Materials Characterization by Thermal Analysis (DSC & TGA), Rheology, and Dynamic Mechanical Analysis (Part 2)

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Afternoon Agenda: Rheology and DMA

- Introduction to Rheology
  - Fundamentals of Stress, Strain and Shear Rate
  - Instrumentation
  - Geometries
- Flow Testing
  - Shear Thinning and Shear Thickening
  - Thixotropy
  - Yield Stress
- Oscillation Testing
  - Viscoelasticity
  - “Hands On” demonstration
  - Characterizing Thermoplastics
- Thermosets and Gels
  - Viscoelastic properties of Gels
  - Characterizing Gelation
  - Experimental considerations
  - Specialized Accessories
- Dynamic Mechanical Analysis
  - Characterizing Glass Transition
  - Comparison of Deformation Modes
- Case Study:
  - Rubber Characterization using DSC, TGA and DMA.

What is Rheology?

Rheology is the study of **flow** and **deformation**.

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

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

Rheology: the study of flow and deformation

Viscosity

- Non-Newtonian Viscosity
  - Shear thinning
  - Shear thickening
  - Thixotropy
  - Yield Stress
- Viscosity under processing conditions

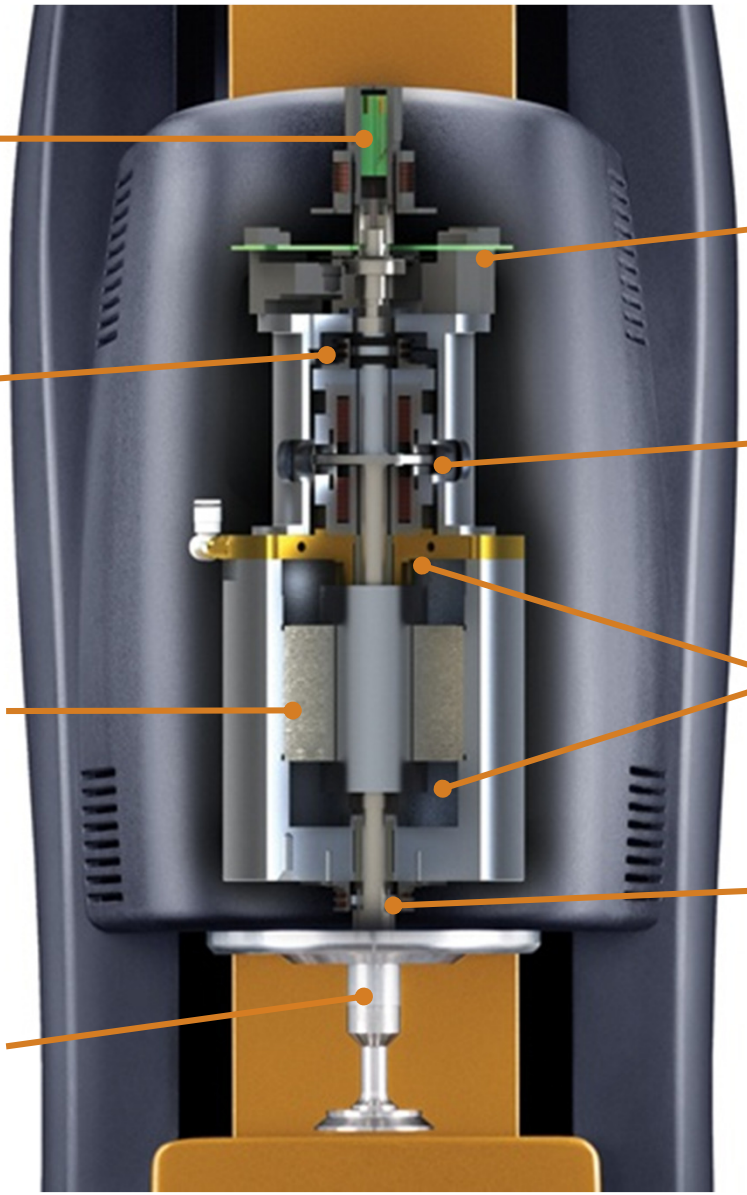
$$\frac{\text{Stress}}{\text{Shear rate}} = \text{Viscosity}$$

Modulus

- Measure viscoelastic properties
  - Storage Modulus
  - Loss Modulus
  - Tan Delta
- Changes with time, temperature

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

Discovery Hybrid Rheometer Technology



Patented Active Temperature Control

Dual Reader Optical Encoder (Patent Pending)

Force Rebalance Transducer Control Electronics

Patented Magnetic Bearing

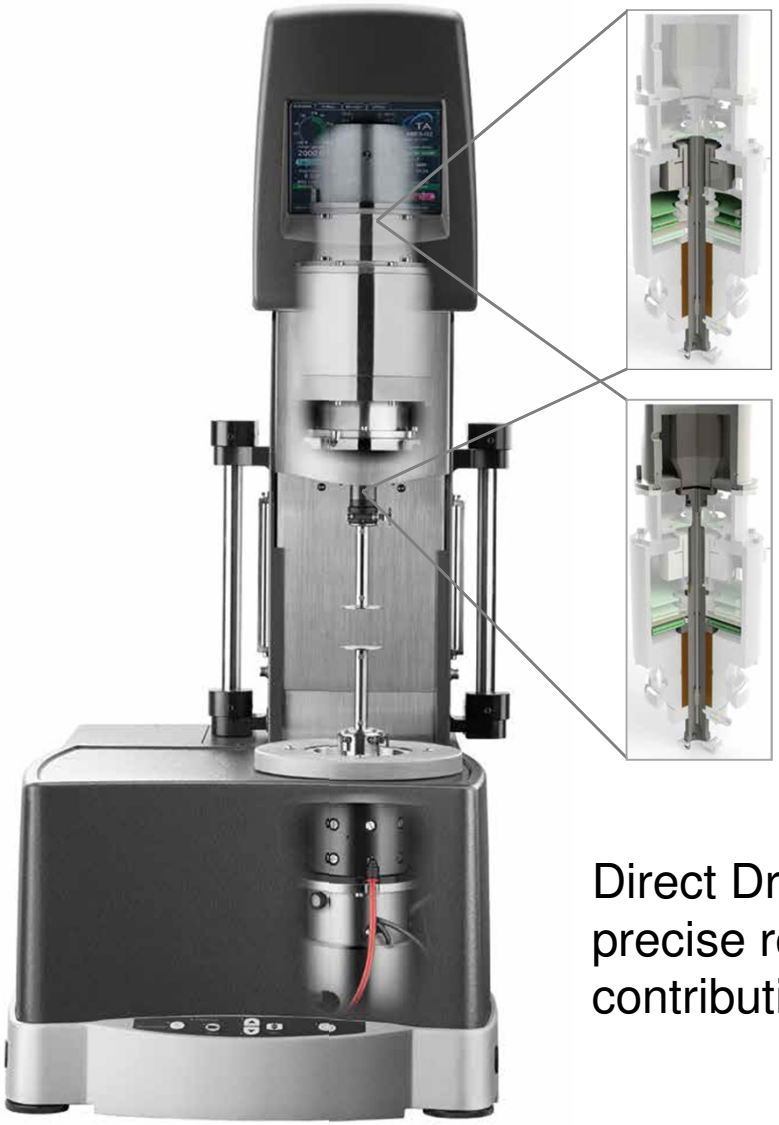
Radial Air Bearing

Patented Advanced Drag Cup Motor

New True Position Sensor (Patent Pending)

Patented Smart Swap Geometries

ARES G2: Separate Motor and Transducer



Torque Transducer maintains the null position as the sample is deformed.

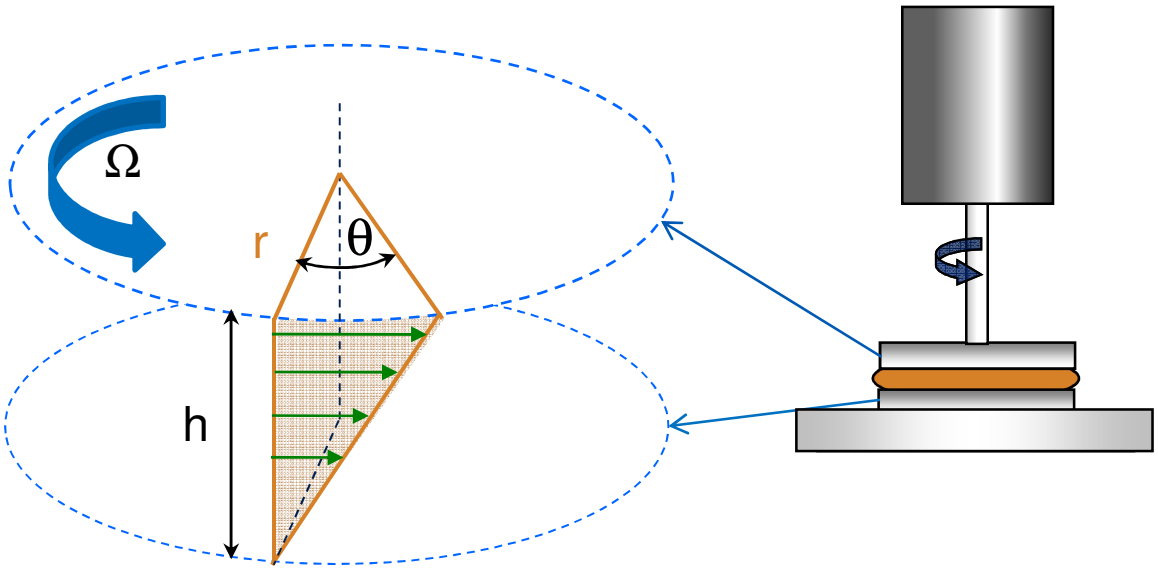
Sample torque to be measured directly, without contributions from motor friction or inertia.

Normal Force Transducer provides highly accurate normal force measurements

High stiffness for precise gap control.

Direct Drive motor applies accurate and precise rotational deformation, without contributing to measured torque.

Torsion Flow in Parallel Plates



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

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

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

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

Geometry Options

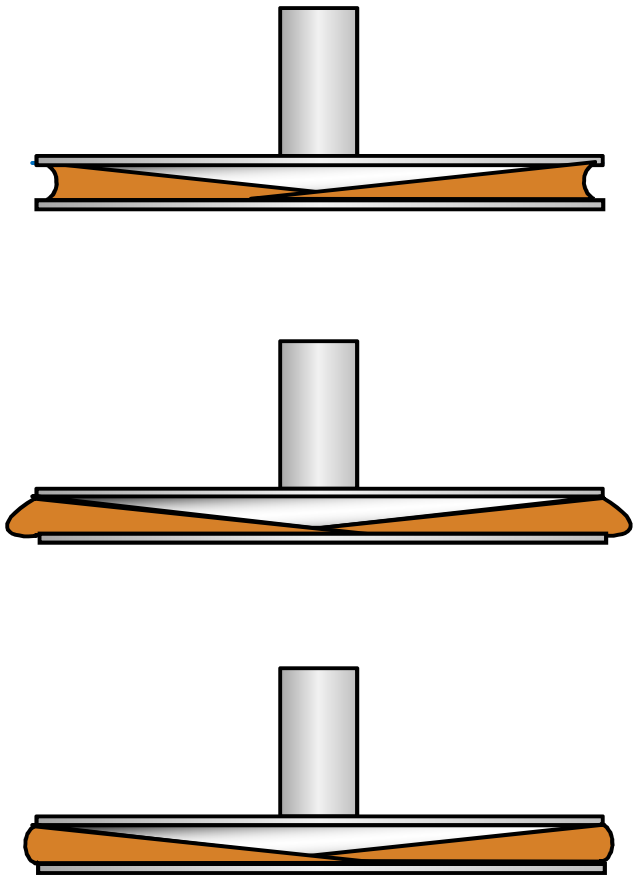
Concentric Cylinders	Cone and Plate	Parallel Plate	Torsion Rectangular
			
Very Low to Medium Viscosity	Very Low to High Viscosity	Very Low Viscosity to Soft Solids	Solids

Water → to → Steel

Choosing a Geometry Size

- Assess the ‘viscosity’ of your sample
- Select diameter appropriate for viscosity of sample
  - Low viscosity (milk) - 60mm geometry
  - Medium viscosity (honey) - 40mm geometry
  - High viscosity (caramel) – 20 or 25mm geometry
- Examine data in terms of torque/displacement/speed and modify geometry choice to move into optimum working range

Correct Sample Loading



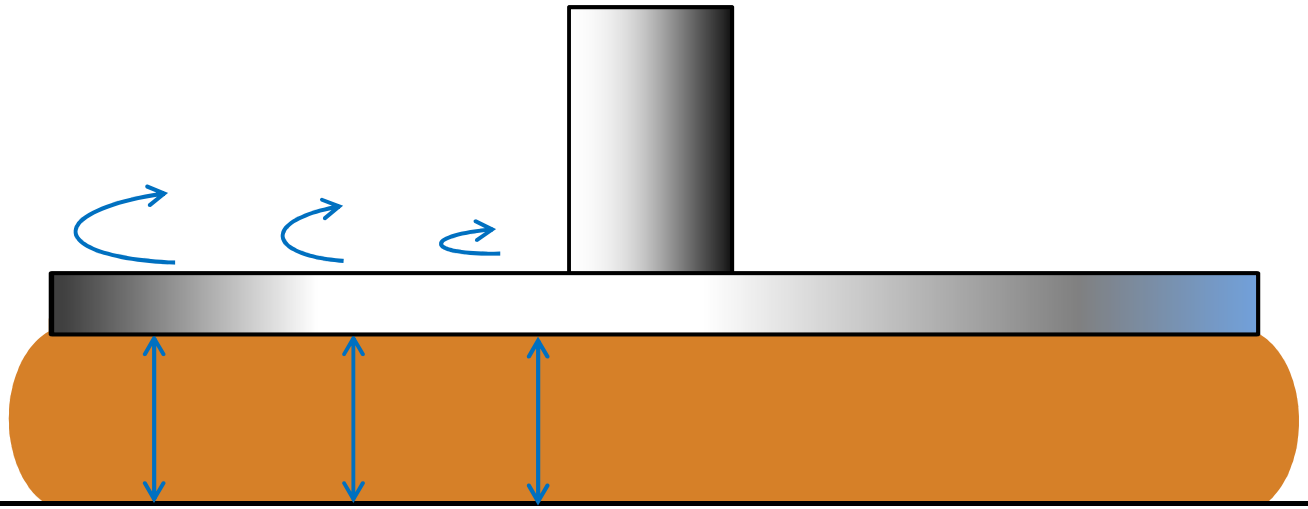
× Under Filled sample:
Lower torque contribution

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

✓ **Correct Filling**

Shear Rate varies across a Parallel Plate

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



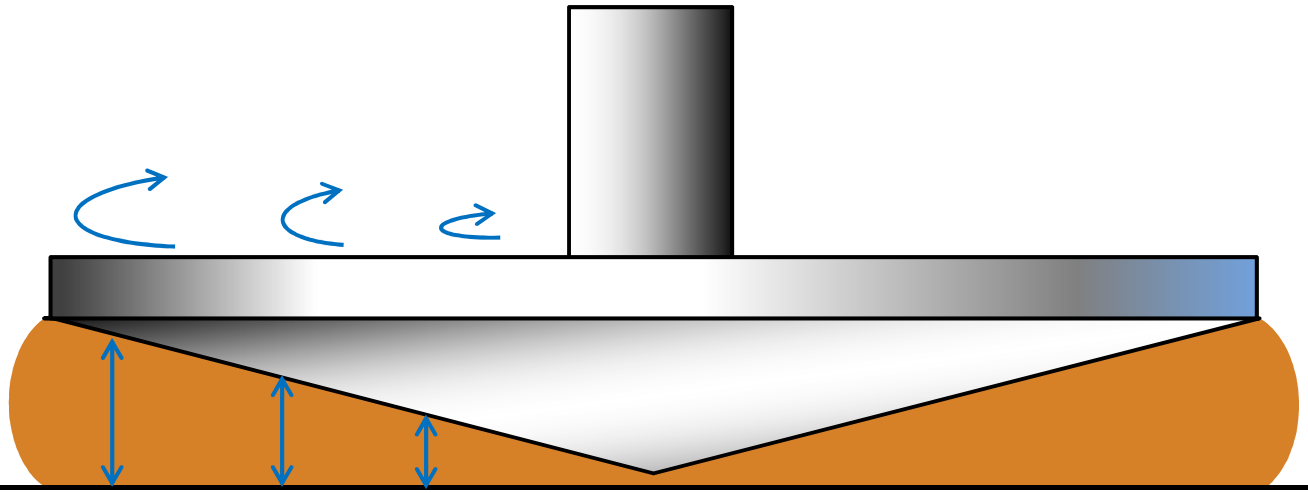
$$\gamma = \frac{dx}{h}$$

dx increases further from the center,
h stays constant

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

Shear Rate is Uniform across a Cone

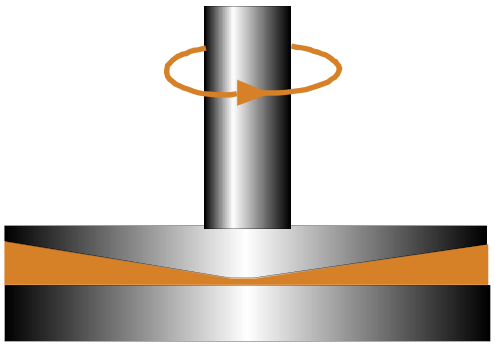
- The cone shape produces a smaller gap height closer to the center, so the shear on the sample is constant



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

h increases proportionally to *dx*, γ is uniform

Limitations of Cone and Plate



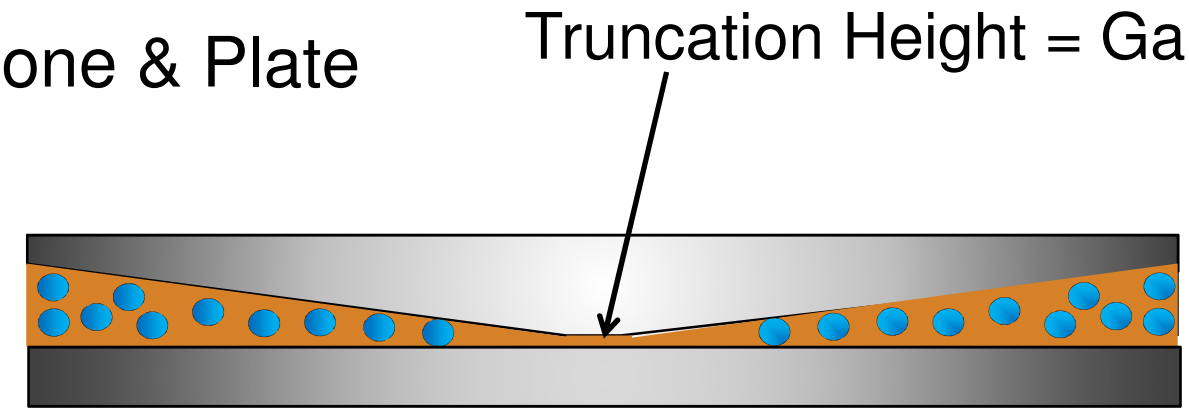
Cone & Plate

Typical Truncation Heights:

1° degree ~ 20 - 30 microns

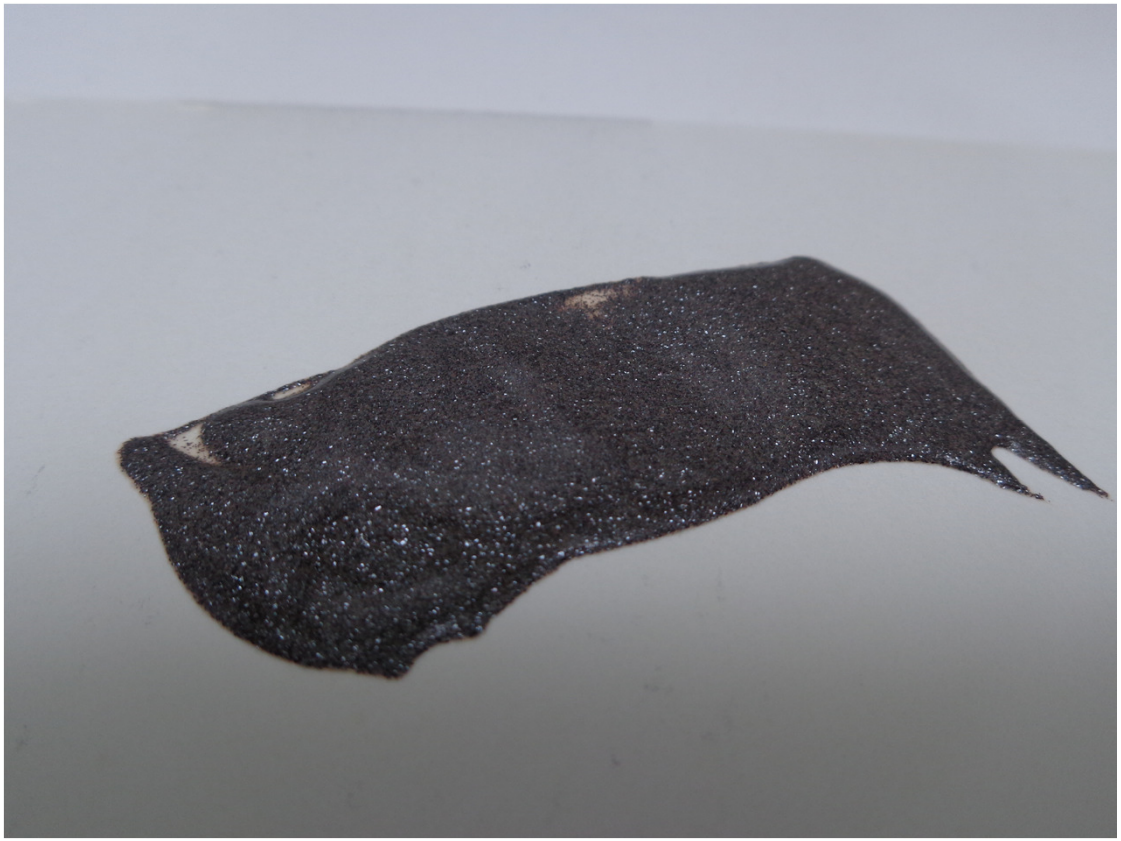
2° degrees ~ 60 microns

4° degrees ~ 120 microns

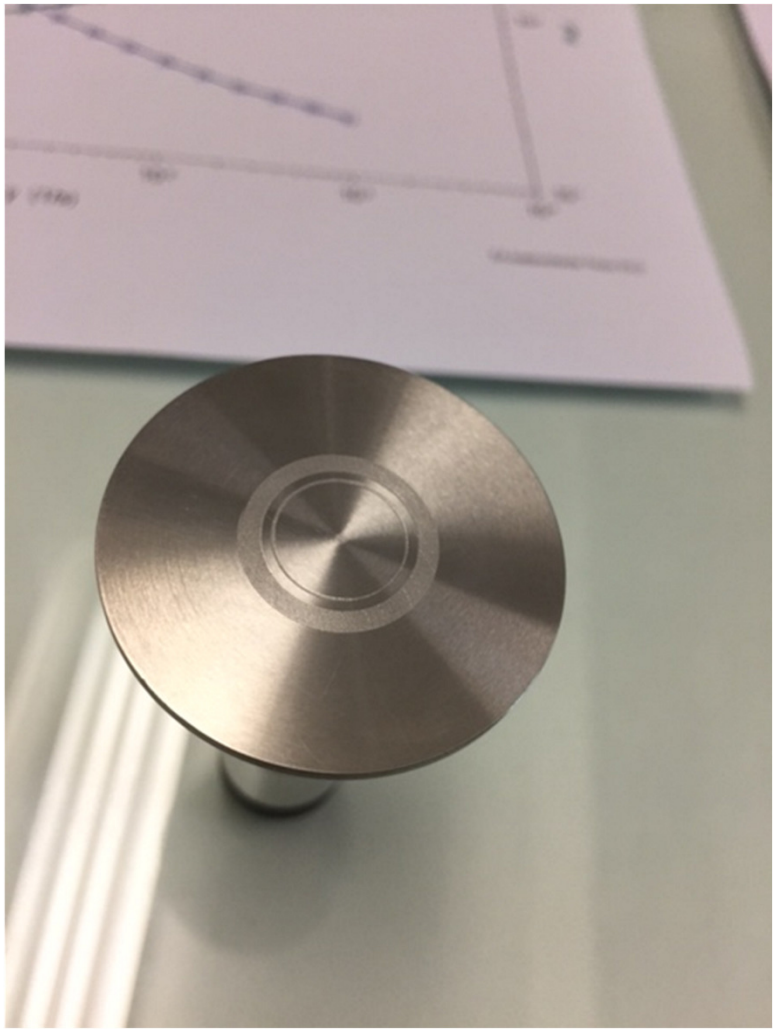


Gap must be > or = 10 [particle size]!!

What Geometry should we use?



Should have used a parallel plate!



When to Use Concentric Cylinders

Peltier Concentric Cylinder

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

Geometry Summary

Parallel Plates	Cone and Plate	Concentric Cylinders
1-2 mL	50-500 µL	7-25 mL
Liquids, gels, soft solids, dispersions, etc.	Unfilled liquids, isothermal tests	“Pourable” liquids, low viscosities, dispersions
Used for all samples. Roughened surfaces available to prevent slip.	Most accurate measurement of non-Newtonian Viscosity, small sample volume.	Least effected by sample loading technique or evaporation.

Flow Testing

Newtonian and Non-Newtonian Fluids

- Newtonian Fluids - Viscosity does not change with changes in shear rate or time.

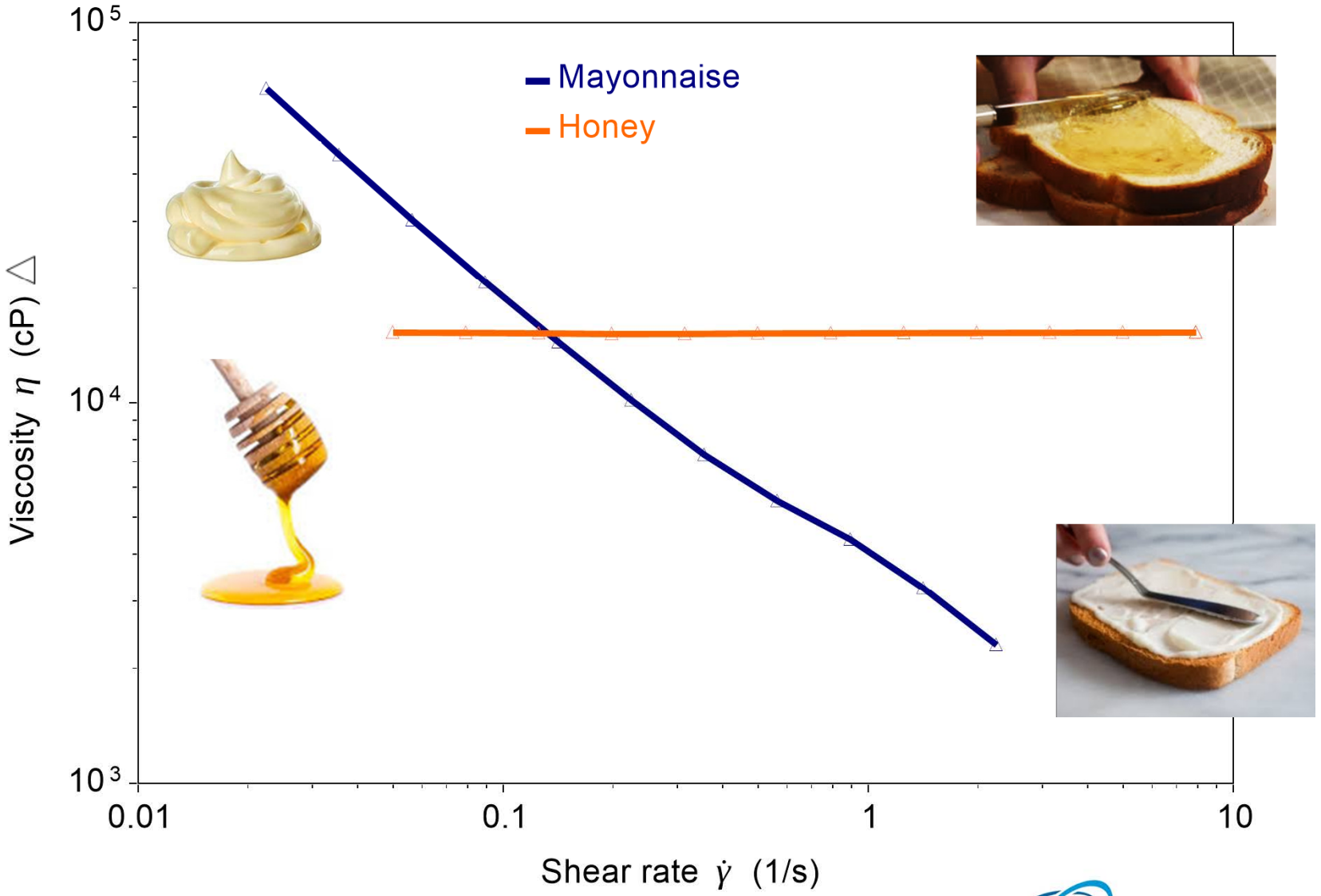
  (examples: water, oil, honey)

- Non-Newtonian Fluids - Viscosity is time or shear rate dependent

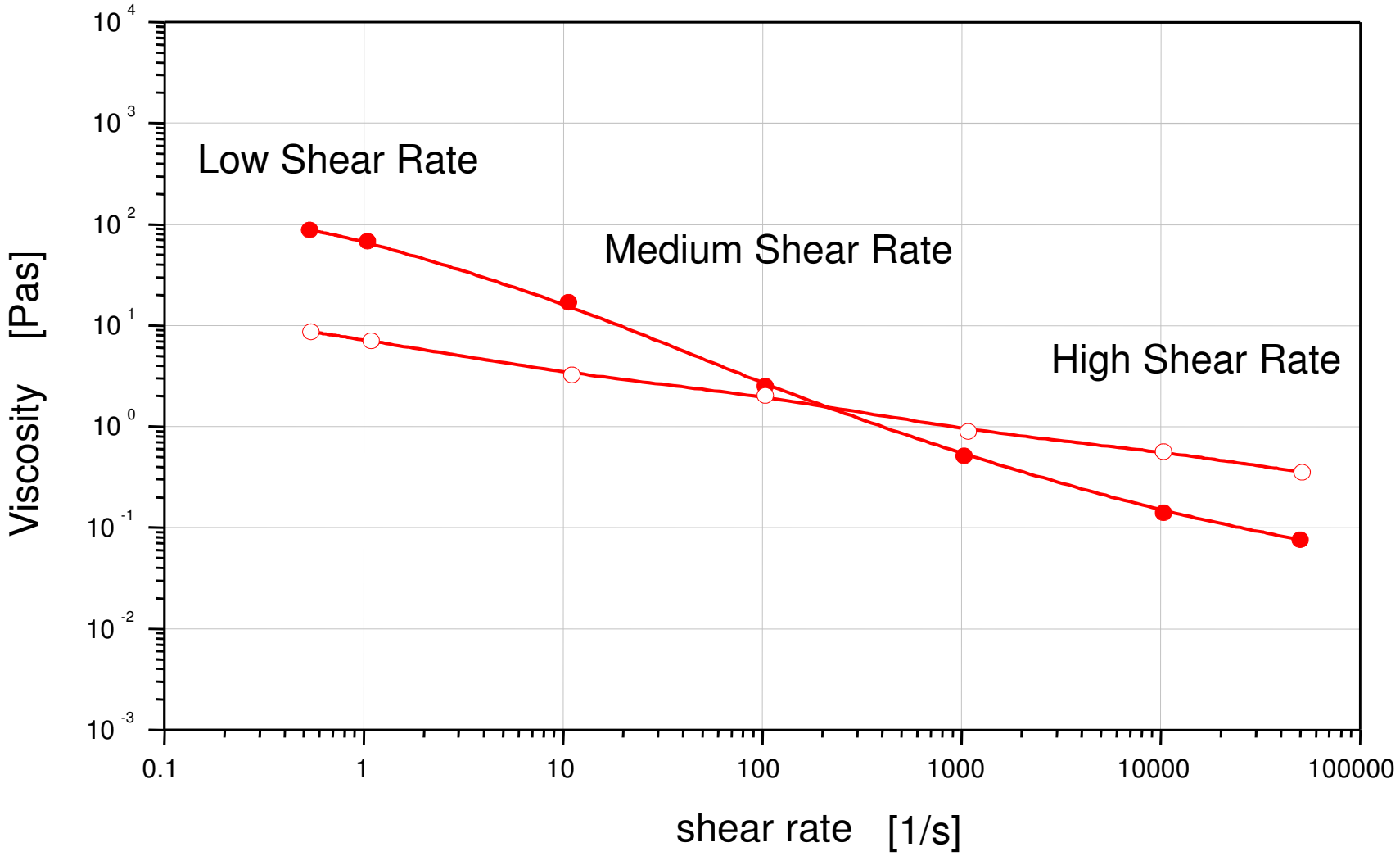
  (examples: mayonnaise, paint, polymer, asphalt)

  - Shear – Thinning: viscosity **decreases** as shear rate increases
  - Shear – Thickening: viscosity **increases** as shear rate increases.

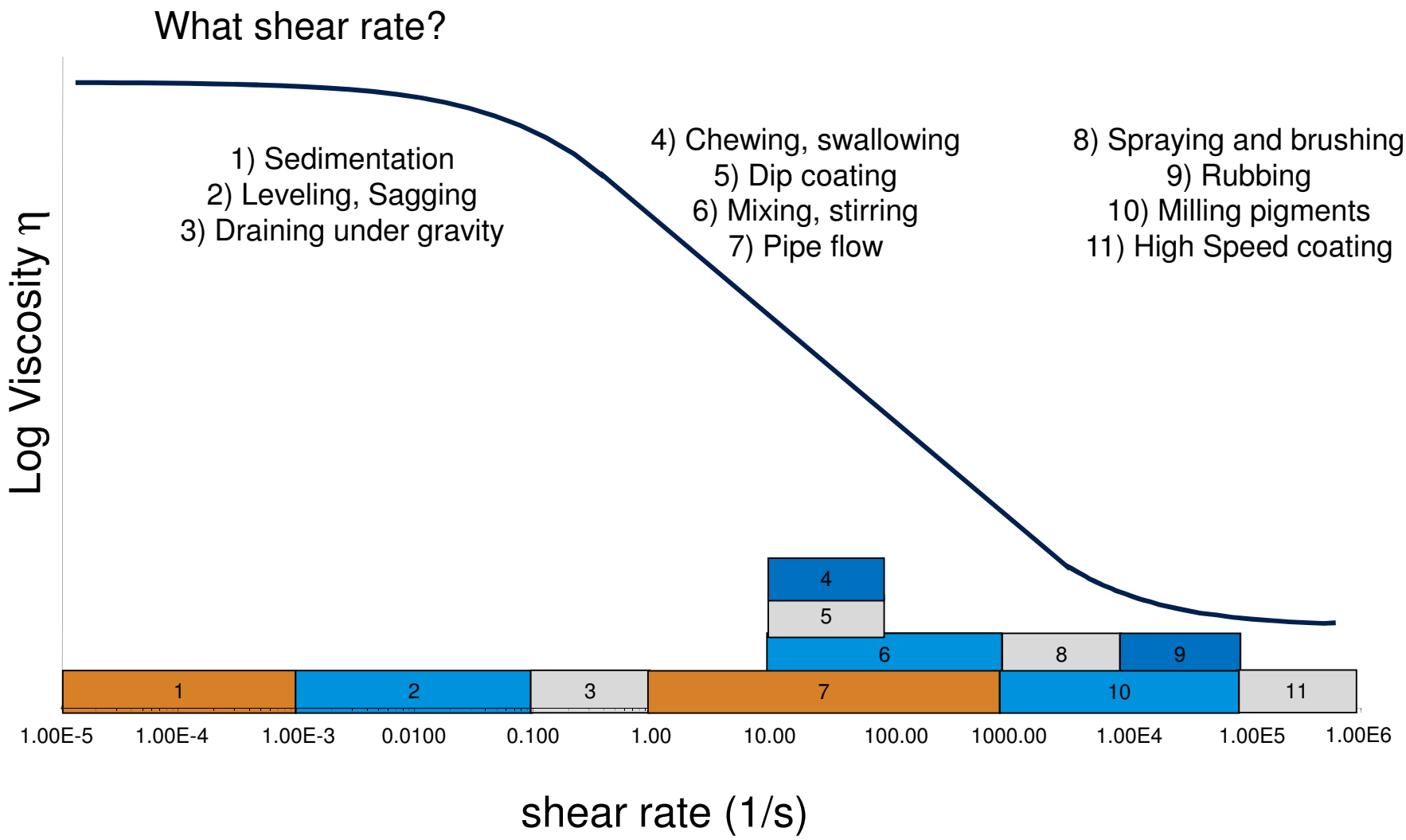
Viscosity of Honey and Mayonnaise



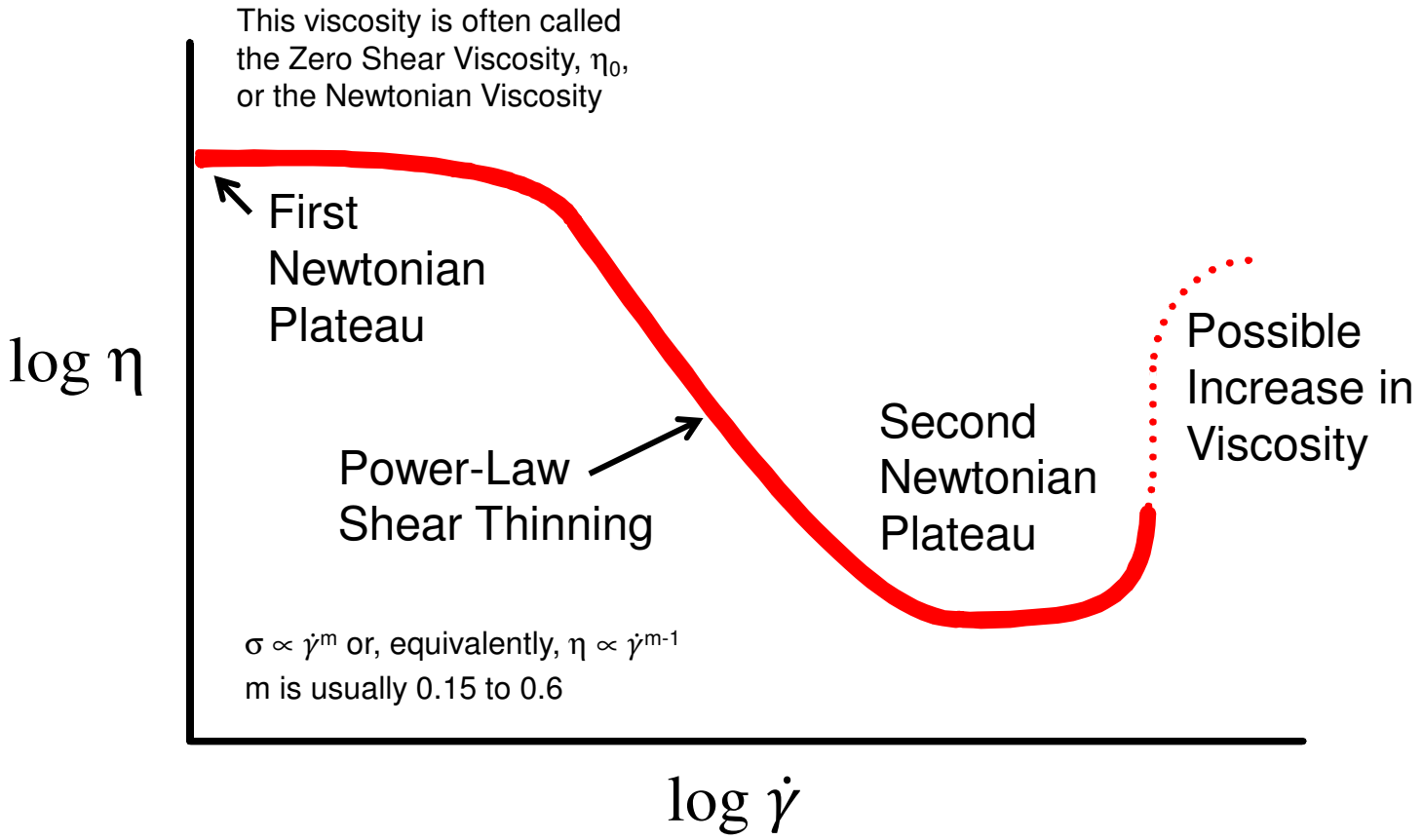
Viscosity is curve, not a single value!



