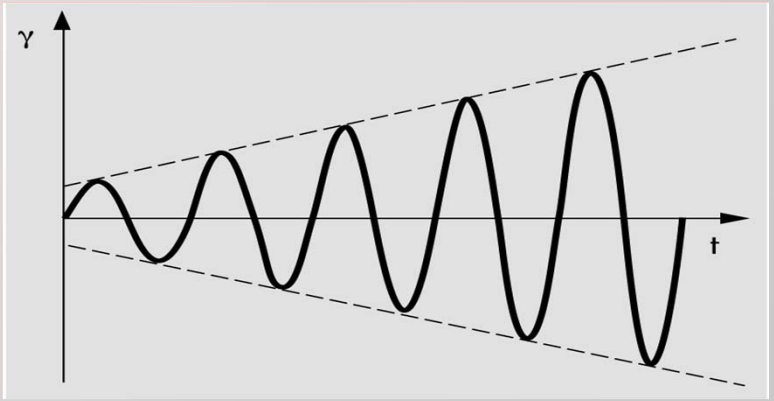
- **Amplitude sweep** – amplitude is ramped while frequency and temperature are held constant.
- **Frequency sweep** – frequency is ramped while amplitude and temperature are held constant.
- **Thixotropy** – frequency is held constant while amplitude is stepped from low to high to low to monitor structure before, during, and after destructive shear.
- **Time test** – amplitude, frequency and temperature are held constant and properties monitored over time.
- **Temperature test** – amplitude and frequency are held constant while temperature is ramped (also called DMTA, Dynamic Mechanical Thermal Analysis).

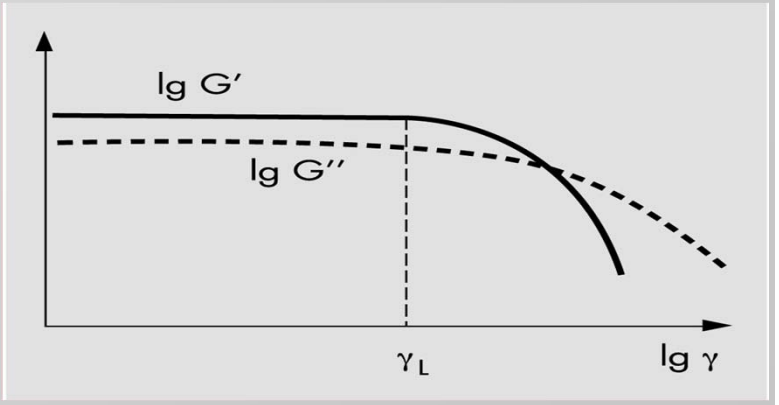




Amplitude Sweep

- The sample is subjected to small angles of increasing deformation in a sinusoidal manner, i.e. small wiggles to large wiggles.
- Determines what deformation eventually damages structure (Linear Viscoelastic Limit).
- Results are typically presented as G’ (elastic component) and G” (viscous component) versus deformation (strain).
- This test determines the:
  - Linear viscoelastic region
  - Structural strength
  - Rigidity (stiffness)
  - Structural stability
  - Dynamic yield point and flow point (for viscoelastic solids)

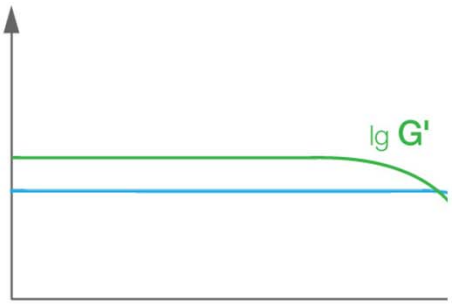




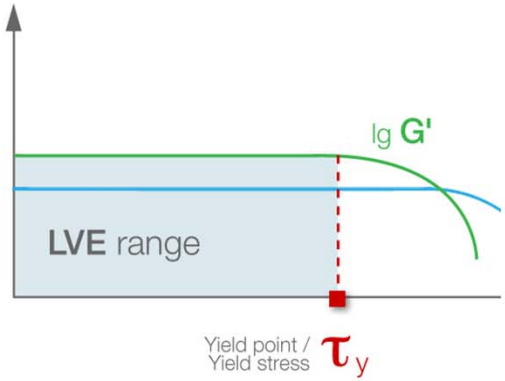
Yield Stress and Flow Stress from the Amplitude Sweep

Anton Paar

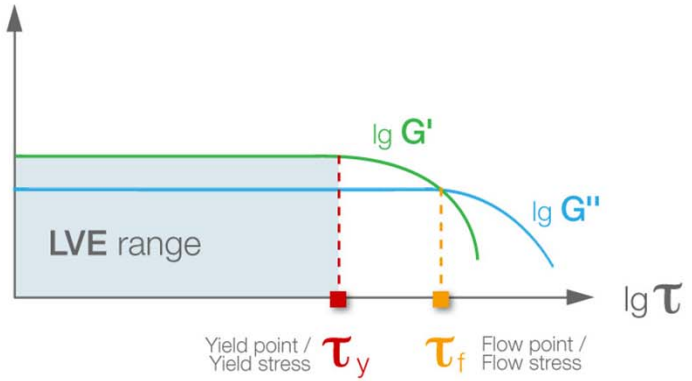
Yield Point / Flow Point



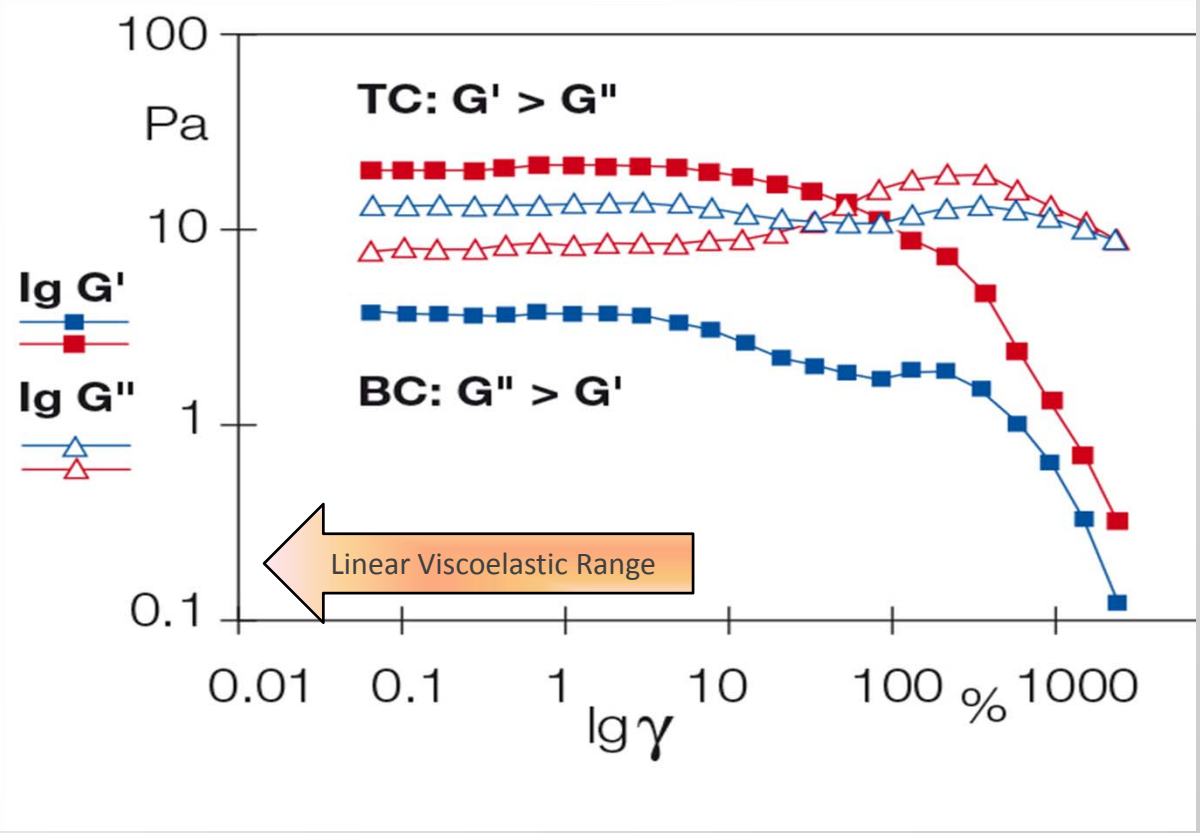
Yield Point / Flow Point



Yield Point / Flow Point



Case Study – Amplitude Sweep of Two Coatings



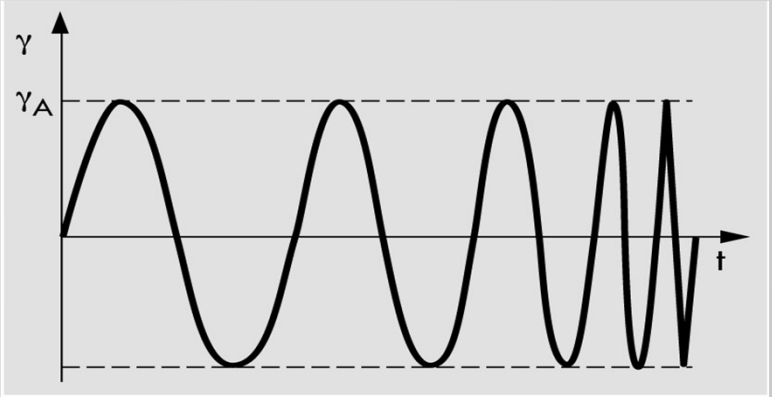
TC Top Coat

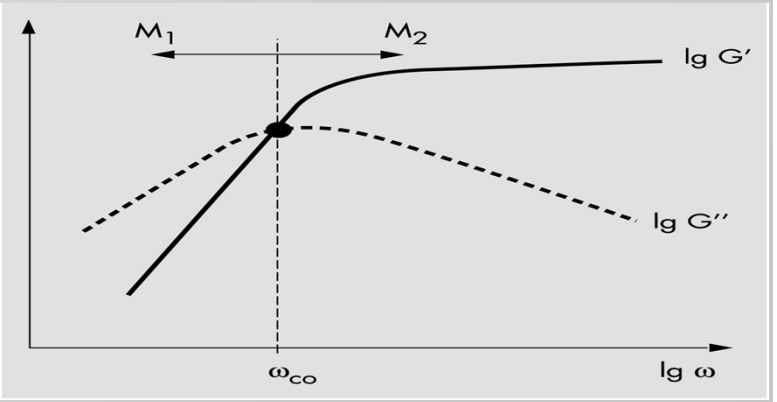
BC Base Coat

- TC is stiffer.
- Similar LVER.
- In LVER, TC is dominated by its elasticity so will have better stability, better sag resistance, greater coating thickness, slower leveling.
- In LVER, BC is thinner and dominated by viscous flow so will be prone to sedimentation but will mix and level more easily into a thin layer thickness.

Frequency Sweep

- Frequency of oscillation is ramped with the amplitude held constant
- Short term relaxation (high frequency) and long term relaxation (low frequency) behavior
- Quantifies zero shear viscosity for viscoelastic liquids
- Shape of G’ and G” curves over frequency characteristic for material type, i.e. gel, emulsion, melt, paste, dispersion
- Provides information in MW, MWD, degree of crosslinking, stability, impact resistance, etc….



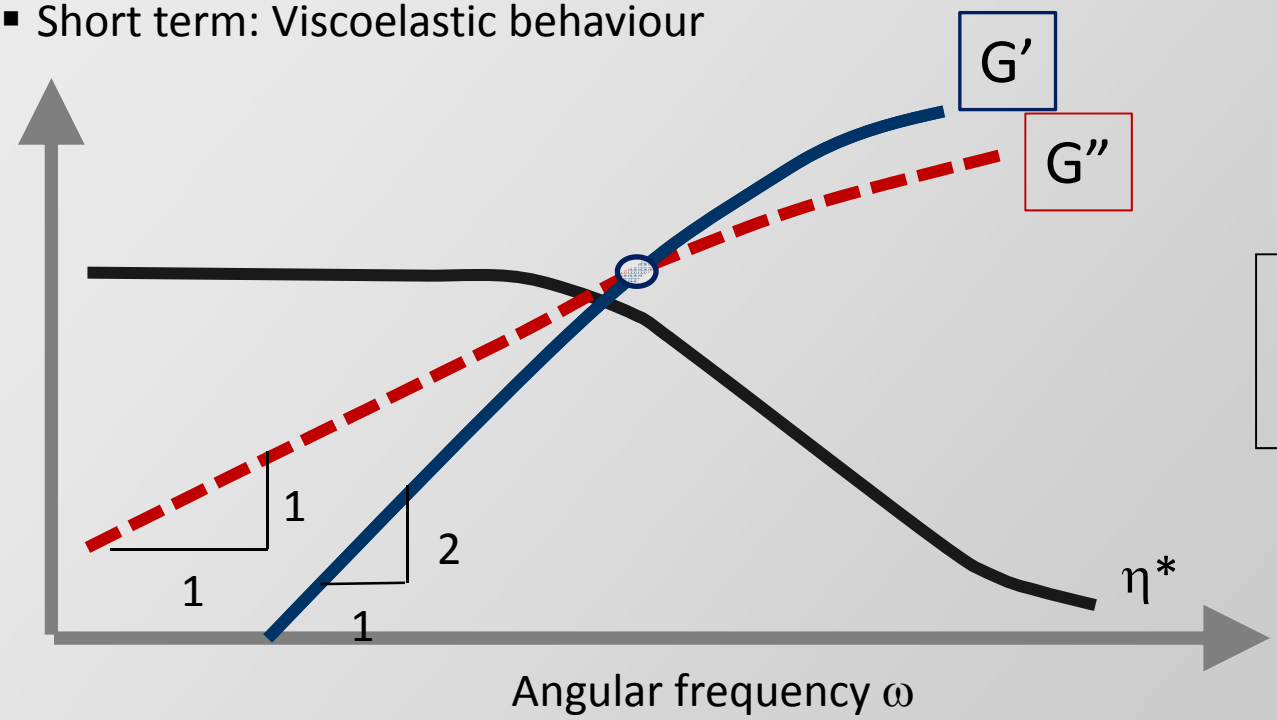


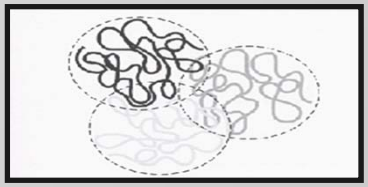
Frequency Sweep – Viscoelastic Liquid

Anton Paar

Viscoelastic Liquid (no gel, no crosslinks, no filler)

- Long term: Newtonian behaviour
- Short term: Viscoelastic behaviour



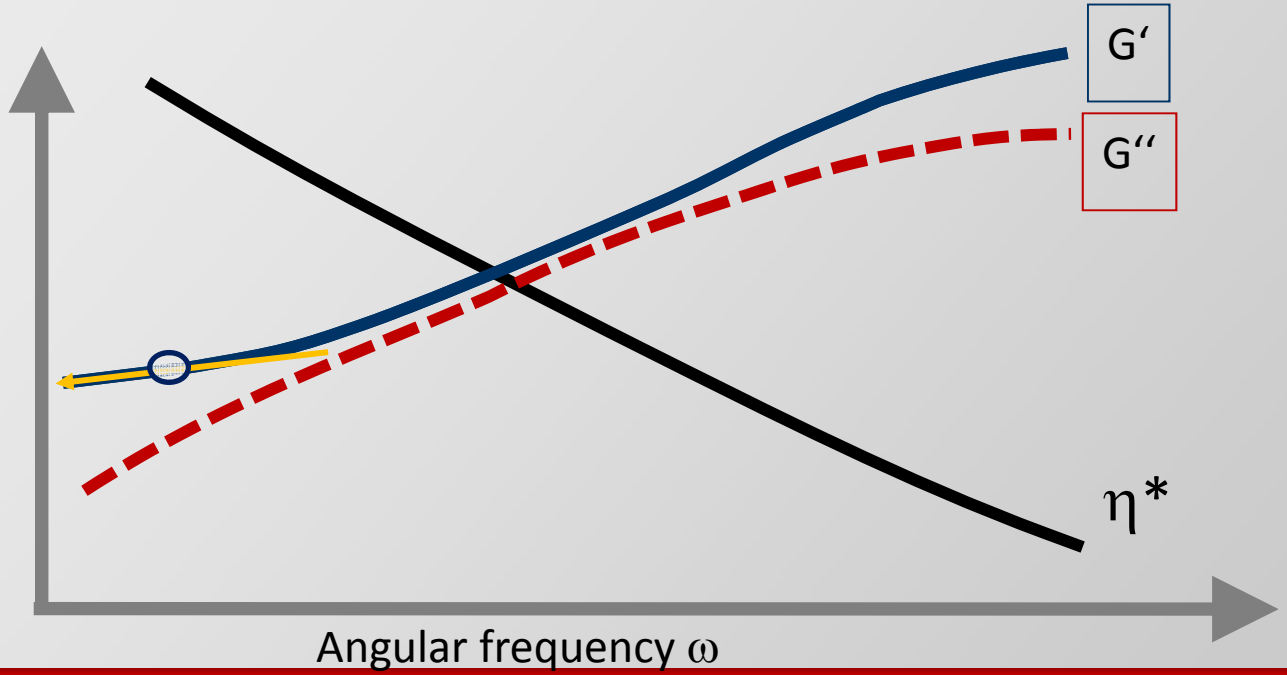


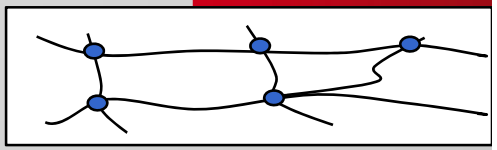
- No network structure
- No links between macro-molecules

Frequency Sweep – Partially Crosslinked Material

Viscoelastic Material Partially Crosslinked

- No long term relaxation
- Gel stability due to 3D-network structure



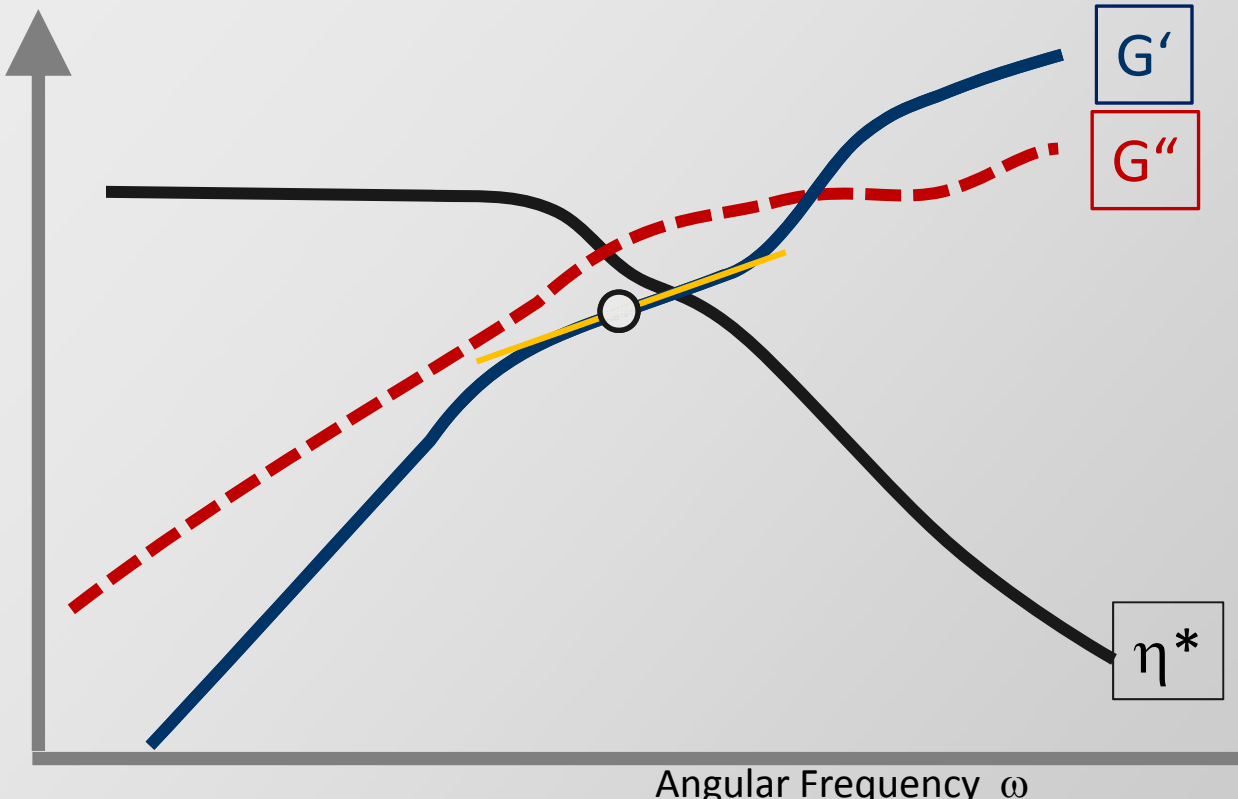


Slope:
- Strength of structure at rest

Absolute value:
- Stiffness of gel

Damping G“/G‘
- Damping behaviour

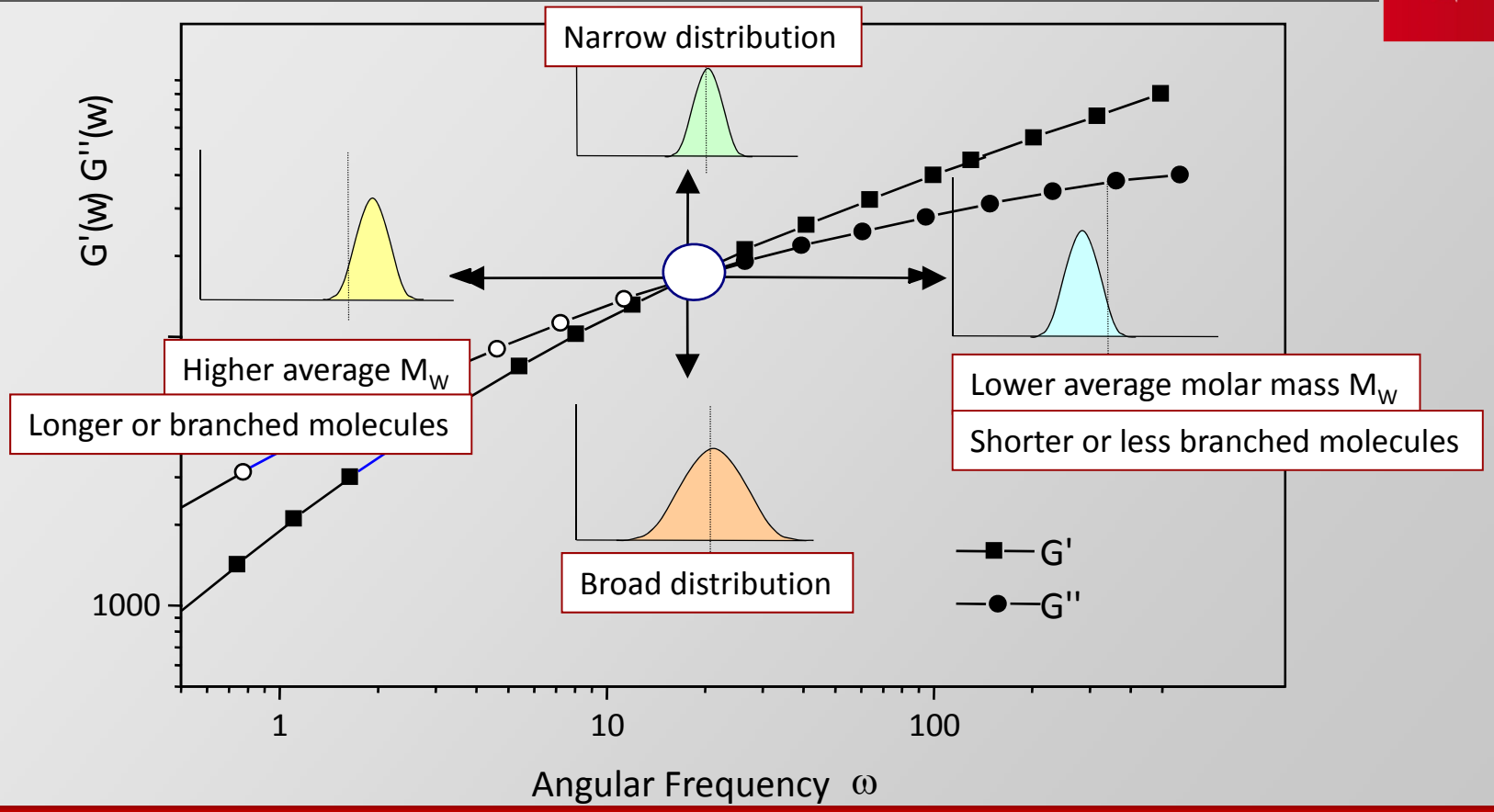
Frequency Sweep – Polymer Blend (Bimodal Distribution)



- Polymer having a short chain dominates at high frequencies
- Long chain polymer behavior dominates at low frequencies

Shoulder:
- Above short chain polymer dominates
- Below long chain polymer dominates

Frequency Sweep - Molar Mass M_w



Anton Paar

Time Temperature Superposition

Background:

- Due to increasing T the relaxation times are getting shorter
- Shift factor $a_T=\lambda(T)/\lambda(T_{ref})$ or based on viscosity $a_T=\eta(T)/\eta(T_{ref})$
- Frequency sweeps (FS) measured at various T can be shifted horizontally
- Only applicable for unlinked and unfilled polymers
- Each FS measured at T can be shifted by a_T to the so called reference temperature T_0

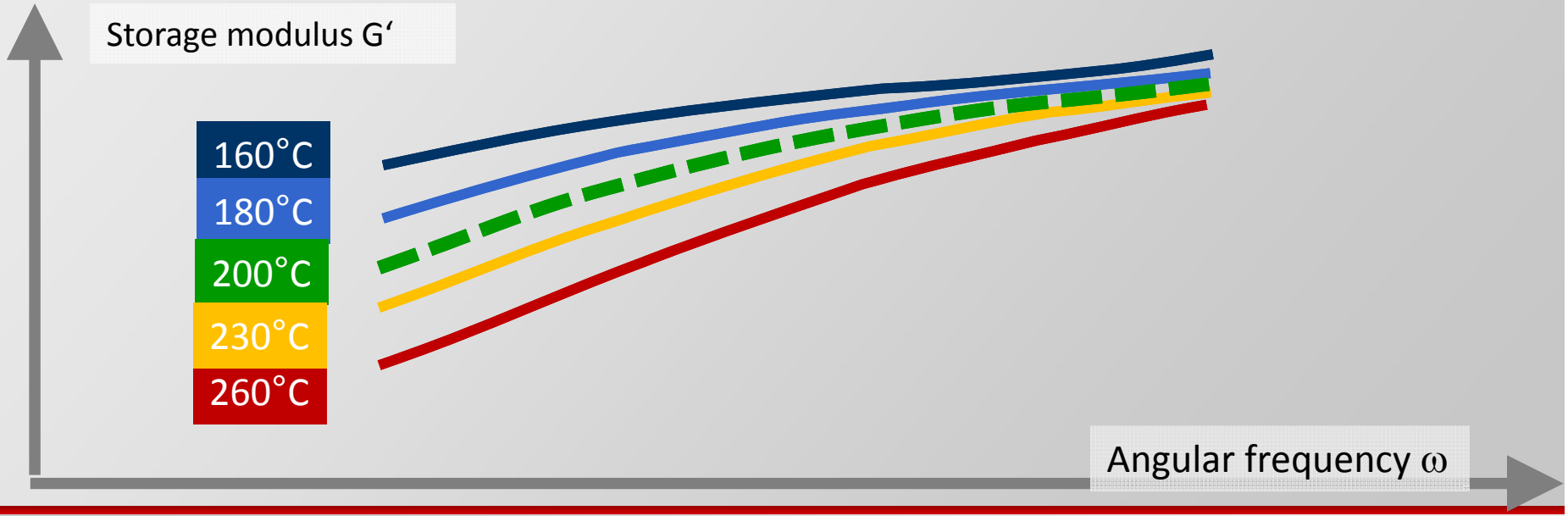
(+) Enlarged frequency range
(+) Information about practically relevant shear rates up to 100,000s^{-1}
(+) Determination of the zero shear viscosity

Frequency Sweep – Master Curve

Anton Paar

Horizontal shift towards the reference temperature T0

- TTS example: horizontal shift of storage modulus G‘

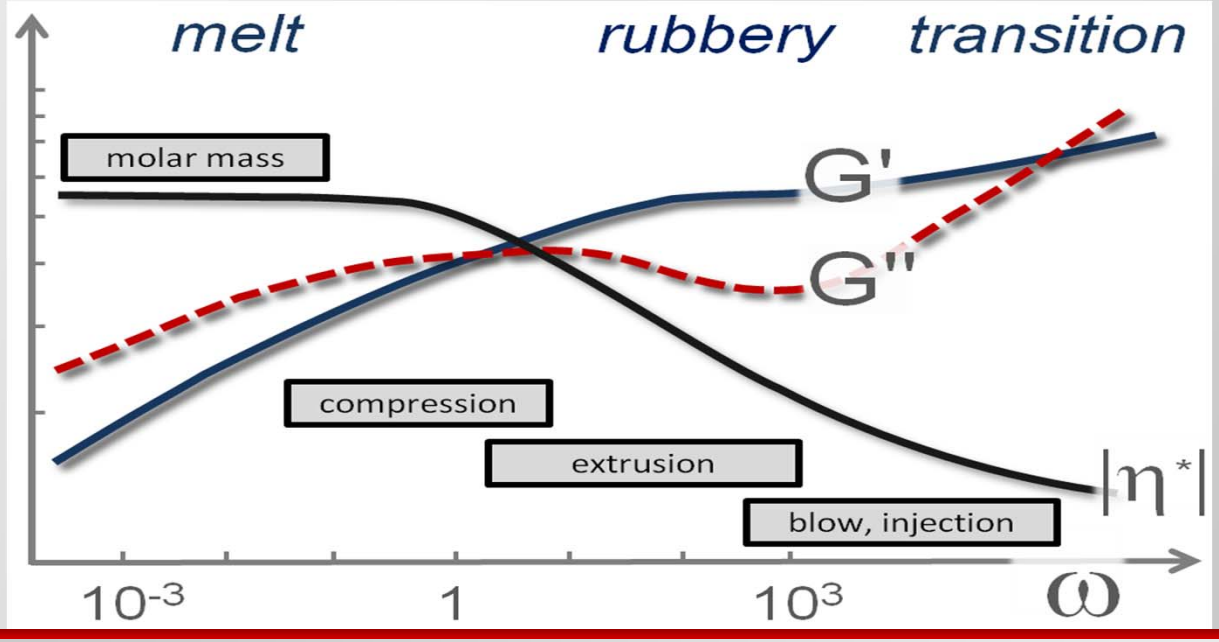


Frequency Sweep – Master Curve

Anton Paar

Horizontal shift towards the reference temperature T0

- TTS example: shift of storage modulus G‘
- The range above the transition region is called glassy region

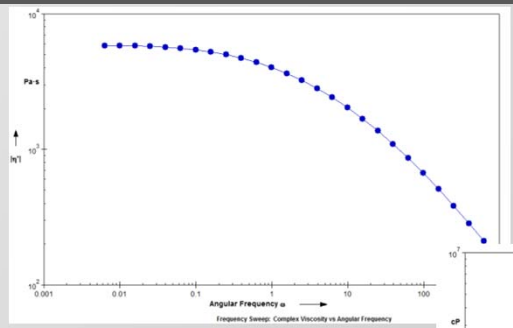


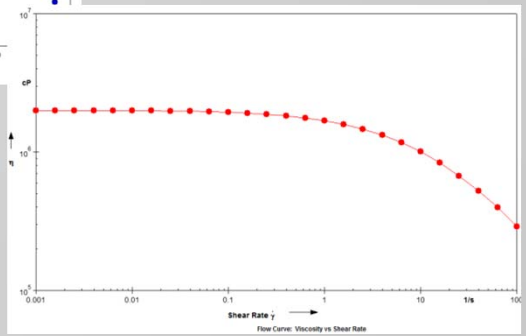
The Cox-Merz Rule

- Empirical rule that establishes a connection between complex viscosity, η*, as a function of frequency sweep in the LVER with the steady shear viscosity as a function of shear rate.

$$|\eta^*(\omega)| \cong \eta(\dot{\gamma})|_{\dot{\gamma}=\omega}$$

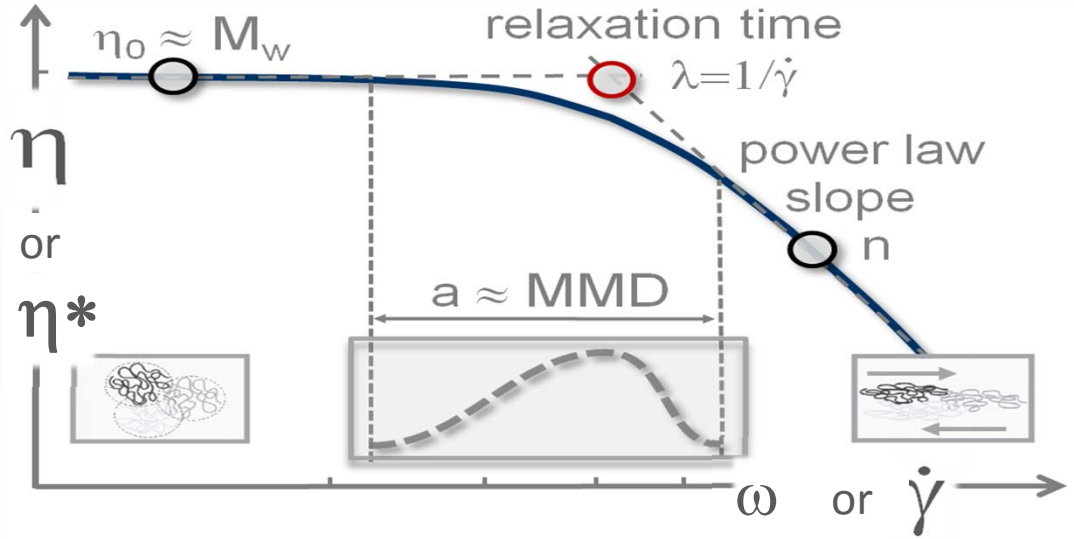
- Cox-Merz does not work well for all samples and conformance must be confirmed.
- Concentrated polymer solutions and melts exhibit edge fracture during steady shear measurements at rates as low as 10 1/s yet their viscosity at higher shear rates is often needed for process control and design.
- Cox-Merz permits complex viscosity obtained at high frequencies to be used in lieu of steady shear viscosity at moderate shear rate.





Linear viscoelasticity		Steady shear
$\eta^*(\omega)$	↔	$\eta(\dot{\gamma})$
$\eta^*(G^*)$	↔	$\eta(\tau)$
$G^*(\omega)$	↔	$\tau\ (\dot{\gamma})$

Viscosity Curve – Carreau-Yasuda Regression



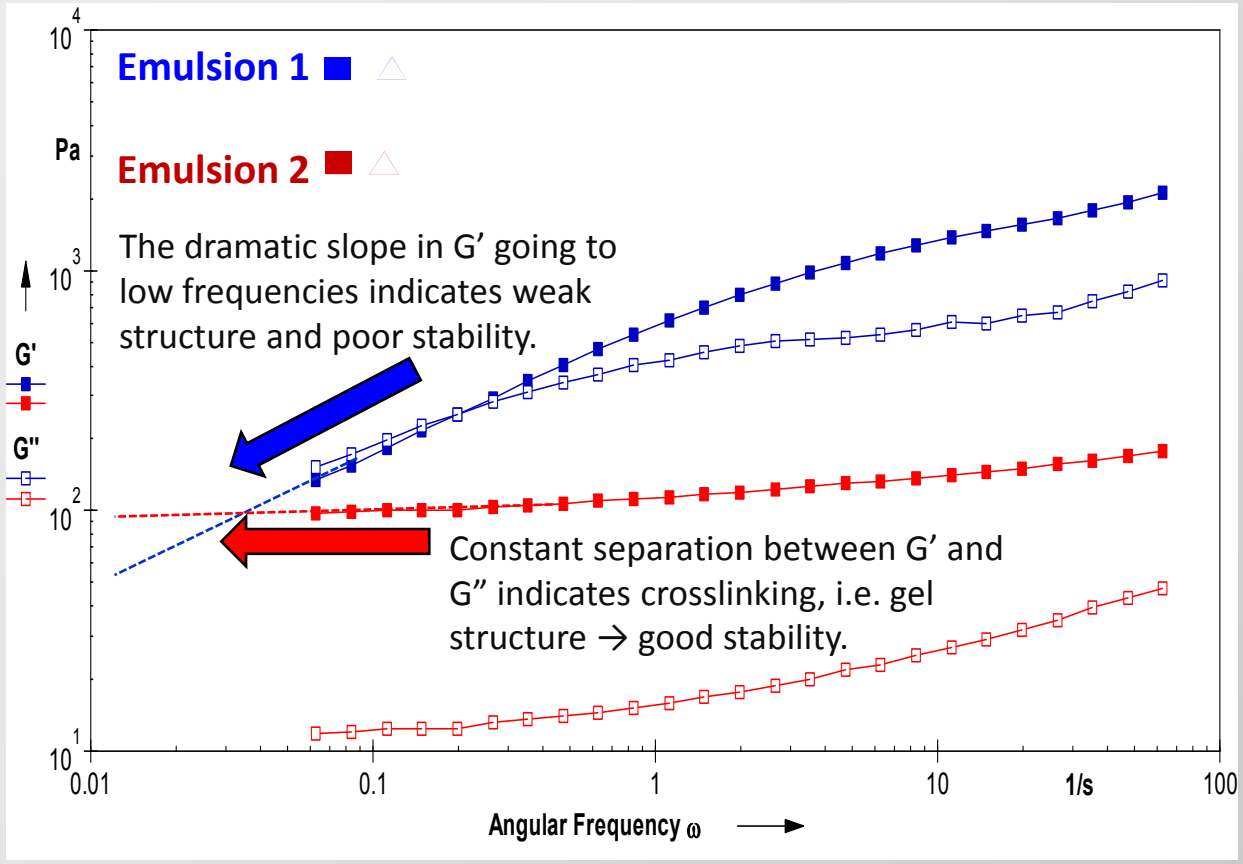
De Deborah Number

$$De = \frac{\text{Relaxation Time}}{\text{Processing Time}} = \lambda \cdot \dot{\gamma}$$

Rule of thumb for processing - make sure that De value is as low as possible, i.e. processing time is long relative to relaxation time.

η_0	*Zero shear viscosity = proportional to molar mass*
n	*Power law exponent = qualitative measure for the ability of the macromolecules to orient in shear direction and to reduce flow resistance*
a	Width of transition range = proportional to MMD and PDI -> narrow MMD=steep, broad MMD=flat)
λ	Relaxation time = time dependent recovery of internal stresses

Frequency Sweep - Emulsion Stability, Pourability, Mixability



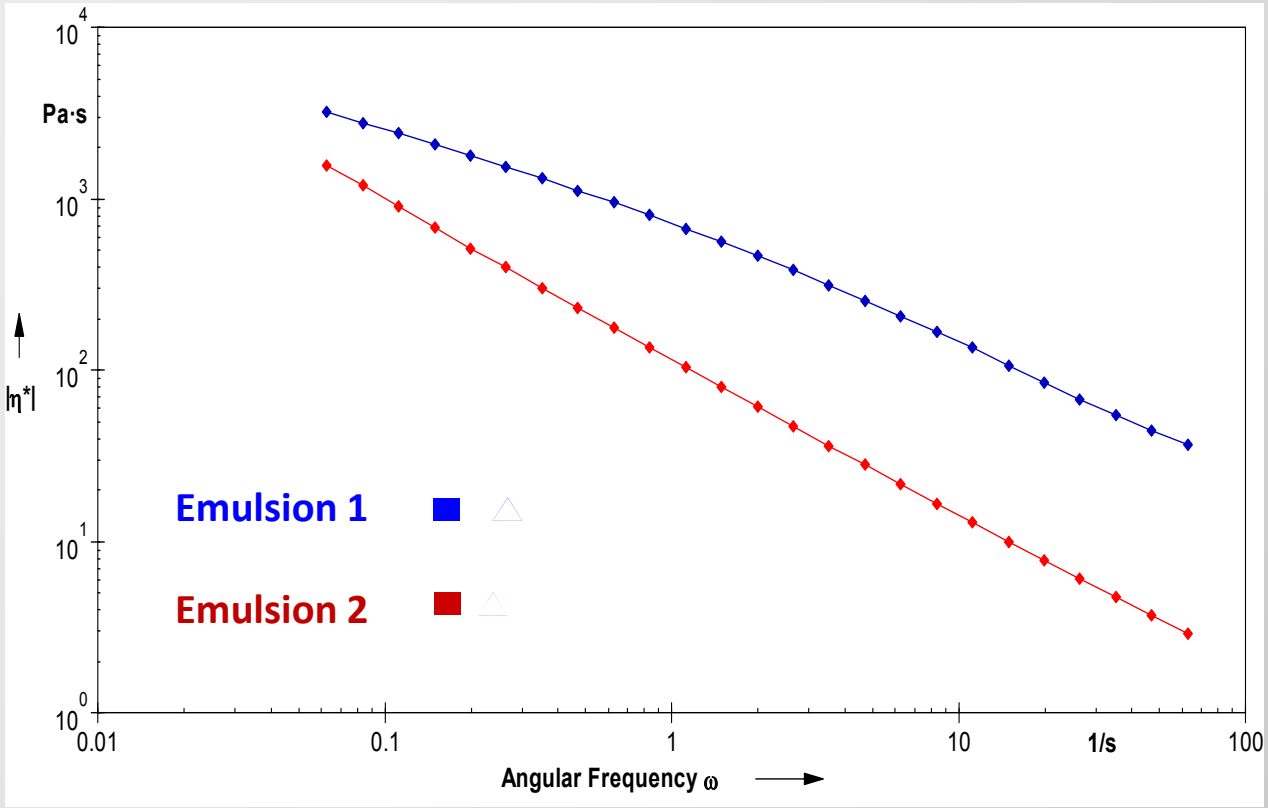
Low Frequency:

- Emulsion 1 has weaker gel structure G"\>G'. Emulsion 2 has a strong gel structure G'\>\>\>G".
- Emulsion 1 will pour easier. Emulsion 2 will have better storage stability.

High Frequency:

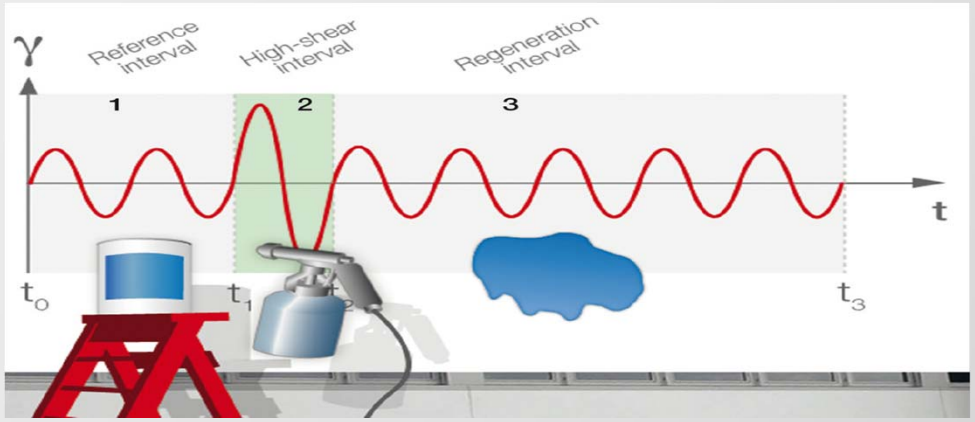
- Emulsion 2 is less elastic and will mix more easily

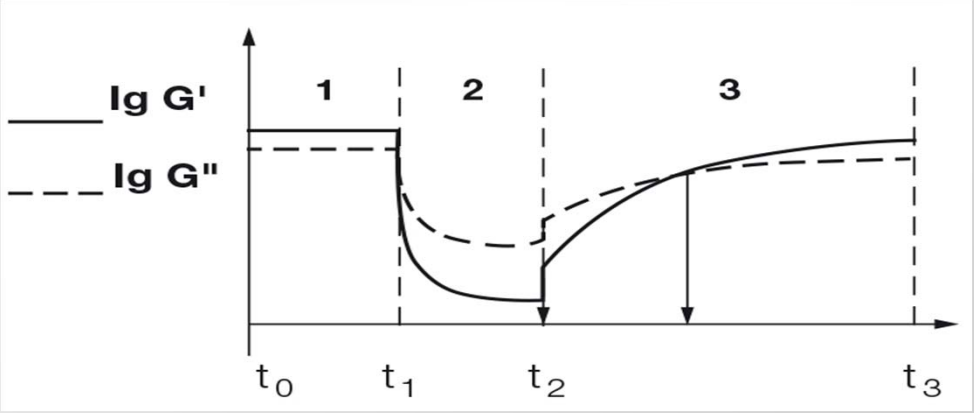
Frequency Sweep - Emulsion (Data Plotted as Complex Viscosity)



- If only viscosity is assessed, one would think that these two samples are very similar.
- Both shear thin readily with Emulsion 1 being thicker than Emulsion 2.
- Whereas the storage and loss modulus really shows they are two very different products and Emulsion 2 will be stable during storage whereas Emulsion 1 will not despite being thicker.

Oscillatory Three Interval Thixotropy Test





Structure Recovery, Step Test (3ITT),

Preset

1. Low shear conditions
2. High shear conditions
3. Low shear conditions

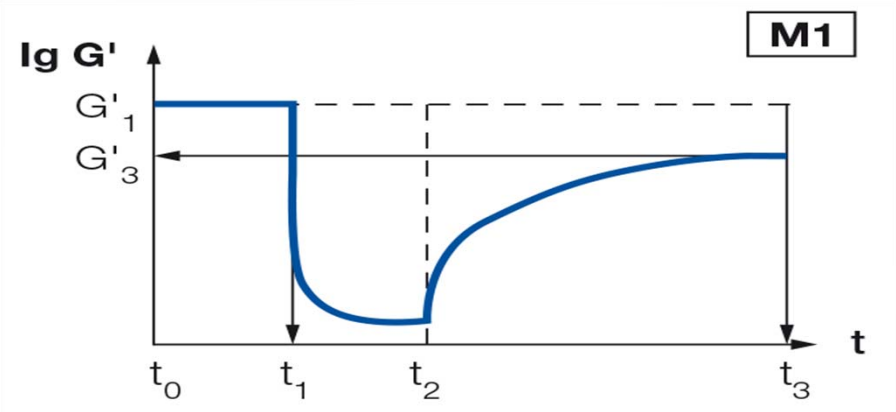
Test Result

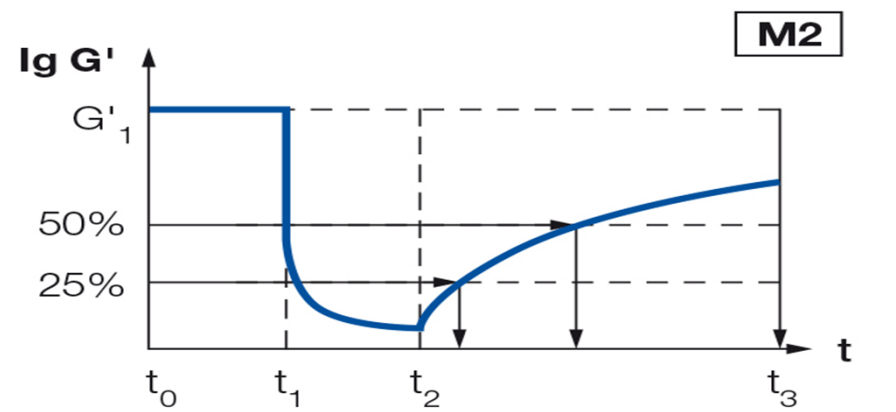
1. At rest
2. Structural decomposition
3. Structural regeneration

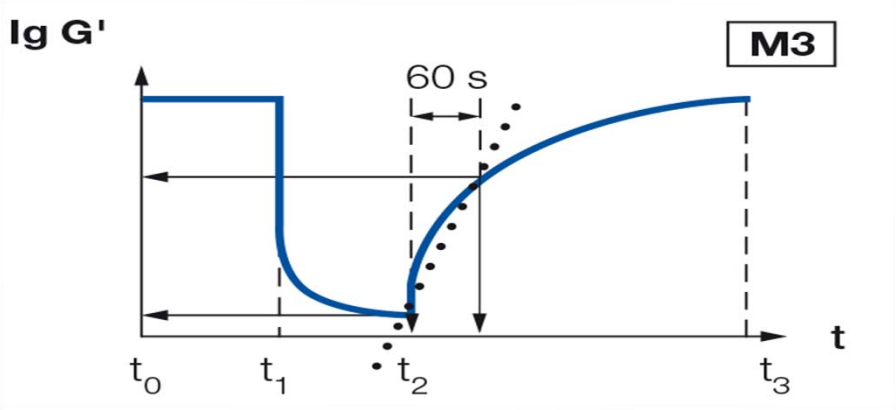
In the 2nd interval: G'' > G‘ (liquid)

In the 1st & 3rd interval: G' > G“, (solid)

Structural Recovery Behavior (Oscillation)



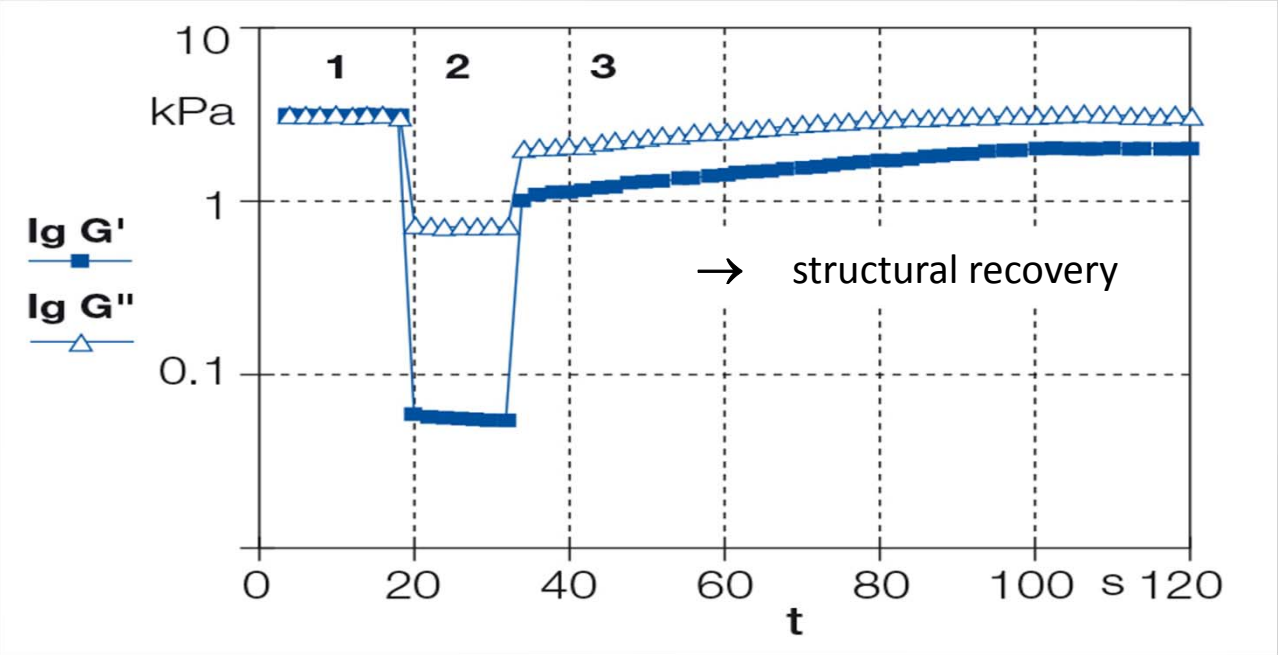




Analysis methods for step tests to evaluate thixotropic behavior relative to **G'** of 1st int.

