Rheology Principles and Applications

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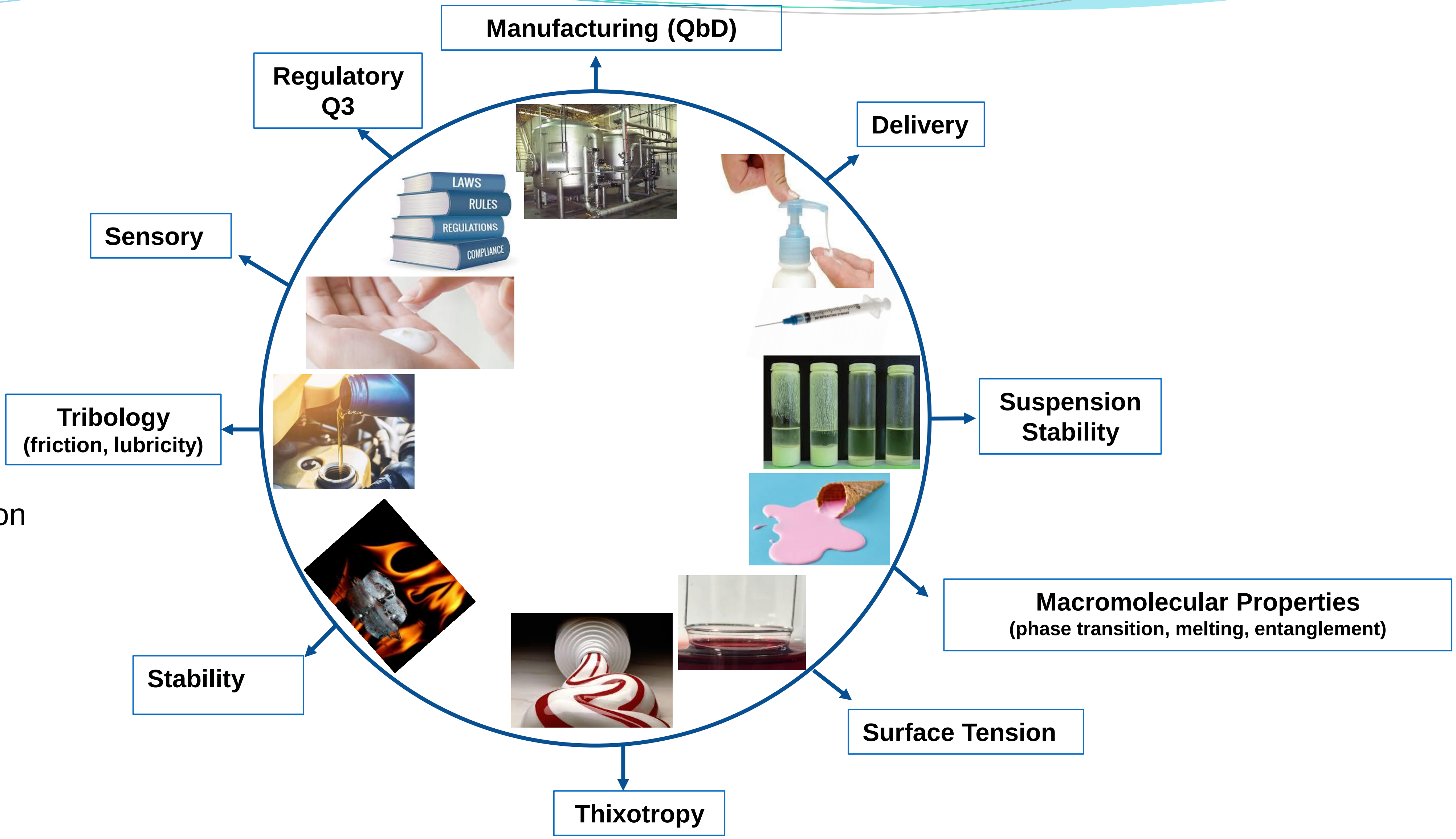
Applications from R&D to Manufacturing

Industries

- •Pharmaceutical
- •Biopharmaceutical
- •Bioengineering
- •Food
- •Cosmetic
- •Many others

Materials

-Polymer
-Cream
-Emulsion/Suspension
-Gel
-Lotion
-Oil
-Ointment
-Solution
-Other Semisolids



Applications from R&D to Manufacturing (CON'T)

- **Product development, optimization & in-process control (Quality by Design (QbD))**

  - batch consistency
  - addition order & rate
  - mixing time & speed
  - temperature (heating/cooling range & rate)
  - bulk transfer (shear, rebuilding)
  - equipment type & size (scale-up)
  - transport (sedimentation, phase separation)

Regulatory Expectations

Confirm Product (Dis)Similarity to RLD (Reference Listed Drug) for ANDA

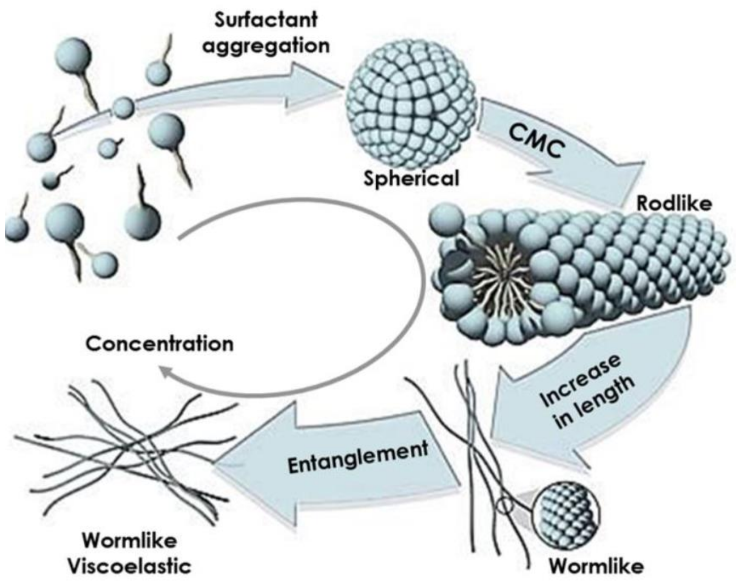
Q1: **Qualitative** ⇒Same components

Q2: **Quantitative** ⇒Q1 & same amount

Q3*: Microstructure

⇒ **Q1 + Q2 + same arrangement of matter**

⇒ stability, batch-to-batch consistency



→ **Rheometer may discern among arrangements based on association (entanglements) and their relaxation time**

→ **Rheological properties may affect biological activity**

* "Draft Guideline on Quality and Equivalence of Topical Products" European Medicines Agency (18Oct2018) (https://www.ema.europa.eu/en/quality-equivalence-topical-products#current-version-section)

* "Generic Development of Topical Dermatologic Products: Formulation Development, Process Development, and Testing of Topical Dermatological Products" AAPS J. 2013 Jan; 15(1): 41-52 (https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3535108/)

* "Testing Topicals: Analytical Strategies for the In-Vitro Demonstration of Bioequivalence" Pharm Tech Sept 2018 (http://www.pharmtech.com/testing-topicals-analytical-strategies-vitro-demonstration-bioequivalence?pageID=1)

Rheometer Overview

Upper Plate

- only <u>moving</u> part contacting sample
- different surfaces
  - -smooth
  - -rough
  - -serrated
- many other attachments

Lower Plate

- does not move
- same surface options as upper plate
- controls temperature (-5 to 200°C)*

*Options to extend temperature ranges are available.

Images from Netzsch

<u>Movements → torque</u>

- Rotational (1 direction)
- Oscillational (bi-directional)
- Vertical

By end of presentation…….

- What assay should I use?
- What experimental parameters should I consider?
- Appreciate which is more viscous – honey or mayonnaise? τ, γ, σ, η?
- Is silly putty viscoelastic solid or liquid? G’, G”, G*, δ, η*, tan delta?

BASIC RHEOLOGY ASSAYS ENTRÉES

…many side options available

⇒ROTATIONAL

- Shear Rate (ramp or step-wise)
- Shear Stress Ramp
- Thixotropy (3-step or more)
- Creep-Recovery
- Temperature Ramp with single shear stress or shear rate
- Tribology (friction, lubricity)

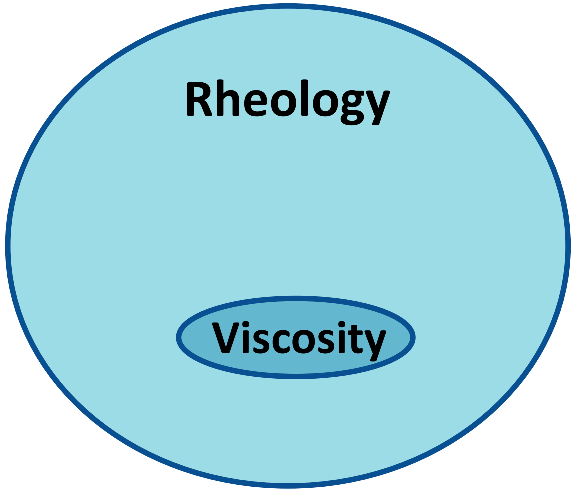
⇒OSCILLATIONAL

- Amplitude Sweep
- Frequency Sweep
- Thixotropy (3-step or more)
- Single Frequency over time for stability
- Temperature Ramp with single frequency

⇒ VERTICAL

- Squeeze-Pull Away (stickiness, model chewing)
- Surface Tension

Rheology is much more than just viscosity!



Principle – Viscosity

Viscosity is "resistance to flow" under applied force, either stress or strain controlled

- Quantifies the <u>push</u> (stress) needed for material to <u>move</u> a certain speed (shear rate) & vice versa

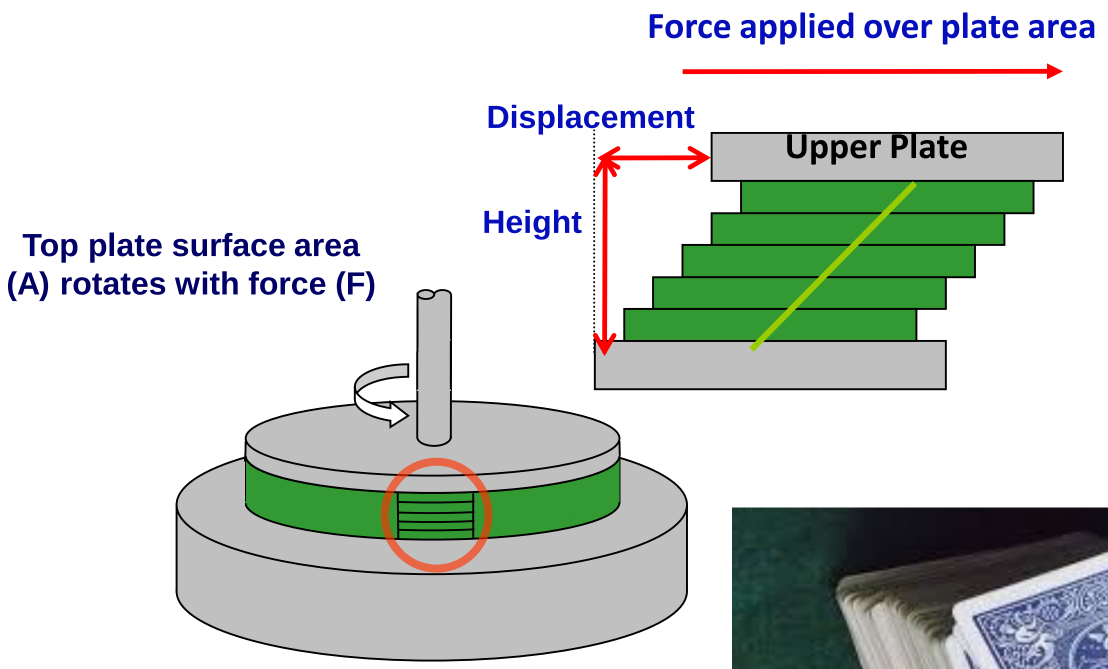


Image from Netzsch

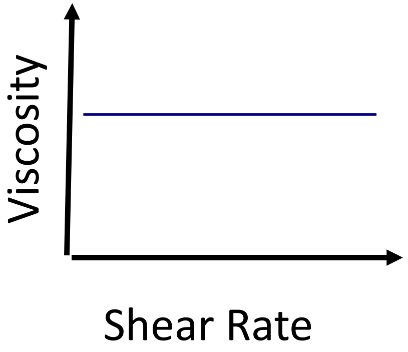
$$\text{Viscosity}(\eta) = \frac{\text{Shear Stress}}{\text{Shear Rate}} = \frac{\tau}{\gamma}$$

$$= \frac{\text{Force/Area}}{\text{Strain/Time}}$$

$$= \frac{\text{Force/Area}}{\text{(Displacement/Height)/Time}}$$

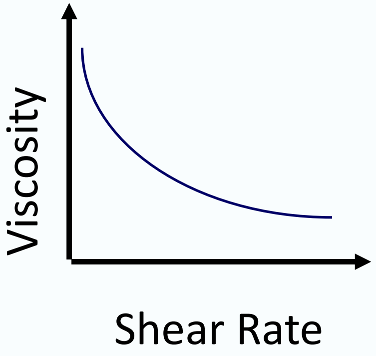
Flow Curves ⇒ Rotational Assay

Newtonian



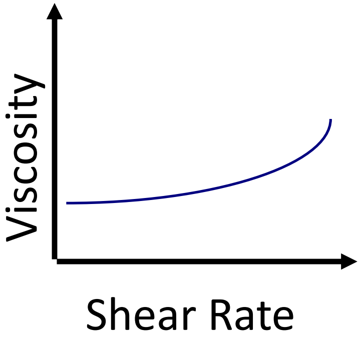
(silicon oil, water)

Shear-Thinning (non-Newtonian)



(most lotions, creams, ointments)

Shear-Thickening/Dilatant (non-Newtonian)



(corn starch)

- **Many semisolids shear thin (non-Newtonian)**
- **Helpful to model processes (spreading, pumping, syringability, feel)**

Shear rate = strain/time
(Strain=displacement/height)

Effect of Shear on Microstructure..”go with the flow”

⇒ Biologicals, polymers, emulsions

⇒ Larger & irregular particles tend to increase viscosity

⇒ Mixtures having more polydisperse particles tend to have lower viscosity

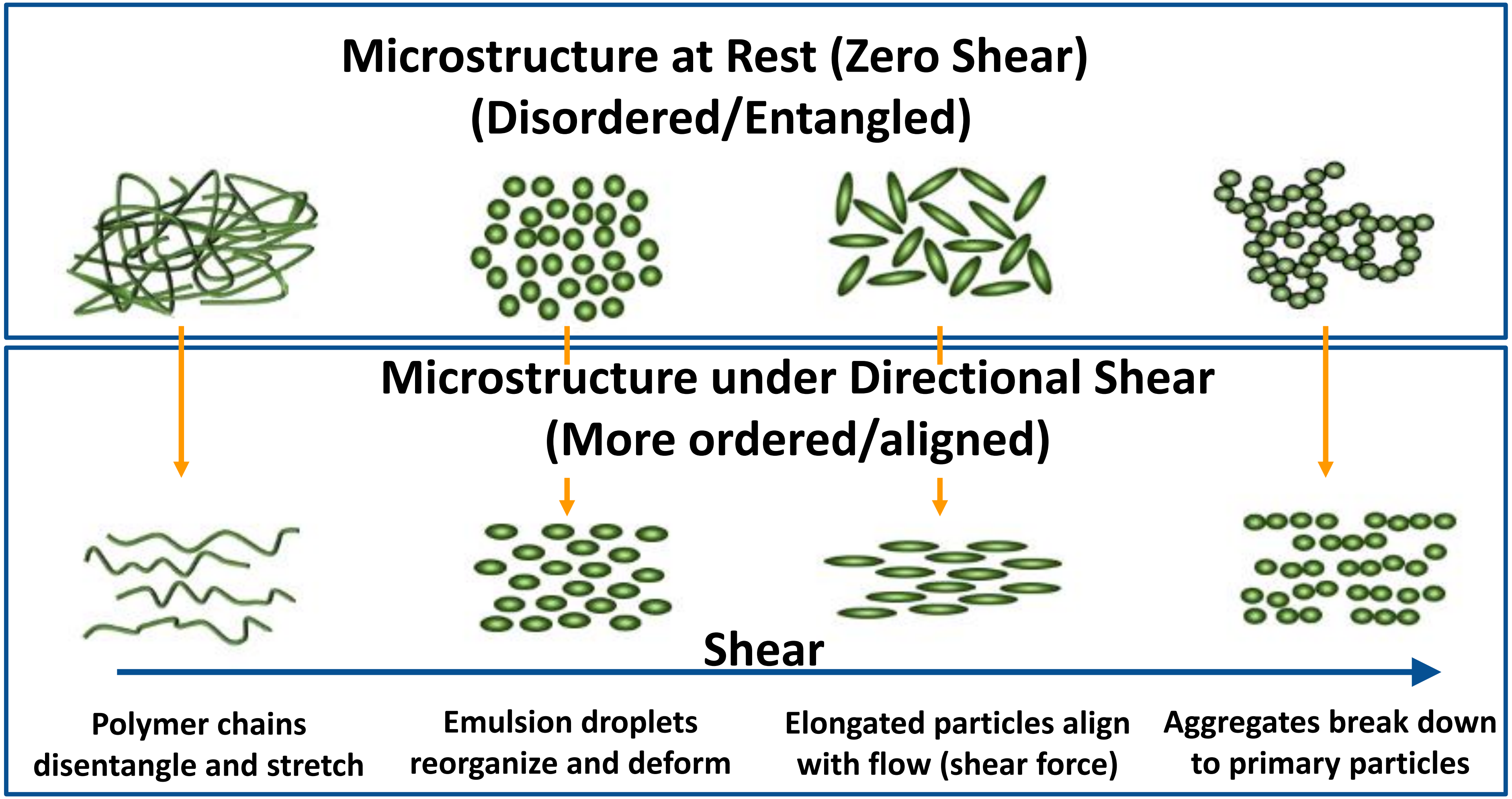
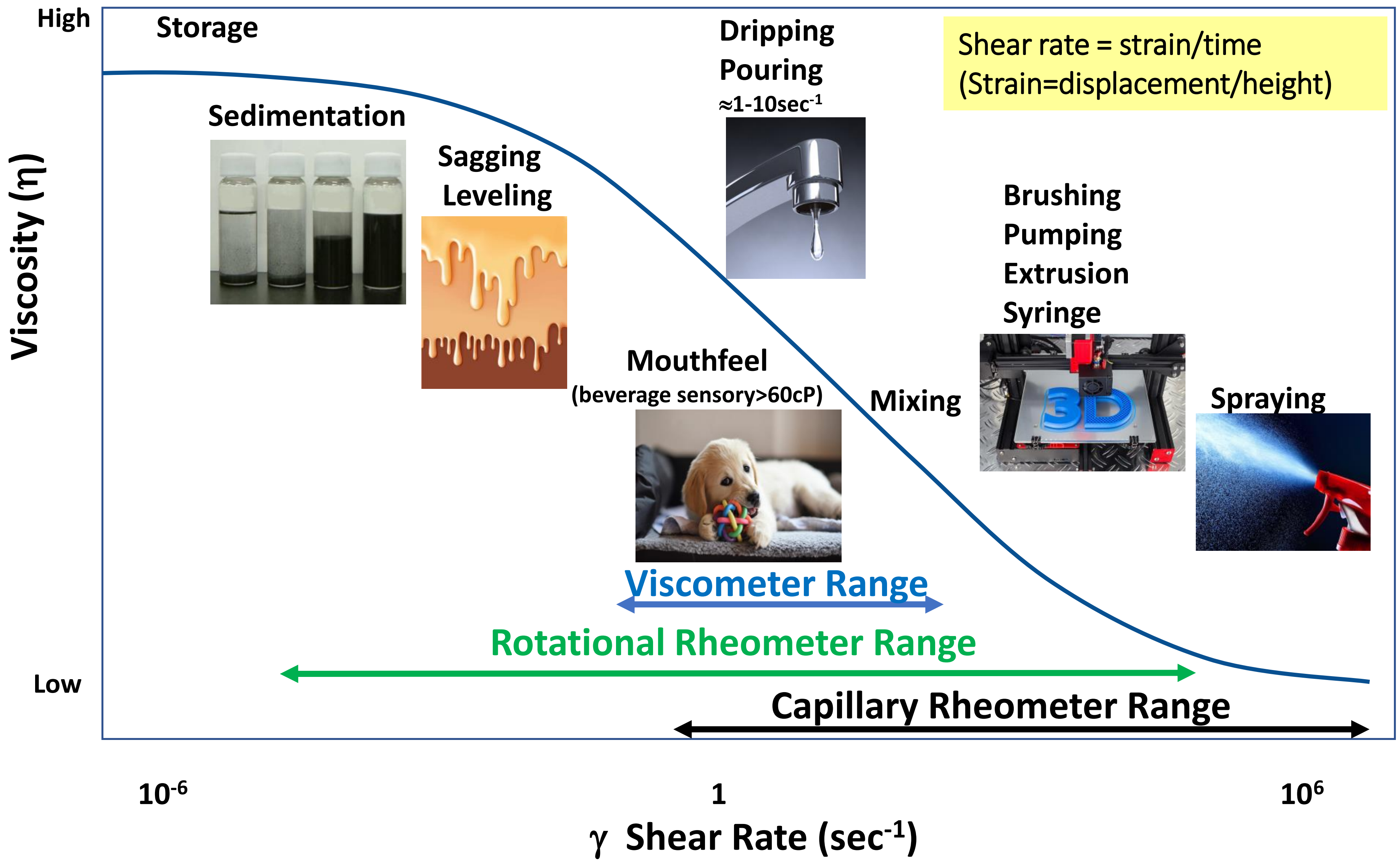


Image from Netzsch

Shear Rate of Processes - range 10^{10} (10 billion)



Shear Rates of Common Processes

Storage

End use

SAMPLE STORAGE

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

How stable is it (sedimentation, phase separation), sample quality…

SAMPLE DELIVERY

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

Pumpability? Scoopability?

SAMPLE APPLICATION 1

Low shear rates: ~$1 s^{-1}$

Too thin? Flows off hand?

SAMPLE APPLICATION - 2

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

Too thick to spread? Nice feel?

Image from Netzsch

Calculation: Shear Rate Calculations of Common Processes

#1 Painting:

Shear rate γ = velocity / height

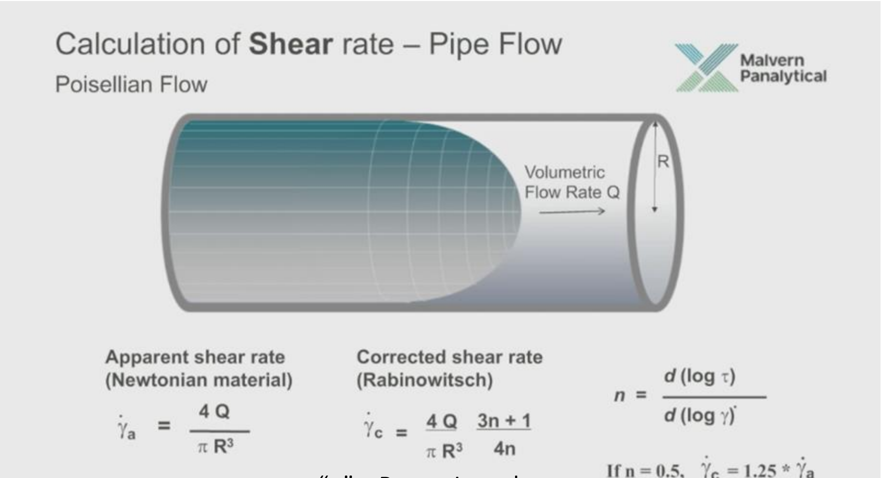
= 0.1m/sec / 0.0002m

= $500 sec^{-1}$

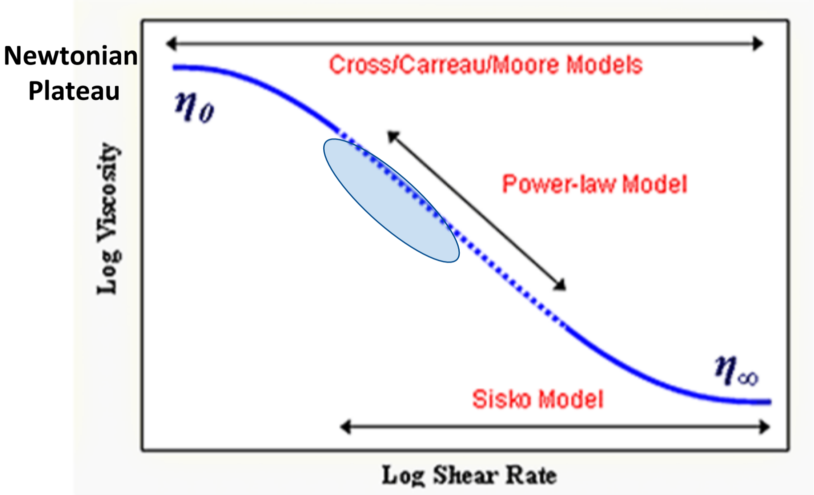
Velocity (v) = 0.1 m/sec (≈4 in/sec)

Paint thickness (h) = 200µm = 0.0002m

#2 Flow in capillaries, tubes, pipes → syringes, needles



"n" = Power Law slope



*water is Newtonian

** toothpaste in non-Newtonian (above calc used Rabinowitsch correction)

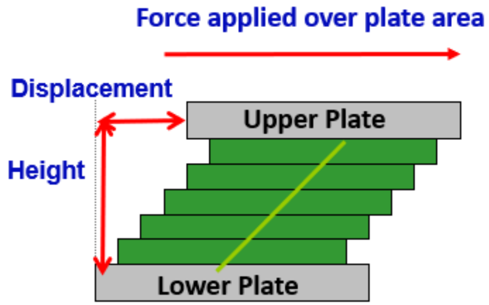
Switching gears…….