Viscosity Flow Curve

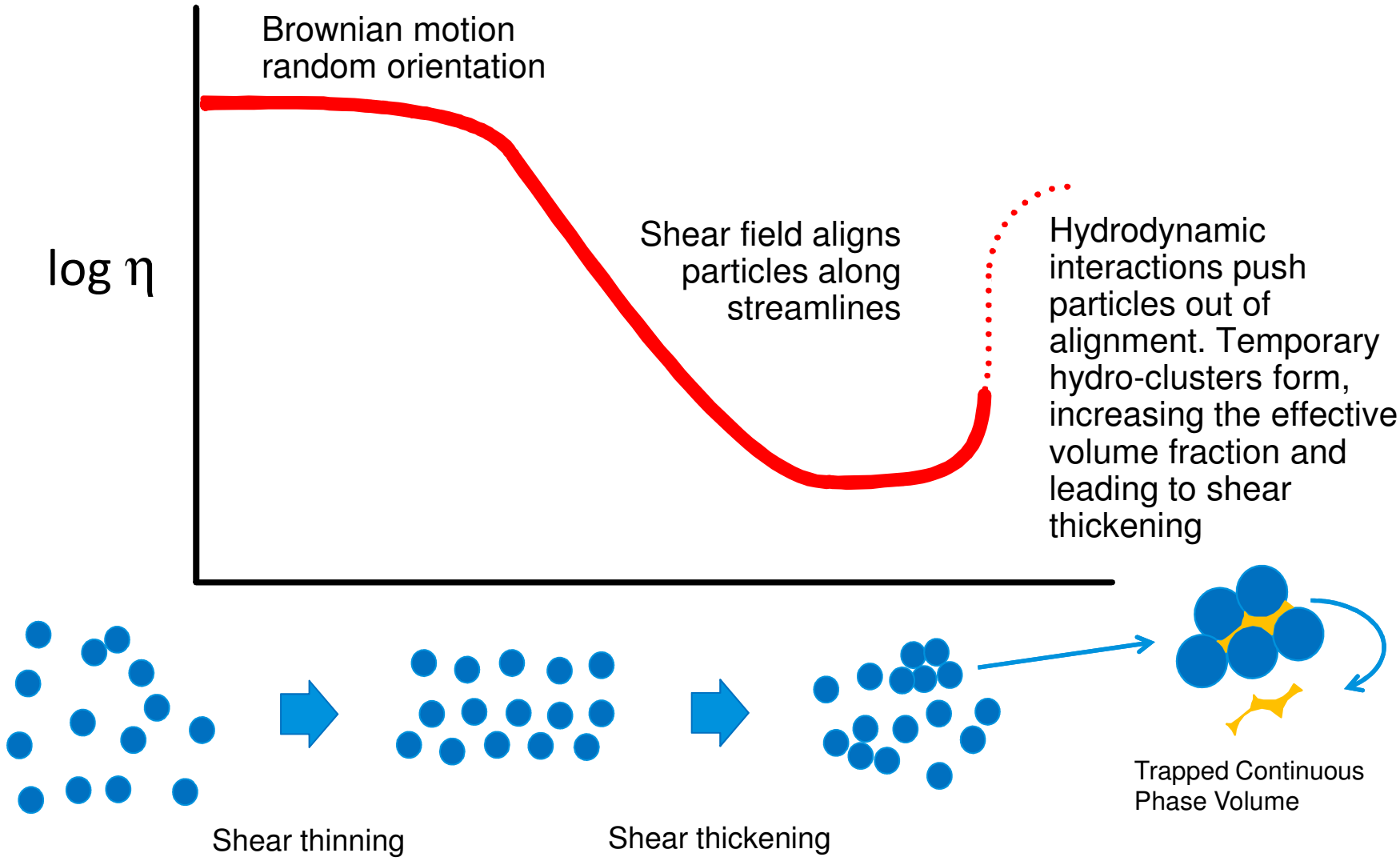


General Viscosity Curve for Suspensions

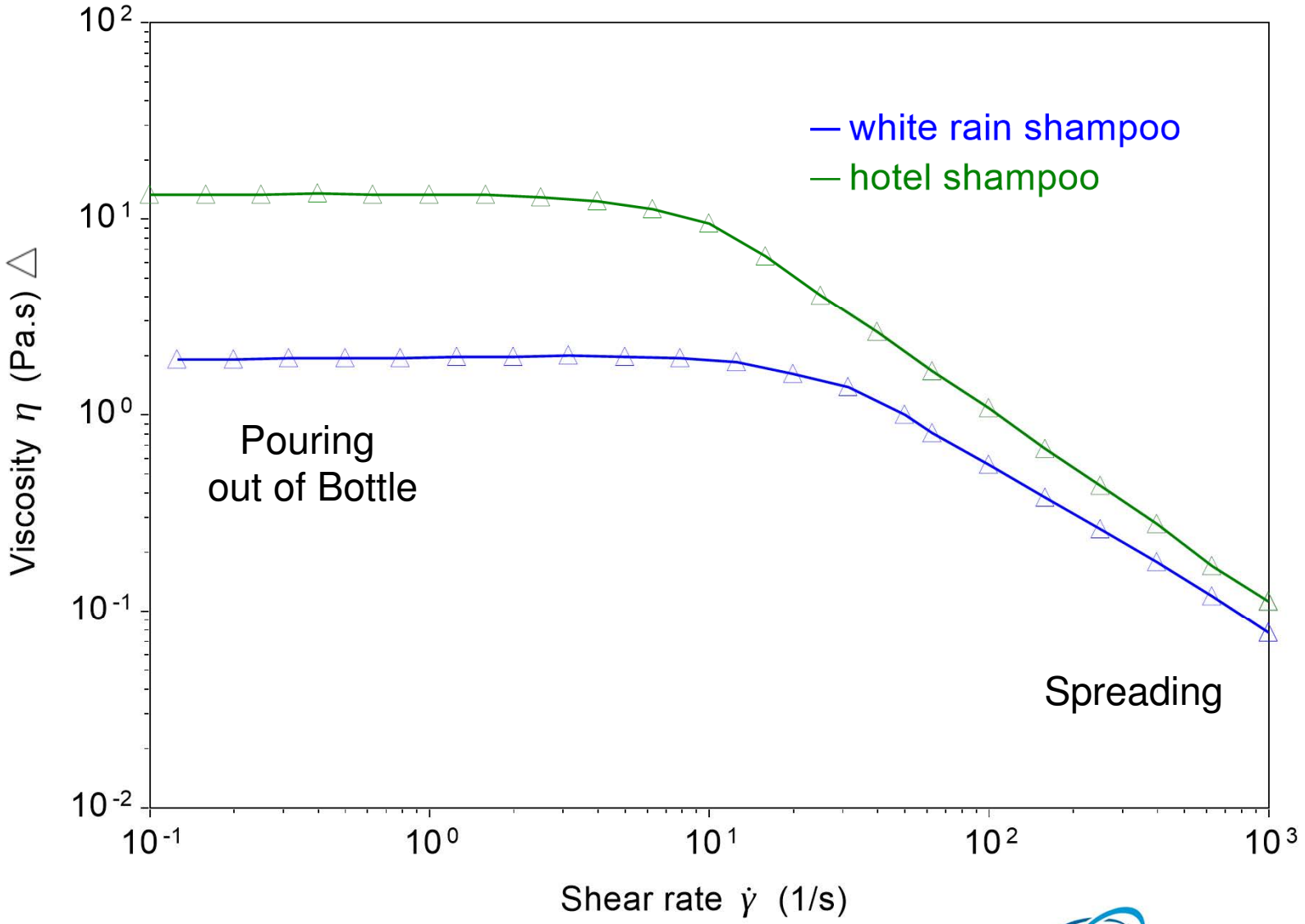


Reference:Barnes, H.A., Hutton, J.F., and Walters, K., An Introduction to Rheology, Elsevier Science B.V., 1989. ISBN 0-444-87469-0

Flow Curve for Suspensions



Viscosity vs. Shear Rate- Shampoo



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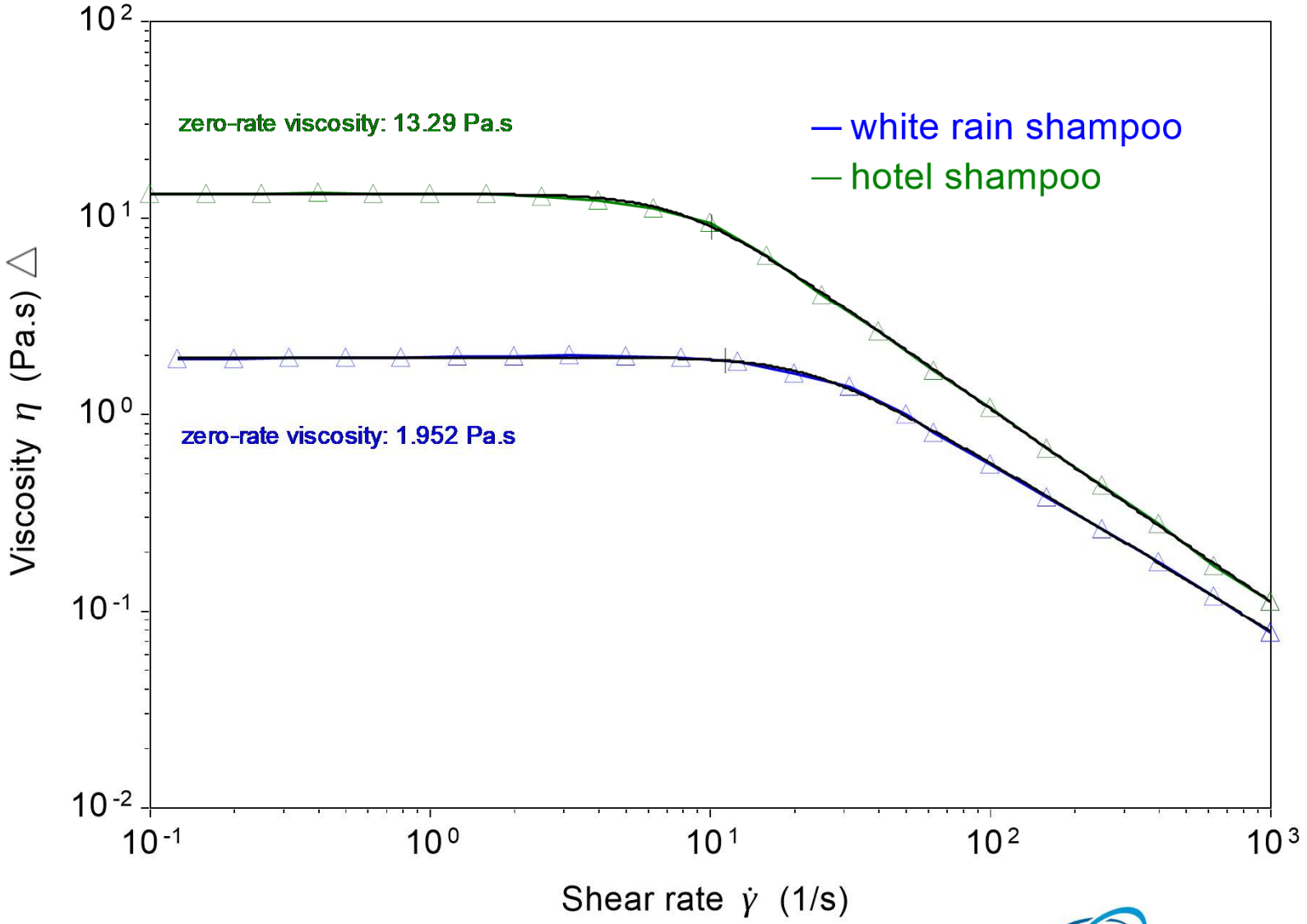
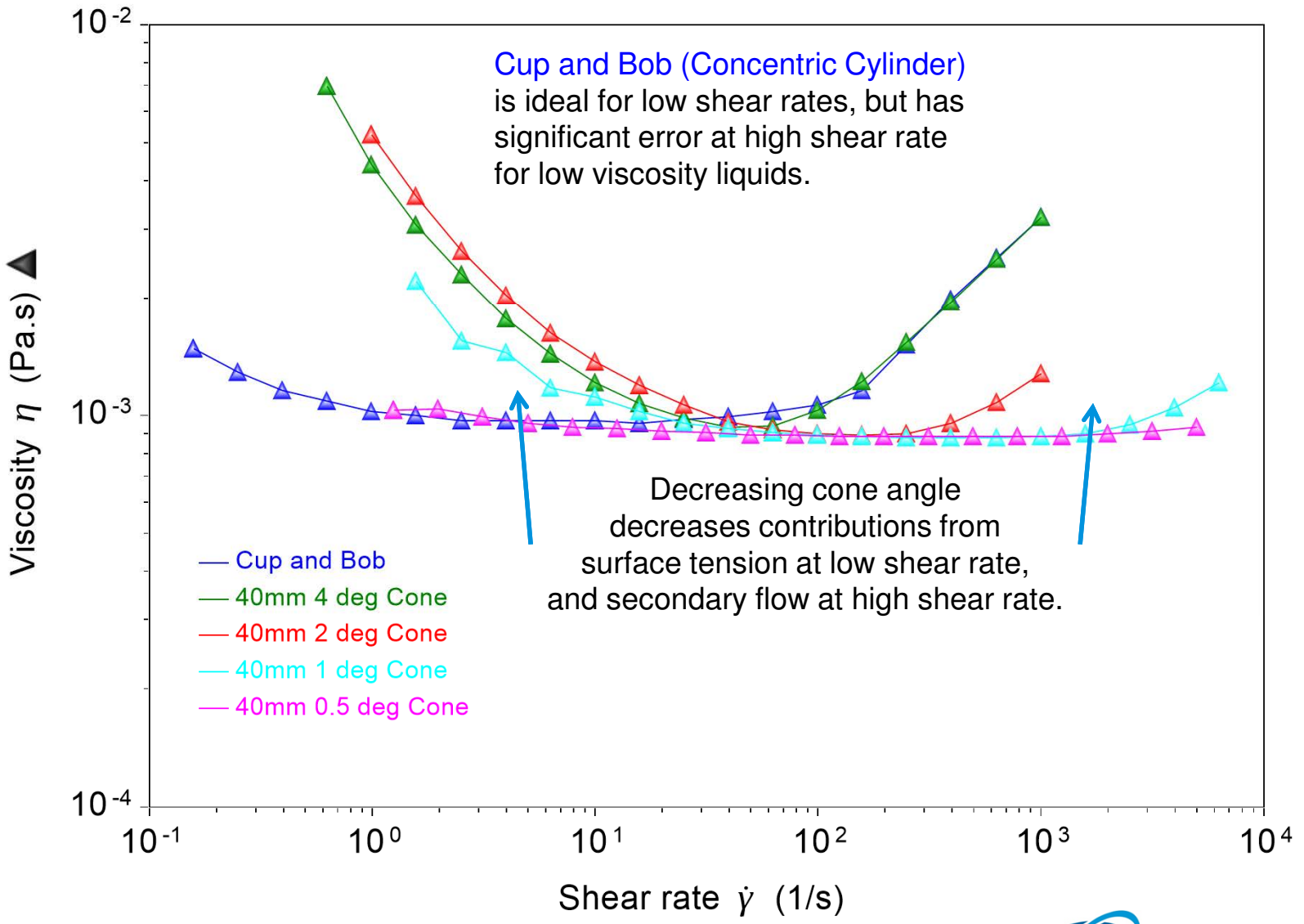
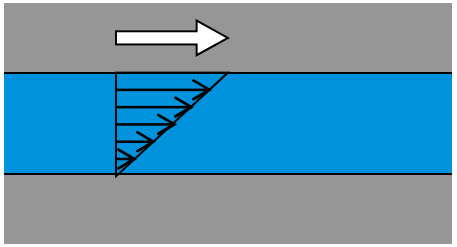


Viscosity of Water: effect of geometry

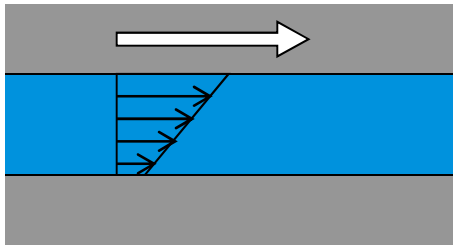


Wall Slip

No slip condition
Ideal, Assumed Velocity Profile

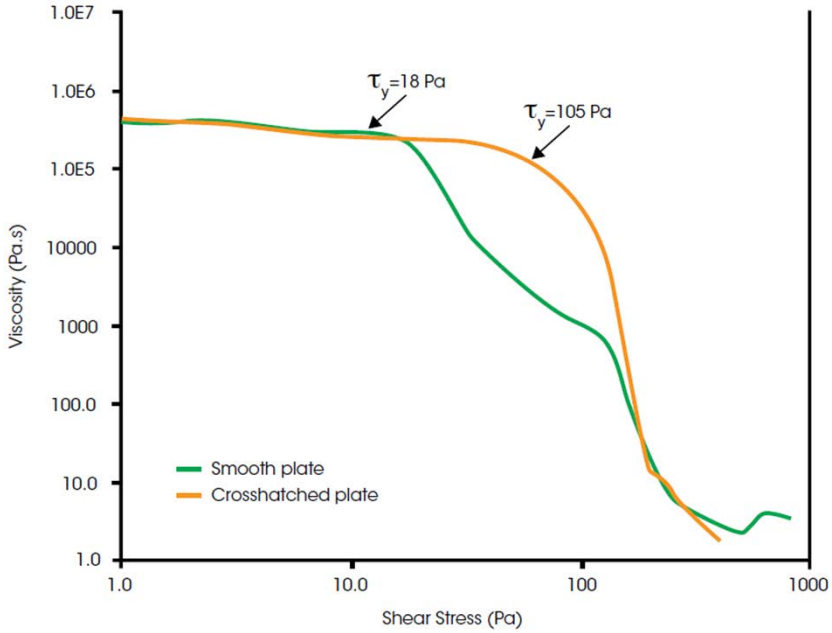


Wall Slip
Incorrect Velocity Profile

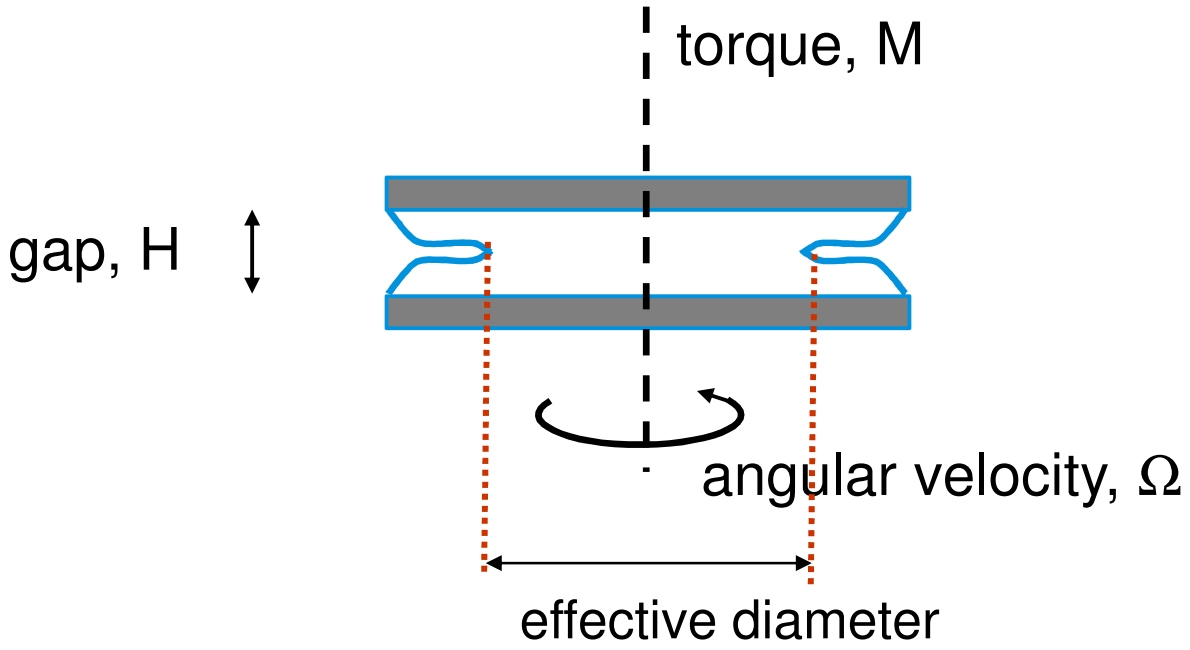


- Can manifest in many ways:
  - Apparent Double Yielding
  - Low Yield Stress
  - Low Viscosity
  - High tan δ
- Test by running the same experiment at different gaps
- For samples that don't slip, the results will be independent of the gap
- Can happen with any geometry: plate, cone, concentric cylinder, etc…

Yield Stress Measurements on Toothpaste



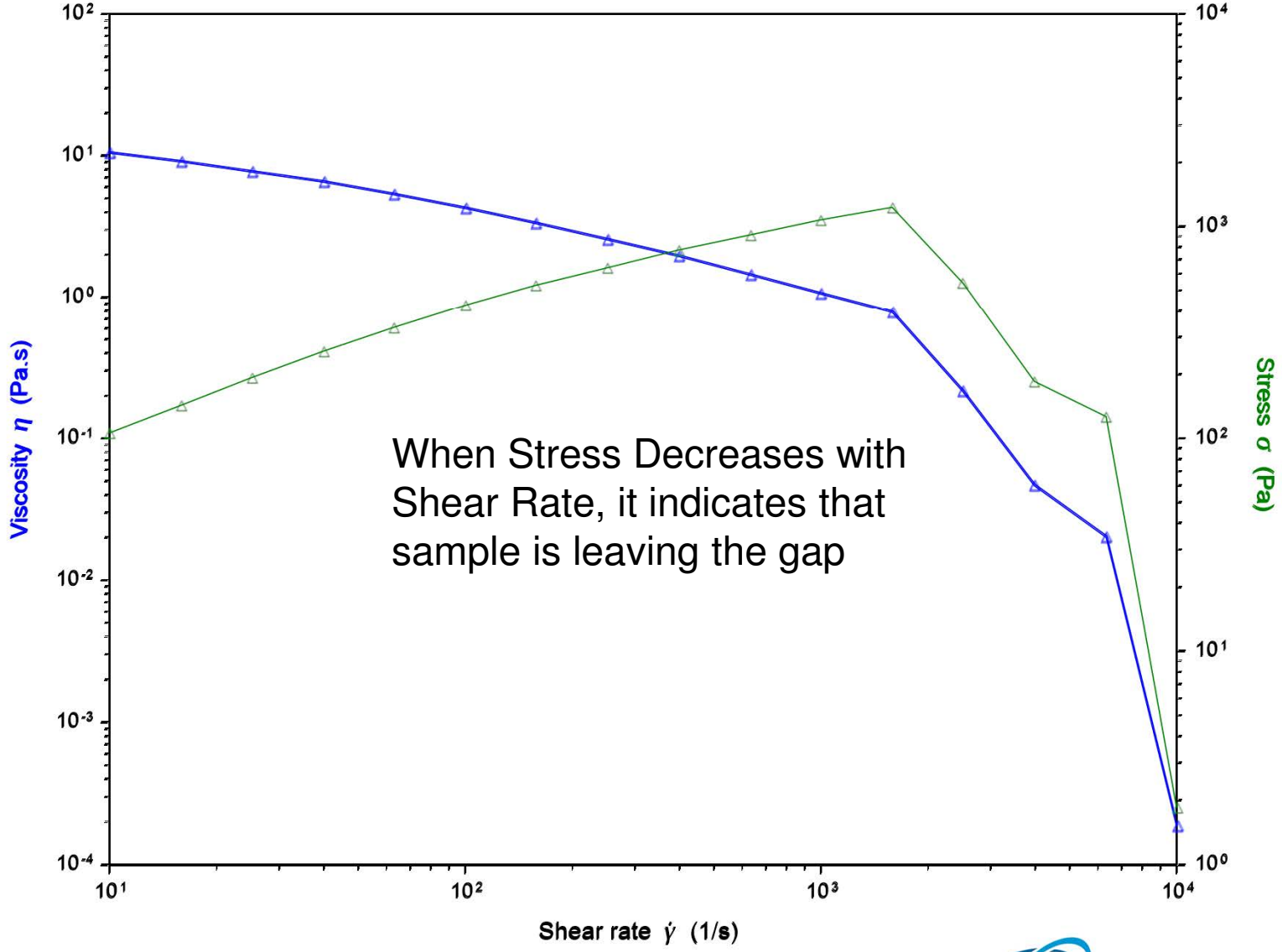
Edge Failure



Large normal stress difference (elasticity) leads to crack formation at free surface

- Results in apparent drop in viscosity
- Remedy: decrease gap to increase stabilizing influence of surface tension

Shear Thinning or Sample Instability?

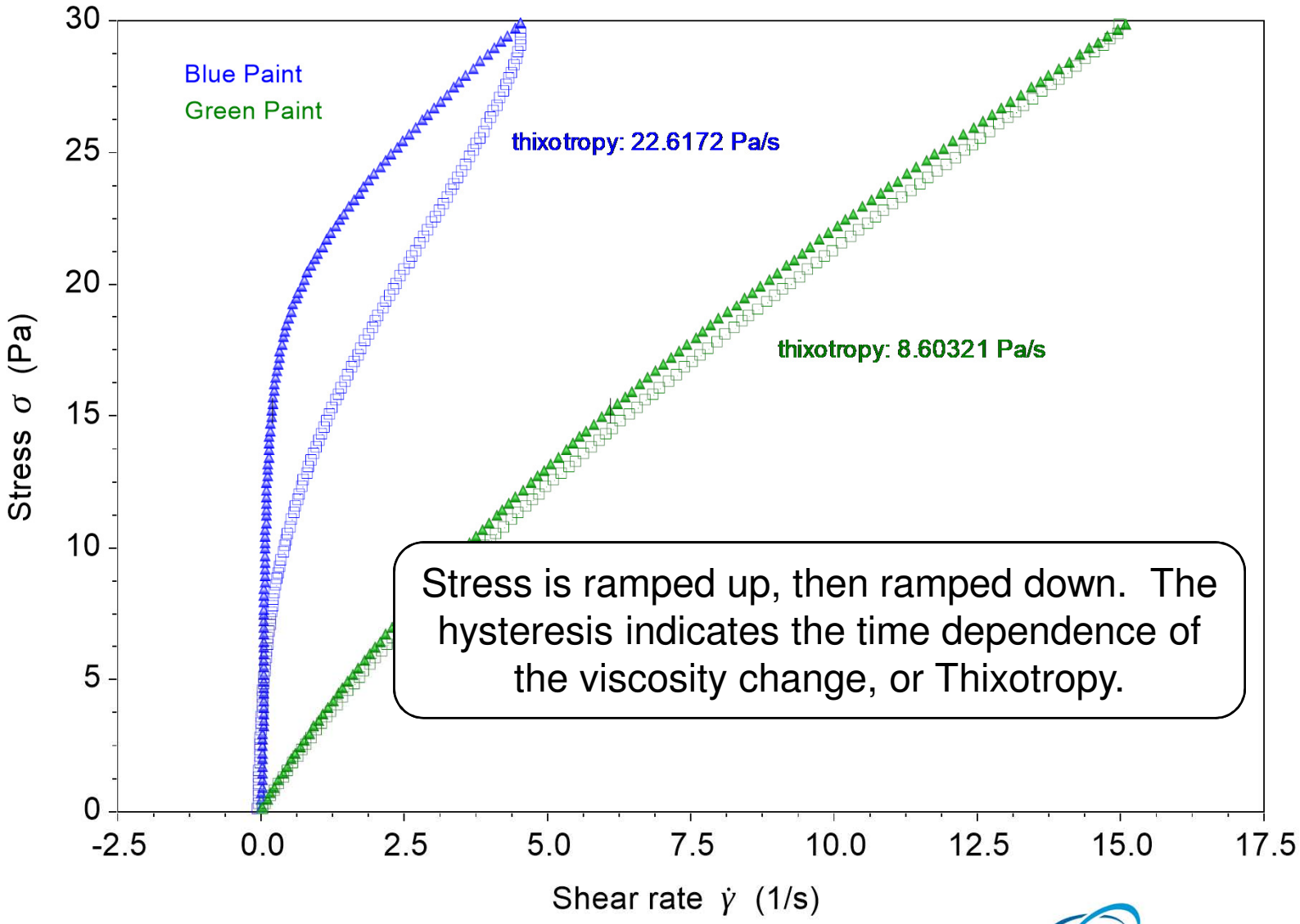


Thixotropy

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

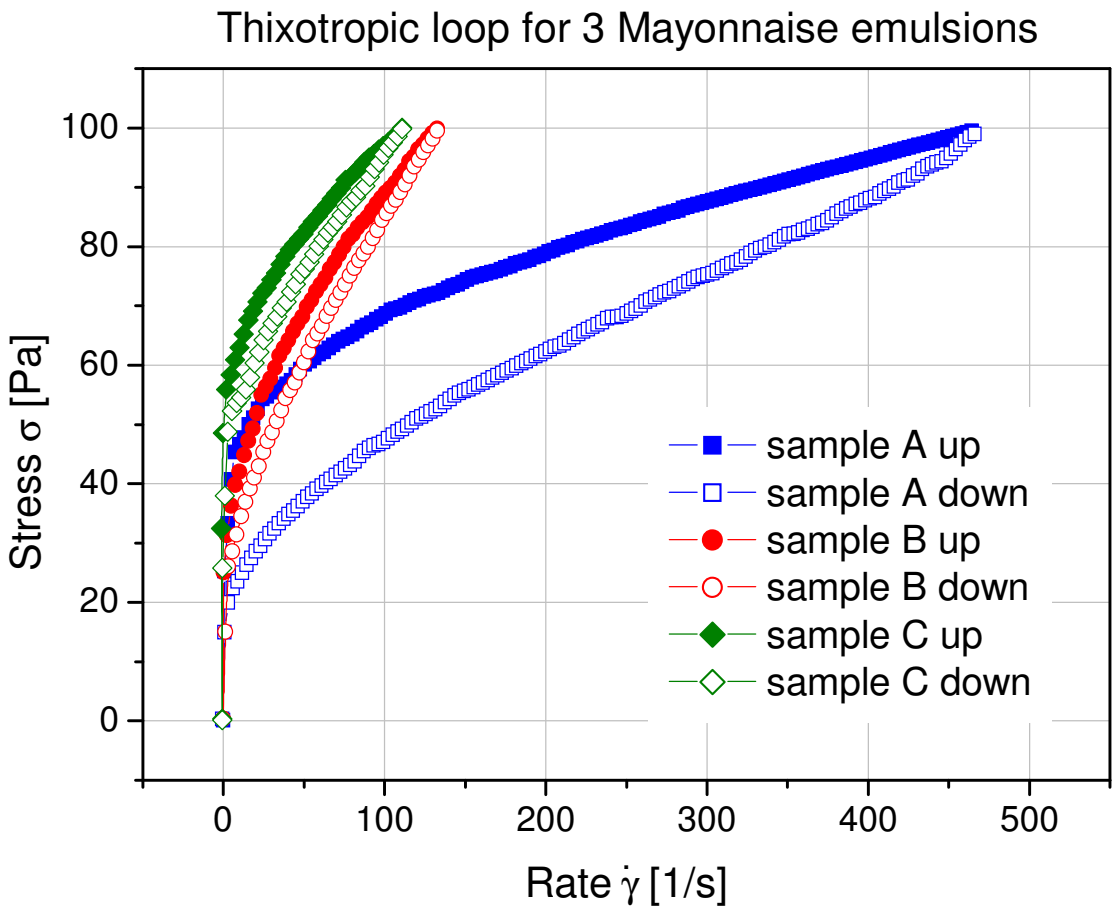
- process conditions; for example, to avoid structure build up in pipes during rest periods
- sagging and leveling; gloss of paints and coatings

Thixotropy of Paint



Stress is ramped up, then ramped down. The hysteresis indicates the time dependence of the viscosity change, or Thixotropy.

Thixotropic Loop- Mayonnaise



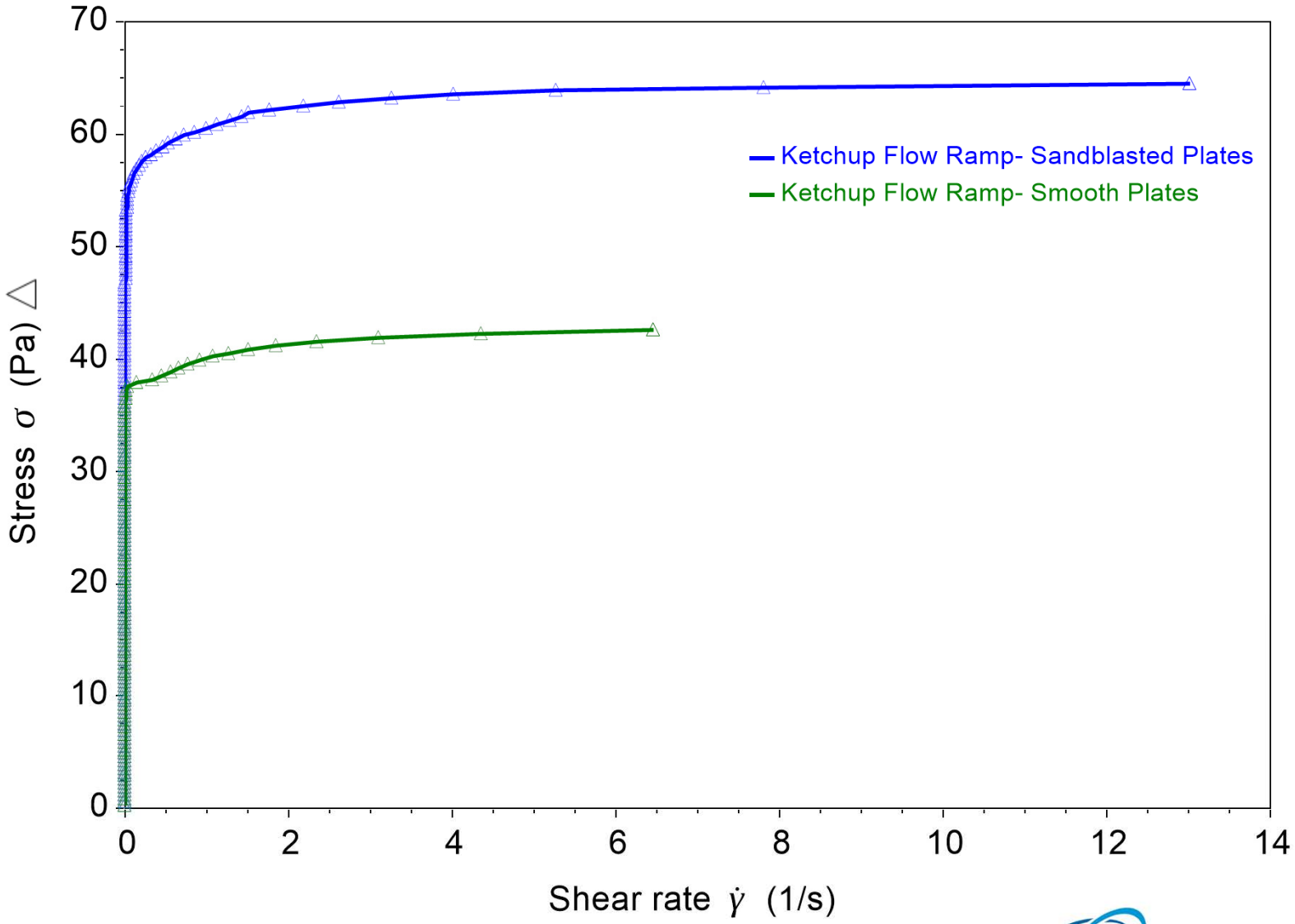
Thixotropic Material

- Up and down rate ramps do not superimpose
- Area under the curve is a measure of thixotropy

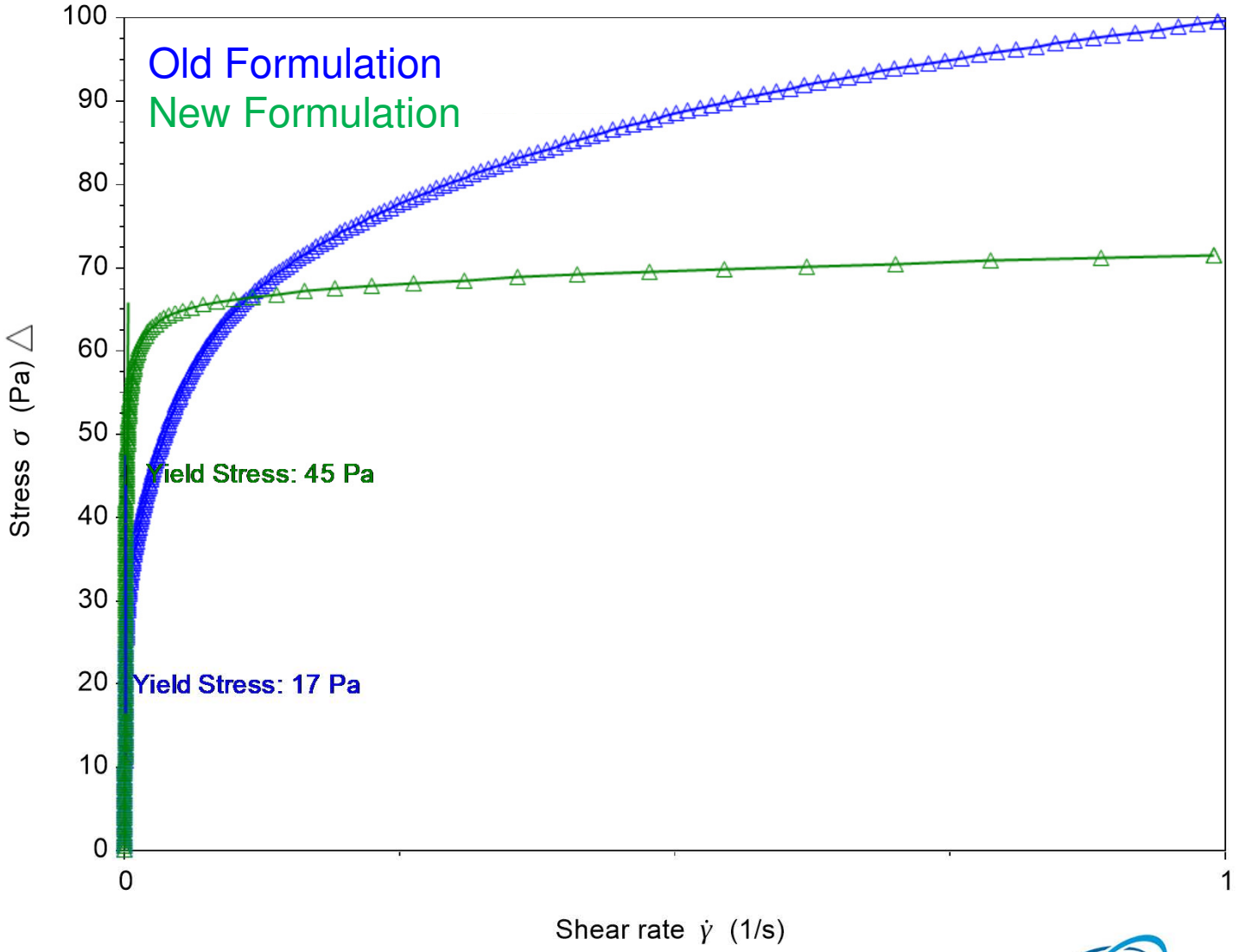
What is Yield Stress?

- Some Structured Fluids behave like “solids” at rest.
- A critical stress must be applied for these materials to flow.
- What does Yield Stress do?
  - Stabilize against sedimentation of separation
  - Improve ease of use
  - Prevent dispensing of product

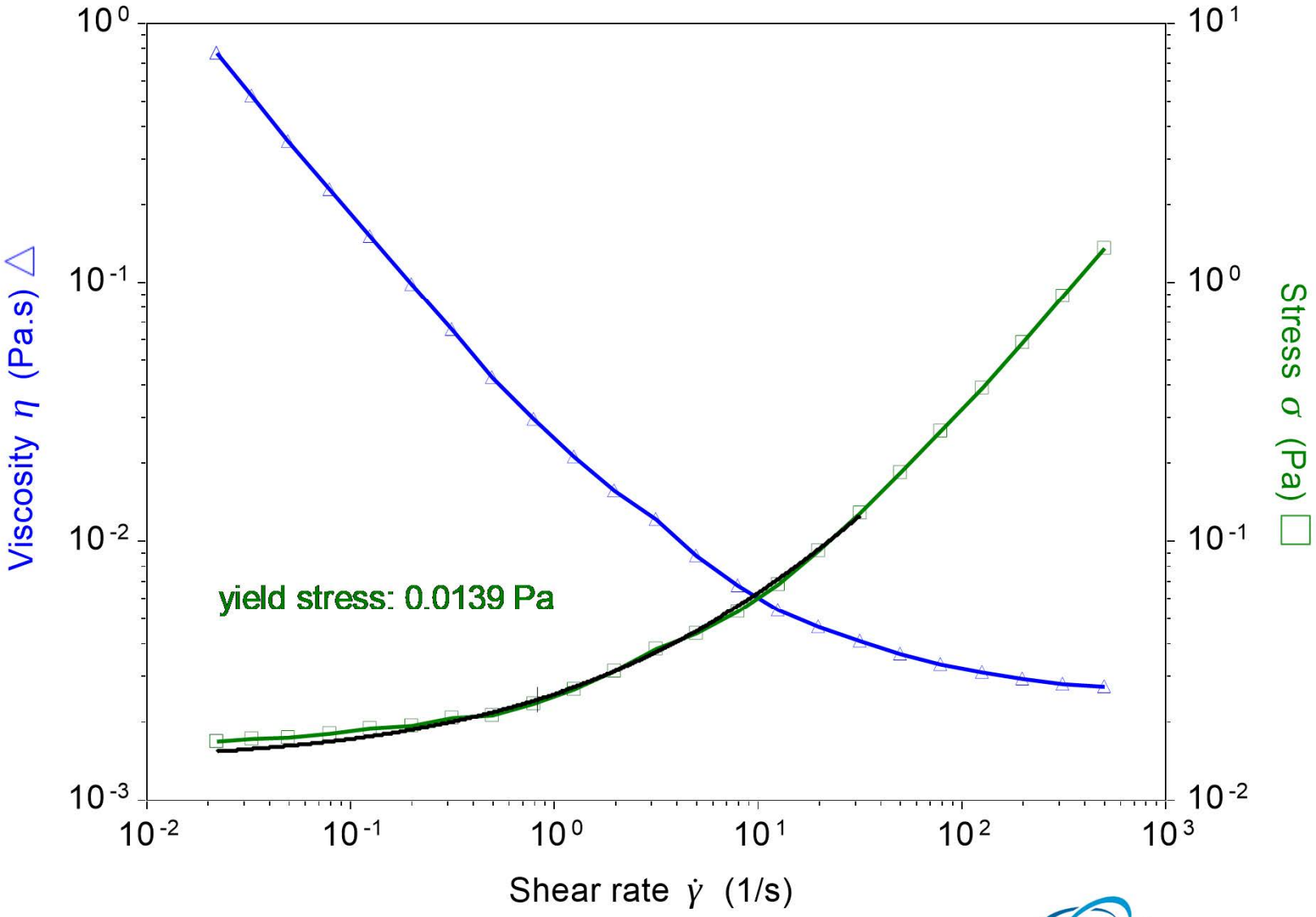
Yield Stress- Ketchup



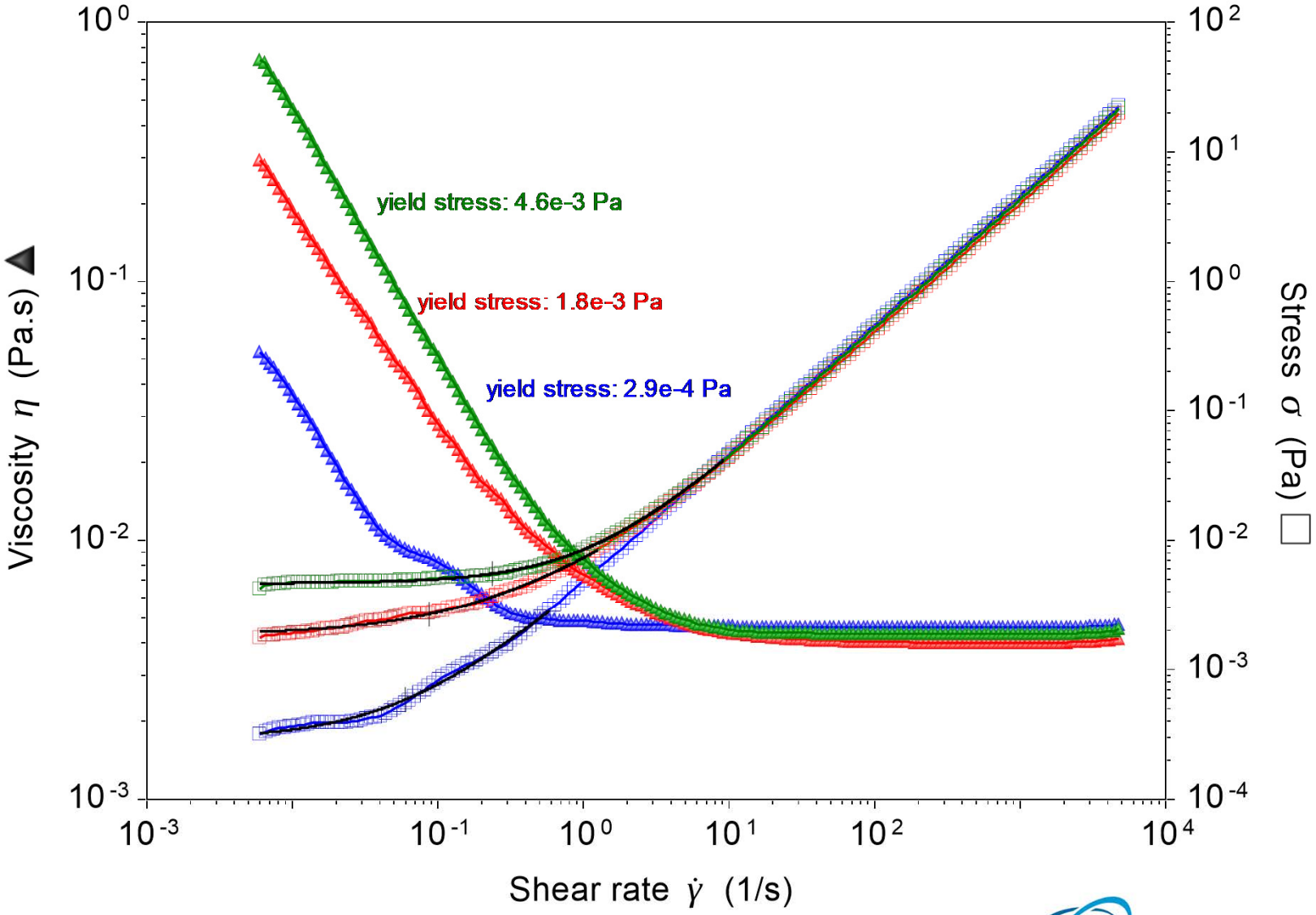
Paint Formulations- Yield Stress



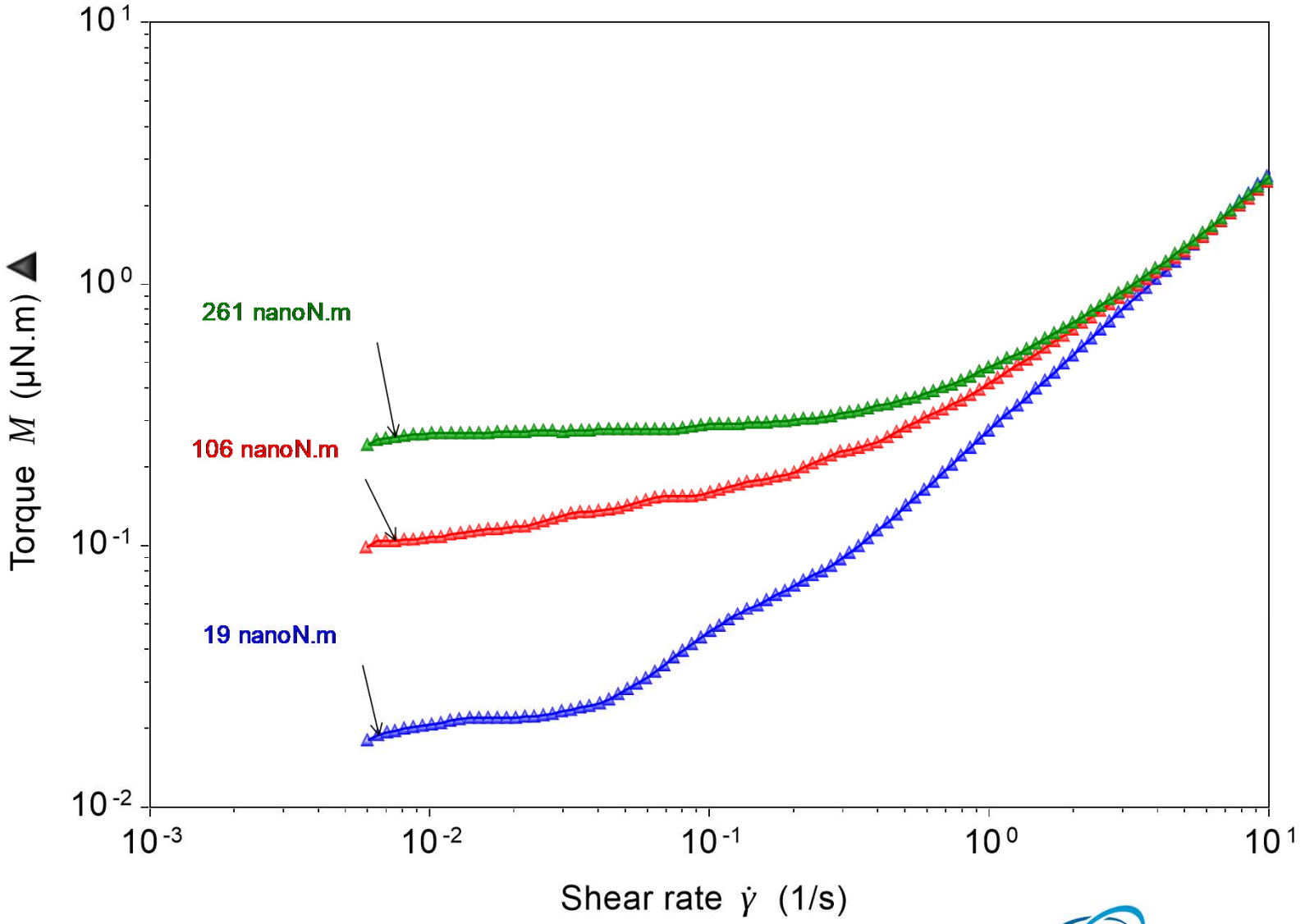
Yield Stress: Orange Juice



Yield Stresses of Protein Solutions



Protein Solutions: Low Torque Sensitivity



Understanding Torque

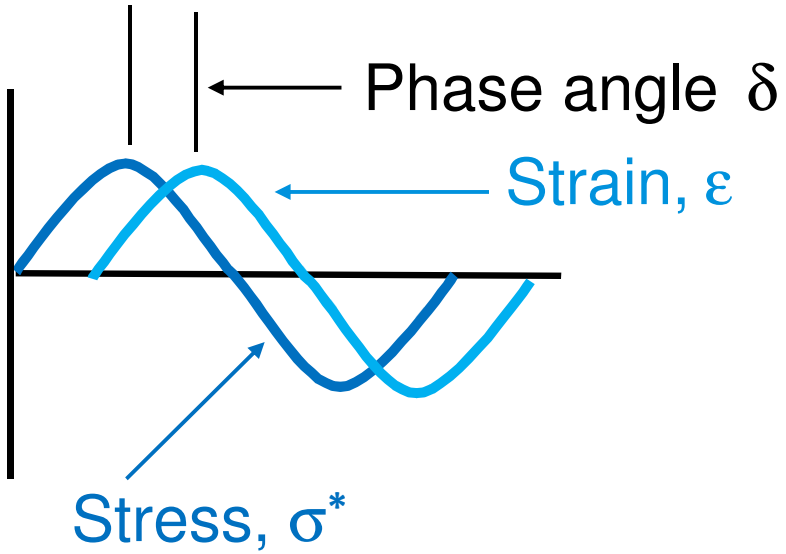
- What is a **N.m**?
  - An apple (about 150 g) on the end of a meter stick
  - **1.5 N.m**

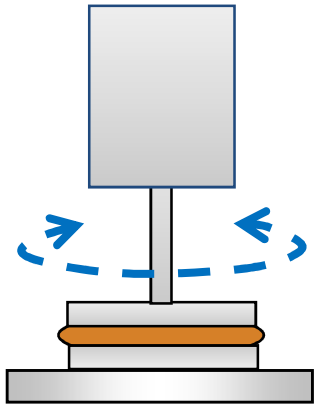
- What is a **µN.m**?
  - A grain of salt (about 0.5 mg) on the end of a meter stick)
  - **5 µN.m**

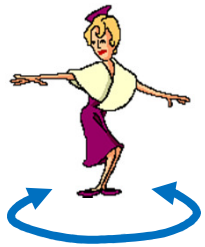
- And a **nanoN.m**?
  - A speck of dust (1 µg) on the end of a meter stick
  - **10 nanoN.m**

Oscillation

What is Oscillation?