- **M1 Total Structural Recovery in Percent**
- **M2 Time to 25% and 50% Recovery**
- **M3 Curve Slope during Recovery**
  e.g. in t = 60s; as ($\Delta G'/\Delta t$) in Pa/s

Three Interval Thixotropy with Oscillatory Settings

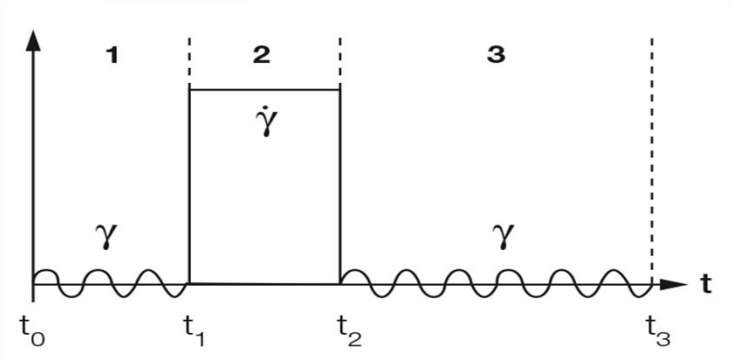


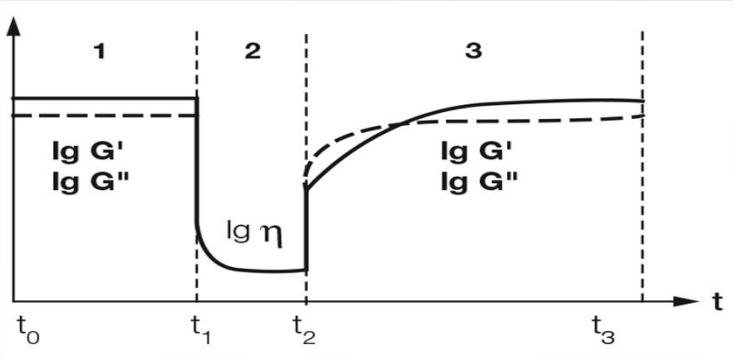
SMD Adhesive
for **s**urface **m**ounted **d**evices, electronics

Step Test:
3x Oscillation
$\gamma_1 = g_3 = 0.2\%$
$\gamma_2 = 100\%$
$\omega = 10$ rad/s
T = +23°C

Problem: dripping
because G'' > G'

Three Interval Thixotropy Test – Oscillation-Rotation-Oscillation





Structure Recovery, Step Test (3ITT)

With Rotational Decomposition Interval to Simulate a Process

Preset

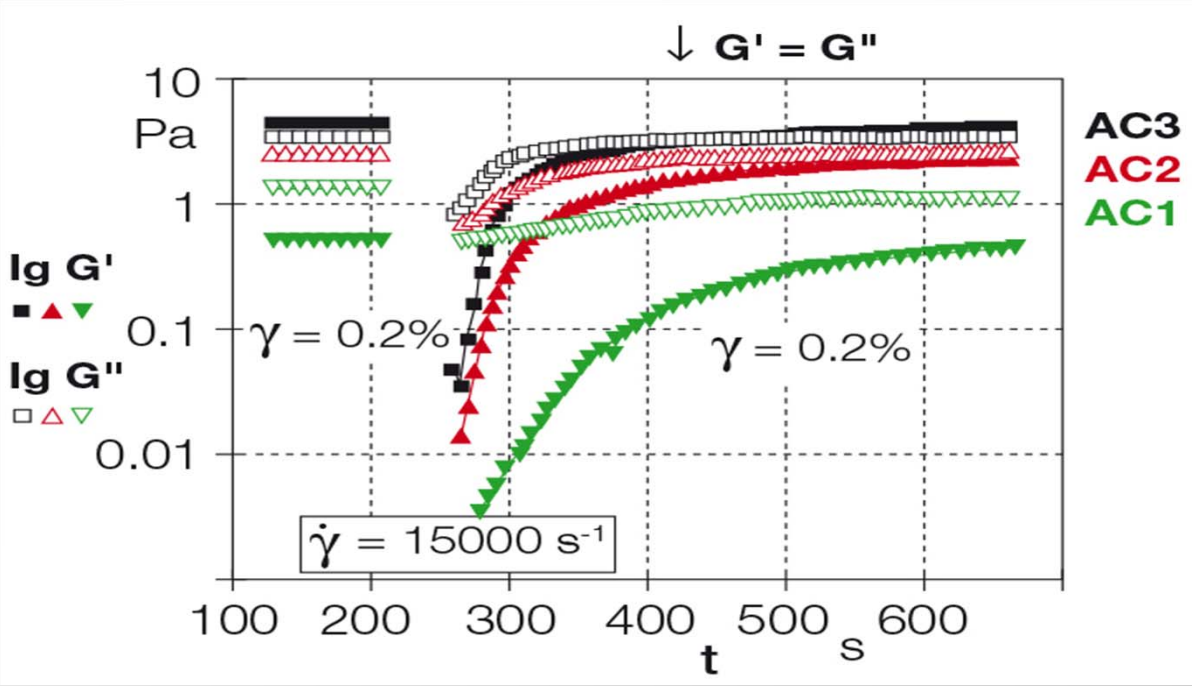
1. Low shear conditions (strain in the LVE range, oscillation)
2. High shear conditions (rotation, process simulation)
3. Low shear conditions (strain in the LVE-range, oscillation)

Test Result

1. At rest
2. Structure decomposition
3. Structure regeneration

Sample is solid-like at rest, becomes a flowable liquid under shear, and after some time recovers its solid-like nature during recover.

Automotive Spray Coatings – Three Interval Thixotropy Test



AC1: ▼ ▽
AC2: ▲ △
AC3: ■ □

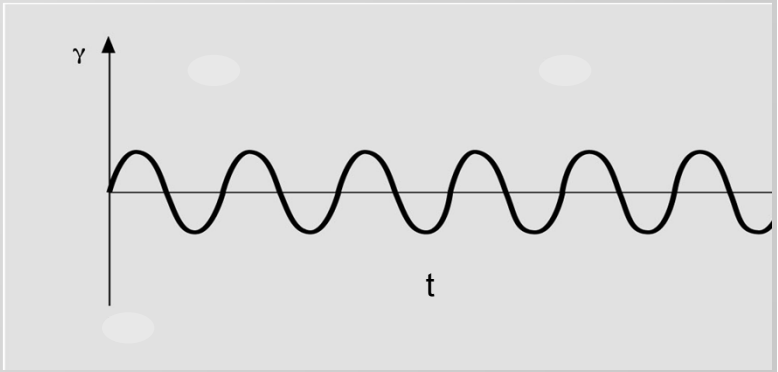
(a) As long as G" > G'
liquid state, flowing, leveling, sagging

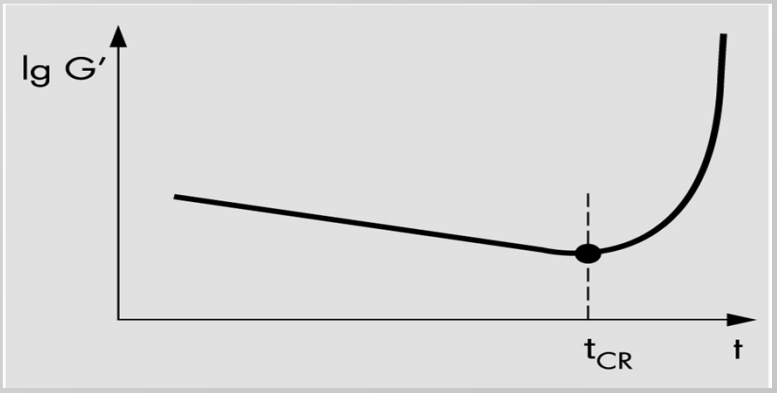
(b) When finally G' > G"
solid state, sagging is stopped

Time Point of Crossover
can be controlled using rheology additives for sag control.

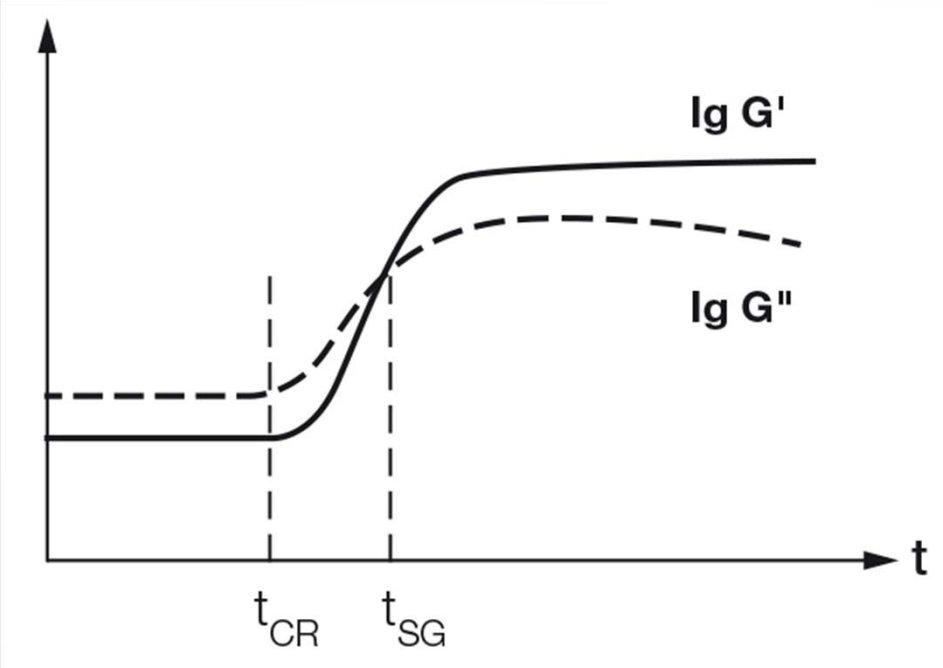
Oscillatory Time Sweep

- Amplitude, frequency, and temperature are held constant
- Amplitude selected to ensure to remain within linear viscoelastic region throughout the test (may require pre-testing on sample at different stages throughout the time)
- Changes in viscoelastic behavior over time are measured
- Properties studied include:
  - Gelation
  - Curing
  - Degradation
  - Freeze thaw stability



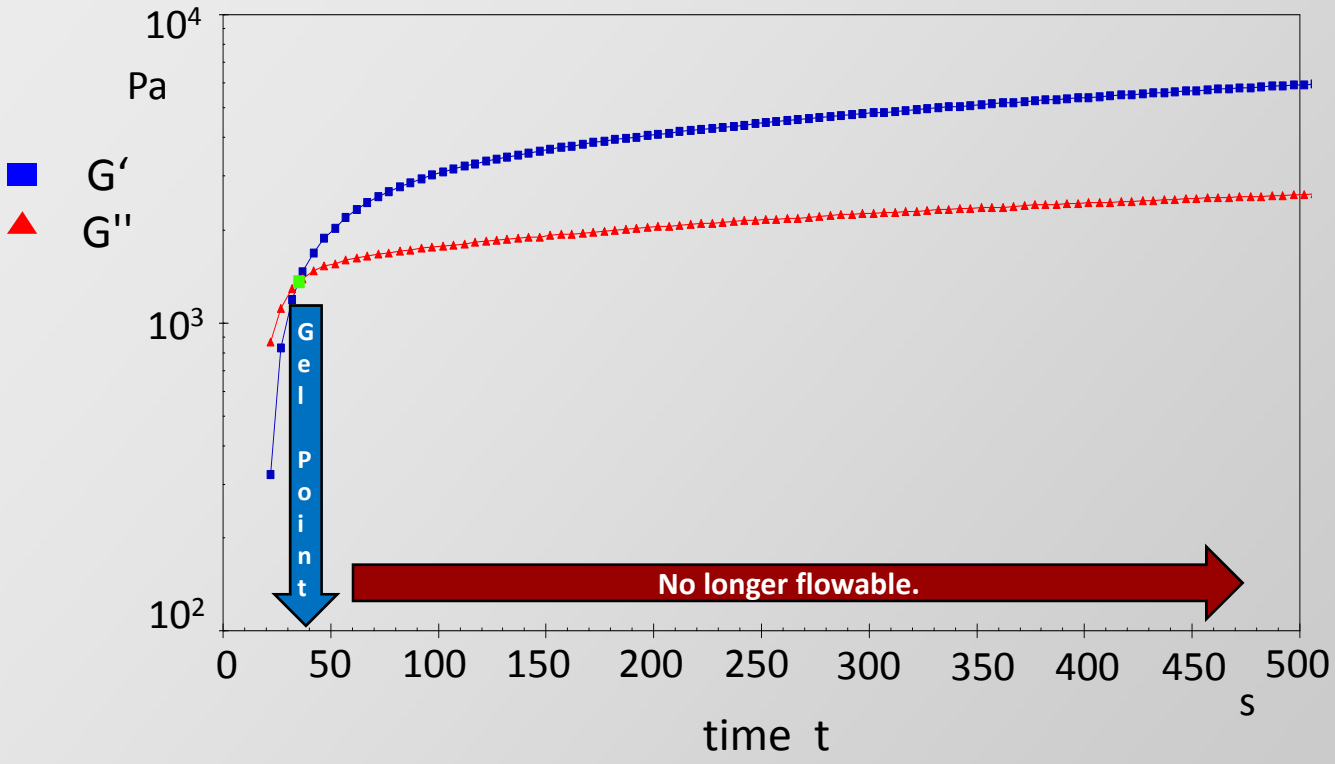


Example: Oscillatory Time Sweep - Gelation



- Sample initial is a liquid.
- At t_{CR} the gelation begins.
- At t_{SG} the sol-gel transition takes place, i.e. G'=G", and the sample is no longer flowable.
- Once G' plateaus, the gelation is complete and the sample is at maximum rigidity.

Two Component Adhesive

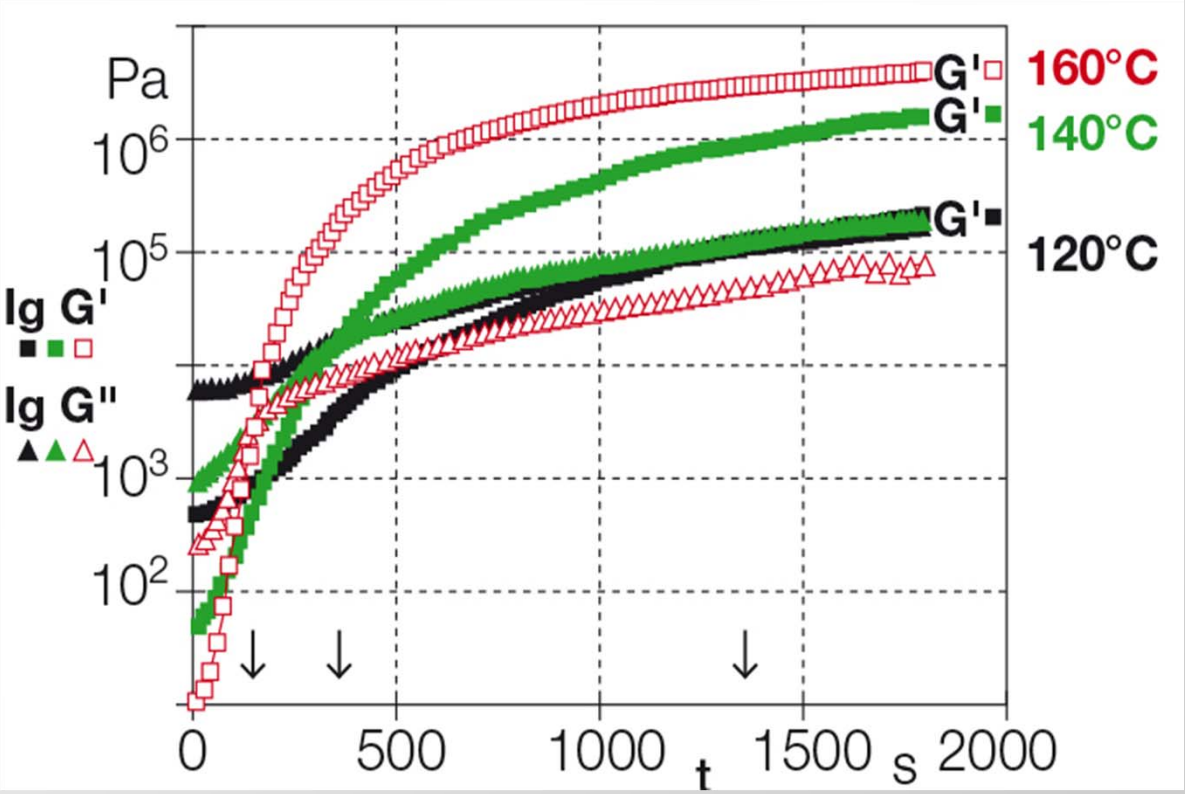


Curing Reaction
Isothermal

T = +23°C

Crossover G' = G''
t = 35s
G' = 1360Pa

Curing Study for a Powder Coating with an Epoxy Resin



Isothermal Curing

Time point t_{SG}
of sol / gel transition
at cross-over point G' = G''

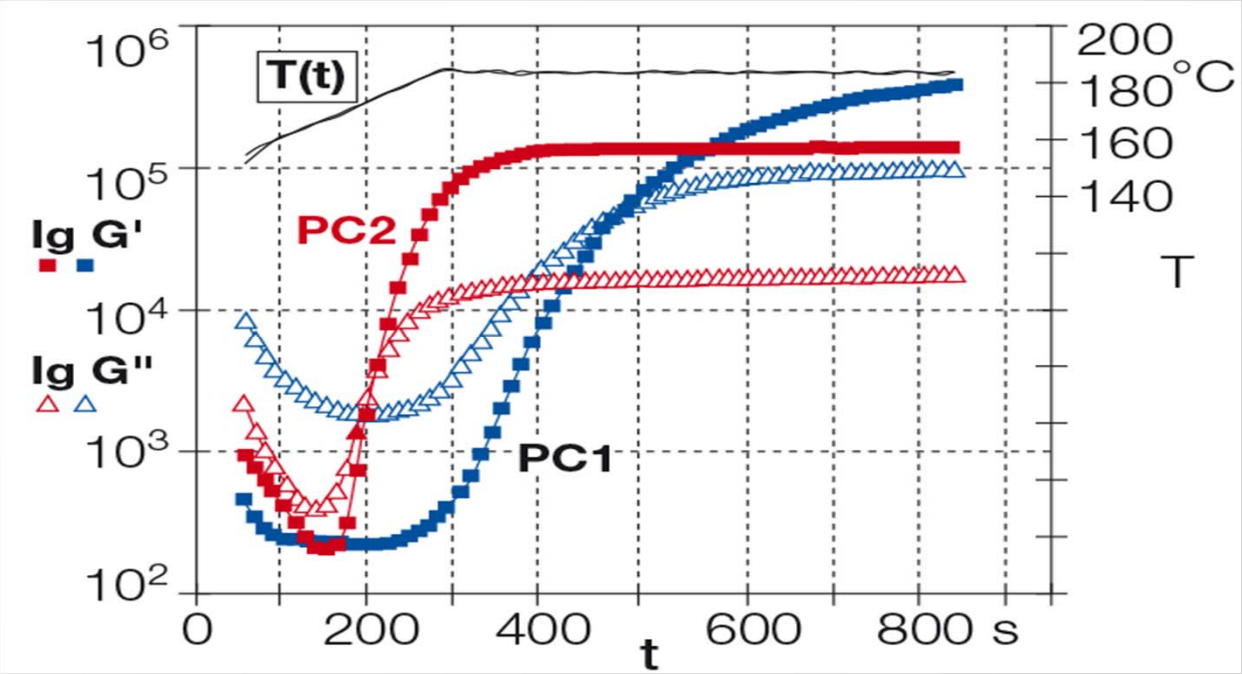
T = 120°C: t_{SG} = 1370s

T = 140°C: t_{SG} = 360s

T = 160°C: t_{SG} = 140s

Time Dependent Behavior (Oscillation)

Melting → Curing →



Powder Coatings

Isothermal Curing

PC1

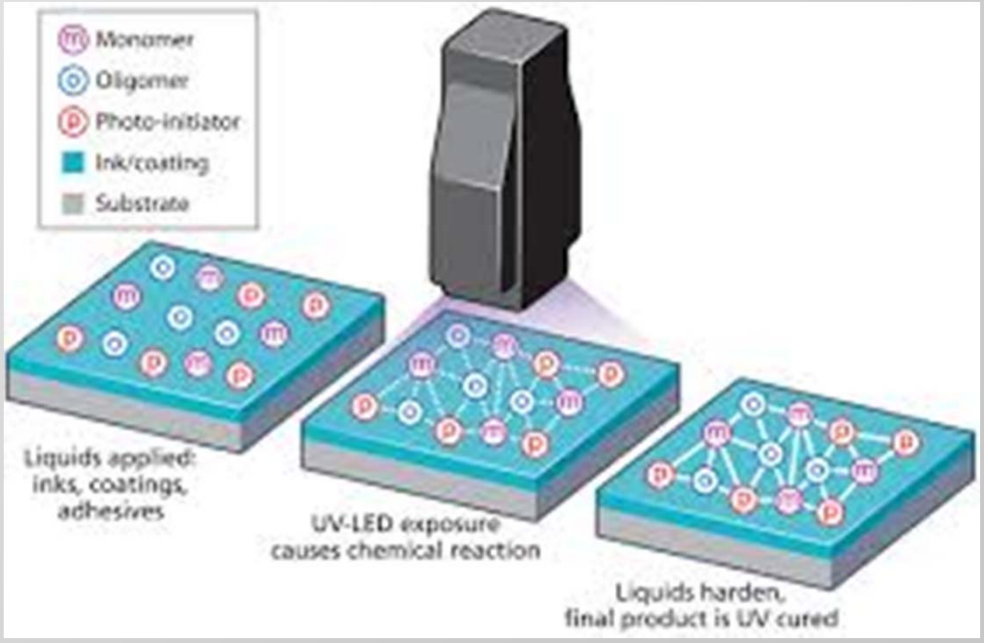
PC2

Analysis:

1) **minimum of G'**
2) **crossover G' = G''**
3) **end of curing**

UV Curing - Background

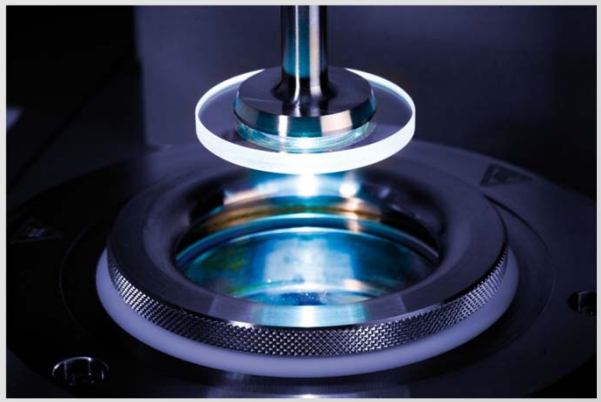
- High intensity ultraviolet light, instead of heat, used to instantly cure or “dry” inks, coatings or adhesives whose formulas incl. photo initiators
- Used in automotive, electronics, telecommunications,, graphic arts, converting, inks, contact lens, nail polish and other metal, glass and plastic decorating industries
- UV curing results in higher productivity in less time, with a reduction in waste, energy use and pollutant emissions