⇒Application of rotational methods

SHEAR STRESS RAMP ASSAY ⇒ “Flow Curve”

Analogous to revolving door

- **Yield Stress**: Force required to start moving door (yield point)
- **Yield Viscosity**: Viscosity at yield point.
- *Very small initial movement (shear rate) at yield point with high stress gives high yield viscosity.*



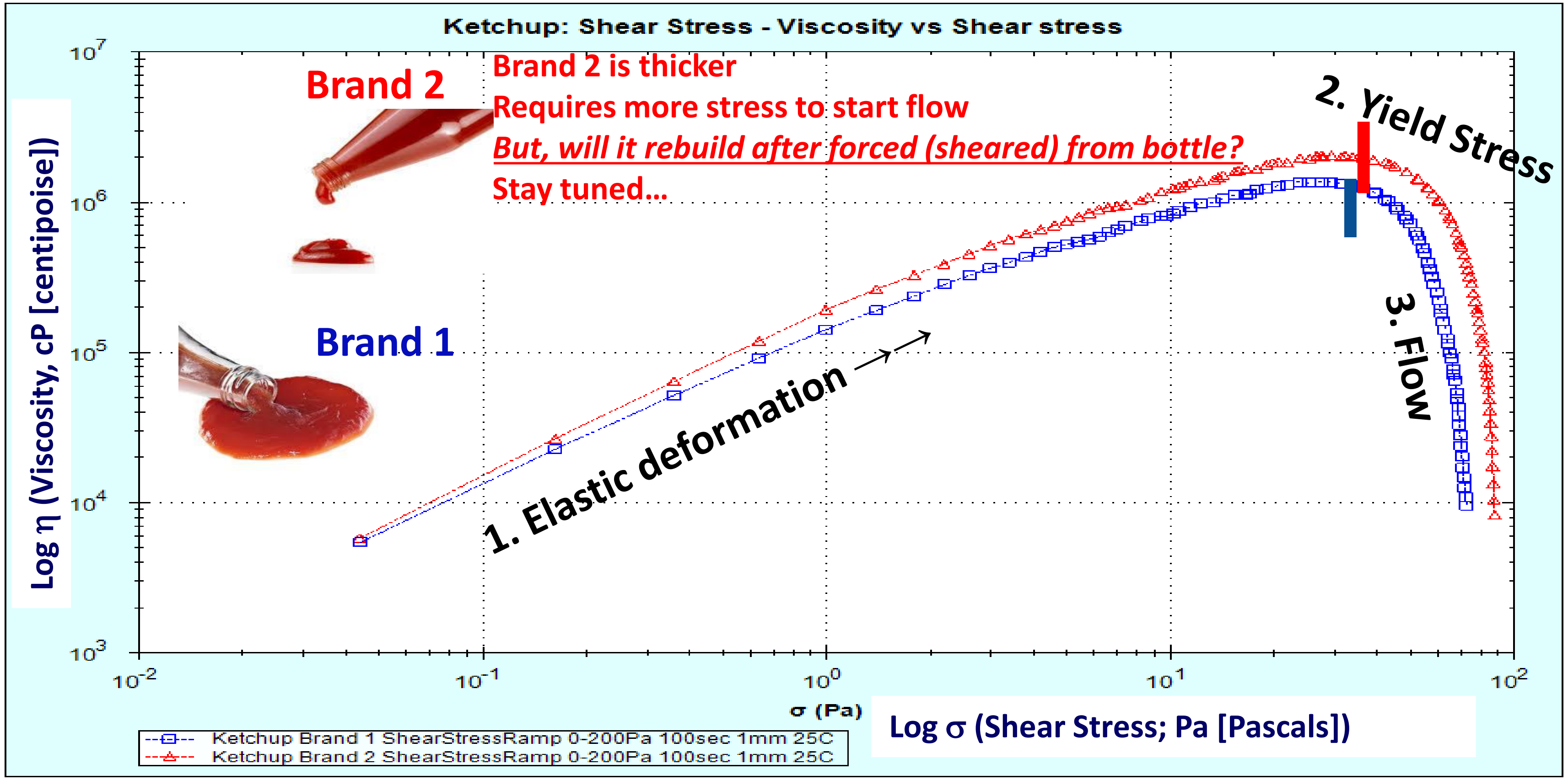
Viscosity(η) = Shear Stress / Shear Rate = τ / γ

= Force/Area / (Displacement/Height)/Time

Stress = Force/Area

Application: Yield Stress Ramp "Flow Curve" - Ketchup

► **Issue:** Client (engineers) needed data for process modelling

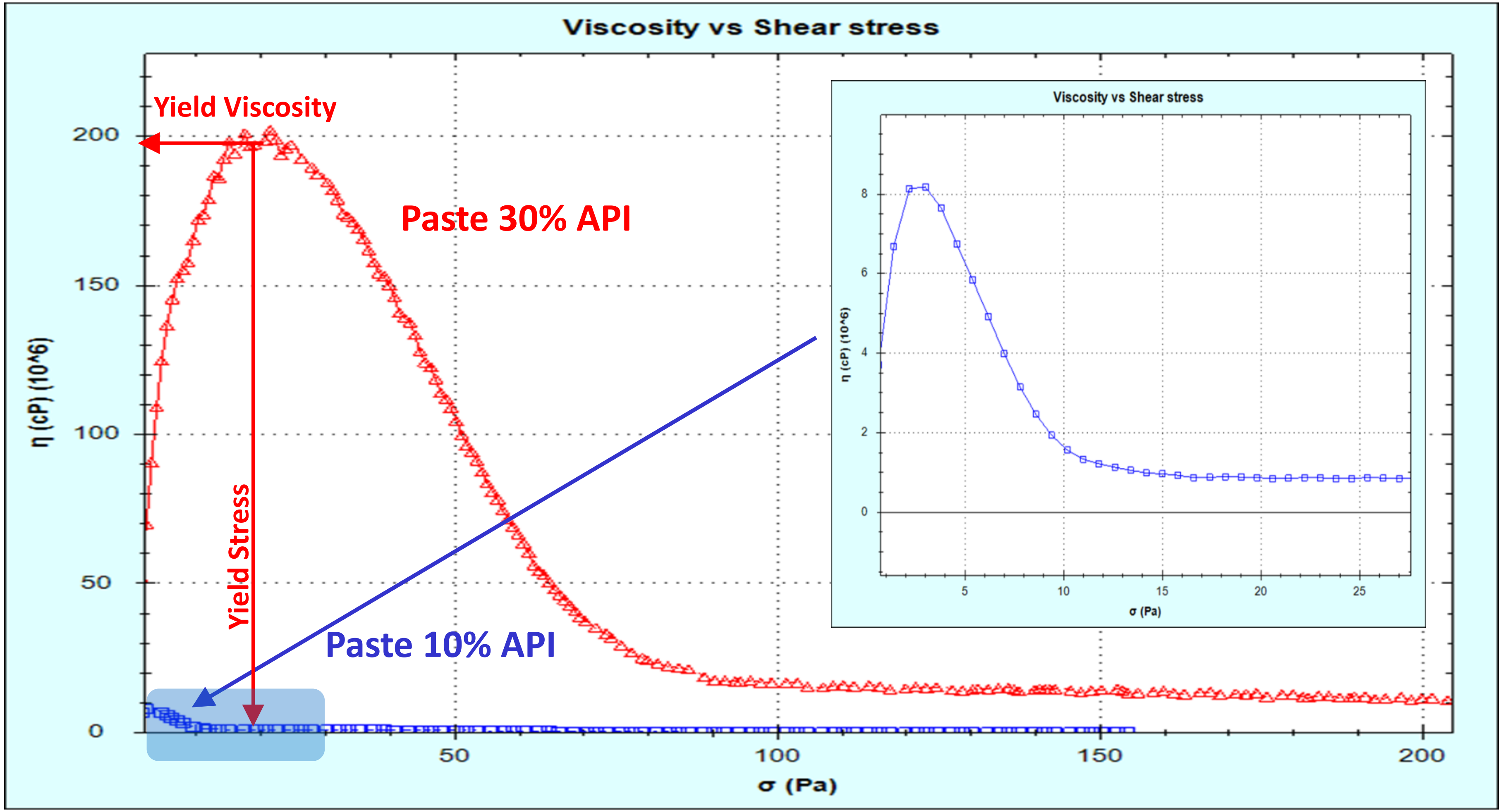


- Helpful model for difficult to pump or stir materials → start up force
- Formulation optimization (type and amount of thickeners, excipients)
- Insight for manufacturing optimization
- Refine customer experience – thicker, creamier
- Assay useful to model if sample is likely to settle. Stokes Law → is downward force on particles > media yield stress?

Application: Yield Stress Ramp - Pharmaceutical paste

Stress = Force/Area

- ► **Issue:** Client needed to quantify impact of % API on processing & application
- ► **Result**: 30% API paste has higher yield stress & yield viscosity → difficult to initiate movement

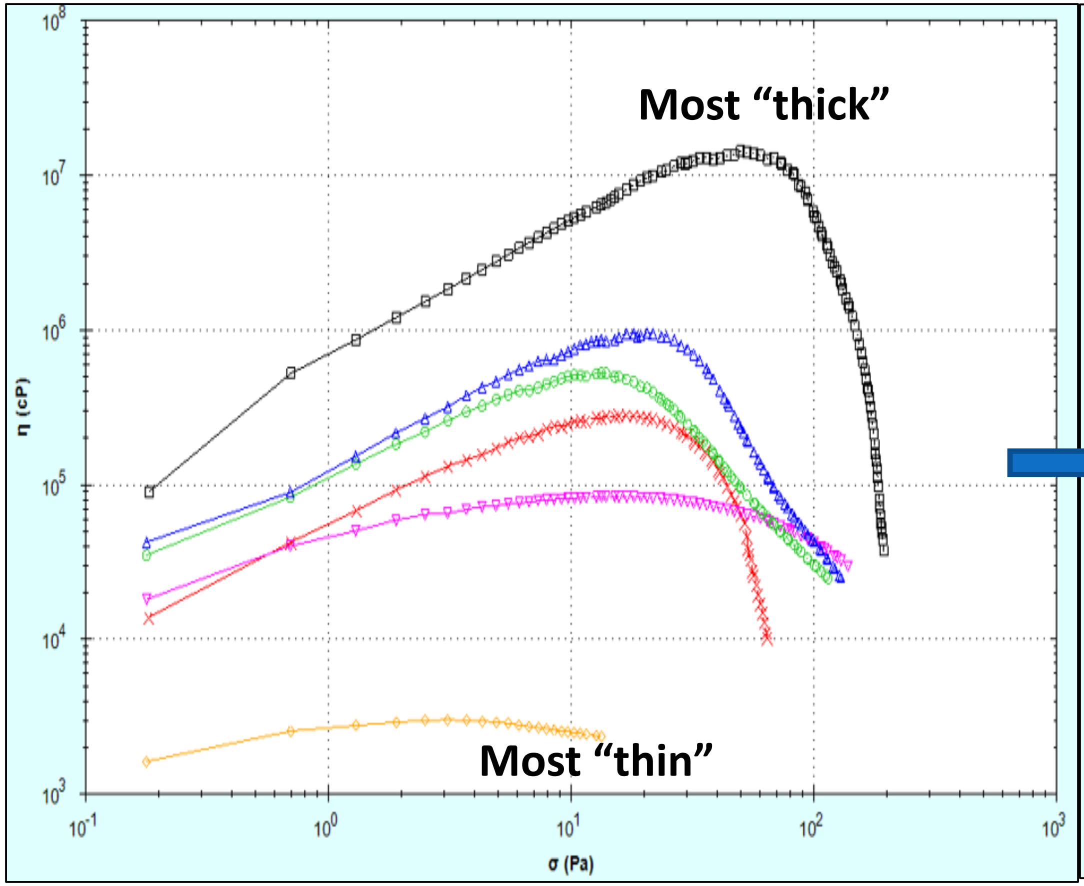


Application: Yield Stress Ramp - Arthritis products

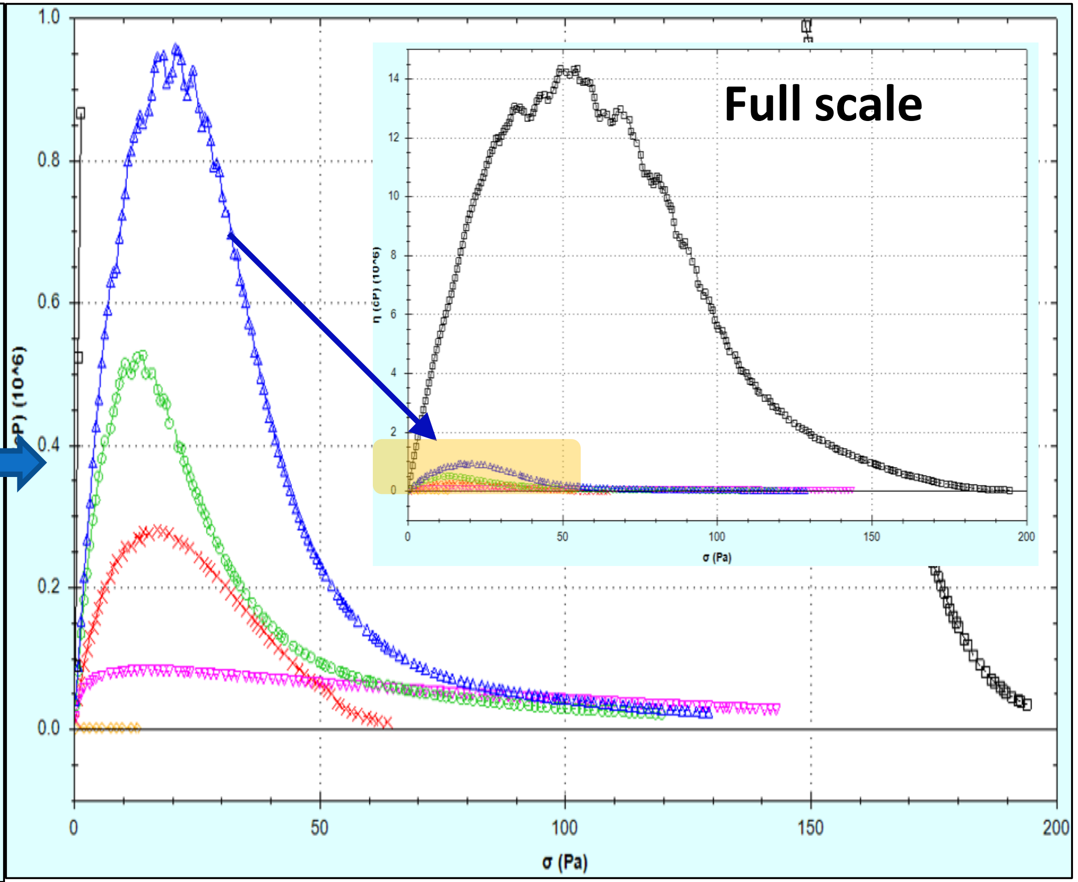
Stress = Force/Area

- ▶ **Issue:** Client requested side-by-side rheological profiles for 6 products
- ▶ **Results:** Orders of magnitude differences!
- Experimental: 25mm rough parallel plate, 200um gap (100uL sample), 0-300Pa/300sec

Log-Log



Linear-Linear



Application: Sedimentation using Yield Stress

Downward stress on a spherical particle in dilute suspension is estimated by Stokes' Law

$$\sigma_s = r * g * \frac{d - \rho}{3}$$

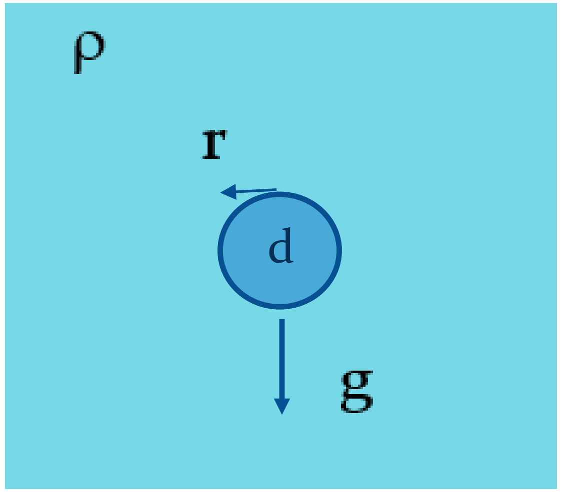
$$V_s = 2\,r^2 * g * \frac{(d\text{-}\rho)}{9\eta_0}$$

σ_s = sedimentation stress on particle
r = particle radius
g = gravitational acceleration
d = particle density
ρ = fluid density
V_s = sedimentation velocity
η_0 = zero shear viscosity

⇒If sample's measured yield stress > σ_s, then sedimentation less likely assuming suspending media doesn't shear thin during transport and handling.

Ref: azom.com/article.aspx?ArticleID=2885

Vodka with suspended gold flakes (non-Newtonian)



Switching gears…….

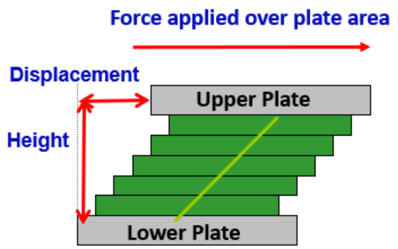
⇒Application of rotational methods

-SHEAR RATE RAMP ASSAY

$$\text{Viscosity}(\eta) = \frac{\text{Shear Stress}}{\text{Shear Rate}} = \frac{\tau}{\gamma}$$

$$= \frac{\text{Force/Area}}{\text{Strain/Time}}$$

$$= \frac{\text{Force/Area}}{(\text{Displacement/Height})/\text{Time}}$$

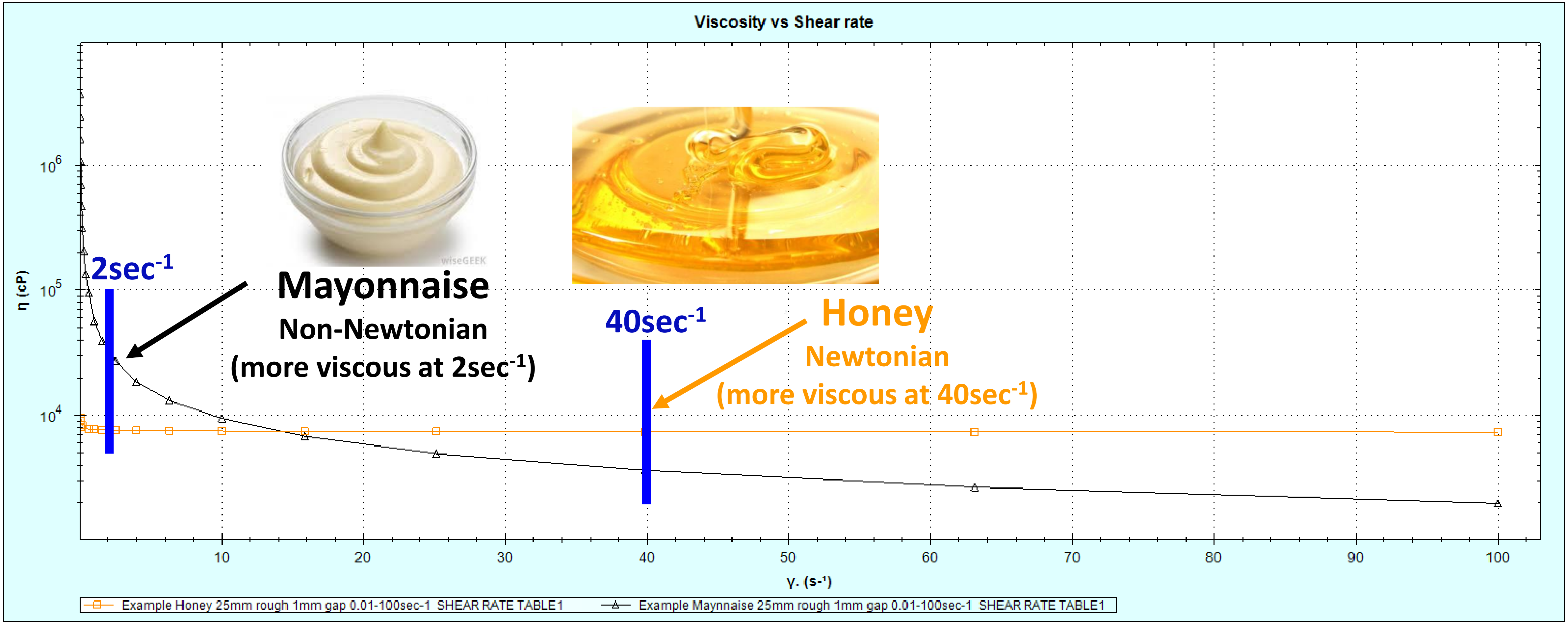


Shear Rate Ramp

Which is more viscous – honey or mayonnaise?

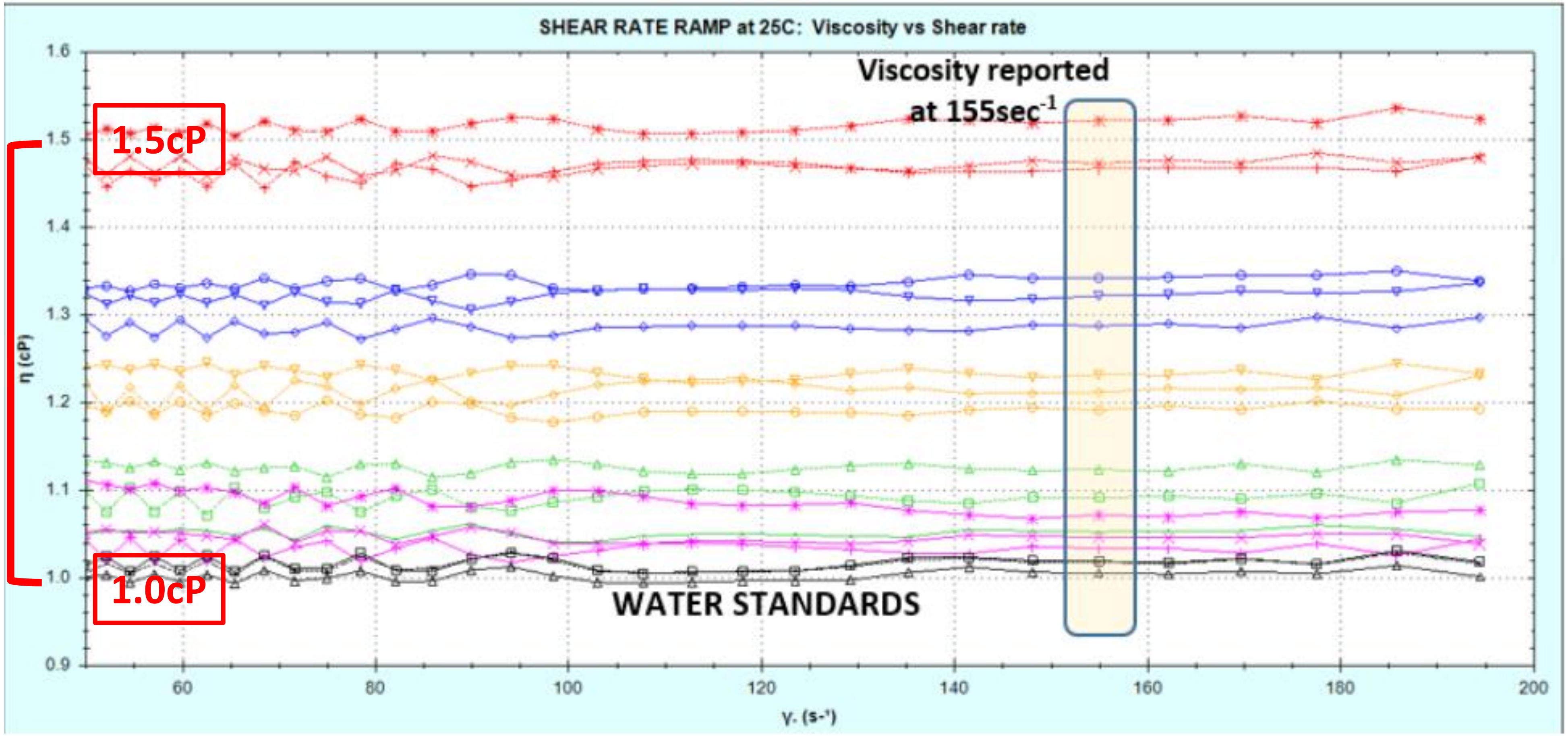
Depends on shear rate…… <u>CRITICAL CONSIDERATION WHEN COMPARING VISCOSITIES</u>

- →At $2sec^{-1}$ $\eta_{Mayonnaise} > \eta_{Honey}$
- →At $40sec^{-1}$ $\eta_{Honey} > \eta_{Mayonnaise}$



Shear Rate Ramp –6 Low Viscosity Samples

- ▶ **Issue**: Client needed to compare viscosity for aqueous formulations vs water
- ▶ **Result:** Able to resolve from water std & trends among very low viscosity samples within a very narrow range
- Experimental: 40mm smooth parallel plate, 300uL gap (380uL sample), 25°C, 50-200sec^{-1}



Sample 1 (RSD 1.6%)

Sample 2 (RSD 2.3%)

Sample 3 (RSD 1.4%)

Sample 4 (RSD 2.7%)

Sample 5 (RSD 1.5%)

