Introduction Rheology

Material Science for Soft Solids & Liquids

Anamet Seminar, 2019

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Agenda

Brno Seminar - Rheology

- Wednesday
  - 13:30 -14:50 Kinexus
  - 14:50-15:00 Break
  - 15:00-15:30 Rosand
  - 16:00-17:00 Complimentary techniques

- Thursday
  - 10:00-12:00 Kinexus/rSpace workshop
    - Hands on the machines, method development for various samples, sample data interpretation
  - 12:00-13:30 Closing remarks & Lunch
  - 13:30-14:30 Remaining, 1:1 Q&A – Booked sessions

Presentation Overview

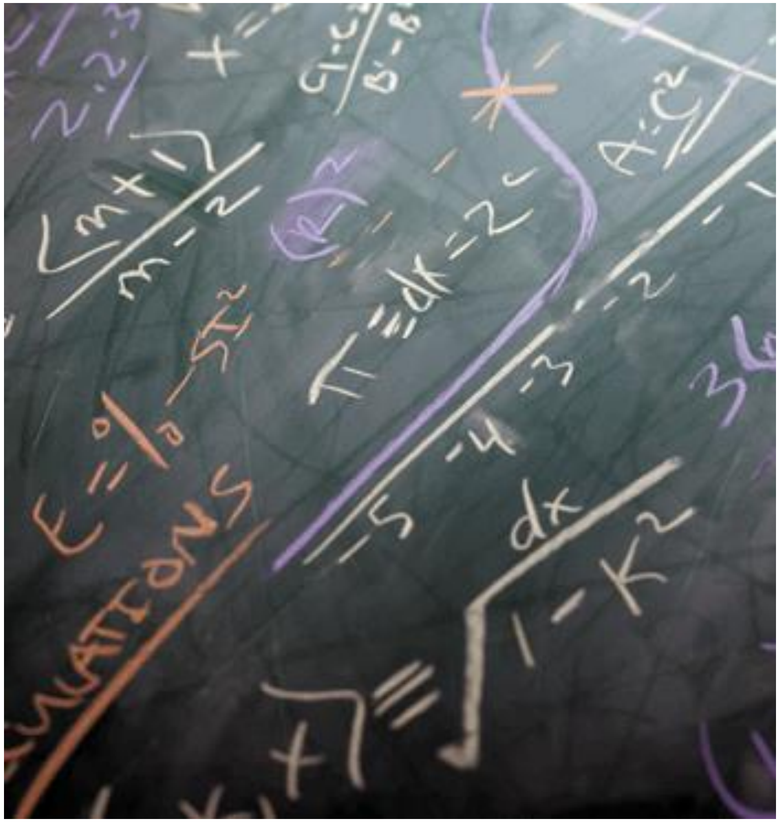
- Overview and Introduction
  - Basic rheology theory
  - How a rheometer works
- Viscosity Measurements
  - Viscosity flow curves
  - Yield stress, Thixotropy
- Viscoelastic Measurements
  - Amplitude sweep
  - Frequency sweep

OVERVIEW AND INTRODUCTION

What is rheology…?

- The technical definition is:

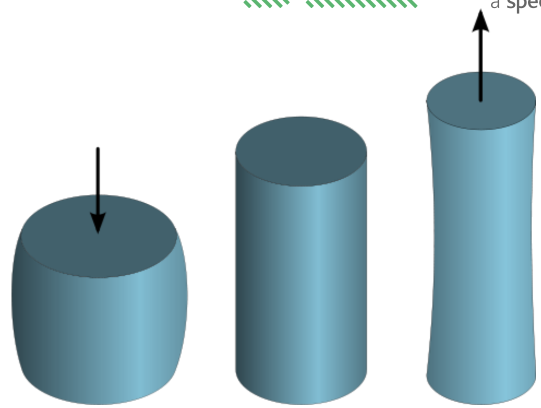
“The science of deformation and flow”

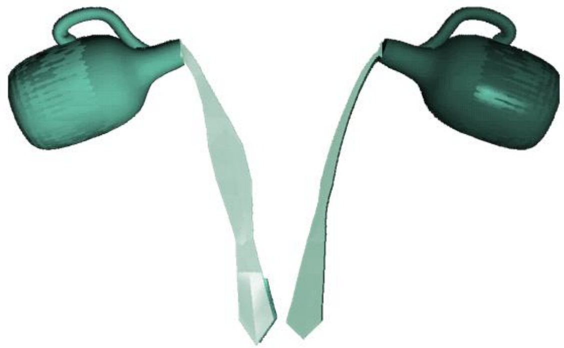


- **But**, what does this **really** mean?

Solids & Liquids

Solids DEFORM when stressed





Liquids FLOW when stressed

- Complex materials can show both SOLID and LIQUID like behaviour.
- Rheology primarily describes the behaviour of these complex materials

Rheology Testing

- Typical testing in rheology splits measurements into *deformation* (oscillation) and *flow* (viscosity)

"The science of *deformation* and *flow*"

DEFORMATION

- Quantifies **VISCOELASTICITY**
- How does a sample behave *before* a sample flows…?
- Predicts sample properties

- Sample classification
- Sample stability – will it settle?

- Types of experiment:
  - Oscillation
  - Creep, Relaxation

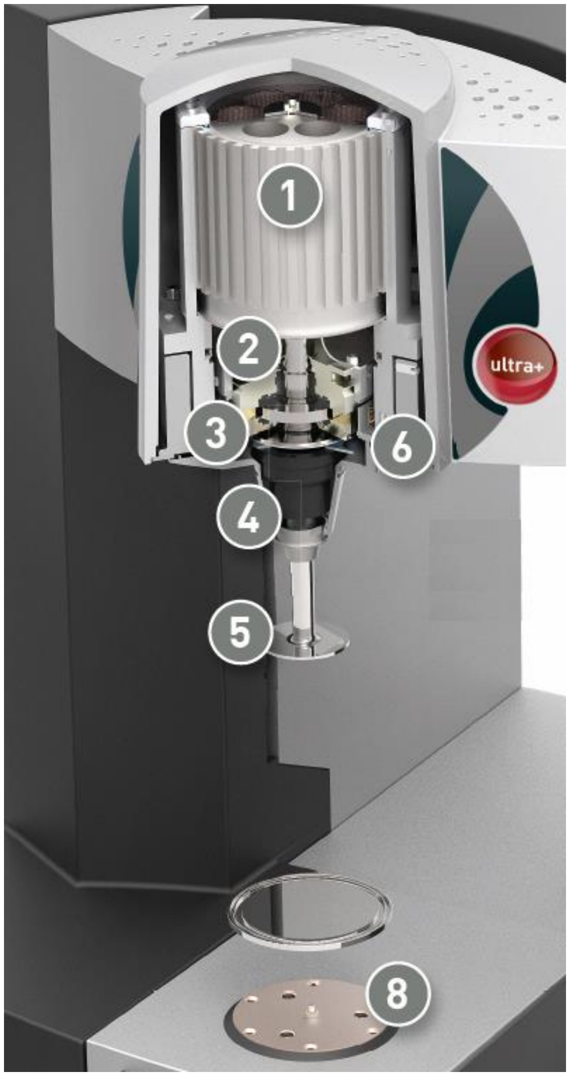
FLOW

- Measures the **VISCOSITY** of a sample
- Mimics typical processing conditions
- The resistance to flow

- How thick is a paint sample
- Will the sample be pumped?

- Types of experiment:
  - Viscometry

Rheometer Principles –Measurement



1. Drag Cup Motor = Stress
   - Directly applies a torque (which is a stress in rheological terms)
2. Air Bearing
   - Enable low torque measurements well beyond viscometer range
3. Position Sensor = Shear Rate (Strain)
   - Independently measures the resultant movement which is determined by the viscosity of the sample. The rheometer literally monitors the displacement in time to convert to a shear rate
   - In controlled rate, the speed (shear rate) is applied directly and the stress required is recorded

$$Viscosity = \frac{Shear\,Stress}{Shear\,Rate}$$

Controlled **Stress** & Controlled **Rate/Strain** are possible

4. Geometry Recognition & Chuck
5. Measurement Geometry / Measuring System
6. Strain Gauge = Normal Force & Automatic Gap
8. Temperature Control

Rheometer Principles

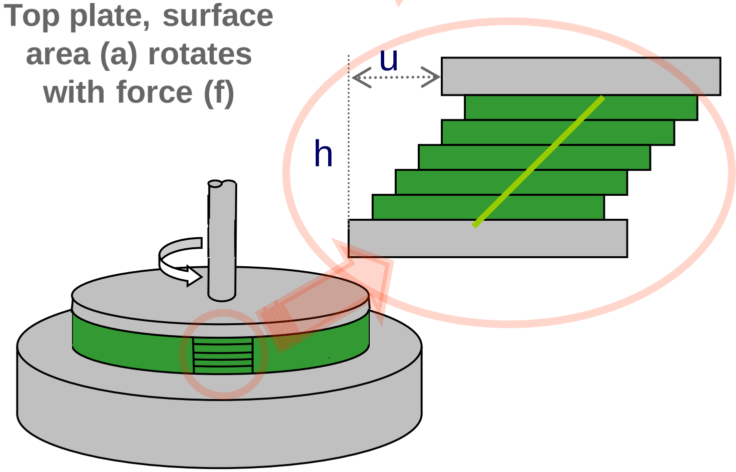
- Rheology testing involves some standard variables:
  - **Shear stress: force (f or p) per area (a)**
  - **Shear strain: displacement (u) divided by height (h)**
  - **Shear (strain) rate: change in strain with time**

- A sample sandwiched between two plates experiences a strain or shear rate depending on the type of stress applied

- The sample experiences a shear profile, and from this typical material properties can be calculated

$$\text{Viscosity}\,(\eta) = \frac{\text{Shear Stress}}{\text{Shear Rate}} = \frac{\sigma}{\dot{\gamma}}$$

$$\text{Modulus}\,(G^*) = \frac{\text{Shear Stress}}{\text{Shear Strain}} = \frac{\sigma}{\gamma}$$



Why different measuring systems?