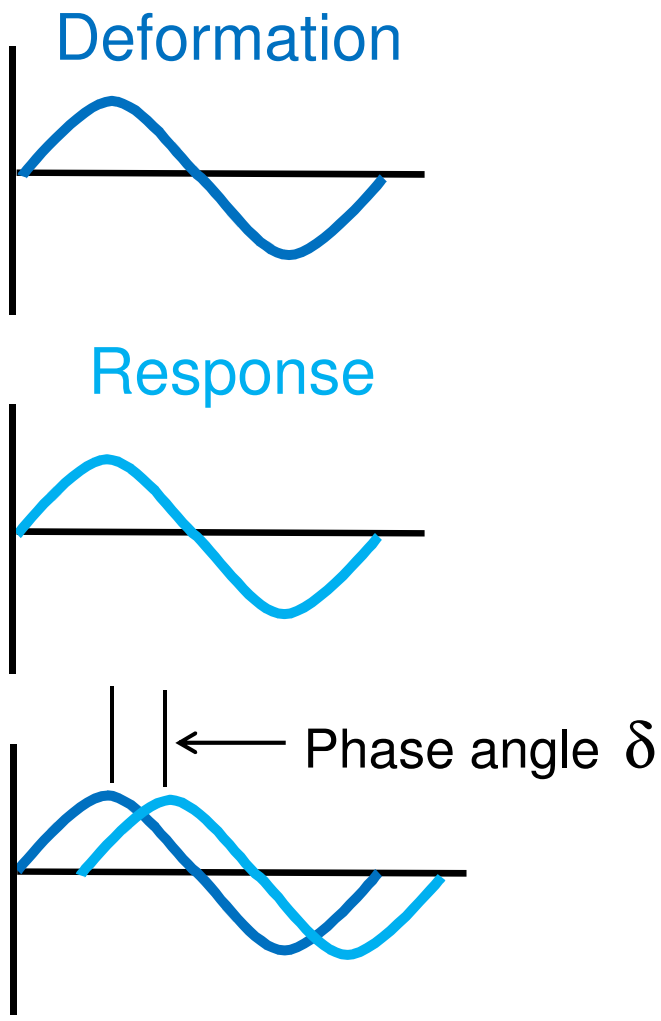


Dynamic stress applied sinusoidally

User-defined Stress or Strain amplitude and frequency

Oscillation Testing

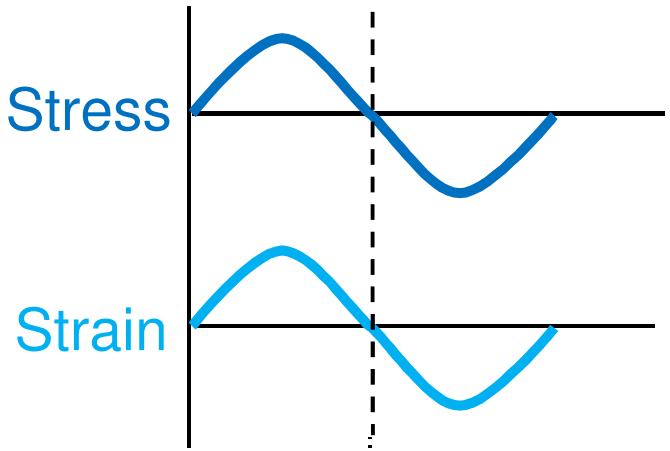
- An oscillatory (sinusoidal) deformation is applied to a sample.
- The material response (stress) is measured.
- The phase angle δ, or phase shift, between the deformation and response is measured.



Oscillation Testing: Response for solids and liquids

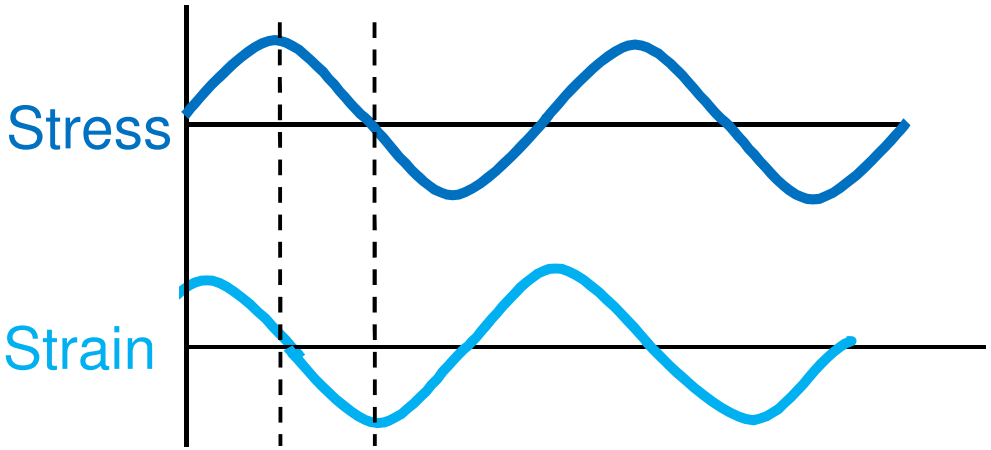
Purely Elastic Response
(Hookean Solid)

$\delta = 0°$

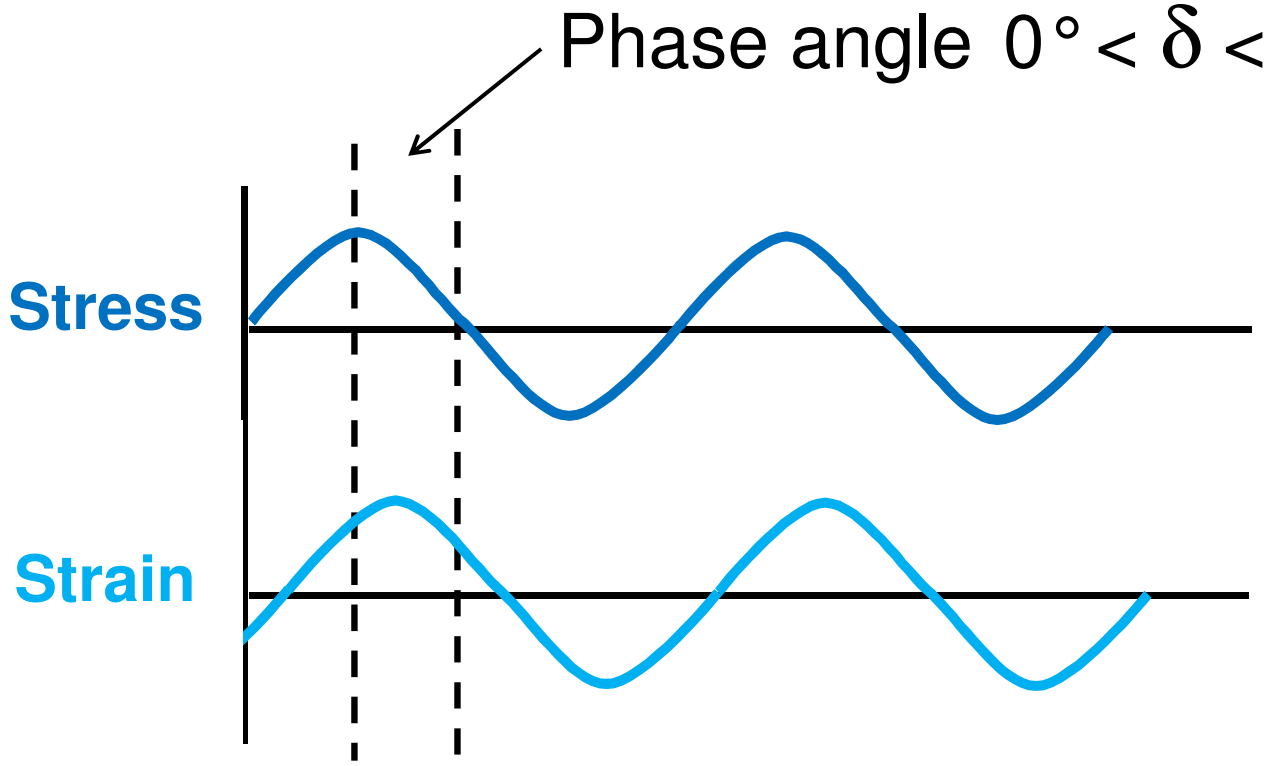


Purely Viscous Response
(Newtonian Liquid)

$\delta = 90°$



Oscillation Testing: Viscoelastic Material



Viscoelastic Parameters

The Modulus: Measure of materials overall resistance to deformation.

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

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

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

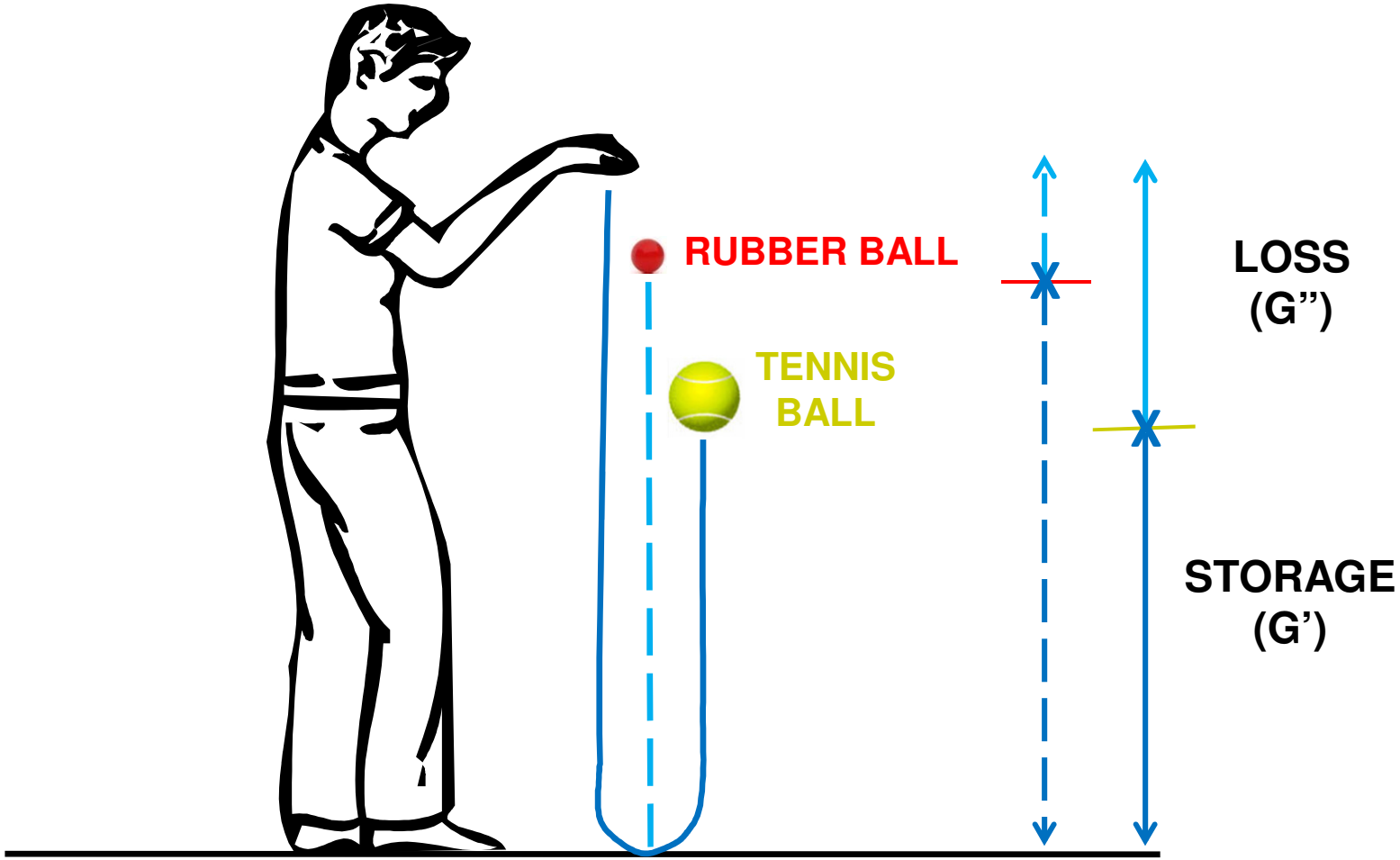
The Viscous (loss) Modulus: The ability of the material to dissipate energy. Energy lost as heat.

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

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

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

Storage and Loss of a Viscoelastic Material



Viscoelasticity Defined

Range of Material Behavior

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

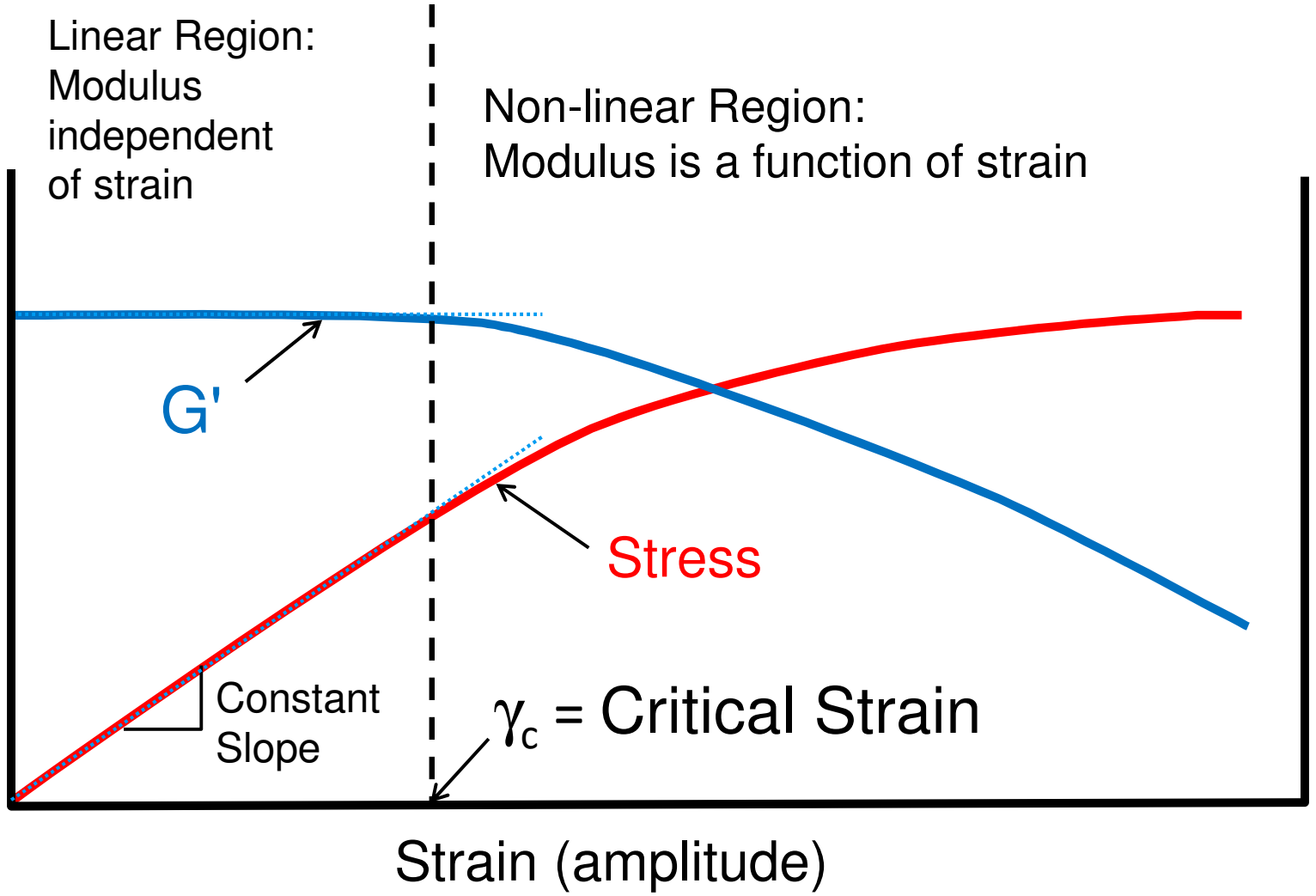
Ideal Fluid ----- Most Materials -----Ideal Solid

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

Viscoelasticity: Having both viscous and elastic properties

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

Oscillation Testing- Linear Viscoelastic Region



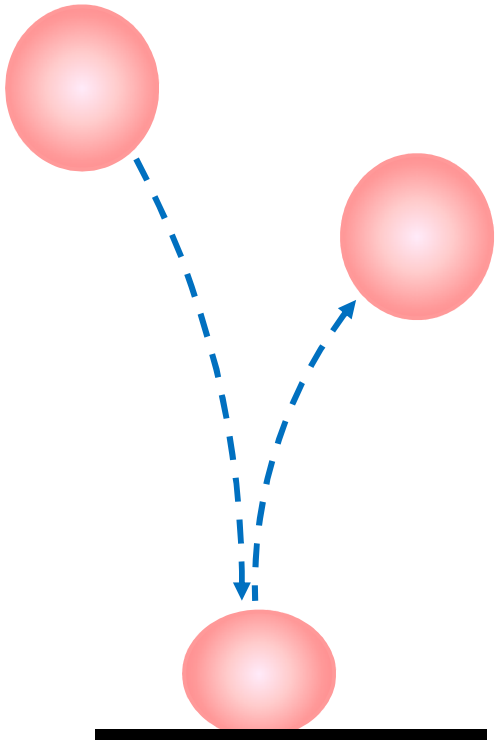
Time-Dependent Viscoelastic Behavior

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

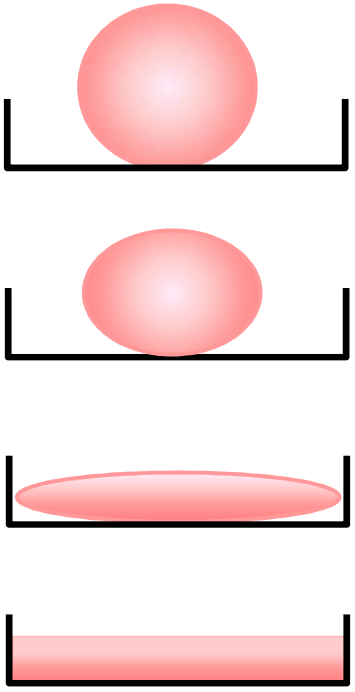
Started in 1927 by Thomas Parnell in Queensland, Australia

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

Time-Dependent Viscoelastic Behavior



T is short [< 1s]



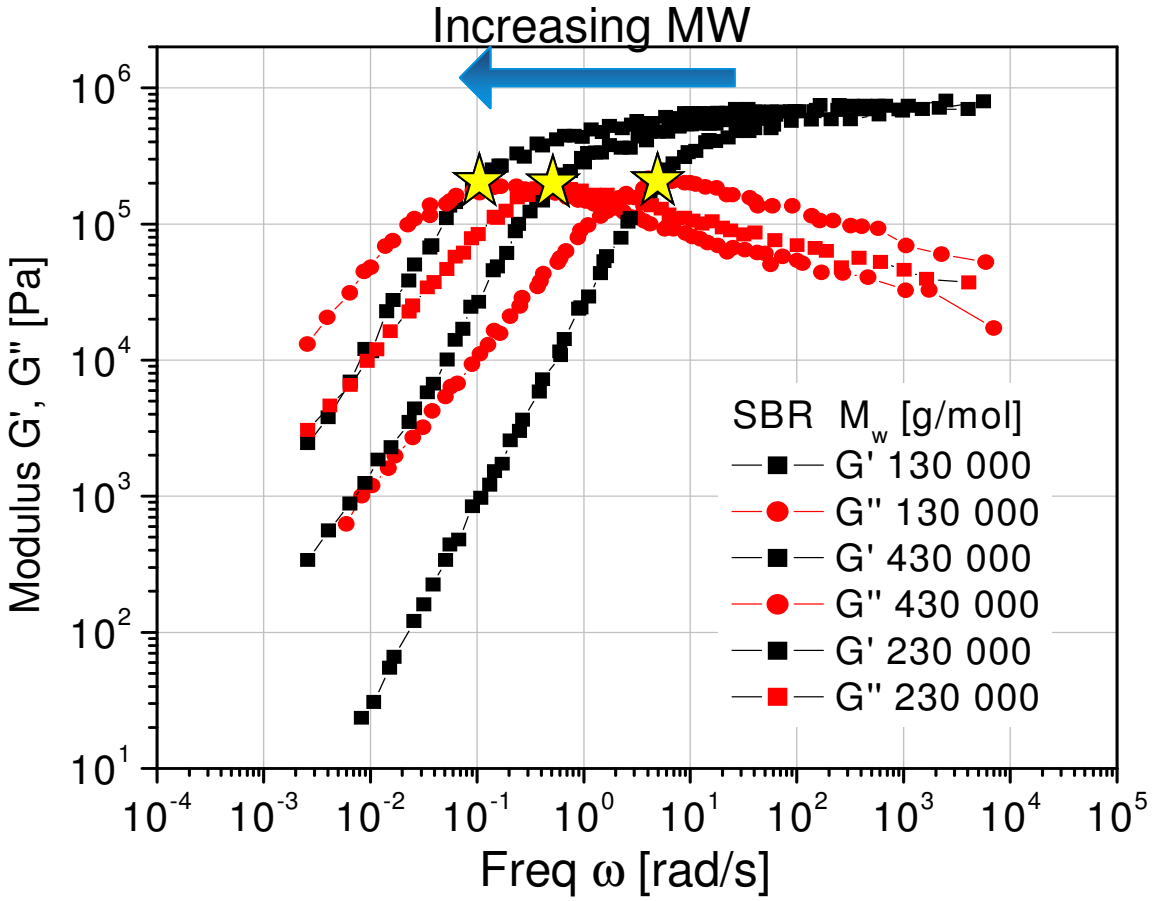
T is long [24 hours]

Viscoelastic Putties

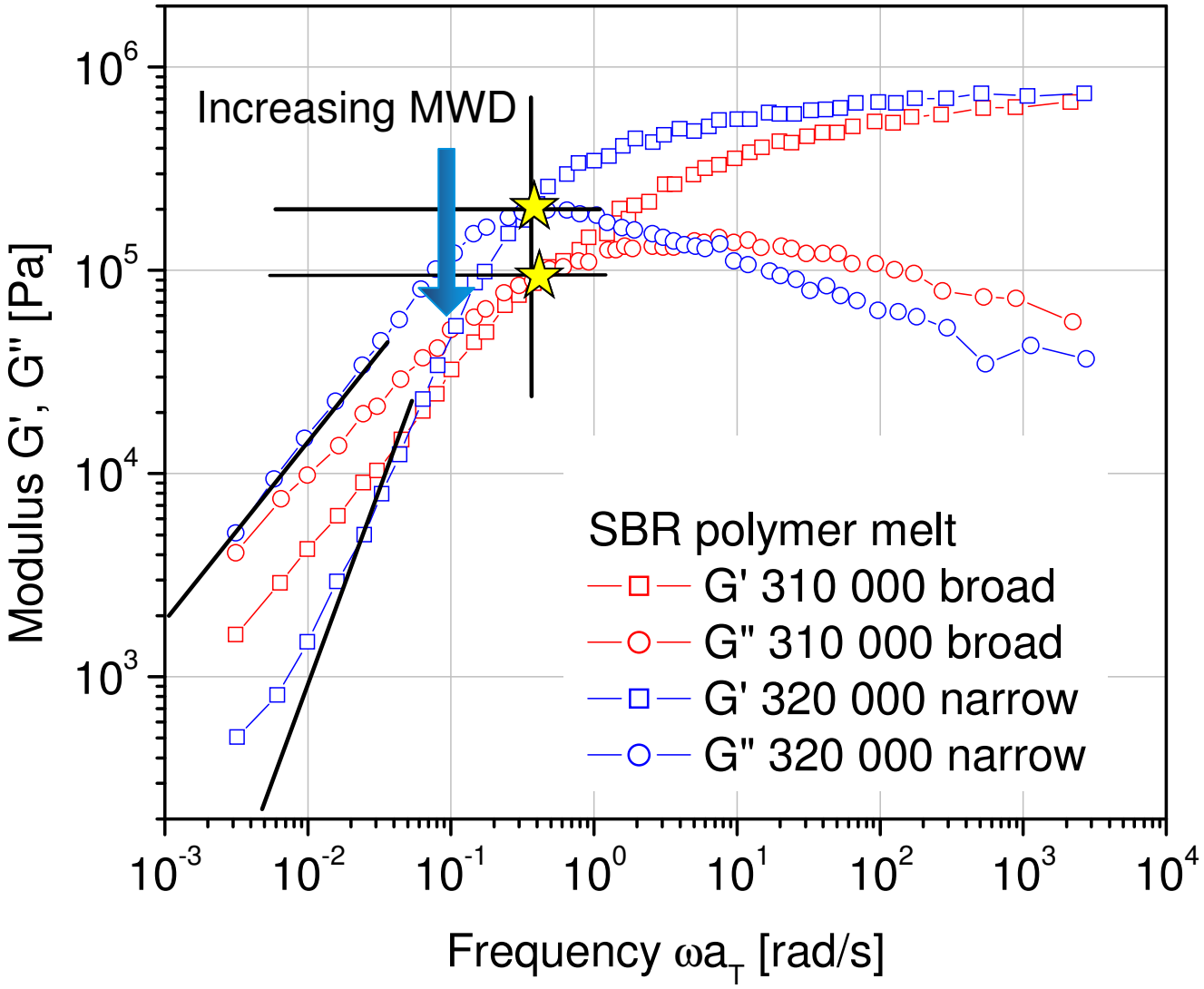
- Compare with your neighbors!
- How do these differ in their rheology?
  - Viscosity
  - Modulus
  - Phase angle
  - Relaxation Time
- How can you test it?
  - “Manual Rheology”
  - With a Rheometer

Influence of Molecular Weight on G' and G"

The intersection of G' and G" shifts to lower frequency as MW increases.



Influence of MWD on G‘ and G“

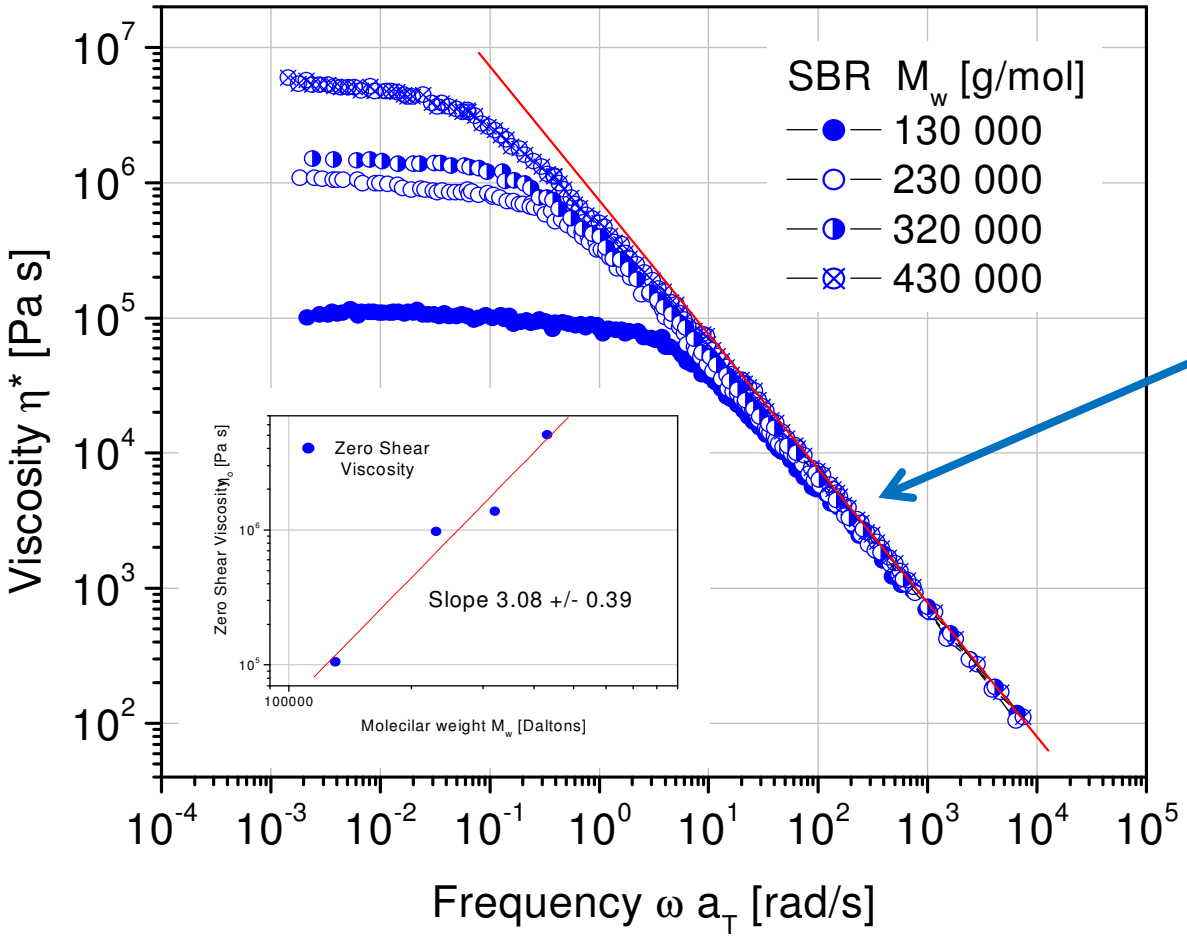


Higher crossover frequency : lower M_w

Higher crossover Modulus: narrower MWD

Influence of MW on Viscosity

The zero shear viscosity increases with increasing molecular weight.
TTS is applied to obtain the extended frequency range.

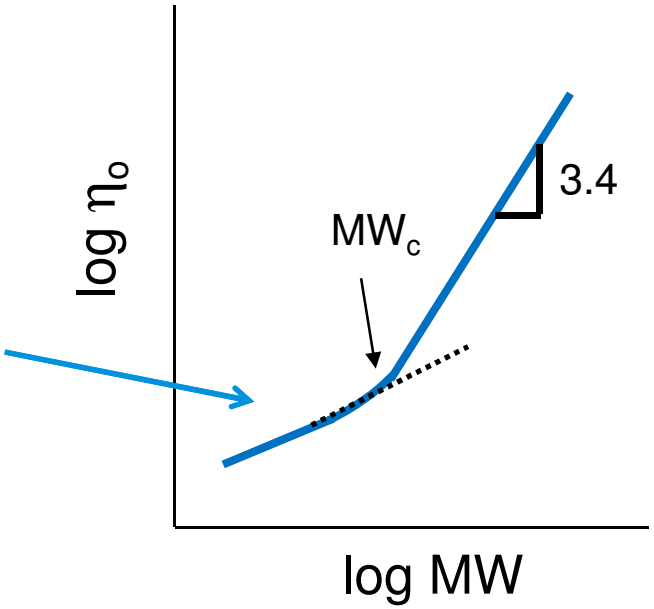


The high frequency behavior (slope -1) is independent of the molecular weight

Melt Rheology: MW Effect on Zero Shear Viscosity

- Sensitive to Molecular Weight, MW
- For Low MW (no Entanglements) η_0 is proportional to MW
- For MW > Critical MW_c, η_0 is proportional to $MW^{3.4}$

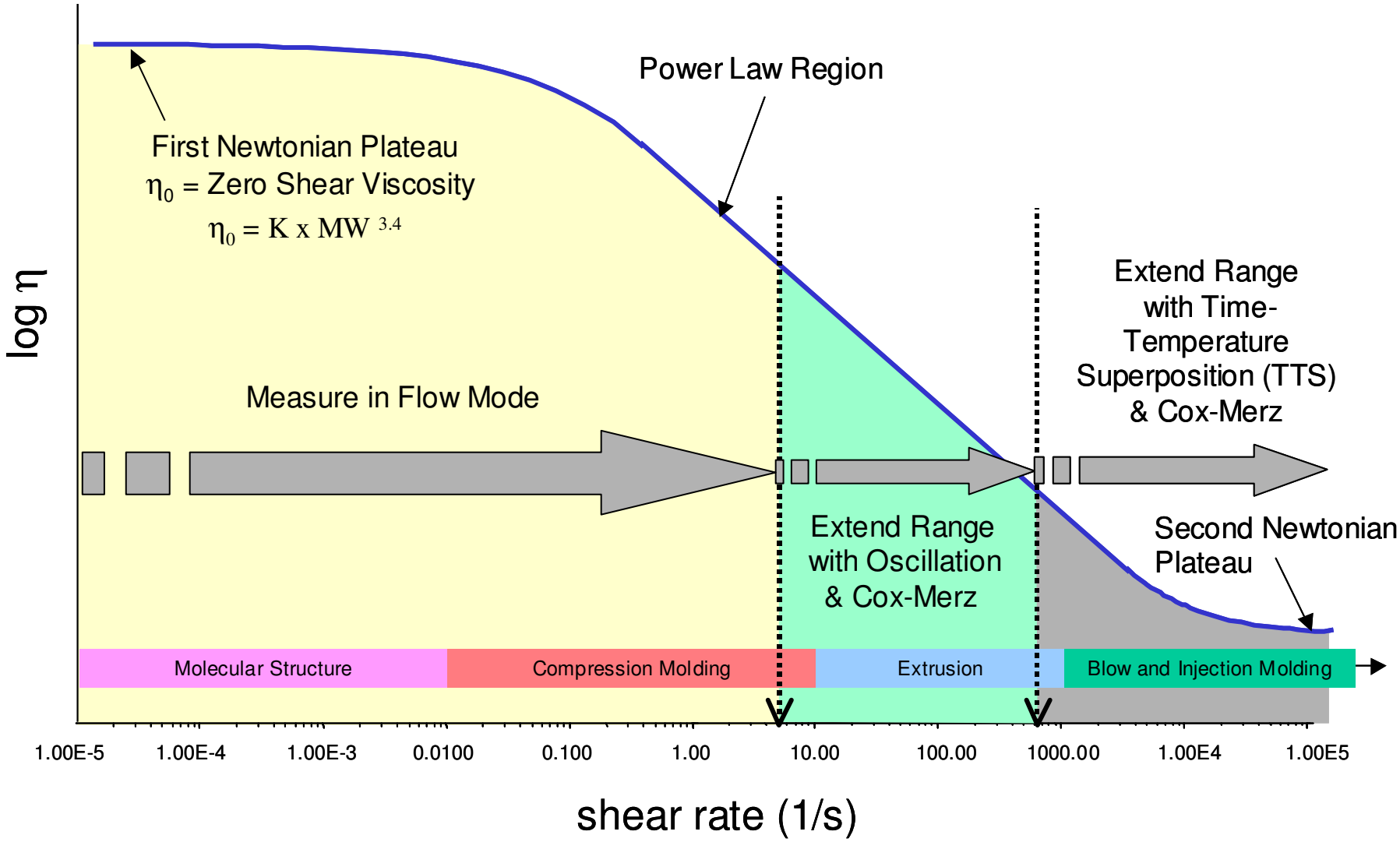
$\eta_0 = K \cdot Mw$



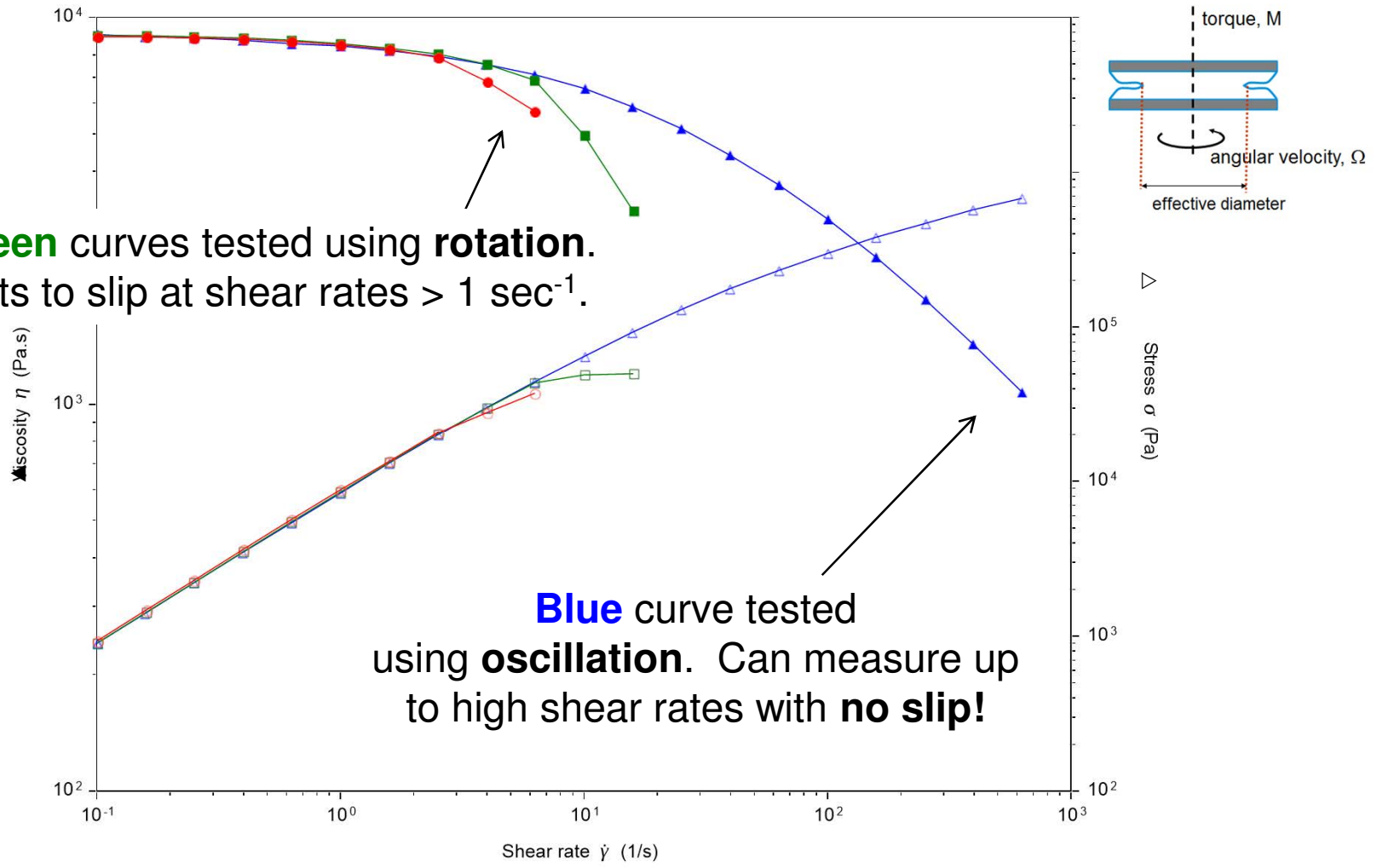
$\eta_0 = K \cdot Mw^{3.4}$

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

Idealized Flow Curve – Polymer Melts



Viscosity Measurements of LDPE at 190°C



Red and **Green** curves tested using **rotation**.
Sample starts to slip at shear rates > 1 sec^{-1}.