UV Curing – Peltier Based System

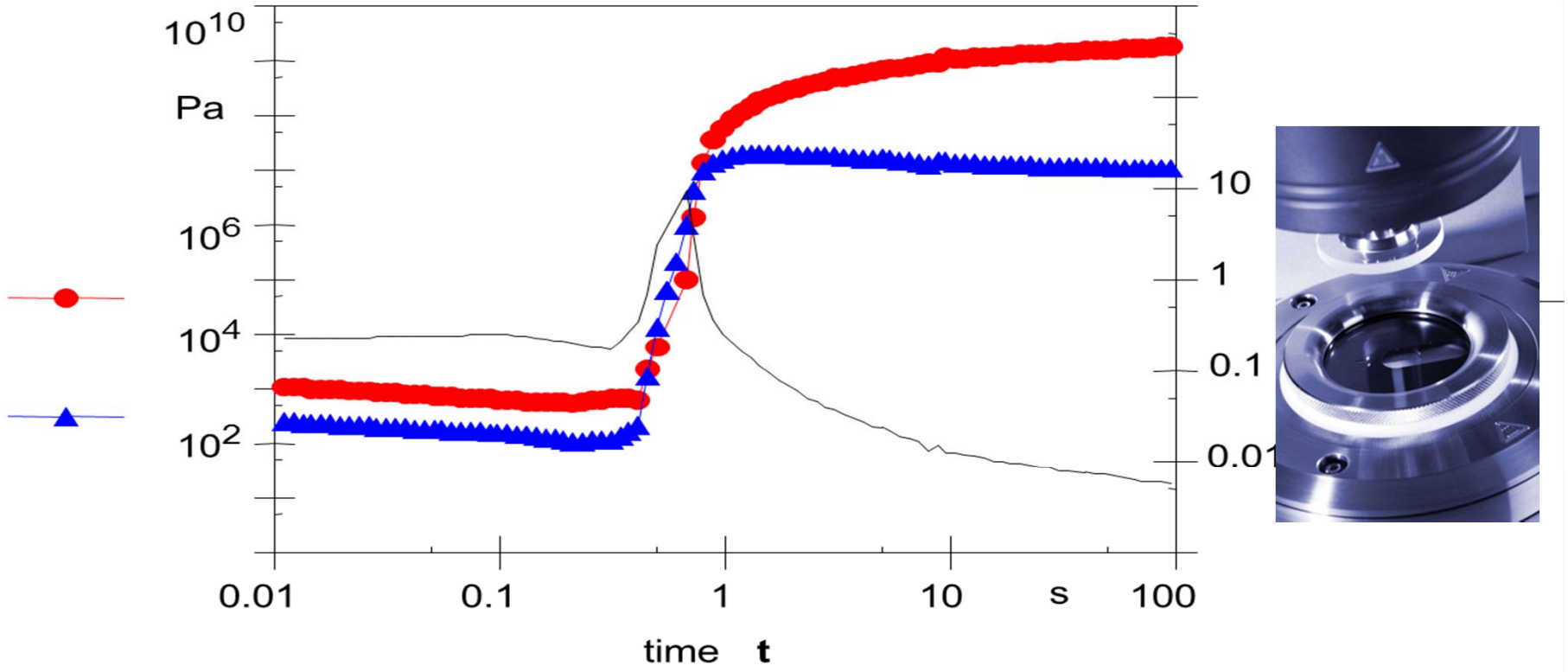
P-PTD200/GL Peltier System

- UV Light Guide
- Adjustable filters
- Can be used with H-PTD200 hood for best temperature control
- TruStrain™ for fast data acquisition
- Nf gap control due to sample shrinkage



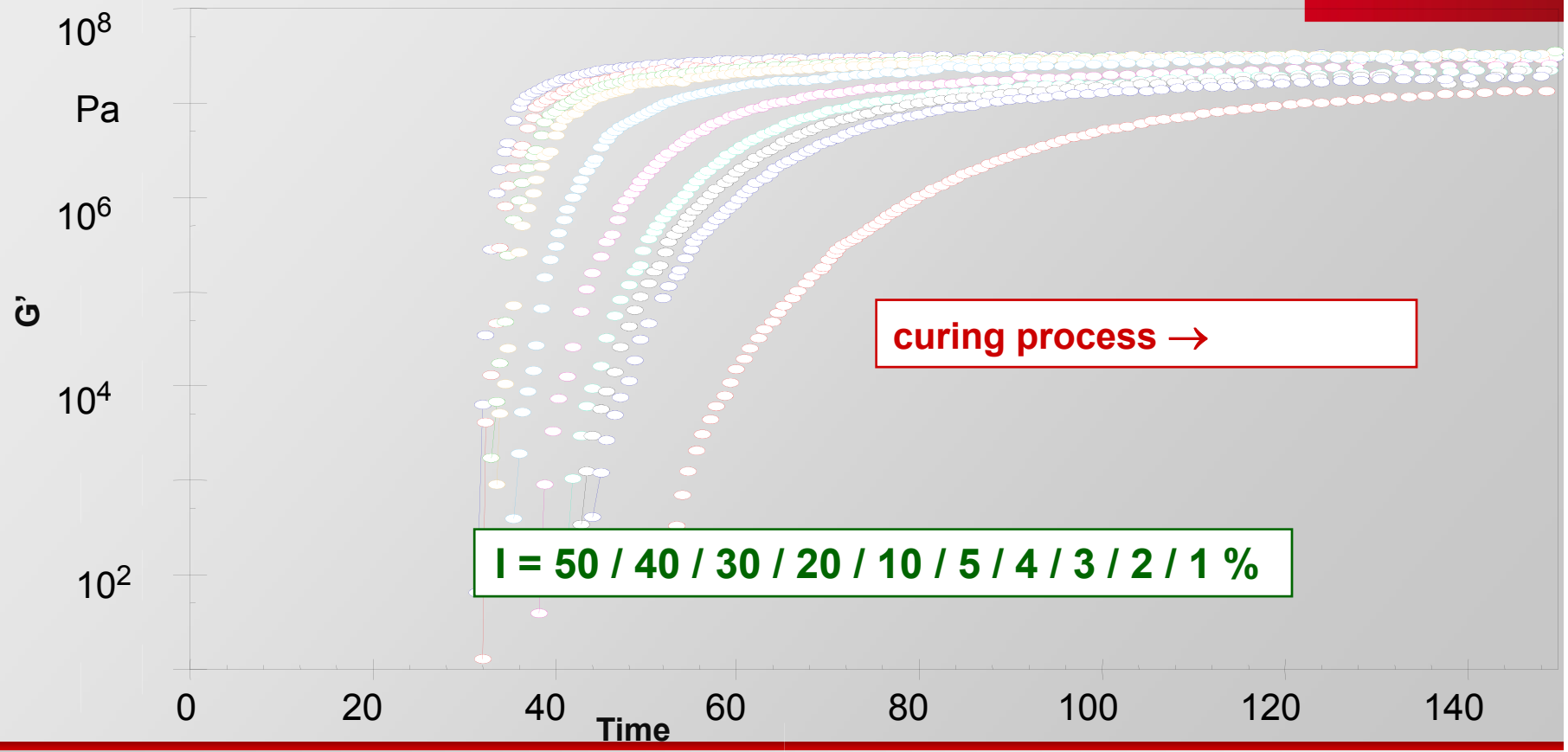
Specifications P-PTD 200/GL and light source	
Temperature range	-20 to 200 °C
UV light source, Peak intensity depending on used filter	
250 nm – 450 nm	22,500 mW/cm^2
365 nm	5600 mW/cm^2
320 nm – 390 nm	10,300 mW/cm^2
320 nm – 500 nm:	21,700 mW/cm^2
Lamp	- High-pressure 100 Watt mercury vapor short arc - Option: LED UV light source
UV safety eyewear	
Parallel-plate and cone-plate systems with diameters up to 50 mm	

UV Curing – Application – Resin Curing

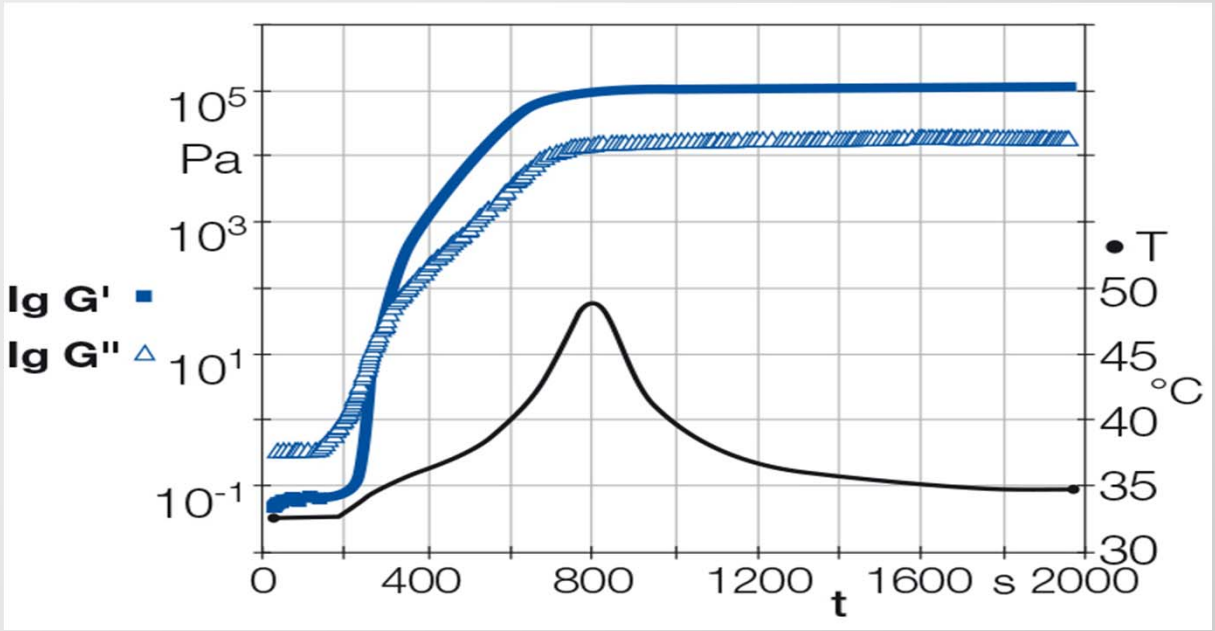


Gel point reached at 1s, rigid cure at 10 s (G' > 1MPa)

UV Curing Application – Ink Curing Impact of Intensity



UV Curing Study



G'' > G' → gel point at G' = G'' → curing → G' > G''

UV Curing Resin

γ = 0.1 %

ω = 10 rad/s

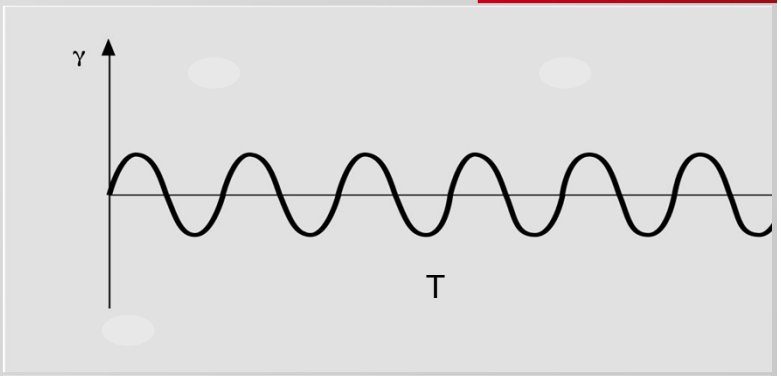
T = +23°C (isothermal)

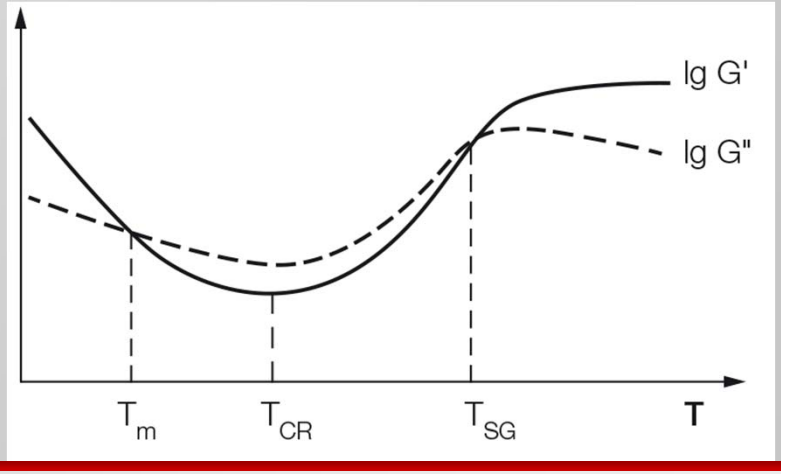
Soft touch, final G' = 0.1 MPa

Temperature peak: end of the **exothermic crosslinking reaction**

Oscillatory Temperature Sweep

- Amplitude and frequency are held constant while temperature is ramped up or down
- Amplitude selected to ensure to remain within linear viscoelastic region throughout the test (may require pre-testing on sample at different stages throughout the test)
- Changes in viscoelastic behavior with changes in temperature are measured
- Properties studied include:
  - Gelation, curing, other reaction kinetics
  - Degradation
  - Freeze thaw stability
  - Phase transitions, crystallization, melting, glass transition





Temperature Sweep - Polymers

Thermoplastics (Amorphous, Partially Crystalline)

- Linear or branched
- Start melting above melting temperature

Elastomers

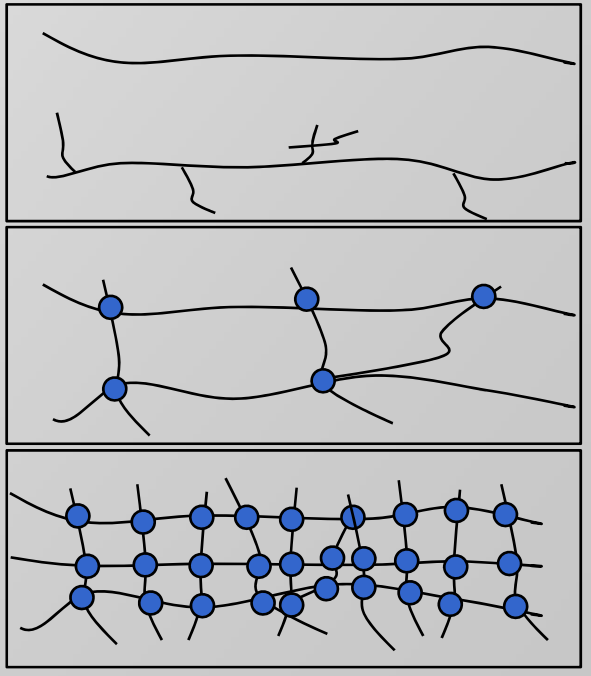
- Sparsely crosslinked
- Do not melt at higher temperatures

Thermosets, Resins

- Densely crosslinked
- 2K adhesives (e.g. epoxy resin based materials)
- Do not melt at higher temperatures

The temperature dependence of these various polymer systems varies greatly due to these differences in their morphology.

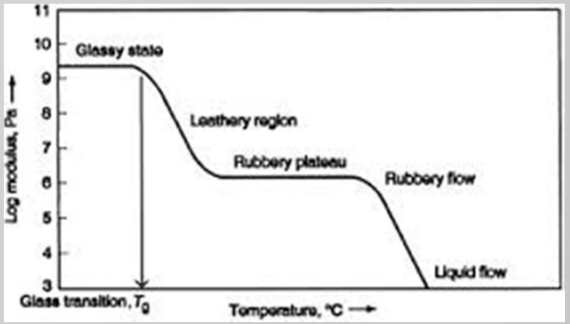
Poly (many) mer (parts)



Glass Transition and Melting Temperatures

The Glass Transition (T_g):

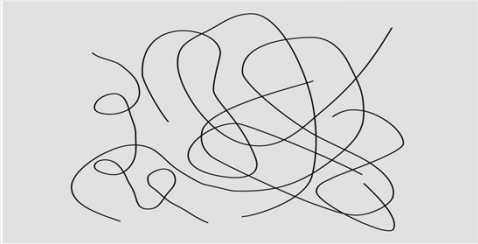
- Reversible transition in amorphous materials (or in amorphous regions within partially crystalline materials) from a hard and relatively brittle "glassy" state into a molten or rubber-like state, as the temperature is increased
  - Above the Tg, these polymers are rubbery; some polymers are used in this temperature range (elastomers like polyisoprene)
  - Below the Tg, these polymers are glassy and brittle; some polymers are used in this temperature range (PMMA, PS)



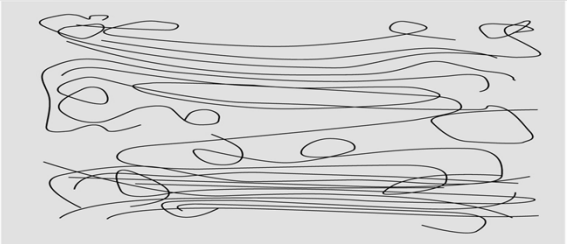
Melting Temperature (T_m):

- Reversible transition in crystalline polymers
  - Polymer chains fall out of their crystal structures and become a disorded liquid
- Amorphous and crystalline polymers have both a T_g and T_m
- Crosslinked polymers have a Tg but no Tm, i.e. they do not melt

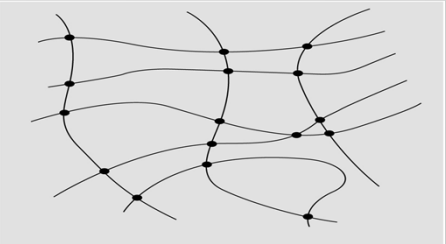
Typical Temperature Sweeps for Polymers



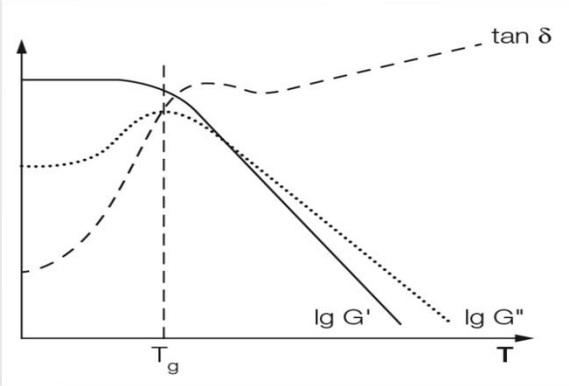
Amorphous
Unlinked, Without Any Order

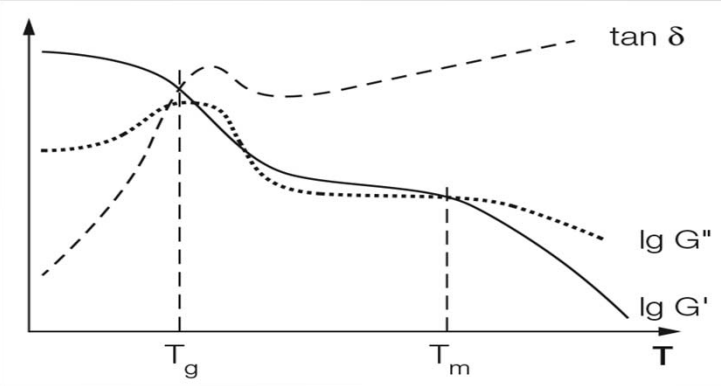


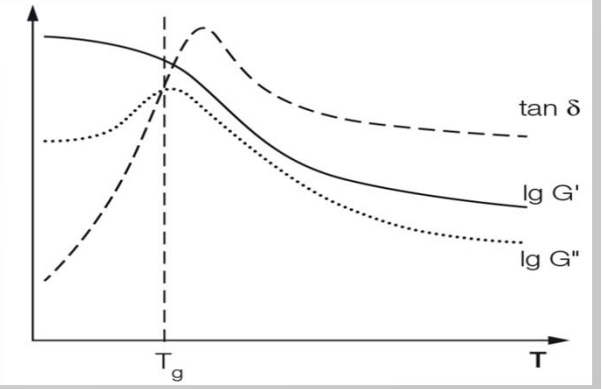
Partially Crystalline
Unlinked, Partially Crystalline Order



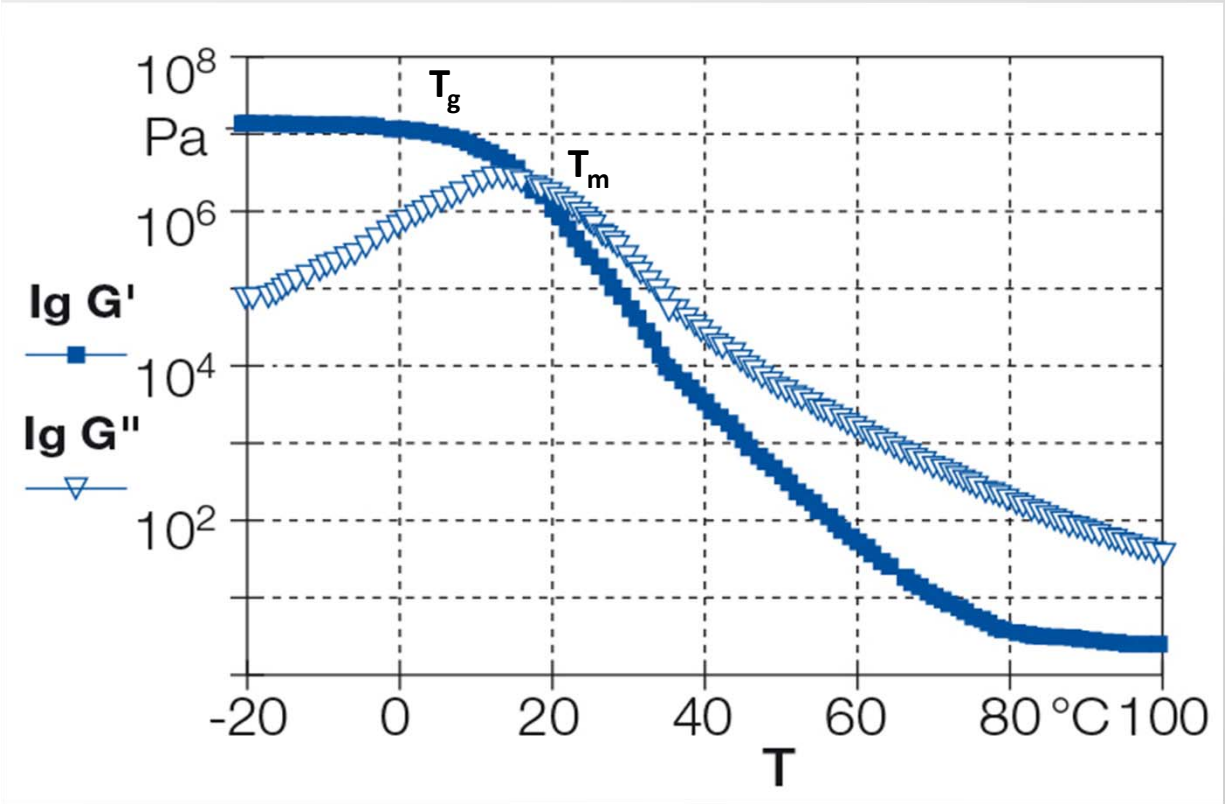
Chemically Cross-linked
Covalent Primary Bonds







Temperature Sweep - Polymer Modified Asphalt



Polymer Modified Asphalt (PMB) with 5% polymer

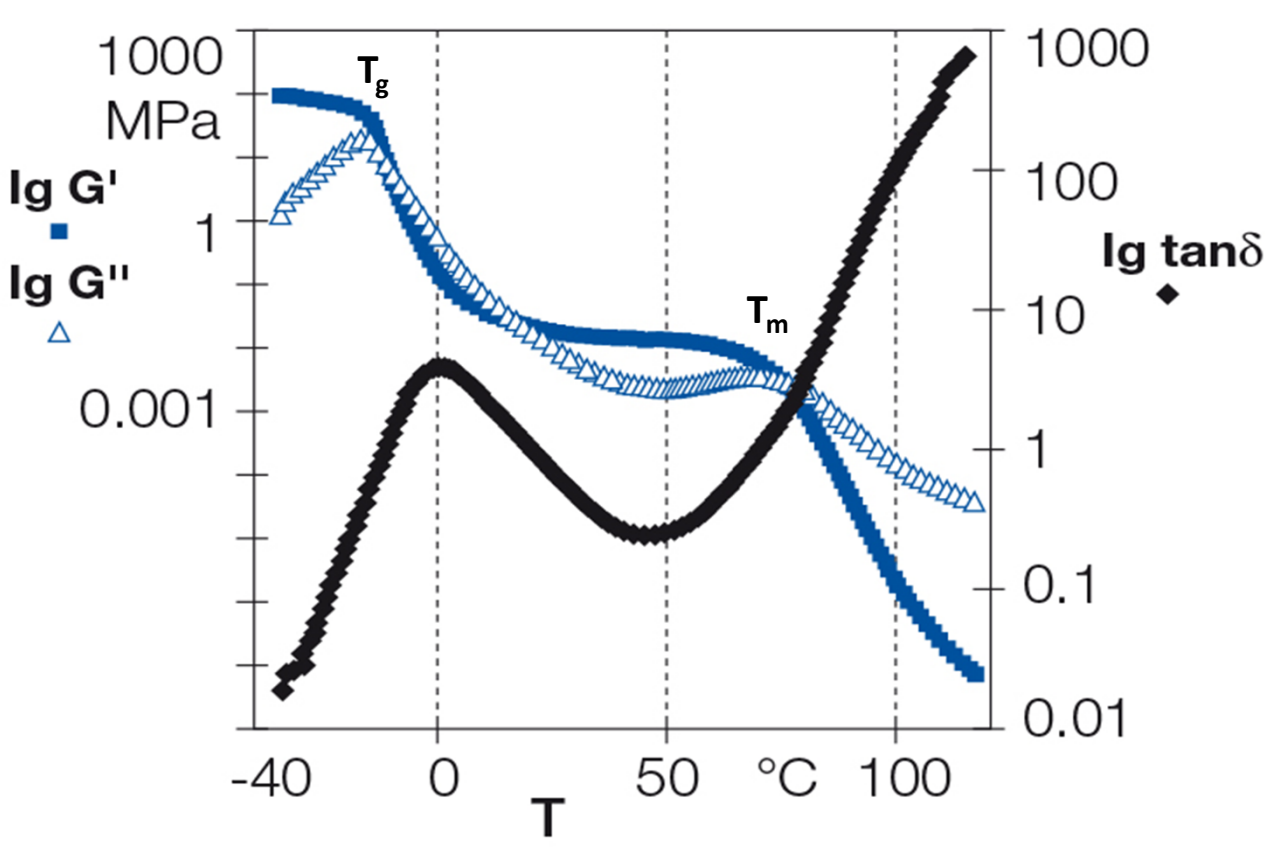
Behaves of an amorphous polymer

Preset in 2 intervals because the G'-values spread over 7 decades and the Linear Viscoelastic Limit changes with temperature