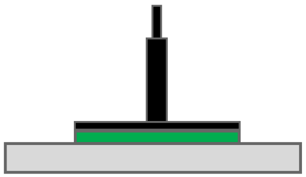
- **A rheometer has a finite range of torque (twisting force)**
  - For thick / tough samples we need to focus this force on a small area – a small plate (PP20)
  - For weak sample we need to spread this force on a large area – a large plate (PP50, PP60)

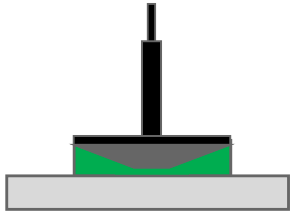
- **Similarly, a rheometer has a finite movement range**
  - Samples rotate more with a larger gap for stiff materials

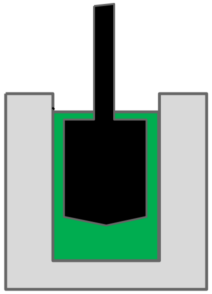
Typical measuring systems

- The most common measuring systems are:

  - Parallel plate
    - First choice for oscillation testing
      - Benefits of flexible gap (~0.5 – 2mm)
  - Cone and plate
    - First choice for viscosity testing
      - Absolute viscosity from uniform shear rate
      - Fixed, small “truncation” gap (~0.03 – 0.15mm)
  - Cup and bobs
    - Legacy/specialist testing
      - Low viscosity at low shear rates
      - Larger dispersed particle testing
      - Volatile sample testing







Special Measuring Systems

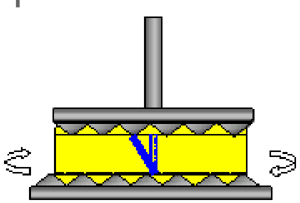
- Some sample types do not lend themselves to be measured using conventional tools and require a modified interface. Here are some common examples:

Vane Tools

- **Reduce wall slip** (e.g. slurries)
- **Measurement of delicate structures** (e.g. yield stress determination for foams and soft solids)

Serrated & roughened surfaces

- **Reduce slip effects** (e.g. concentrated dispersions & semi-solids)



VISCOSITY MEASUREMENTS

Viscosity

- Introduction to Viscosity
  - Defining shear stress and shear rate
  - Viscometers and rheometers
  - Identifying the appropriate shear rate
  - Shear thinning and why it occurs
- Viscosity Measurements
  - Viscosity flow curves
  - Yield stress
  - Thixotropy

Rheology Testing

- Typical testing in rheology splits measurements into *deformation* (oscillation) and *flow* (viscosity)

"The science of *deformation* and *flow*"

DEFORMATION

- Quantifies **VISCOELASTICITY**
- How does a sample behave *before* a sample flows…?
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- Sample classification
- Sample stability – will it settle?

- Types of experiment:
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FLOW

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- Types of experiment:
  - Viscometry

What is Shear Rate?

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- Really just a deformation rate. How much work are we putting into the sample?

Process	Typical shear rate range (s^{-1})		
Reverse gravure	100,000	-	1,000,000
Roller coating	10,000	-	1,000,000
Spraying	10,000	-	100,000
Blade coating	1,000	-	100,000
Mixing/stirring	10	-	1,000
Brushing	10	-	1,000
Pumping	1	-	1,000
Extrusion	1	-	100
Curtain coating	1	-	100
Levelling	0.01	-	0.1
Sagging	0.001	-	0.1
Sedimentation	0.000001	-	0.0001

Faster processes, squeezing materials through smaller gaps

Measurable on a **Rosand** capillary rheometer

Measurable on a **Kinexus** rotational rheometer

Match Shear Rate to Processes…

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- Take an everyday simple example… hand cream

Storage

End use

SAMPLE STORAGE

Very low shear rates: ~ $0.001s^{-1}$

How stable is it, sample quality…

SAMPLE DELIVERY

Medium shear rates: $\sim 10s^{-1}$

Pumpability? Scoopability?

SAMPLE APPLICATION 1

Low shear rates: $\sim 1s^{-1}$

Flows away? Flows off hand?

SAMPLE APPLICATION 2

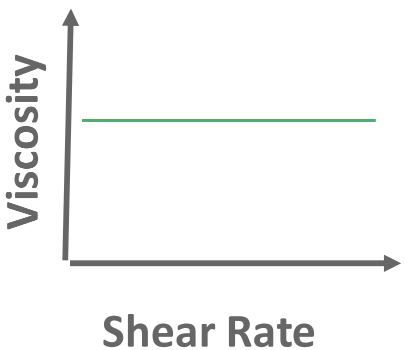
Higher shear rates: $\sim 100s^{-1}$

Too thick to spread? Nice feel?

Flow Curves

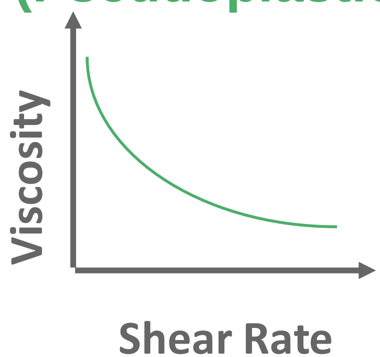
- Three general flow behaviours
  - Viscosity is a function of shear rate

Newtonian



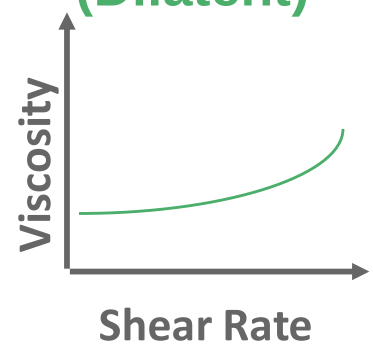
e.g. silicone oil, low concentration dispersions

Shear-Thinning (Pseudoplastic)



e.g. polymers, dispersions

Shear-Thickening (Dilatent)



e.g. cornflour, high solid content TiO_2

› Most, real, samples are shear thinning with Newtonian regions

› Viscosity testing is most powerful when it is used to simulate or mimic processes

Simple Flow

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Not Simple Flow

- Need to measure to understand behaviour
- Shear thickening

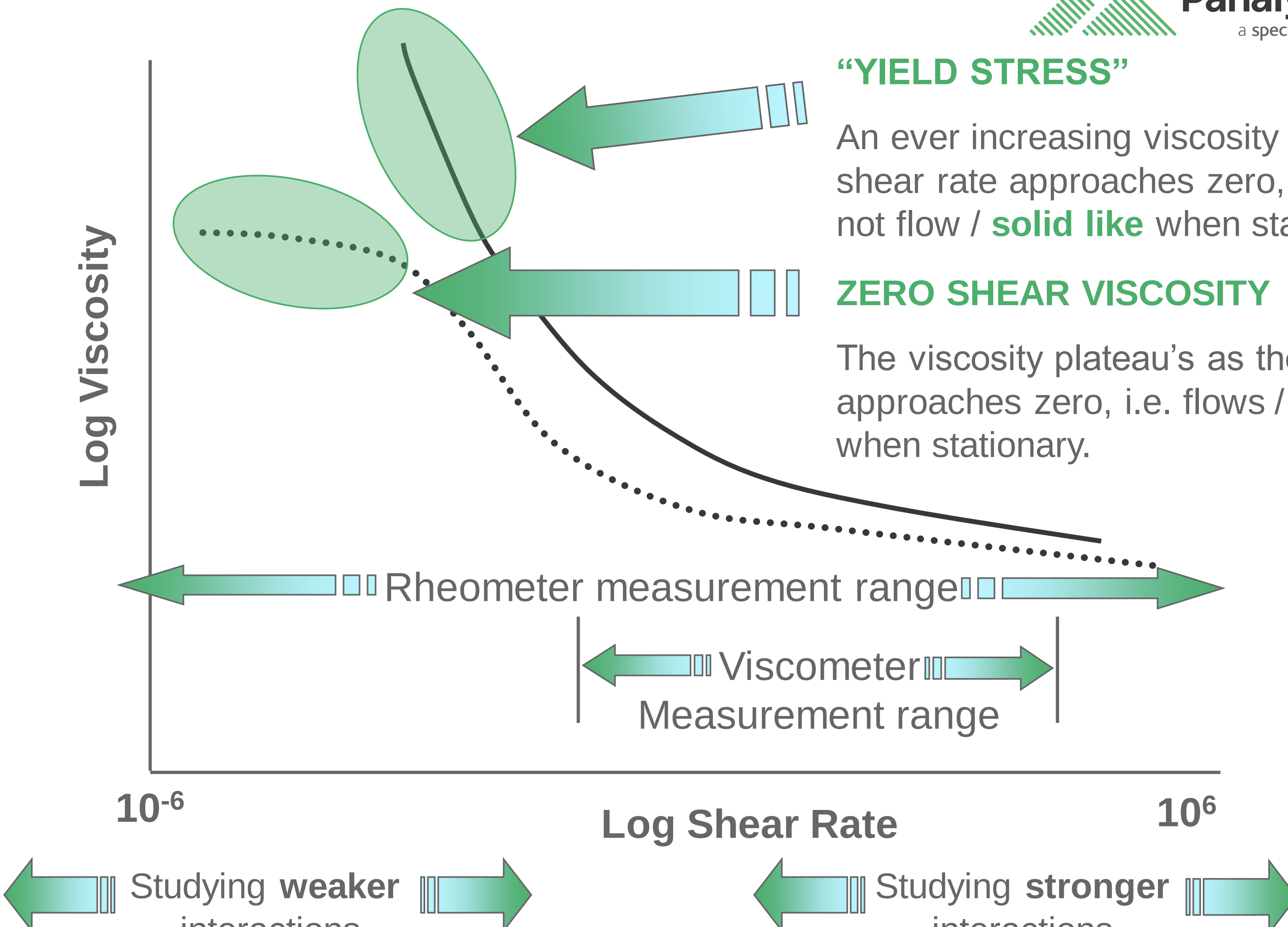
Flow Curve Measurements

"YIELD STRESS"

An ever increasing viscosity as the shear rate approaches zero, i.e. a does not flow / **solid like** when stationary.

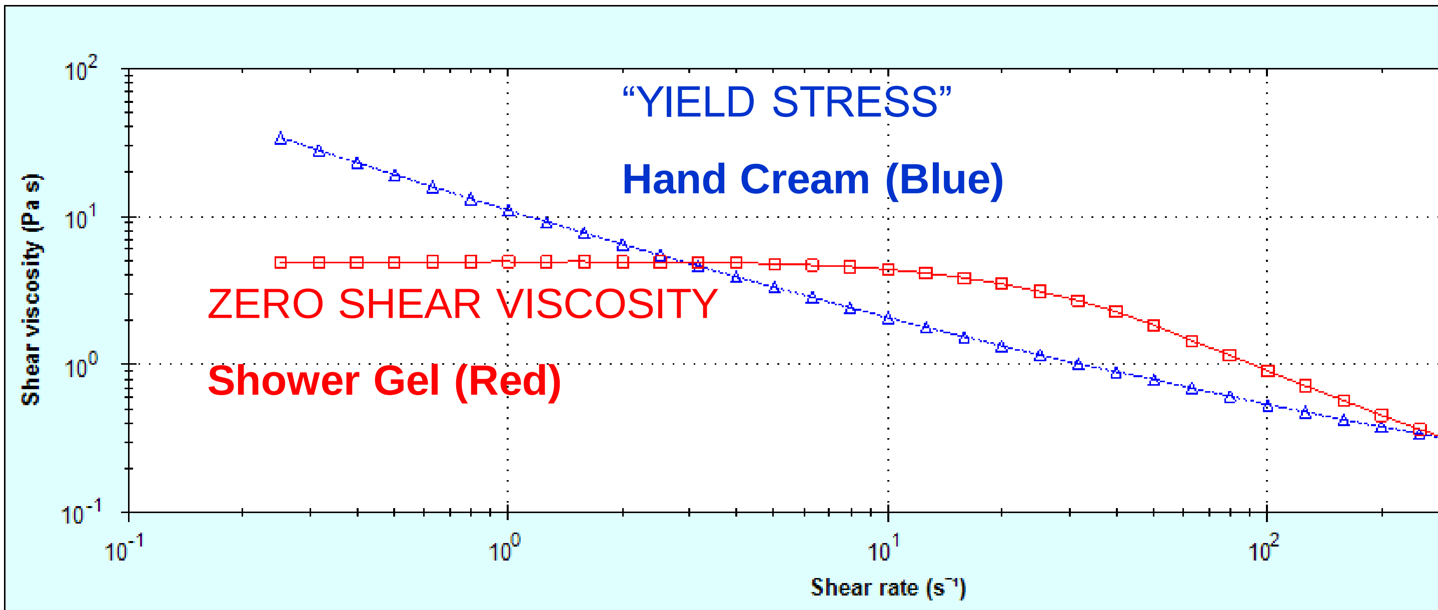
ZERO SHEAR VISCOSITY

The viscosity plateau's as the shear rate approaches zero, i.e. flows / **liquid like** when stationary.