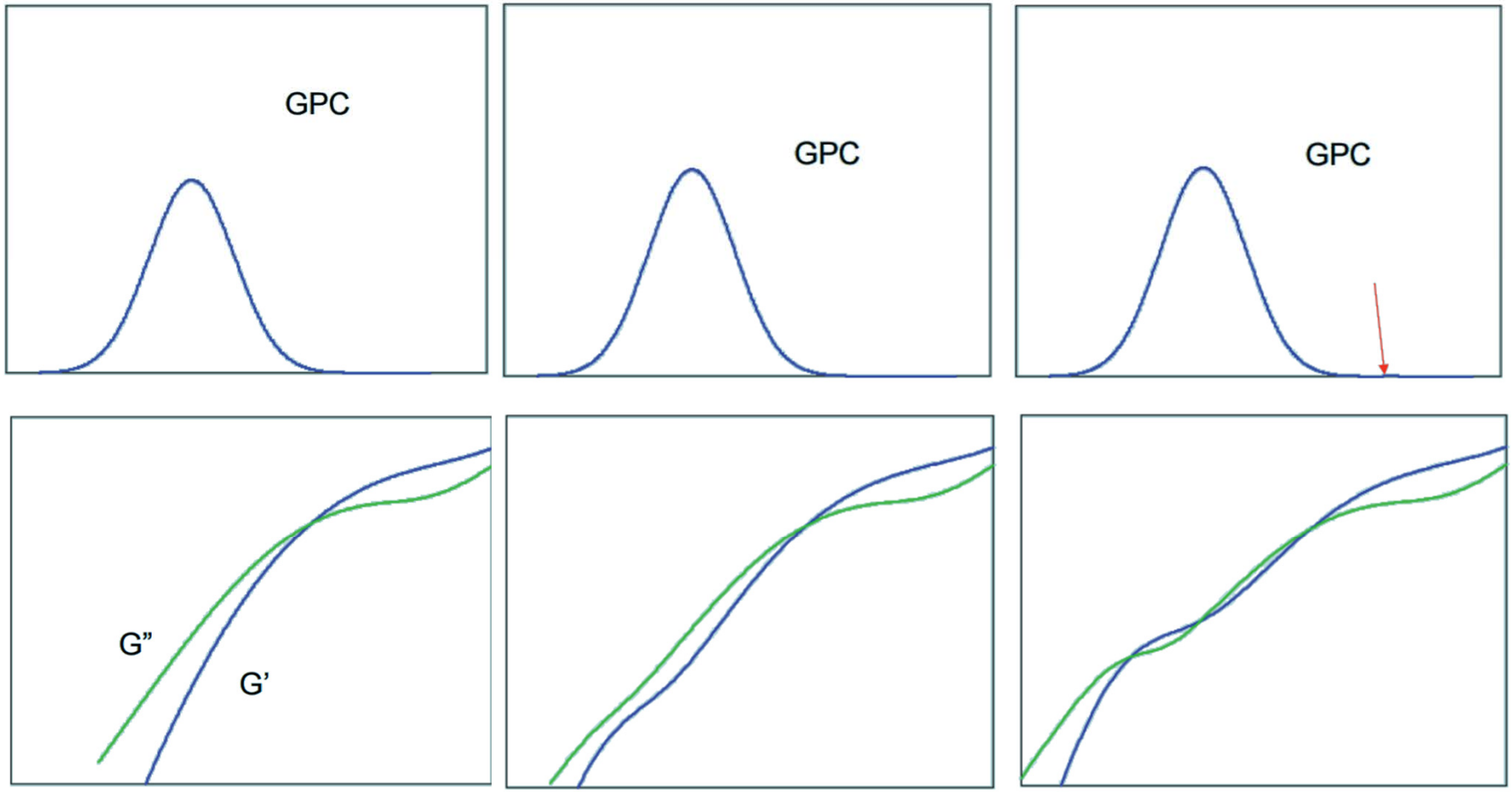
Blue curve tested using **oscillation**. Can measure up to high shear rates with **no slip!**

High MW Contributions

400,000 g/mol PS

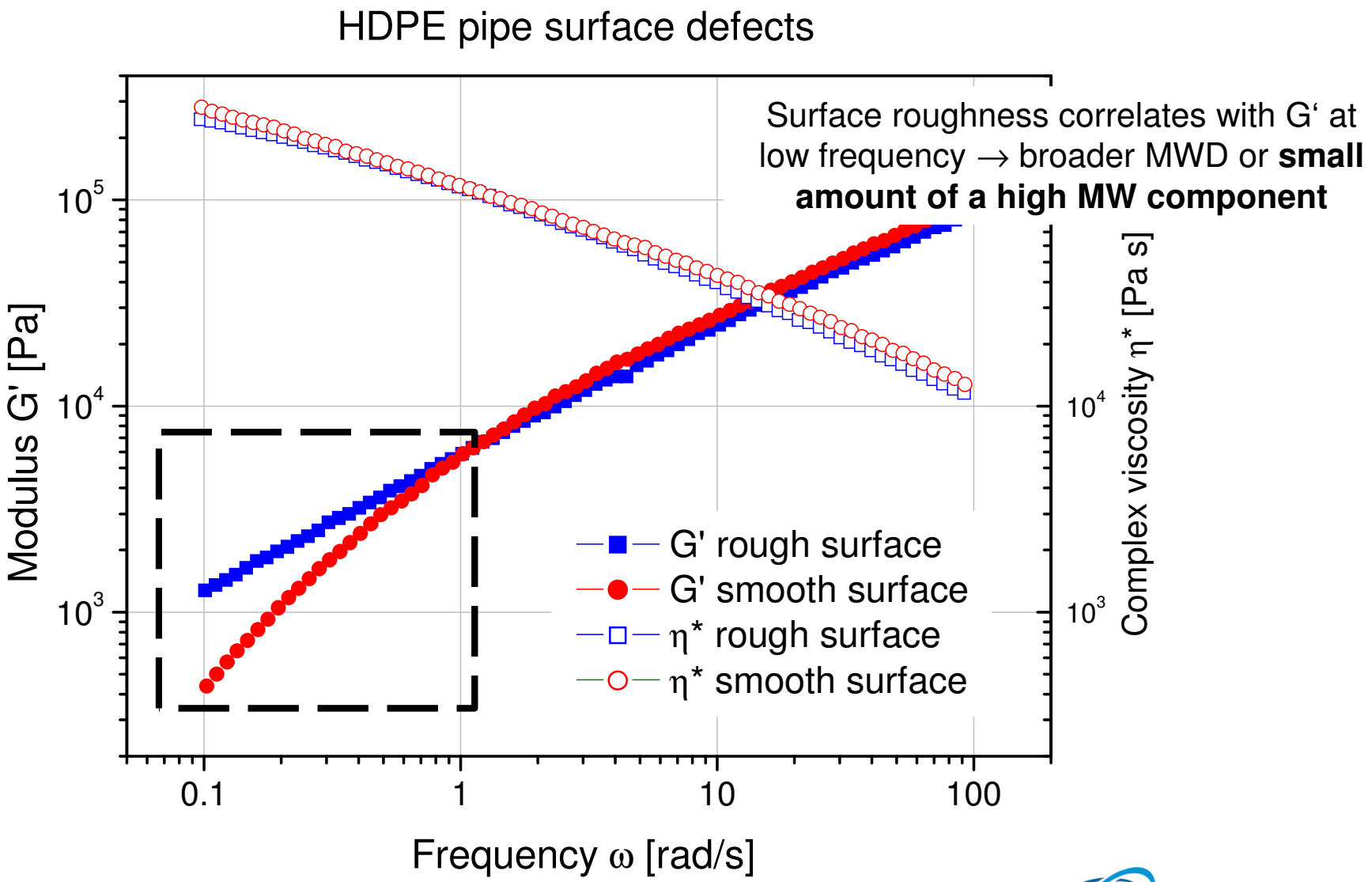
400,000 g/mol PS
+ 1% 12,000,000 g/mol

400,000 g/mol PS
+ 4% 12,000,000 g/mol



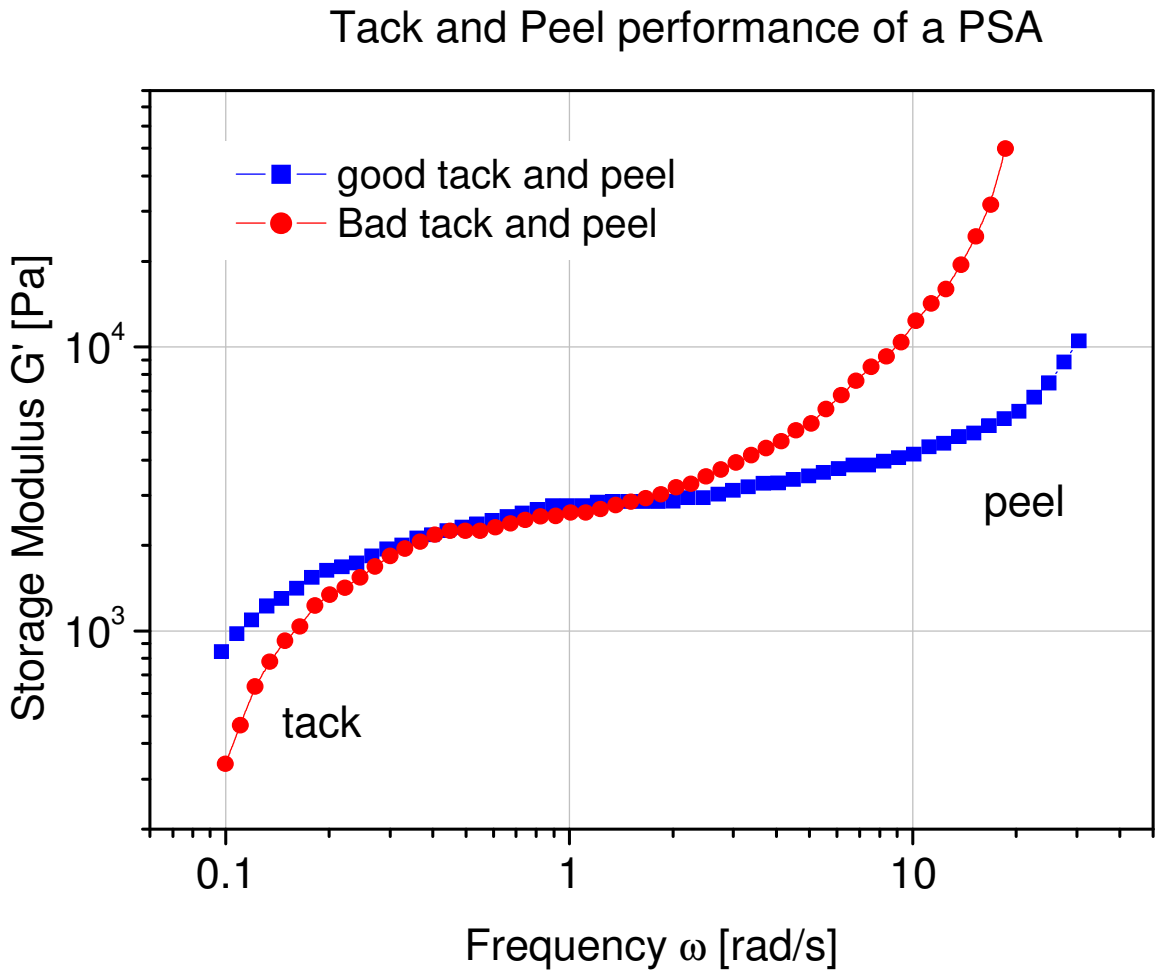
Macosko, TA Instruments Users' Meeting, 2015

Example: Surface Defects during Pipe Extrusion



Tack and Peel of Adhesives

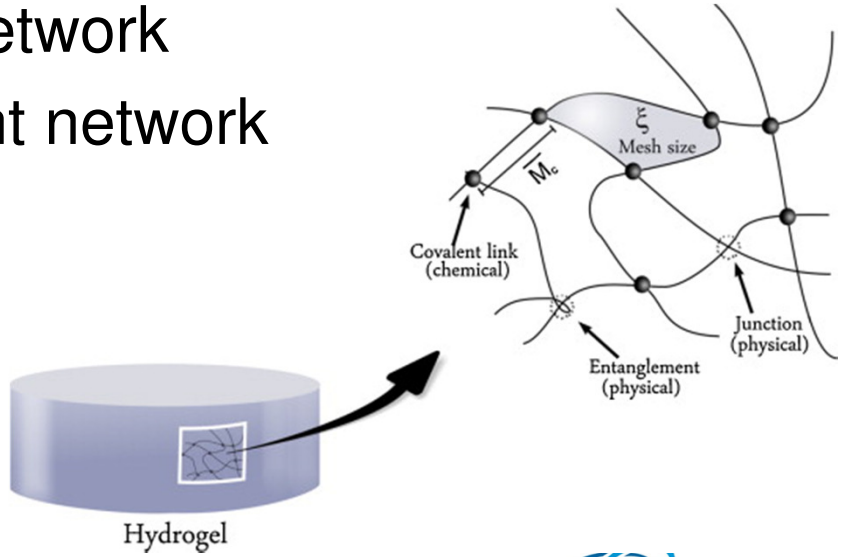
- Bond strength is obtained from peel (fast) and tack (slow) tests
- Tack and Peel are a function of viscoelastic properties at different frequencies



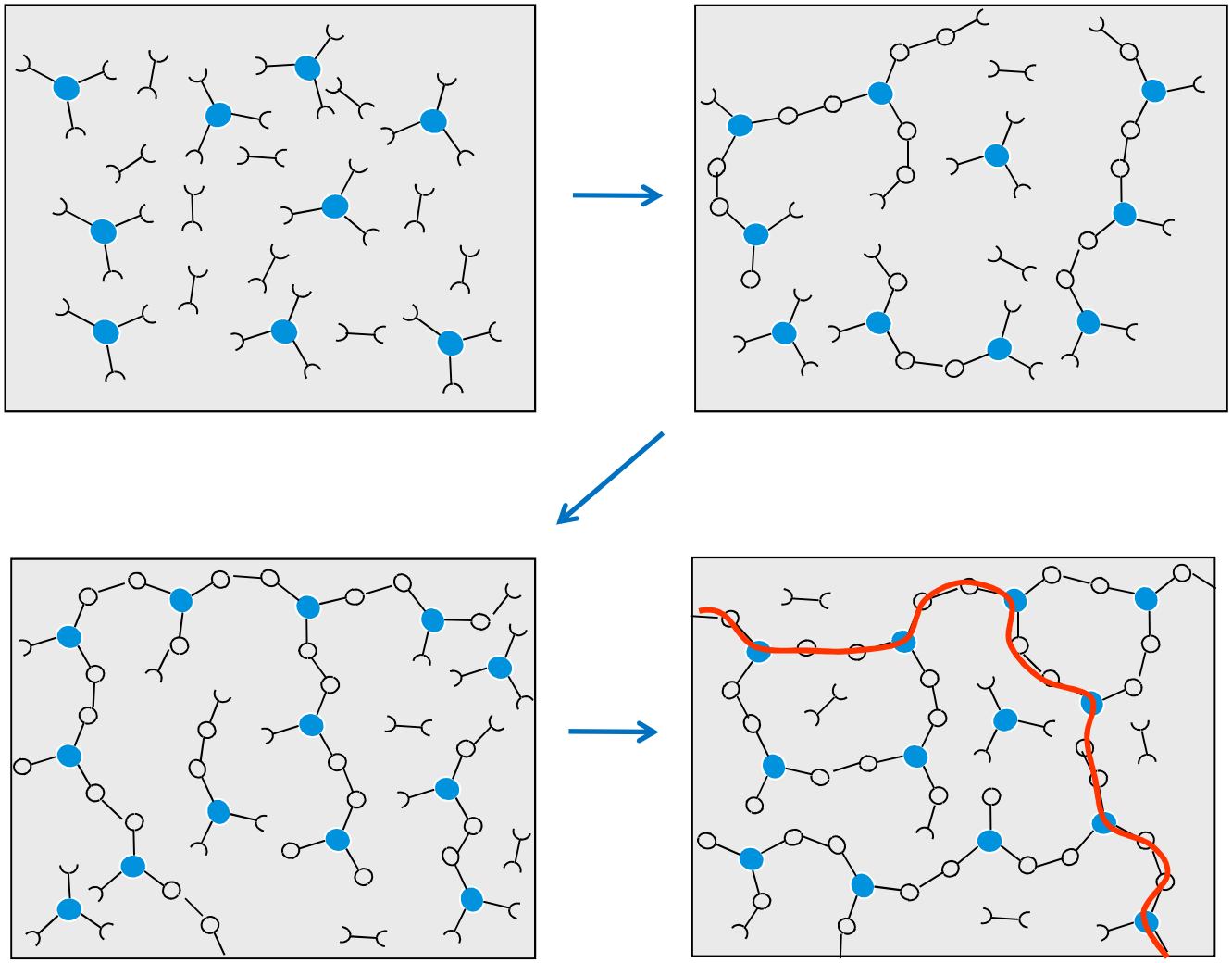
Thermosets and Gels

What is a Gel?

- A soft solid that contains a polymeric network and a substantial fraction of solvent
  - Latin: *gelatus* (frozen; immobile)
- "A substantially dilute crosslinked system that exhibits no flow in the steady state."
  - J.D. Ferry, Viscoelastic Properties of Polymers, 1980.
- Chemical Gel: covalent network
- Physical Gel: non-covalent network
- Hydrogel: network with significant water content

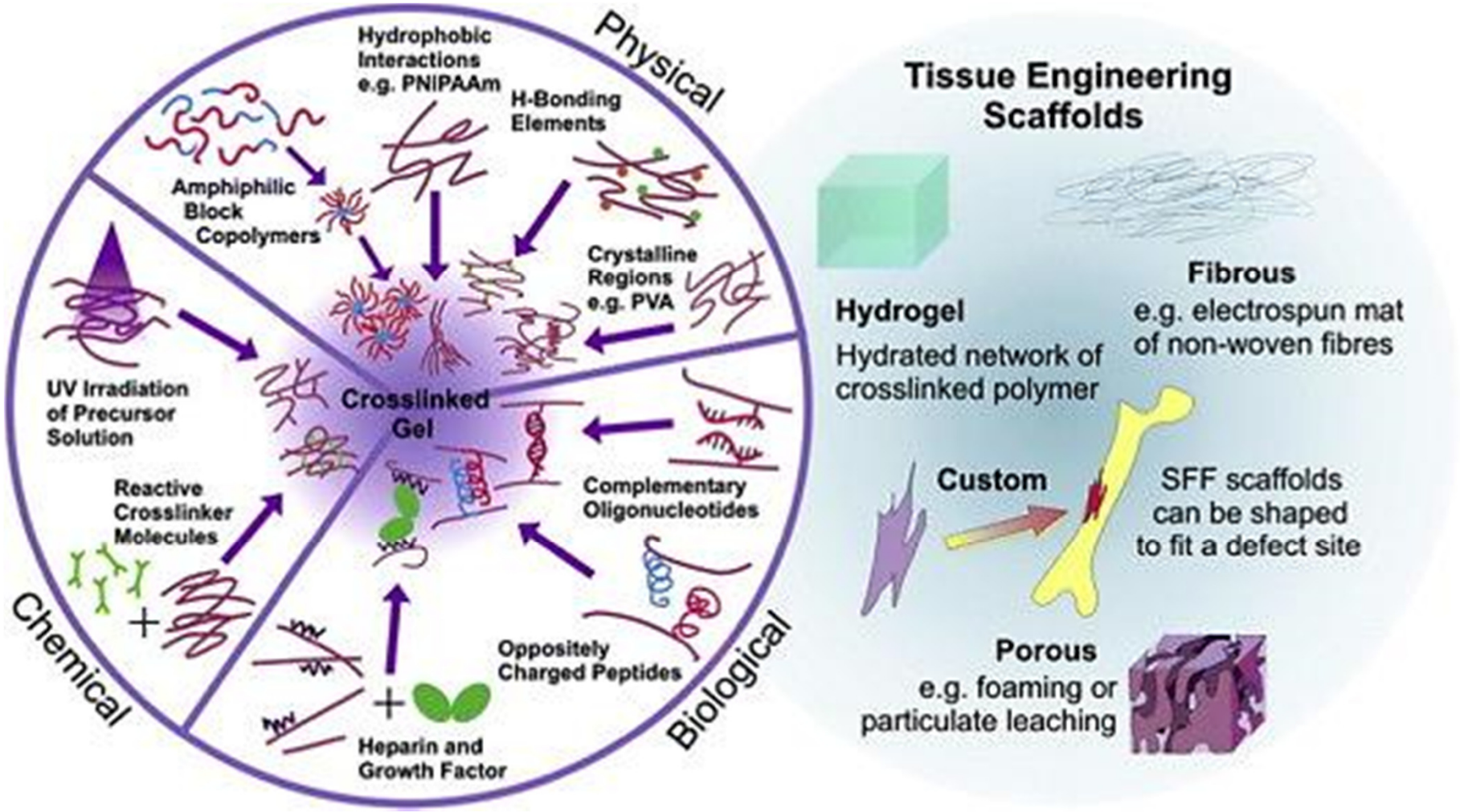


Gelation



Gel point

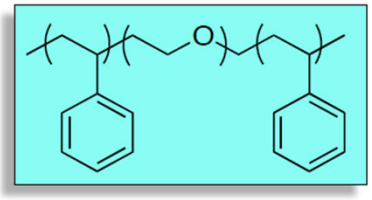
Physical, Chemical and Biological Hydrogels

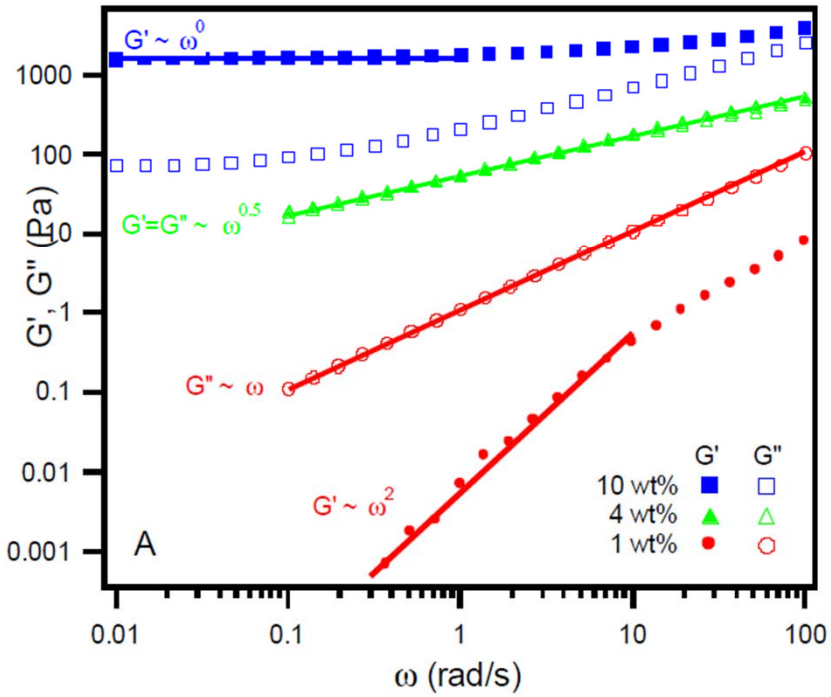


E.S. Place, J.H. George, C.K. Williams, M.M. Stevens, Chem. Soc. Rev. 2009, 38, 1139–1151

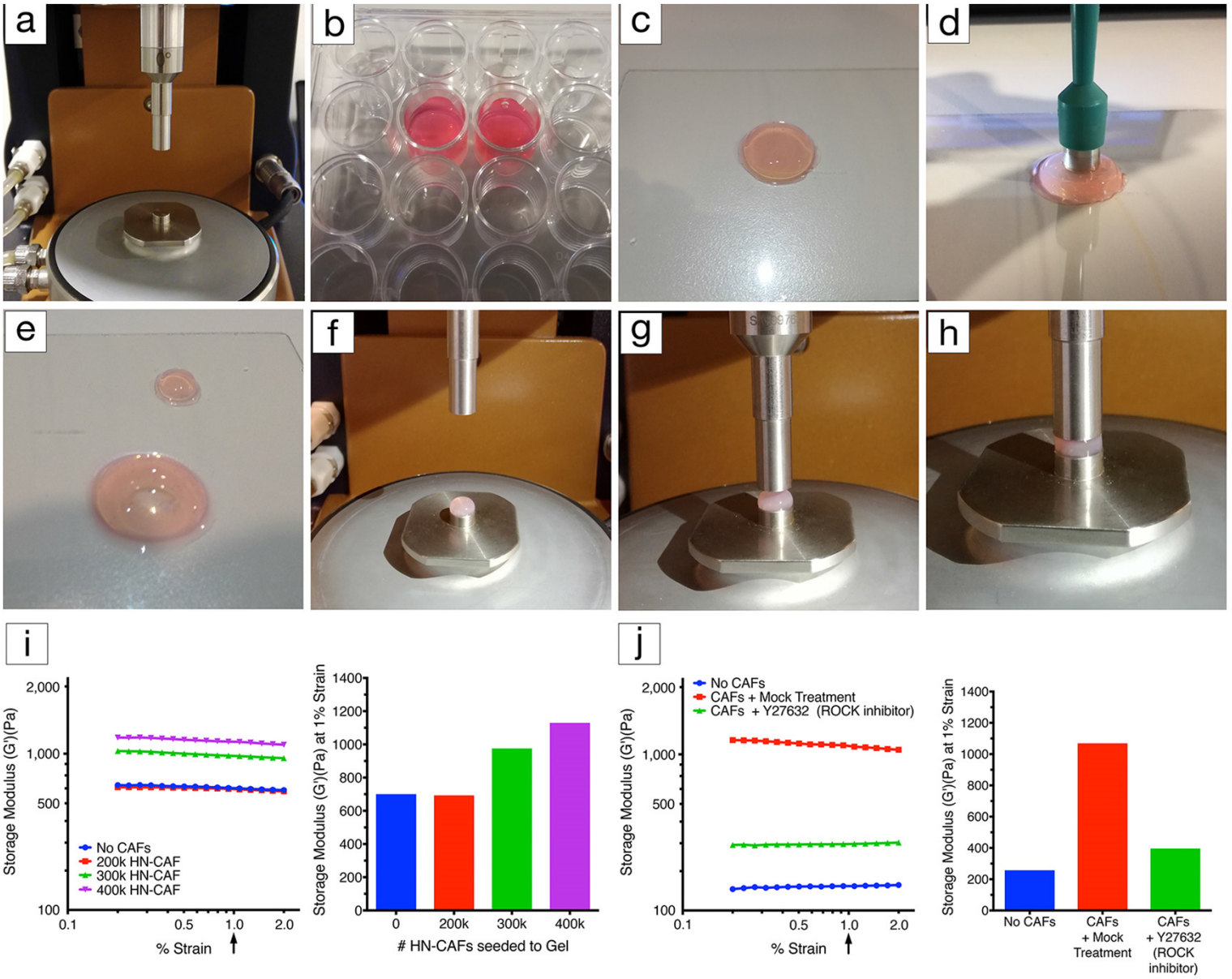
Viscoelastic Properties: "Is it a Gel?"

- PS-PEO-PS triblock copolymer in ionic liquid.
- **1 wt%:** Viscoelastic Liquid
  - Flow behavior seen at low frequency
- **4 wt%:** Gel Point
  - G' = G"
- **10 wt%:** Physical Gel
  - G' independent of frequency





Sample Preparation



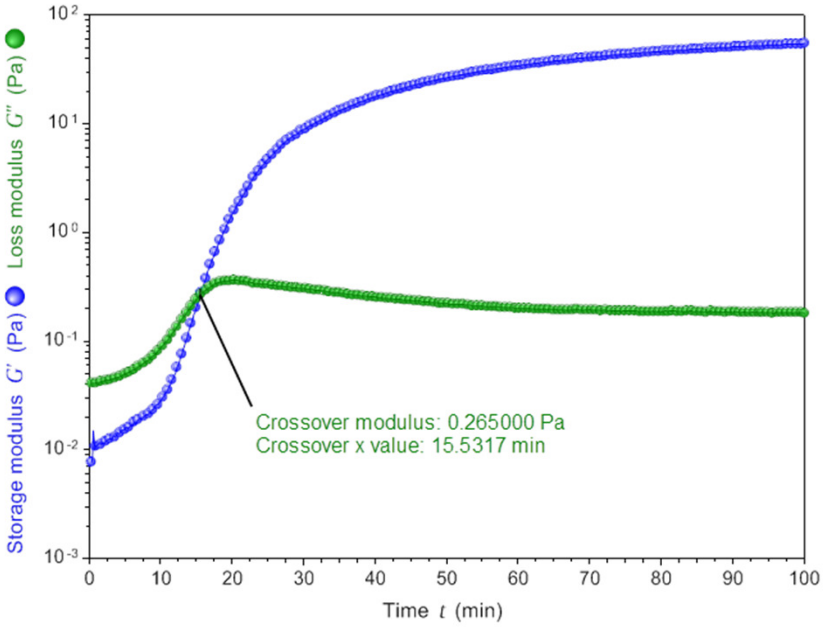
Cox, T. R. and Madsen, C. D. (2017).

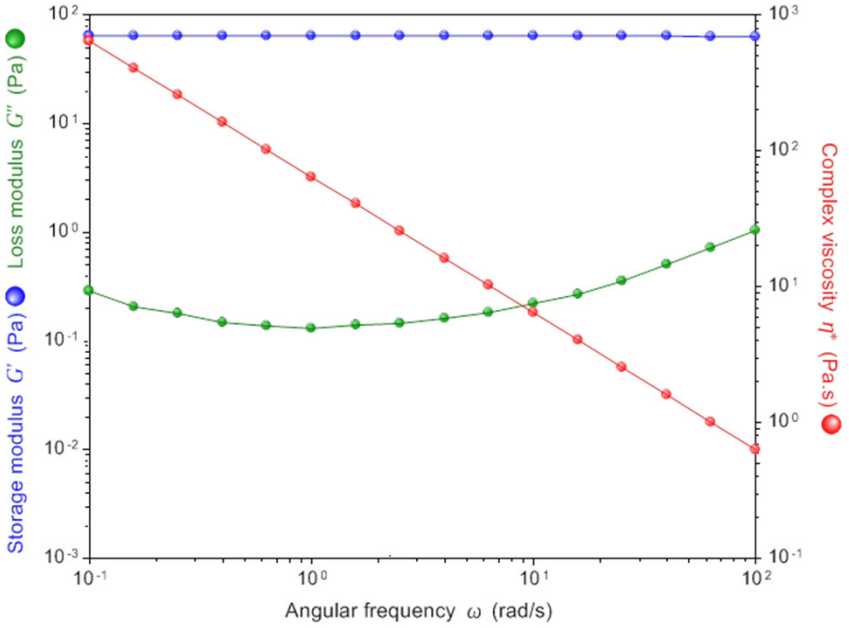
Relative Stiffness Measurements of Cell-embedded Hydrogels by Shear Rheology *in vitro*.

Bio-protocol 7(1): e2101.
DOI: 10.21769/BioProtoc.2101.

Isothermal Gelation: Hyaluronic Acid Gels

- Hyaluronic acid gels are used as lubricating agent during abdominal surgeries to prevent adhesion and also for join lubrication, wound healing etc.
- Rheology can monitor gelation and evaluate gel

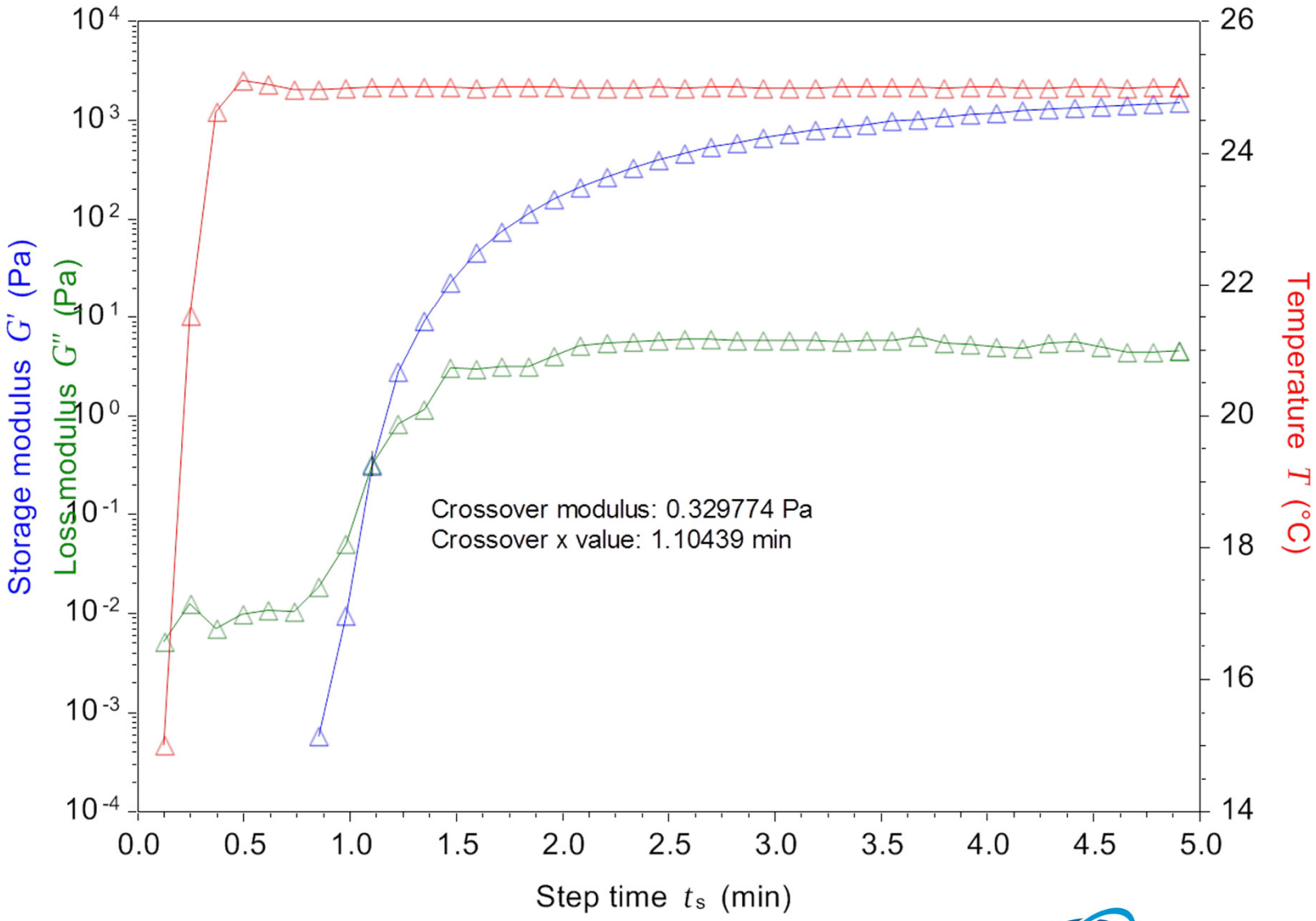




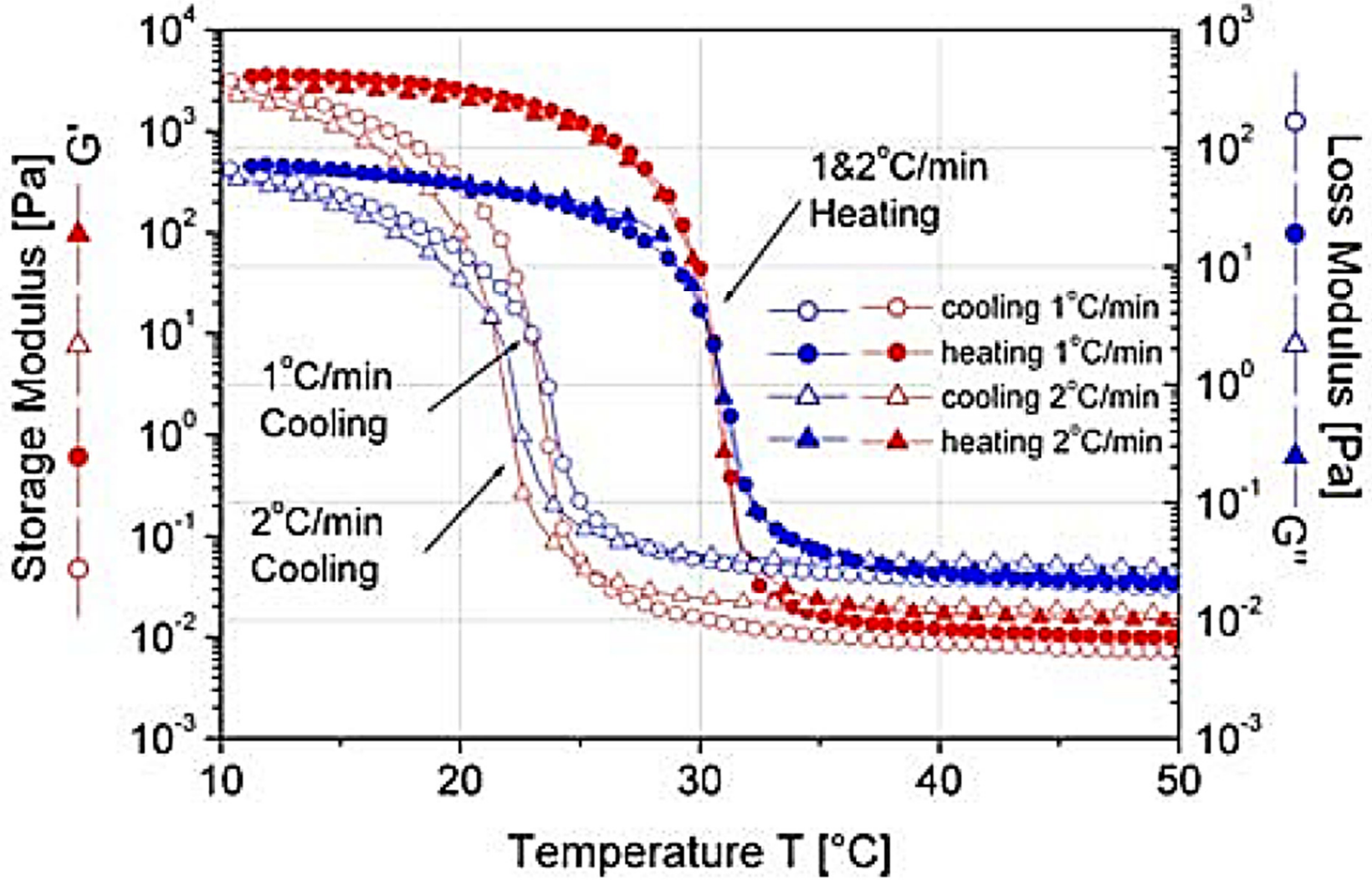
Rapid Gelation of 2-component system

- Experimental Challenge:
  - 2 components form a gel upon contact
  - Used to create small encapsulating beads and drug delivery devices.
- Upon mixing, gelation occurs in seconds and cannot be easily loaded.
- **Decreased temperature to delay gelation.**

Characterizing short Gel Time

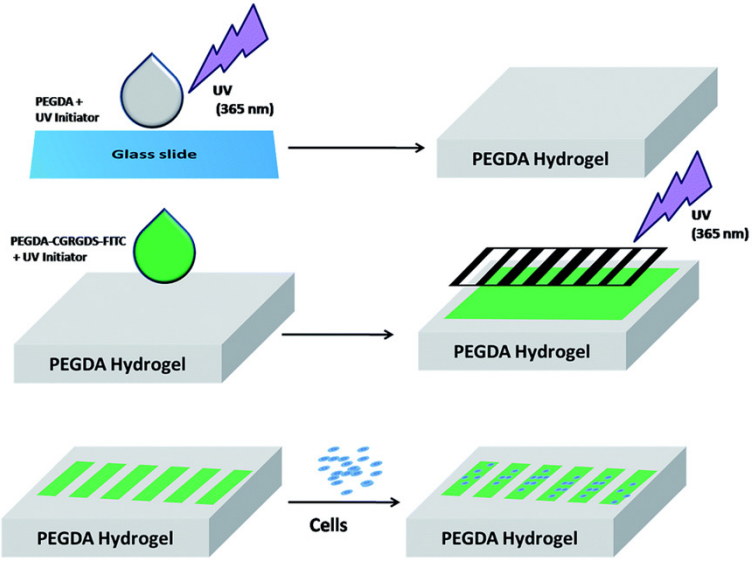


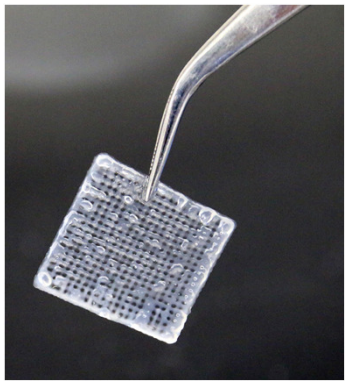
Thermo-Reversible Gelation: Gelatin



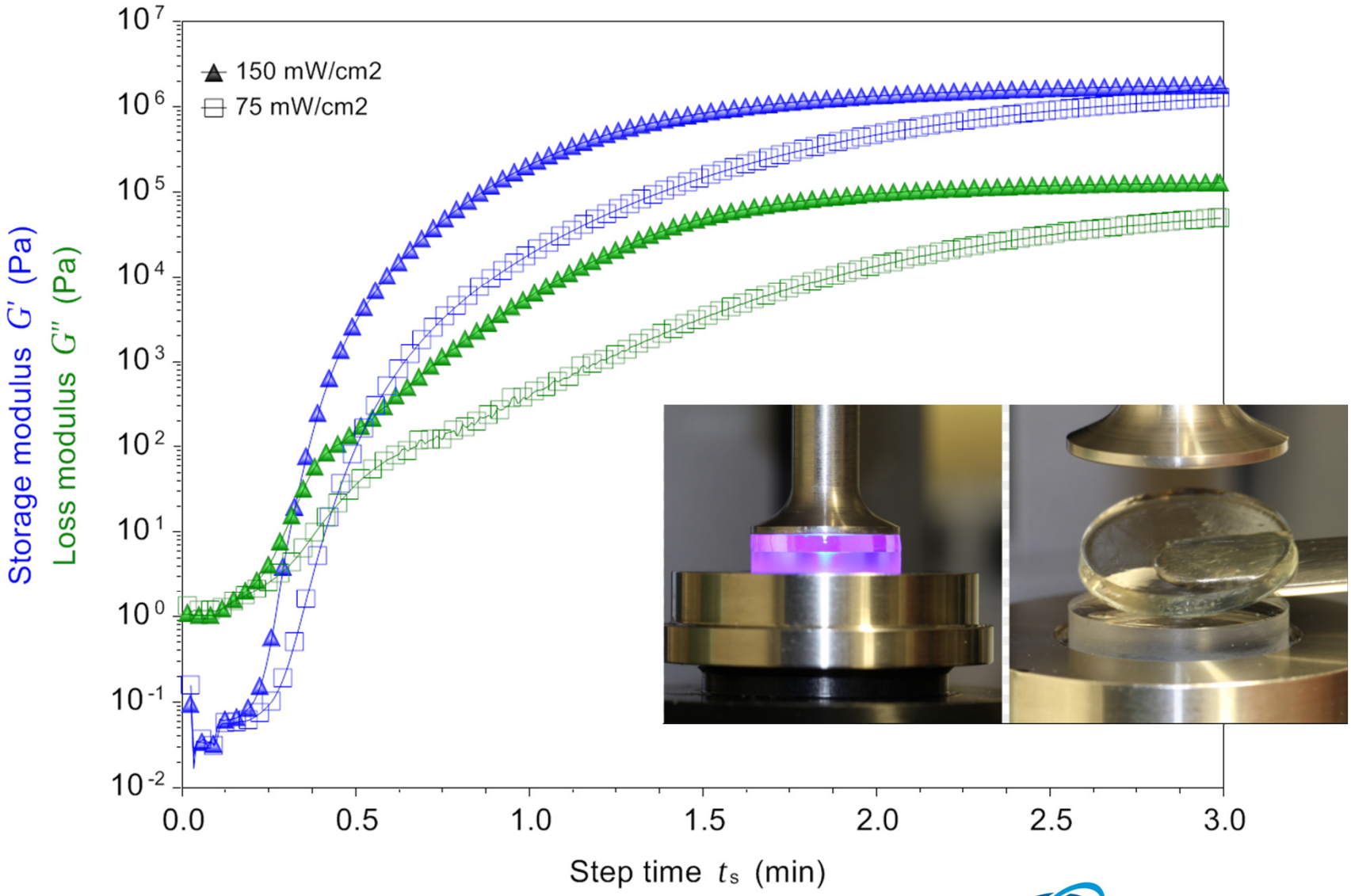
UV-Cured Hydrogels

- Widely used systems
  - 3D curing
  - Photolithography
  - On-demand gelation
- UV accessory attachment for Rheometer
  - Allows for in-situ gelation and optimum measurement of modulus.
  - Characterize gelation kinetics with controlled:
    - irradiance
    - wavelength
    - exposure time
    - temperature