1. γ_1 = 0.1% (for T < 35°C)
2. γ_2 = 1% (for T > 35°C)

ω = 10 rad/s

Temperature Sweep - Hotmelt Adhesive



Hotmelt Adhesive

Unlinked Partially Crystalline Polymer

Shows a pronounced rubber - elastic region

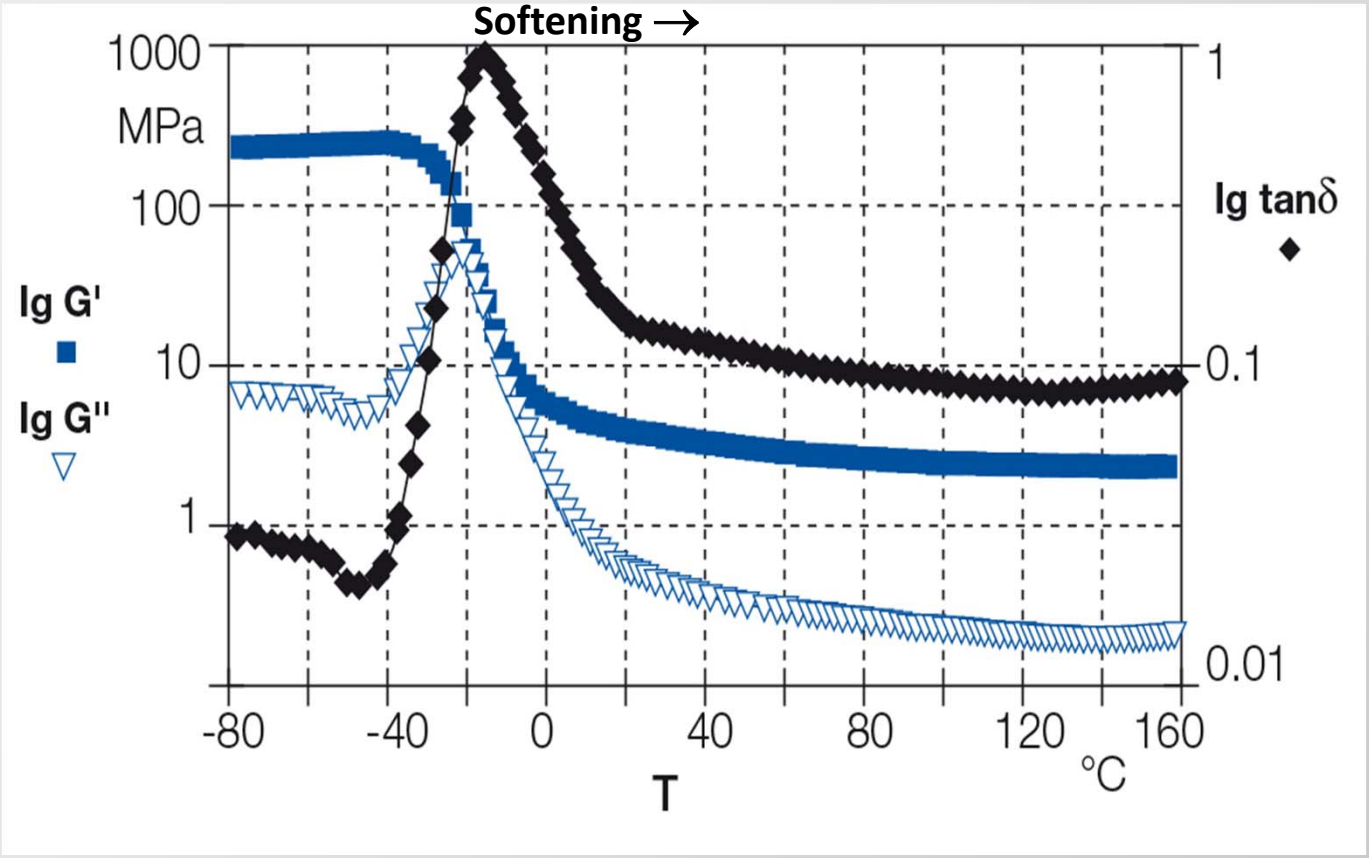
T_g = -18°C (G'' max)
T_g = 0°C (tanδ max)

Melts at 78°C

G'' > G' for T > T_m

tanδ = G'' / G'

Temperature Sweep - Rubber



Rubber
Cross - linked Polymer

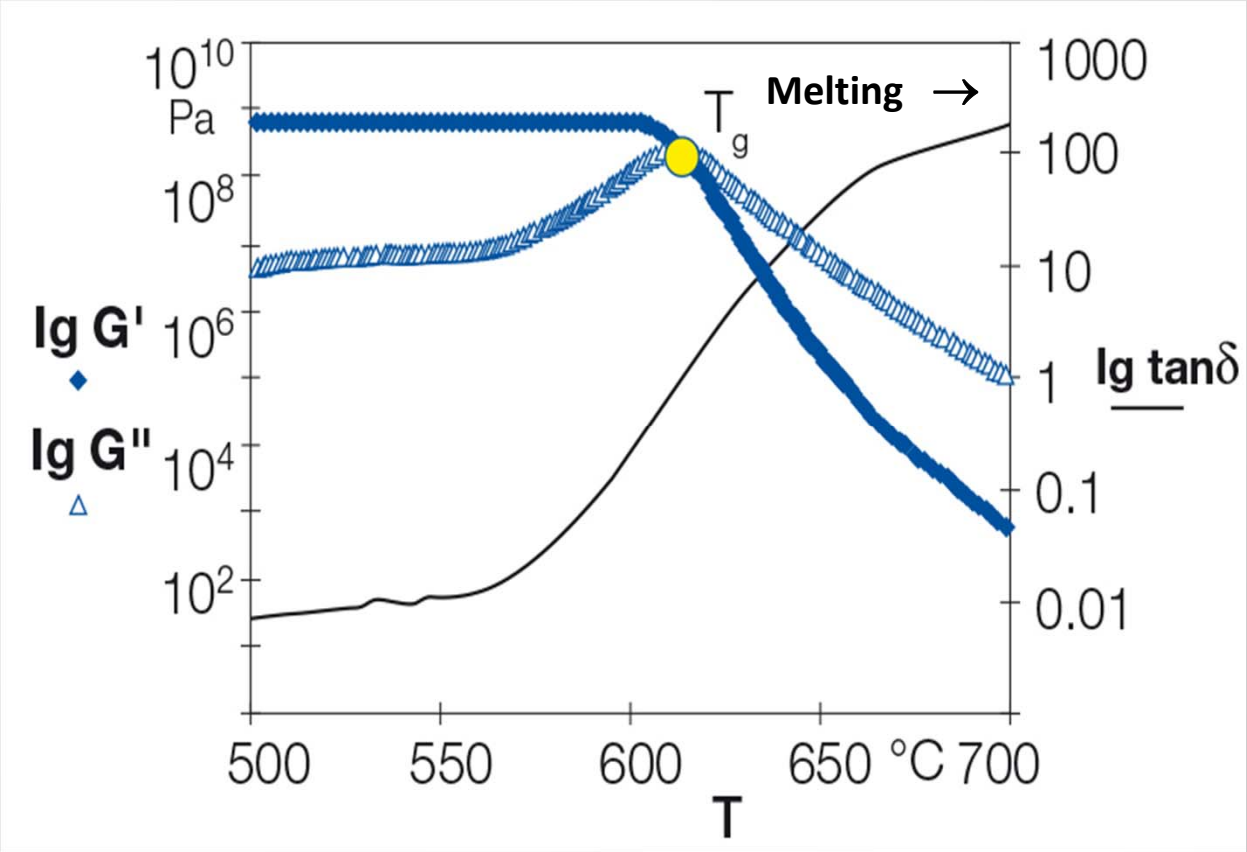
T_g = -22°C (G'' max),
T_g = -16°C (tanδ max)

No melting

G' > G'' also
at high temperatures

γ = 0.25 %
ω = 10 rad/s
tanδ = G'' / G'

Temperature Sweep - Glass



Glass
$G' > G''$ at $T < T_g$

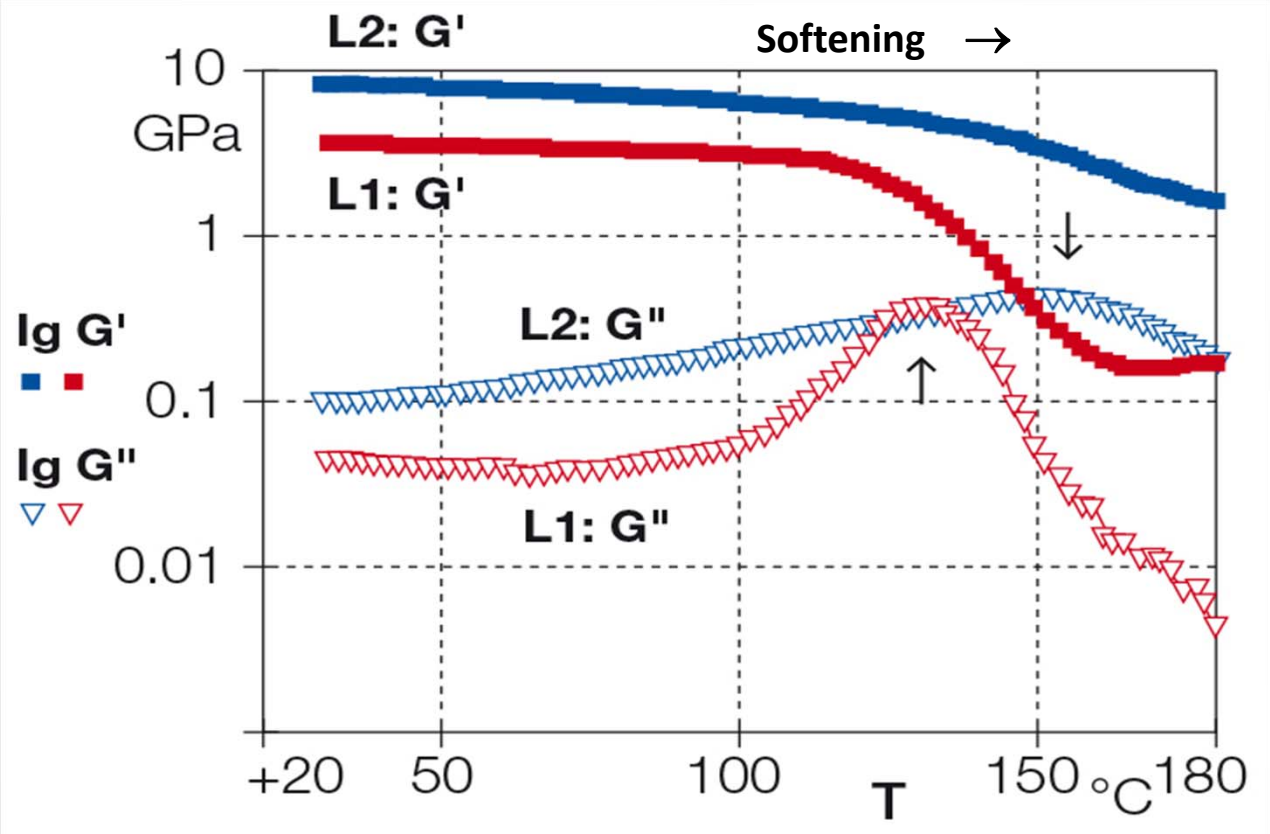
Glass is not an undercooled liquid but is an **amorphous solid** as indicated by the continuously increasing tanδ curve without any peak

T_g = +612°C (at G''_{max})

tanδ = G'' / G'

Measuring System: PP 08

Temperature Sweep – Two Laminates



Laminates

Reinforced laminate

Unmodified laminate

Shifting T_g from +132°C to +152°C

ω = 10 rad/s
γ = 0.01 %

Torsion bar (SRF)

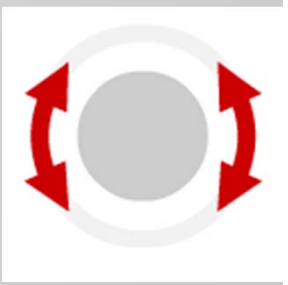
50 x 10 x 1 (in mm)

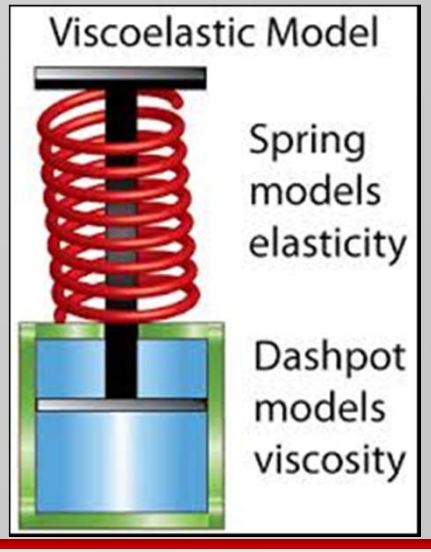
Summary of Viscoelastic Properties

- Viscoelastic materials exhibit both liquid-like (viscous) and solid-like (elastic) behaviors.
- Materials dominated by viscous behavior (G”>G’, viscoelastic liquid) flow, apply easily, but may suffer from stability and sagging issues.
- Materials dominated by elastic behavior (G’>G”, viscoelastic solid) do not flow rather deform, have good stability but may suffer from leveling issues.
- Oscillatory tests provide means to characterize:
  - Structural strength (LVER), rigidity, yield stress, and flow stress
  - The frequency sweep provides insight into behavior at both long (storage) and short (impact) time scales.
  - Inherent structural properties over changes in time and temperature, including measuring recovery after shear, all while imparting no behavior
- The viscoelastic balance in a material is that which imparts the desired performance characteristics in most cases.

Summary of Oscillatory Test Types

- Rotational tests measure the response of a material to the test conditions applied.
- Oscillatory tests measure the inherent behavior of a material without imparting any behavior.
- Oscillatory tests allow to quantify the balance between viscous liquid behavior and elastic solid behavior in a sample.
- The amplitude sweep identifies stiffness, LVER, yield stress, and flow stress.
- Frequency sweeps describe the behavior of a sample at different time scales, i.e. short relaxation times, long relaxation times.
- Oscillatory testing for thixotropy, time, and temperature sweeps provides a means to watch structural changes without impeding the structures development.



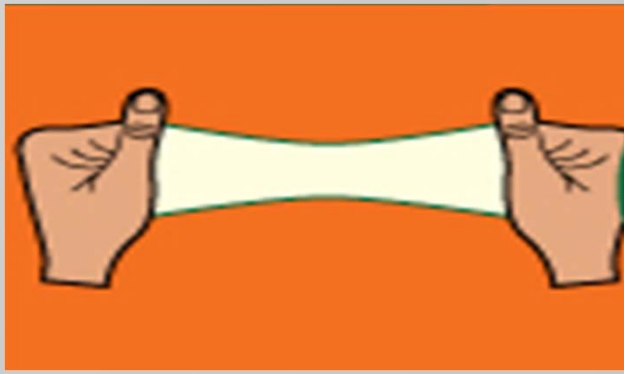


Summary of Benefits of Rheological Measurements

- Provides Comprehensive Analysis of Both Flow and Viscoelastic Properties
- Sensitivity to Distinguish Between Very Similar Samples
- Simulation of Process Conditions
- Ability to Characterize At Rest Properties of Materials
- Non-Destructive Probing of Sample Structure
- Objective and Reproducible Methodology
- Process design, product development, reverse engineering, QC parameters, QA incoming materials, formulation
- Low viscosity liquids to solids
- Controlled temperature, humidity, UV
- Absolute, comparable data

Recap – Audience Participation!

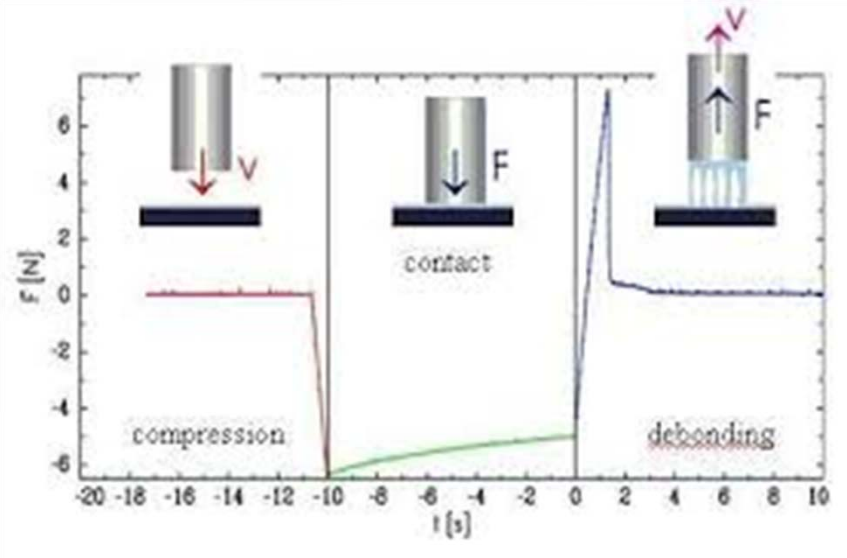
- What test would you conduct first to start evaluating the rheological properties of a material?
  Amplitude sweep to determine LVER
- What do you expect to happen when the bread dough shown a right being stretched is released?
  Will recoil fully if deformation was within LVER
- Is elasticity a good or bad thing?
  Depends
- Does water have any elasticity?
  Not at temperatures where it is fluid. Yes near and below freezing
- At what frequency would a material used to dampen impacts be measured?
  As high as possible

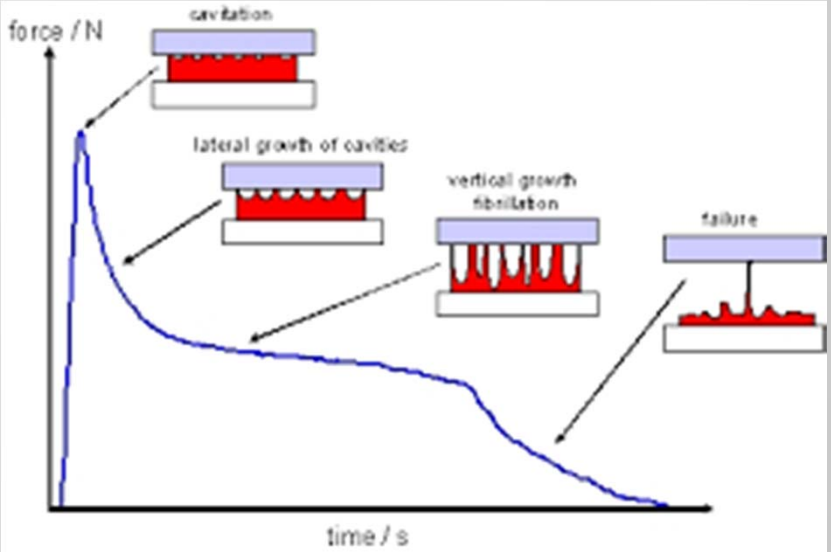


Rheology

Non-Traditional Measurements

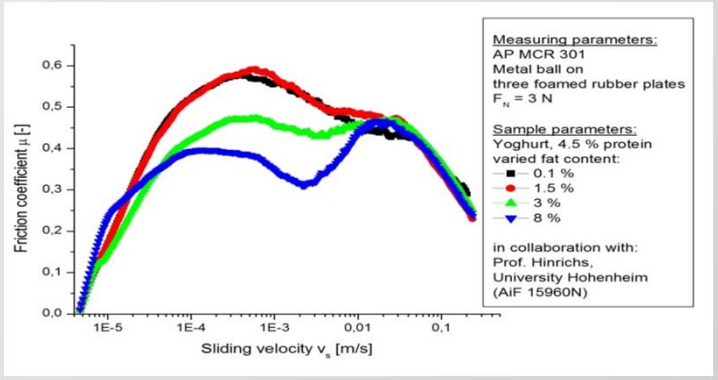
Tack Measurement



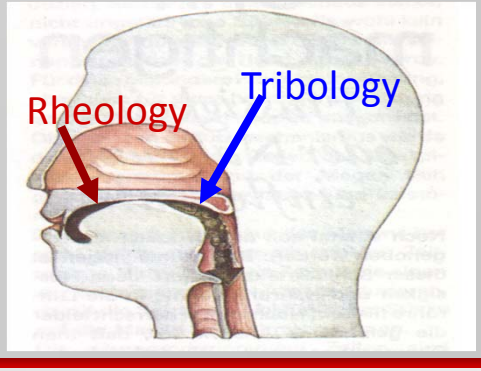


- Measuring system moves up with a well defined speed (1mm/s) and measures the force (FN) acting between the sample and the measuring system surface.
- Test characterizes the sample's stickiness (tack).
- The stickiness or tack is calculated by integration of the area under the curve

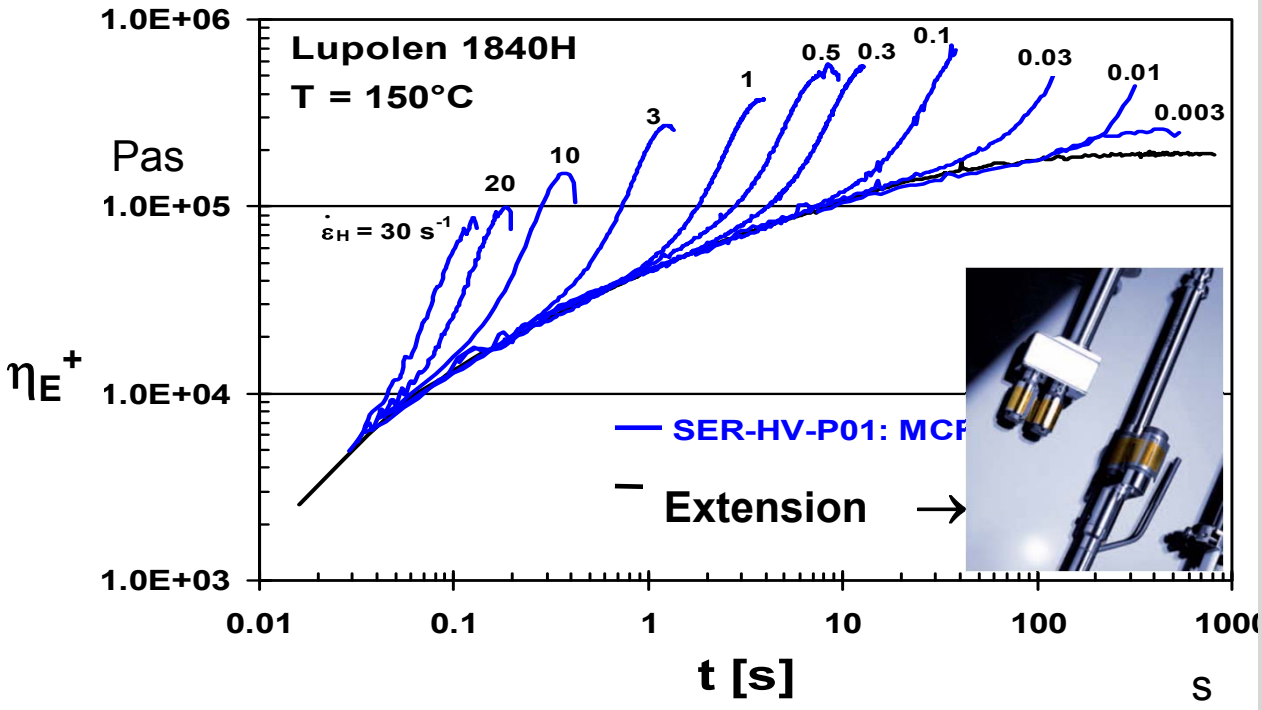
Lubrication, Tribology, Friction, Wear Measurement



- Effect of lubrication properties as a function of viscosity, speed, load, and surface.
- Material of both surfaces can be varied.
- Temperature and humidity can be controlled.
- Used to determine coefficient of friction, static friction, stick slip behavior.