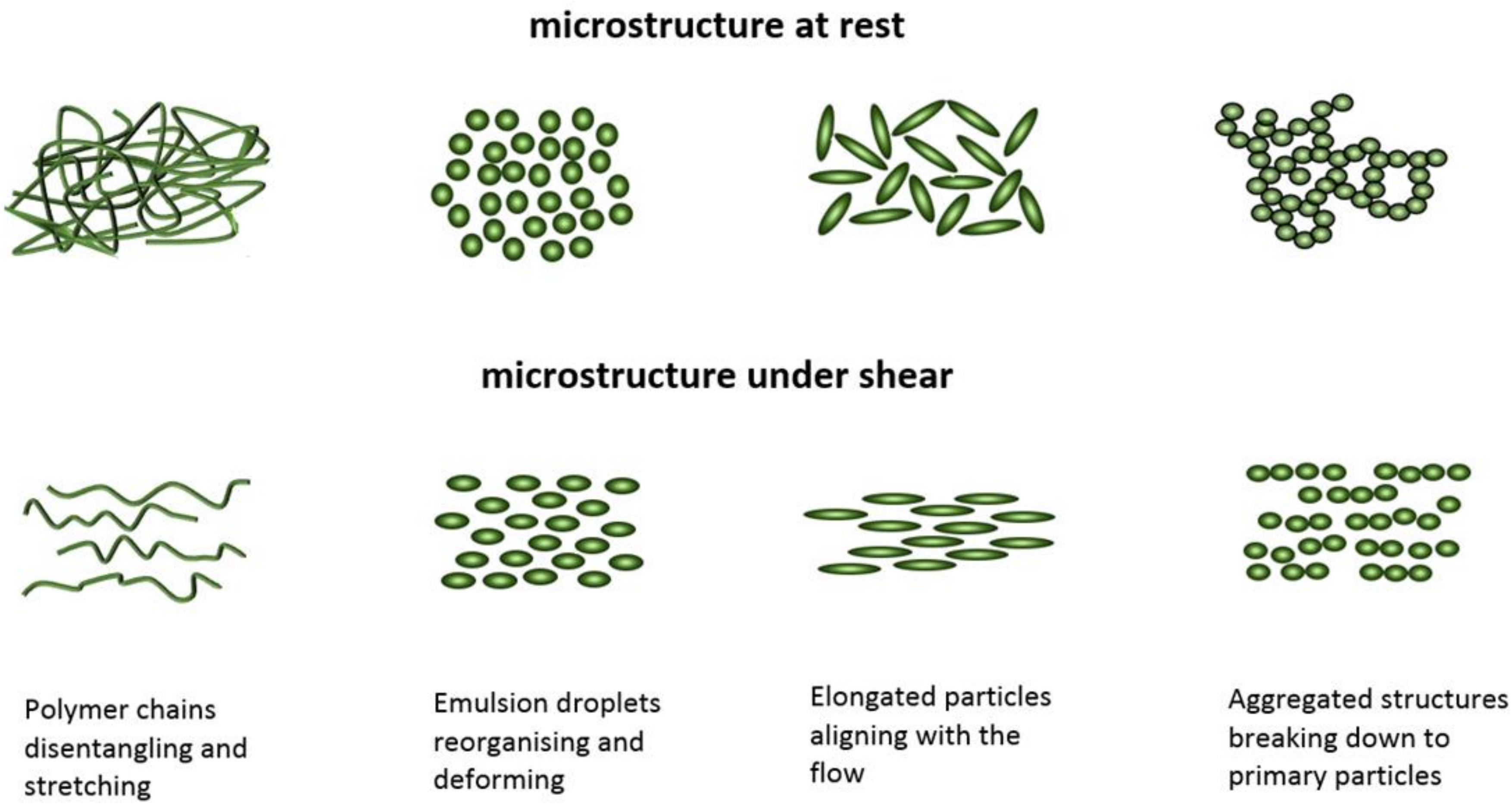
V001 – Flow Curve: Typical Results

- This tests shows how materials behave under different conditions, which are mimicked by shear rates



- Notice how it is **only at low shear rates** that shower gel and hand cream are different; they are different when in the bottle
- At higher shear rates, i.e. being applied, they have similar viscosities, as both are expected to behave the same under these conditions

Why does shear thinning occur?



YIELD STRESS

Yield Stress

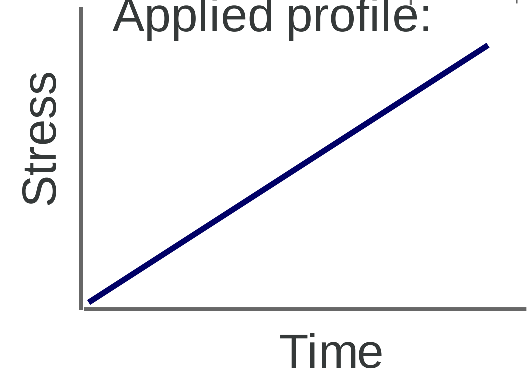
- Some samples require a certain stress until they flow – **a yield stress**
- A transition to go from solid to liquid

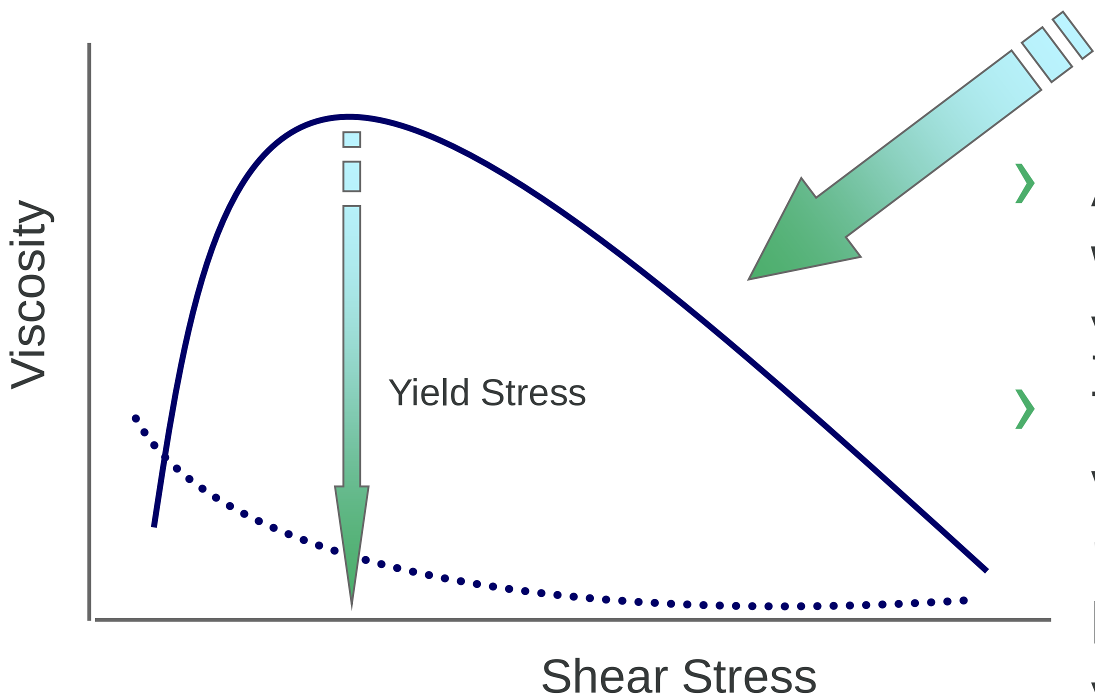
- For example:
  - Why toothpaste needs to be squeezed to get out of the tube but does not flow into bristles on tooth brush
  - Why Heinz tomato sauce needs a whack but still looks thick on the plate
  - Or why pumps have a start-up time

Yield Stress Measurement

- Apply an increasing rotational “squeeze”, i.e. shear stress to a material

Applied profile:

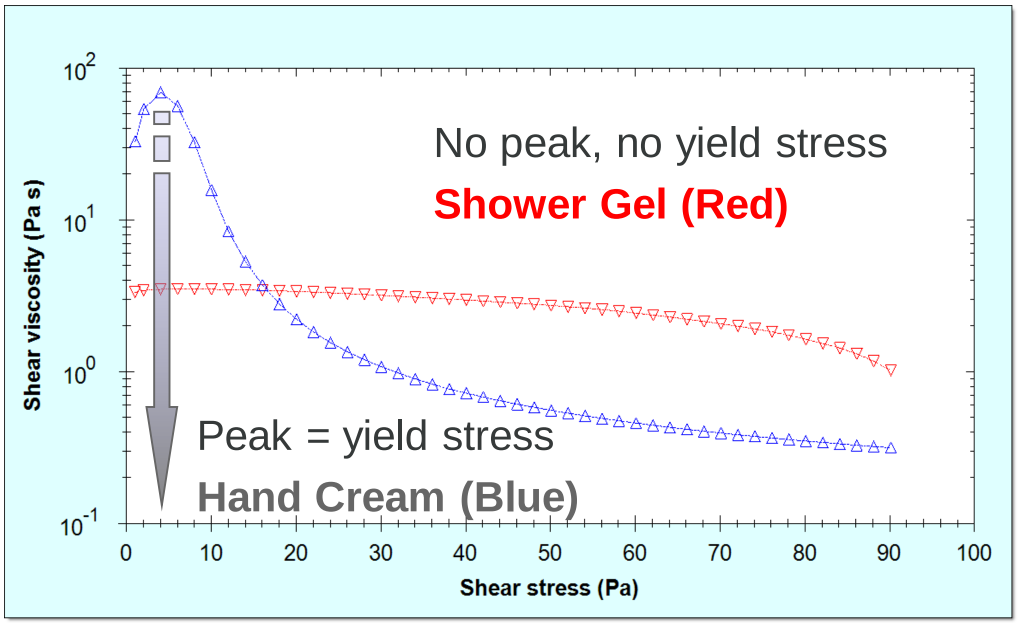


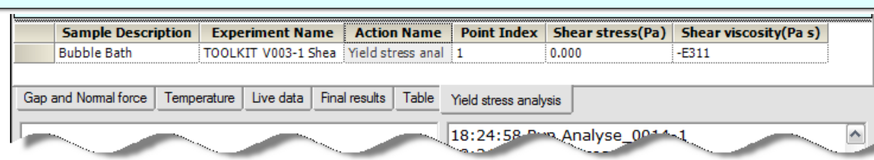


- A material with yield stress will stretch easily, until the yield point, then flow
- The stress at the peak in viscosity is the force required to go from solid like to liquid like, i.e. the yield stress
- No peak (dotted line), no force needed

V003 – Stress Ramp: Typical Results

- Typical results from a stress ramp experiment shows clear differences between a yield stress type material, and that of a zero shear viscosity system





Sample Description	Experiment Name	Action Name	Point Index	Shear stress(Pa)	Shear viscosity(Pa s)
Bubble Bath	TOOLKIT V003-1 Shea	Yield stress anal	1	0.000	-E311

› It is typical to only quantify the yield stress when a sample exhibits one in the flow curve

› rSpace can measure the peak in the data directly

THIXOTROPY

Thixotropy – Not Just Shear Thinning

- Viscosity is not only dependent on shear rate it is also **time dependent**
- Think of paint. Thick in the can when left in the shed for months, but thins when stirred
- However, it is thixotropic as it does not rebuild straight away on stopping the stirring

Store paint

Low shear rate

Appears "thick"

Stir paint

High shear rate

Becomes thinner, shear thinning.