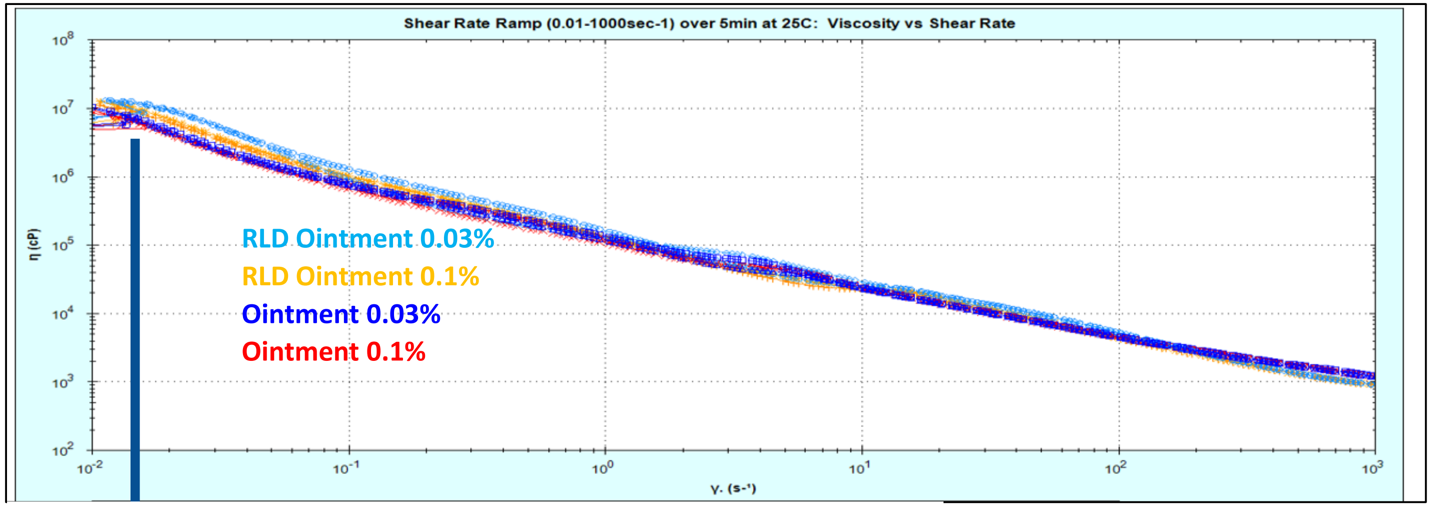
Water Std (RSD 1.1%)

Shear Rate Ramp – 2 RLD vs 2 Generic Ointments

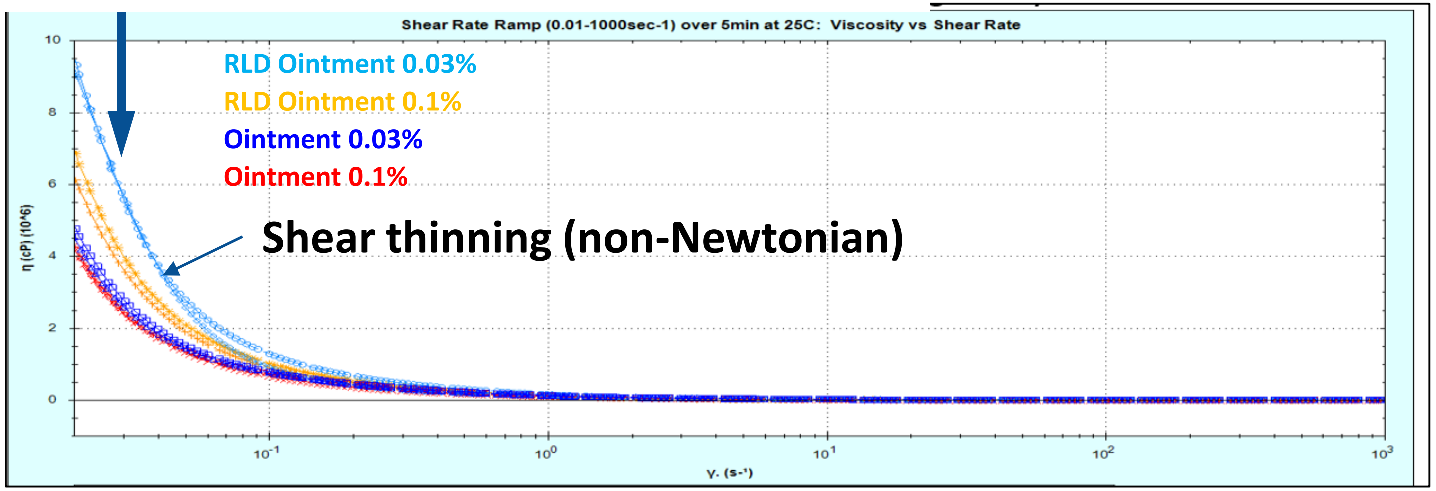
-Shear rate ramp (0.01-1000sec^{-1}) over 5min at 25°C , 25mm rough plate

-0.03% > 0.01% among both RLD and Generic ointments with good reproducibility (n=2)

log-log → Samples look reasonably similar in plot



log-linear → Not so much at low shear rates!



Principle: Viscosity – <u>Stepwise</u> Shear Rate

-Incrementally step up, then can also step down thru shear rates

-Can define viscosity stabilization (i.e. 5% change/5sec) or timeout (30sec) criteria before next shear rate.

-Helpful to model manufacturing processes, quantify post-shear thinning (ir)reversibility (hysteresis)

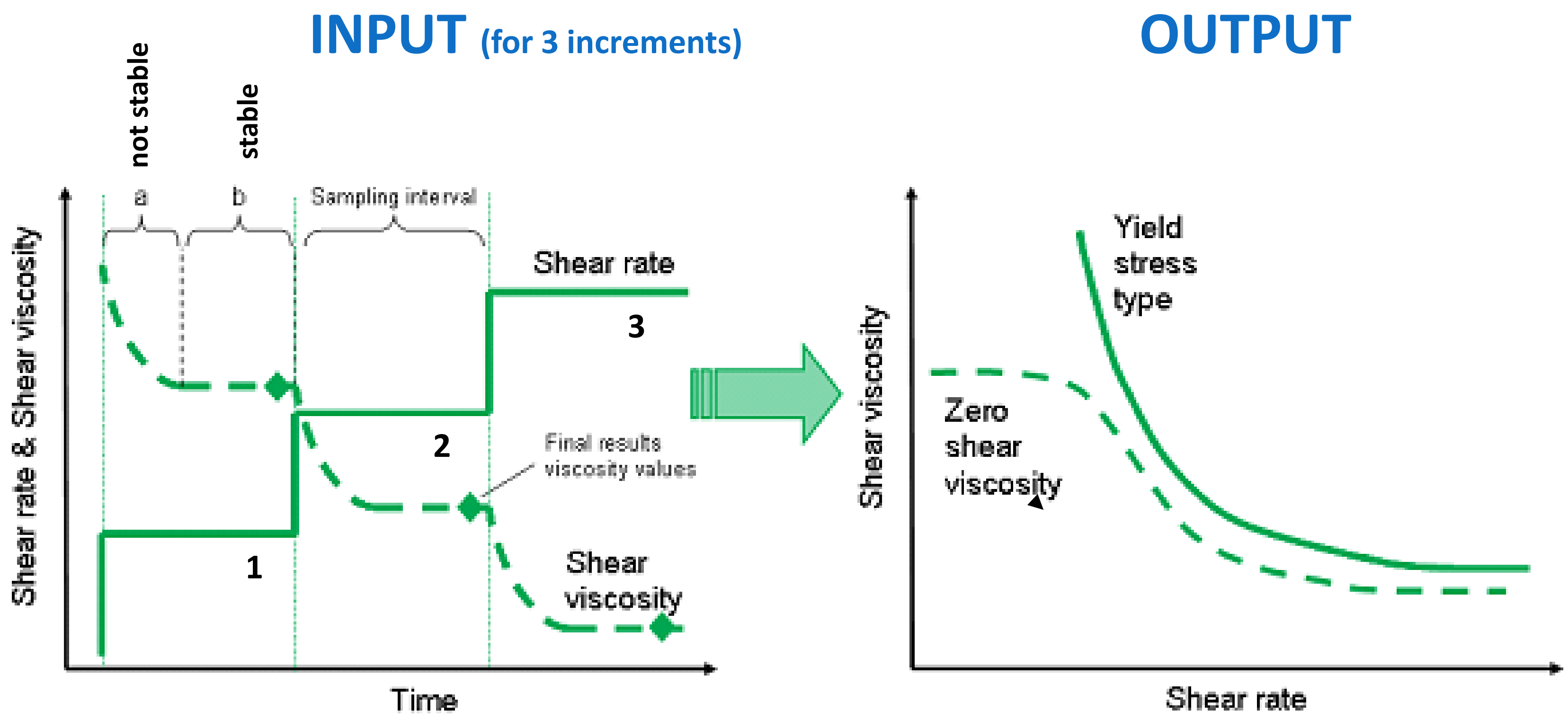


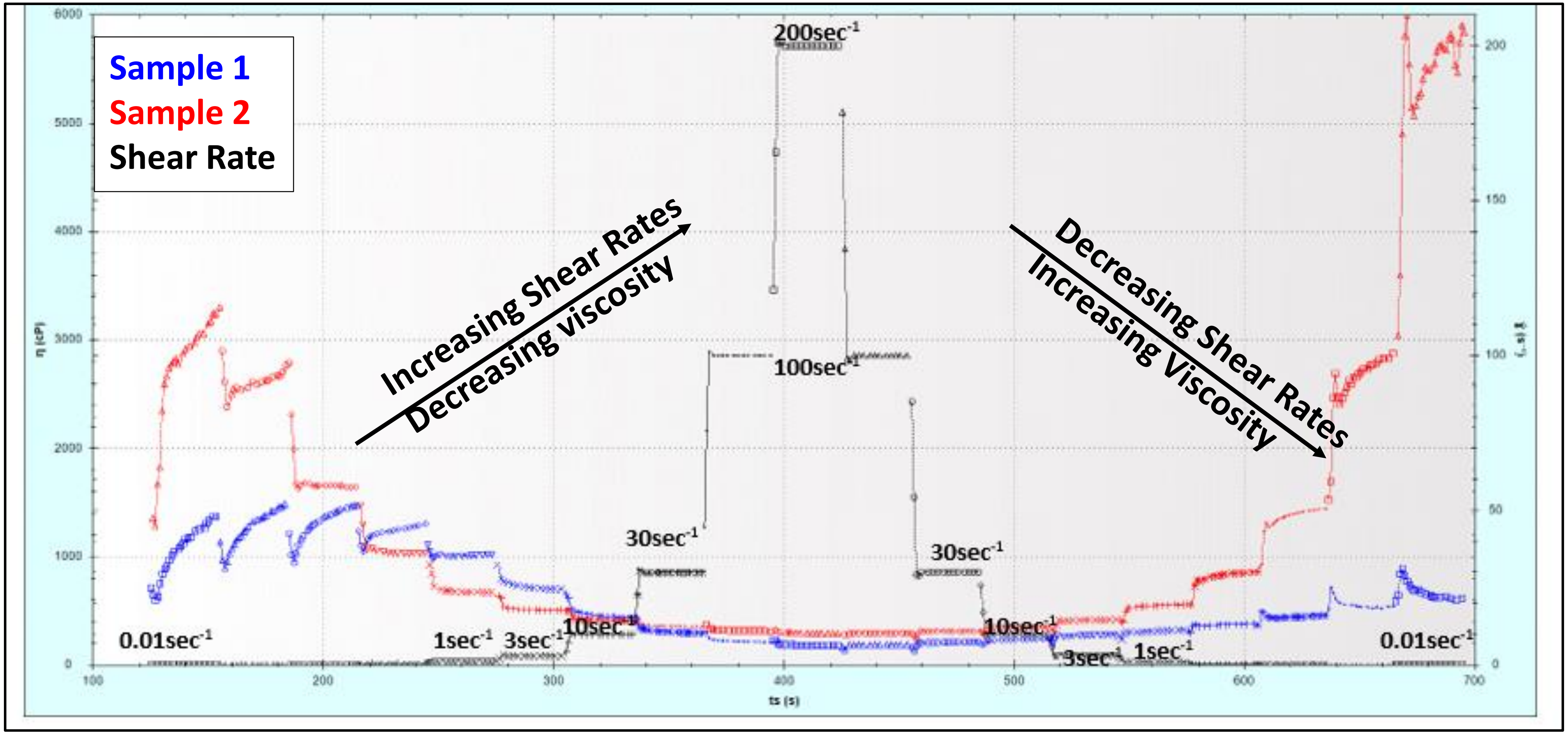
Image from Netzsch

Stepwise shear rate over increasing/decreasing rates for 2 polish samples

- Experimental: 25mm rough plate, 300um gap (150uL), 0.01 → 200 → 0.01sec^{-1}
- 30 seconds hold at each step (10 steps up / 9 steps down)

Results: -Samples thinned with increasing shear rate, then rebuilt with decreasing shear rate

-After shear thinning, Sample 1 under-rebuilt 0.53-fold vs initial, Sample 2 over-rebuilt 1.86-fold.



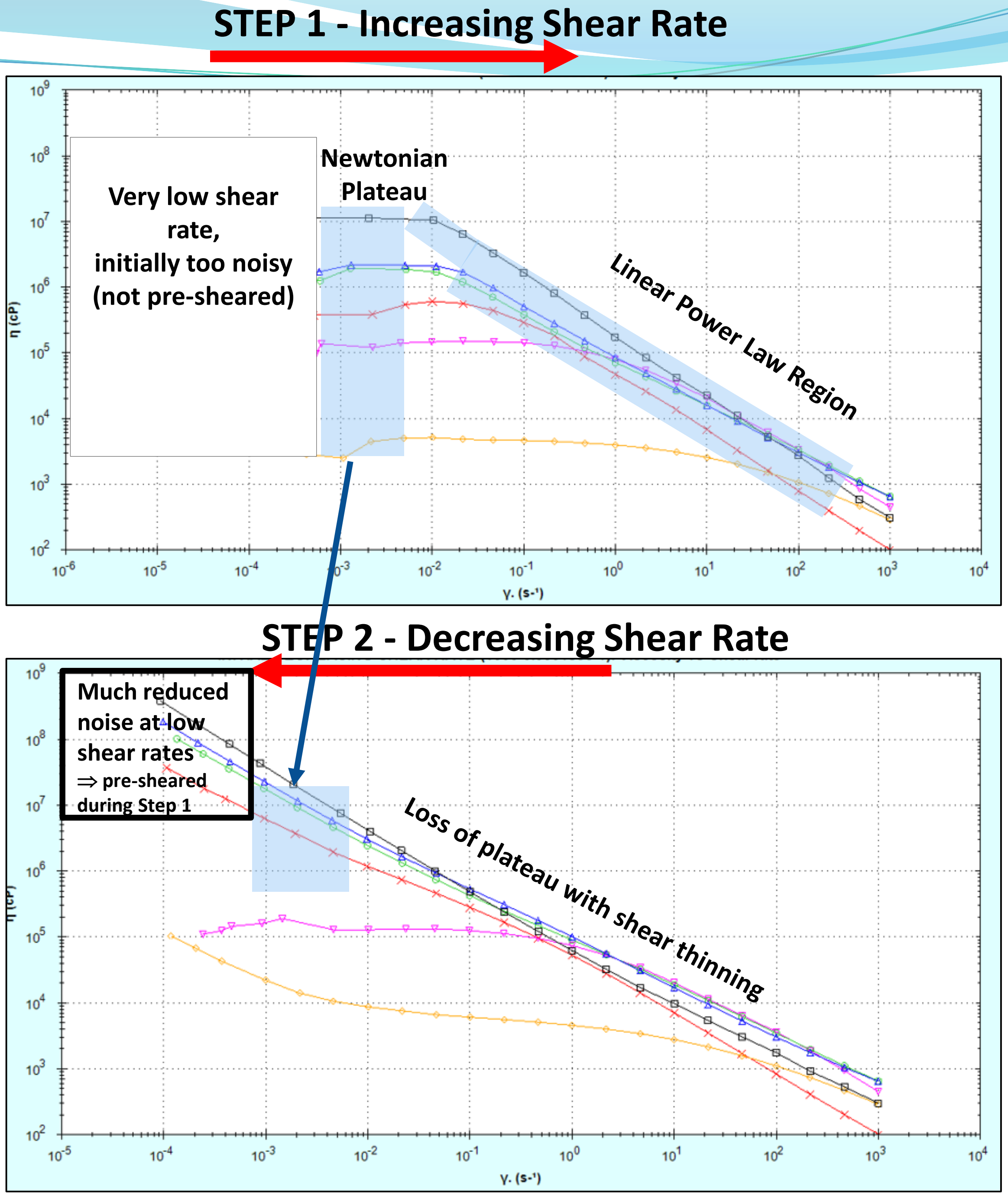
Application: Stepwise shear rate for arthritis products

- Move to next step after stability criteria met(5%).
- Report average over each step.

► **Issue:** Client requested side-by-side rheological profiling for comparison.
1 of many methods.

► **Results:**
-Very different among samples.
-Increasing vs decreasing shear rate results different.

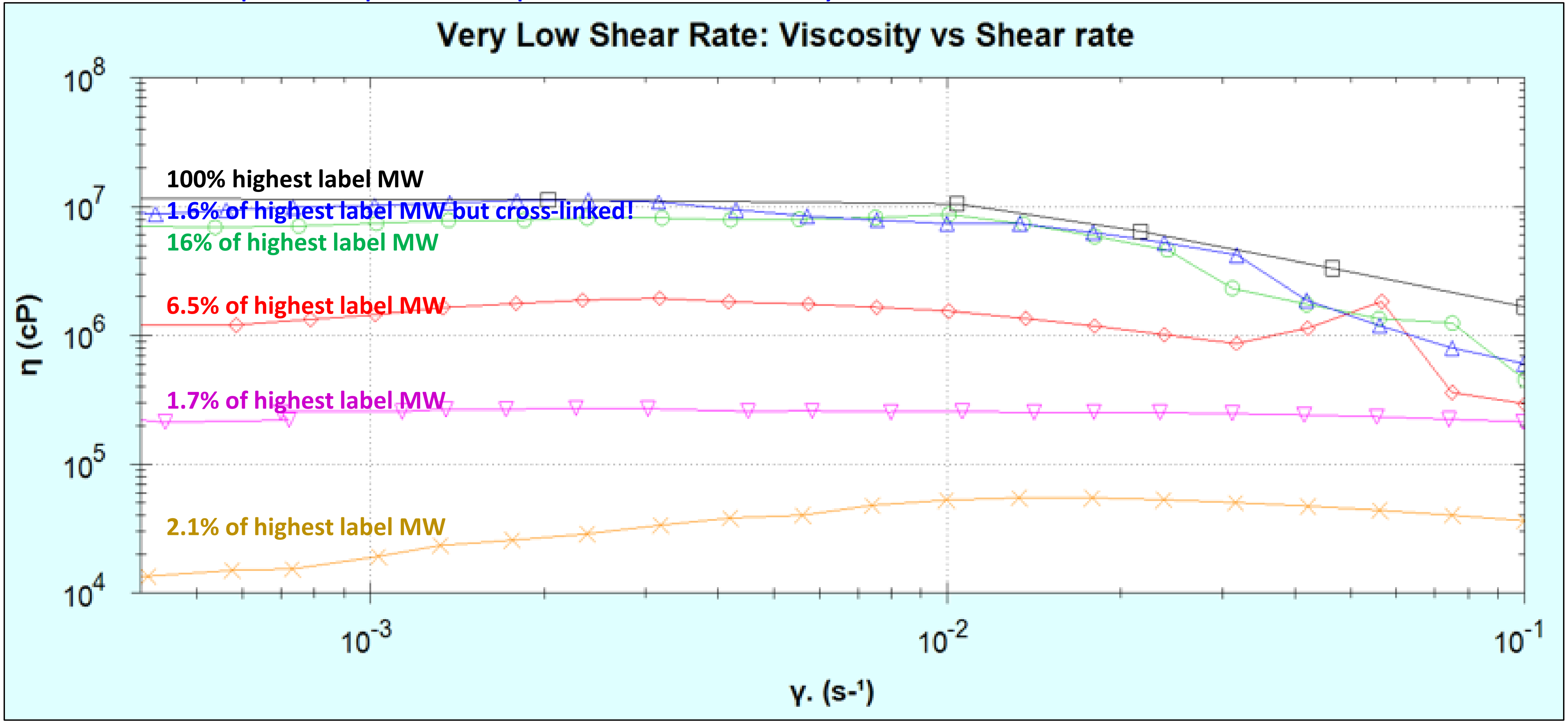
- Experimental: 25mm rough plate, 200um gap (100uL), 0.0001-1000sec^{-1}



Application: Stepwise shear rate - Rank order macromolecule MW vs “zero” shear rate

- **Issue:** Client requested side-by-side rheological profile for several products
- **Results:** Viscosity at Newtonian Plateau correlate with molecular weight (MW).

Expanded plot from previous slide at very low shear rates.



Application: Single Shear STRESS vs Temperature - 6 dispersed polymers

- ▶ **Issue**: Client interested to screen for rheological differences & stability brief exposure to heat
- ▶ **Result:** Difference among batches. All appeared to be rheologically stable.
- Experimental: 25mm rough parallel plate, 0.2mm gap, 15Pa over 5-90-5°C (5°C/min)

Fig 1. Preliminary yield stress assay IDed stable stress (15Pa) for subsequent stress-temperature assay

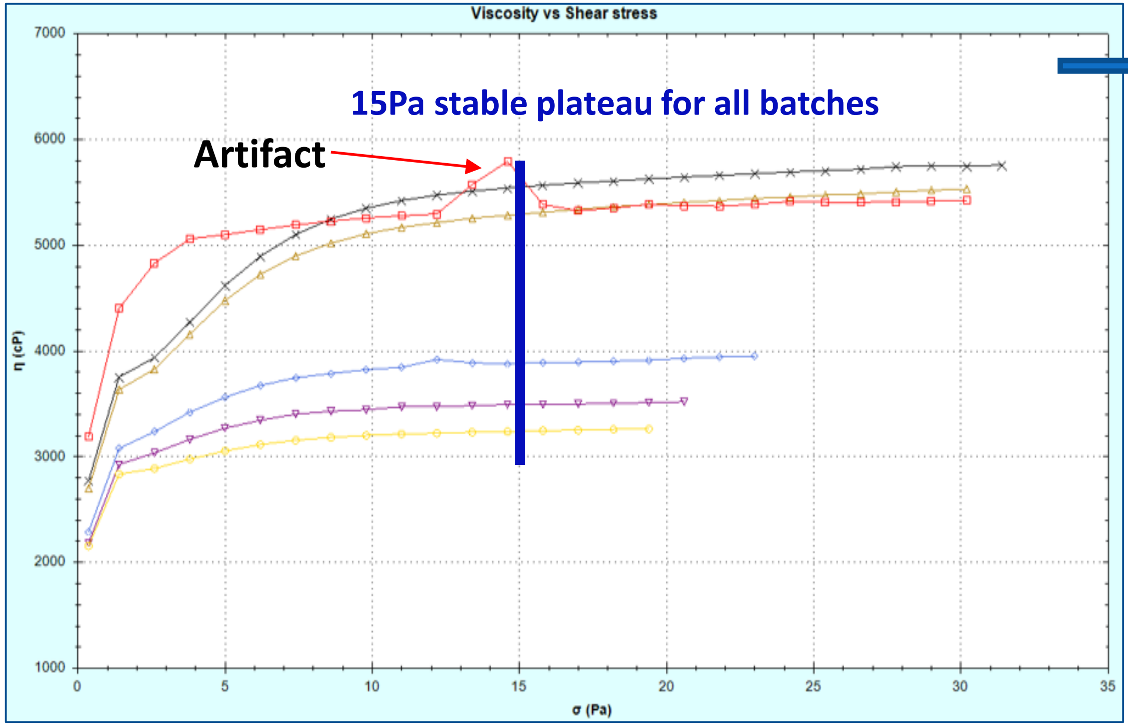
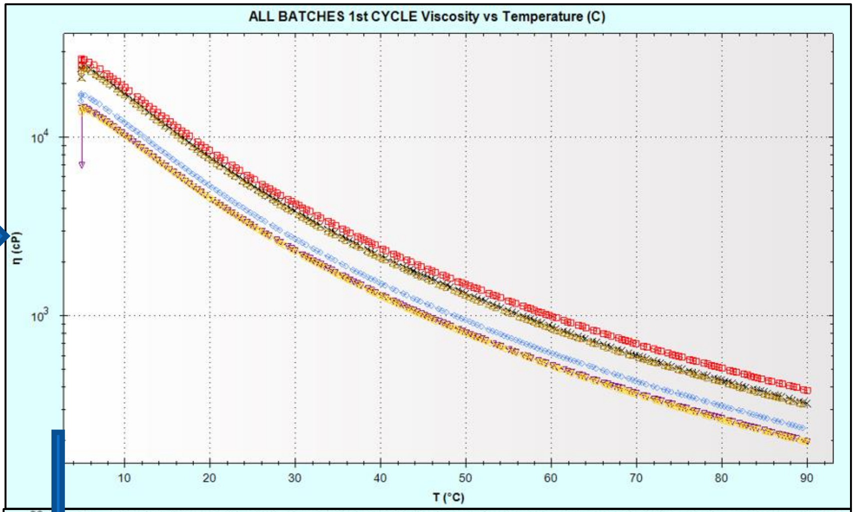


Fig 2. Increasing Temperature Ramp (6 lots)



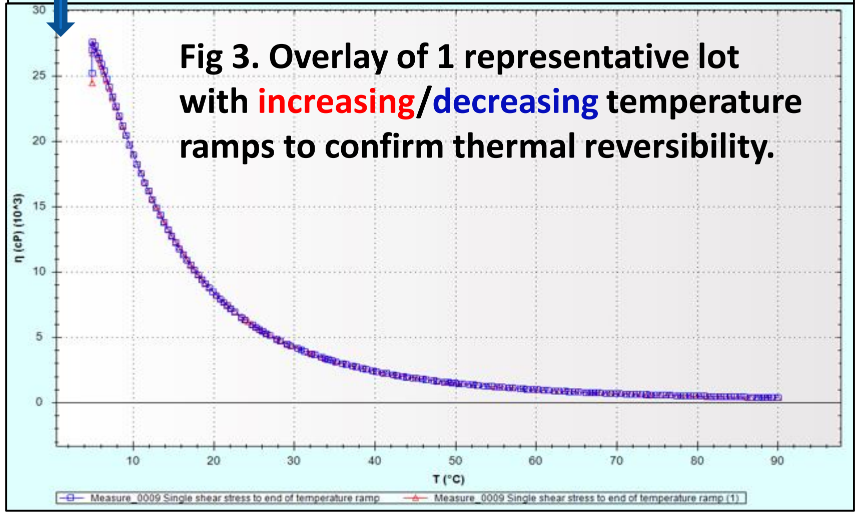


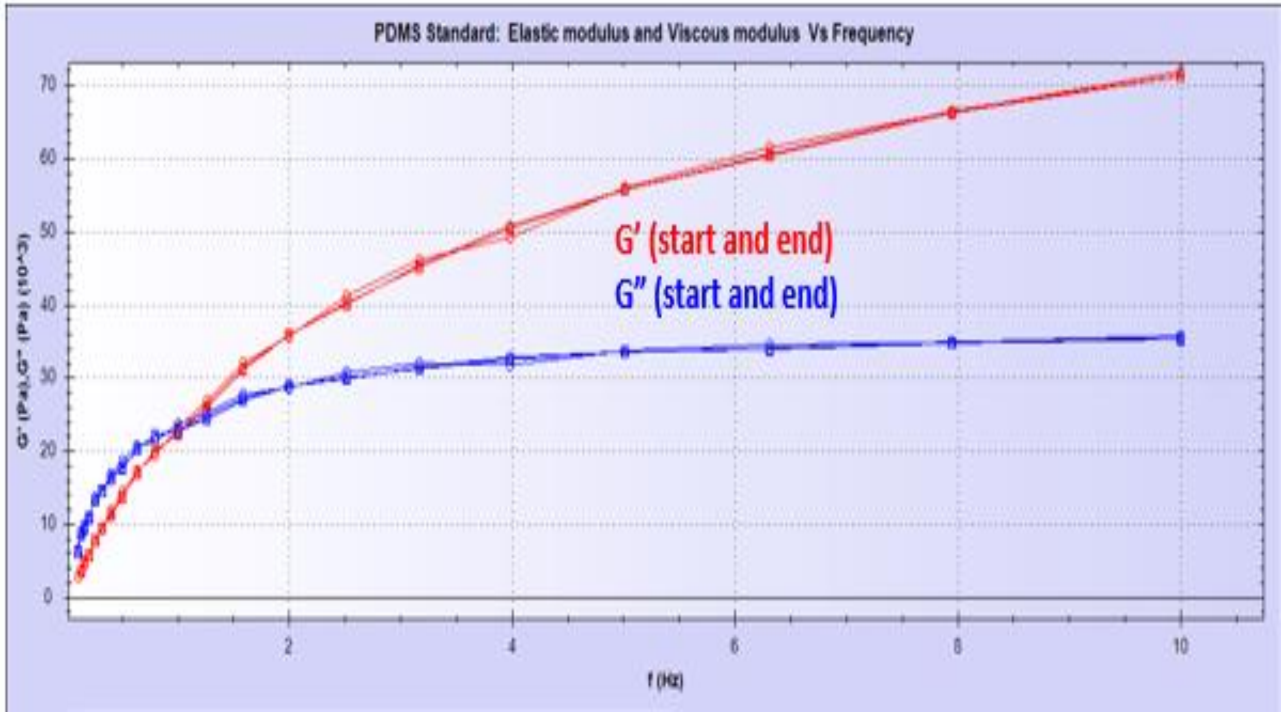
Fig 3. Overlay of 1 representative lot with increasing/decreasing temperature ramps to confirm thermal reversibility.