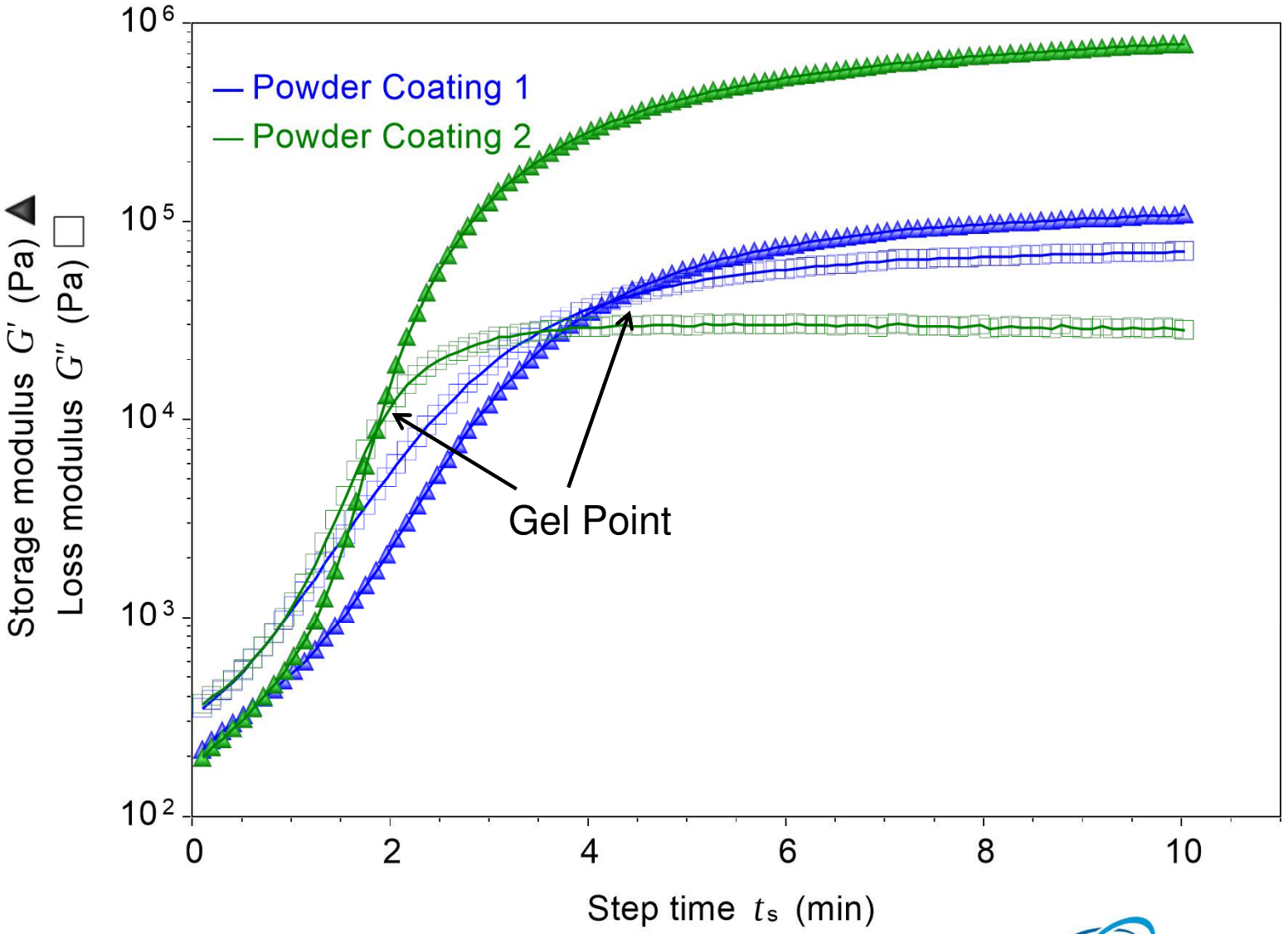




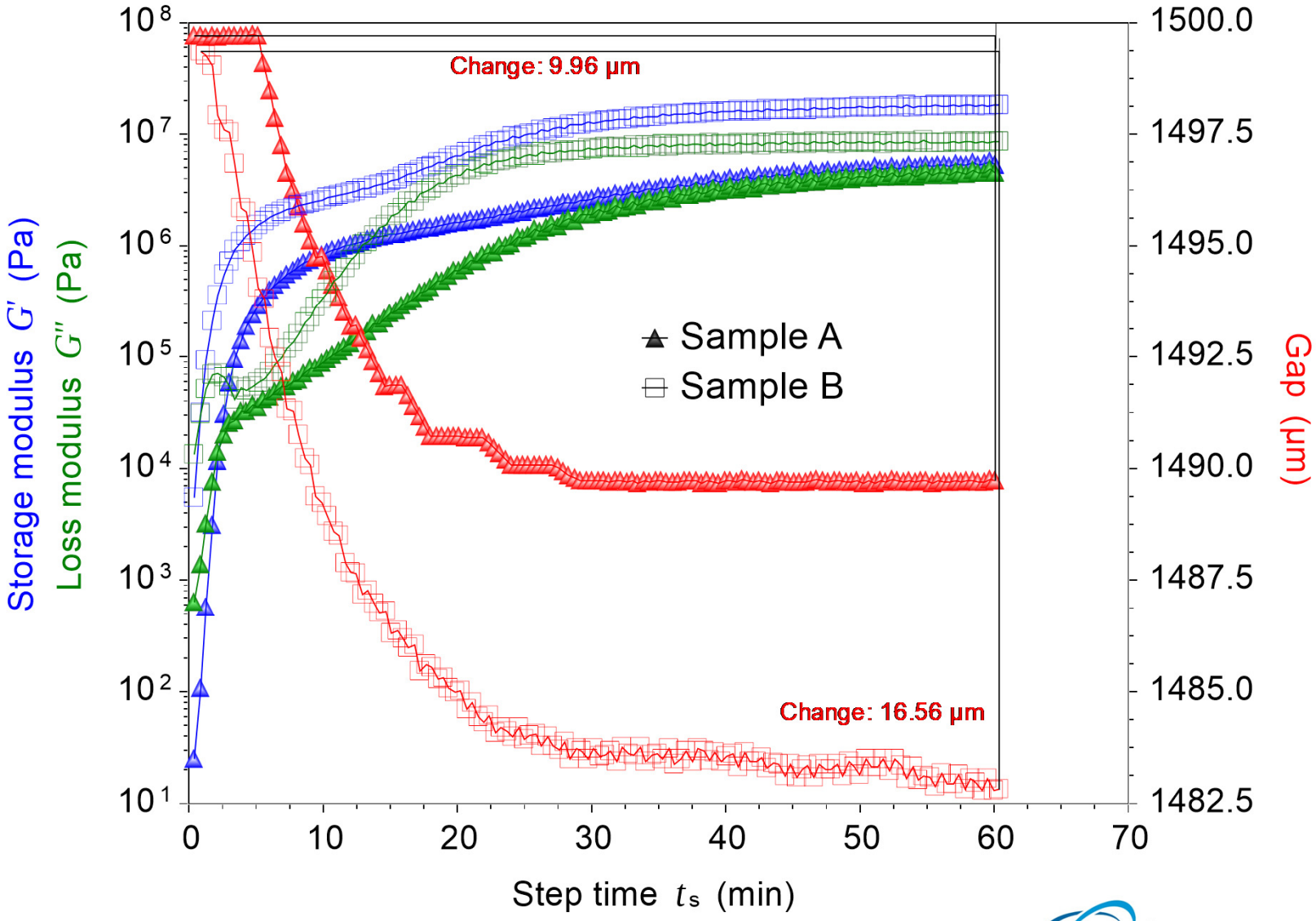
UV Gelation, 365 nm LED



Powder Coating: Cure Test

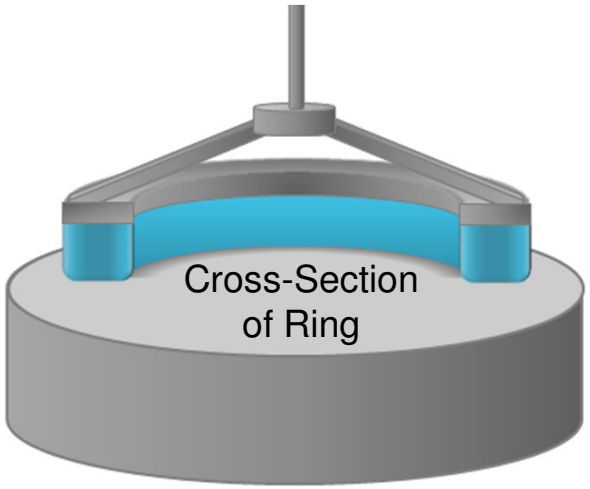


Cure Testing- Dimensional Change

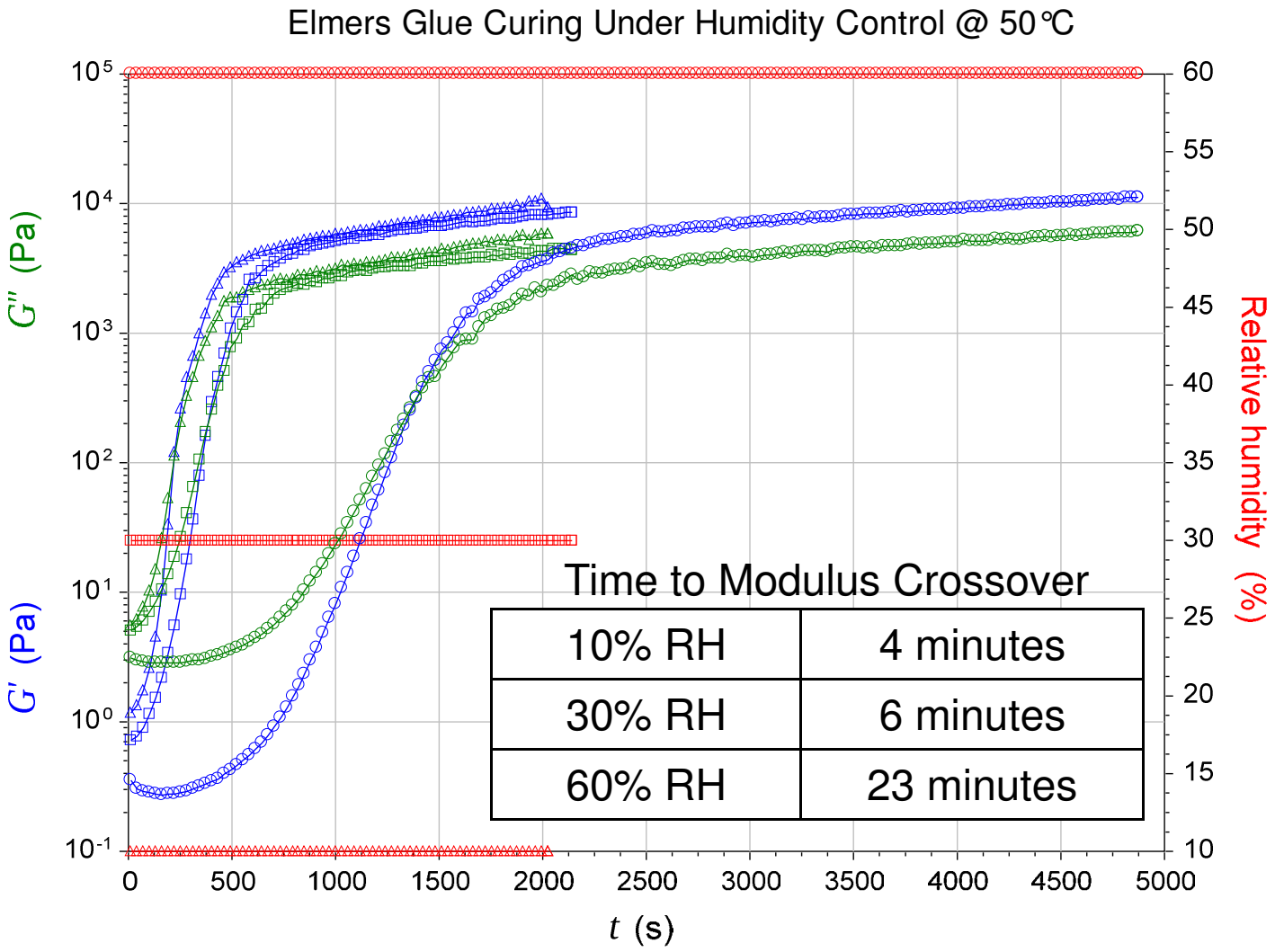


Change in Mechanical Properties During Drying

- Relative Humidity and Temperature Controlled Chamber
- **Quantitative** measurement of modulus during drying of the bulk material.
- Characterize time of drying
  - Time needed to “set” (Crossover point)
- Determine conditions needed to achieve drying
- Test Method: constant temperature and humidity



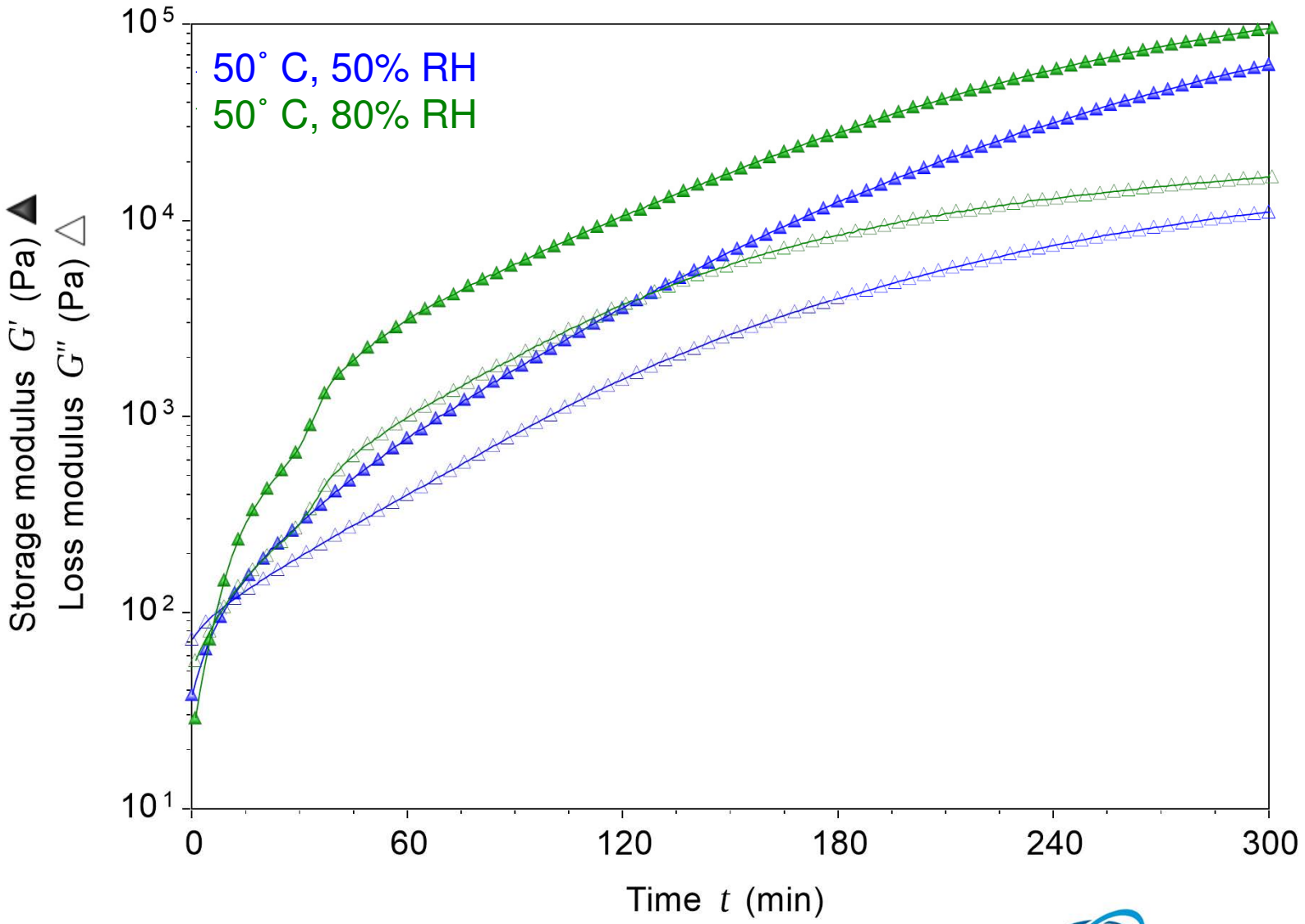
Example: Glue Drying under Different Humidity



Time to Modulus Crossover

10% RH	4 minutes
30% RH	6 minutes
60% RH	23 minutes

Moisture-Cured System- Humidity Control



Dynamic Mechanical Analyzers

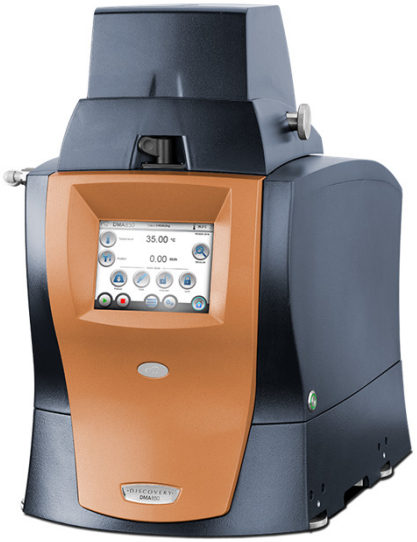
Is DMA Thermal Analysis or Rheology?

- ***Thermal Analysis***
  - measurement as a *function of temperature or time*.
- ***Rheology***
  - the science of *stress* and *deformation* of matter.
- ***DMA*** mechanically *deforms a sample* and measures the sample response. The response to the deformation can be monitored as a *function of temperature or time.*

DMAs from TA Instruments

RSA G2

Discovery DMA850

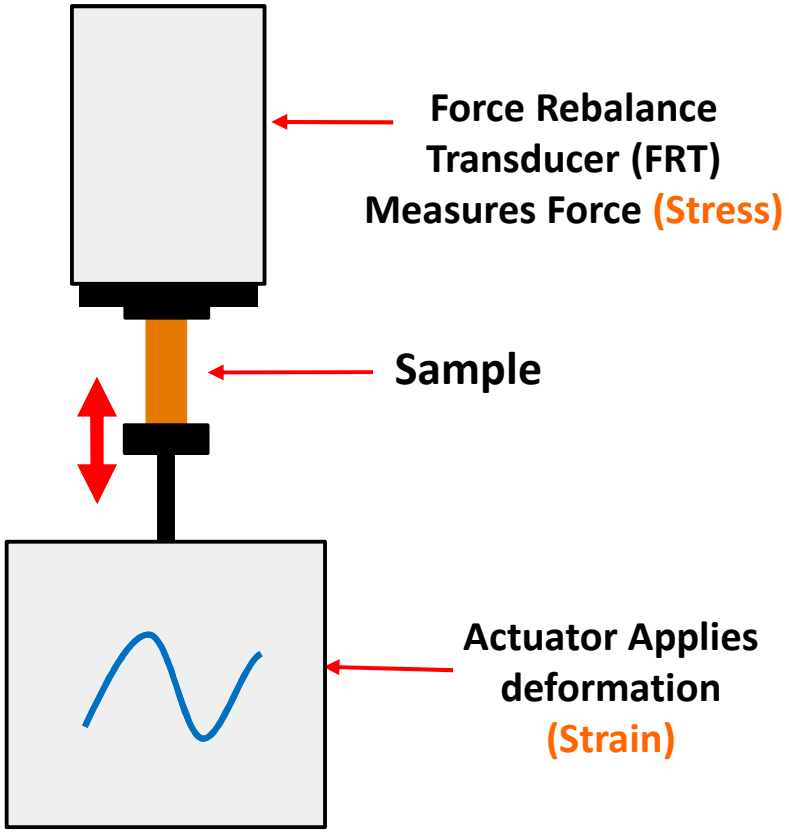


Q800

DMAs from TA Instruments

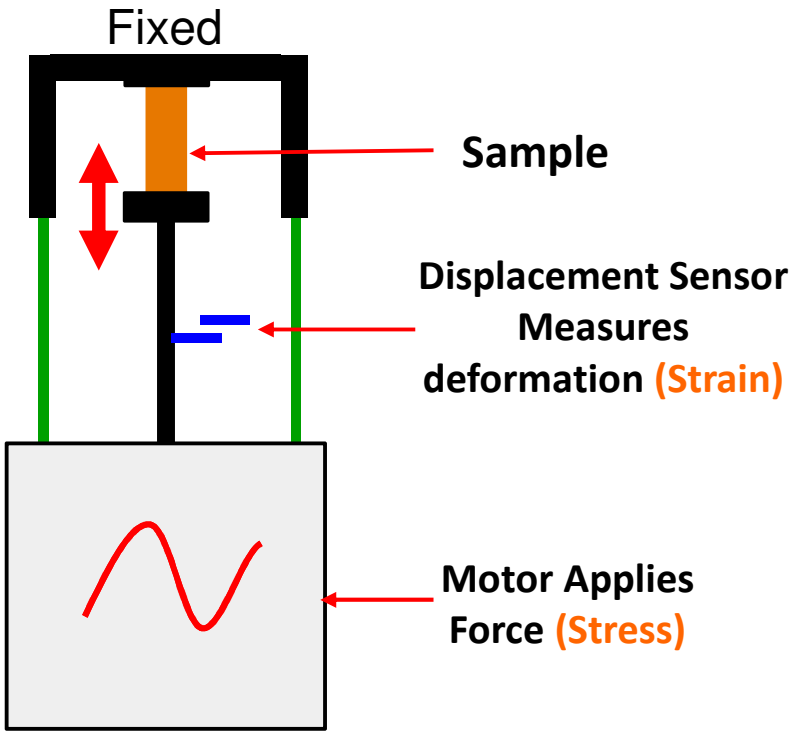
RSA G2

Separate Motor & Transducer



DMA850 and Q800

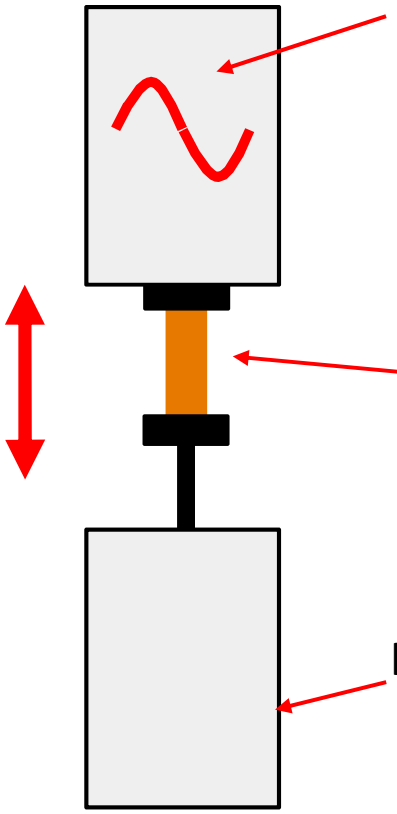
Combined Motor & Transducer



DMA Mode on DHR and ARES-G2

ARES G2 and DHR DMA Mode

Strain control & dynamic test only



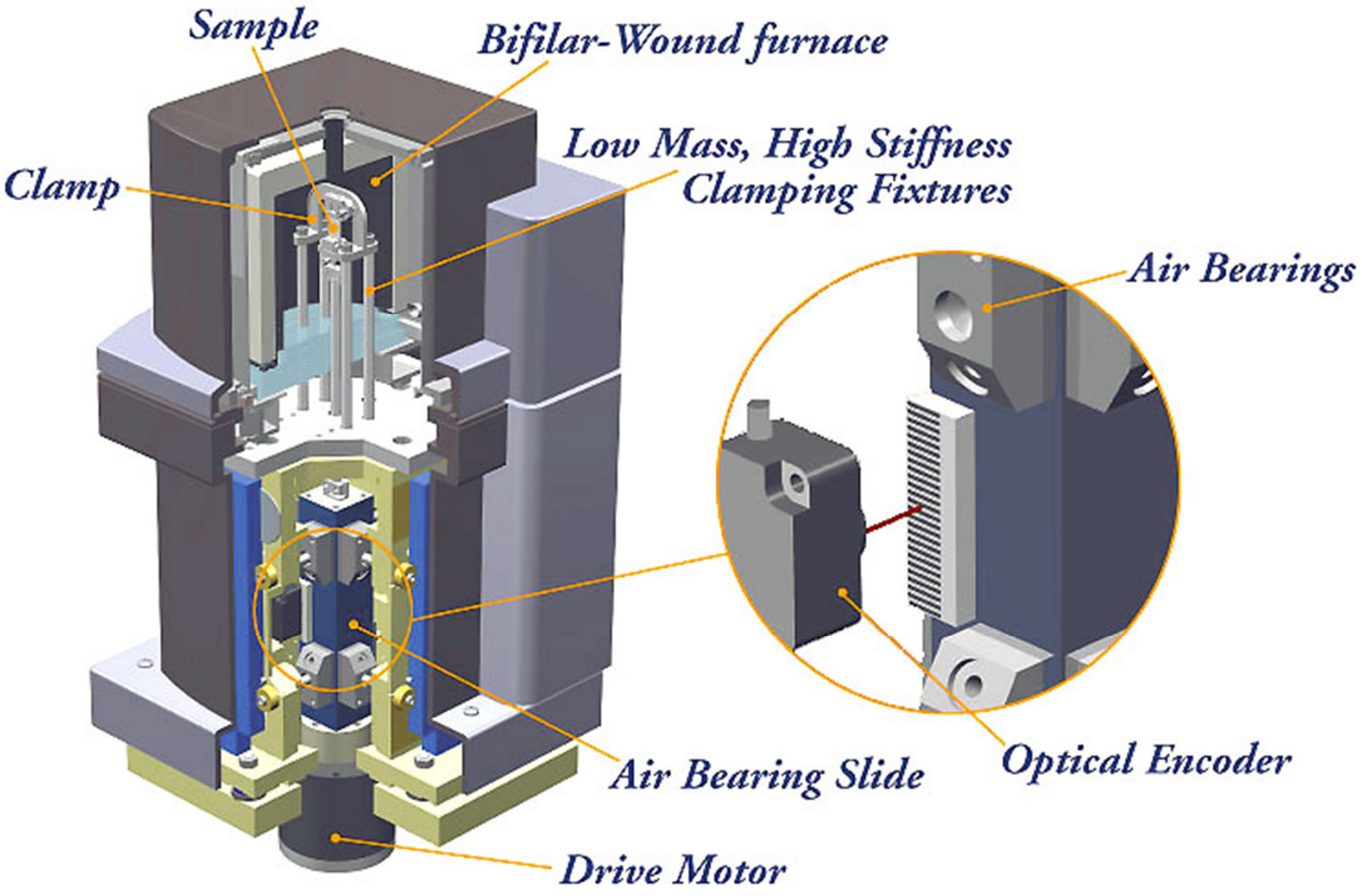
Force Rebalance Transducer (FRT)
(Measures Stress)

Servo control on Null position
(Strain)

Sample

For the ARES-G2, the bottom Actuator remains locked during DMA function

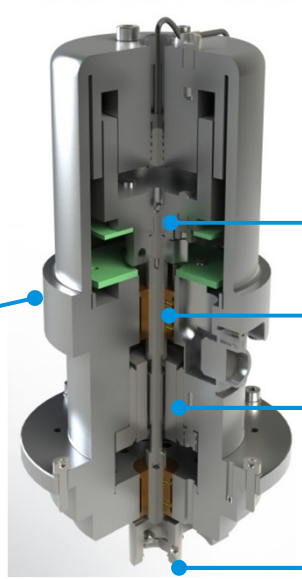
DMA Q800: Schematic



RSA G2 Schematic: Dual Head Design

Transducer

Motor

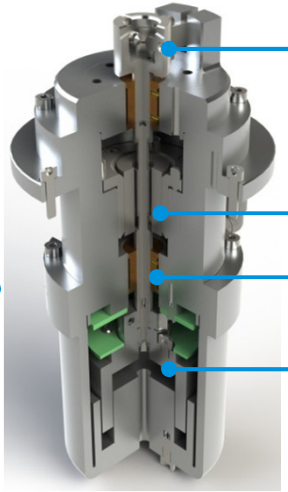


Transducer Motor

Air Bearing

LVDT

Upper Geometry Mount



Lower Geometry Mount

LVDT

Air Bearing

Drive Motor

DMA Viscoelastic Parameters

The Modulus: Measure of materials overall resistance to deformation.

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

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

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

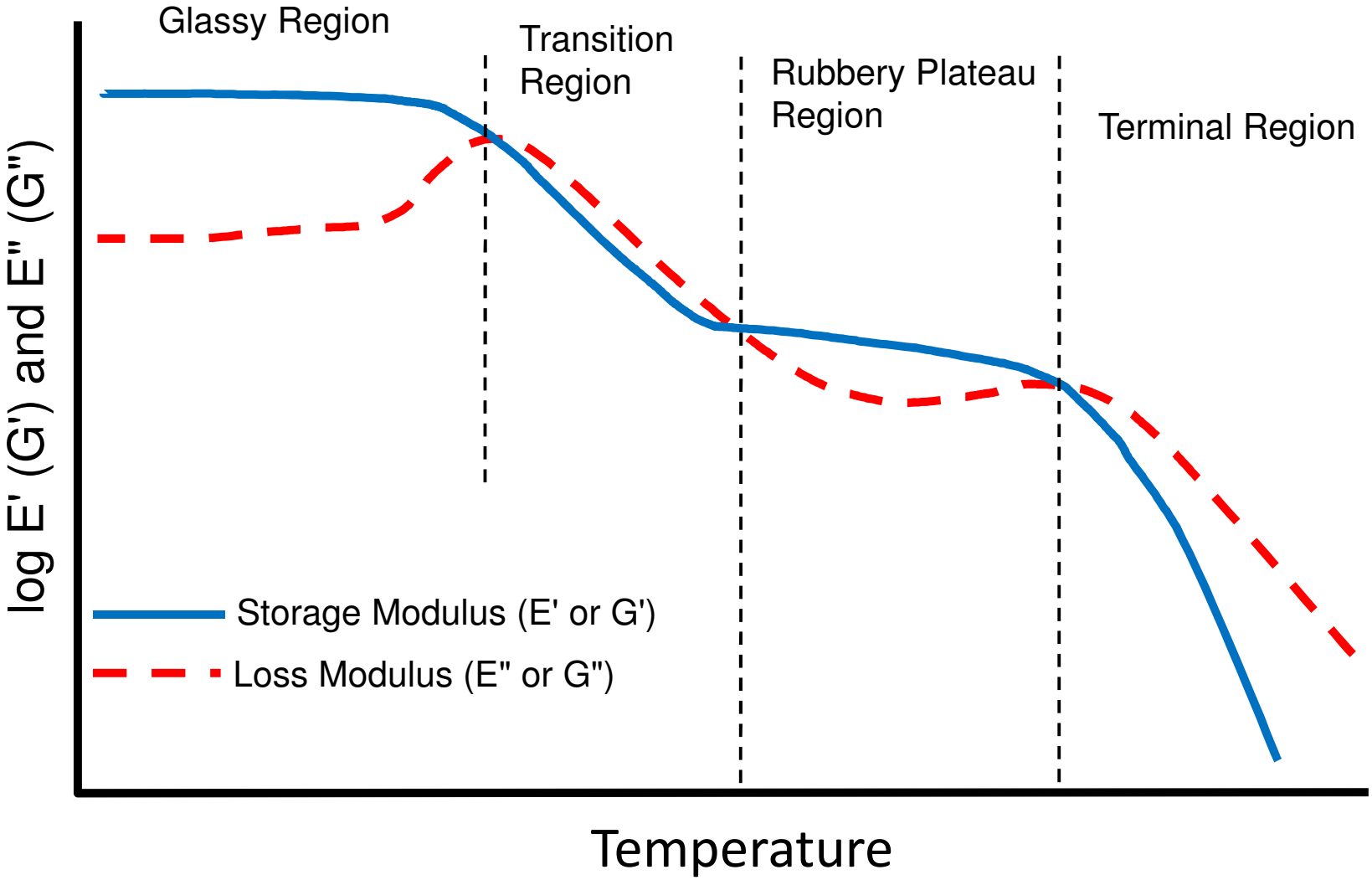
The Viscous (loss) Modulus:
The ability of the material to dissipate energy. Energy lost as heat.

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

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

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

Dynamic Temperature Ramp



Dynamic Mechanical Analysis of Glass Transition

- DMA more sensitive to Tg than DSC, directly measures changes in mechanical and viscoelastic properties as a function of temperature.
- Materials whose glass transitions cannot be resolved by DSC can often be measured easily in DMA
  - Semi-crystalline materials with low amorphous content
  - Composites in which the polymer weight fraction is small
  - Glass Transitions that occur over a wide range, or overlap with other thermal events
- Glass Transition measurement by DMA particularly relevant to characterizing materials for their end-use properties

Glass Transition E' Onset, E" Peak, and Tan δ Peak

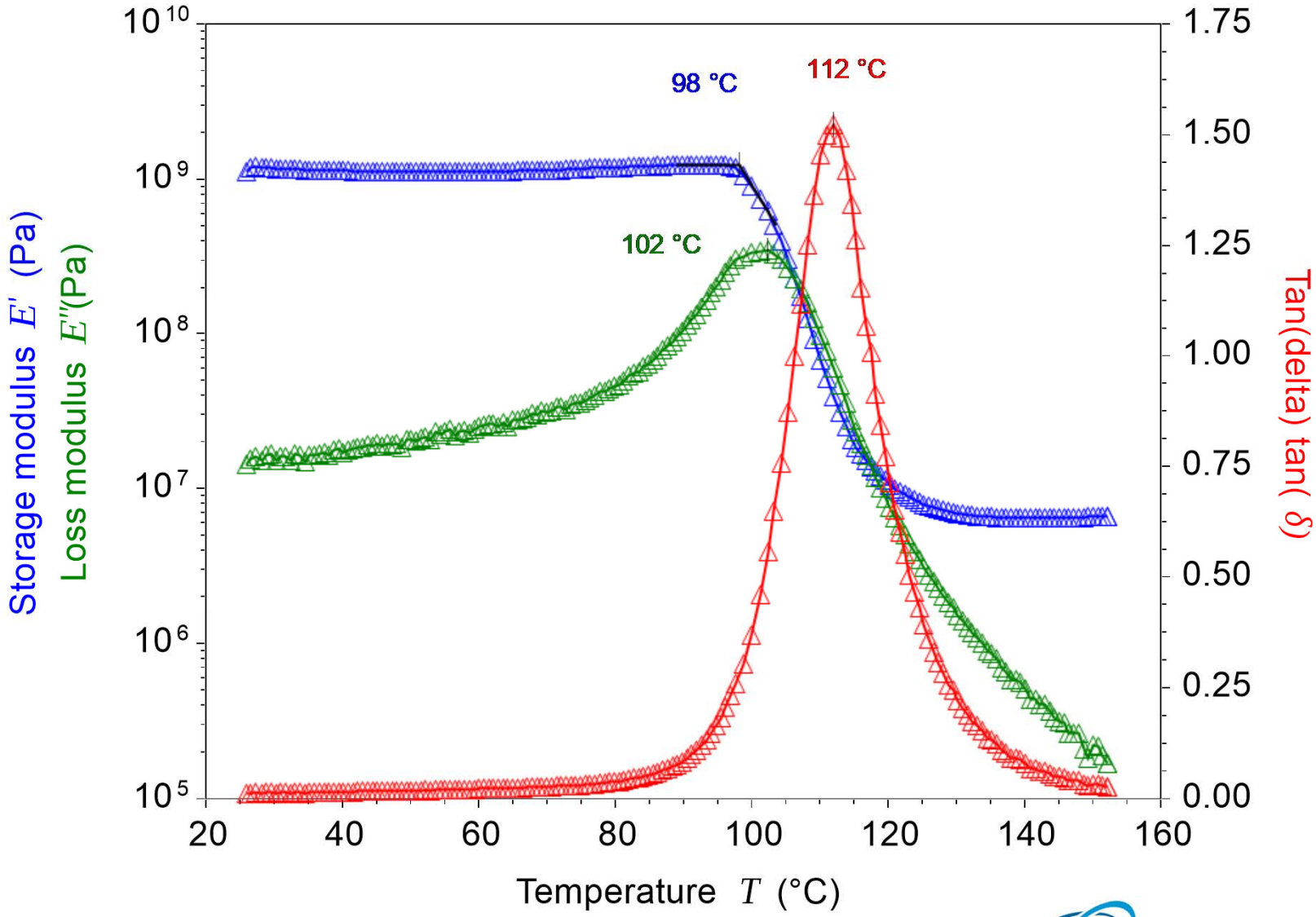
- **Storage Modulus E' Onset**:
  - Occurs at lowest temperature, relates to mechanical failure

- **Loss Modulus E" Peak**:
  - Occurs at middle temperature
  - Related to the physical property changes
  - Reflects molecular processes - the temperature at the onset of segmental motion

- **Tan Delta Peak:**
  - Occurs at highest temperature; Used historically in literature
  - Measure of the "leatherlike" midpoint between the glassy and rubbery states
  - Height and shape change systematically with amorphous content.

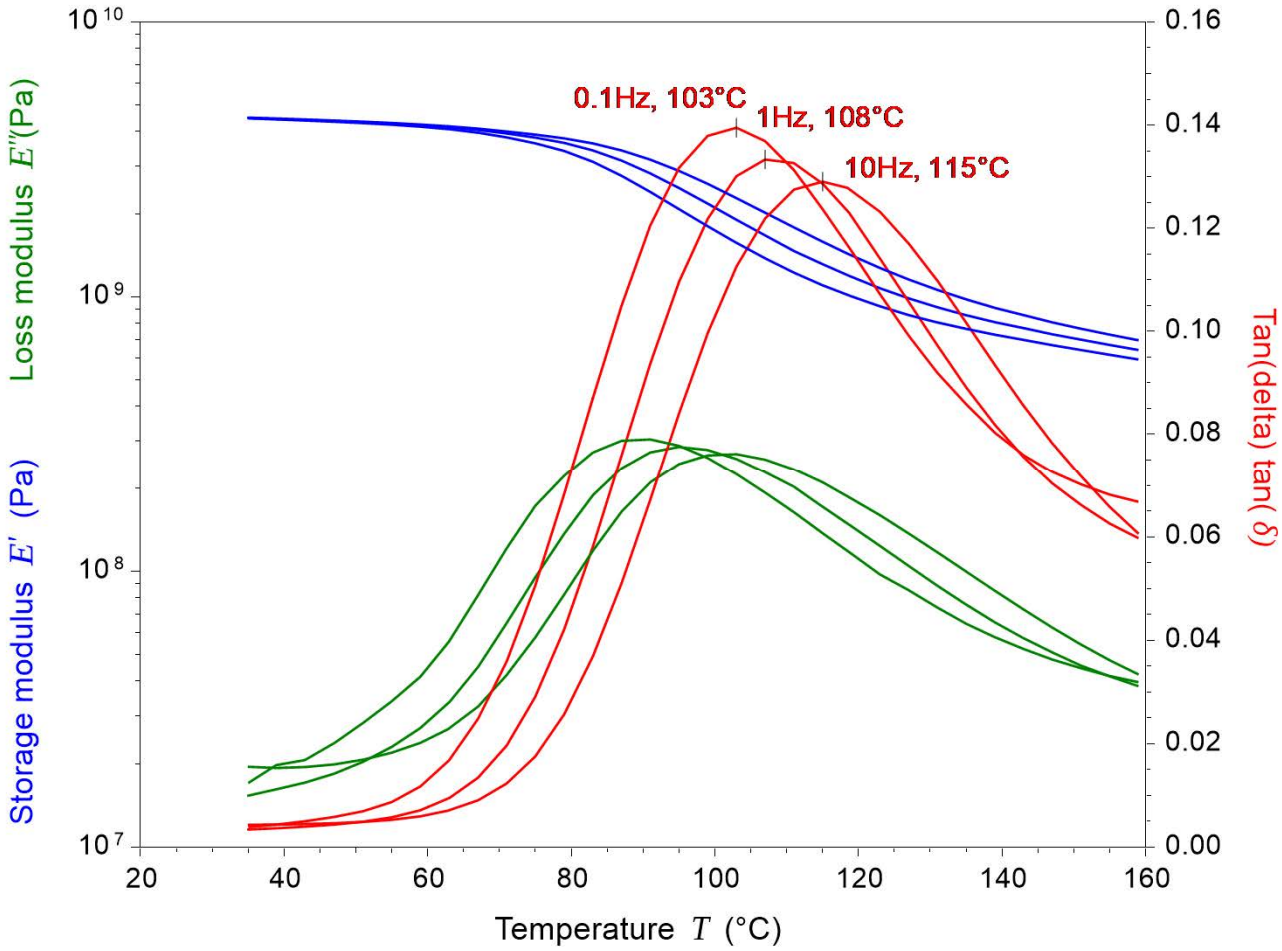
Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 980.