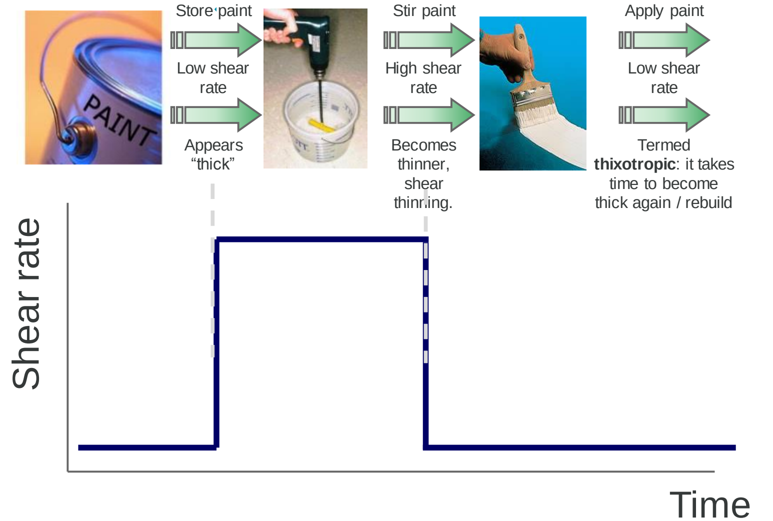
Apply paint

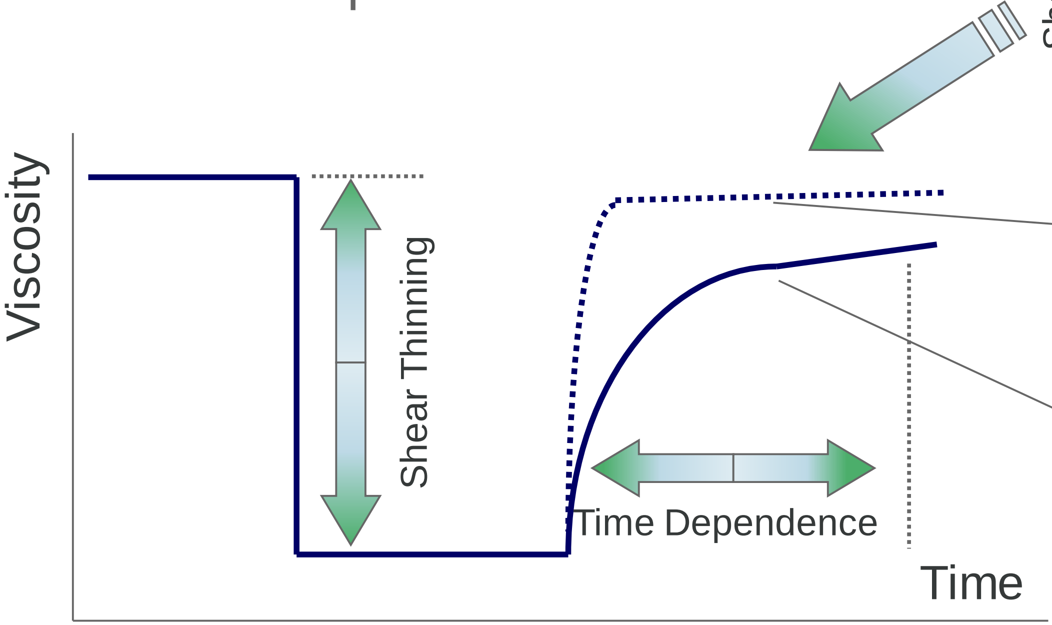
Low shear rate

Termed **thixotropic**: it takes time to become thick again / rebuild

V002 Thixotropic Measurement

- Apply a step sequence of shear rates. Simulate a process





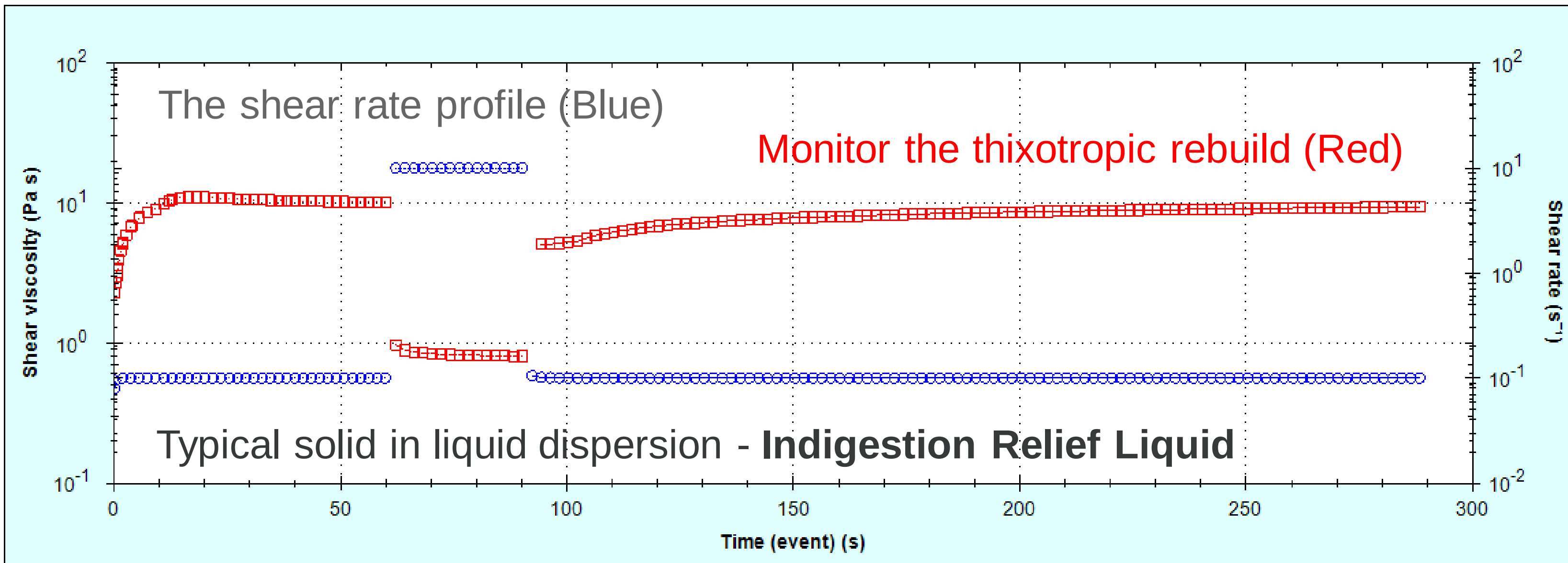
Bad paint – leaves brush marks
Rebuilds too thick too quickly

Good paint – leaves smooth finish
Rebuilds quite slowly. Enough time to allow ridges to smooth out

- A shear thinning material may be thixotropic
- However, a thixotropic material will always be shear thinning

V002 – Three Step Test: Typical Results

- This tests shows how a material **rebuilds** its structure **after a high shear** process



- The **longer** a material takes to rebuild, the **more thixotropic** the sample is
- Thixotropy also affects how long a sample takes to get to steady flow
- Thixotropy is not only an important material parameter. It is important to understand for **reproducible measurements**, i.e. repeat when fully rebuilt

VISCOELASTIC MEASUREMENTS

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Overview

- Viscoelastic Measurements
- Oscillation Amplitude Sweep
- Frequency Sweep
- What is a solid, and what is a liquid!

Rheology Testing

- We have looked at the first part of rheology… flow… now:

“The science of *deformation* and *flow*”

DEFORMATION

- Quantifies **VISCOELASTICITY**
- How does a sample behave *before* a sample flows…?
- Predicts sample properties

- Sample classification
- Sample stability – will it settle?

- Types of experiment:
  - **Oscillation**
  - **Creep, Relaxation**

FLOW

- Measures the **VISCOSITY** of a sample
- Mimics typical processing conditions
- The resistance to flow

- How thick is a paint sample
- Will the sample be pumped?

- Types of experiment:
  - **Viscometry**

Viscoelasticity

- All this means that most materials are not completely solid nor completely liquid like…
- They are **viscoelastic**

An example would be a paint:

› During storage it needs to behave like a **solid** to prevent sedimentation

› When painting it needs to behave like a **fluid** so that it flows in the bristles of the brush and can be evenly painted

Pitch Drop Experiment

- Timescale is also important in Rheology!

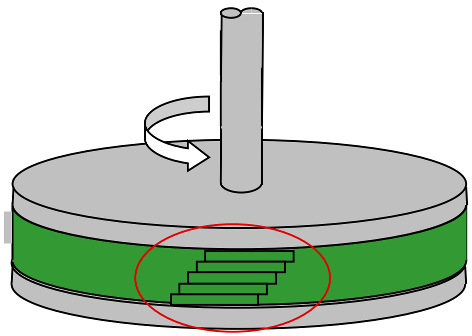
› Pitch behaves as a SOLID on short timescales (high frequency) – *shatters when hit with a hammer*

› ….but behaves like a LIQUID on long timescales (low frequency) – *drips at rate of 1 drop every 10 years*

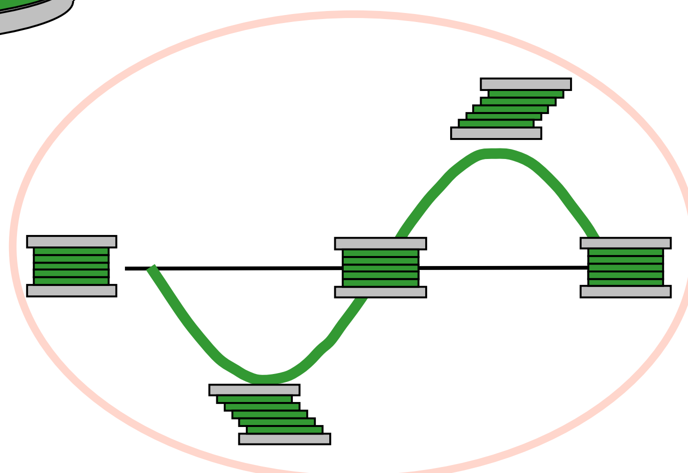
http://www.science.uq.edu.au/uq-science-webcams

Oscillation Testing

TOP PLATE ROTATES AT A CONSTANT ROTATIONAL VELOCITY

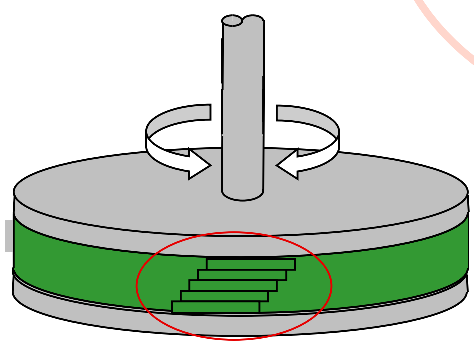


- To determine the Viscosity we apply a constant Shear Stress and measure the resultant Shear Rate (or vice versa)