Now that we've looked at some examples, some experimental considerations….

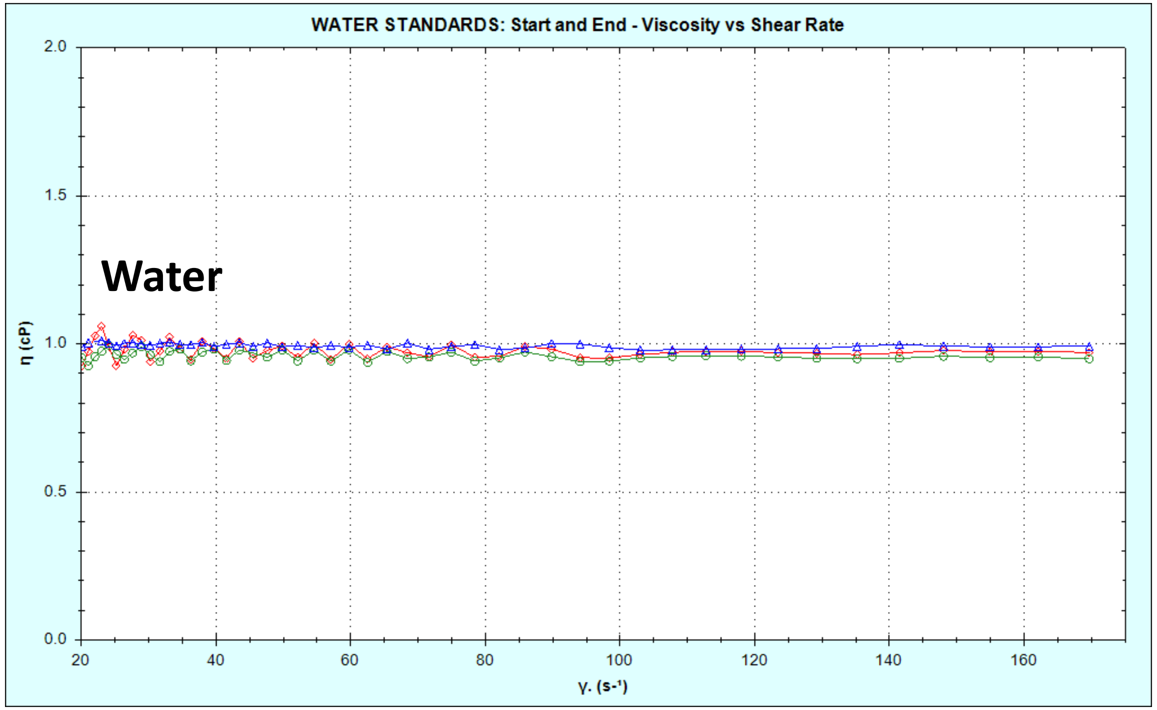
Preliminaries to ensure & confirm rheometer performance:

- Motor Warmup, Torque Mapping, Geometry Inertia
- Performance standards: <u>bracketing</u> water or silicone oil for rotational assays and PDMS for oscillational assays

<u>Oscillational Assays (PDMS)</u>: Frequency sweep 10→0.1Hz
25°C, 0.5% strain, 0.5mm gap with 25mm rough plate vs label claim



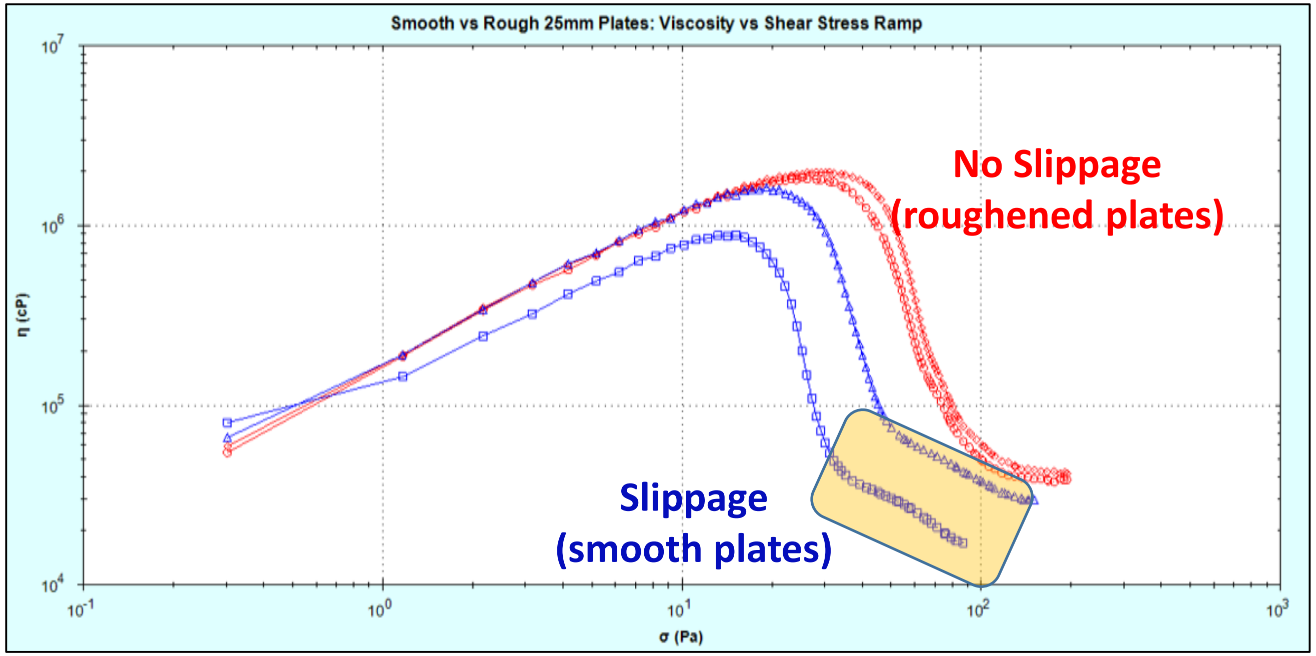
<u>Rotational Assays:</u>
- **Water for highly aqueous, low viscosity samples**
- **Silicone oil standards for higher viscosities**

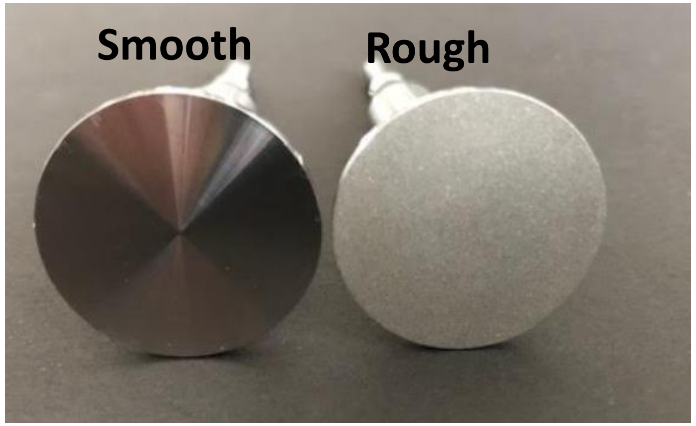


Mindful about slippage at plate-sample interface

- Plate must impart force through sample, not just at plate-sample interface
- Slippage leads to experimental error, variability and conclusions

▶ Use roughened or serrated plates to reduce potential for slippage





Example of "Slippage" at of top cards→

Other Experimental Considerations

- **Consistency is critical!**

  -Handling during loading (minimize shear, bubbles, volatiles loss (more later))

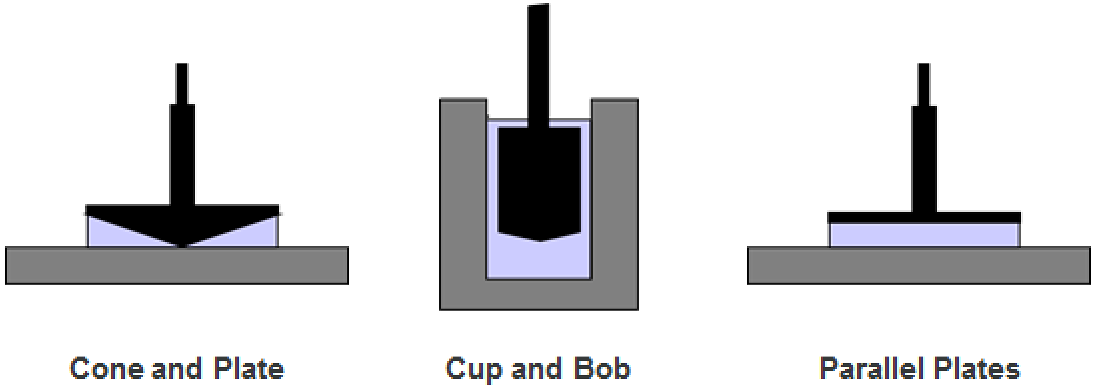
  -Trim to remove excess sample

- **Geometry: Cone, Plate or Cup & Bob, vane, many options**

  -Cone gives more consistent shear across sample vs plate.

  -Cone not recommended for temperature sweeps if not compensate for thermal expansion

  -Plate allows flexible and smaller gap to generate higher shear rate without losing sample. Cone has default gap.



- **Plate/Cone Size**

  -Larger diameter provides more sample contact to provide more torque; but requires more sample

  -Larger diameter is more sensitive for less viscous samples and achieves smaller strain amplitudes for oscillatory assays.

  -Smaller diameter better for increasingly viscous and viscoelastic samples.

Other Experimental Considerations (continued)

- **Consistency is critical! …repeating**

Shear rate = strain/time
(Strain=displacement/height)

- **Gap (sample height)**

-Typically 0.2-1mm. Depends on sample and assay parameters. (human hair ≈70+/-20um)

-Smaller gap requires less sample (100ul for25mm plate for 200um)
-Smaller gap:
  -facilitates assay at higher shear rate
  -reduces potential to lose sample from gap at high shear rate
  -small gap inaccuracies may lead to modest % assay error
-Larger gap facilitates smaller strain amplitude

-1/10 rule: plate-plate gap > 10x largest particle or droplet. Default gap for cone tip = 30um.

-Gap setting options to provide consistent sample loading:
  -<u>height</u> → Typical 200-1,000um.
  -<u>force</u> → For samples with inconsistent thickness (i.e. cheese) or difficult to compress (polymer films). Rheometer software accounts for sample height.

⇒Kinexus rheometer tracks both gap height and force for each datapoint throughout assay

Other Experimental Considerations (continued)

- **Pre-Shear or not to pre-shear…..**

  -Depends on question to be answered

  -Any sample movement (loading) may irreversibly shear thin sample, maybe not!?! Screen with thixotropy assay (later)

  -Can apply very low pre-shear to "normalize" for handling effects

  BUT*… can "erase" other rheological properties especially if sample easily shear thins with poor rebuilding.*

- **Sample change during handling and analysis**

  -Curing, degradation, rebuilding, cross-linking, volatiles loss, etc

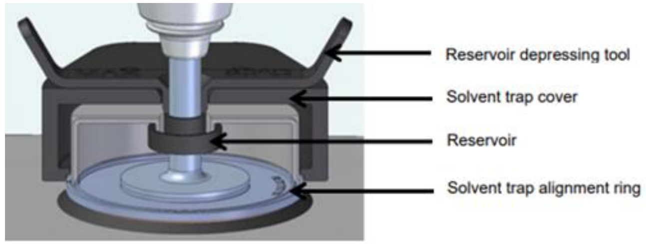
  -Rotational: Screen with <u>single</u> shear rate or shear stress vs time at assay temperature(s) and monitor viscosity

  -Oscillational: Screen with <u>single</u> frequency vs time & monitor G', G", δ, G* changes

  what are G', G", δ, G* ?   *Stay tuned……*

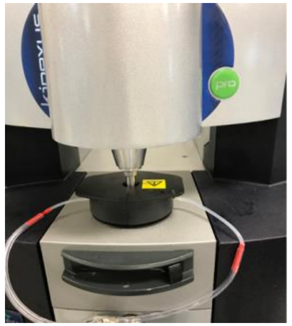
-Got volatiles? Use a solvent trap

-Maintain sample in enclosed volatiles saturated environment (i.e. humidity)



-Sensitivity to oxidation at elevated temperature →

enclosed, low N_2 flow



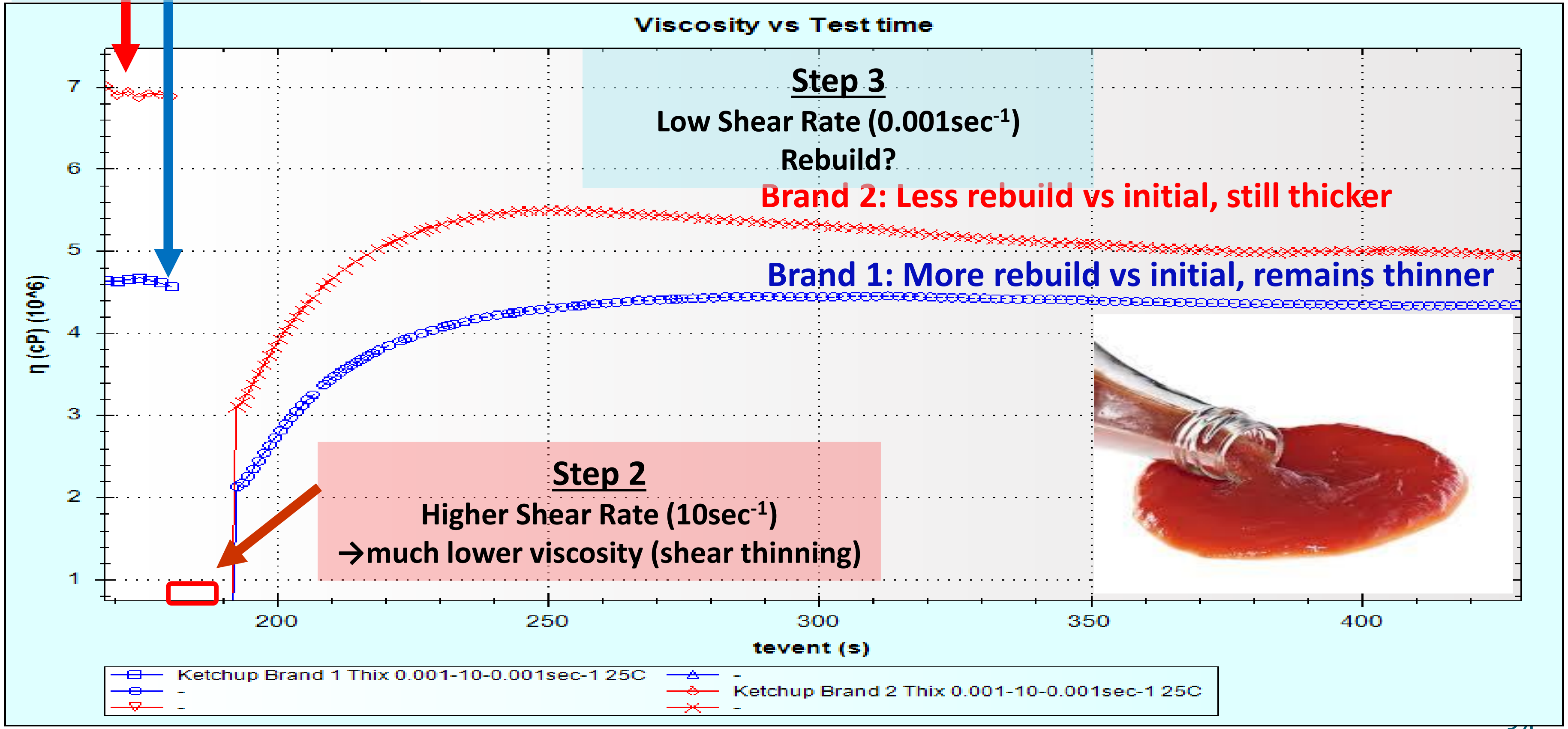
Application: Thixotropy (3-Step) – Ketchup…again

▶**Issue:** Client (engineers) requested ketchup data for process modelling
Determine rebuild extent and rate after exposure to higher shear

- Careful about selection of shear rates for each step…not too low, not too high

⇒Depends on question seeking to answer……..

Step 1
Low Shear Rate (0.001sec^{-1})
Baseline



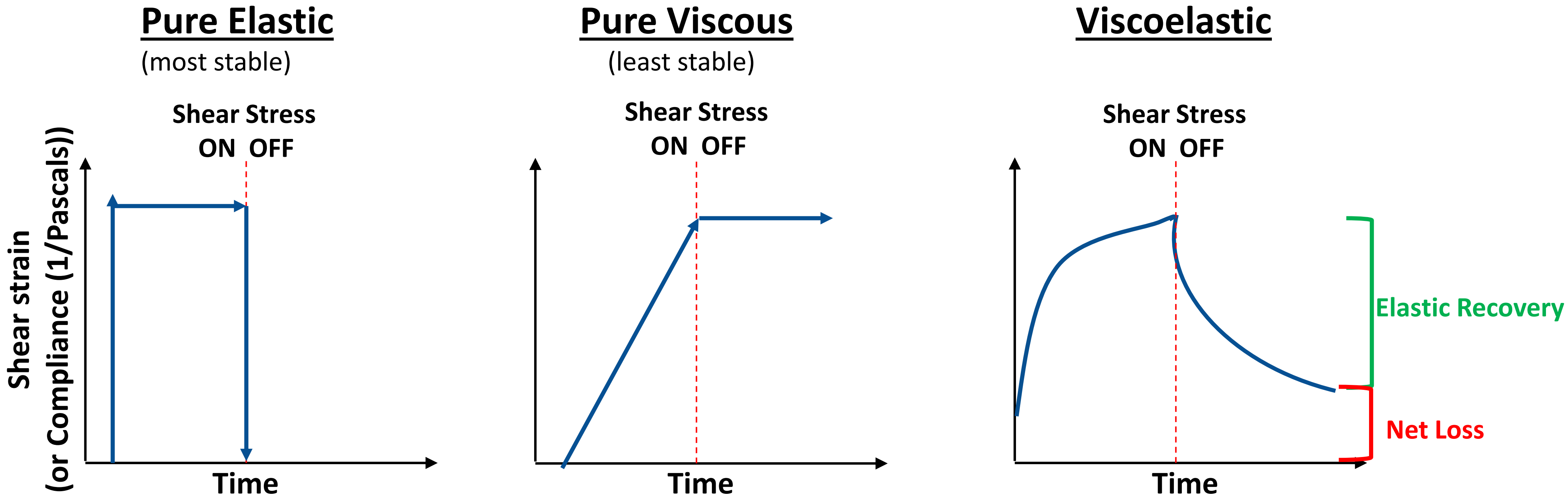
Creep-Recovery

Response to applied stress and release

⇒ Quantitate net loss of elasticity following stress

⇒ Used to determine zero-shear viscosity and evaluate suspension stability

Squeeze/twist and release



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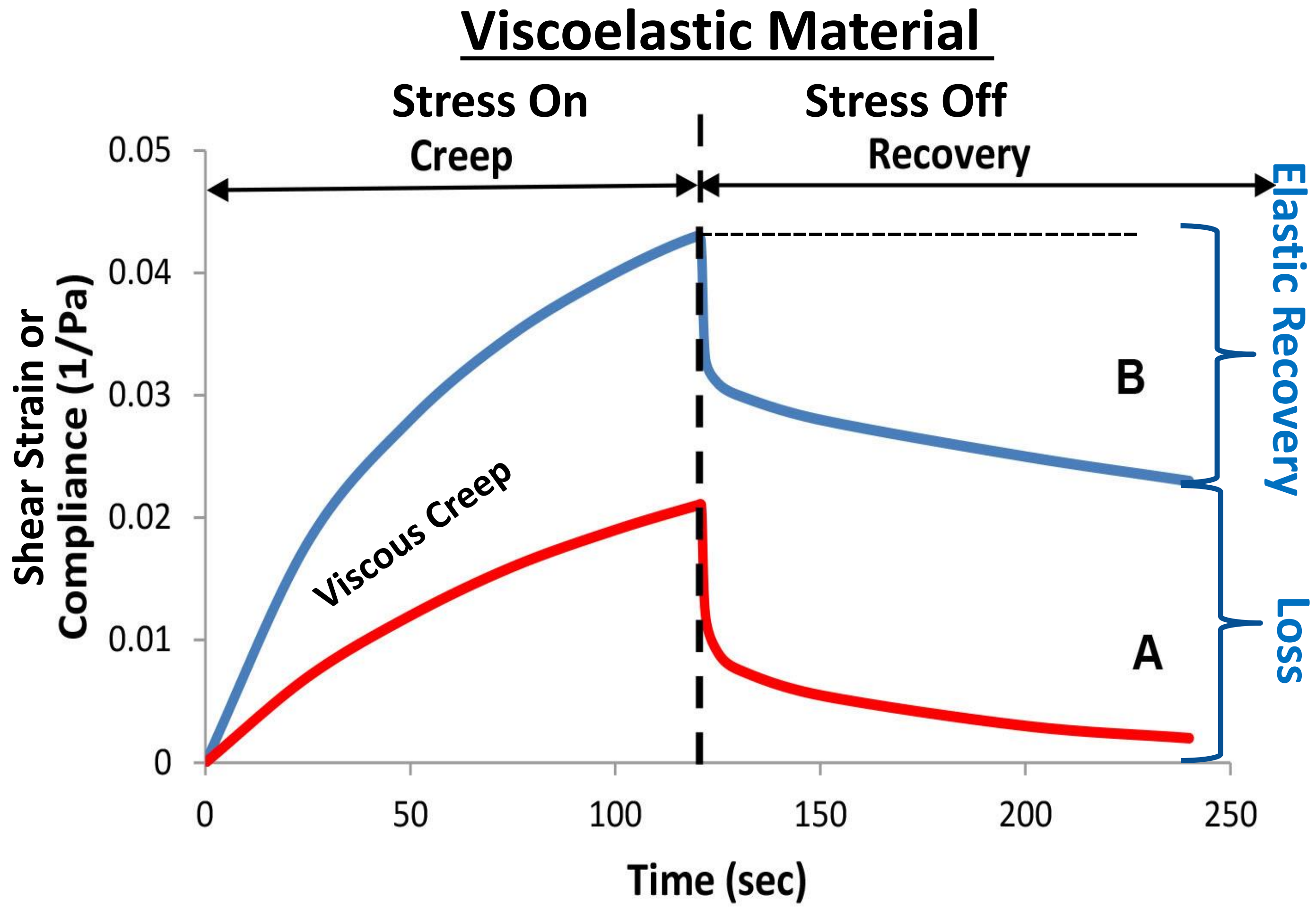