Extensional Measurements

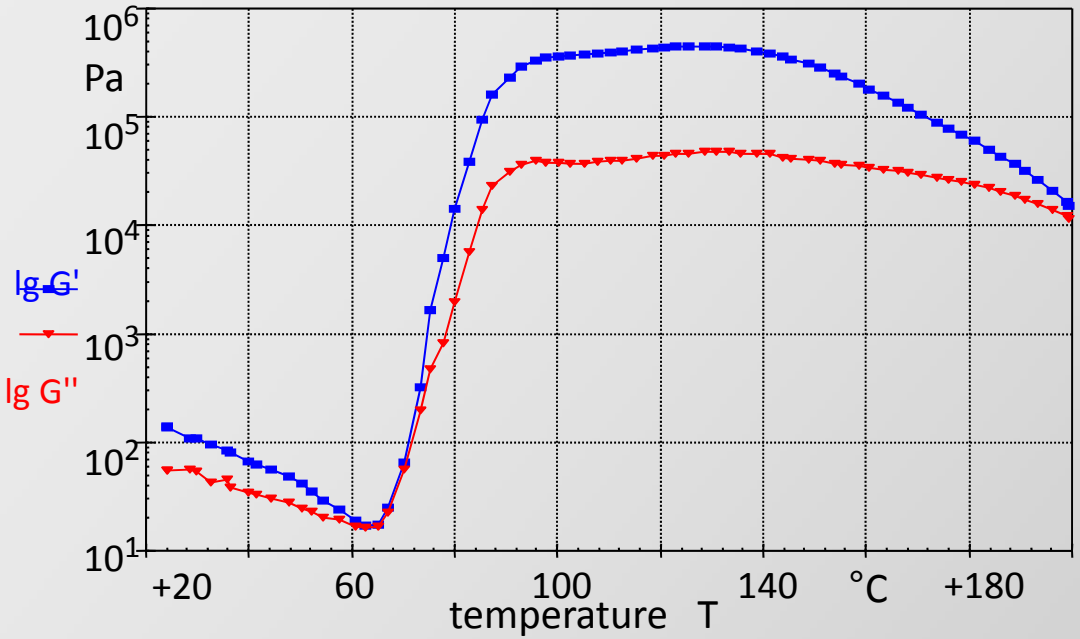


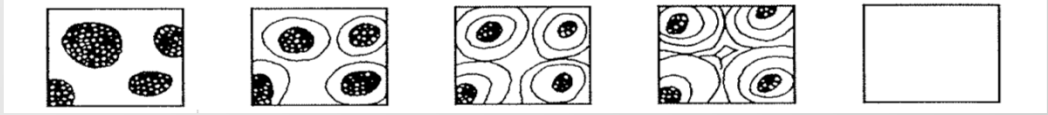
Extensional Viscosity η_E (in Pas), rotational test

Branched Polymer
LDPE, T = 150°C,
Extensional tests (SER)
at Various Extension Rates
(Hencky Strain rRates)

Extensional Tests (Blue) and Shear Test (Black) are overlapping until growth curve of shear viscosity, using cone-plate, showing $\eta_E^+ = 3 \cdot \eta^+$ until the break of each sample → **strain hardening** stemming from branching.
Shear Test does not detect branching.

Rheo-Microscopy + Temperature Sweep - Fusion





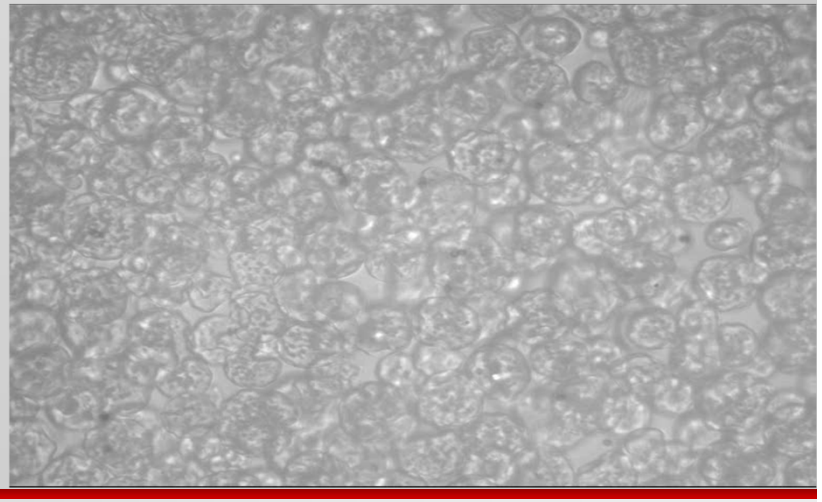
Softening → Swelling → Thickening → Fusion → Gelation

PVC Plastisol

Fusion process from plastisol paste to elastomer

Onset of gelation: T = +65°C

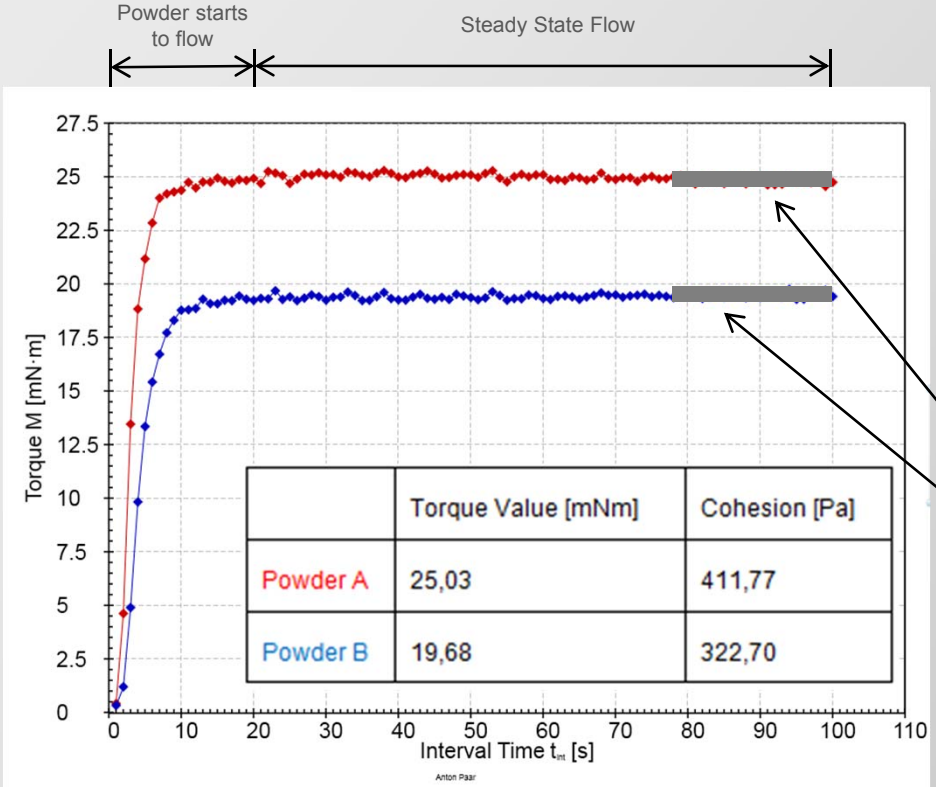
End of fusion: T = +96°C



Rheology of Powder and Granular Media

- The Powder Cell Accessory
- Highly reproducible measurement of cohesion strength of powders
- Full scale fluidization studies of powders
- All rheological test types on powders

Example of Cohesion Strength Measurement



	Torque Value [mNm]	Cohesion [Pa]
Powder A	25,03	411,77
Powder B	19,68	322,70

The **red curve** has a higher Cohesion Strength. The particles stick together tighter, the powder flows less.

The **blue curve** has a lower Cohesion Strength. The particles stick together less, the powder flows better.

Linear regression across last data points

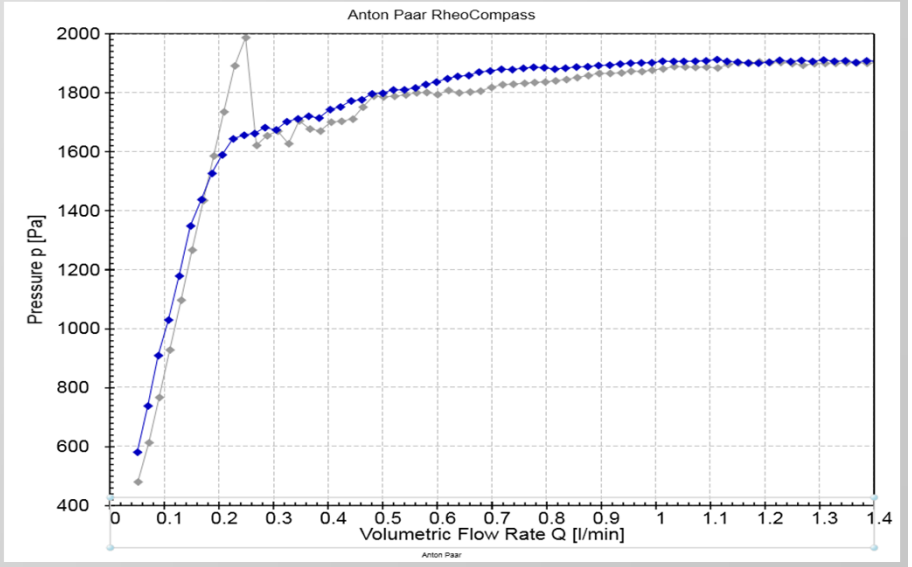
Fluidization Studies

- Air stream is introduced to the powder through a porous material at the base of the powder column
- Gravity and inter-particle adhesive forces are overcome due to the air stream
- Powder behavior changes uniformly from a static solid-like state to a dynamic fluid-like state, depending on the air velocity through the powder
- If air velocity is increased further, the powder bed starts bubbling or/and spouting
- Fluidization also clears "powder memory" which is important in case of measurements on powder, meaning it does not matter how the powder was stored before or how it was filled into a measurement cell.

Powder Transport

- A pipe with the diameter 50 mm would need a minimum flow of 1.2 l/min to fully fluidize and therefore transport powder
- This would vary extensively depending on the powder used.
- Different Volumetric Flow Rates for other pipe diameters can be calculated easily:

  Volumetric Flow Rate = Air Velocity * Pipe Cross Section Area

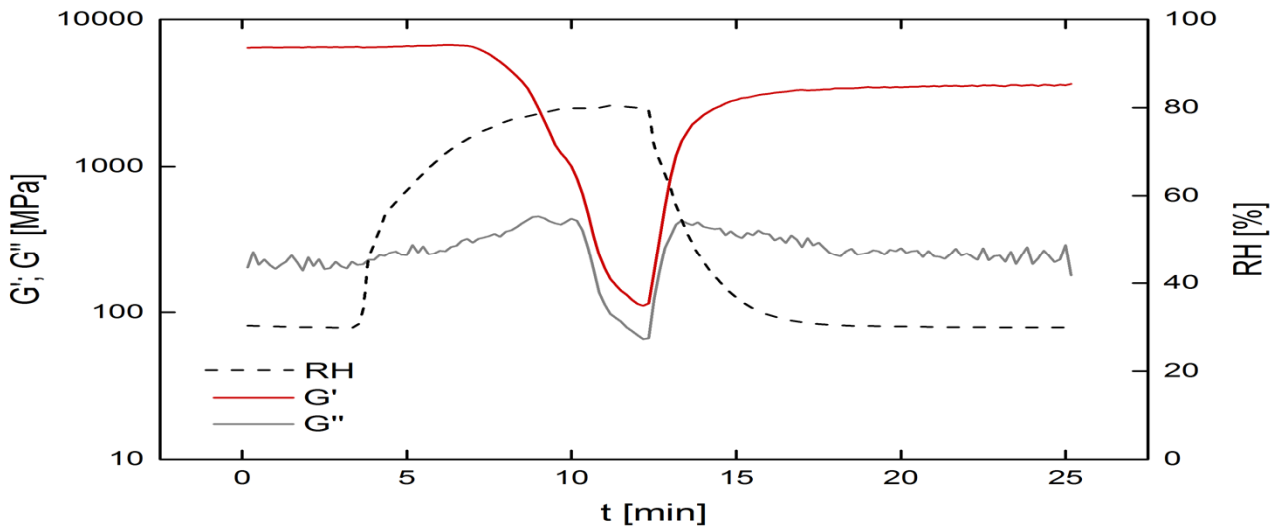


Humidity Controlled Rheology

- A humidity generator connected to the new CTD 180 (Humidity Ready) allows to control the humidity around the sample in addition to the temperature.
- The humidity generator MHG 100 allows to control the humidity in the convection oven in the range from 5 to 95% relative humidity within the temperature range from 5° to 120°C.
- The system fits on all MCR rheometers and consists of: New CTD 180 “humidity ready”, humidity sensor, humidity kit (tubing) and humidity generator.

- All fixtures UXF, SER, UXF TD, SRF, PP, CP, Tribo etc. can be used together with the humidity option
- Humidity generator is controlled manually or via separate software. The humidity generator can be synchronized with the rheometer via trigger and the temperature and humidity sensor is directly read in the rheometer software.

Humidity Controlled Rheology of Gelatin



Time Test,
TruStrain™
SRF, CTD180, 50°C

Gelatin
(35 x 10 x 0.2 mm)
Strain: 0.01 %
Frequency: 1 Hz

RH = 30 %; t = 4 min
RH = 80 %; t = 8 min
RH = 30 %; t = 13 min

30% Relative Humidity: Stable values G´>> G´´, brittle solid gelatin plate
80% Relative Humidity: Both G´ and G´´ decrease due to wetting and swelling of the gelatin plate. Sample turns to a soft viscoelastic solid, G´ > G´´ (less brittle)
Again 30% Relative Humidity: Drying of the gelatin, returns almost to the initial mechanical properties with slightly higher water content.

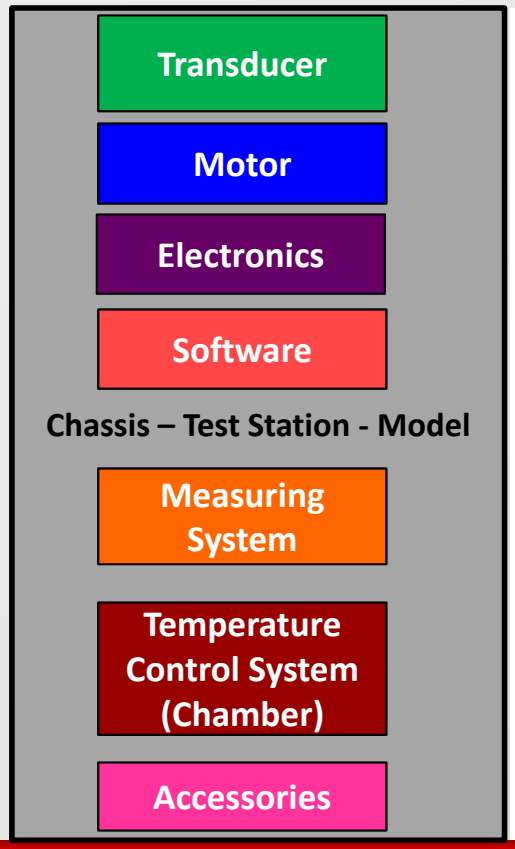
Recap – Audience Participation!

- What is the main advantage of oscillatory testing over rotational testing?
  - Non-destructive
- Would rotational testing be appropriate for a solid sample?
  - No as solids do not flow
- Would G’ or G” be larger at low frequencies for a material with a yield stress?
  - G’
- Which would be larger at low frequencies for a materials with zero shear plateau?
  - G”
- What is the main use of the Cox-Merz rule? Does it work for all materials?
  - No
- What does having a narrower linear viscoelastic region mean?
  - Less structural strength

Rheometers

Bascis

Rheometer Basics - Components



Torque — **Controller (CSS)**, **Detector (CSR, CSD)**

Speed or displacement — **Controller (CSR, CSD)**, **Detector (CSS)**

Signal processors, controllers

Test programming, data collection, analysis

Modularity, stiffness, footprint, ease-of-accessibility, aesthetics

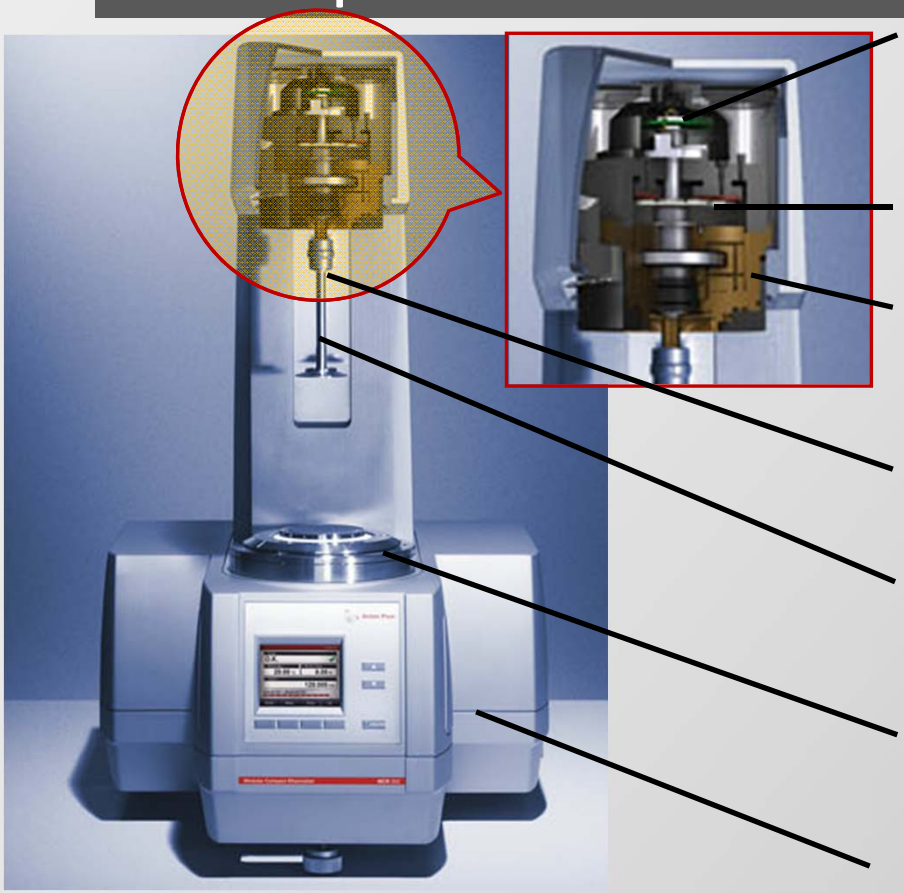
Sample "container", finite range, rigid, design

Heating/cooling, temperature range

Additional settings, advanced capabilities, research platform

CSS = controlled shear stress; CSR = controlled shear rate; CSD = controlled shear deformation

Basic Components of An MCR Rheometer



Optical Encoder
Measures or controls speed → shear rate
Measures or controls displacement → strain

Electronically Commutated Motor
Measures or controls torque → shear stress

Air bearing, capacitive Normal Force Sensor
Positions motor
Measures or controls normal force → normal stress

Motor coupling
Precision quick connection of measuring systems

Measuring System
Sample holder → defined flow field (sample shape)
→ CP, PP, CC, SRF

Chamber
Temperature control, additional settings, accessories

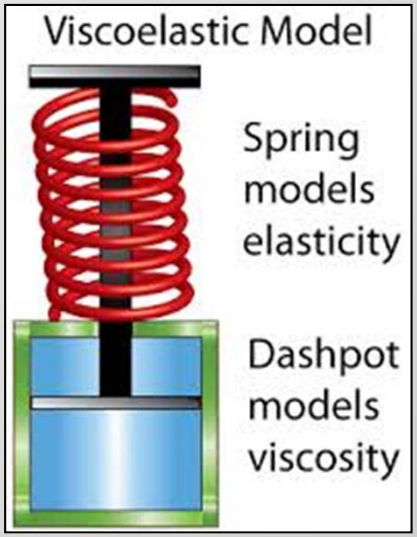
Chassis
Stainless steel, lowest compliance ever

CP=cone-plate; PP=parallel plate; CC=concentric cylinder; SRF=solid rectangular fixture

Basics of the Viscoelastic Model – Shear Stress and Strain

Sir Isaac Newton
1643-1727

Viscosity was first described by Newton who found the velocity at which a liquid moved was proportional to the force applied to it.



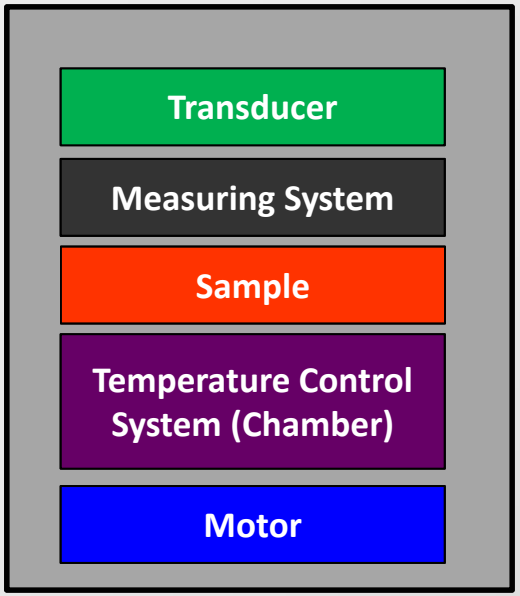
Robert Hooke
1635 - 1703

Elasticity was first described by Robert Hooke who found that a spring deformed proportionally to the force applied to it.

$$\text{Viscosity} = \frac{Shear\ Stress}{Shear\ Rate} = \frac{\tau}{\dot{\gamma}}$$

$$\text{Shear Modulus} = \frac{Shear\ Stress}{Strain} = \frac{\tau}{\gamma}$$

Rheometer Basics – Separate Motor and Transducer Design SMT

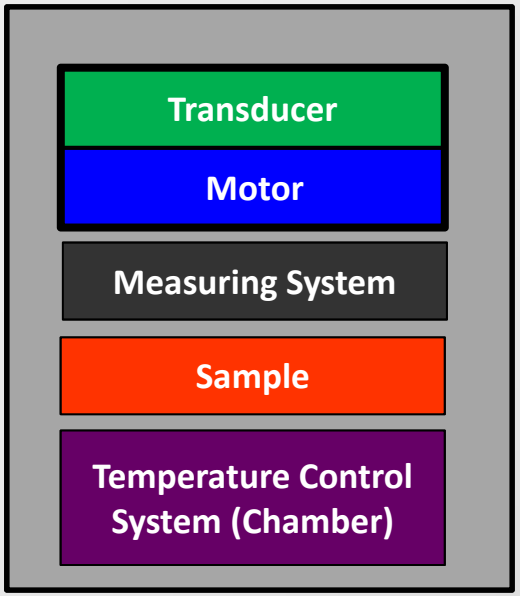


Torque Detector

Speed or Displacement Controller

- Motor beneath the sample drives to a commanded speed or displacement (strain).
- Sample response is measured via a torque detector(shear stress) above the sample.

Rheometer Basics – Combined Motor and Transducer Design CMT



Torque Detector

Speed or Displacement Controller

- Motor above the sample drives to a commanded speed or displacement (strain).
- Sample response is measured as the torque (shear stress) the motor required to accomplish the motion.

Rheometer Basics – Controlled Stress and Controlled Strain

- Controlled **Strain** Measurement
  - A finite **strain** (deformation) is commanded.
  - The device instantly achieves the commanded **strain** independent of the sample.
  - The stress required to achieve that finite **strain** is measured as the sample response.
  - The device maintains the commanded **strain** independent of changes in the sample.
  - In oscillatory measurements:
    - The **strain** wave must always be sinusoidal.
    - The stress wave must be non-sinusoidal once the linear viscoelastic region is exceeded.

If a rheometer controls this way, it is a Controlled Strain Rheometer.

τ = γ

Shear Stress = Shear Strain

Shear Modulus = Shear Stress / Shear Strain

The MCR Rheometers can do both just as all Anton Paar rheometers since way back in 1985.

- Controlled **Stress** Measurement
  - A finite **stress** (torque) is commanded.
  - The device instantly achieves the commanded **stress** independent of the sample.
  - The strain achieved by that applied **stress** is measured as the sample response.
  - The device maintains the commanded **stress** independent of changes in the sample.
  - In oscillatory measurements:
    - The **stress** wave must always be sinusoidal.
    - The strain wave must be non-sinusoidal once the linear viscoelastic region is exceeded.

If a rheometer controls this way, it is a Controlled Stress Rheometer.