- To determine the Modulus we apply an oscillatory Shear Stress and measure the resultant Shear Strain (or vice versa)

TOP PLATE OSCILLATES AT A GIVEN STRESS OR STRAIN AMPLITIDE

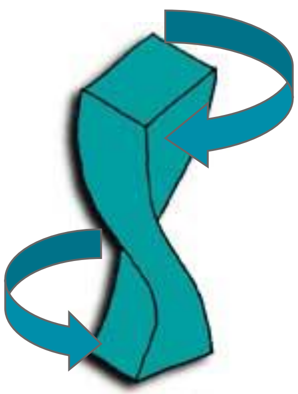


- Modulus is given by the max stress (amplitude) divided by the max strain

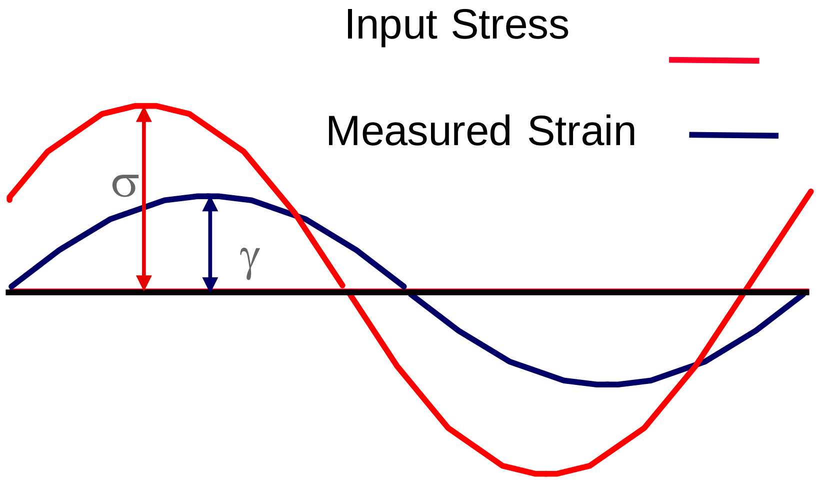
Complex Modulus - G*

- G* is measure of overall material stiffness with contributions from viscous and elastic elements
  - **Some stress required to stretch the elastic components**
  - **Some stress required to translate viscous components**

Calculated from how much a sample moves for a given force.



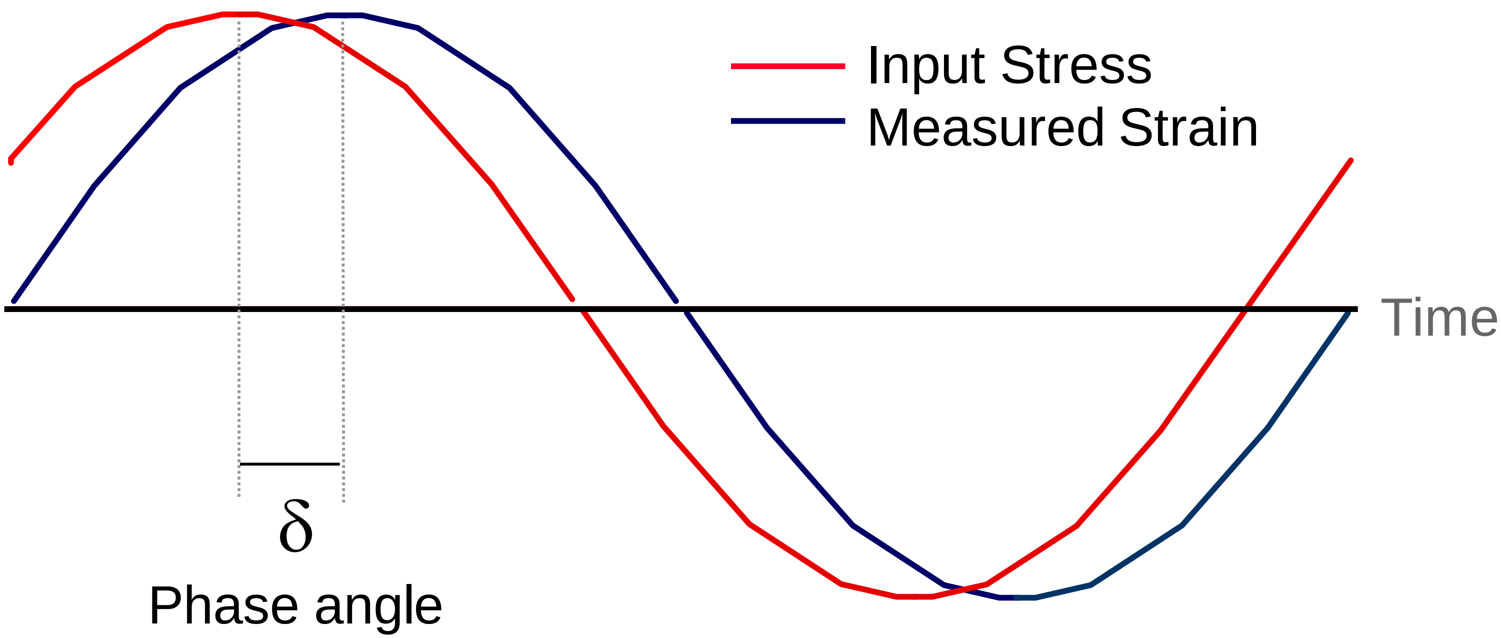
Units of Pascal's (Pa)



$$G^* = \frac{Max\ Stress}{Max\ Strain}$$

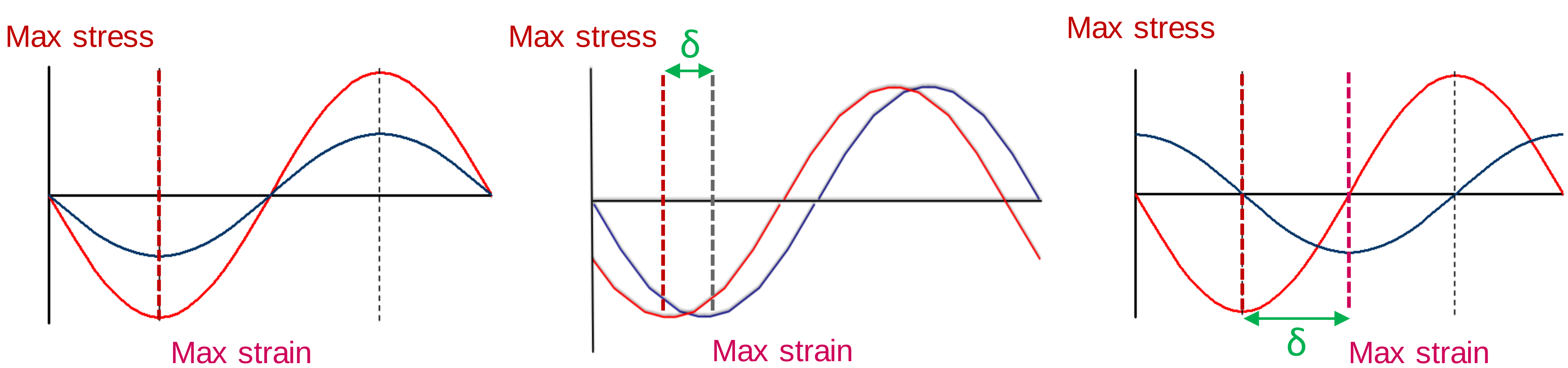
Phase Angle

- We can also calculate the phase angle
- Different types of materials have a different lag / phase angle between the applied and measured sinusoidal signal



Phase Angle - δ

- For a Purely Elastic Material – Solid-like behaviour
  - the stress is in phase with the strain ($\delta = 0$)
- For Purely Viscous Material – Liquid-like behaviour
  - the stress is in phase with the shear rate ($\delta = 90°$)
- For Viscoelastic Material – Mixed behaviour
  - The phase angle is somewhere in between ($0 < \delta < 90°$)



Elastic ($\delta = 0$)

Viscoelastic ($0 < \delta < 90°$)

Viscous ($\delta = 90°$)

Solid or liquid like…?

- Yogurt and honey can have the same complex modulus or same stiffness, however...

- Yogurt is elastically dominated, it behaves as a solid
  - **Pour it and it drops**
  - **Leaves ridges, doesn’t flow well**

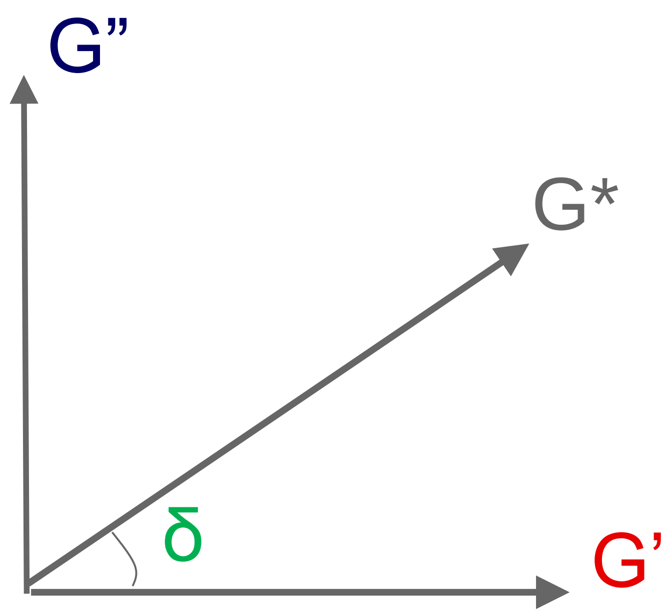
- Honey is viscously dominated, it behaves as a liquid
  - **It pours and strings**
  - **Settles with a smooth finish**

Elastic and Loss Modulus

- G* can be broken down into its component parts using simple trigonometry
- These components are termed:
  - Storage (elastic) modulus, given by G' = G*cosδ
  - Loss (viscous) modulus, given by G'' = G*sinδ

- G' is a measure of the energy stored and is related to the stress contribution (or stiffness) from the materials elastic structure

- G'' is a measure of the energy dissipated (or lost) and is related to the stress contribution from the viscous elements



Storage and Loss Modulus

- Rheology language tends to use a combined form of complex modulus and phase angle