Temperature Ramp- Glass Transition

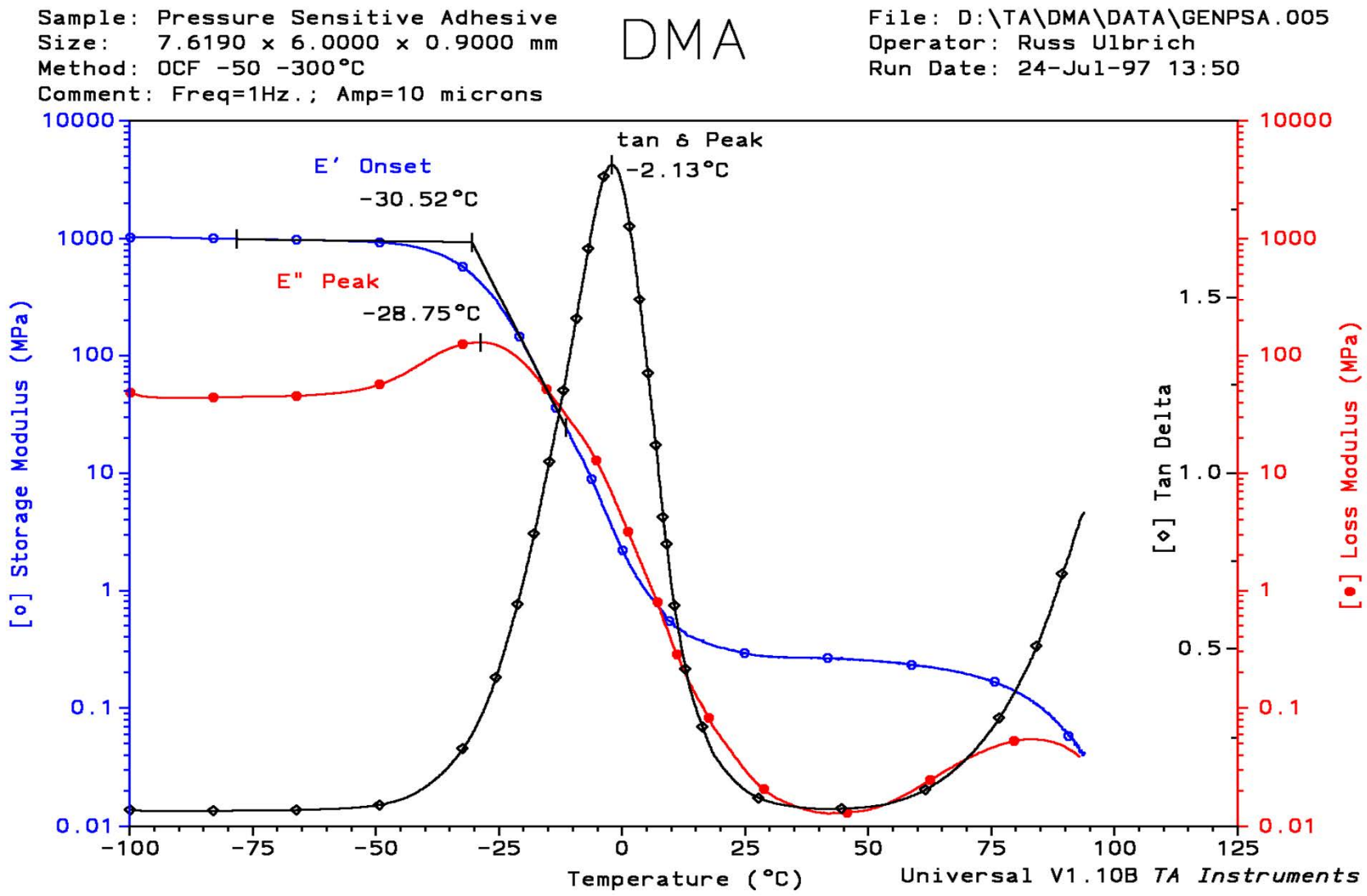


PET Film: Effect of Frequency on Tg

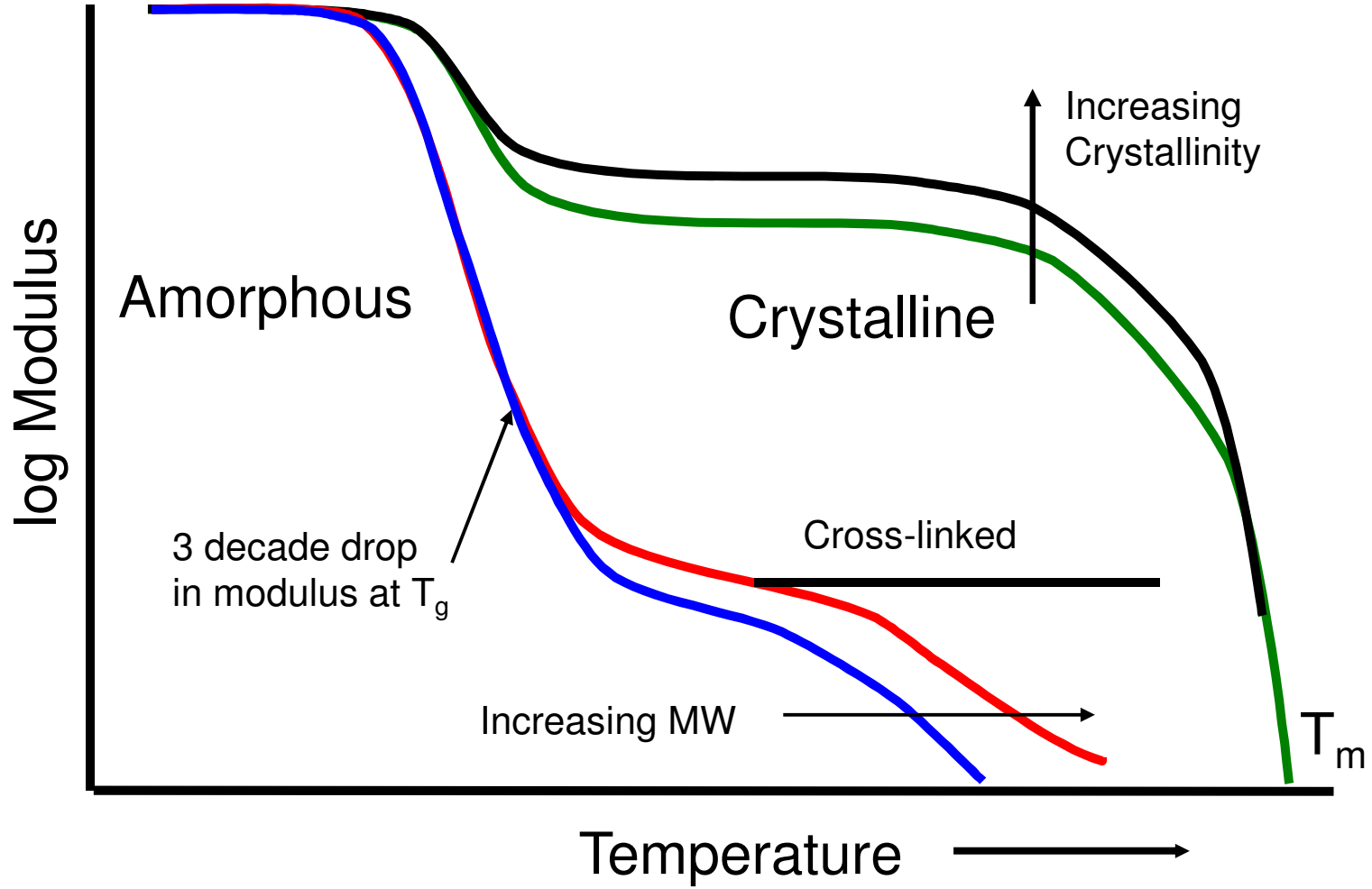
- PET film tested at 0.1 Hz, 1Hz and 10 Hz



Glass Transition is a Range, not a Temperature



Crystallinity, Molecular Weight, and Crosslinking



DMA Deformation Modes

Axial

Tension

- Thin Films
- Fibers

Compression

- Soft solids
- Foams
- Gels

Bending

- Thermosets
- Composites

Rotational

Parallel Plate

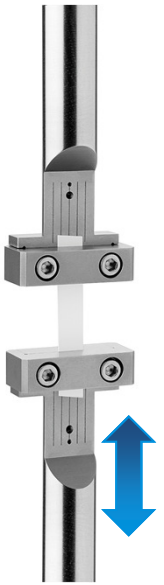
- Thermoplastic
- Thermosets
- Elastomers

Torsion

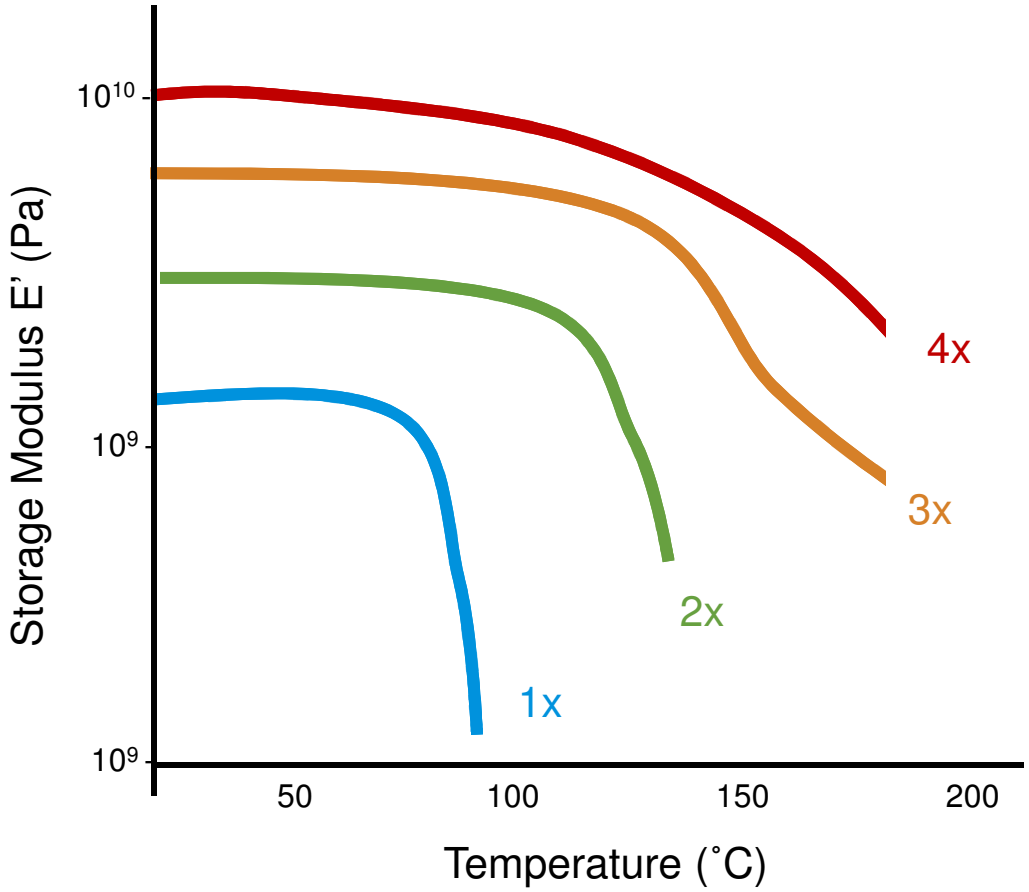
- Thermoplastic
- Thermosets
- Composites

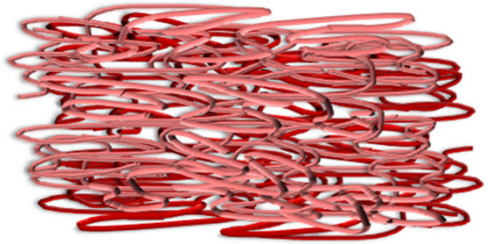
Tension DMA

- **Young's Modulus (E)**
  - Easy to adjust clamps to accommodate different samples. Allows for thermal expansion or shrinkage.
- **Dimensions:**
  - Length can be adjusted directly, measured by instrument.
  - Thickness up to 2 mm
- **Materials:**
  - Polymer films (Mylar, Kapton)
  - Elastomers (o-rings, seals)
  - Free films of coatings (dried paint)
  - Fibers, bundled or single.

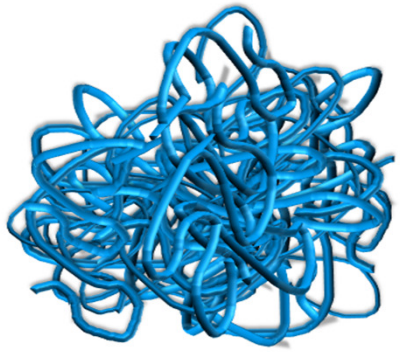


Storage Modulus of PET Fiber- Draw Ratios





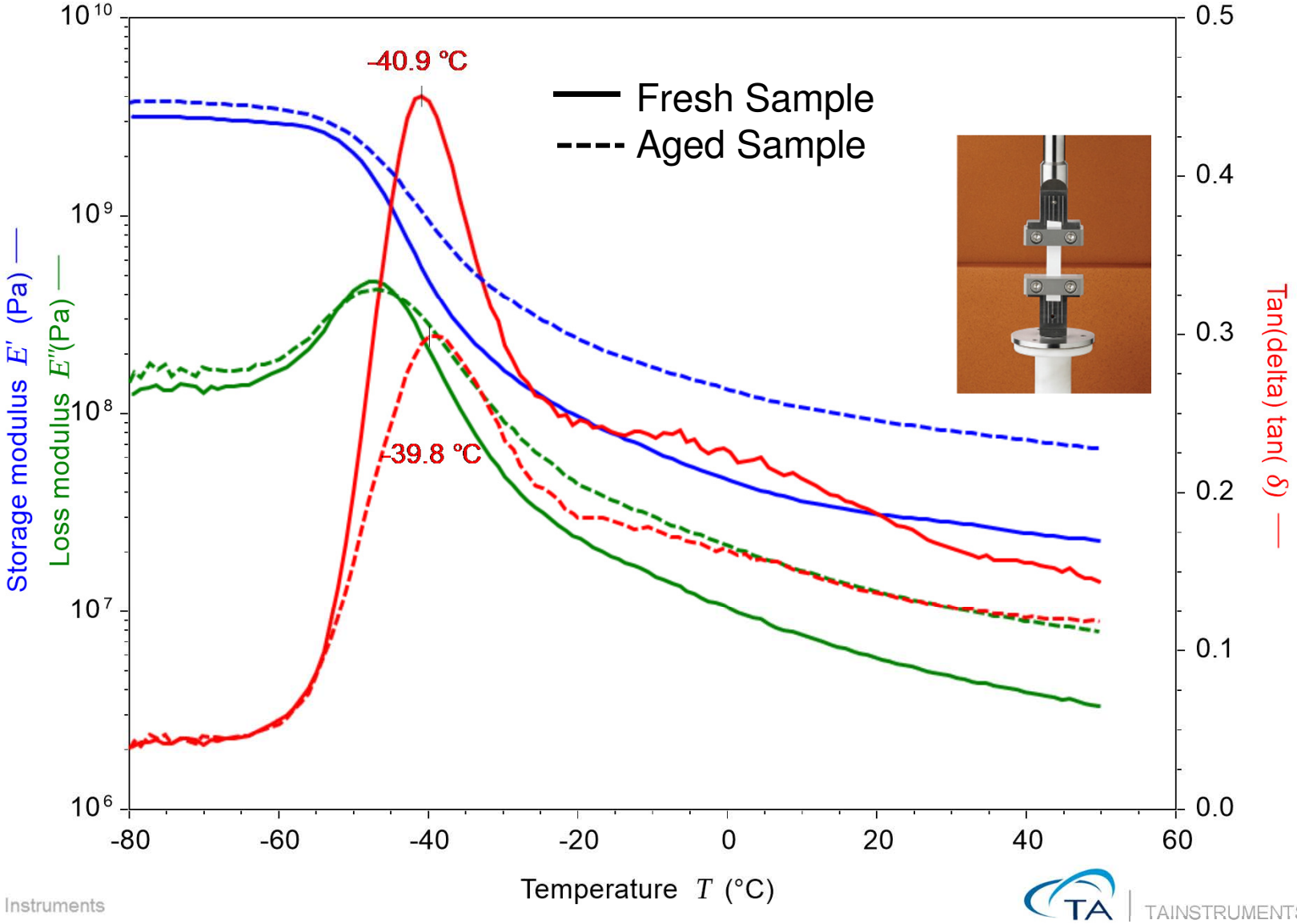
High uniaxial orientation



Random coil- no orientation

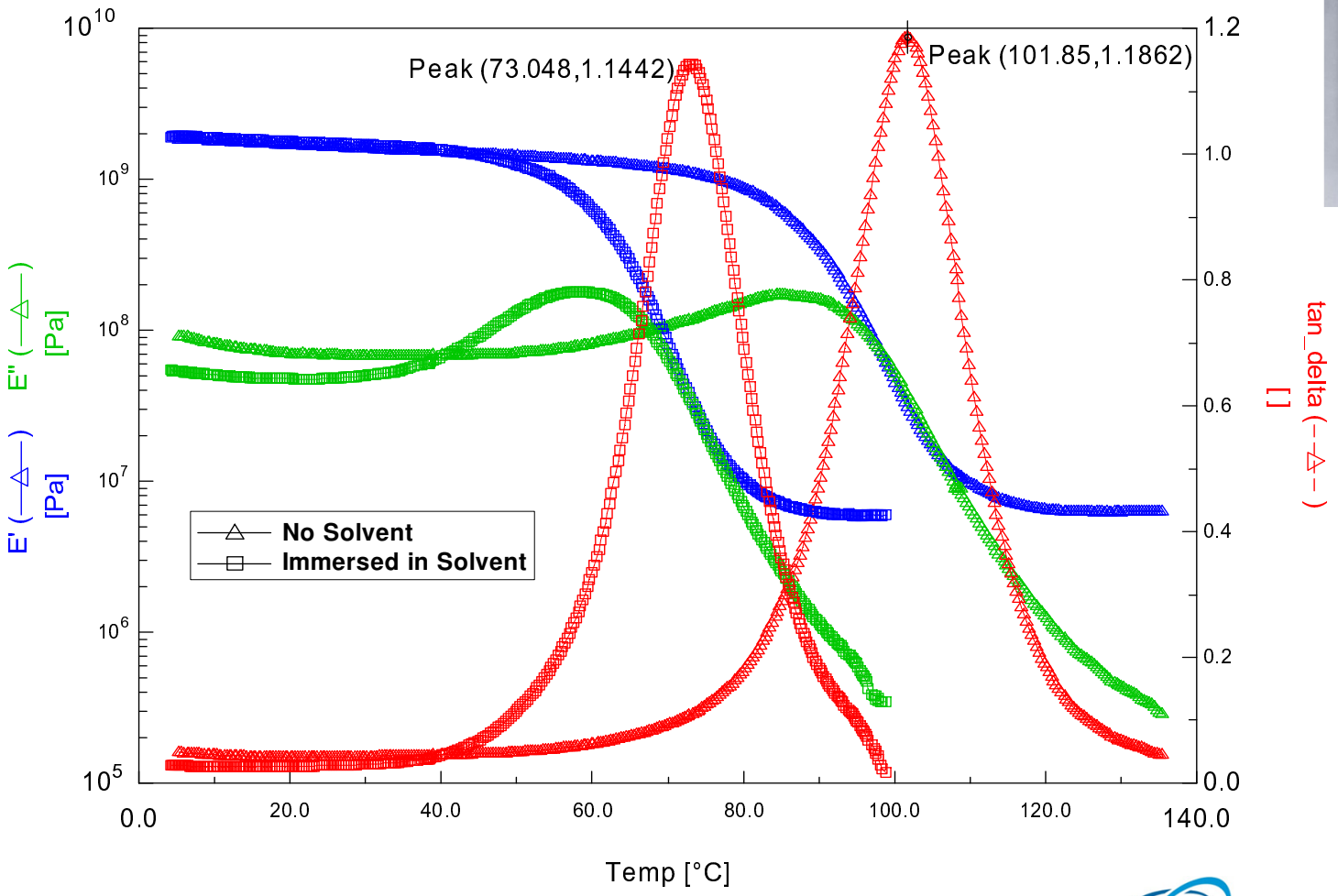
Murayama, Takayuki. "Dynamic Mechanical Analysis of Polymeric Material." Elsevier Scientific, 1978. pp. 80.

Glass Transition of EPDM- DHR DMA Tension

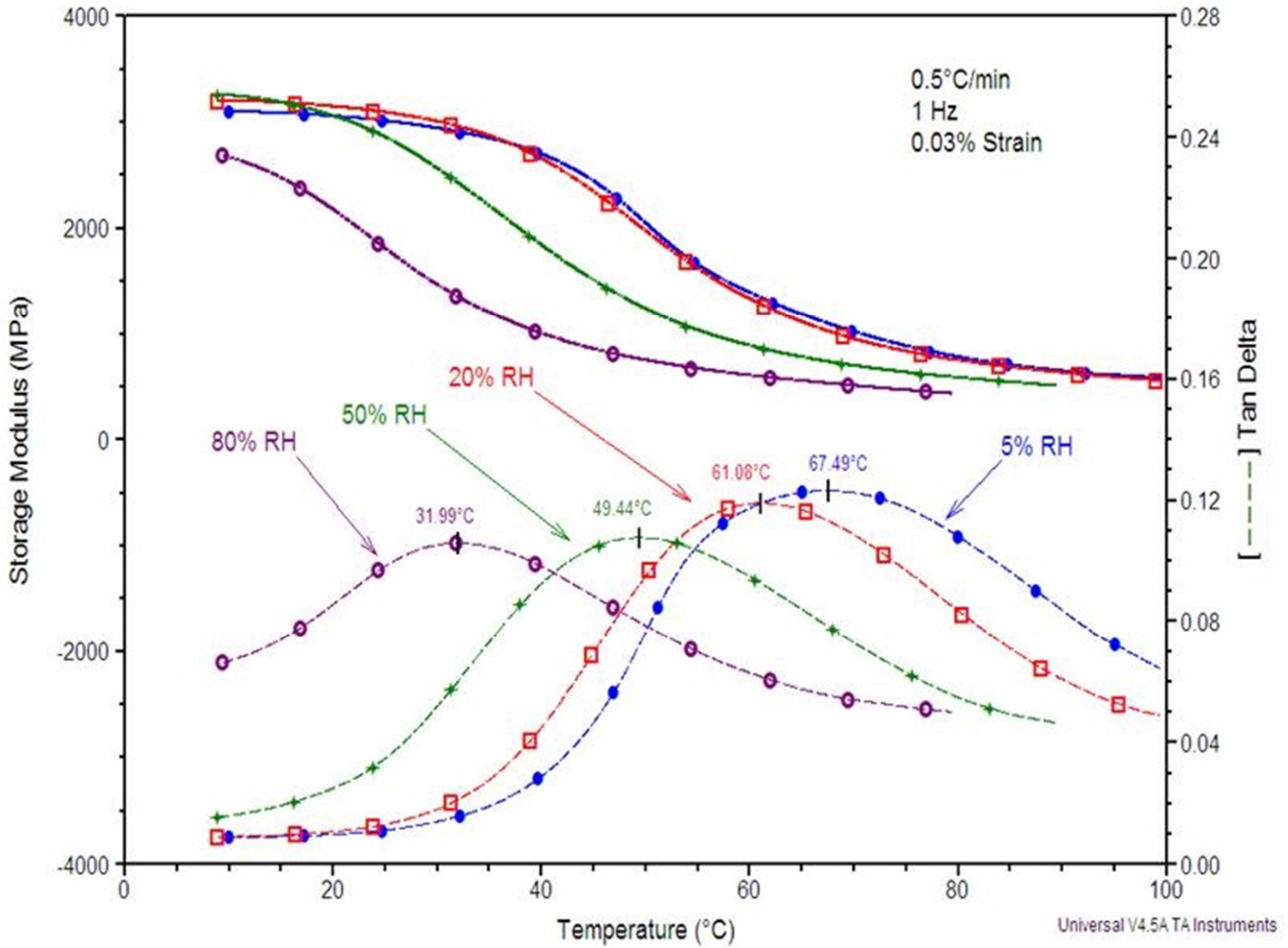


Effect of Solvent

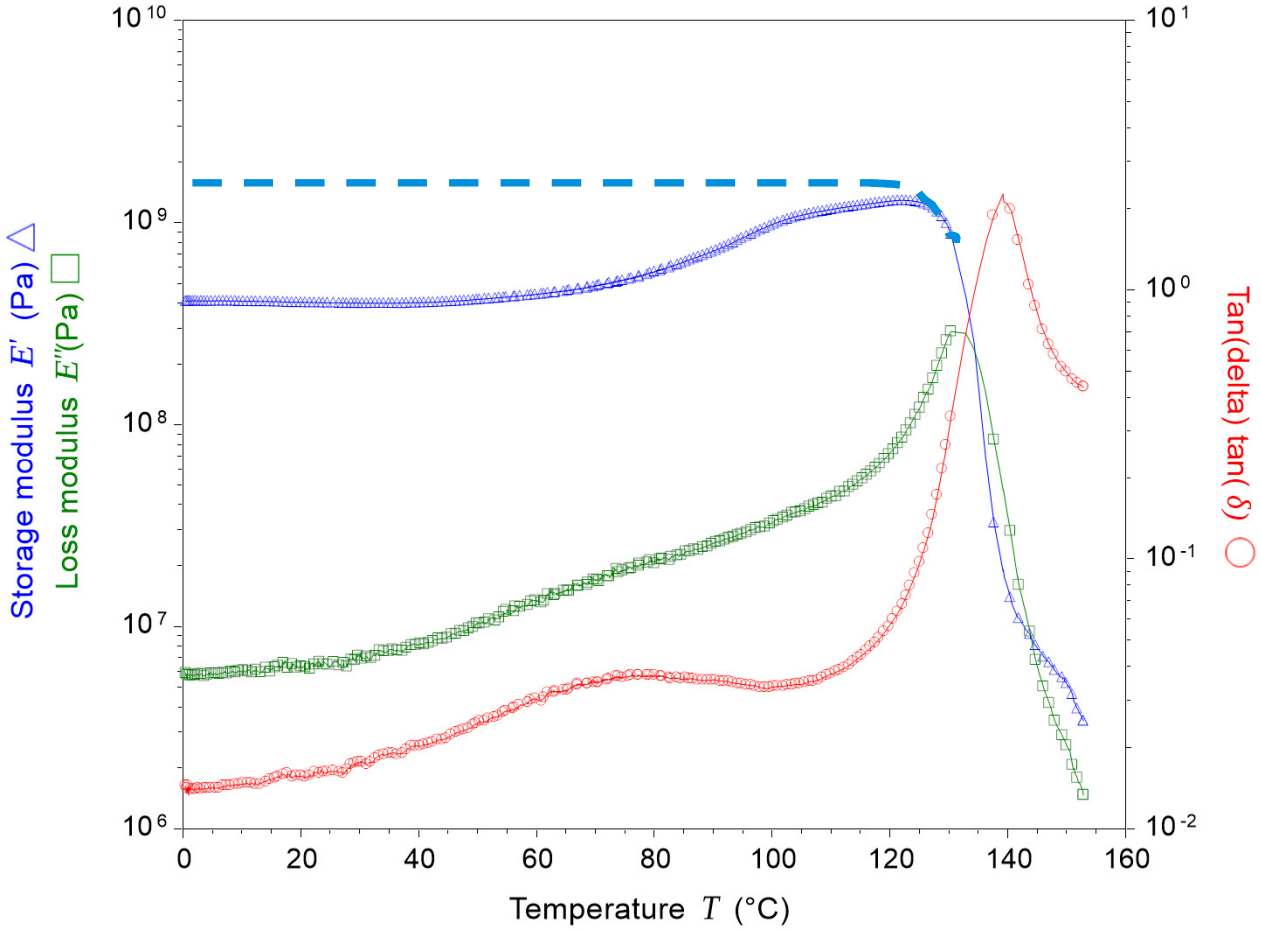
- Automotive coating measured with and without solvent

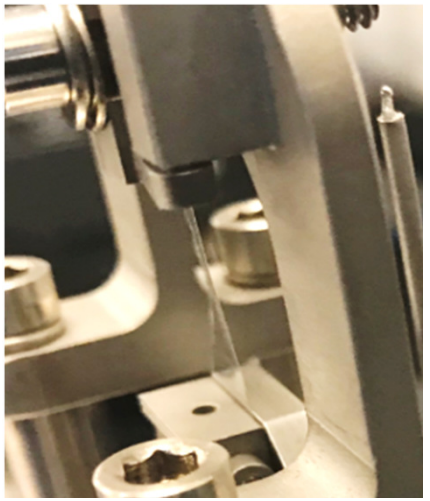


Nylon 6: Effect of Humidity on Glass Transition



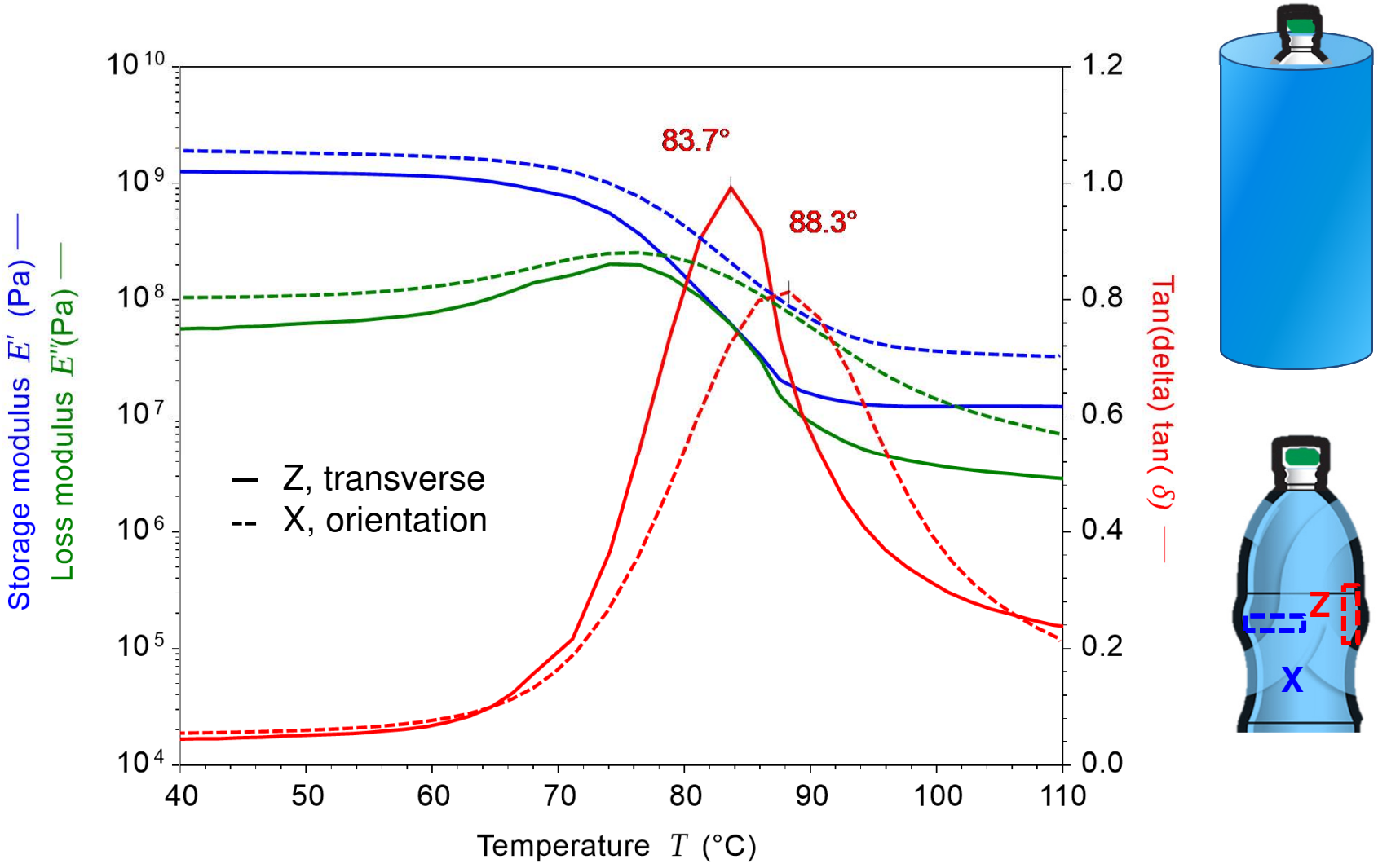
Error: Film Sample not Loaded Flat



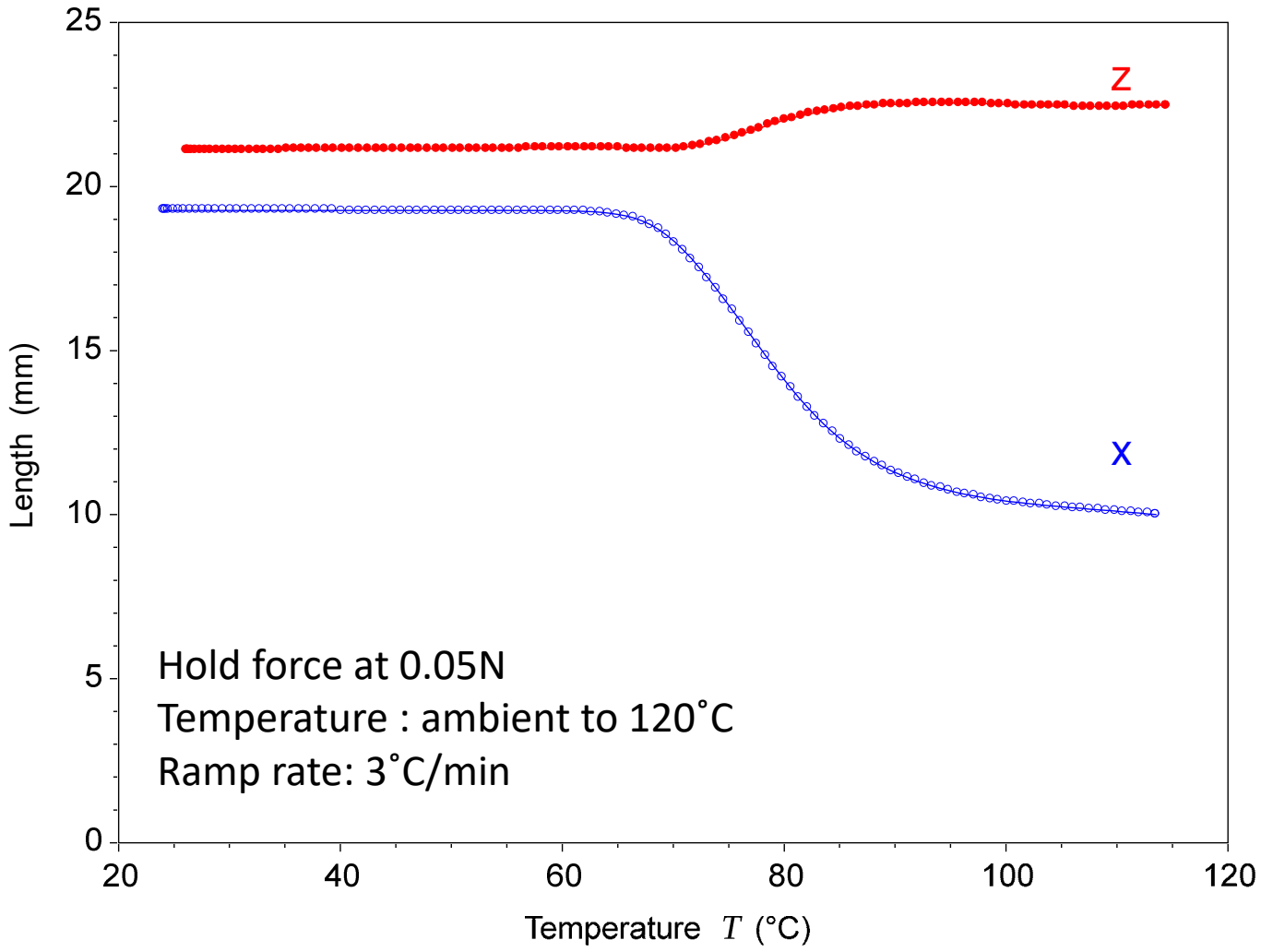


Instrument: Q800
Clamp: tension
Temperature:
0℃ to 180℃
Heating rate: 3℃/min
Frequency: 1Hz
Amplitude: 10 µm

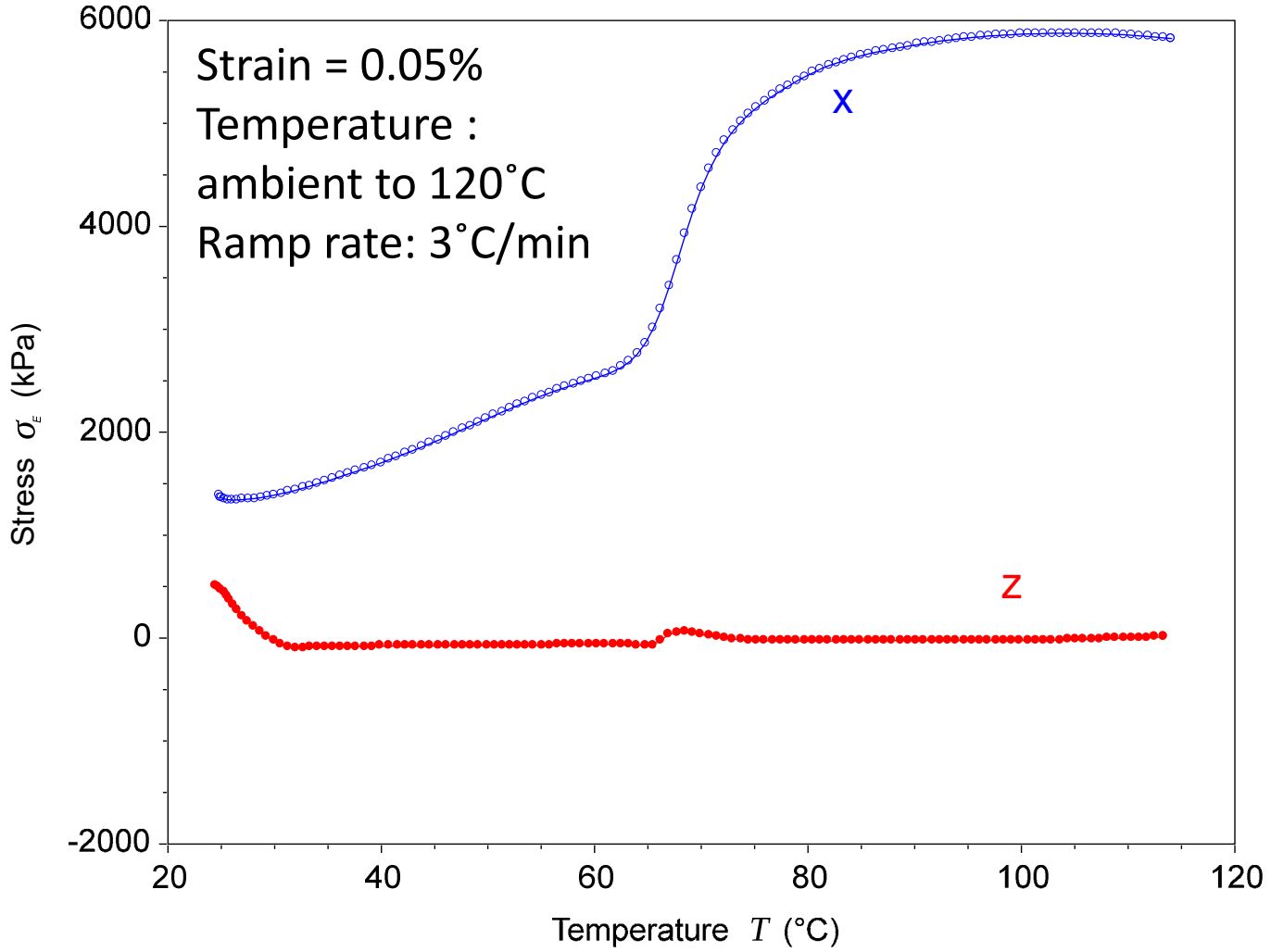
PET Film Measured at X and Z Direction



Iso-force Temp Ramp: measure shrinkage



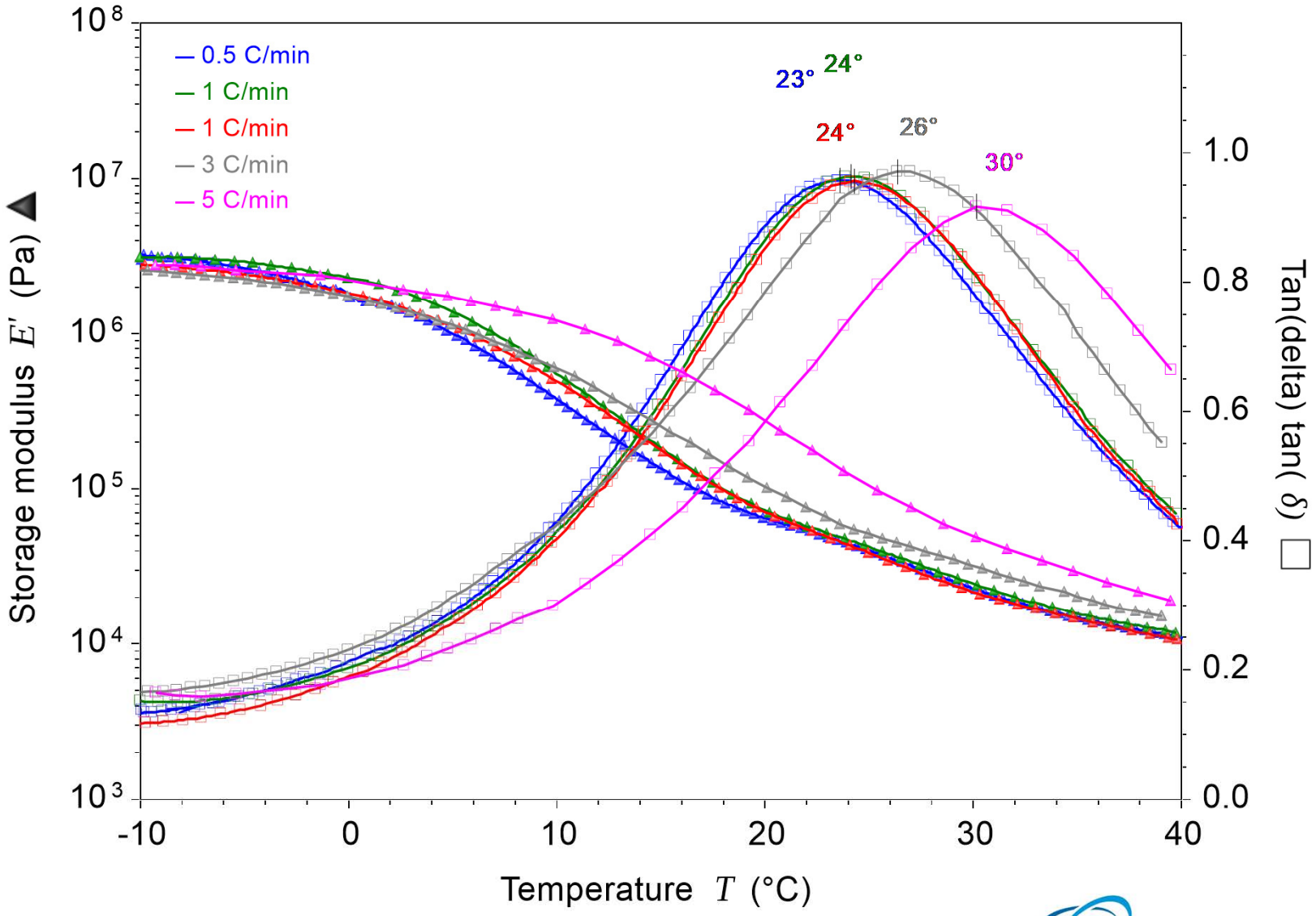
Iso-strain Temp Ramp: measure shrinking force