Application: Tribology (friction) of 5W-30 motor oils at 15, 25 & 125°C

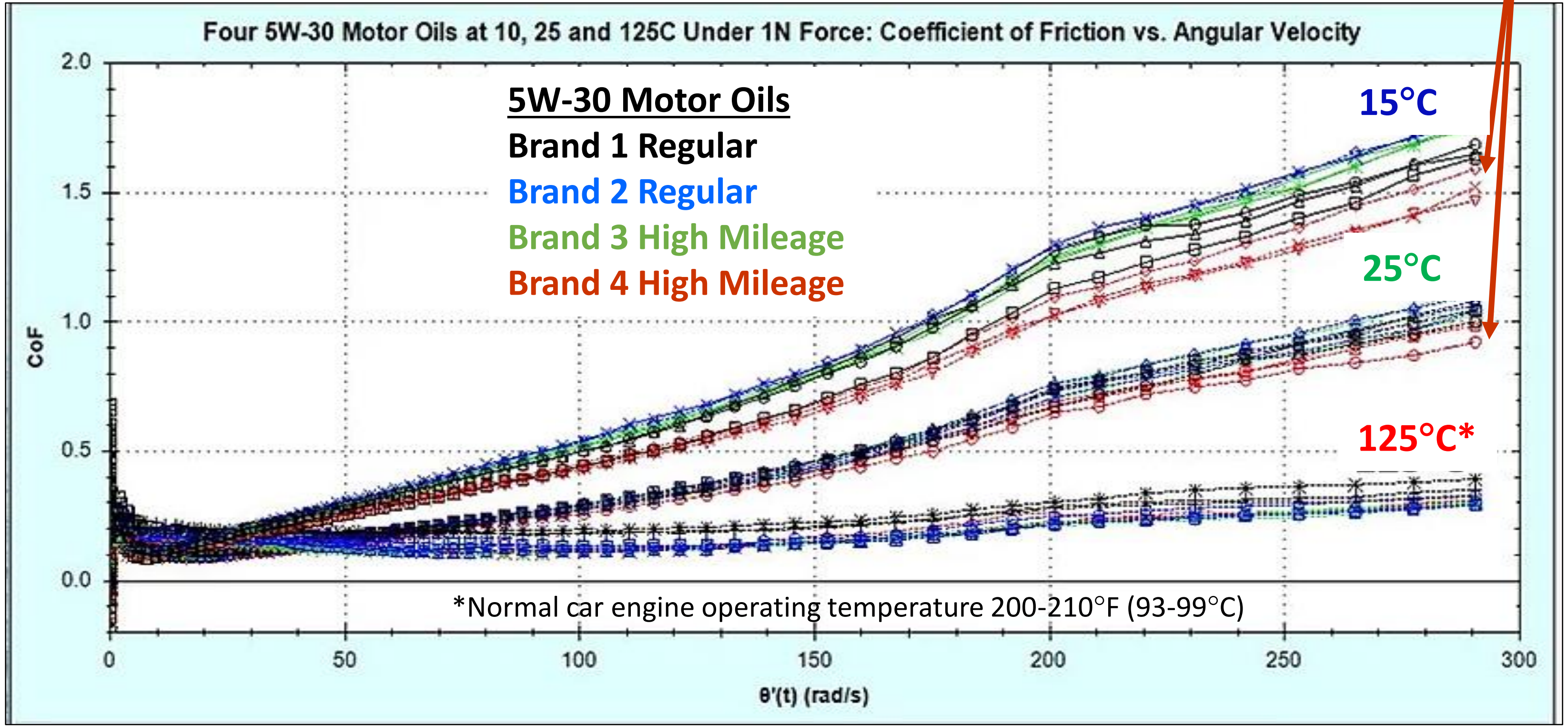
►**Result:** Differences among samples decrease with increasing temperature and decreasing shear

⇒ food and cosmetics applications

per ISO7148

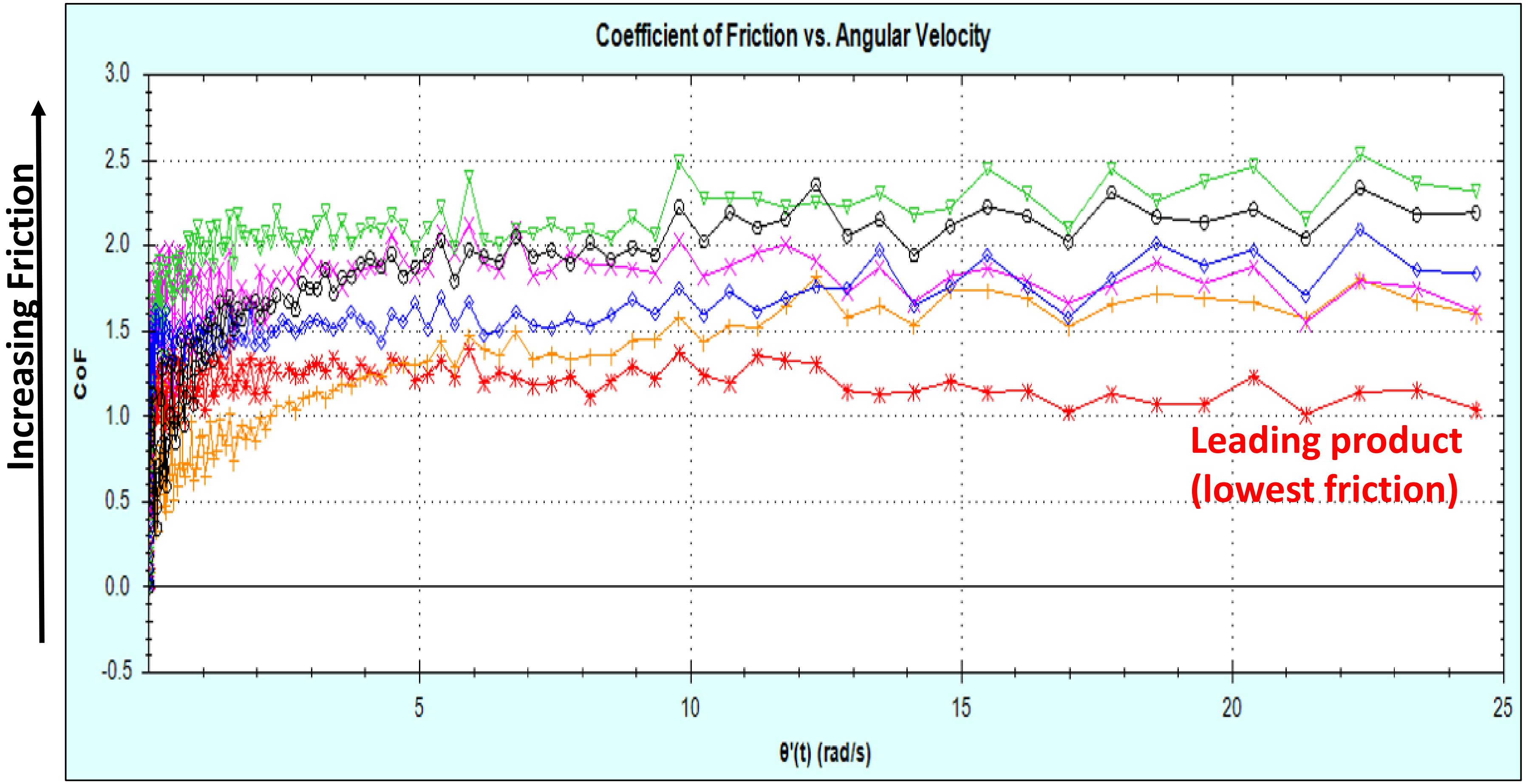
Stribeck Curves

Increasing Friction



Application: Tribology (friction) for arthritis products

- ▶ **Issue**: Client wanted to compare friction properties of 6 products
- ▶ **Result:** Observed ≈2-fold difference with leading product having least friction among samples
- Experimental: 36°C, 0.2N over 0.0001 to 100 radians/sec. Requires ≈300uL sample



Switching gears from rotational to oscillational assays

<u>Movements → torque</u>

- Rotational (1 direction)
- Oscillational (bi-directional)
- Vertical

Rheology Testing Services

Oscillation ≈ washing machine agitator…sort of

2 ways to modulate oscillation

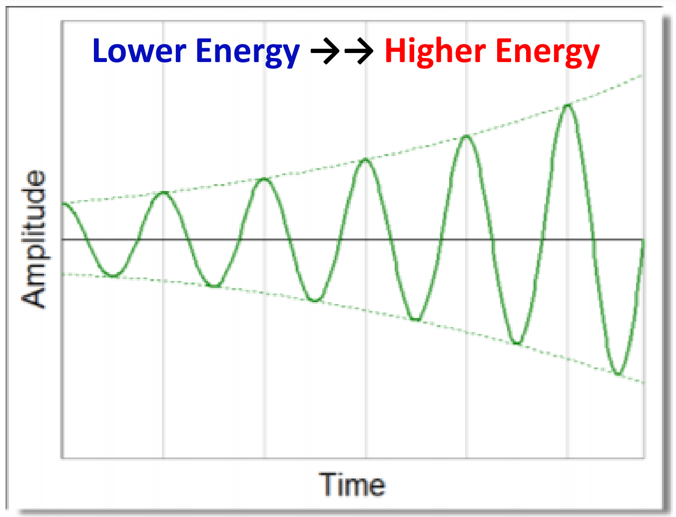
1. Amplitude (destructive)

- Determine Linear Viscoelastic Region (LVER)
  ⇒"Breaking point" of structure ∝ stability

- Textural properties: stiffness, springiness, structural strength, brittleness

2. Frequency (non-destructive)

- Measure response to event time =1/freq
  -Probe structural properties within LVER to maintain rheological integrity during assay



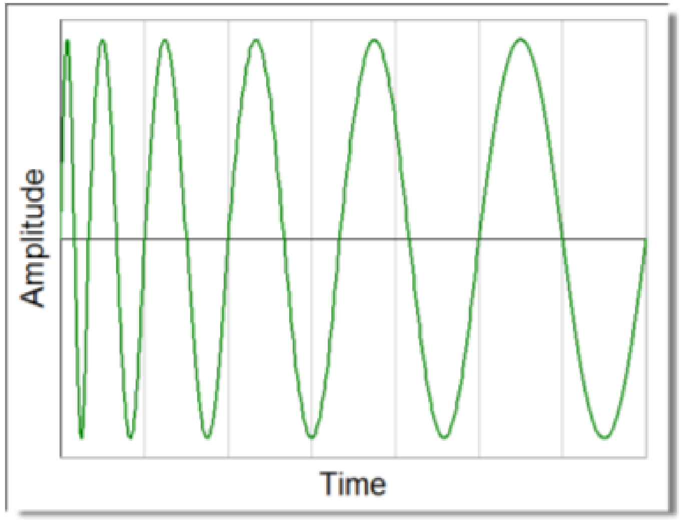


Image from Netzsch

Oscillation - Amplitude Sweep

⇒ Increase amplitude (energy) until "break" macrostructure

⇒ Determine LVER before perform frequency sweep to ensure sample integrity

⇒ LVER can be frequency and temperature dependent

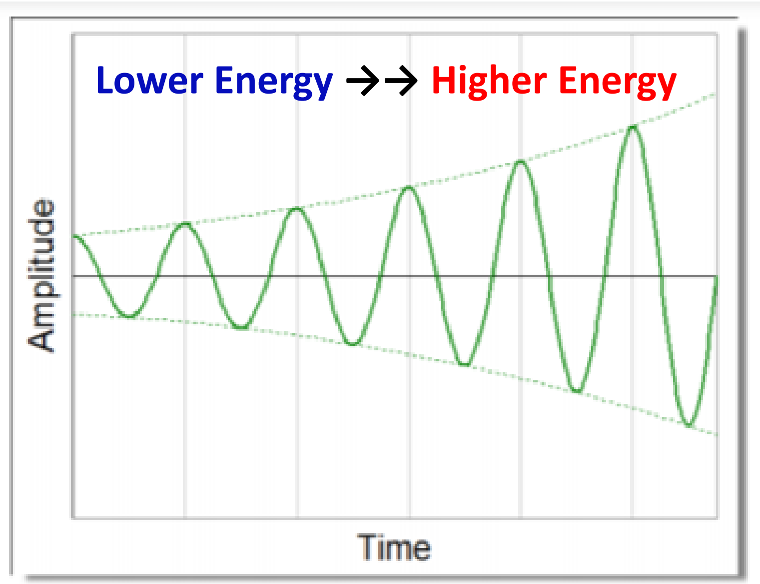
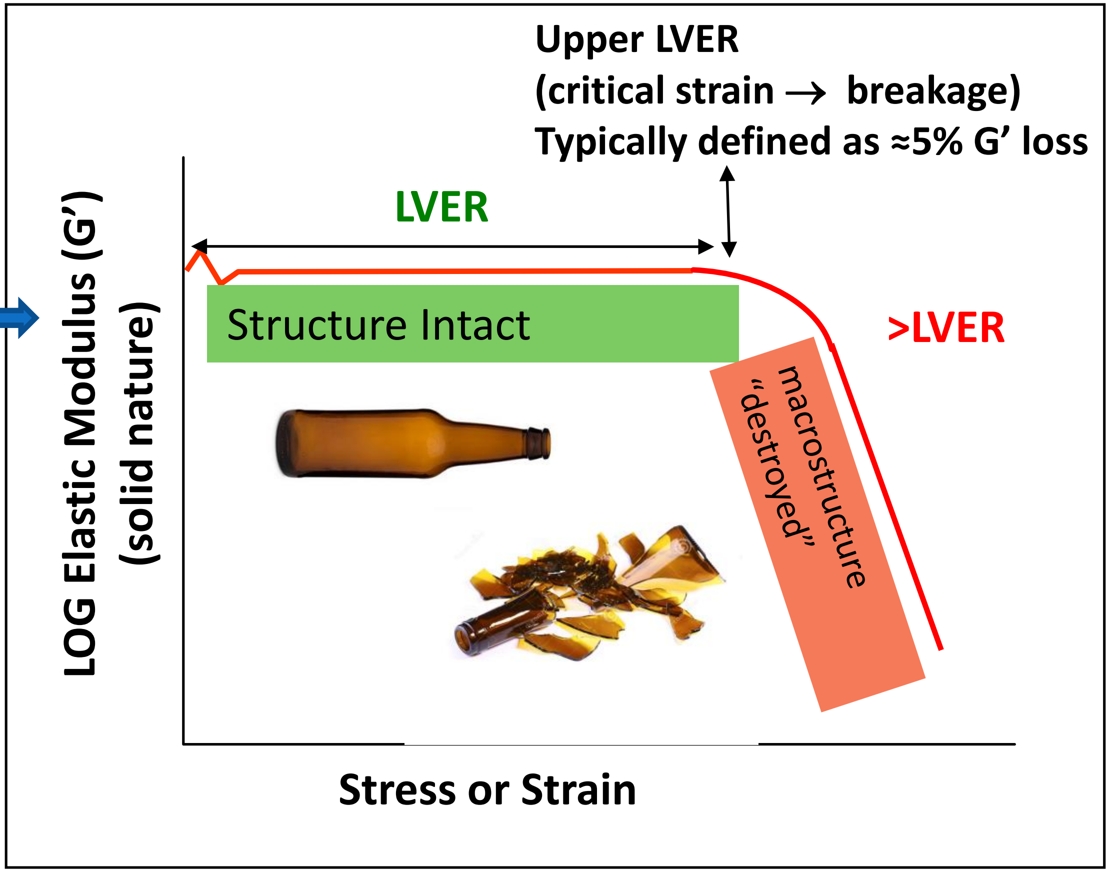


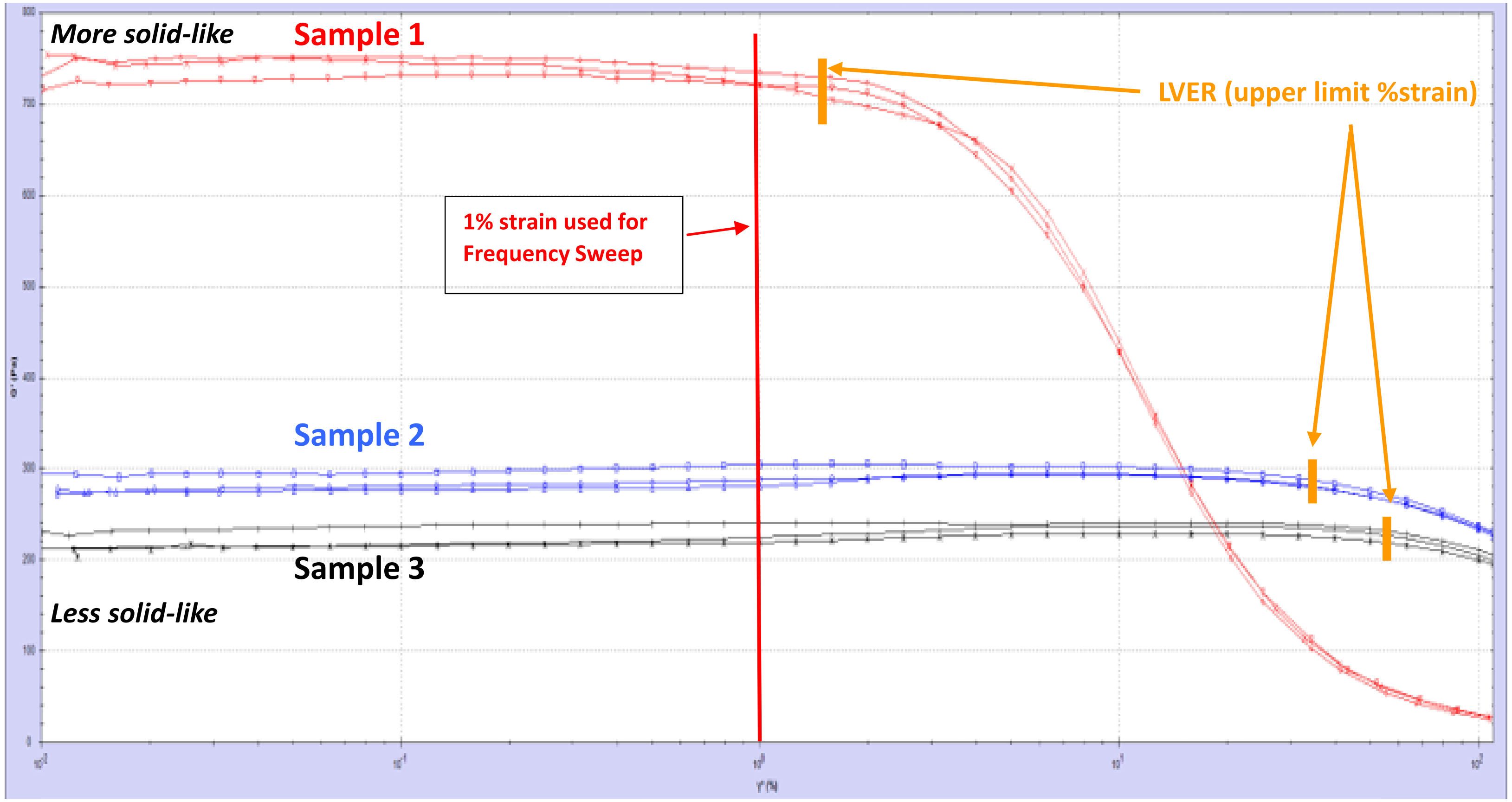
Image from Netzsch



Application: Amplitude Sweep: G' vs % strain → LVER for biomedical gels containing hyaluronic acid

► **Issue**: Compare properties. ALSO needed LVER from amplitude sweep for subsequent frequency sweep assay input.

► **Result:** Observed large G' differences. Determined input %strain for subsequent frequency sweep



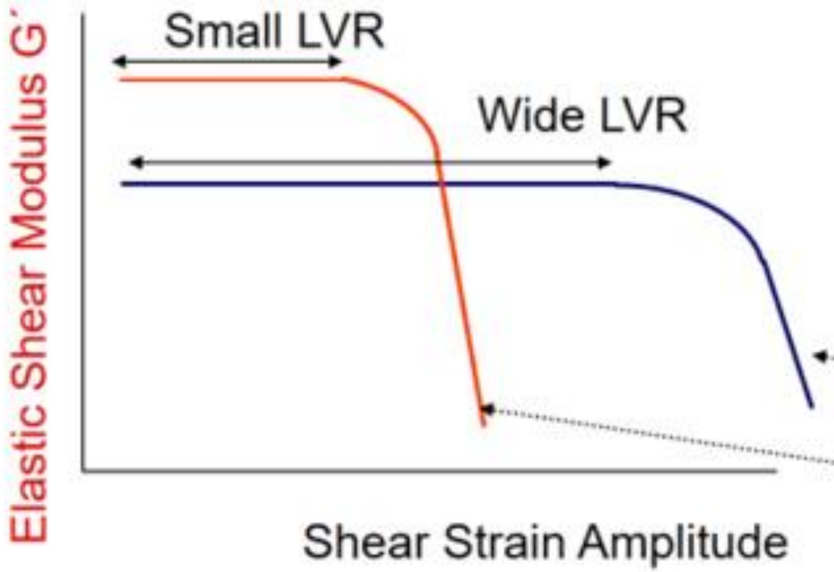
Sample	G' (plateau) Pa	$LVER_{upper\ limit}$ % strain*	% strain for frequency sweep
Sample 1			
AVG (n=3)	**743**	**1.8**	**1**
Std Dev	9.7	0.3	
%RSD	1.3	19.7	
Sample 2			
AVG (n=3)	**298**	**31.6**	
Std Dev	5.2	0.008	
%RSD	1.8	0.026	
Sample 3			
AVG (n=3)	**235**	**63.1**	
Std Dev	5.0	0.005	
%RSD	2.1	0.007	

* LVER typically defined as 5% G" decrease determined from data tables, not from plots.

Interpretation of Amplitude Sweeps: Shelf Life of Dispersions

NETZSCH

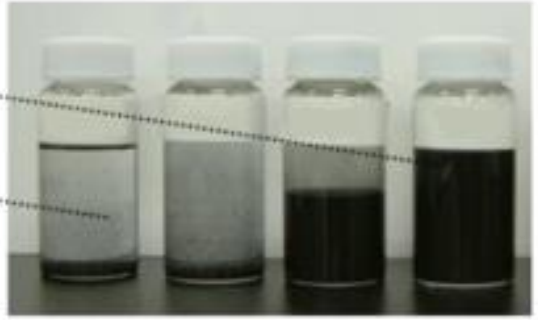
Quick Check of Shelf Life without Prediction of Timescale!



Cohesion Energy Density

$$E/V = \tfrac{1}{2}\, G' \times \gamma_{kr}^{2}$$

Units: $\frac{J}{m^3} = \frac{kg \cdot m^2}{s^2} \cdot \frac{1}{m^3} = \frac{kg}{m \cdot s^2} = \frac{N}{m^2} = Pa$



Long-Range Interactions increase the Cohesion Energy by enlarging the LVR.

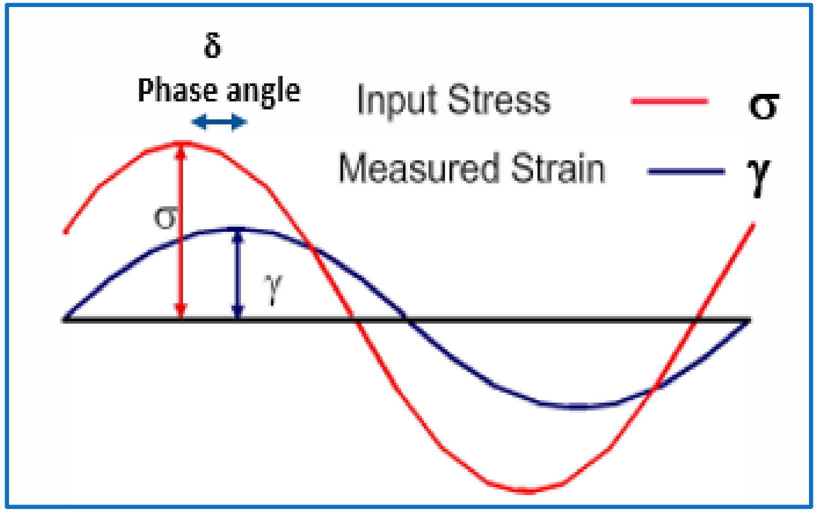
Slide from Netzsch

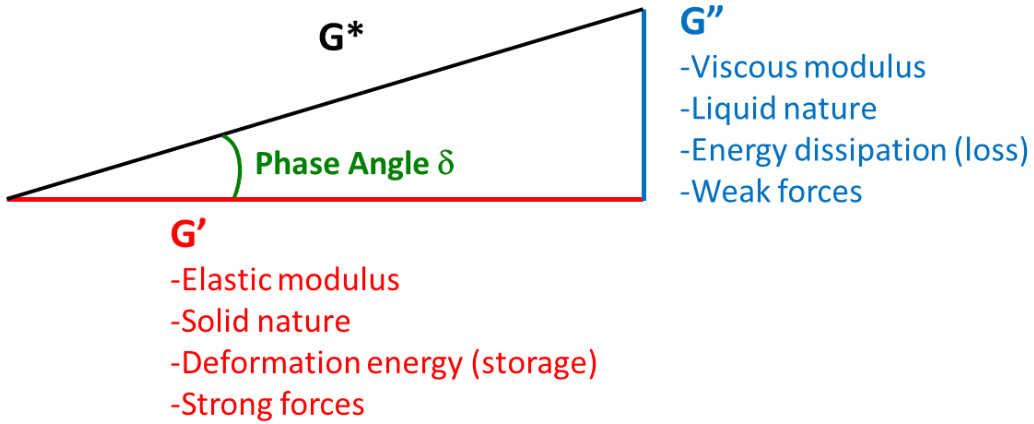
FREQUENCY SWEEP: Outputs G', G", δ, G*, η* and tan delta

- **G' (Pascals)** = elastic or "storage" modulus ≈ solid nature
- **G" (Pascals)** = viscous or "loss" modulus ≈ liquid nature
- δ **(degrees)** = phase angle → increasingly solid 45° to 0°
  → increasingly liquid 45° to 90°
- **tan δ = G" / G' =** energy lost/energy stored during cyclic deformation
  tan δ < 1 → particles highly associated due to colloidal forces, sedimentation could occur

- **G* (complex modulus) = Stress$_{(max)}$ / Strain$_{(max)}$ ∝ Stiffness**

- **η* (complex viscosity) = G*/ 2πf where f= angular frequency (rad/sec)**

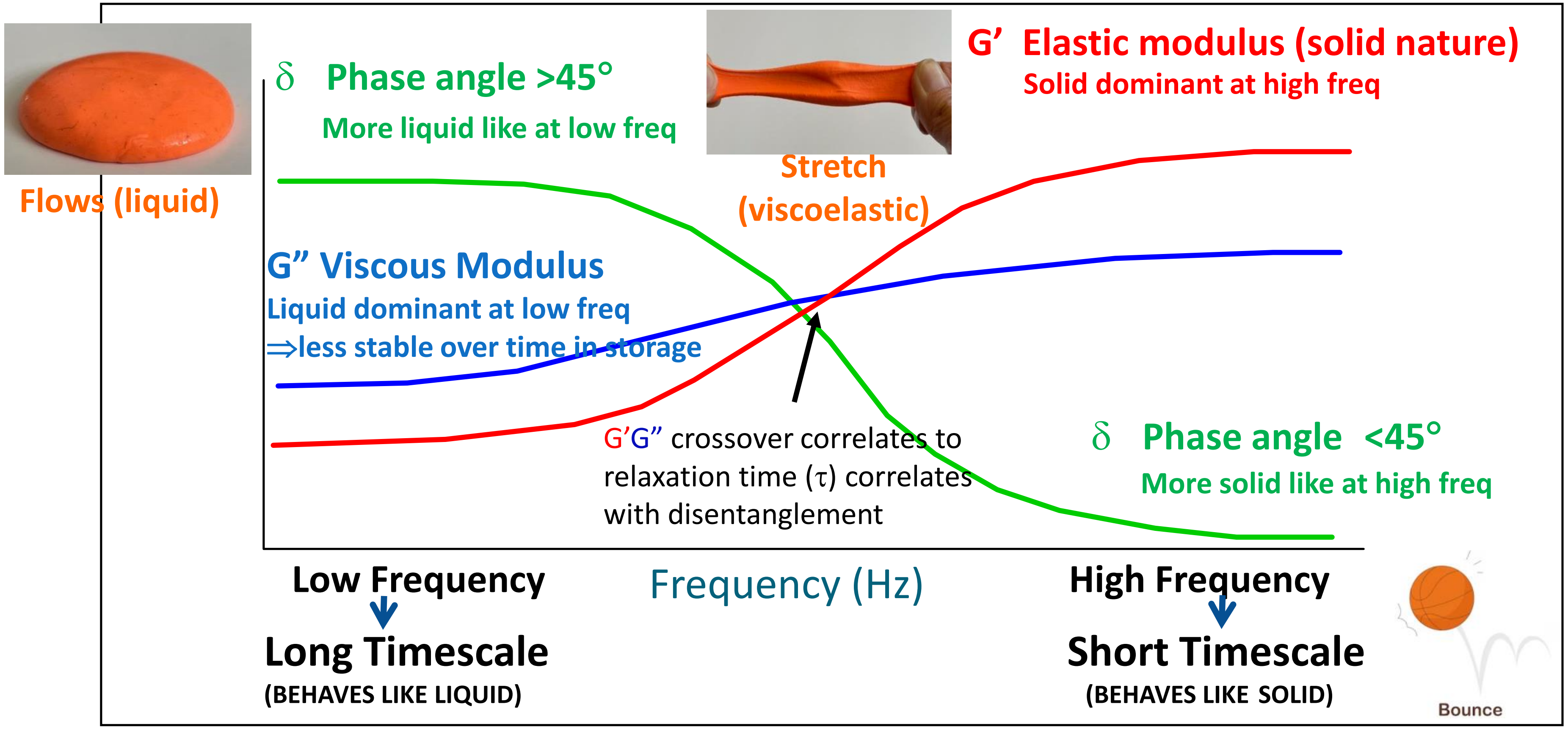




Frequency Sweep: Example Silly Putty → Liquid or Solid?