- **Storage (elastic) modulus G'**
- **Loss (viscous) modulus G''**

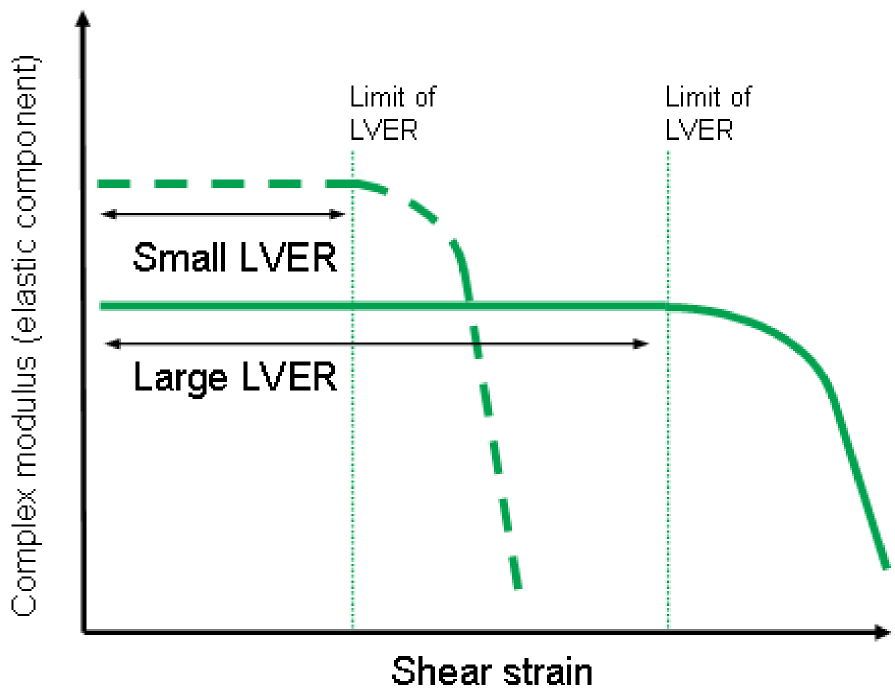
- If **G' > G''**, phase angle less than 45° - **SOLID LIKE**
- If **G'' > G'**, phase angle greater than 45° - **LIQUID LIKE**

- G* - modulus, is still a measure of toughness

AMPLITUDE SWEEP

Amplitude Sweep

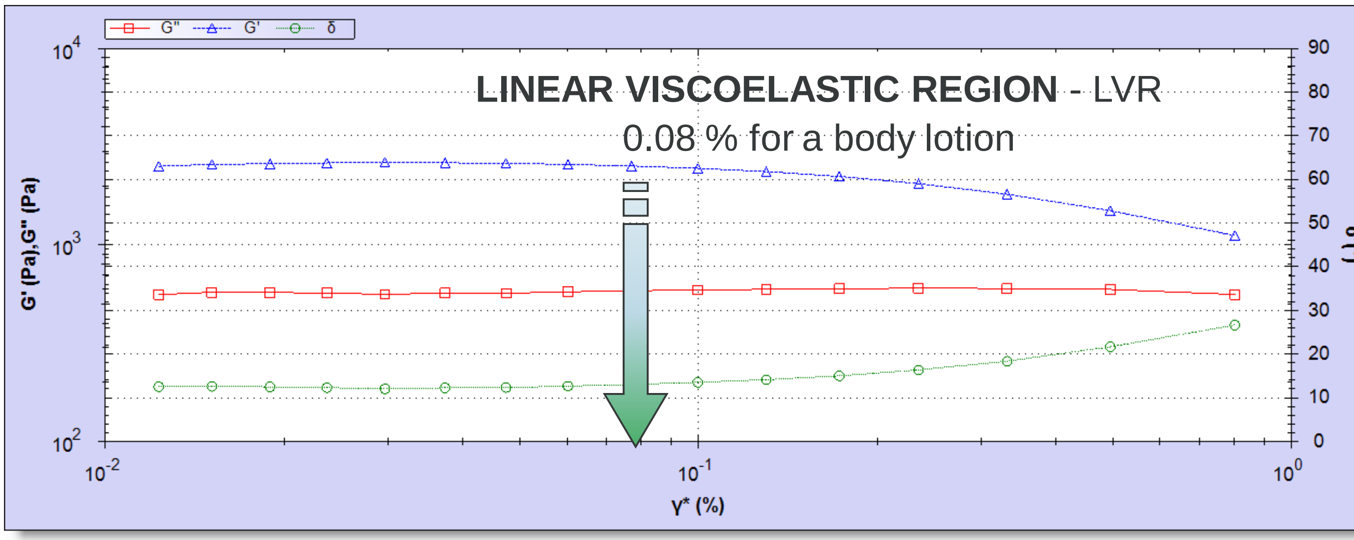
- Determines the Linear Viscoelastic region (LVR) where stress/strain ratio and hence G*, G’ and G” are constant
- Hookes law is only applicable within the LVR so stress or strain value kept within LVR for further linear testing



- Structural breakdown (yielding) is observed at stresses/strains outside the LVR which is why G’ drops
- A large LVR means a ‘more ductile’ material and a small LVR “ a more brittle” material

O001 Amplitude Sweep: Typical Results

- **This tests records the linear viscoelastic region (LVER) of a material**

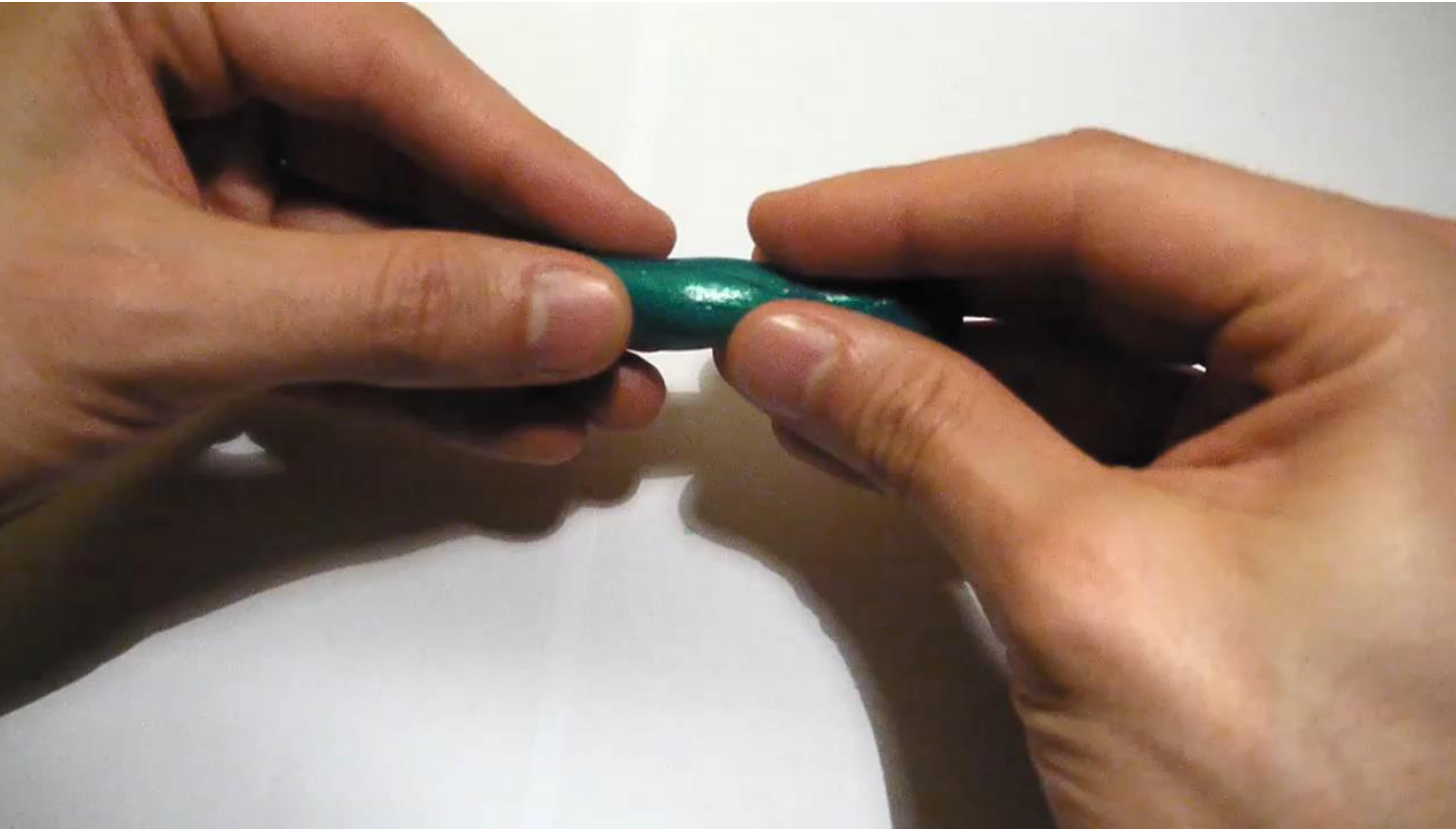


- **Typically G' is the most sensitive to the LVER**
  - The limit of the LVER is where the structure of the material starts to break down
  - **G'** is a direct measurement of the **structure** in the sample
  - **G''** is the viscous or **flow** property, as such this tends to flow instead of breaking down

FREQUECY SWEEP

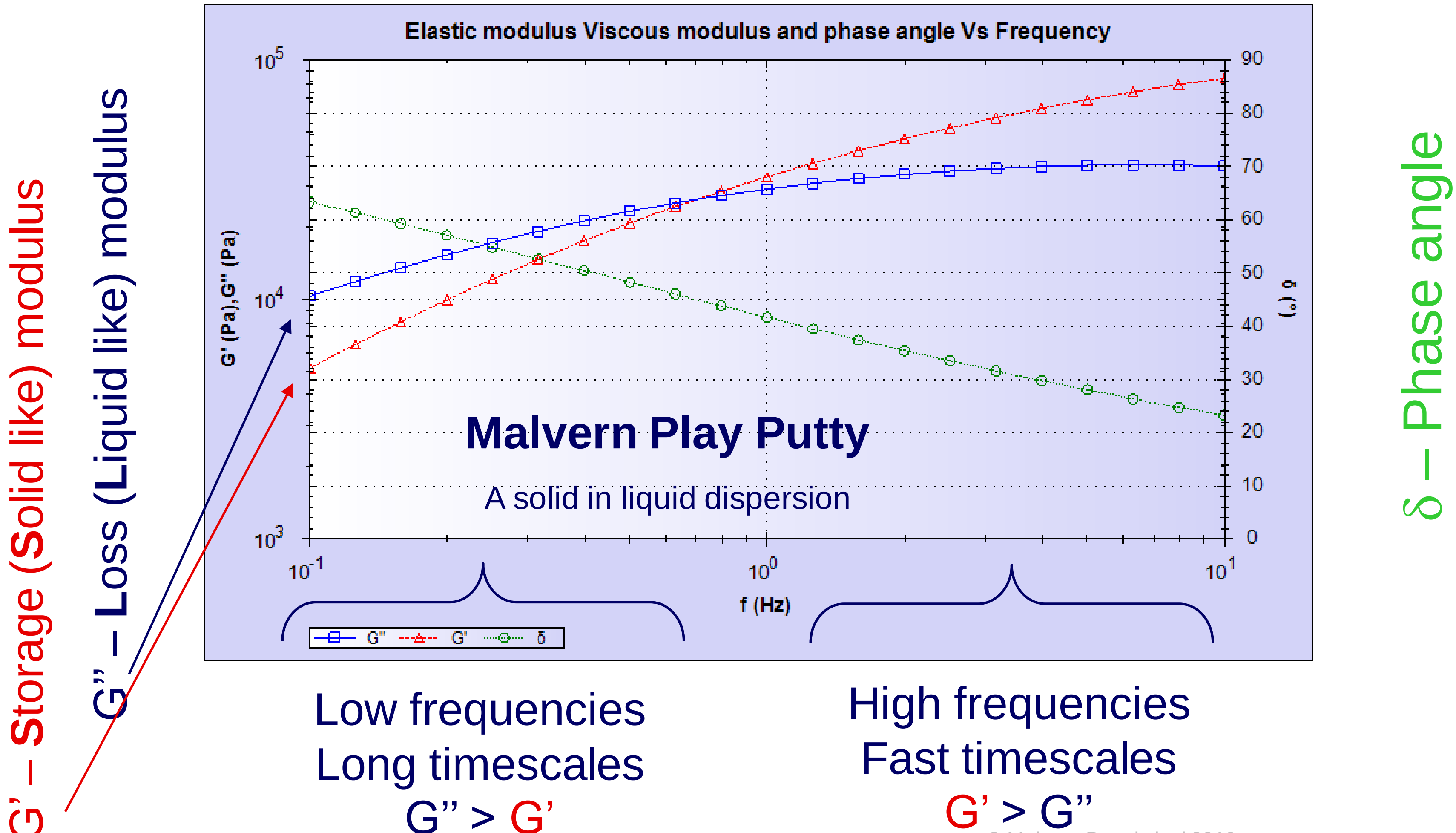
Solid AND Liquid "like"