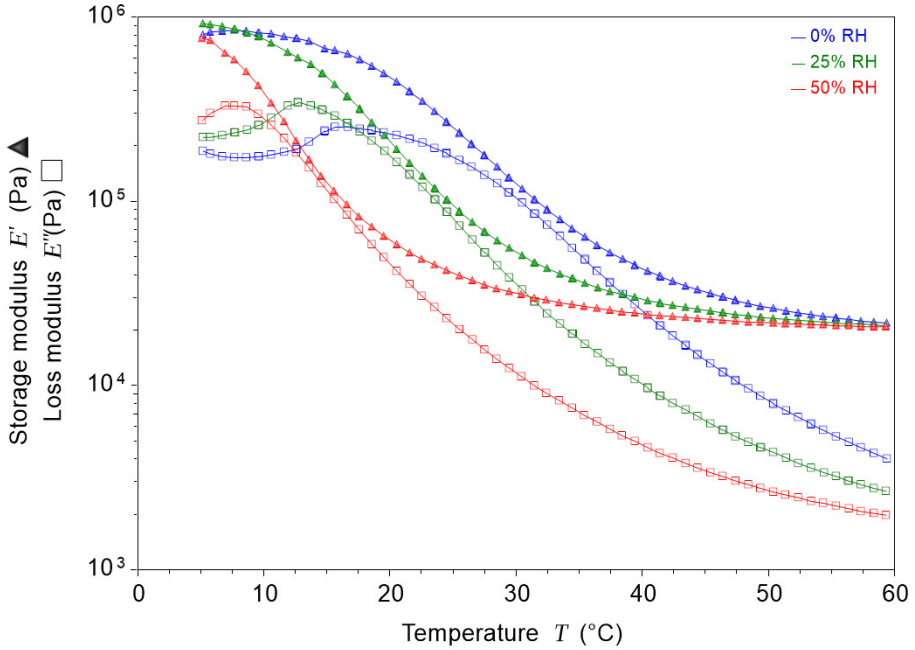
Compression DMA

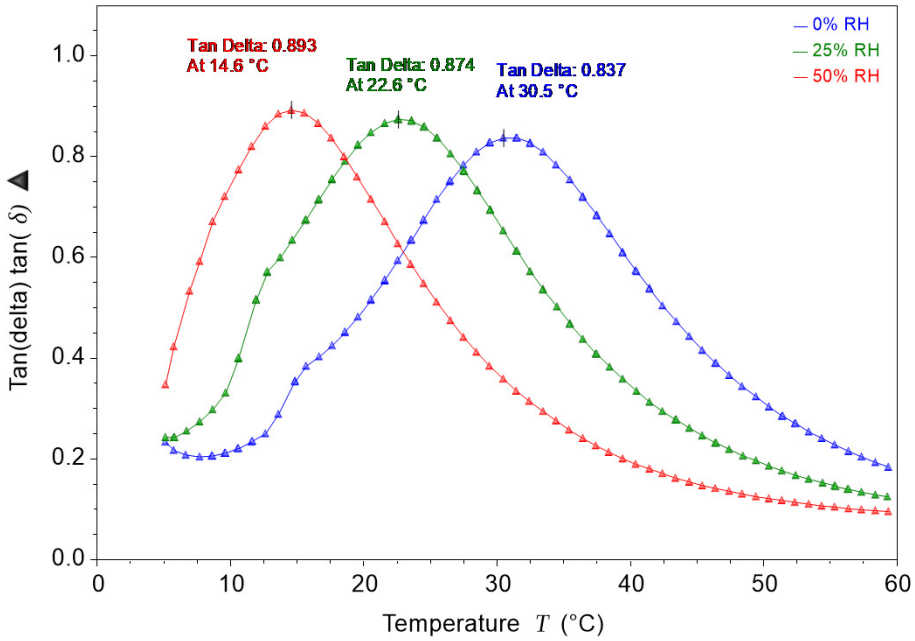
- Compression Modulus (E)
- Soft materials with high elasticity.
- Must be compressible, without yielding under deformation.
- Dimensions:
  - Ideally cut to diameter of the plates. Can also accommodate smaller disks or rectangles.
  - 1-10 mm thick
- Materials:
  - Foams (mattress, packaging, anti-vibration)
  - Soft Elastomers (above Tg only!)
  - Stiff hydrogels, biological tissue

Foam Compression DMA: Temperature Ramp Rate



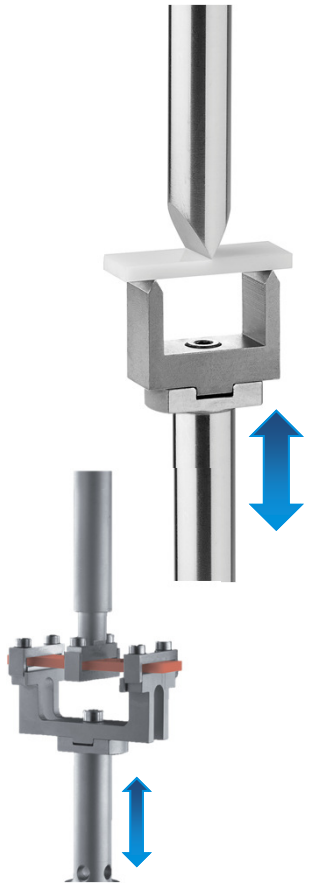
Effects of Humidity on Glass Transition of Foam



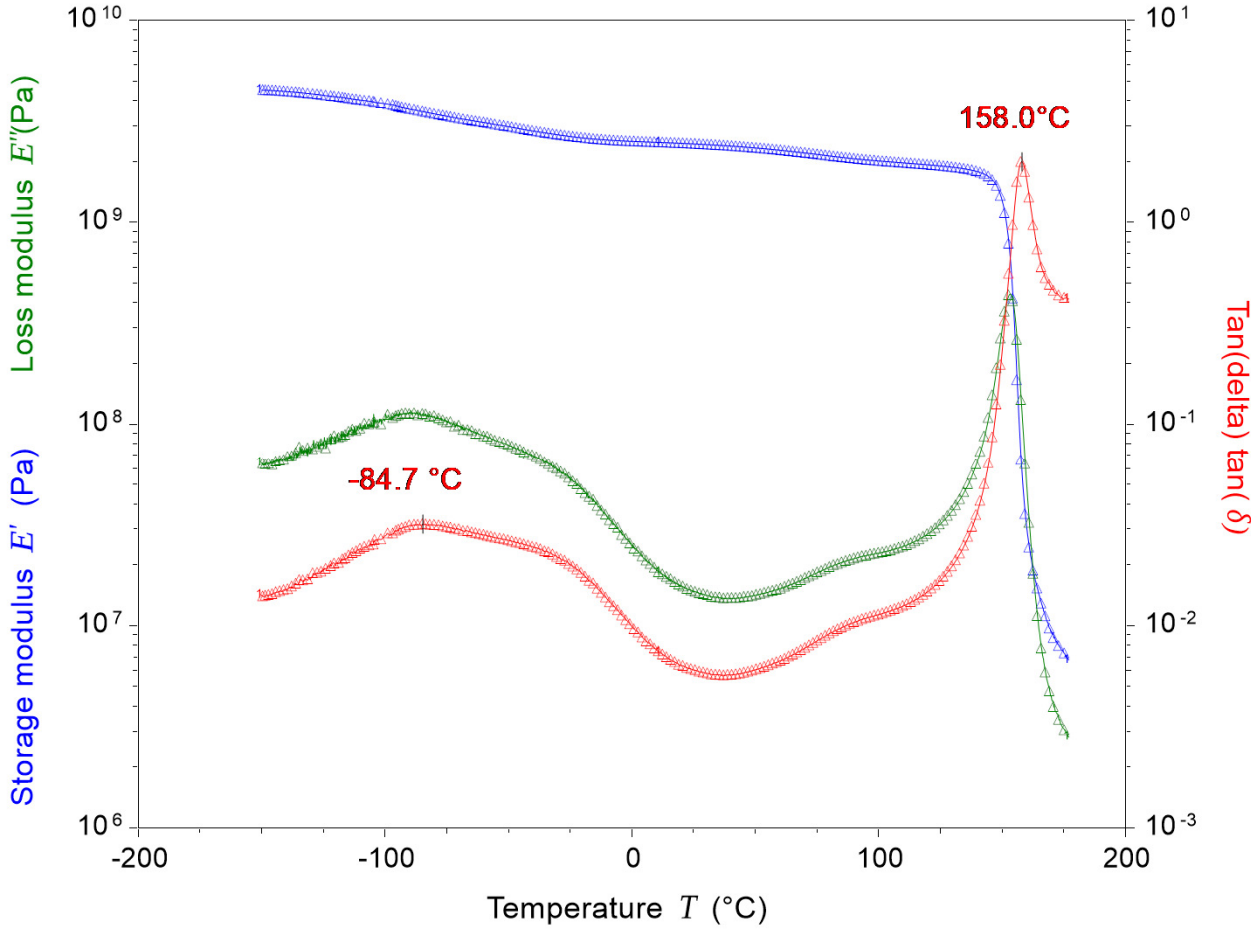


Bending DMA

- **Flexural Modulus (E)**
- 3 Point Bend (unclamped) and Cantilever (clamped)
- **Dimensions**
  - Fixed lengths: (i.e. 40, 25 and 10 mm 3PB)
  - Width up to 12.5 mm
  - Thickness ideally less than 1/10 length.
- **Materials**
  - Unfilled thermoplastics (Cantilever only > Tg)
  - Elastomers (Cantilever)
  - Thermosets (3PB)
  - Composites (3PB)
  - Metals (3PB)



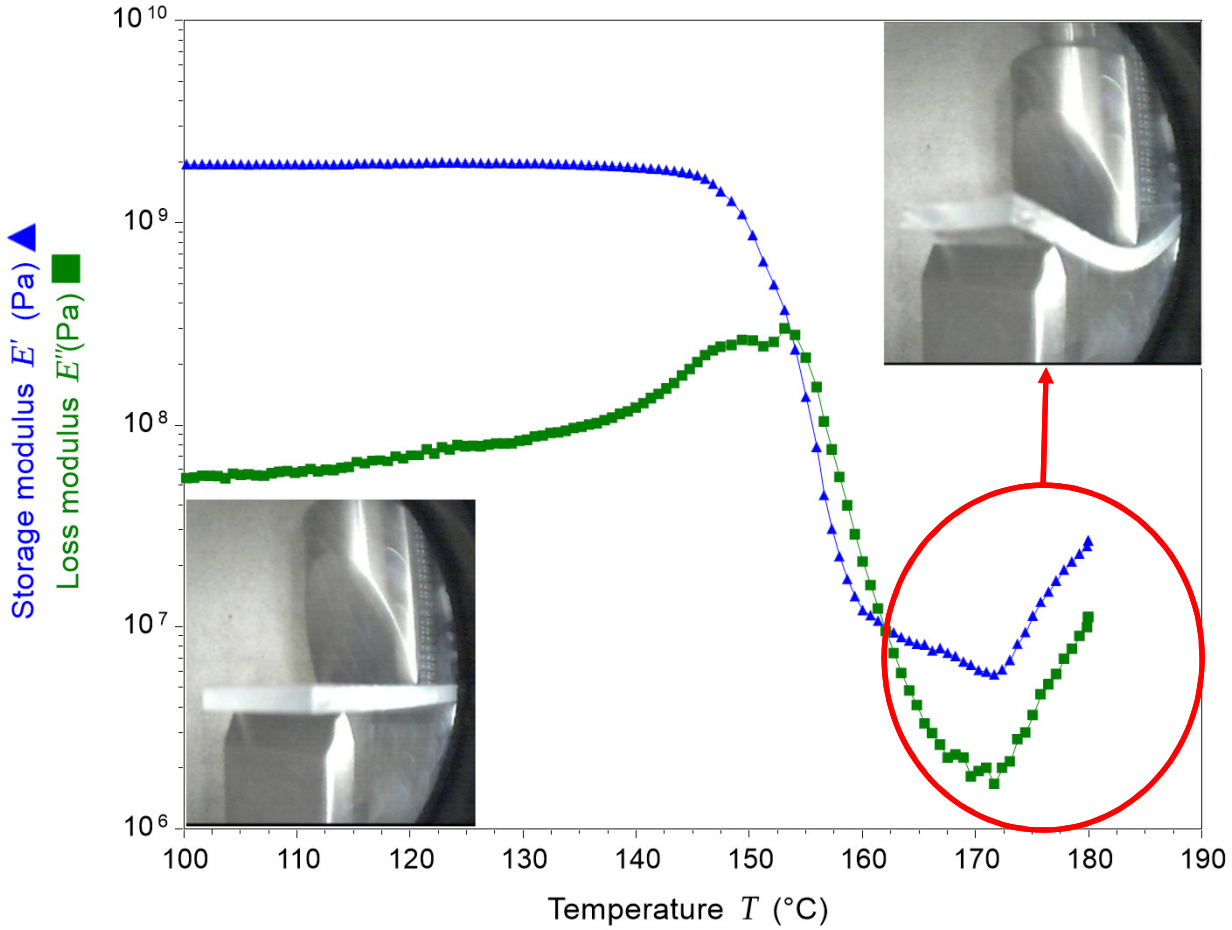
Primary and Secondary Transitions in PC



Instrument: DMA850
Temperature:
-150℃ to 180℃
Heating rate: 3℃/min
Frequency: 1Hz
Amplitude: 15 μm

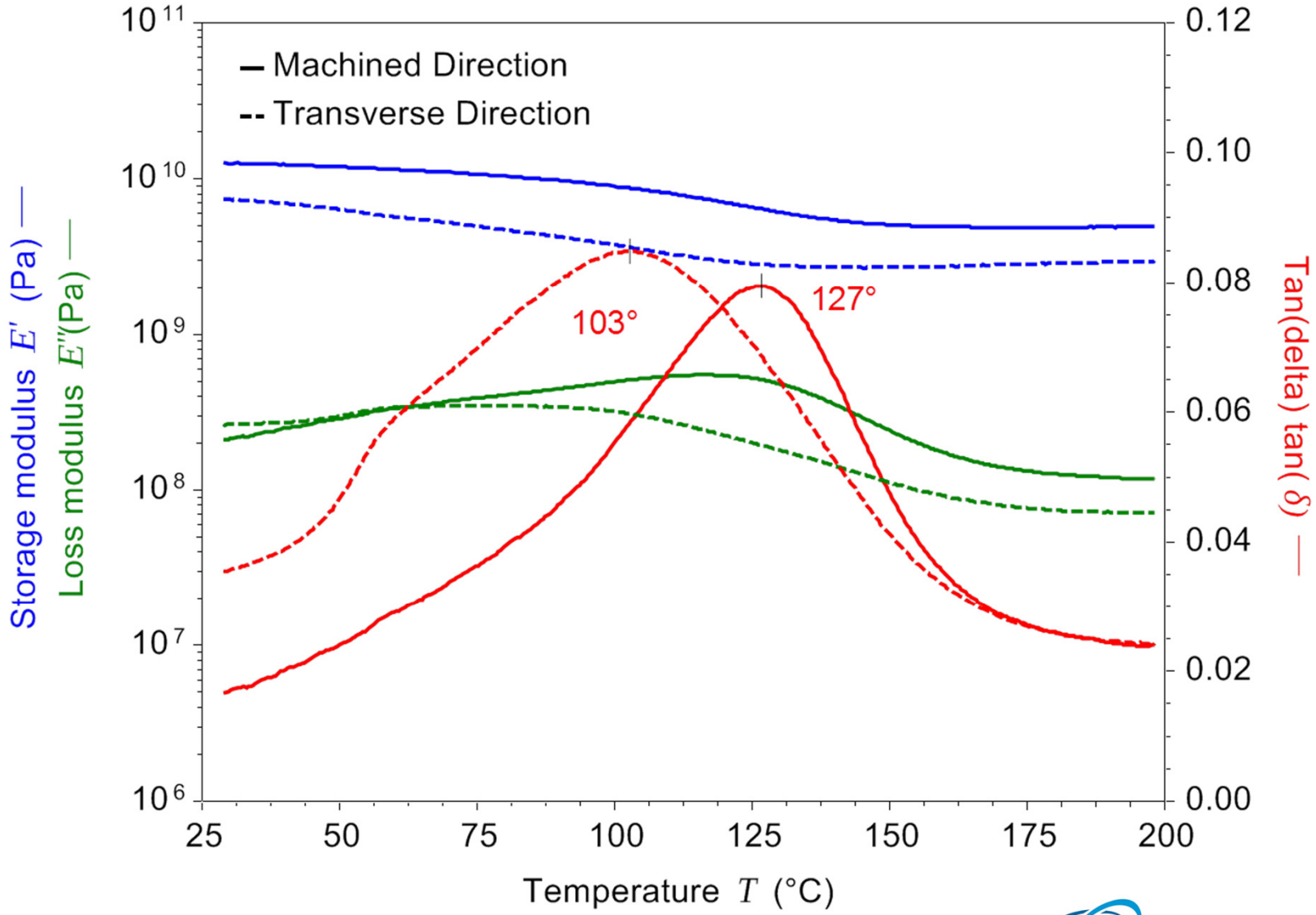
What Causes E' Increase after Tg?

- Sample sagging after Tg
- Solution: use cantilever clamp instead of 3-p bending



Instrument: RSA G2
Clamp: 3-p bending
Temperature:
50°C to 180°C
Heating rate: 3°C/min
Frequency: 1Hz
Amplitude: 10 µm

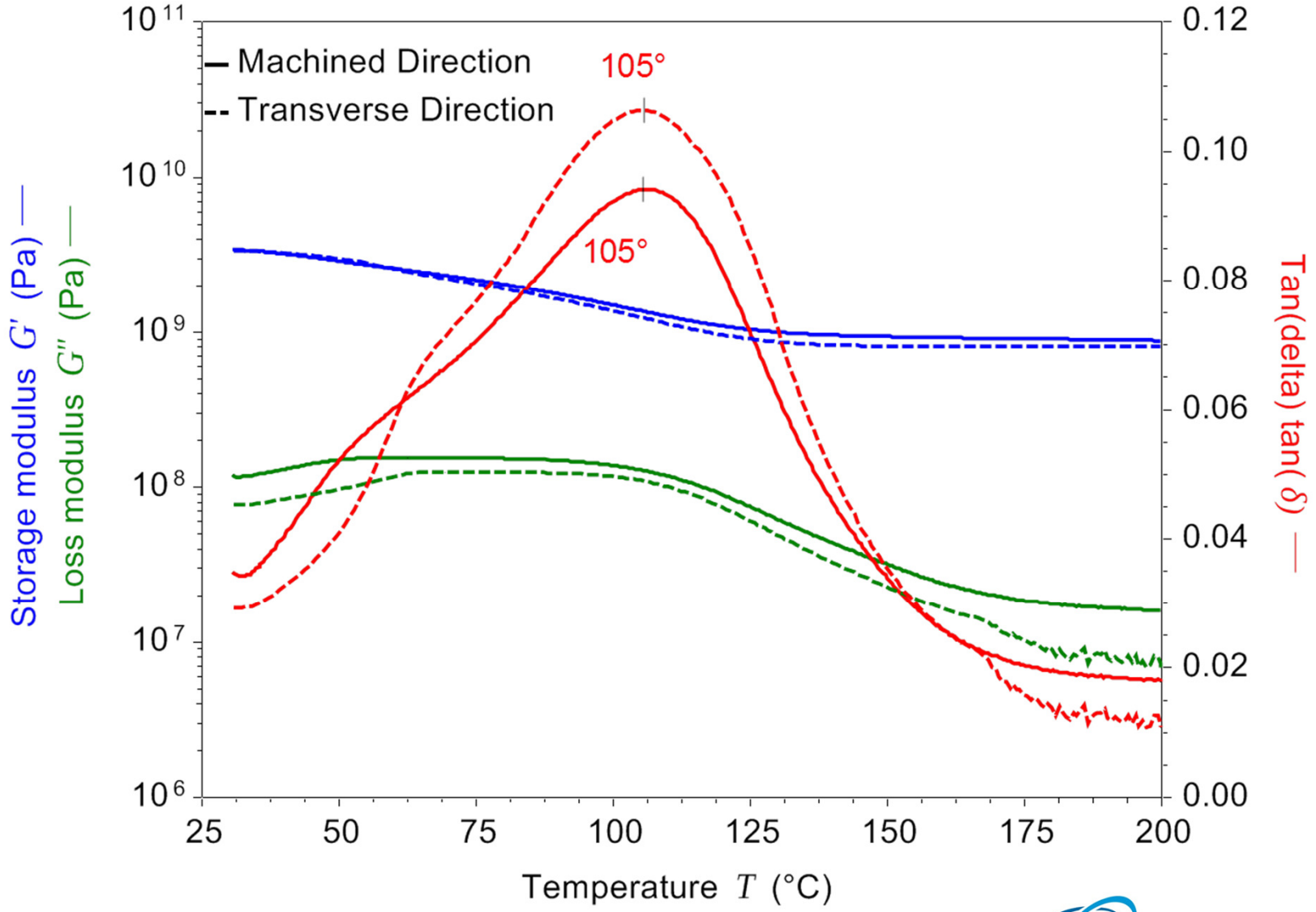
Fiber Reinforced Polymer- 3 Point Bending



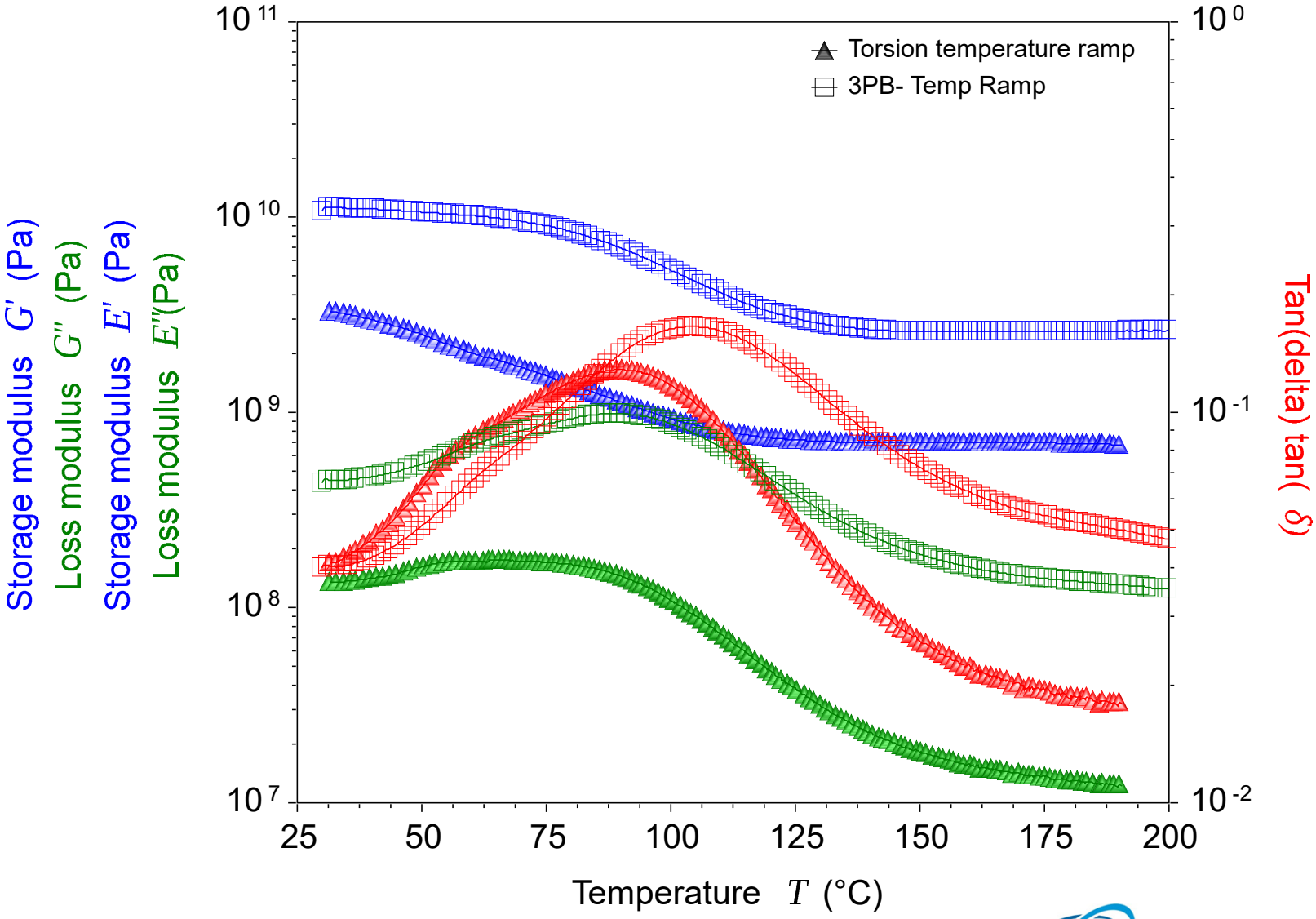
Torsion DMA

- **Shear Modulus (G)** “Modulus of Rigidity”
- Ideal for very high modulus materials; accommodates wide range of dimensions.
- **Dimensions:**
  - Small: 7 mm long, 3 mm wide, 0.5 mm thick
  - Large: 40 mm long, 12.5 mm wide, 4 mm thick
  - Cylinder: 1.5, 3 or 4.5 mm diameter
- **Materials:**
  - Thermoplastics and Thermosets
  - Elastomers
  - Composites
  - Metals

Fiber Reinforced Polymer- Torsion



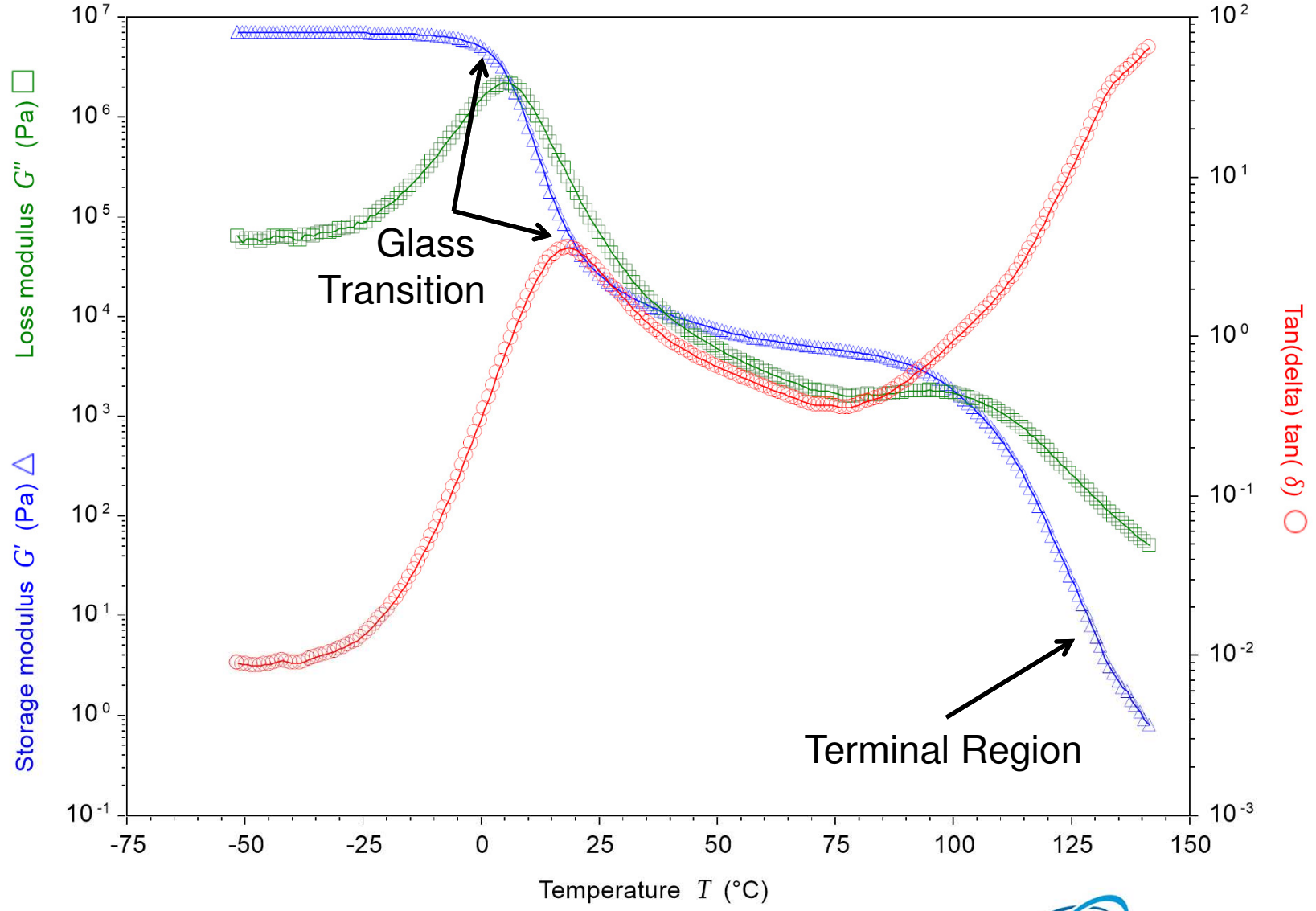
Torsion vs. 3 Point Bending



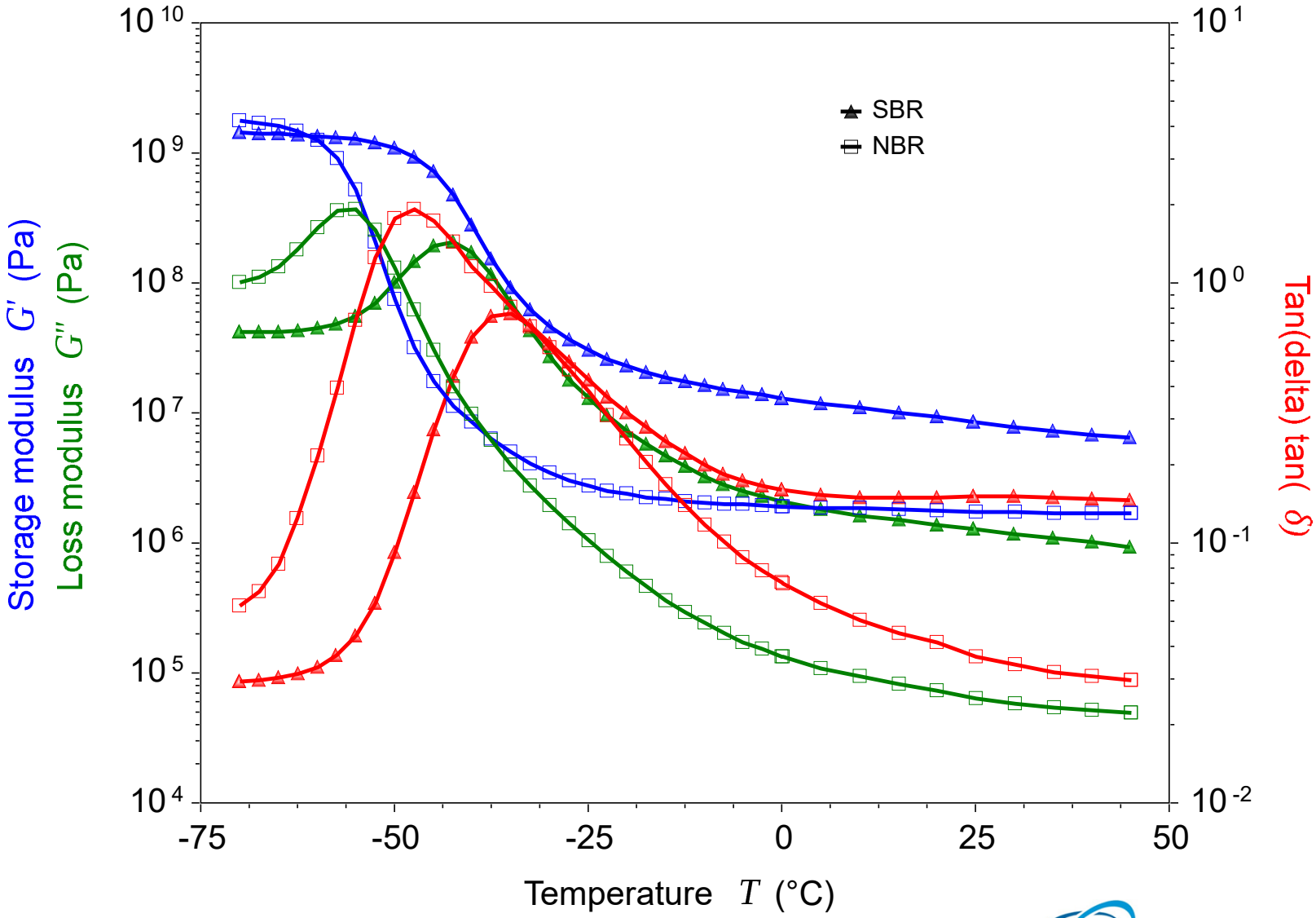
Parallel Plate DMA

- **Shear Modulus (G)**
- Full range of viscoelastic behavior (glassy, rubbery and terminal region).
- **Dimensions:**
  - 25, 8 or 4 mm parallel plates
  - 0.5 – 3 mm gap thickness
- **Materials:**
  - Thermoplastics: load above softening point, ramp temperature down.
  - Thermosets: cure in place on disposable plates.
  - Elastomers: cut disk and glue to plates.
  - Adhesives: too soft to test with linear DMA

Hot Melt Adhesive: Parallel Plates



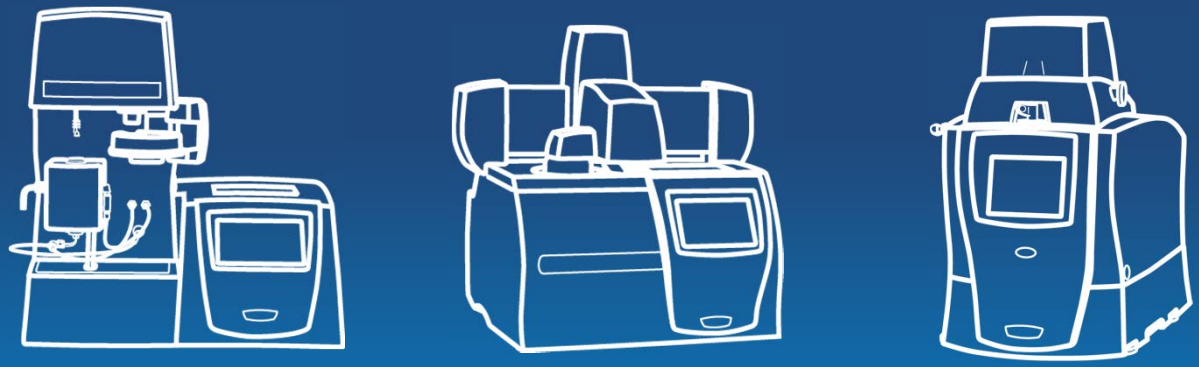
Rubber DMA: Parallel Plates



Thermal Analysis Techniques for Rubber Characterization

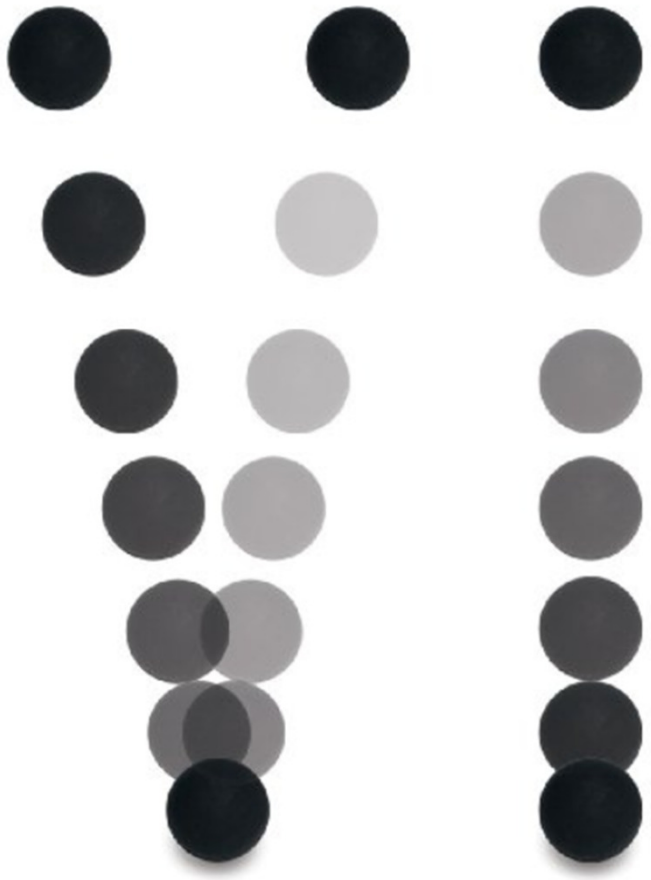
"Happy and Sad Balls"

TGA, DSC and DMA



What are Happy and Sad Balls?

- Set of 2 black rubber balls used as demonstration of viscoelastic behavior.
  - When dropped, the Happy Ball bounces and the Sad Ball does not.
- Quality varies between vendors!
- Thermal Analysis can help understand why these materials perform differently.



Amazon Reviews, “Vendor 1”

★★★☆☆ **Three Stars**

By SciTeachSF on May 20, 2017

Verified Purchase

Sad ball bounced to much

▸ Comment | Was this review helpful to you? Yes No Report abuse

★★☆☆☆ **Not a happy ball.**

By Amazon Customer on January 10, 2017

Verified Purchase

The happy ball wasn't happy did not bounce at all.

▸ Comment | Was this review helpful to you? Yes No Report abuse

Can we measure, and quantify, the “bounce”?

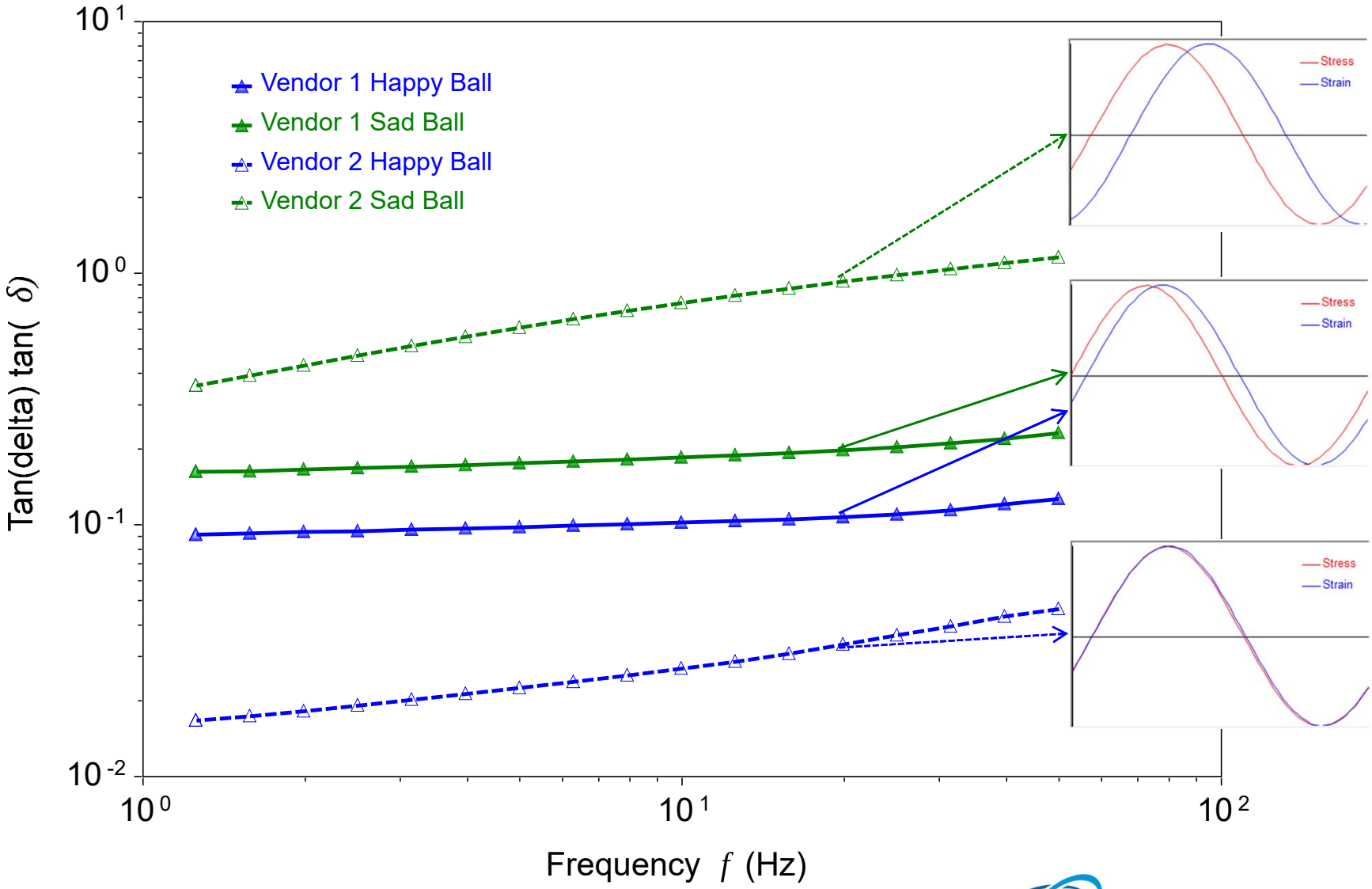
★☆☆☆☆ **One Star**

By Nicholas S. on October 16, 2016

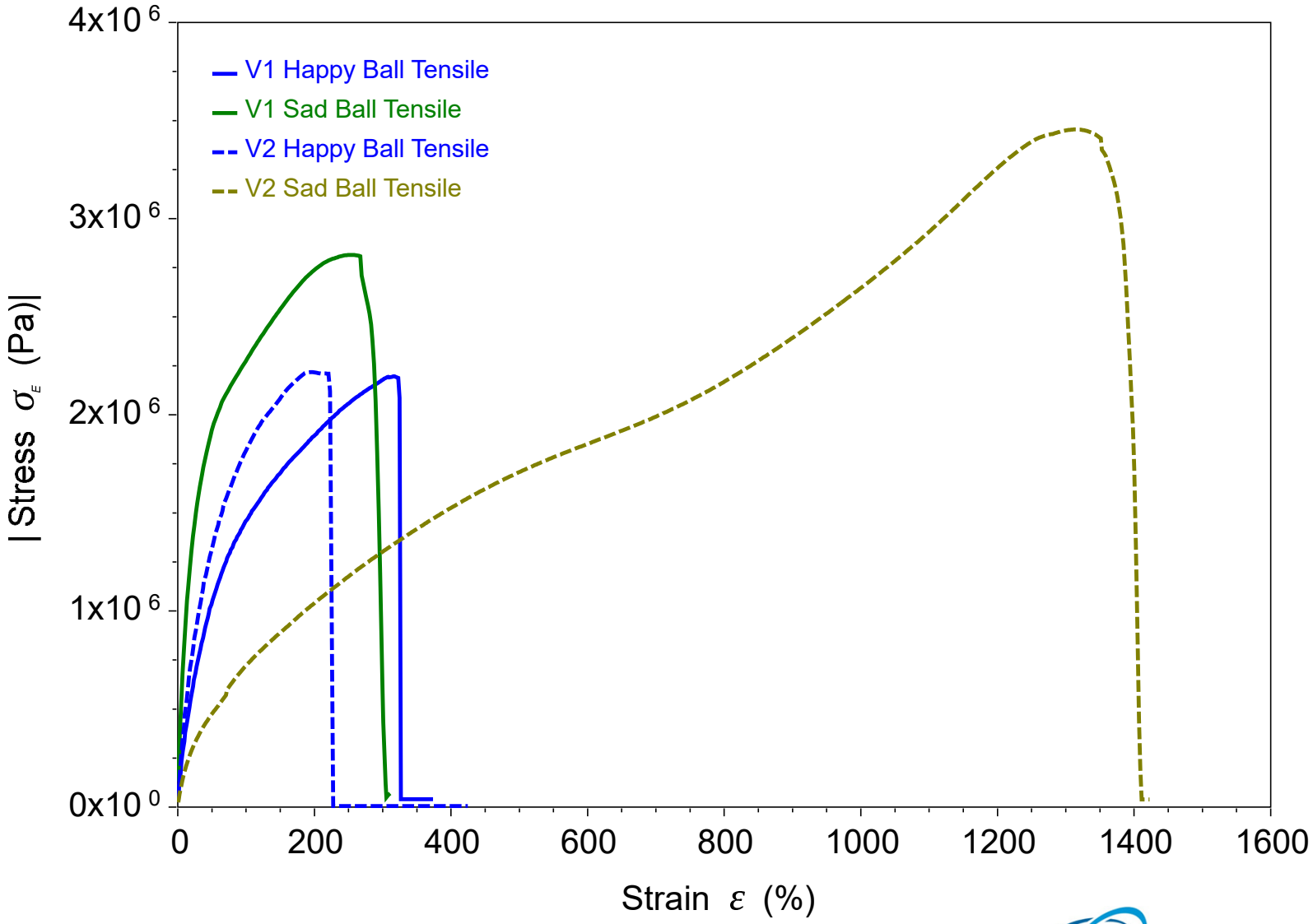
Verified Purchase

Sad ball not sad enough. Happy Ball was... well pretty sad actually.