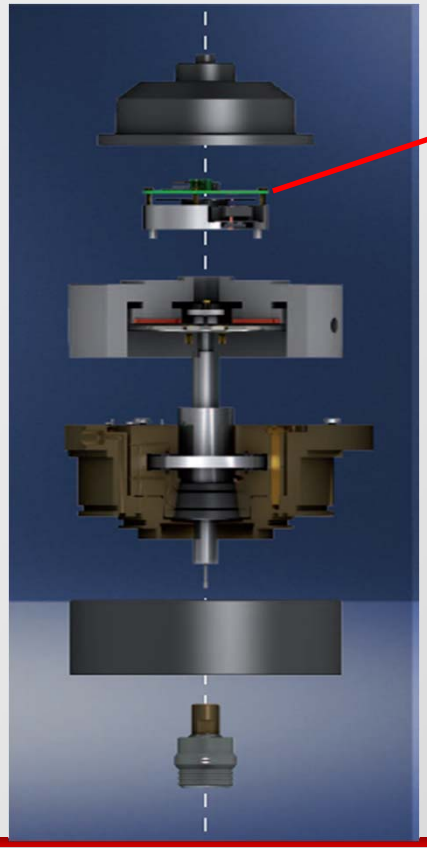
The Most Important Rheometer Considerations

- **Control**
  - Torque and angle resolution are paramount
  - Inertia free measurements to sample inertia limit
  - Extremely rapid and precise stress and strain control even in rapidly changing samples
- **Temperature Quality**
  - No temperature gradients within sample
  - Automatic thermal equilibrium check
  - Automatic temperature calibration
- **Gap Accuracy**
  - Active control based upon temperature at sample to prevent drift with room temperature
- **Error Proofing**
  - Automatic tool and chamber recognition
  - Precision measuring system connection
  - Smart software with warnings
- **Future Proofing**
  - Duality between R&D and QC
  - Generational compatibility
  - Modularity

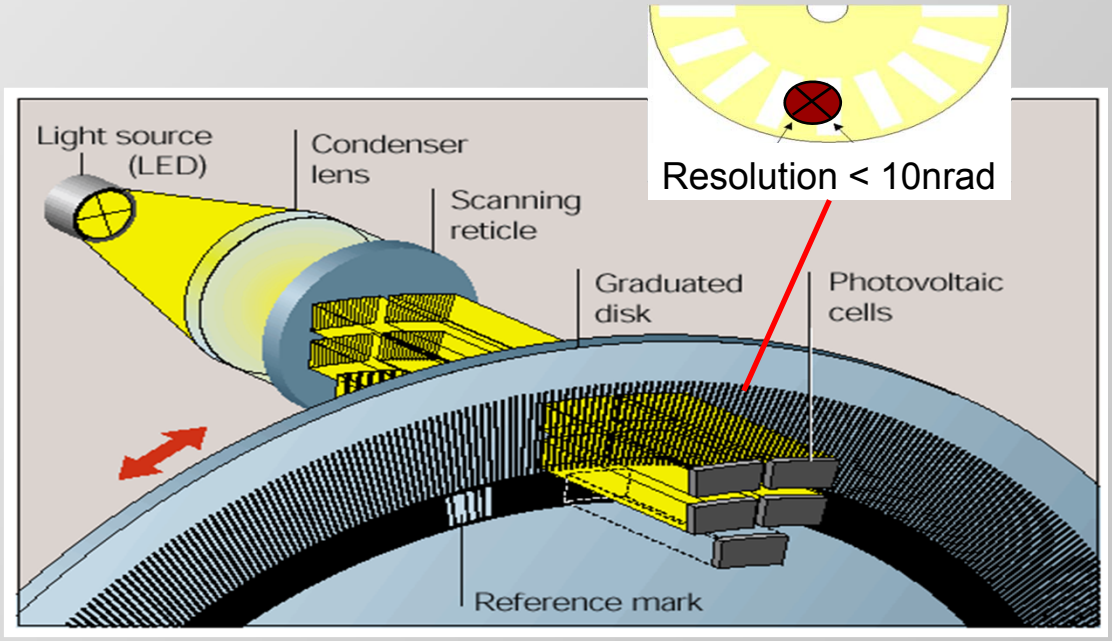
Important Rheometer Characteristics

Motor Control

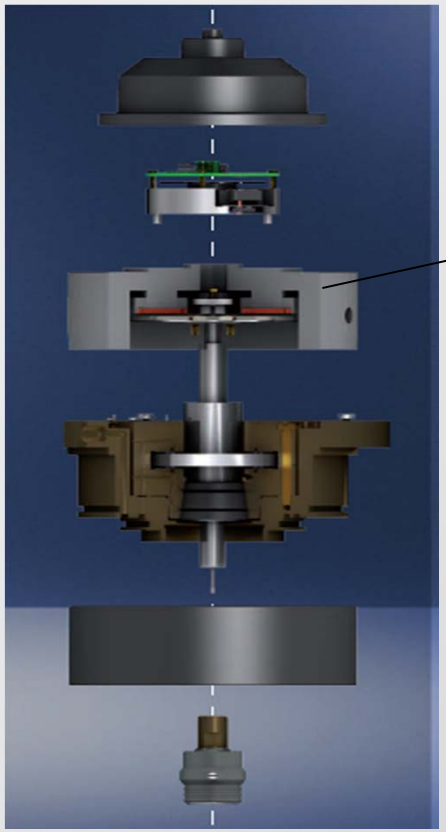
Control: Ultra-High Resolution Optical Encoder



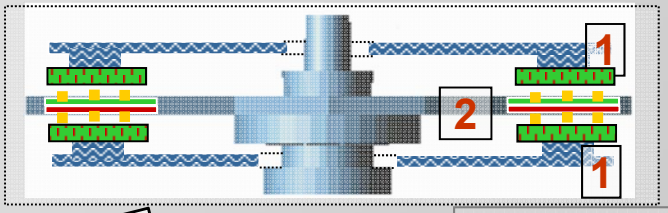
Online, precise position control of shear rate & strain



Control: Unique Synchronous EC Motor –Generations of Expertise



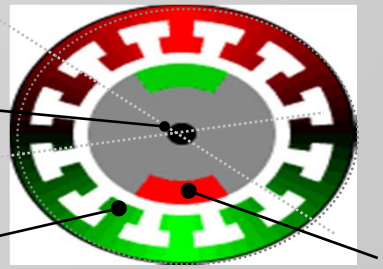
Non Contact Magnetic Drive Motor



1 Electronic field
2 Magnetic disk

The rotor is ALWAYS in sync with the stator even at high frequency.

$\omega_I = \omega_{II}$



Geometry Shaft from Top

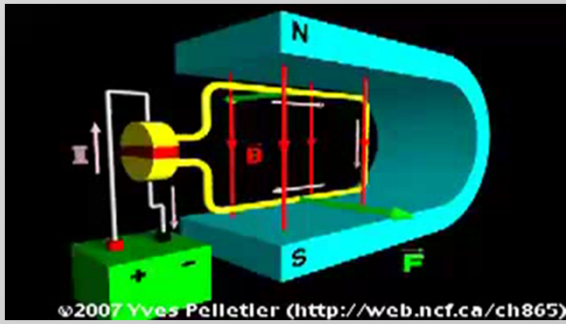
Electronic Field - Stator -

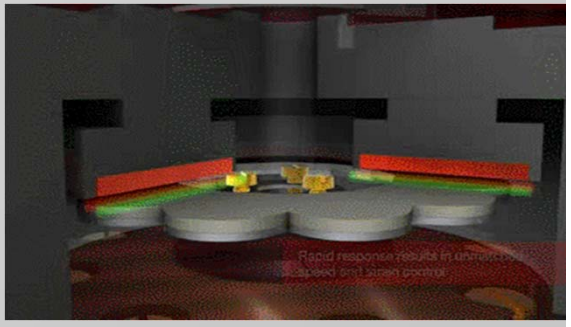
Magnetic Disk - Rotor -

Control: MCR's EC Motor is the Key to Precise, Inertia Free Control

Anton Paar

- **Instantaneous availability of the magnetic field and the torque, i.e. no time lag due to induction.** **Benefits:**
  - Extremely fast response times
  - Control of very small speeds at small torques
  - Oscillation at higher frequencies
- **No induction needed.** **Benefit:**
  - No eddy currents → No heat production on the rotor → No change in motor characteristics → High torques for long times possible (300 mNm)
- **Known and constant magnetic field and linear relationship between electro-magnetic torque and stator current(M ~ I).** **Benefit:**
  - Only one motor constant for calibration
- **Virtually no dependence on the type of geometry.** **Benefit:**
  - No difference between small low inertia and large high inertia geometries
- **Extremely efficient.** **Benefit:**
  - No heat build up even at long operation at high torques → No drift in torque signal over time





Control: Intelligent Adaptive Controllers - TruRate™ and TruStrain™

TruRate™ fast and accurate strain and strain rate setting in **rotation**

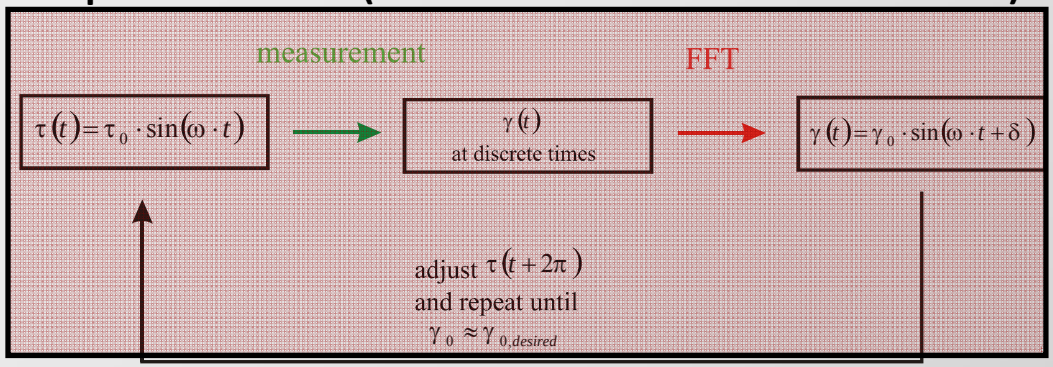
- A fully adaptive controller
- Starts with highest dynamics and adapts the dynamic as required
- Does not need pre-tests or other information about the sample
- Controls and measures precisely smallest speeds and torques

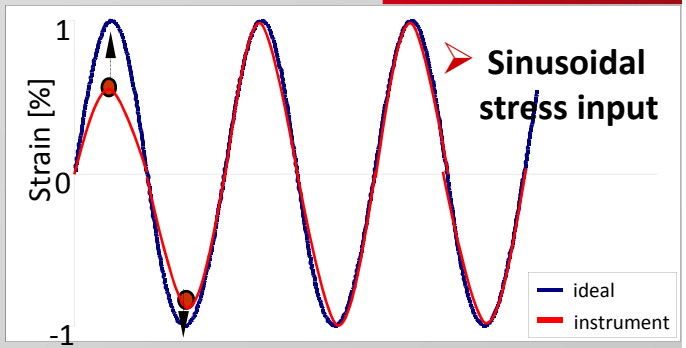
TruStrain™ real time position controlled **oscillation**

- Sets a perfectly sinusoidal strain by real time position control
- Does not require any pre-test or other information about the sample
- Controls and measures precisely smallest deflection angles and torques
- Allows LAOS with sinusoidal strain setting with a controlled stress instrument
- Is a further developed version of the former Direct Strain Control (DSO)

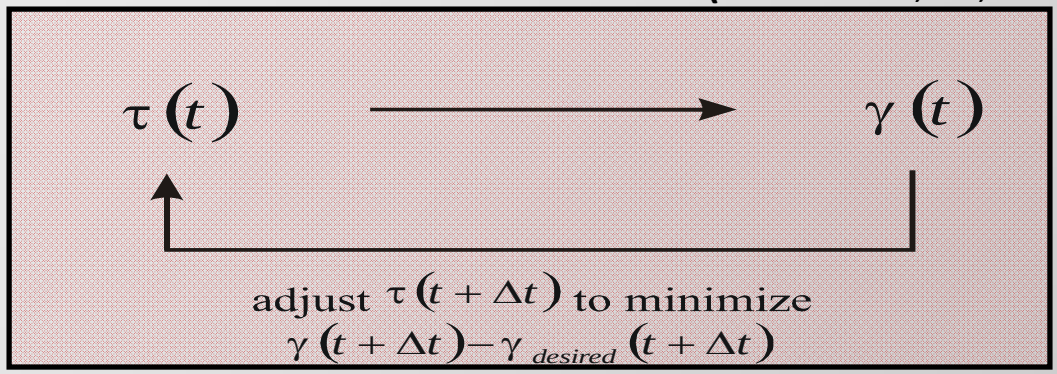
Control: Adaptive TruStrain™ in Action

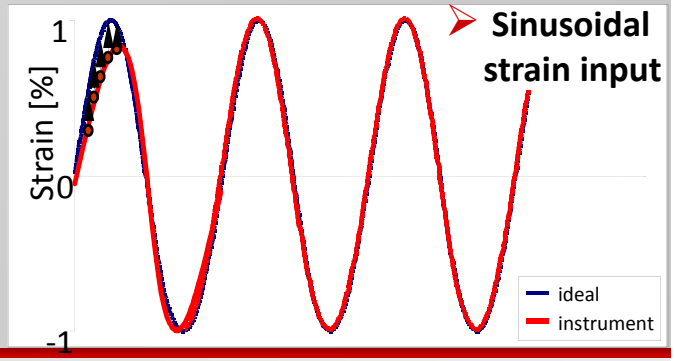
Amplitude Control (Controlled Shear Deformation - CSD)





Real Time TruStrain™ Position Control (*Rheol. Acta*, **41**, 356-361 (2002))

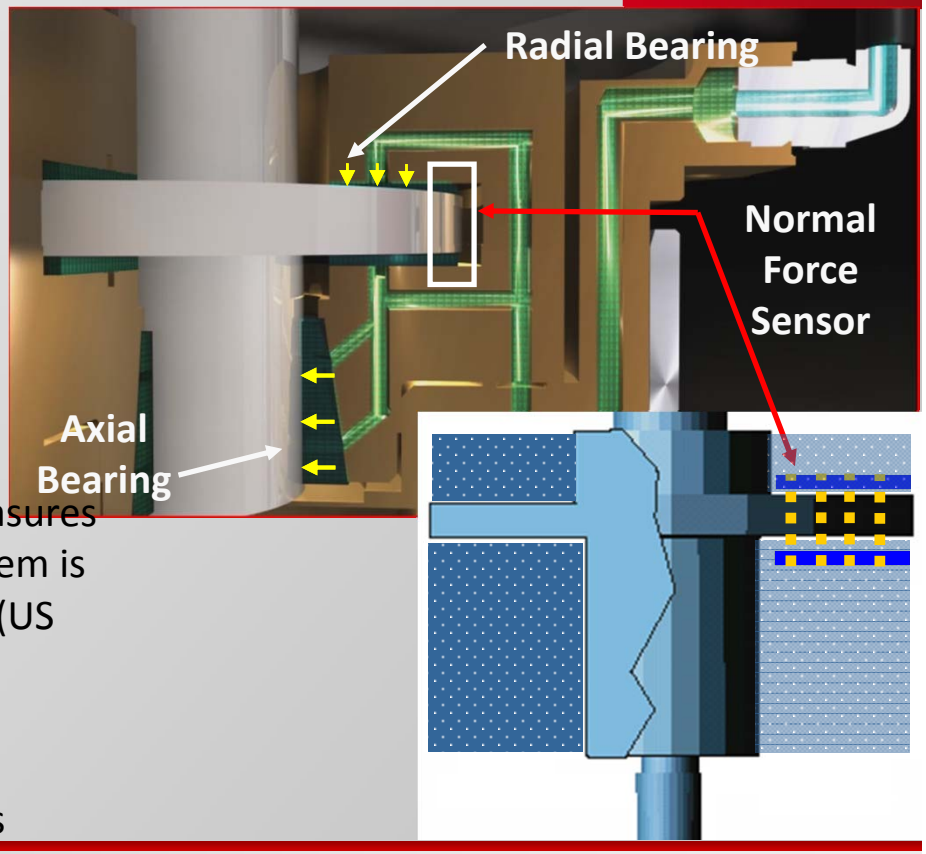




Control: Air Bearings and Normal Force

Air bearings

- Axial bearing centers the shaft
- Radial bearing holds the rotating part
- Constant high quality (less variation) of air bearings due to improved manufacturing process → best low torque performance
- MCR502 and 702: Temperature stabilization of the air bearing increases the lifetime of motor adjustments and reduces drifts in normal force



Normal Force Measurement

Patented normal force sensor in the air bearing measures the natural deflection of rotor when measuring system is pushed or pulled by an electrical capacitive method(US Patent 6,167,752)

Benefits:

- Large NF range with high resolution
- NF measurements in fast transient measurements

Important Rheometer Characteristics

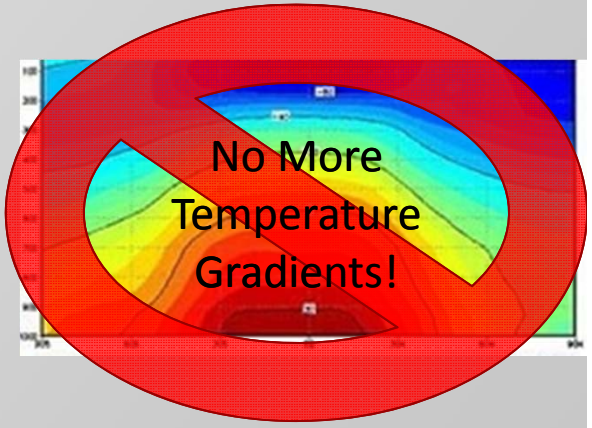
Temperature Control

Temperature Quality

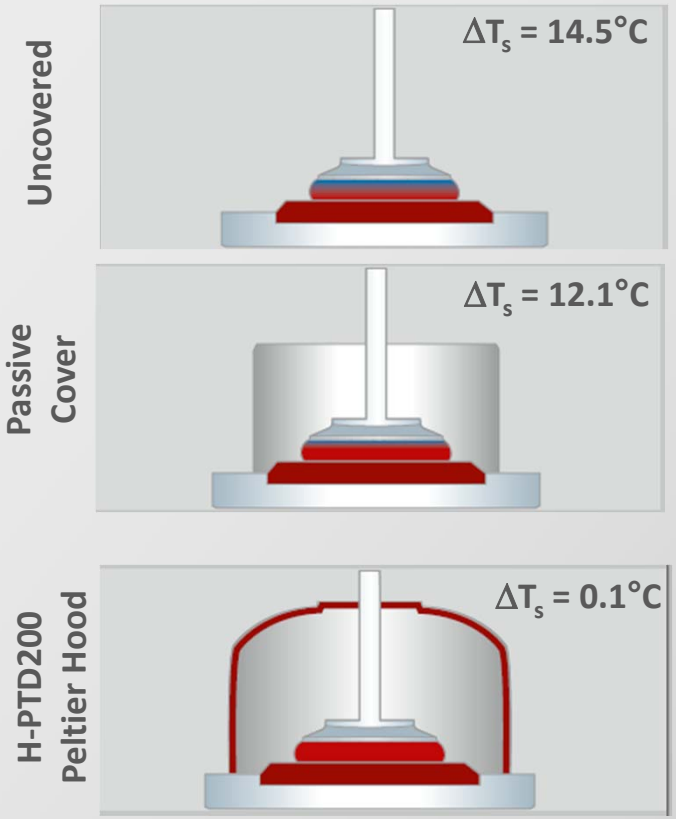
- Right behind Drive Control in importance is Quality of Temperature Control.
- The three most important aspects of rheometer temperature control are:
  - The temperature control systems should be engineered so that the sample does not have temperature gradients.
  - The sample temperature can be measured directly and a simple automatic calibration routine conducted to insure that when a temperature of 100°C is commanded, the rheometer understands to “go to a chamber temperature that results in a sample temperature of 100°C AND that the sample temperature is used as the basis for the temperature control and NOT the upper or lower plate temperature. The sample temperature is what is important, not the plate temperatures.
  - Some automated means for check of thermal equilibrium within the sample be possible which permits test start only after equilibrium is reached.
- Rheology is so highly impacted by temperature that the most precise control of the sample temperature is required.

Temperature Quality: Temperature Gradients

- In 1999 Anton Paar engineers developed sensor systems to permit study of temperature within several locations of the sample when placed in a standard rheometer chamber.
- They found that when using a Peltier lower plate, even if using a passive cover, when testing at 100°C the sample contained thermal gradients on the order of **12°C** within the gap.
- In the cylinder systems, they found that unless the chamber was specifically designed to prevent gradients, the sample had gradients within the gap on order of **14°C**.
- In the convection (forced air) ovens, they found that a "heat gun" design with heated air coming from only one direction resulted in sample gradients between plates up to 5°C and in torsion fixtures much greater.
- These findings lead to the Patented H-PTD200 Peltier Hood for use with Peltier lower plate chambers, the Patented C-PTD200 Peltier Cylinder Chamber and the CTD ovens.
- The sensor system resulted in the first every fully automatic temperature calibration routine available for commercial rheometers.

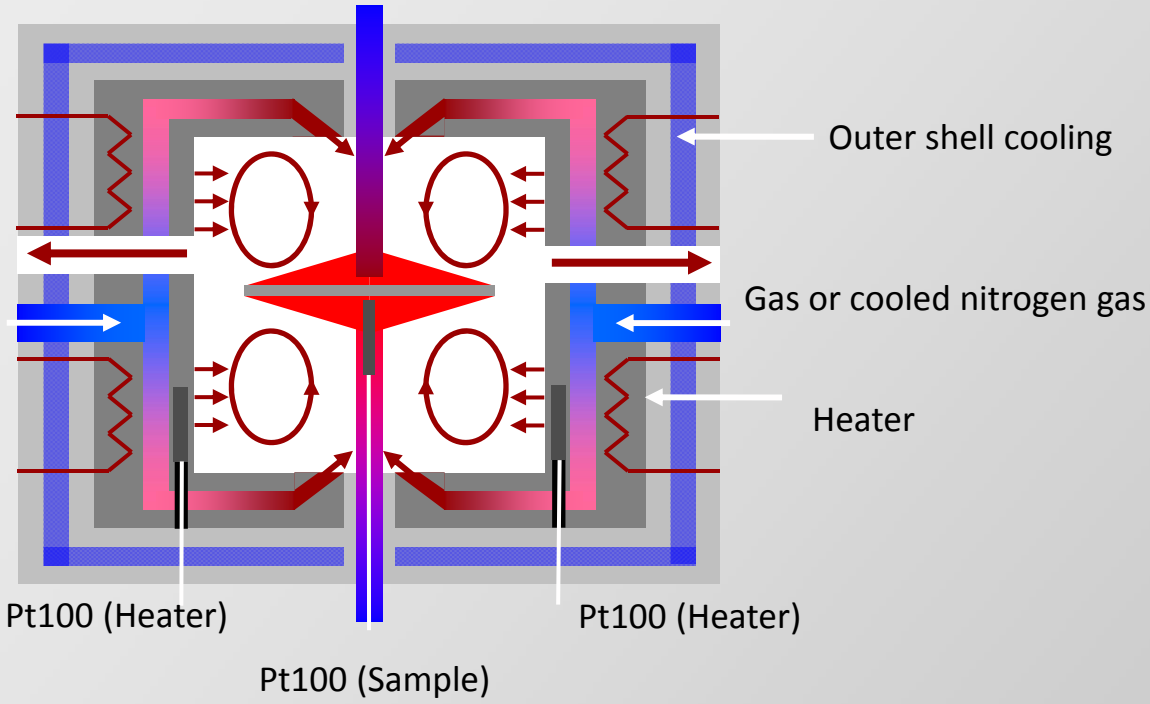


Temperature Quality: Consistency Across the Sample Matters



- Patented active Peltier control of upper and lower plate
- Perfectly symmetric percolation of thermostated dry purge gas into hood with adjustable flow rate results in no loss of low end torque range while also preventing icing at sub-zero range
- Solvent channel on hood top coupled with clip on solvent traps form complete vapor barrier from ambient

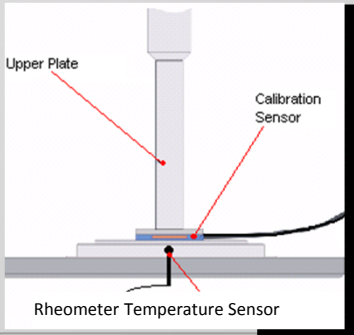
Temperature Quality: Great Engineering is Required

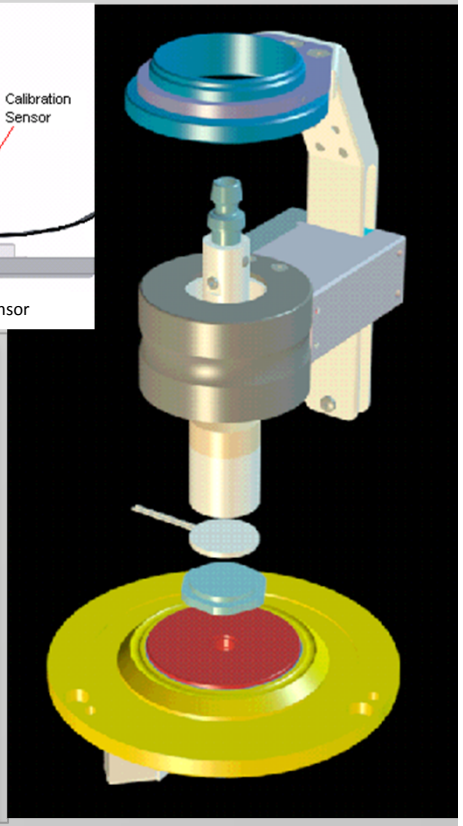


- Heat transfer by convection and radiation
- Symmetric design for no gradients
- Sample temperature measured at sample…not in the air far from sample
- Integrated power supply and controller, i.e. no external boxes required
- Low LN2 consumption for cooling
- Safety first – automatic shut off when open, shell cooling