- Your inks want to behave like…



O002 Frequency Sweep: Results

- The test records the viscoelastic spectrum of the material

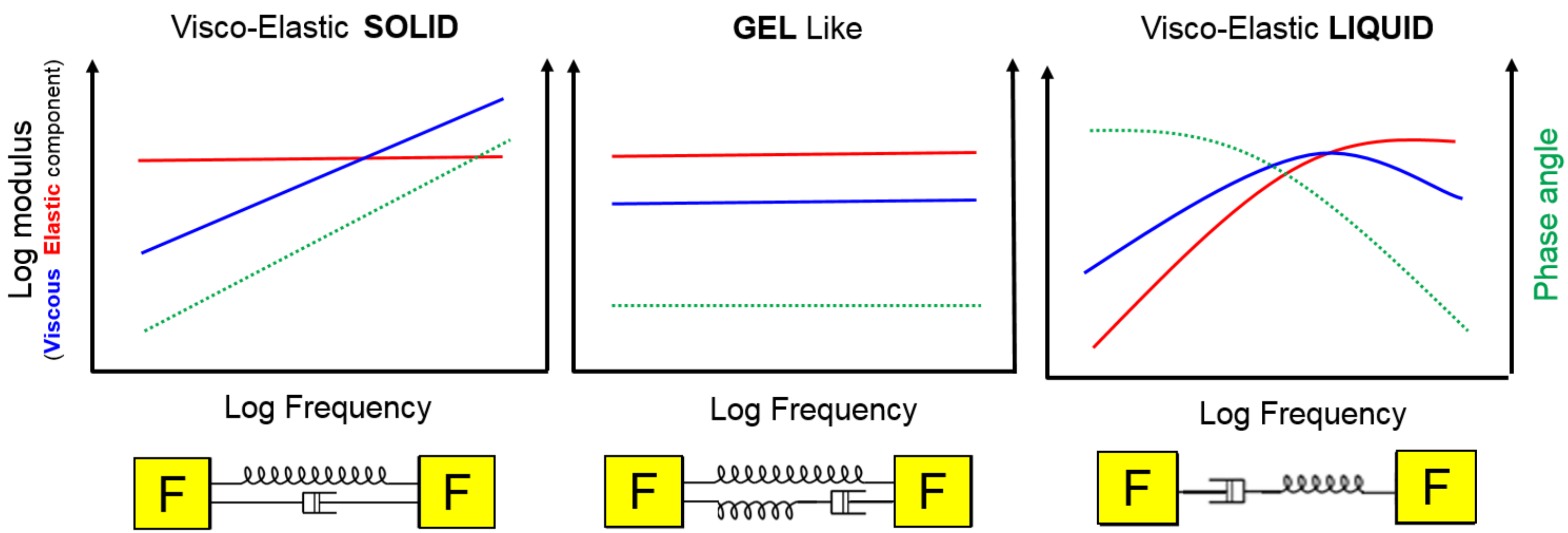


Low frequencies
Long timescales
G'' > G'
LIQUID LIKE

High frequencies
Fast timescales
G' > G''
SOLID LIKE

Material Behaviour

- Three general material behaviours
- Material property at rest (0Hz) classifies behaviour

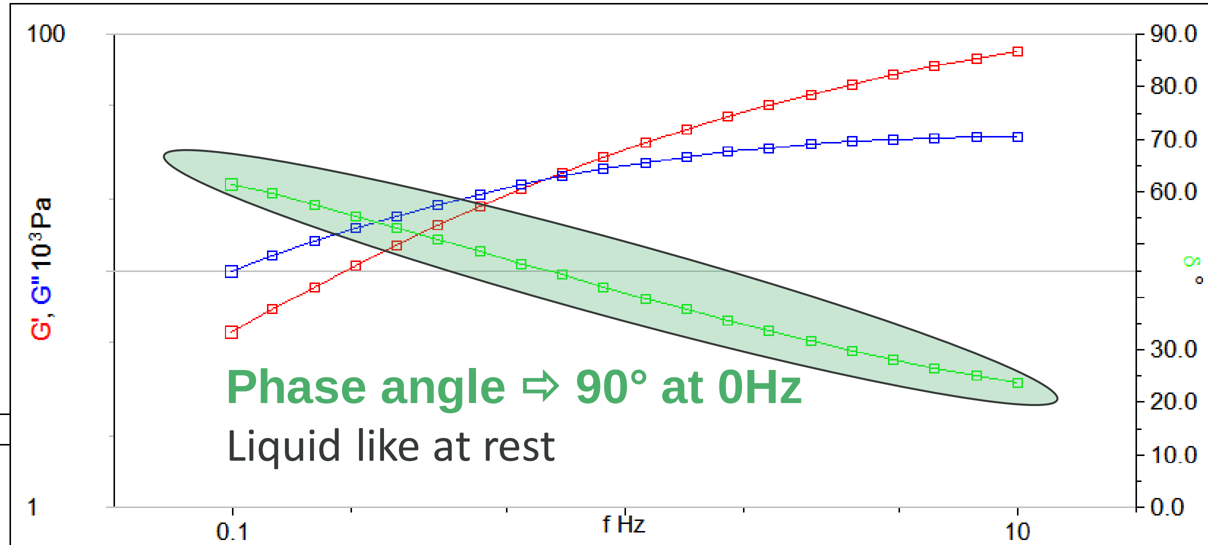


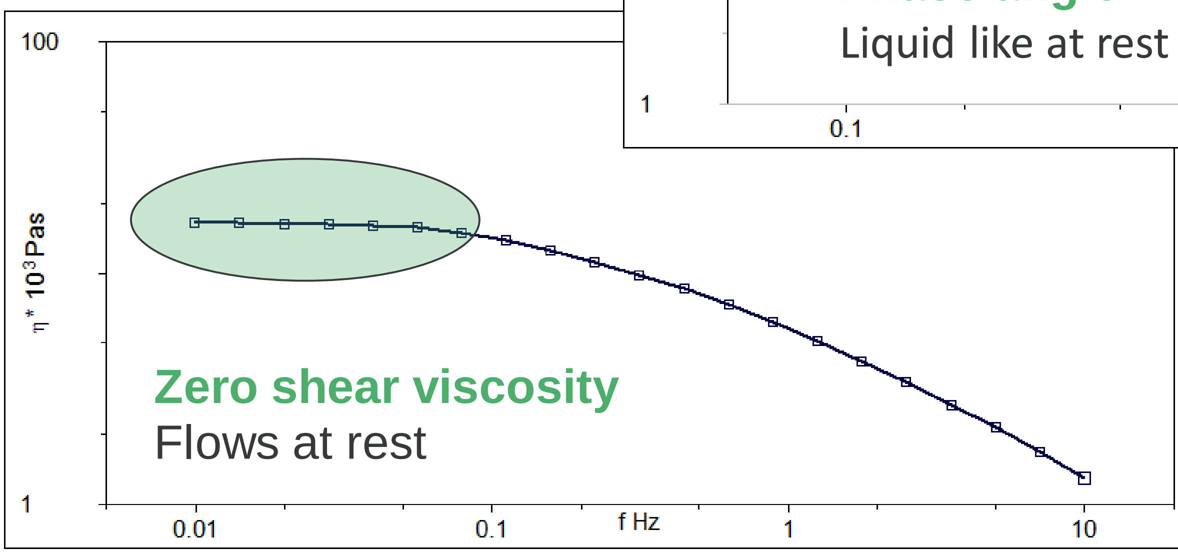
- VISCOELASTIC **SOLID**: phase angle ⇨ 0° at 0Hz.
- VISCOELASTIC **LIQUID**: phase angle ⇨ 90° at 0Hz.
- GEL: phase angle independent of frequency.

VISCOSITY VS. OSCILLATION

Solid or Liquid? Play Putty

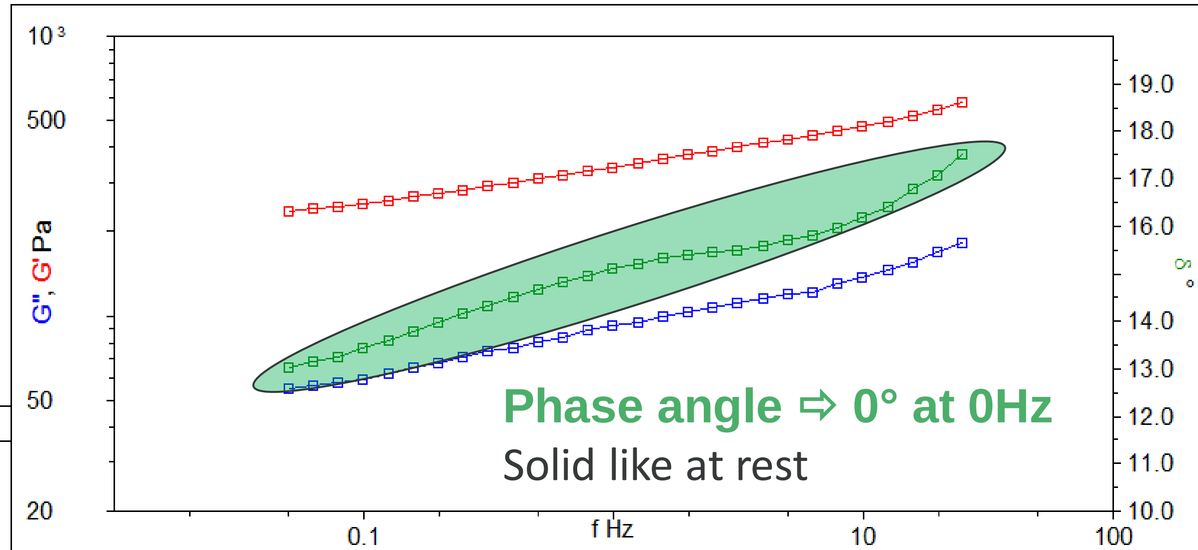
- Play Putty is actually a **VISCOELASTIC LIQUID!**

