

# Rheology: Basic Theory and Applications Training

## Section #2

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TA Instruments – Waters LLC



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# Agenda

## Section 1 (2 hours)

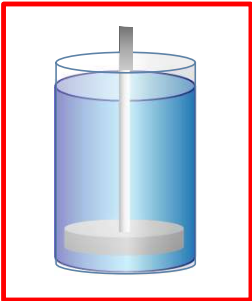
- Basics in rheology and instrumentation
  - Rheology theory
  - How rheometers work and geometry selections
- Introduction to all rheological methods
  - Flow experiments
  - Oscillatory experiments
  - Transient experiments

## Section 2 (2 hours)

- Rheology Applications- how to select correct geometries and test methods
  - Structured fluids
    - Low viscosity liquids
    - Creams/slurries/pastes
    - Gels and soft solids
  - Polymers
    - Polymer melts
    - Reactive polymers
    - Solid polymers

# What Rheology Measures

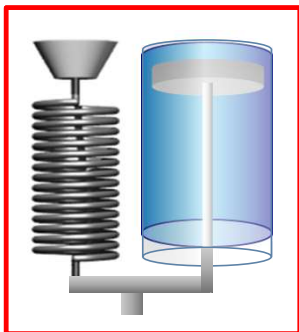
- **Viscosity (Liquids)**



- **Elasticity (Solids)**



- **Viscoelasticity (Liquids to Solids)**



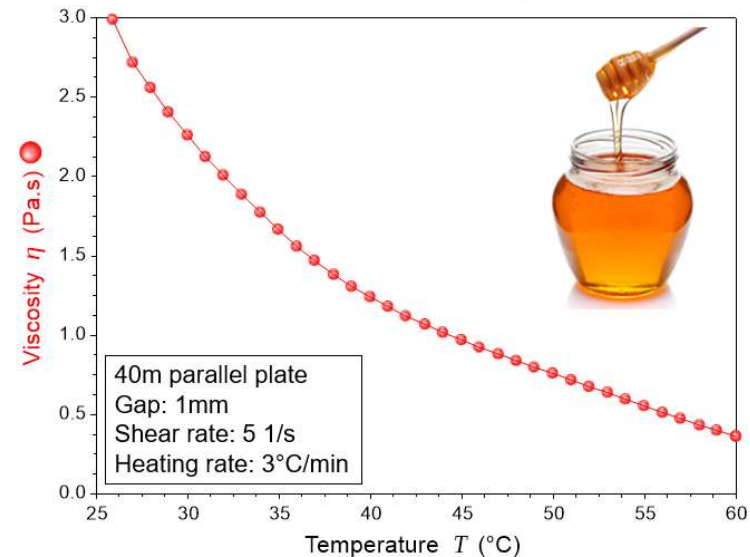
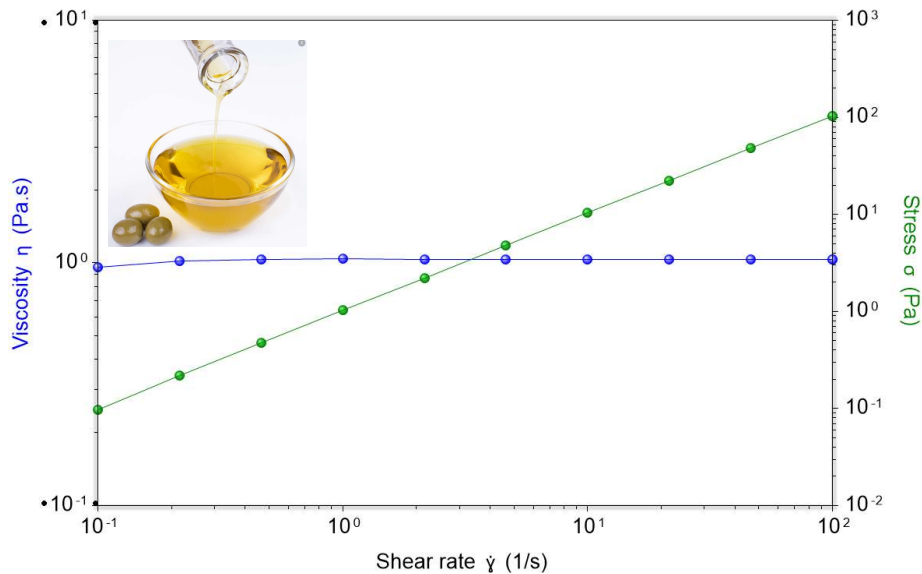
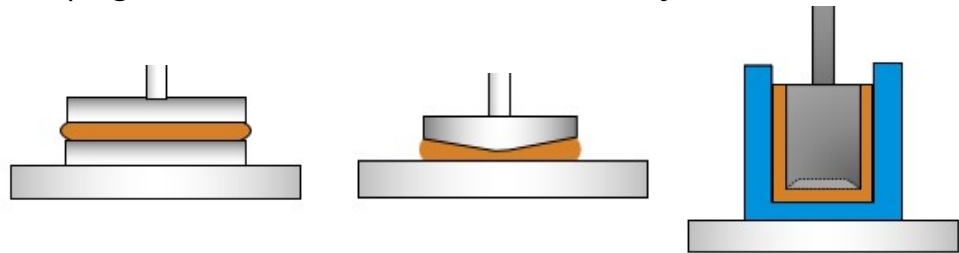
# Rheology Applications