- Probe properties across a time domain. Frequency = 1/time (sec)
- Unique rheological "fingerprint" or "spectrum"
- Use % strain as assay input < LVER from amplitude sweep

At lower Hz, the molecular relaxation time is shorter than test freq, more liquid-like with G" > G' ⇒ flows.

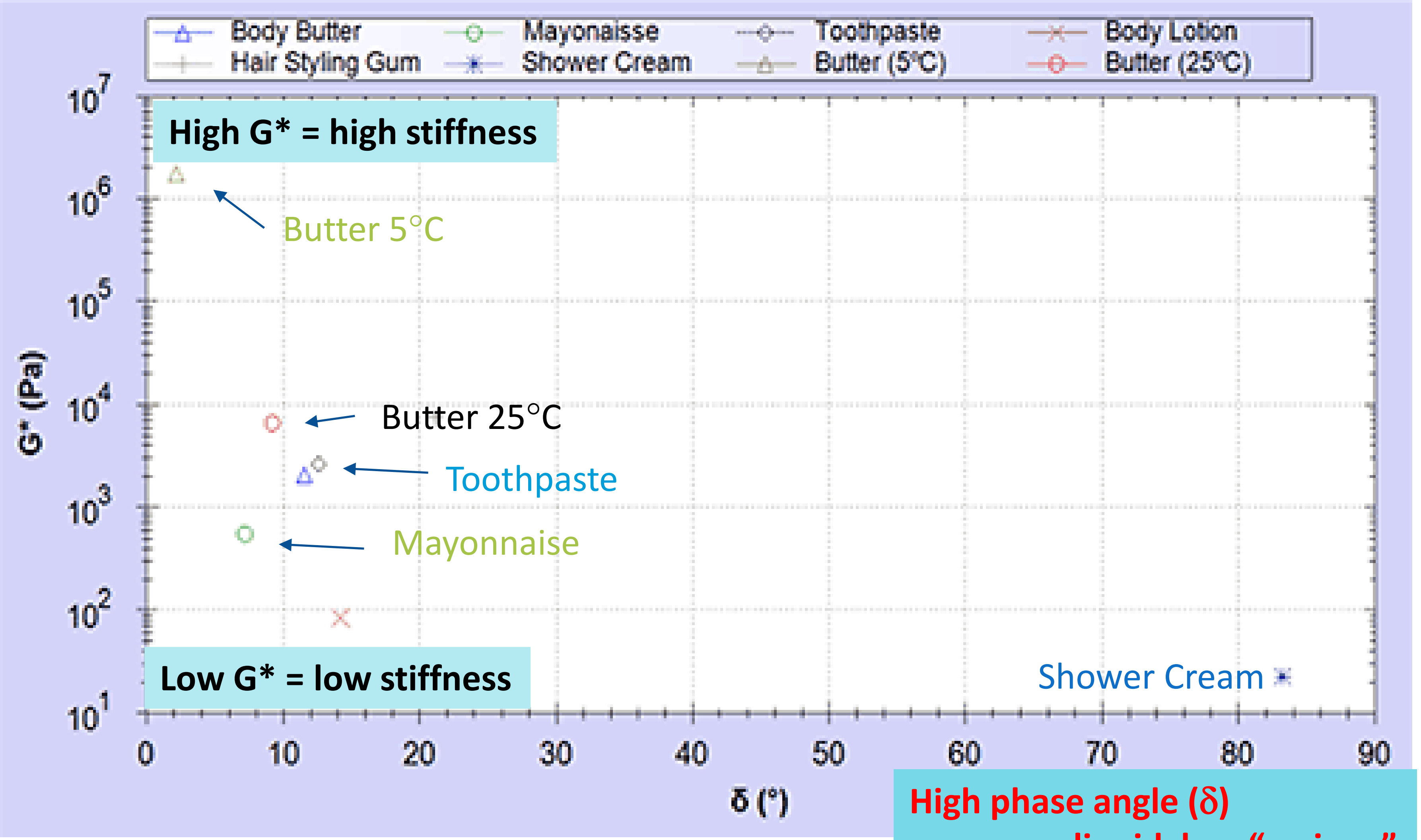


At higher Hz, the molecular relaxation cannot follow the test freq, therefore, G' >G", more solid-like.

Bounces (solid)

Quantifying Texture

Complex modulus (G*) vs Phase Angle (δ) at 1Hz and consistent %strain

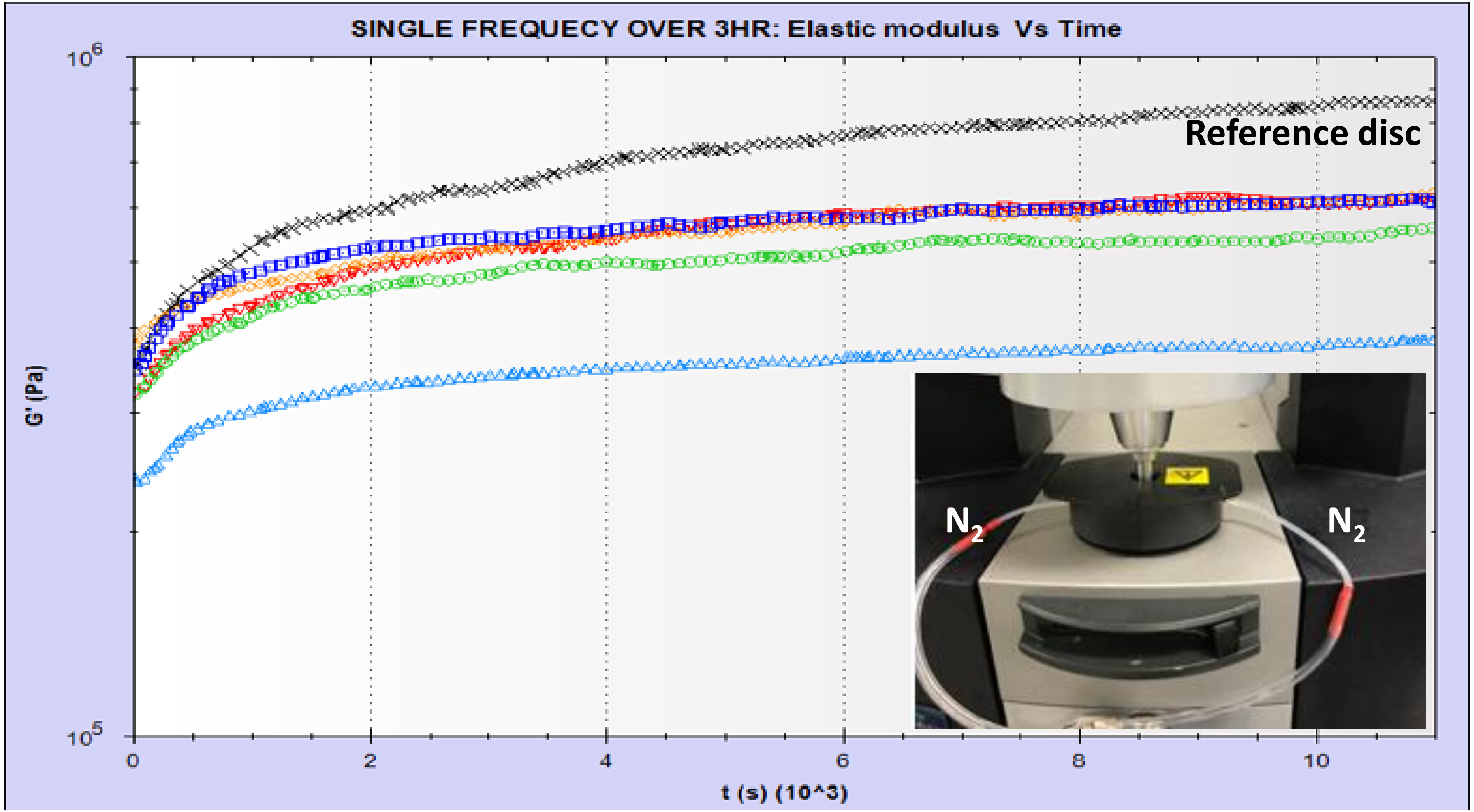


High phase angle (δ)
= more liquid, less "springy"
= less elastic

Image from Malvern Pananalytical /Netzsch

Application: Primary assay: Single frequency for polymeric discs gapped with 4N downward force, then assayed 3hrs at 180°C under N_2 using 1.59Hz at 0.5% strain

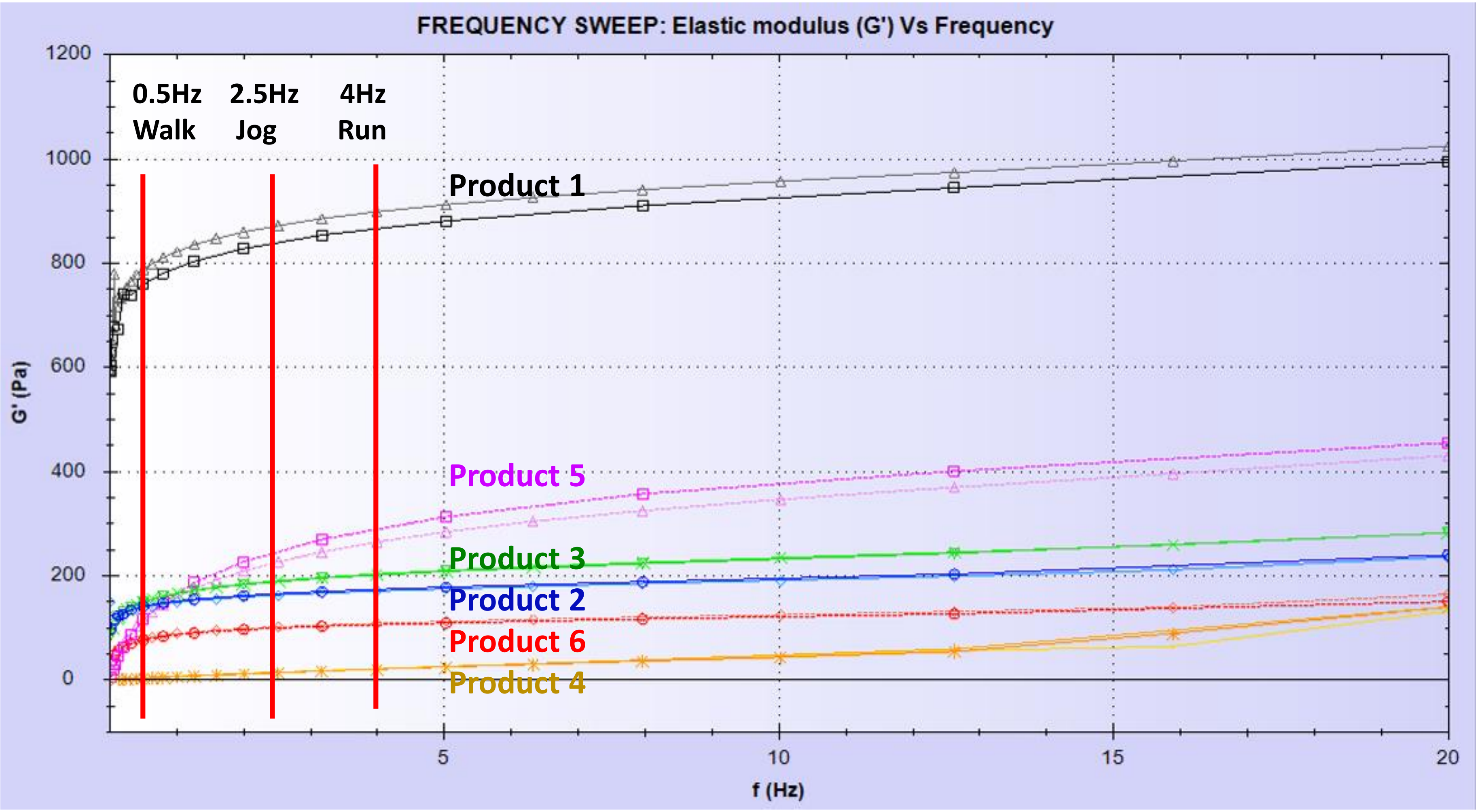
- **Issue**: Compare thermal stability discs vs % anti-oxidant
- **Result:** Samples different regarding G'$_{(plateau)}$ and stabilization rate



Application: Frequency sweep - G' from 20 to 0.01Hz, 3% strain* – 6 Arthritis products (n=2 each)

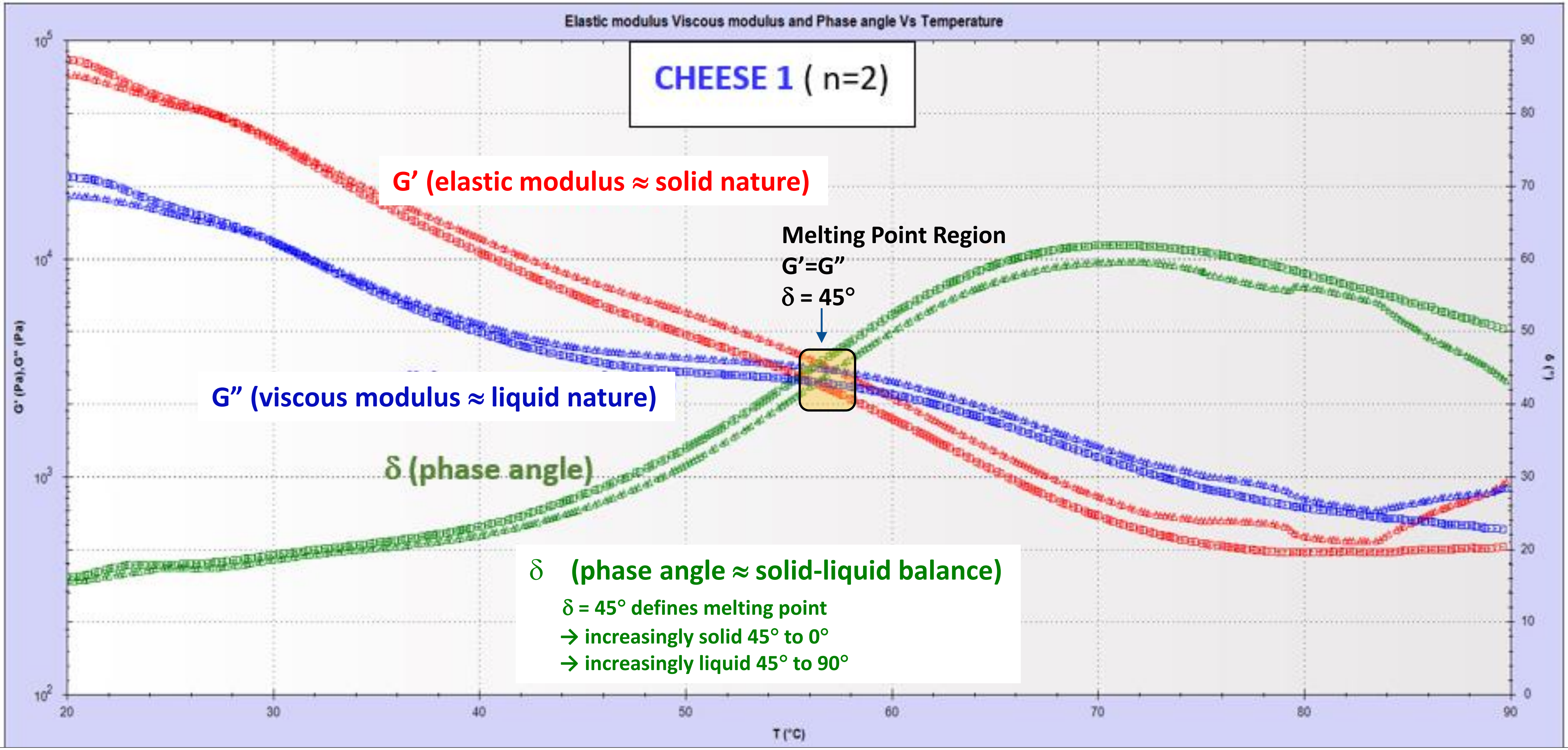
⇒Illustrate products stiffen more than others with increasing frequency (∝ exercise) as shown in results

- **Issue:** Client requested detailed side-by-side rheological profile of 6 products for comparison
- **Results:** Significant differences. Helpful for Q3 (ANDA) pharma, ID counterfeit and adulterated products



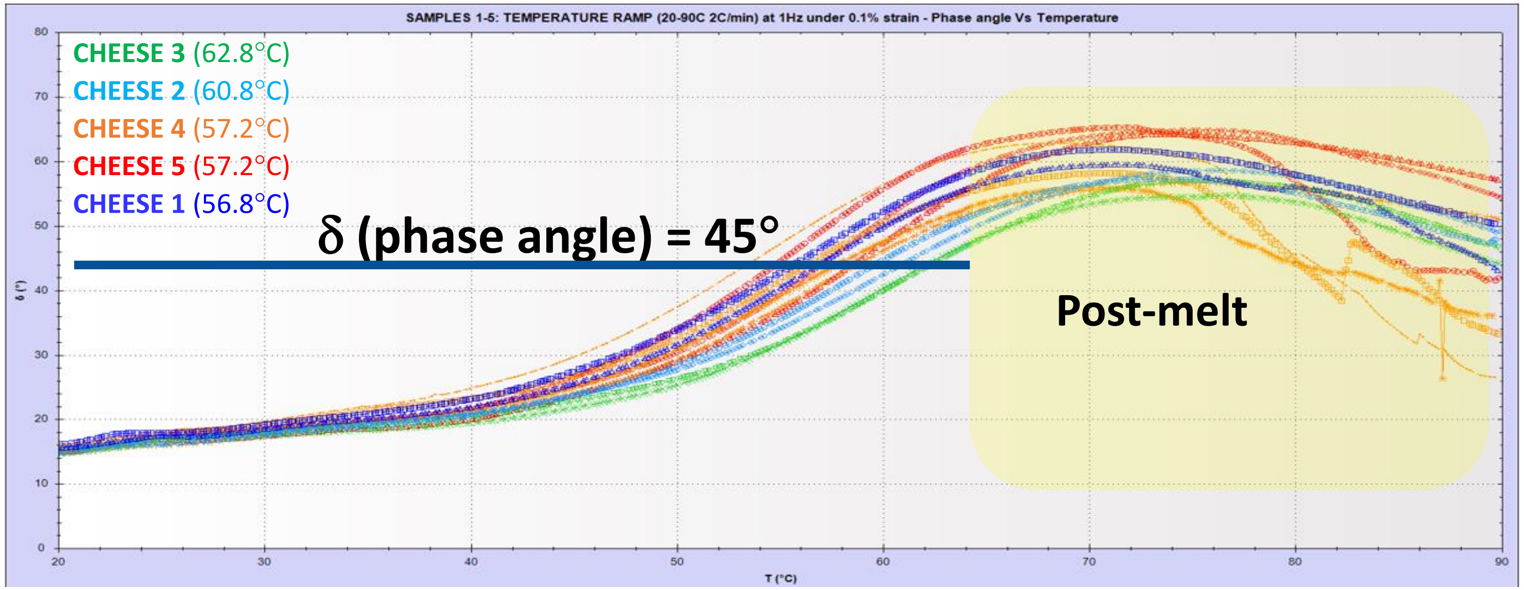
* 3% strain obtained from literature and also confirmed with amplitude sweep

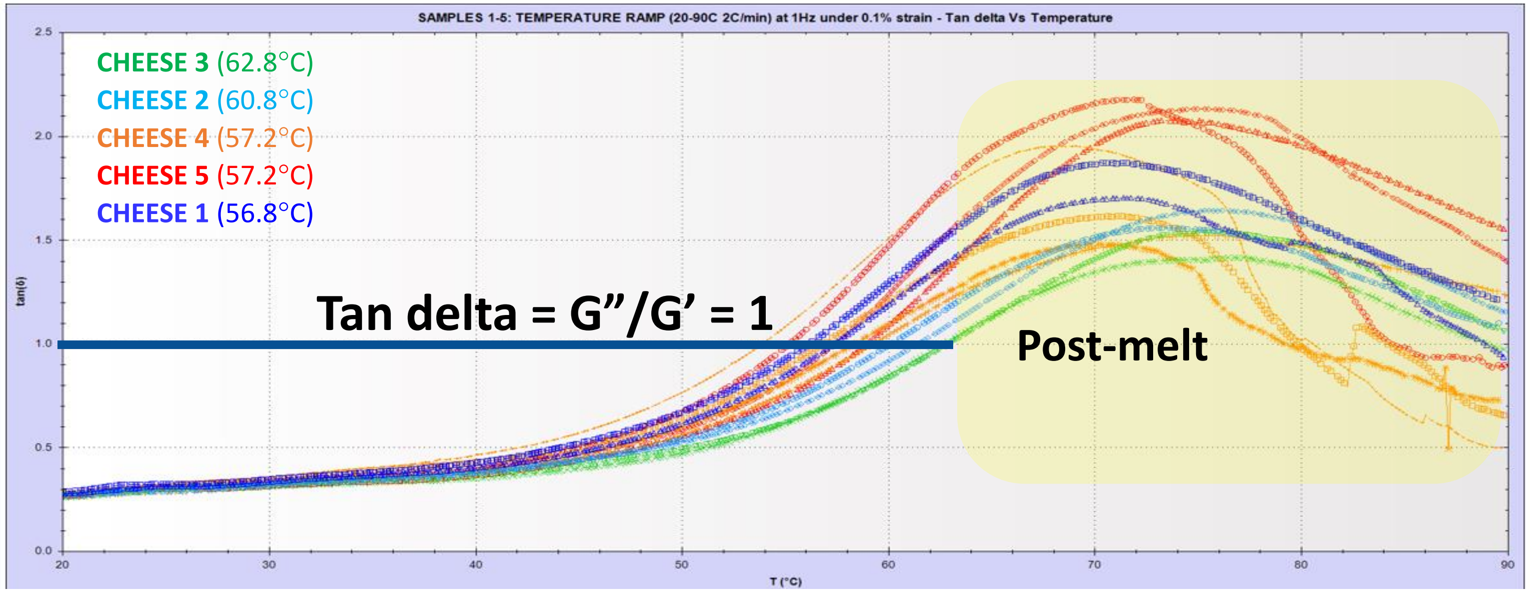
MELTING BY TEMPERATURE SWEEP – OSCILLATION MODE: SINGLE FREQUENCY vs TIME



MELTING BY TEMPERATURE SWEEP – OSCILLATION MODE: SINGLE FREQUENCY

Quantify by phase angle (δ=45°) and Tan delta (G”/G’=1)





REPRODUCIBILITY*	
Sample	**Melt Point °C**
CHEESE 1	56.28
	57.35
AVG	**56.8**
CHEESE 2	60.21
	61.41
AVG	**60.8**
CHEESE 3	62.93
	62.69
AVG	**62.8**
CHEESE 4	59.39
	58.46
	53.95
	56.96
AVG	**57.2**
CHEESE 5	58.93
	55.32
	57.49
AVG	**57.2**

*Values determined directly from data file not from figure.