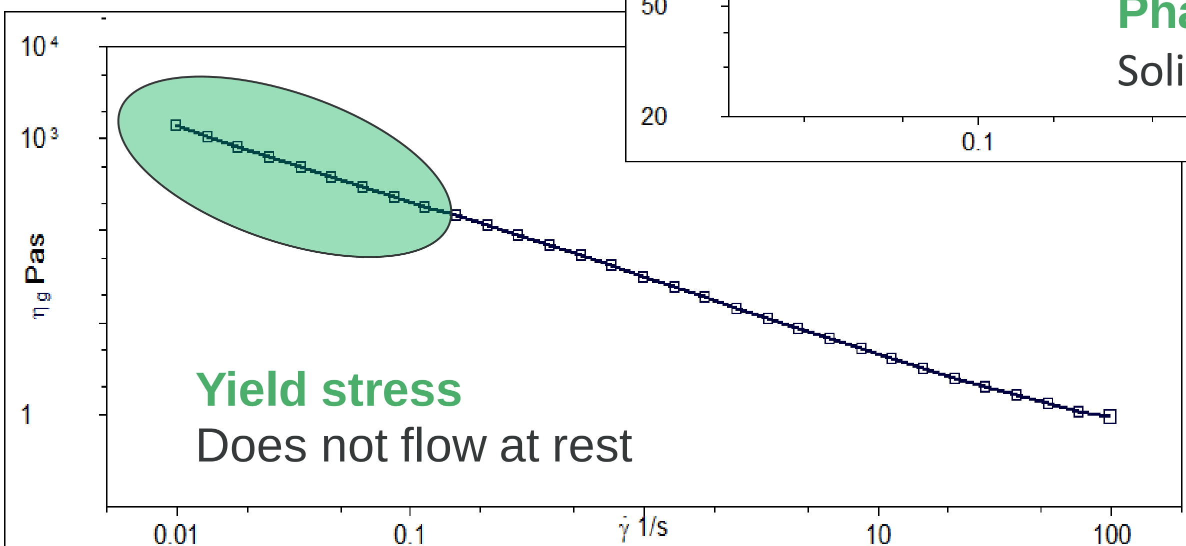




Solid or Liquid? Hand Cream

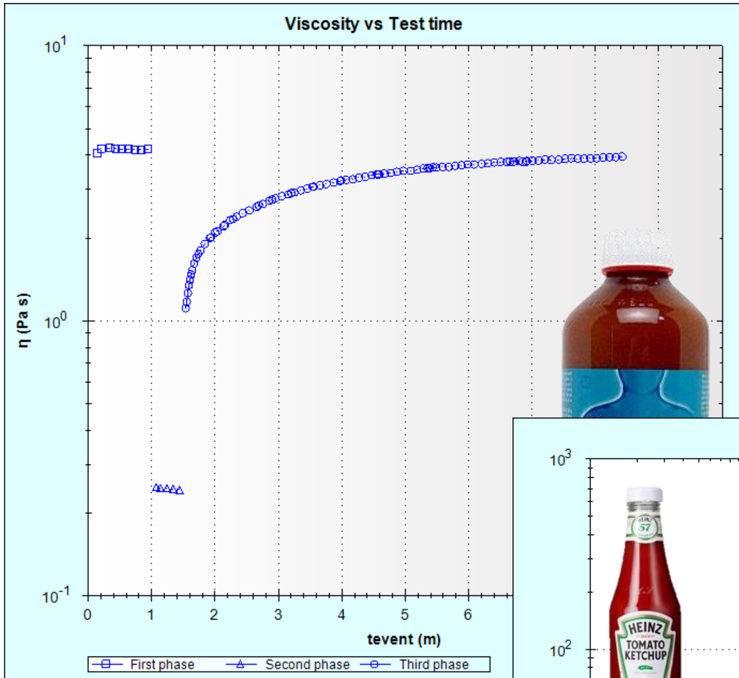
- Hand cream is actually
  VISCOELASTIC SOLID!

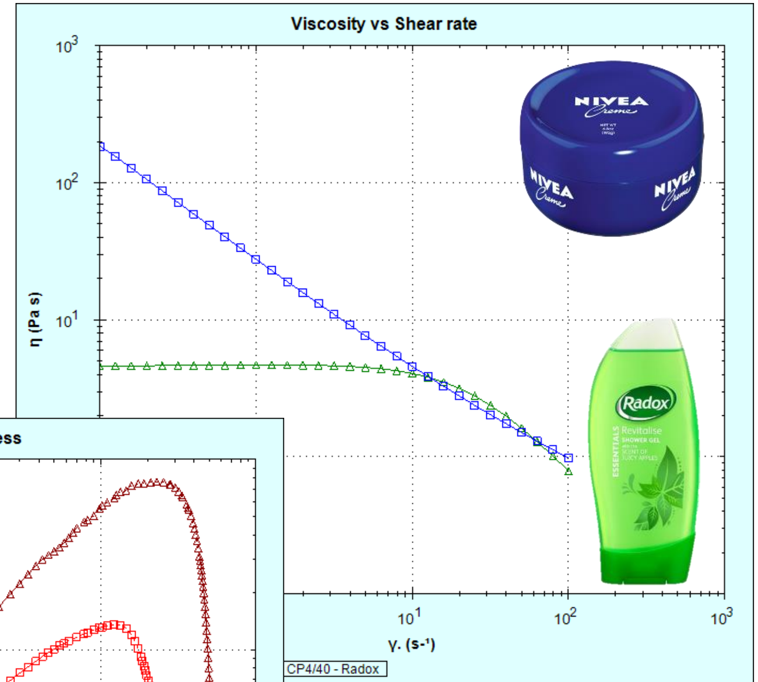




SUMMARY & OVERVIEW

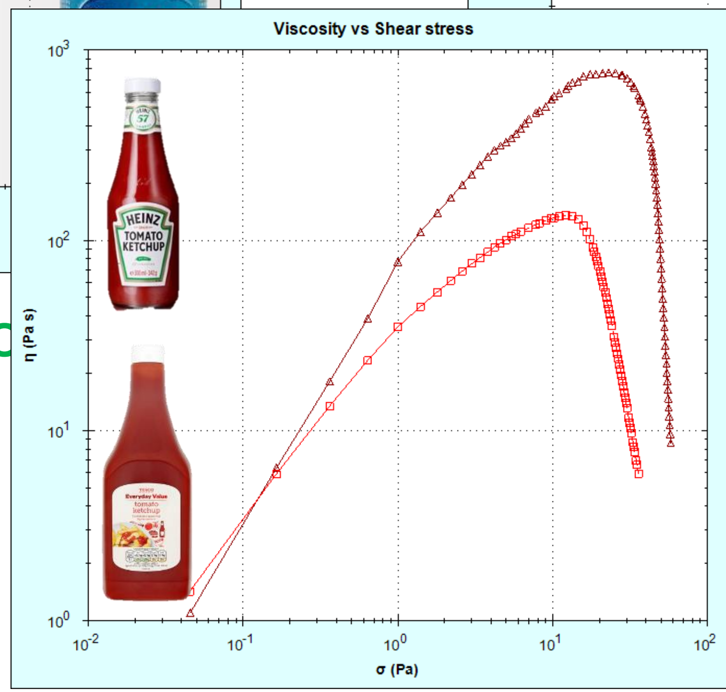
Malvern Panalytical





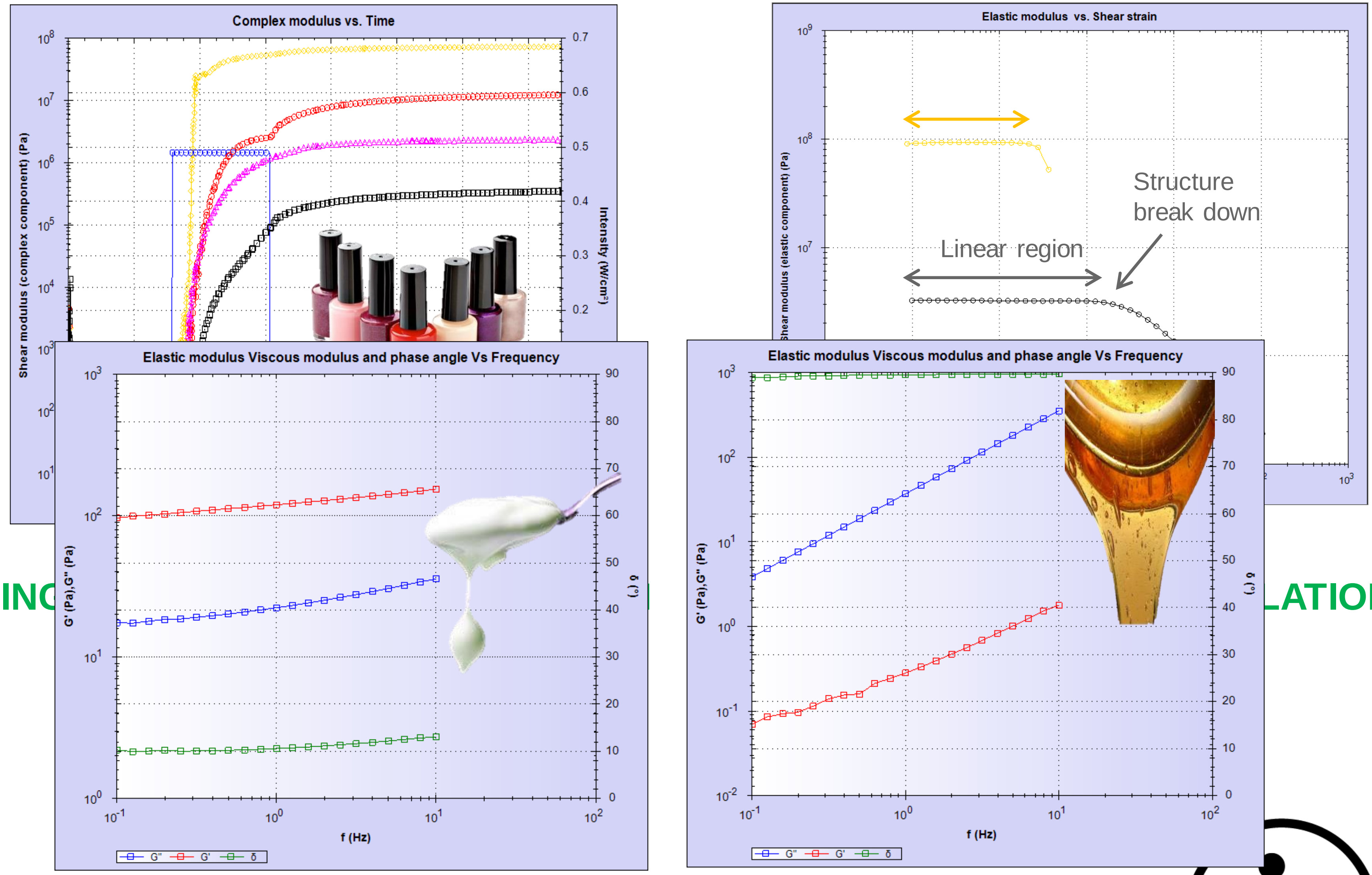
THIXOTROPY- VISCO

RVES - VISCOMETRY



YIELD STRESS - VISCOMETRY

RHEOLOGY MEASUREMENTS



SINC … LATION

FREQUENCY SWEEP - OSCILLATION

RHEOLOGY MEASUREMENTS

Thank you for your attention

Any questions?

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