Temperature Quality: Calibration - Sample Temperature Matters

- Temperature calibration eliminates the temperature offset between the rheometer temperature sensor and the sample between the plates
- The GMH 3710 thermometer and calibration sensor provide a traceable unit and fully automatic, unassisted temperature calibration
- A calibration report is provided which documents the offset determined at each calibrated temperature and the exact devices used during the calibration





Temperature Calibration Report
==========

Date, time : 7/25/2013, 8:39:11 AM
Application : RHEOPLUS/32 Multi6 V3.61 21005973-33033

Temperature Calibration
==========

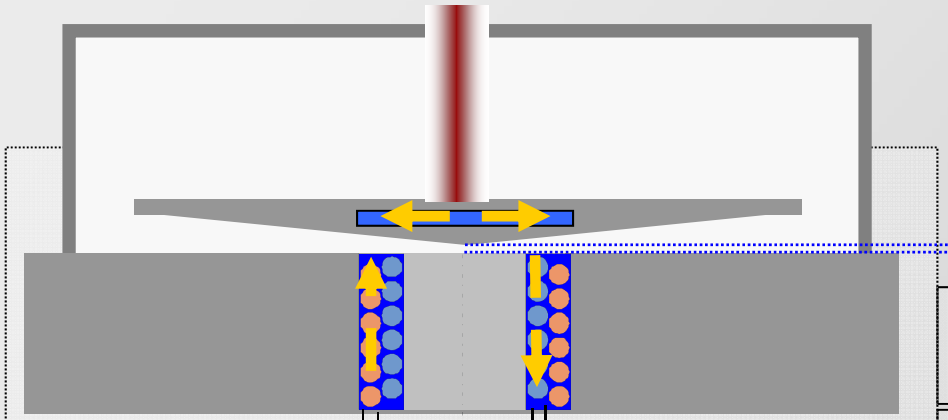
Remark : Full AASHTO T315 Temperature Range
Instrument : SmartPave102 SN81330881
Set Value : P-PTD200+H-PTD120-SN81336296-81336258
Display : P-PTD200+H-PTD120-SN81336296-81336258
Output List : (4.00;7.00;10.00;13.00;16.00;19.00;22.00;28.00;31.00;34.00
40.00;46.00;52.00;58.00;64.00;67.00;70.00;76.00;82.00;88.00;25.00)°C
Settings : Tolerance +/- 0.03°C, Test Time 600s, Mean Time 180s
Start : 7/24/2013, 5:12:27 PM
Duration : 6:43:57

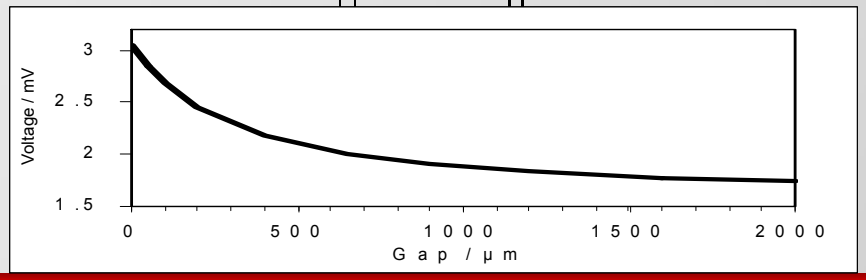
Time	: Set Value	Display	Calib.Probe	Unit
0:23:07	: 4.00	4.00	4.13	°C
0:39:31	: 7.00	7.00	7.09	°C
0:55:36	: 10.00	10.00	10.06	°C
1:11:05	: 13.00	13.00	13.03	°C

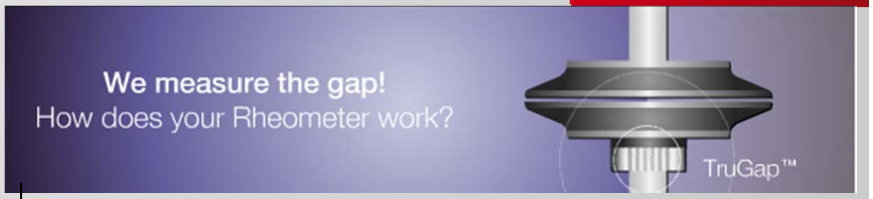
Important Rheometer Characteristics

Gap Accuracy

Gap Accuracy: How Does TruGap™ Work?







Typical 50µm cone/plate gap

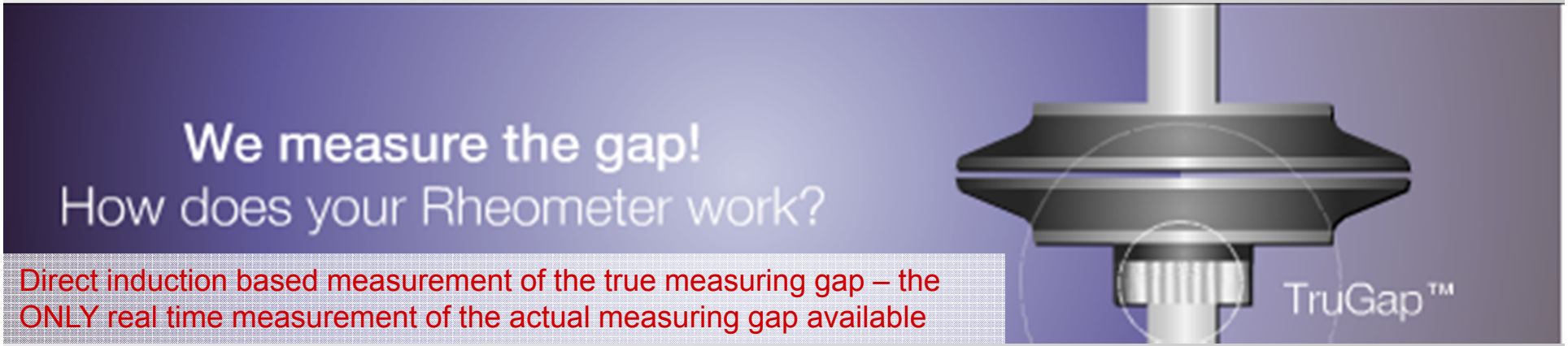
Primary coil: constant applied current I = const.

Secondary coil: voltage signal (U) depends on the gap distance

- Larger gap = less induction = lower voltage induced
- Smaller gap = higher voltage induced

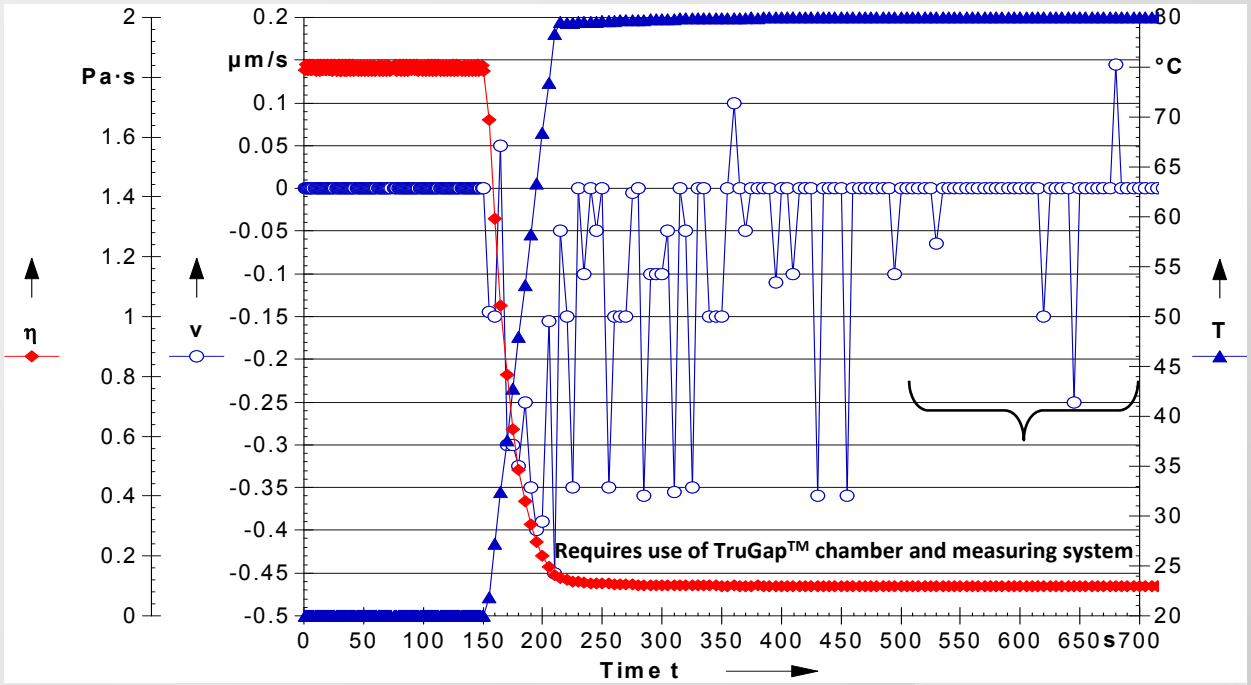
All calibration data stored in ToolMaster™

Gap Accuracy: TruGap™ (US Patent 6,499,336)

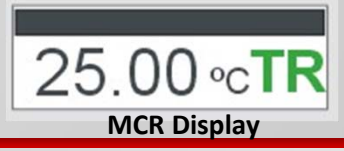


- Gap accuracy of + / - 0.6 µm from -150°C to 280°C
- No more waiting for temperature equilibration during zero gap setting
- No more additional Zero-Gap
- No more gap errors due to changes in room temperature
- TruGap is a direct 'in position' gap reading and active gap control
- Static gap correction for thermal expansion is no longer needed the true gap is measured immediately
- Accurate gap even under non-isothermal conditions

Gap Accuracy: T-Ready™ Automatic Detection of Thermal Equilibrium



Under 3 µm change within 200 s → T-Ready™

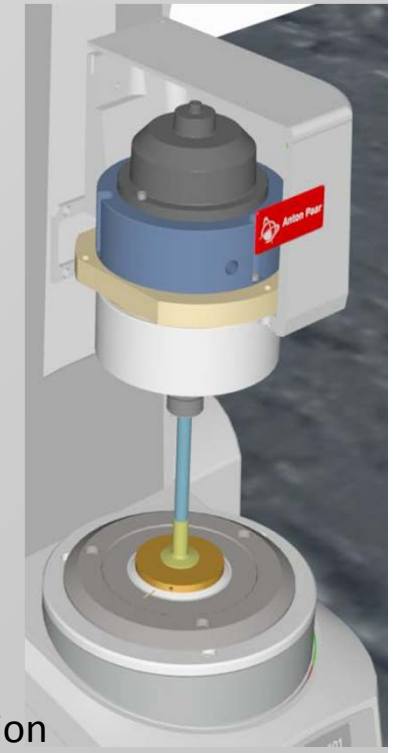


MCR Display

- Patented T-Ready™ ensures the desired **sample temperature** (US Patent 8,904,852)
- Reduces and optimizes waiting times
- Uses the TruGap™ hardware and functionality to detect sample temperature equilibrium
- T-Ready™ is clearly displayed on the color display signaling start of test
- RheoCompass permits T-Ready as criteria for autostart of test
- Removes all guess work from thermal equilibrium time

Gap Accuracy: AGC Automatic Gap Compensation – Standard in All MCRxx2s

- MCR rheometers operated without TruGap™ and all other rheometers on the market use AGC for gap compensation
- Zero gap determined by “touchdown”
- Gap setting based on high precision stepper motor
- Static* thermal expansion of :
  - Geometry shaft (*) after temperature equilibration
  - Expansion is compensated based on temperature signal(s) in chamber
- It is not possible to compensate for the thermal expansion of
  - Geometry shaft -> during the temperature equilibration phase
  - Accessory
  - Rheometer frame
- Example:
  - AGC = 1.0 µm /K = thermal expansion coefficient
  - T increases from 0°C to 100°C
  - Measuring system shaft length is 100.1 mm instead of 100mm
  - Head is lifted by 100µm to compensate for the calculated thermal expansion



Important Rheometer Characteristics

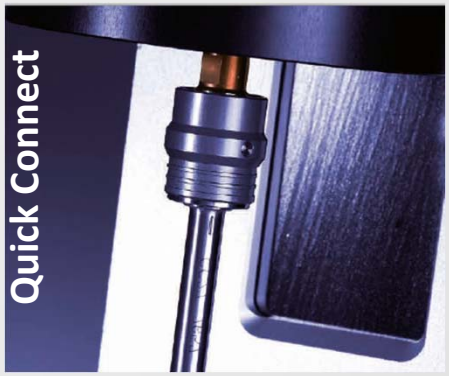
Error Proofing

Error Proofing

- Bits of error here and there can add up to big errors in data
- Beyond having the best motor control and best temperature control, the best rheometers have the most build-in error proofing to ensure the highest quality data and safest operation of the rheometer
  - MCR High Precision Quick Connect Motor Coupling
  - ToolMaster™ Patented Intelligent Auto-Recognition System for Measuring Systems and Chambers
  - TruGap™ Patented Real Time Gap Measurement
  - T-Ready™ Patented Automatic Check for Thermal Equilibrium
  - Keyed plugs/sockets make set up simple and error free every time
- Reduce mistakes, prevent errors, save time, save money

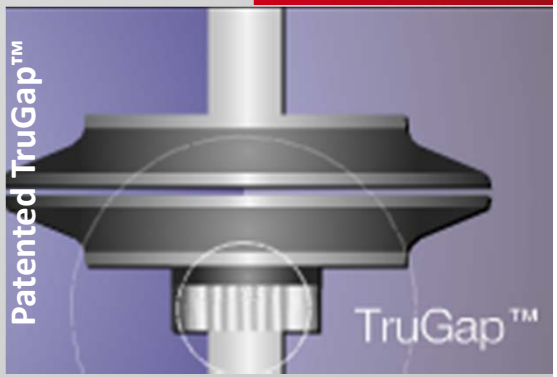
Error Proofing: Prevent Mistakes, Save Time and Save Money

Anton Paar



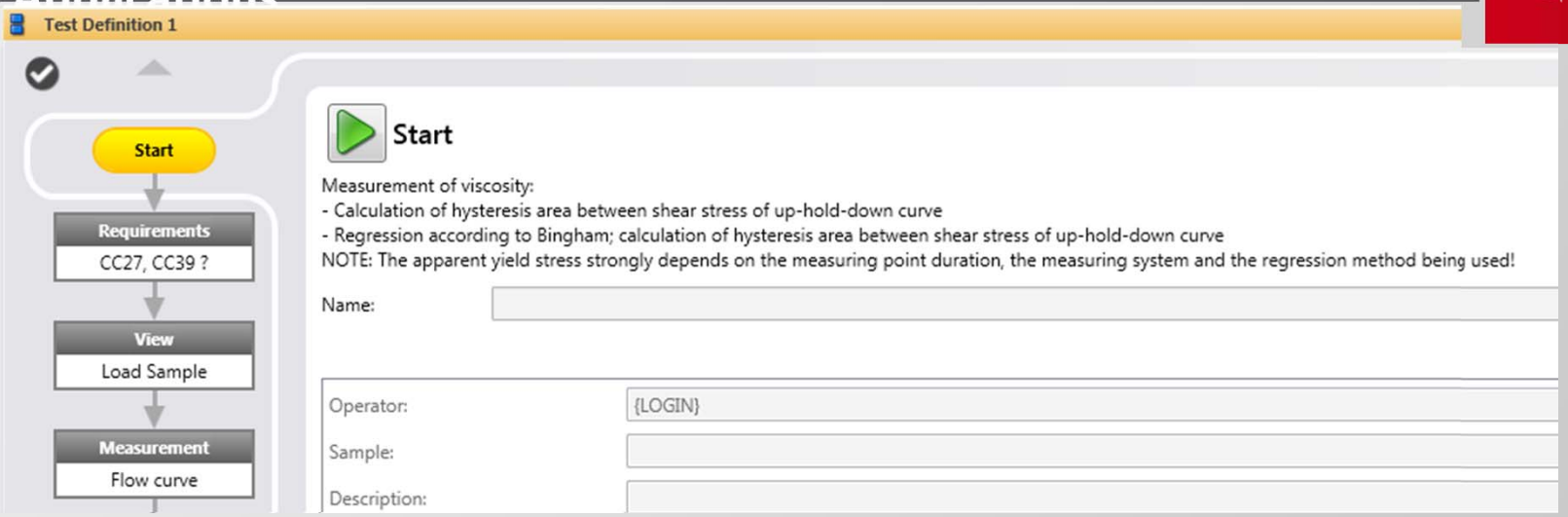
- Precision machined
- Single hand operation
- No zero gap needed after removal for cleaning
- No tools needed
- Perfect alignment every time

- Intelligent auto configuration
- Auto calculation of real geometry factors
- Traceable identification of measuring system and chamber
- Error free documentation
- Compatibility check between chamber and measuring system
- Keyed plugs, no wrong connections



- No gap errors
- Automatic detection of thermal equilibrium
- No zero gap between runs

Error Proofing: RheoCompass™ Software Smart Applications



- Pre-configured test settings for optimal data quality
- Easy to follow action blocks
- Applications can be locked from editing
- Multiple levels of log in accounts to limit access within software
- Automatic check for steady state (rotational testing)
- Notification when outside instrument range and when inertial effects may be contributing

Important Rheometer Characteristics

Future Proofing

MCR's Speak a Common Language

- Duality Between R&D and QC
  - All MCR models share chambers, measuring systems, software, and ease-of -use features
  - Handling and operation of all MCR models are the same
- Generational Compatibility
  - Chambers and measuring systems from MCR xx0 and MCR xx1 series rheometers are compatible with the MCR xx2 rheometers
  - Most MCR xx2 rheometer standard chambers are compatible with MCR xx0 and MCR xx2 rheometers
  - Compatibility from generation to generation is a core belief within Anton Paar's product development team
- Modularity is the MCR's first name
  - No other rheometer system in the world offers the breadth of testing capabilities, chambers, and accessories that the MCR series does

The Most Advanced, Innovative, and Complete Rheometer Portfolio

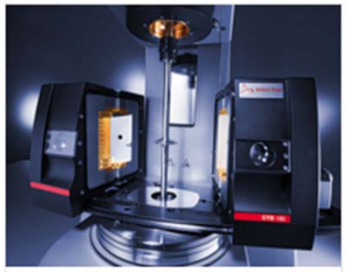
Anton Paar

RheolabQC	MCR 72 and 92	MCR 102, 302, SmartPave	MCR 502 TwinDrive™ Ready	MCR 702 TwinDrive™
Manual stand	Automatic stand	Normal force	TwinDrive™ Ready	TwinDrive™
ROT	ROT & OSC	nNm – 230 mNm	Isolign flange	
CC / DG / ST	PP / CP / CC / DG / ST	TruGap	Higher stand	
LTD / PTD	LTD / PTD / ETD	CTD		
Stand alone or PC+RheoCompass	PC+RheoCompass			





The MCR Series – Unrivaled Versatility



MCR 702 TwinDrive™

MCR 502 TDR, MCR 502 S, MCR 302, MCR 102

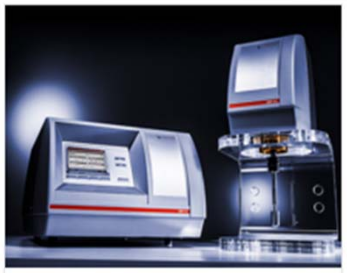
MCR 92 and MCR 72

MCR 302 WSP Without Supporting Plate

HTR High Throughput Rheometer

SmartPave 102 Asphalt Rheometer

FRS 1600 Furnace Rheometer



DSR 502 Rheometer Measuring Head

MCR 302 WESP With Exposed Supporting Plate

HTR Light

Additional Chambers and Accessories (Partial List)

Structural Analysis Simultaneous to Rheological Measurement
Microscopy- Light, Polarized, Fluorescence, Stagnation Plane
SALS, SAXS, SANS, WAXS Birefringence, Dichroism
Particle Imaging Velocimetry (PIV)
Dielectric Spectroscopy

Additional Parameter Settings Simultaneous to Rheological Measurement
Pressure
Magnetic Field Electric Field
UV Exposure
Humidity
Vacuum (Immobilization Kinetics)

Extended Material Characterization Going Beyond Rheology
Dynamic Mechanical Analysis (DMA)
Extensional Rheology
Large Particle Rheology
Starch Rheology
Squeeze, Tack, Penetration
Tribology Friction, Wear, Lubrication
Powder Flow and Fluidization

Conclusion

- Rheology provides a means to characterize the flow and viscoelastic properties of materials ranging from low viscosity liquids to rigid solids.
- No one rheological test can provide the full scope of a material's behavior thus the appropriate test for the desired information should be chosen.
- A research rheometer also provides a means to characterize other mechanical properties such as tack, tribology, tensile properties, optical monitoring via microscopy, and powder flow characteristics.

Information

References

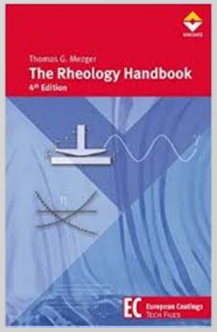
About Us

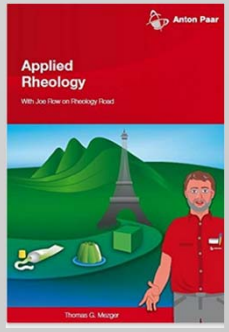
Works Cited

- Iona, Urma. “elasticity (TV set art) (3)”. Web blog post. IOANA.blog. IONA. 02 Mar. 2011. Web. 22 Feb. 2016.
- "Lesson 14 Mechanical Properties of Materials." Lesson 14 Mechanical Properties of Materials. Web. 22 Feb. 2016.
- Mezger, Thomas G. Applied Rheology with Joe Flow on the Rheology Road. Anton Paar GmbH, 2015. Print.
- Mezger, Thomas G. The Rheology Handbook: For Users of Rotational and Oscillatory Rheometers. Hannover: Vincentz Network, 2006. Print.
- Rao, Anandha. Rheology of Fluids, Semisolid, and Solid Foods: Principles and Applications. Springer US, 2015. Print.
- Wikipedia. Wikimedia Foundation. Web. 22 Feb. 2016.

Anton Paar Professional Development Resources

- Recommended Reading
  - The Rheology Handbook by Thomas Mezger
  - Applied Rheology by Thomas Mezger
- Workshops, Seminars, and Webinars
  - Rheology Boot Camp MCR User Courses offered several times at year at Anton Paar USA in Ashland, VA and Houston, TX.
  - Introduction to Rheology Seminars offered throughout the year at various locations throughout the U.S.
  - Industry specific workshops offered across the U.S. (asphalt, paints/coatings, foods, polymers)
  - Beginner and Advanced RheoCompass™ Software training
  - http://www.anton-paar.com/us-en/events/seminars/
- Educational webinars offered throughout the year
  - http://www.anton-paar.com/us-en/events/webinars/
- Learn at your desk with our eLearning Courses
  - http://www.anton-paar.com/us-en/footer/mediagallery/category/5/
- Free unlimited customer support by phone and email for the lifetime of Anton Paar rheometers



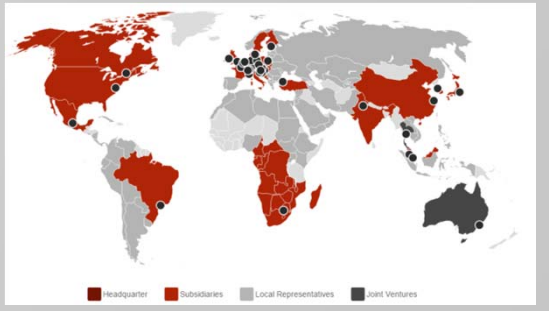


Anton Paar

A Bit About Our Company

A little about Anton Paar…

- Mr. Anton Paar created our company in 1922 in Graz, Austria.
- Decedents of Anton Paar manage the company today.
- In 2003, the decedents of Anton Paar created The Santner Foundation and gave ownership of the company to this charitable foundation.
- So…Anton Paar will never be bought up by the big lab instrumentation companies and the vision of the company will remain focused on making the highest quality instrumentation in the world while maintaining our core belief in “people first”.
- A fixed percentage of annual sales are by charter divided among several charities with focus on helping those with drug and alcohol addictions.
- With sustained annual growth rates in the double digits, Anton Paar is a strong, well-run private company.



And now a little about Anton Paar USA …

- Established in 1986 with headquarters in Ashland, VA.
- Anton Paar USA is responsible for sales, support, and service of Anton Paar products in the USA.
- We have enjoyed double digit sales growth for the past ten years and, in accordance with our fundamental principles, have grown headcount every year since 2001 and have never had a layoff.
- We believe in maintaining a highly technical, specialist sales force. Each division has as their sales representatives a scientist with expertise in the products of that division.
- In addition to your local sales representative, Anton Paar USA employs a staff of application experts whose purpose is to ensure you get the best use of your instrument over its lifespan.
- Regional facilities in Houston (est. 2014) and Los Angeles (late 2016) for demonstrations, training courses, and repair service.

Thank You for Your Attention!

Anton Paar

Great People :: Great Instruments

www.anton-paar.com