Apparent outlier

TEMPERATURE SWEEP – OSCILLATION MODE

G* ∝ stiffness

- Spreadable butter contains fats & oils that melt at lower temperatures making it easier to spread at lower temperature.

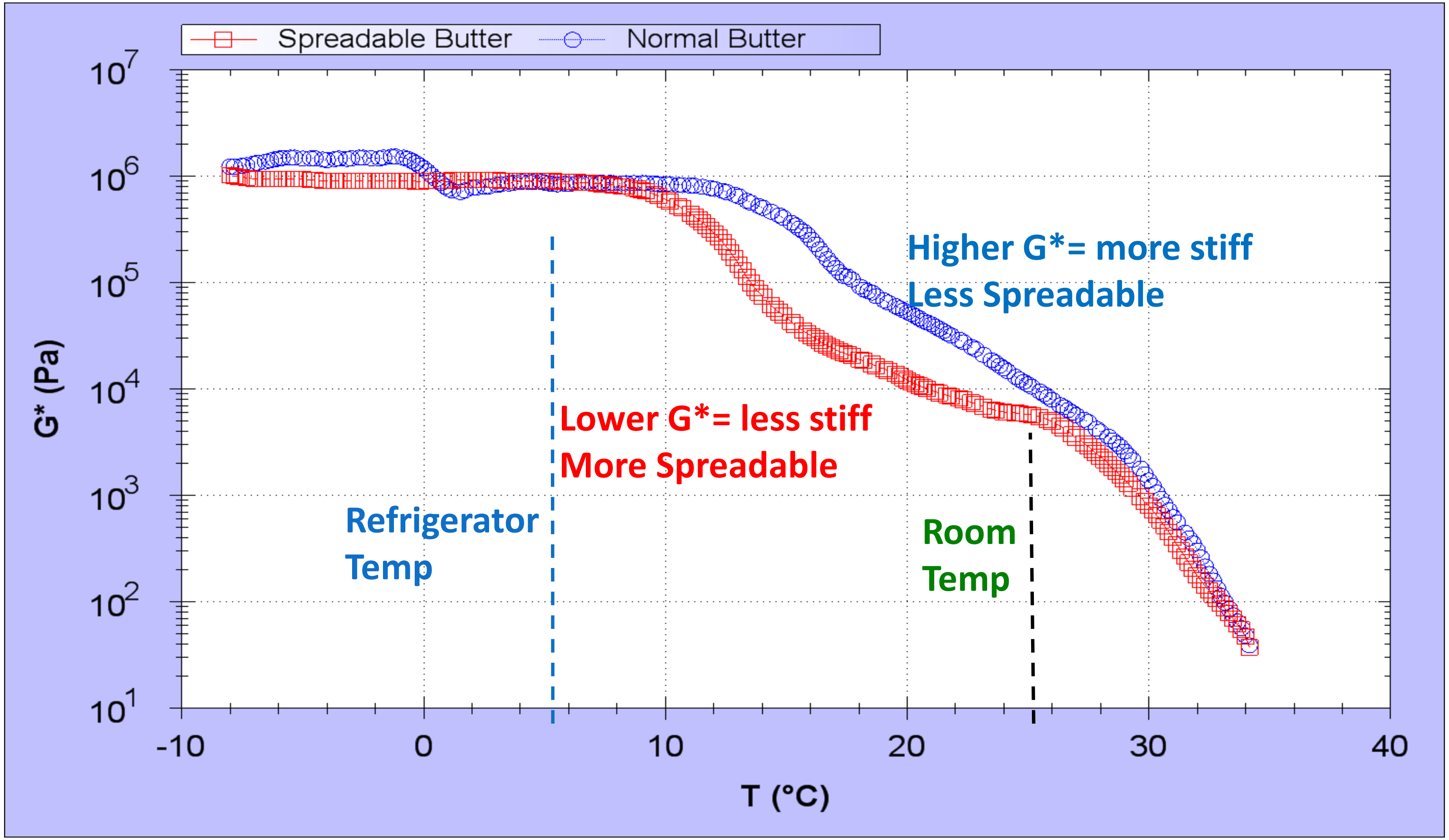
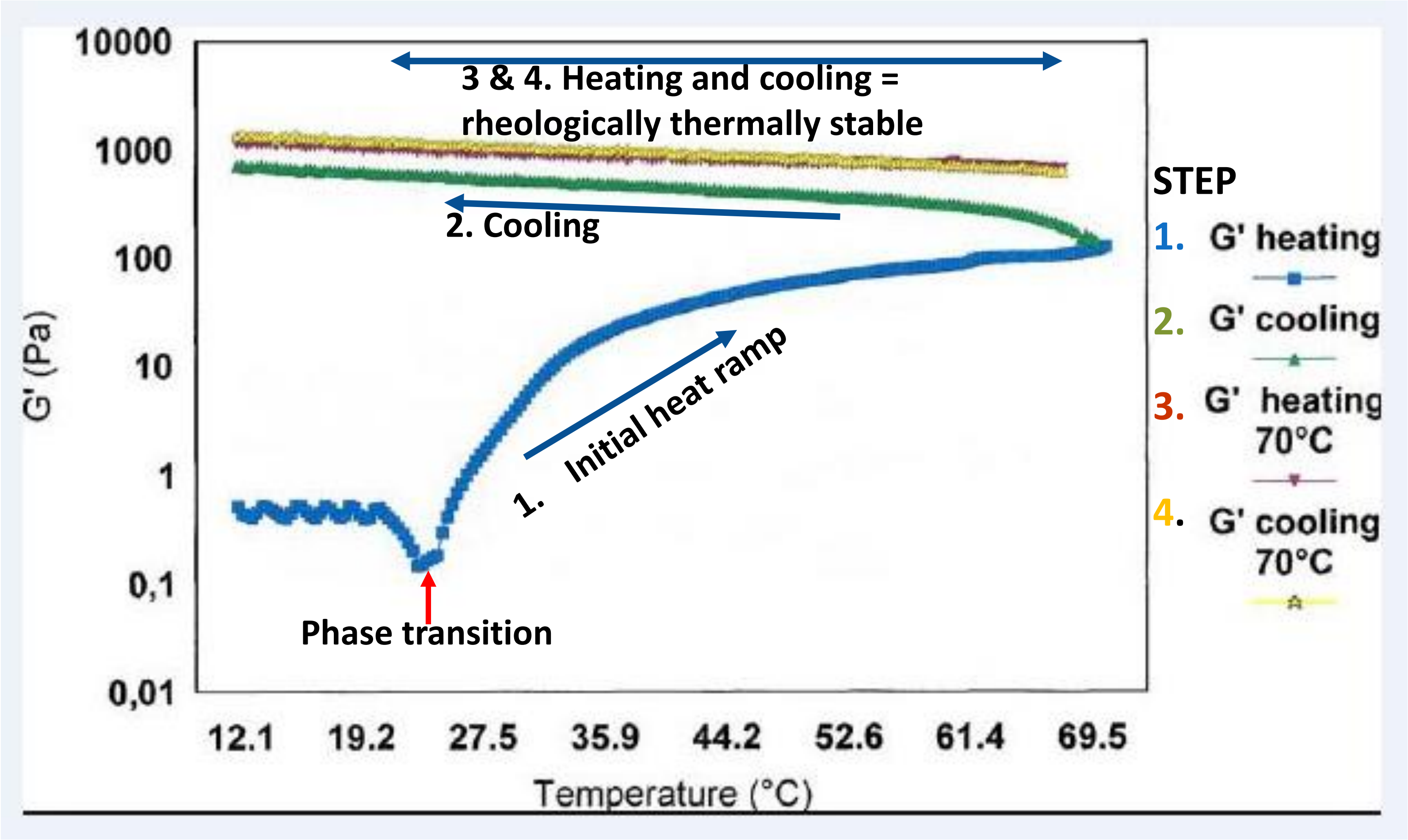


Image from Malvern Pananalytical/Netzsch

TEMPERATURE SWEEP TO PROBE THERMAL (IR)REVERSIBILITY

- Can do in either rotational or oscillational mode
- Probe properties with multiple temperature up/down sweeps.
- Important for manufacturing and low/high temperature exposure (winter/summer)

Example showing irreversible rheological change to more thermally stable material



FREQUENCY SWEEP

- pull-away assay also correlates with sensory

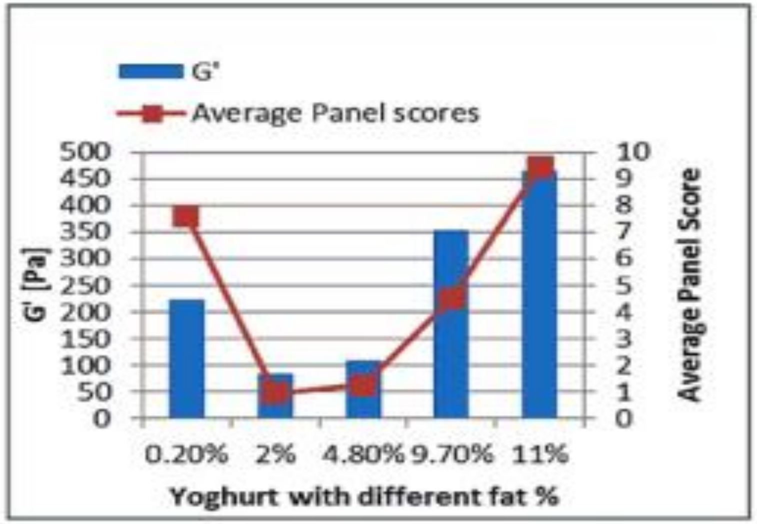
Dairy Innovation Australia Sensor Analysis Lab

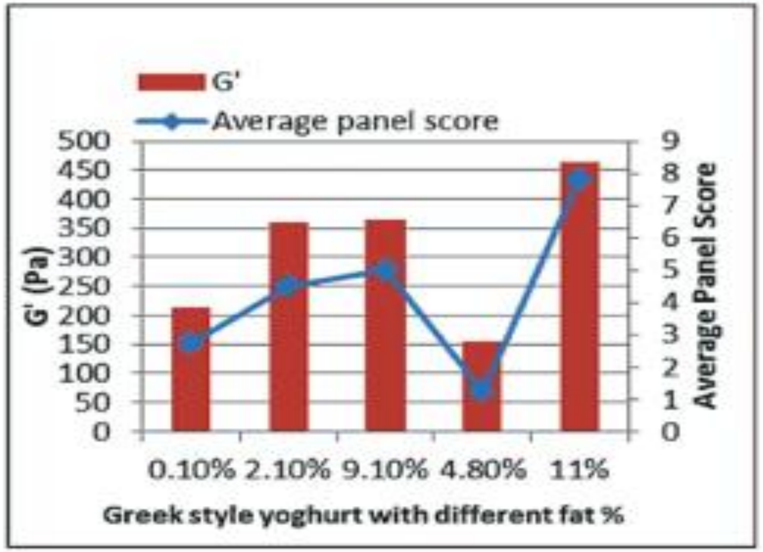
Yogurt - sensory-rheology

Firmness vs elastic modulus relationship

High fat always scores well.....

Note G' here – correlates to panel score....





Ranjan Sharma Dairy Australia/NCDEA

"Sensory Quality Aspects of Yoghurt" Webinar - 11 July 2013

Image from Malvern Pananalytical/ Netzsch

Switching gears to vertical assays

-pull away

-model chewing

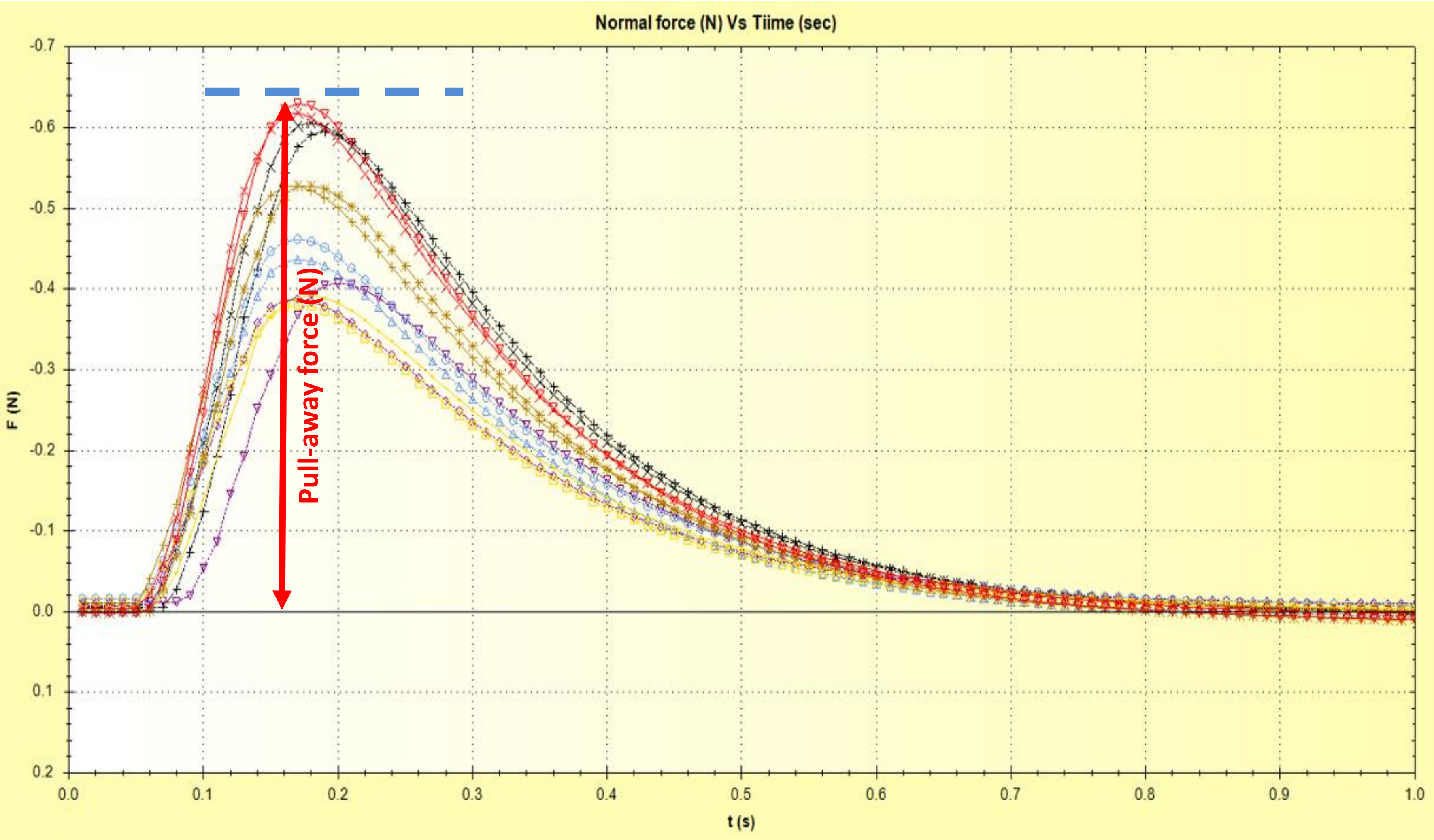
-surface tension

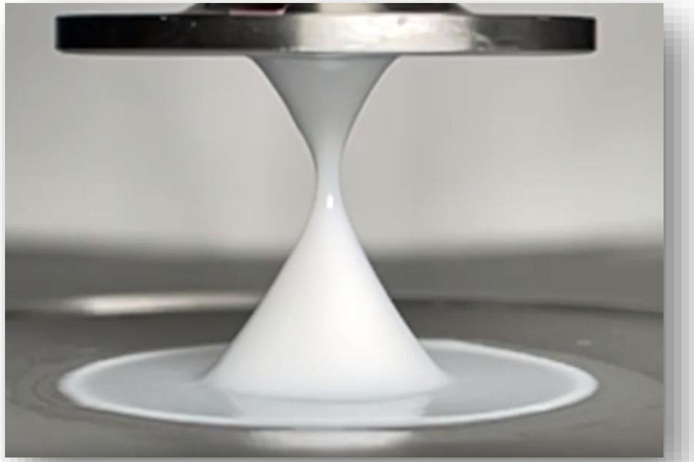
<u>Movements → torque</u>

- Rotational (1 direction)
- Oscillational (bi-directional)
- Vertical

Squeeze-Pull Away for Several Manufacturing Input Sources

- Models adhesion/cohesion, stickiness, mastication (chewing)
  - -peak pull-away force (Newtons) for tack
  - -area under the curve (N-sec) for adhesion/cohesion strength
  - -time (sec) for 90% of force reduction for failure





Squeeze-Pull Away to Model Chewing

Food Research International 49 (2012) 161–169

Contents lists available at SciVerse ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Instrumental mastication assay for texture assessment of semi-solid foods: Combined cyclic squeezing flow and shear viscometry

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[a] Department of Food Science, University of Massachusetts, Amherst, MA 01003, United States
[b] ConAgra Foods, Six ConAgra Drive, Omaha, NE 68102, United States

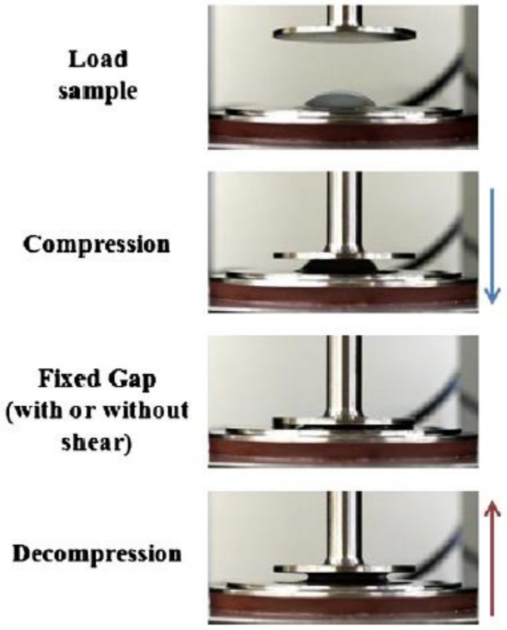
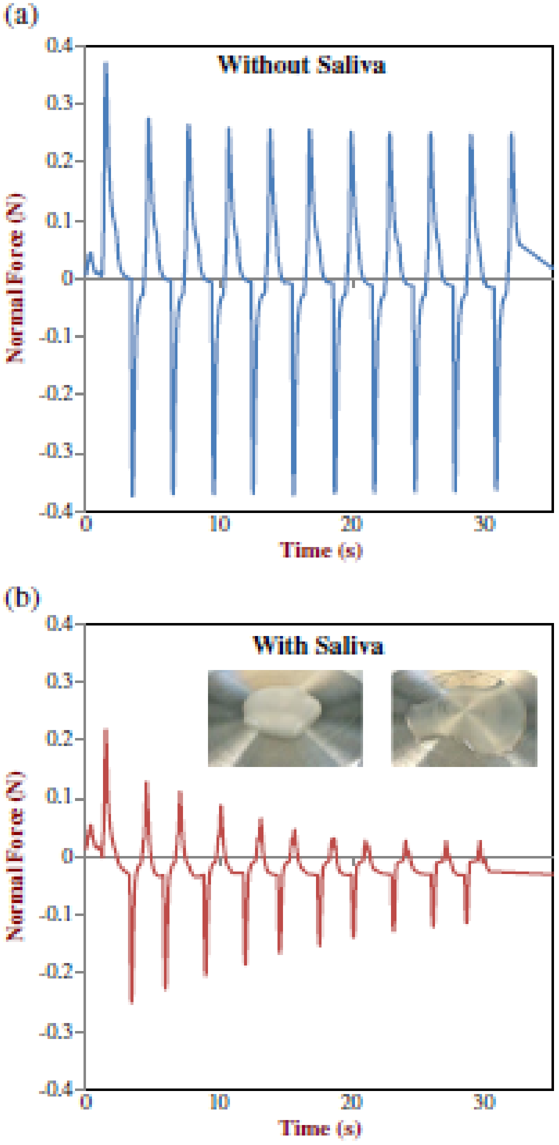
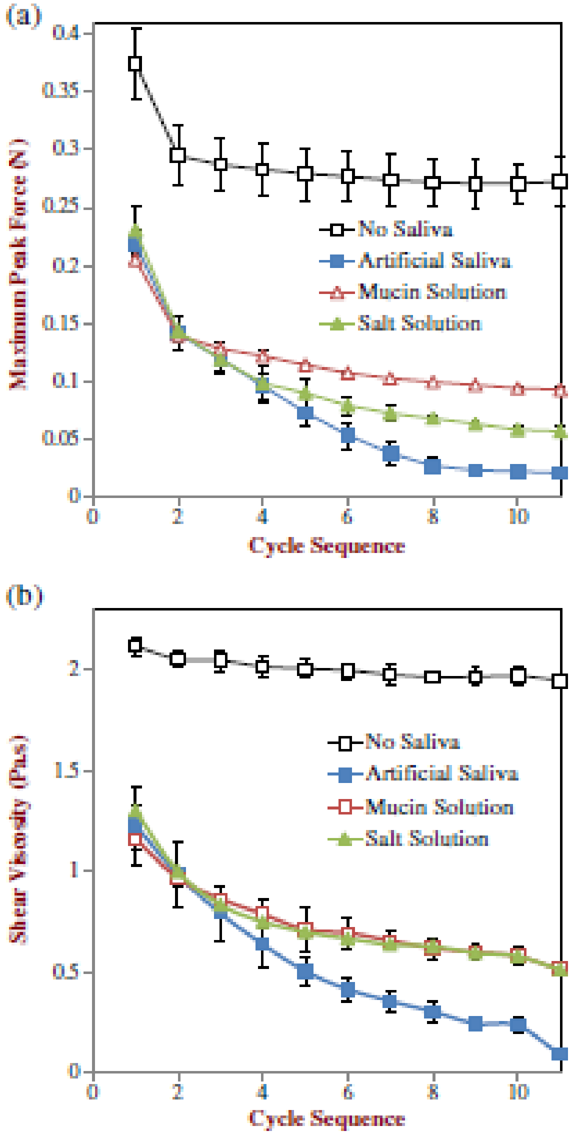


Table 1
Chemical composition of artificial saliva (Mandel et al., 2010; Sarkar et al., 2009).