Frequency Sweep: Tan Delta (RSA G2)



Tensile Testing (RSA G2)



Physical Properties

	Vendor 1		Vendor 2	
	Happy Ball	Sad Ball	Happy Ball	Sad Ball
Shore A Hardness	60	63	44	42
Density (g/cm^3)	1.53	1.39	1.09	1.54
Tensile Strength (MPa)	2.2	2.7	2.2	3.5
Elongation at Break	320%	250%	190%	1,290%
Tan δ (damping) at 50 Hz	**0.127**	**0.232**	**0.046**	**1.158**

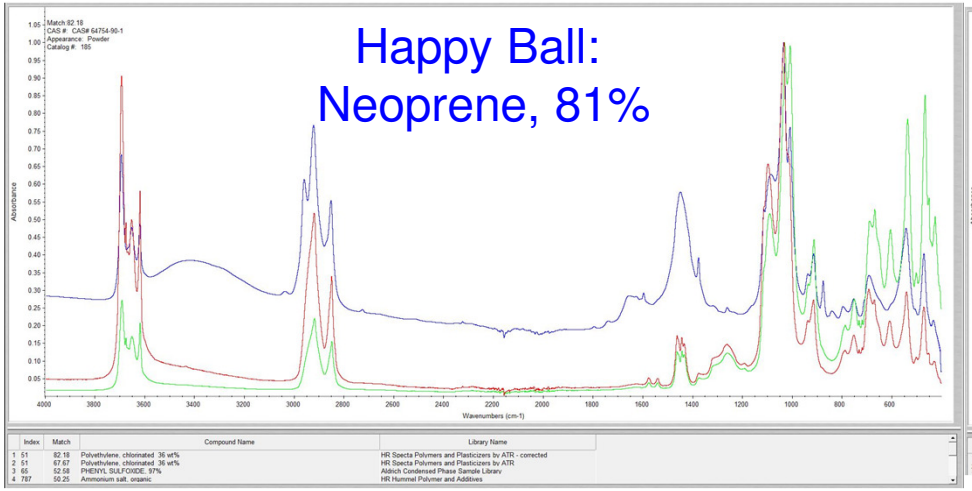
What is the source of the difference in physical properties?

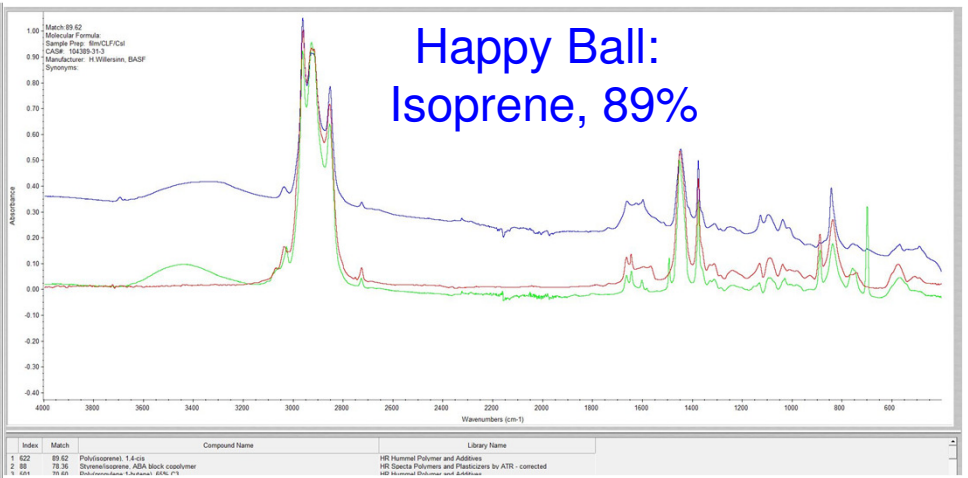
- Chemistry of elastomer?
- Degree of crosslinking?
- Amount of additives or filler?

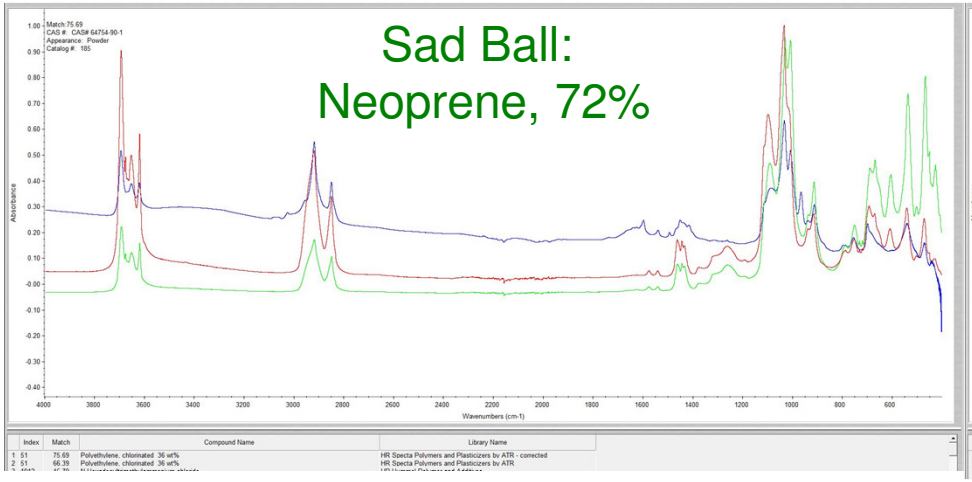
FT-IR: Useful, but not conclusive

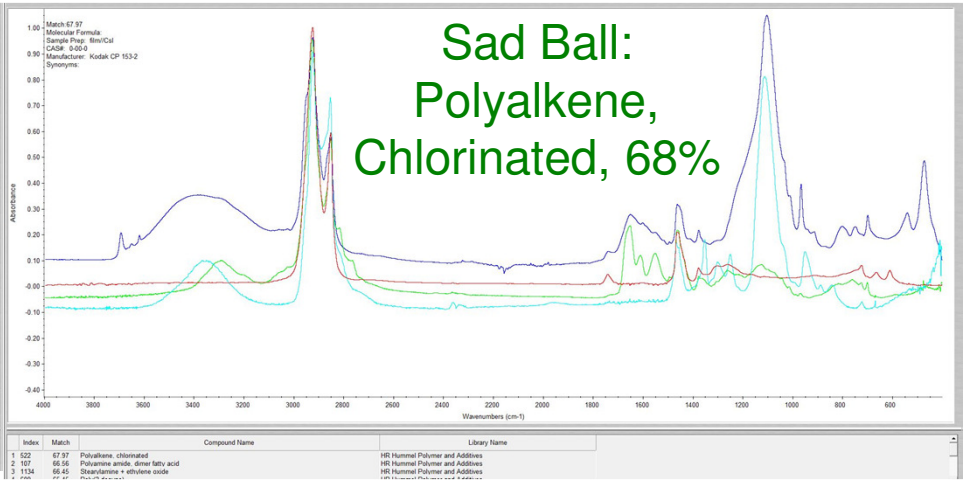
Vendor 1

Vendor 2









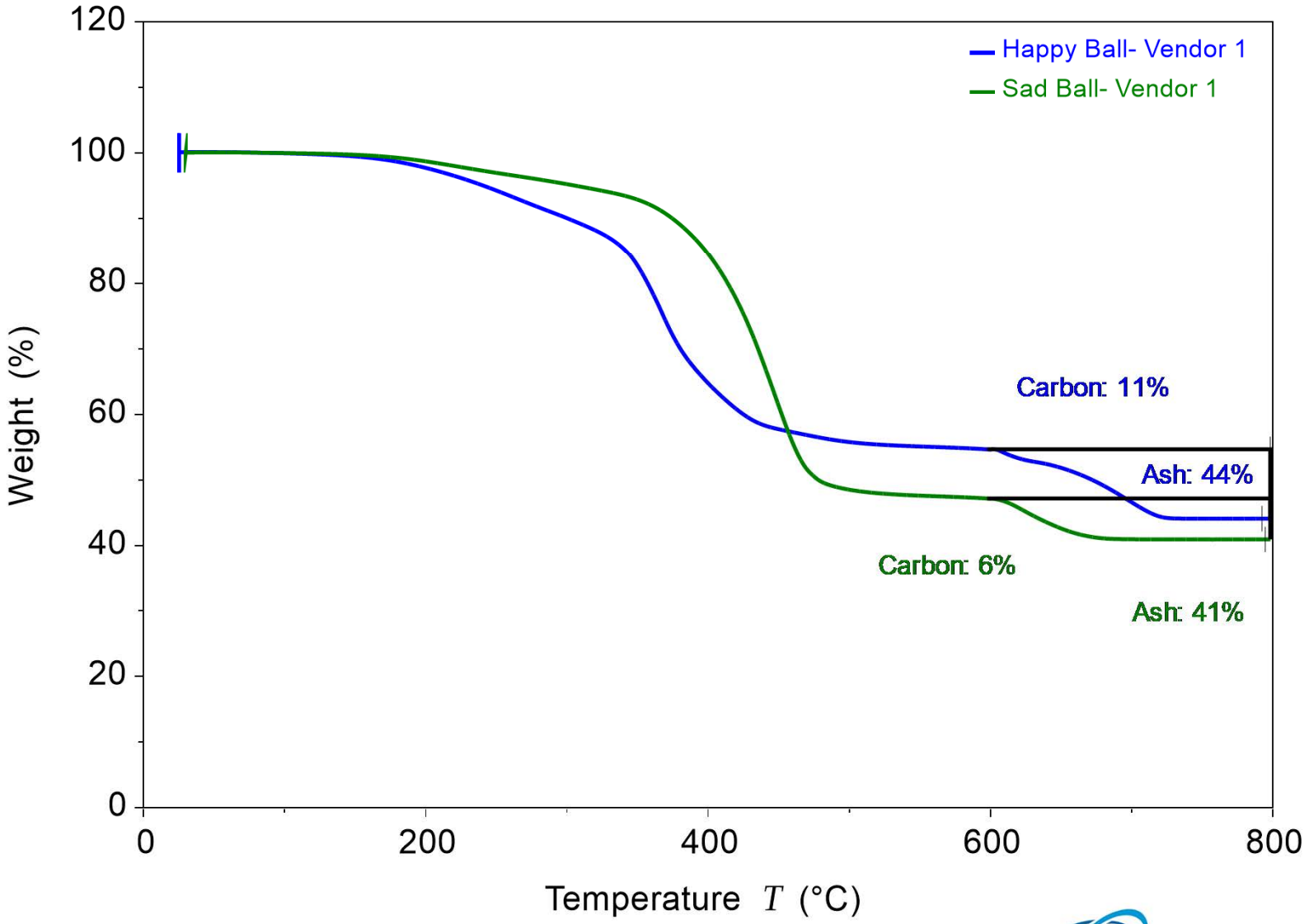
Thermal Analysis Characterization Techniques

1. **Thermo-Gravimetric Analysis (TGA)**
   - Measure weight change while increasing temperature.
   - Quantify the content of volatiles, elastomer, carbon black and inorganic filler (ash).

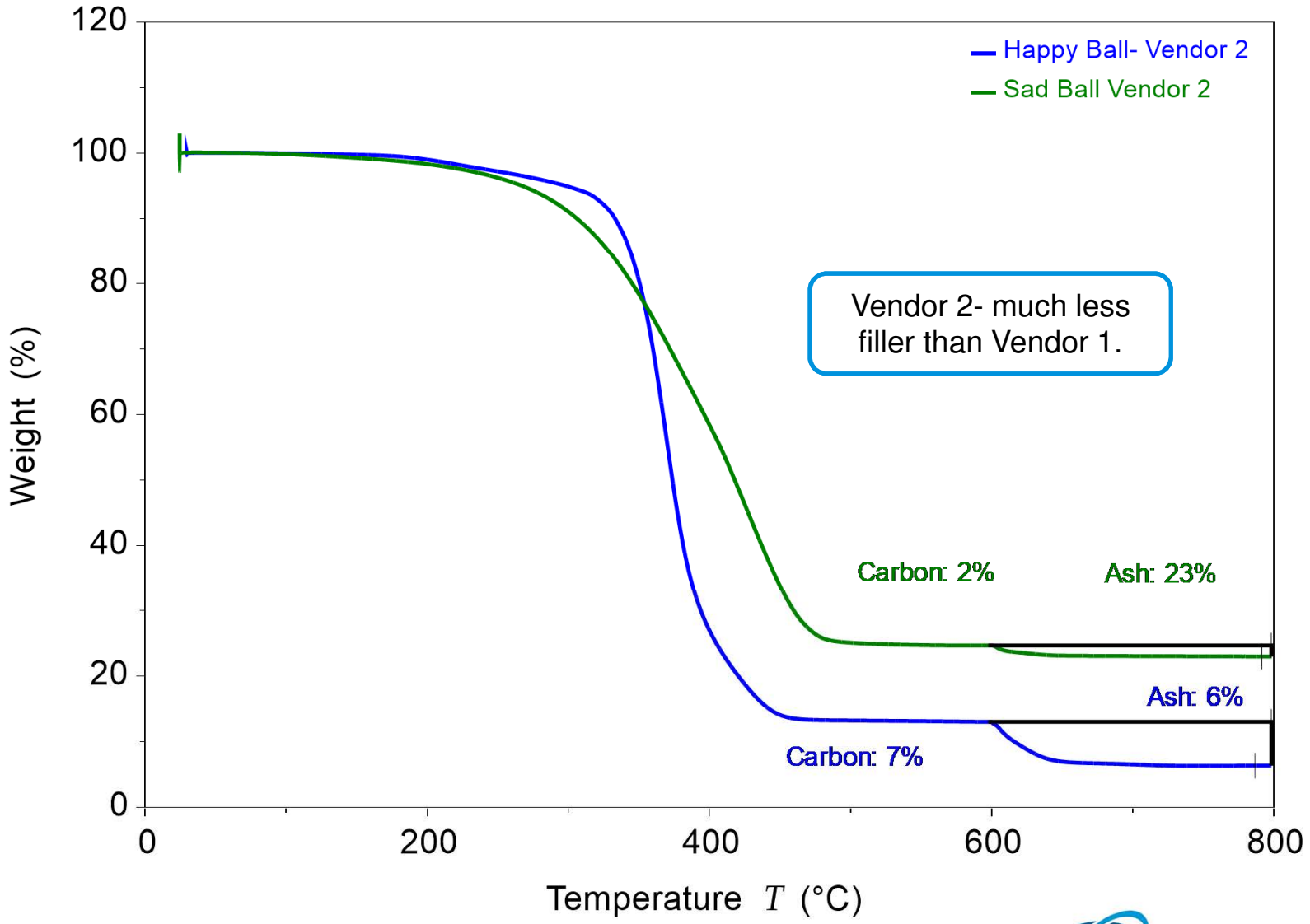
2. **Differential Scanning Calorimetry (DSC)**
   - Measure Heat Flow as a function of temperature.
   - Identify glass transition, melting/ crystallization, and any polymerization or curing.

3. **Dynamic Mechanical Analysis (DMA)**
   - Measure viscoelastic properties as a function of temperature.
   - More sensitive characterization of glass transition.

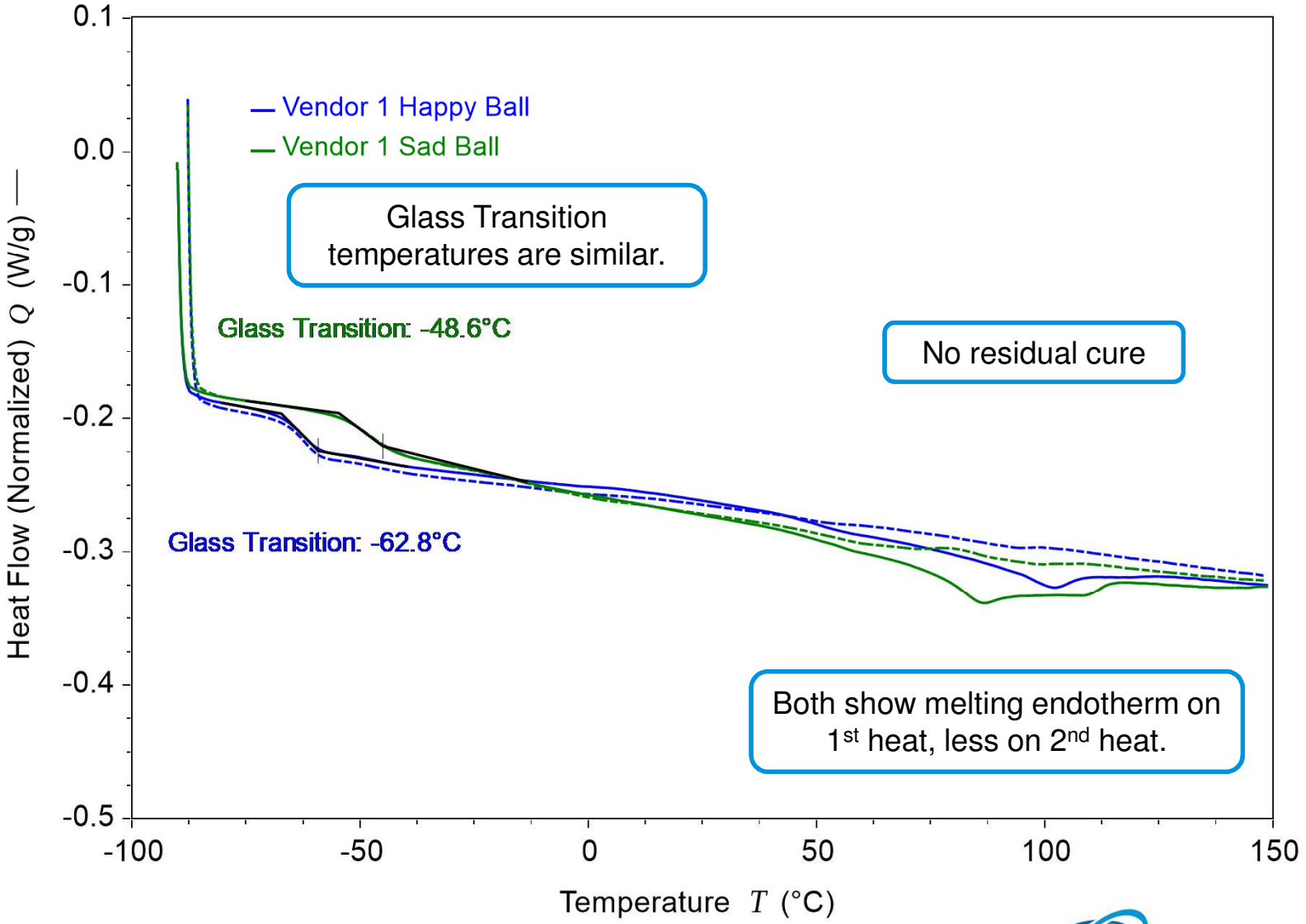
TGA: Vendor 1, filler



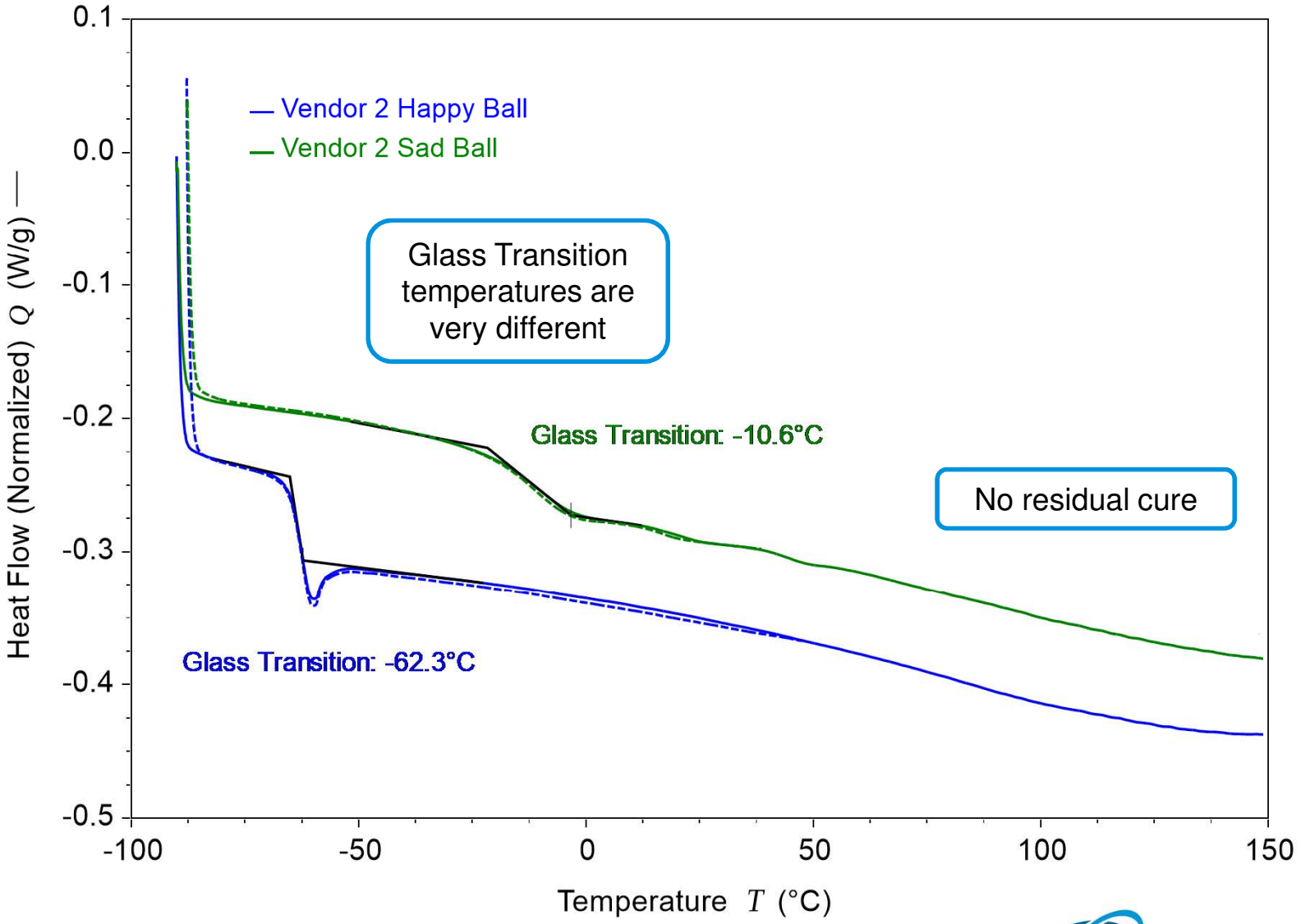
TGA: Vendor 2, filler



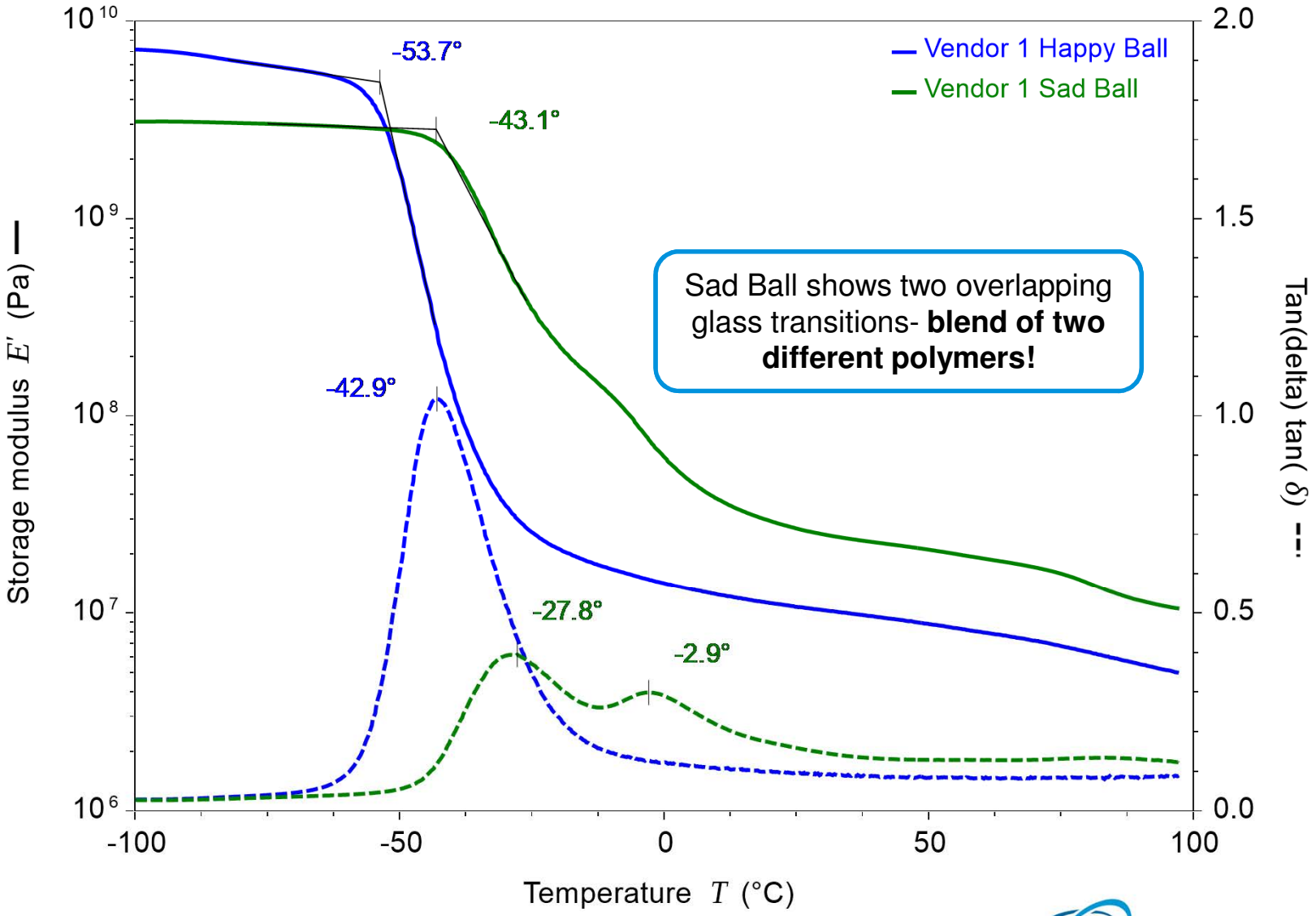
DSC: Vendor 1



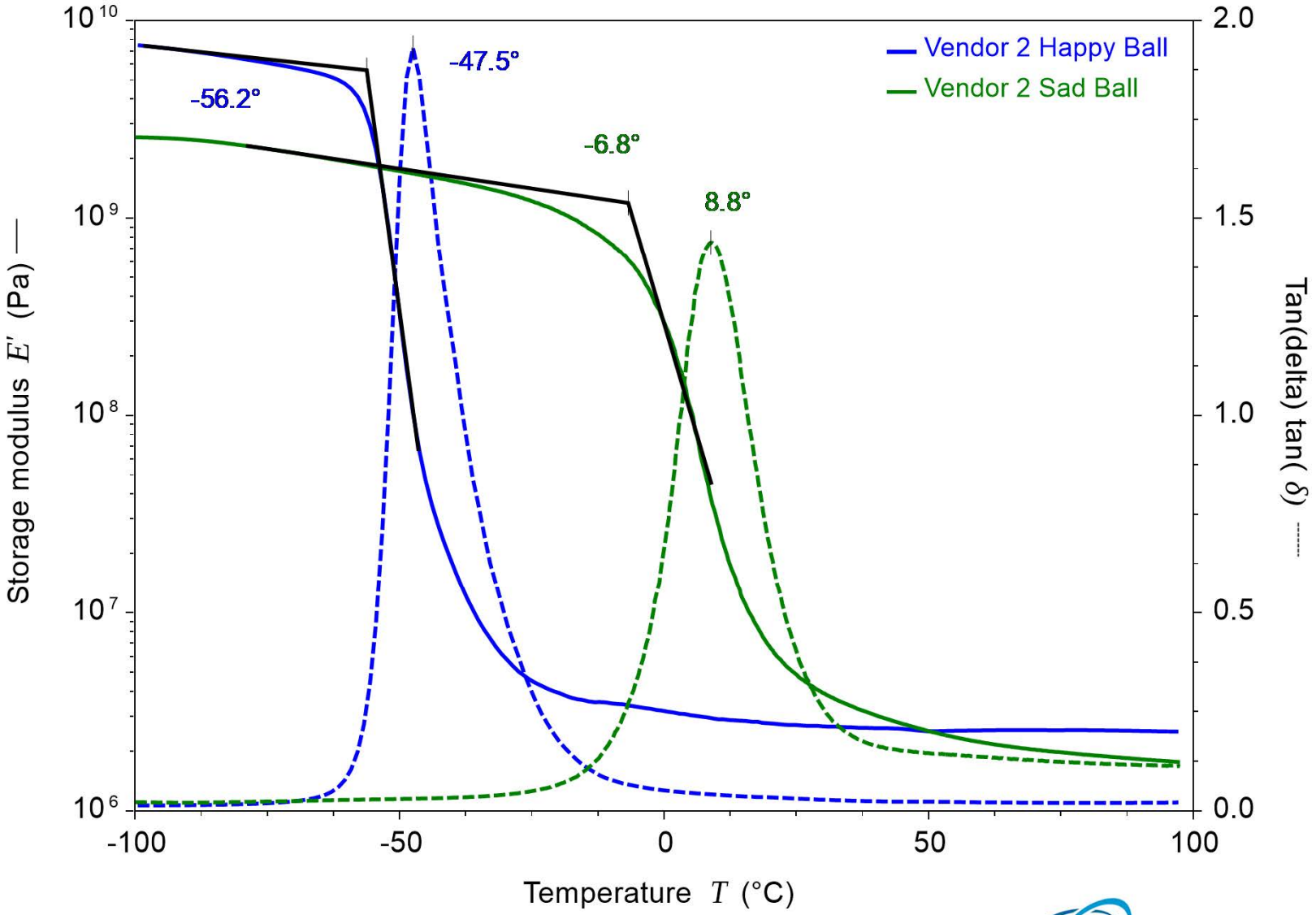
DSC: Vendor 2



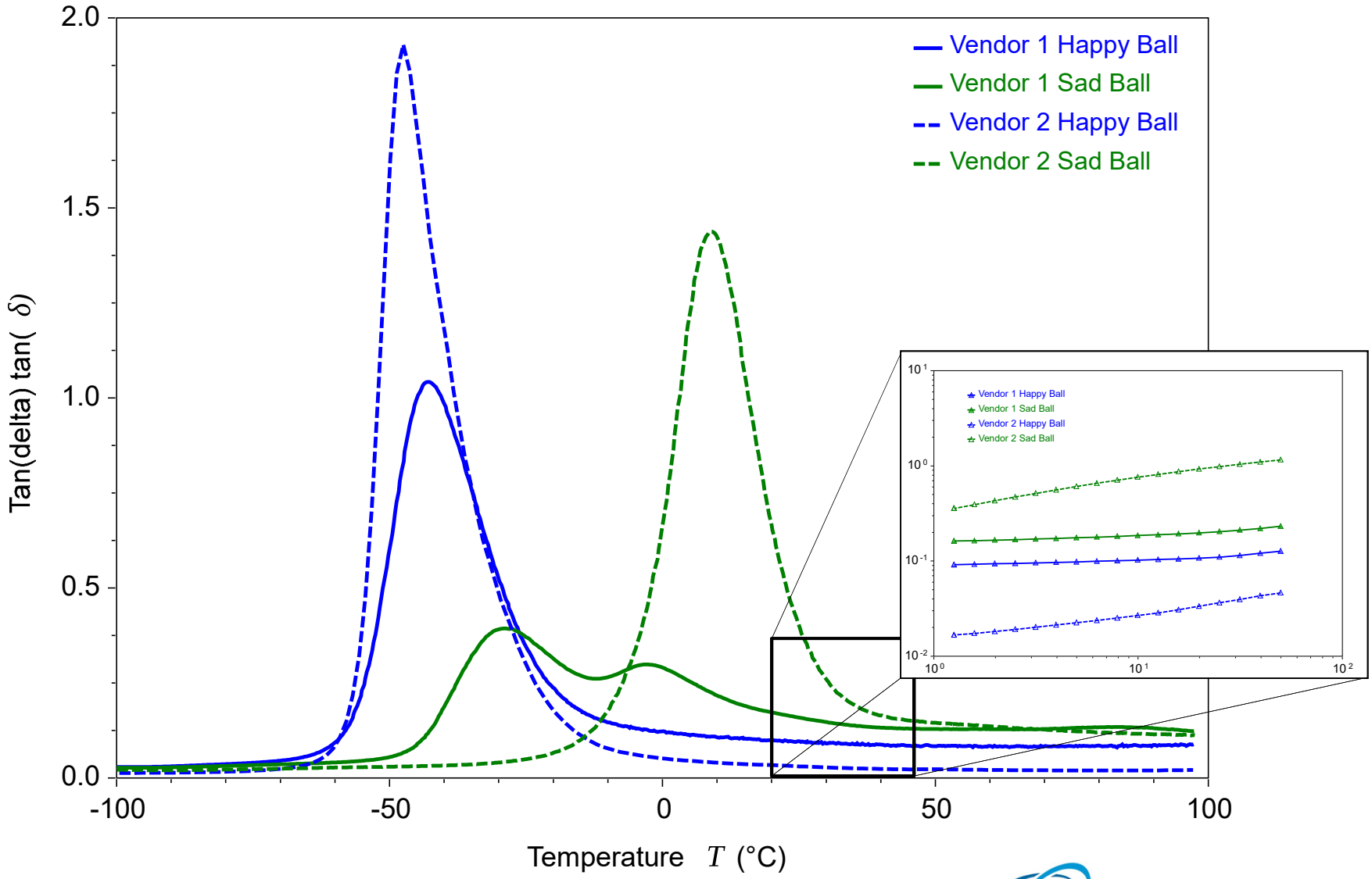
DMA: Vendor 1



DMA: Vendor 2



Comparison of Glass Transitions, Vendors 1 & 2



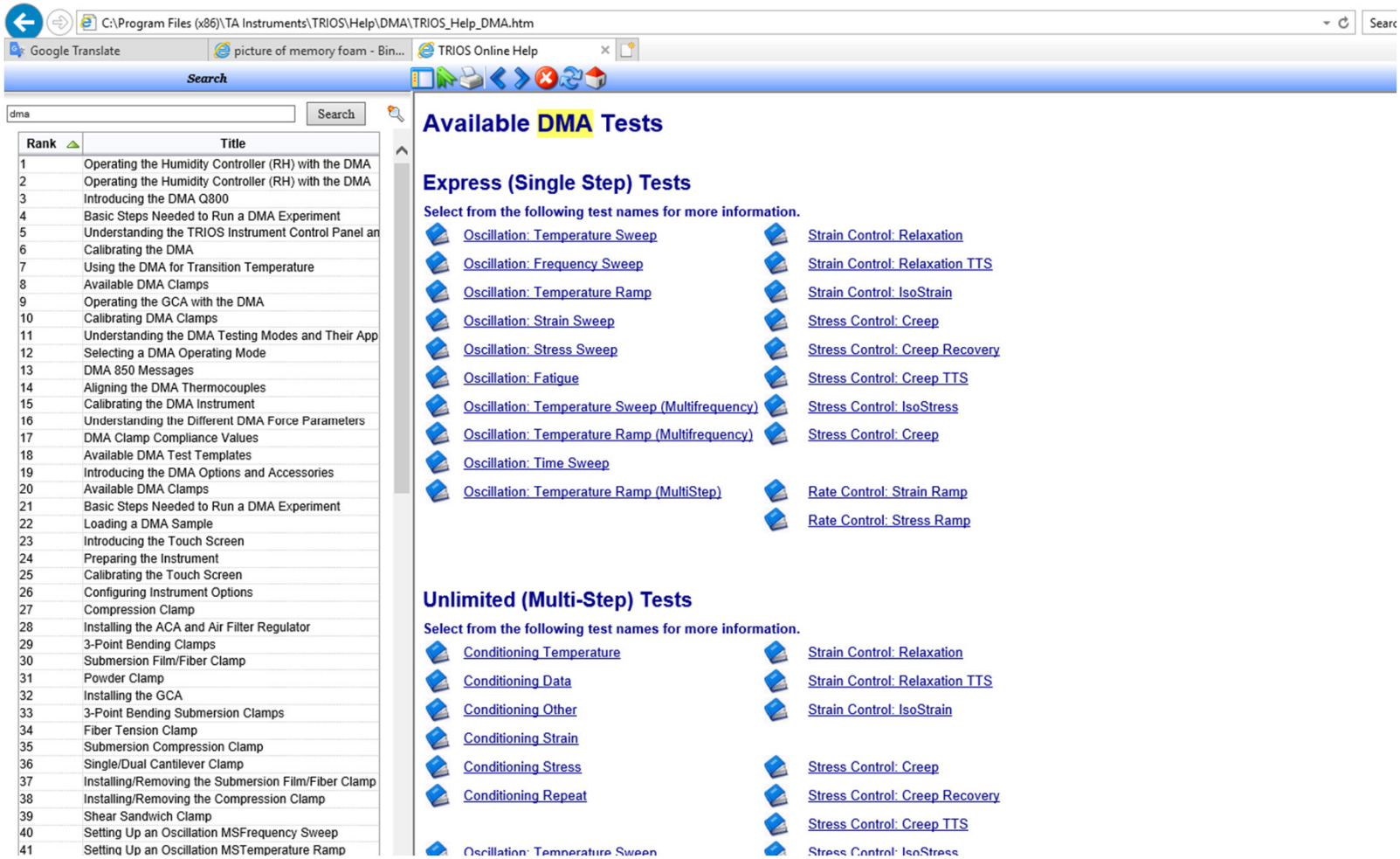
Summary of Results

- TGA
  - Quantified the basic components of the compound.
  - Saw **higher filler loading** in rubber from Vendor 1.
  - Other applications:
    - Use evolved gas analysis (mass spec, FT-IR) to identify components separately
- DSC
  - **Ruled out extent of cure** as a root cause for performance problems.
  - Saw differences in glass transition, melting in rubber from Vendor 1.
- DMA
  - Measured Tan Delta, **quantifying the performance difference**.
  - Observed glass transition in detail, learned the Vendor 1 Sad Ball is a **blend of elastomers.**
  - Other applications:
    - Creep-Recovery and Stress Relaxation, to mimic response in end use.

Rheology Applications Resources

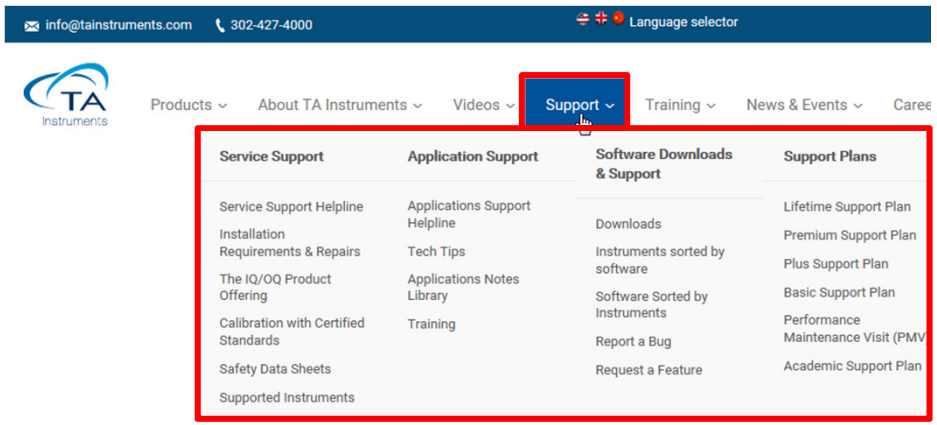
How do I get started using my new rheometer?	• Quick Start Guides (e-Training) video • "Getting Started Guide"(desktop shortcut)
How do I load my sample?	• TA Tech Tips
What kind of test should I use on my sample?	• Applications Notes • "Practical Approach to Rheology"
What parameters should I use in my procedure?	• TRIOS Help files • TA Tech Tips • rheologysupport@tainstruments.com
What do these measurements tell me about my sample?	• Webinar: "Essential Tools for the New Rheologist," Neil Cunningham
How can I be confident in the quality of my data?	• "Strategies for Better Data" • Webinar: "Experimental Challenges of Shear Rheology; How to Avoid Bad Data" Randy Ewoldt
How do I analyze my data in TRIOS?	• Quick Start Guide: TRIOS Analysis • TRIOS Help files

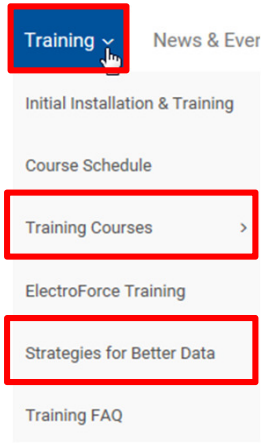
Trios Online Help Manual



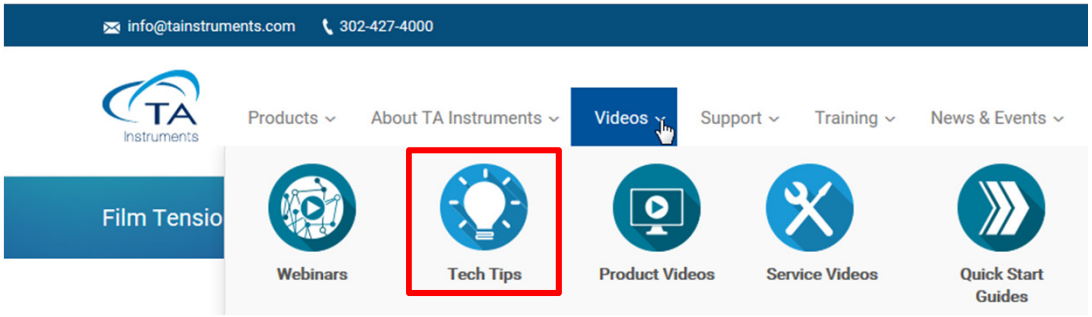
Instructional Videos

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





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



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

Instructional Video Resources

Quickstart e-Training Courses

DMA Q800 Quickstart Course – Instrument and Experimental Setup

DMA Q800 – Analysis Quickstart

Universal Analysis QuickStart Course

Universal Analysis Advanced E-Training

Universal Analysis Custom Report

Web based e-Training Courses

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

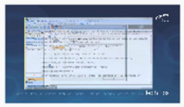
QUICKSTART e-TRAINING COURSES

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

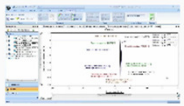
Contact Us for Web based e-Training Courses

Search Results for "TRIOS"

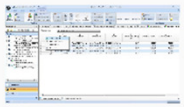
Discovery DSC – TRIOS Data Analysis



TRIOS Guardian — a tool to aid in 21 CFR 11 compliance



TRIOS – Analysis in Overlay



TRIOS – Analysis Reports

TRIOS – Cox Merz Transformation

Help with TA Instruments

- Check the manuals, TRIOS help.
- Contact the Applications Helpline
  - rheologysupport@tainstruments.com
  - thermalsupport@tainstruments.com
- Contact the Service Helpline
  - servicehelpline@tainstruments.com
- Call your local Technical or Service Representative
- Visit our Website www.tainstruments.com for training videos, TA Tech tips, application notes and much more!

Thank You

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