Chemical type	Concentration (g/L) or activity (units/mL)
Sodium chloride	1.594
Ammonium nitrate	0.328
Potassium phosphate	0.636
Potassium chloride	0.202
Potassium citrate	0.308
Uric acid sodium salt	0.021
Urea	0.198
Sodium DL-lactate/lactic acid sodium salt	0.146
Mucin from porcine stomach, type II	30
Alpha amylase activity	93 units/mL

168 C. Chung et al. / Food Research International 49 (2012) 161–169





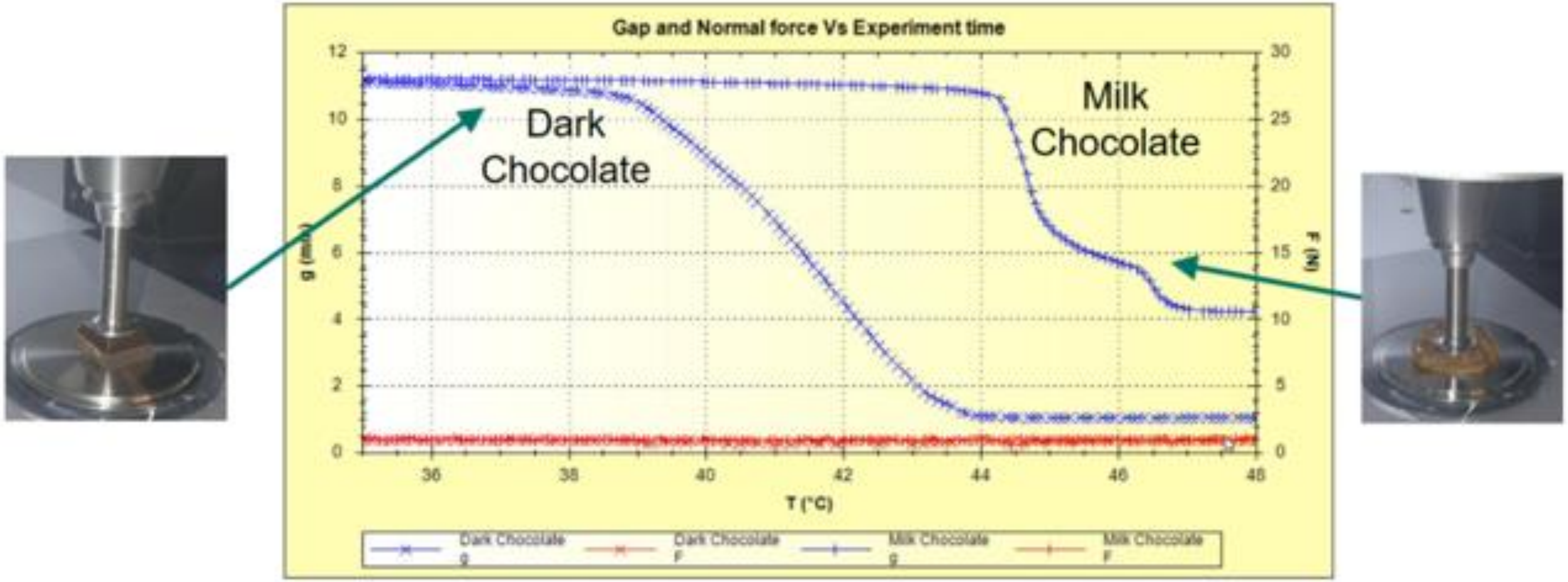
Axial Testing to Quantify Texture with Heating- Chocolate

Chocolate

Rheometry Axial Testing Results

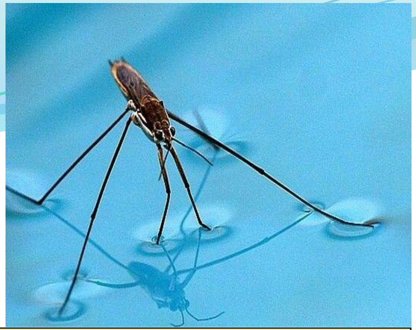
NETZSCH

- These relative tests allow for a close correlation, under more scientific control, of properties that we “feel” and know

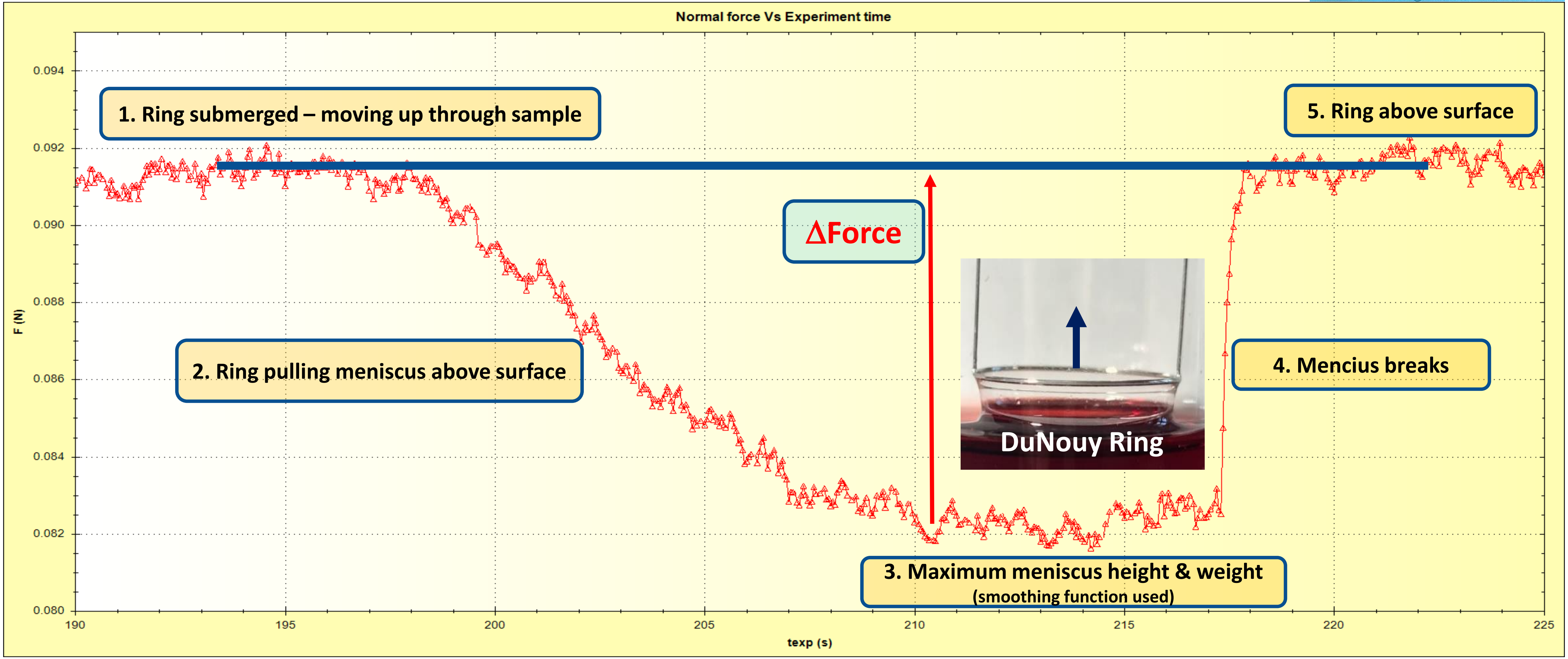


Slide from Netzsch

Principle: Interfacial surface tension (liquid-air, liquid-liquid)



- Applications in pharmaceutical, cosmetics, paint, food industries
- Surface Tension (milliNewton/meter) = ΔForce * Ring factor (normalized to bracketing water standards 71.99mN/meter at 25°C or at other assay temperature.)



Principle: Interfacial surface tension (liquid-air, liquid-liquid)

- Applications in pharmaceutical, cosmetics, paint, food industries
- Surface Tension = ΔForce * Ring factor (normalized to bracketing water standards 71.99mN/m at 25°C or at other assay temperature.)

Example Results

Sample Description	# Pulls	Average Surface Tension (milliNewton/meter)	%RSD
HPLC grade water START	12	71.99	5.3
1mg/mL SET 1	6	**72.99**	4.4
1mg/mL SET 2	6	**72.90**	3.6
HPLC grade water INTERIM 2	6	71.99	4.6
10mg/mL SET 1	6	**63.84**	3.4
10mg/mL SET 2	6	**63.89**	5.1
HPLC grade water END	6	71.99	1.8

CONCLUSIONS

√ **Rheology is <u>much</u> more than viscosity!**
√ **Many approaches to characterize materials. Depends on the questions to be answered.**
√ **Viscosity will often decrease with increasing shear rate = shear thinning (non-Newtonian).**
  →Report viscosity with associated shear rate.
√ **Regulatory considerations!**
√ **Numerous experimental considerations**

⇒ROTATION

- Shear stress ramp and stepwise: “Flow curve”. Model delivery, performance & processes.
- Shear rate ramp and stepwise: Compare products
- Thixotropy: Rebuild after shear thinning? Ketchup, paint, toothpaste
- Single shear rate or stress over time: Stability
- Temperature sweep: Change with temperature, model processes
- Creep-Recovery
- Tribology (friction, lubricity): motor oil, arthritis products

⇒OSCILLATION

- Amplitude sweep: Define LVER $\propto$ breaking point $\propto$ rheological stability
- Frequency sweep: Rheological fingerprint across frequency (1/time) domain. Silly putty. Model arthritis products. Texture.
- Temperature sweep and cycling: Polymeric discs, thermal (ir)reversibility, melting point

⇒ VERTICAL

- Squeeze - Pull Away: stickiness, model chewing, texture
- Surface Tension

Backup Slides

Plate Considerations

Geometry Size	Advantages	Disadvantages
Larger surface area	-Use for lower viscosity samples	-Requires more sample
Smaller surface area	-Use for higher viscosity samples -Requires less sample	-May not provide adequate response since less sample area

Geometry Surface	Advantages	Disadvantages
Smooth	-Easy to clean	-May give slippage
Roughened	-Easy to clean -May reduce potential for slippage	-May still give slippage
Serrated	-Most aggressive to reduce slippage	-May need brush to clean -May "gouge" sample surface

Geometry Type	Advantages	Disadvantages
Flat (parallel)	-Good for high viscosity fluids	-Variable shear rate across radius. Sample may yield at edge before center.
Cone (2 & 4°)	-Good for low viscosity fluids -Constant shear rate in gap	Don't use for temperature sweeps unless rheometer compensates for thermal expansion

Optimizing Dispersion, Colloidal and Emulsion Stability

(dispersed phase <1mm)

Property	To Improve Stability	How	
Zero Shear Viscosity (η_0)	↑	Add thickeners to prevent particles from settling	
Yield Stress	↑	Provides high resistance to sedimentation.	
Thixotropy	↓	Decrease rebuild time to near pre-shear value	
Cohesive Energy	↑	Determine with strain controlled amplitude sweep (CE=1/2G’ x γ^2)	
Viscoelasticity	↓δ	-Viscoelastic liquids with high phase angle (δ) at low freq are less stable -Use structured gel having δ <45° and independent of freq -If heavy or large particles, decrease δ <45° at low freq	

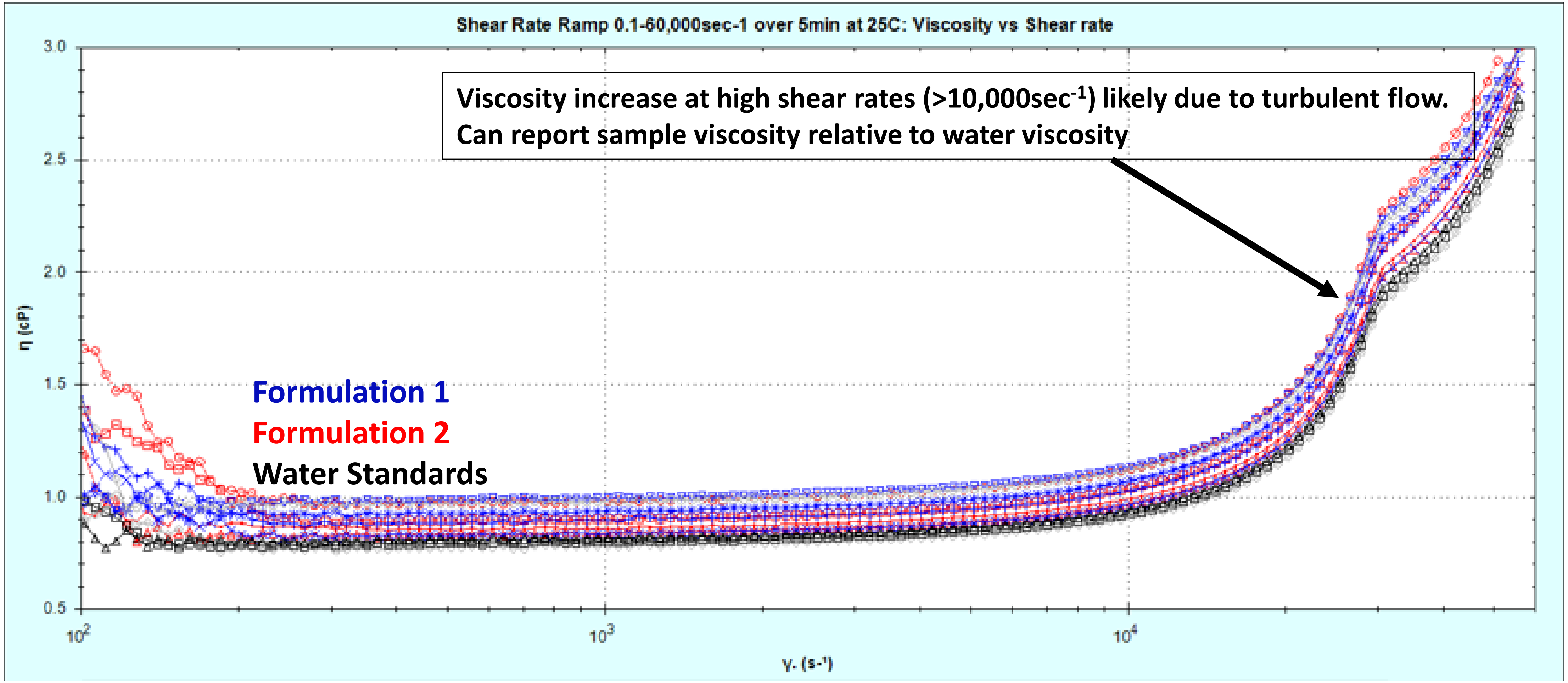
- Larger particles increase viscosity
- Irregular particles increase viscosity

https://www.azom.com/article.aspx?ArticleID=11442

Application: Shear Rate Ramp - Low viscosity formulations with high shear rate

- Experimental: 40mm smooth parallel plate, 100uL gap* (130uL sample), 25°C, 1-60,000sec^{-1} over 5min

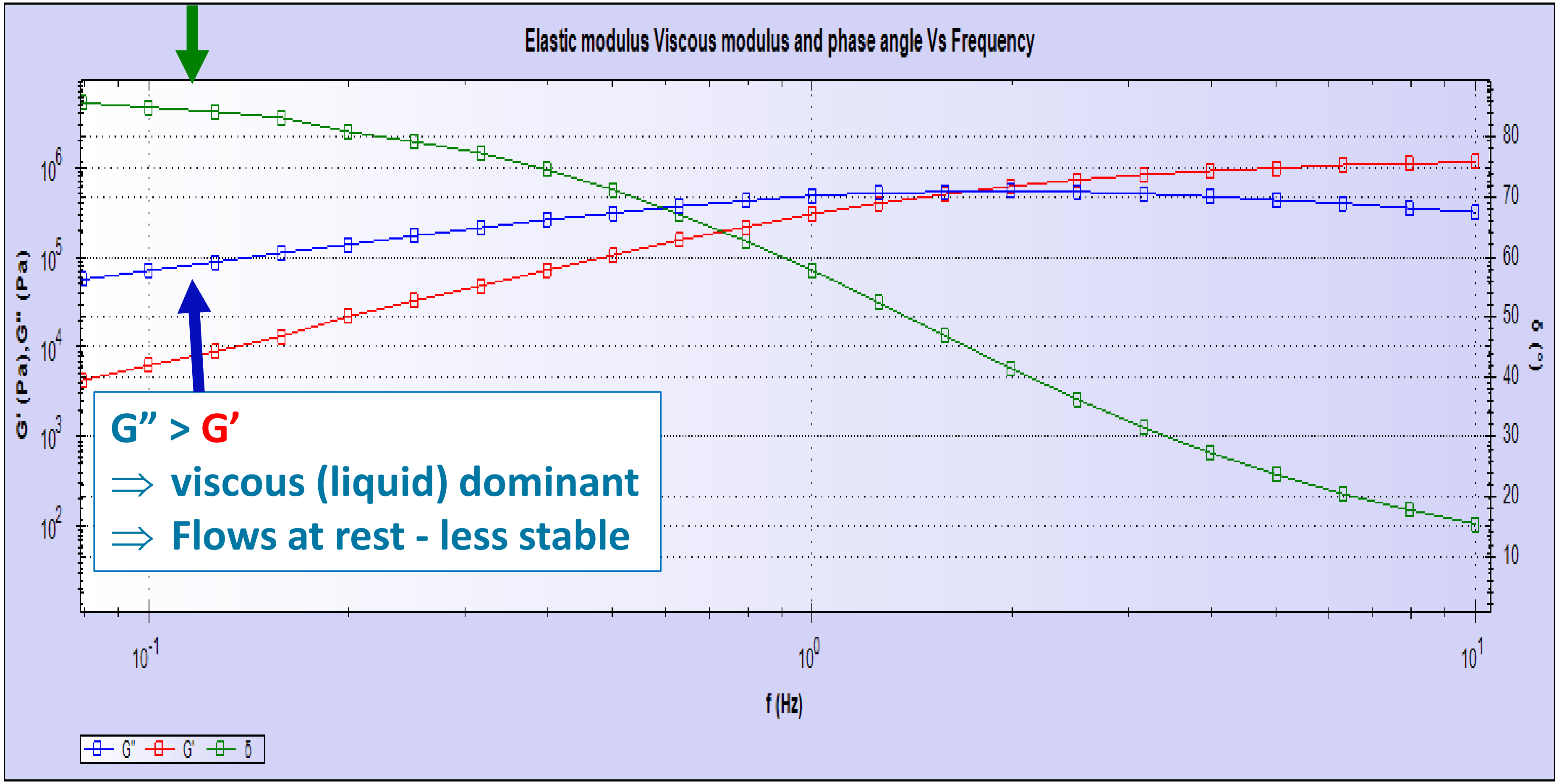
Figure 3.1A. Overlay of samples and water standards with shear rate ramp (0.1 - 60,000sec^{-1}) over 5min using a 100um gap (log-linear)



* Small gap (100um) is required to retain sample within plates at high shear. Human hair is 70+/-20um.

Is silly putty a viscoelastic solid or liquid at rest?

phase angle starts >45°
⇒ liquid dominant



G" > G'
⇒ viscous (liquid) dominant
⇒ Flows at rest - less stable

PROCESSING OF A PROTEIN-STABILIZIZED EMULSION

Influence of Processing Variables on Rheological & Textural Properties of Lupin Protein-Stabilized Emulsions

J. M. Franco, A. Raymundo, I. Sousa, and C. Gallegos   J. Agric. Food Chem. 1998, 46, 3109−3115

PURPOSE

- Mayonnaise and salad dressing-type emulsions are stabilized by an adsorbed layer of protein at the oil-water interface.
- Previous studies show poorer gelation and thickening properties of lupin protein compared to commercially used soy protein.

EXPERIMENTAL (rheology only)

- **Steady-state flow curves (rotational)**: Serrated plate (20 mm) to prevent wall-slip.
- **Frequency Sweep (oscillational):** Within LVER, using a cone/plate (35 mm, 2°) across 0.05-200 rad/s (0.01-31.8Hz).

CONCLUSION:

- Emulsion stability and physical properties improved by heating lupin solution prior to the addition of the oil phase or inducing a chemical or enzymatic reaction that increases the entanglement protein molecules along with hydrophobicity.

- Processing variables (temp, time, impeller/stir type & speed) affect viscous and viscoelastic behavior by droplet size distribution, interdroplet interactions and entanglement.

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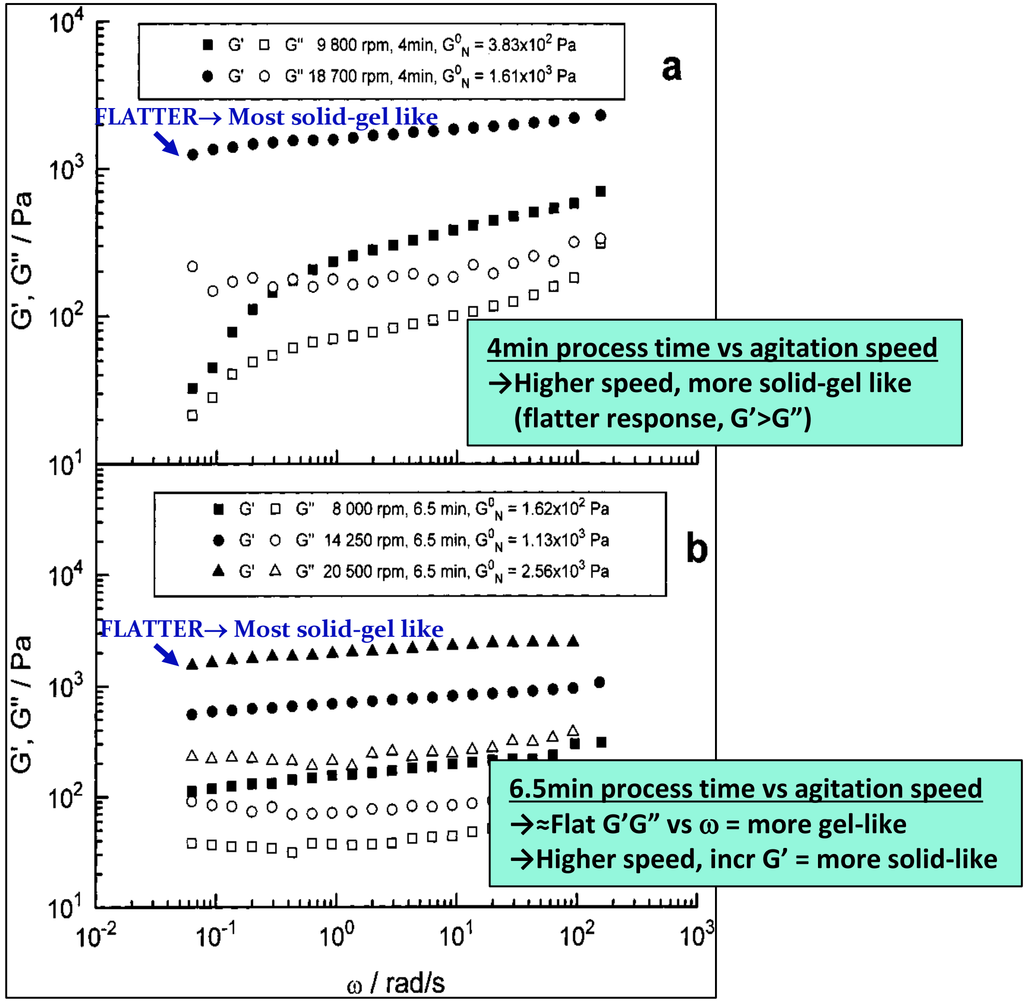
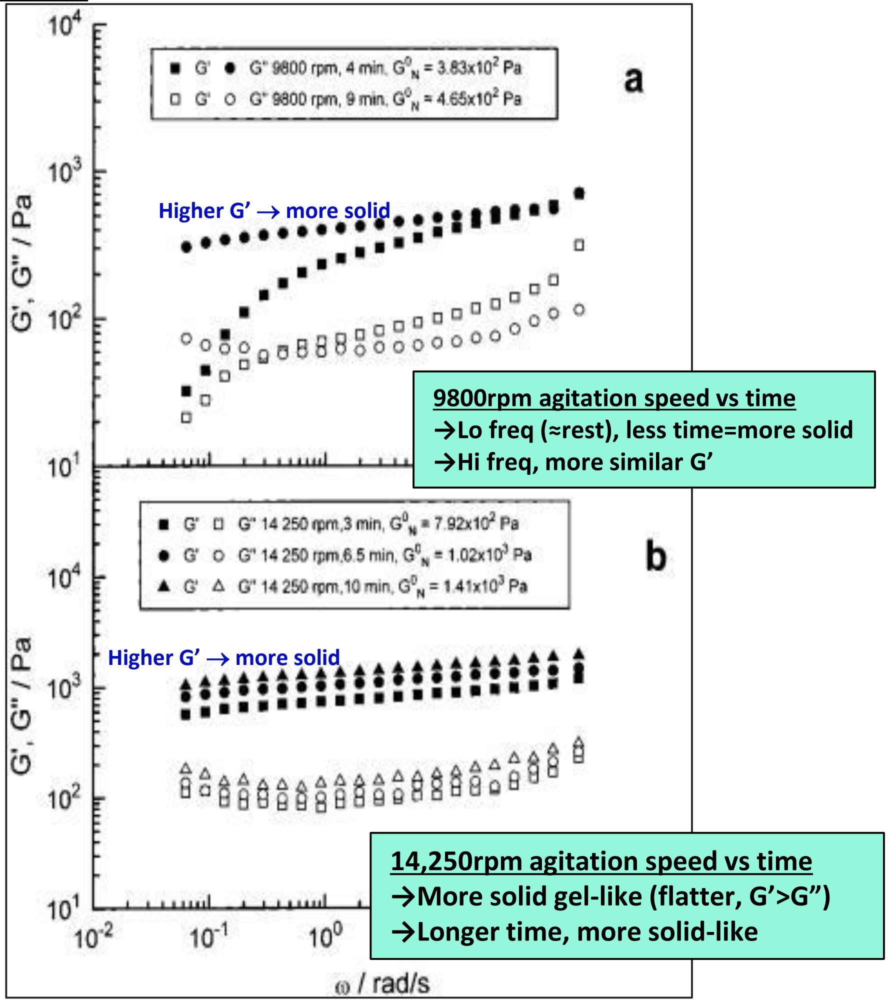


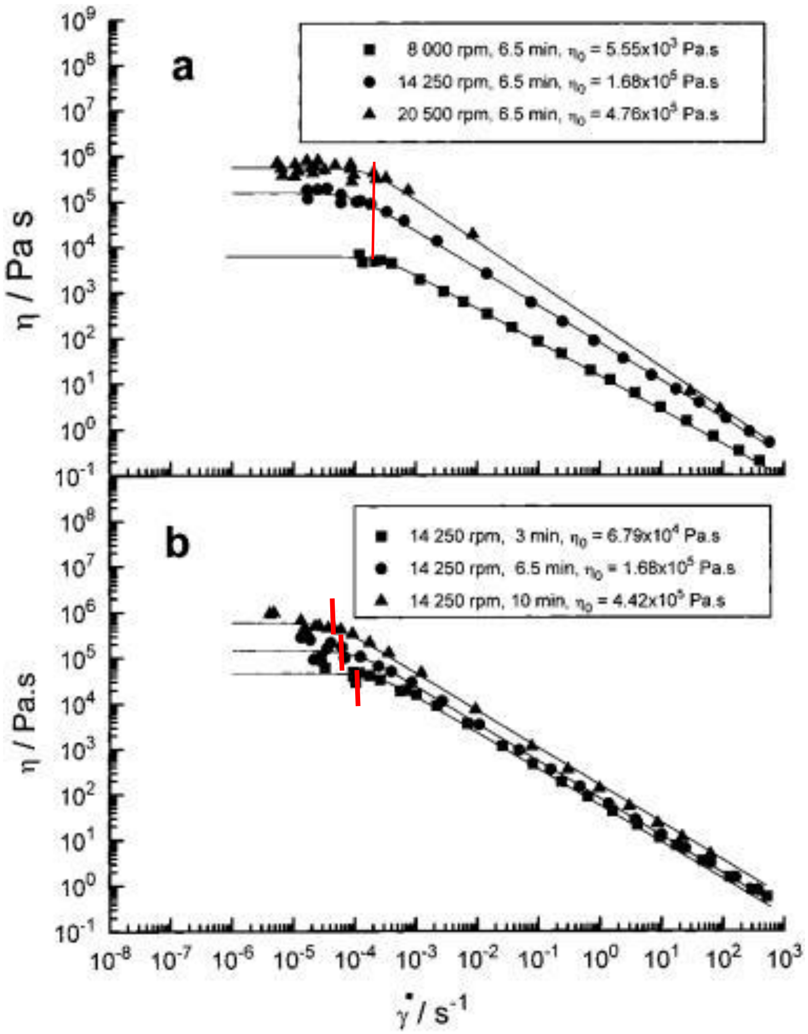
Freq Sweep: G' and G" of lupin protein-stabilized emulsions vs agitation speeds.



Freq Sweep: G' and G" for lupin protein-stabilized emulsions prepared vs emulsification times

PROCESSING OF A PROTEIN-STABILIZIZED EMULSION (con't)

J. M. Franco, A. Raymundo, I. Sousa, and C. Gallegos J. Agric. Food Chem. 1998, 46, 3109−3115



Steady-state flow curves: (a) agitation speed and (b) emulsification time for lupin protein stabilized emulsions.

<u>**6.5min process time vs agitation speed**</u>
→Higher speed, more viscous
→All shear thin, with 20,500rpm more rapidly
→Generally, similar breakpoint

<u>**Agitation speed (14,250rpm) vs time**</u>
→Longer time, more viscous
→Shorter time, later breakpoint