## 1. Structured Fluids and Soft Solids



# Low Viscosity Liquids – 1. Newtonian

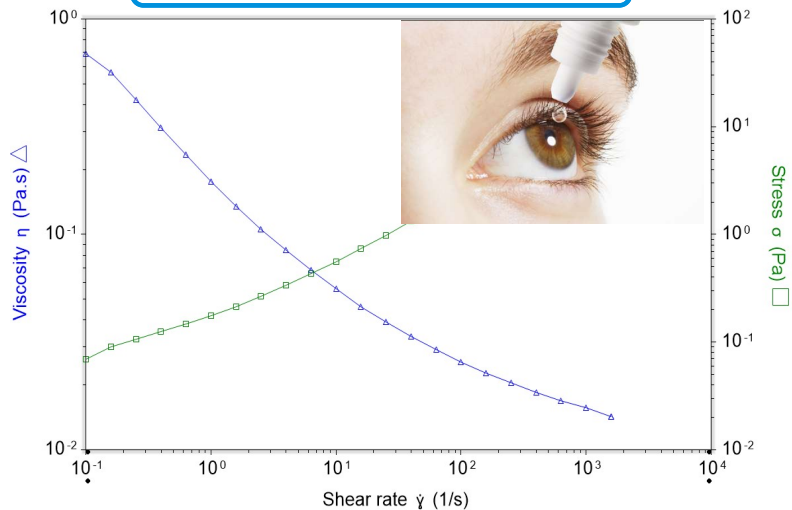
- What geometry to use?
  - Large diameter cone-plate or parallel plate (e.g. 60mm, 40mm, concentric cylinder cup/rotor).
- What methods?
  - Isothermal viscosity
  - Viscosity versus temperature



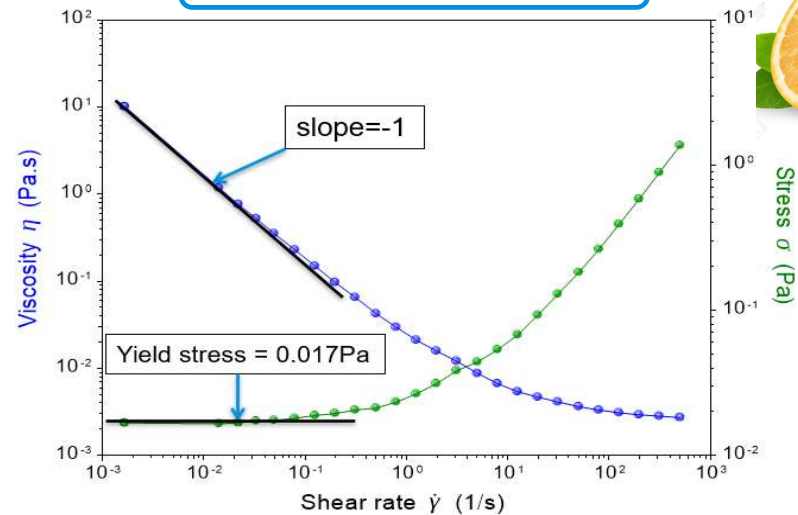
# Low Viscosity Liquids – 2. Non-Newtonian

- What geometry to use?
  - Large diameter cone-plate or parallel plate(e.g. 60mm, 40mm, concentric cylinder cup/rotor.
- What methods?
  - Isothermal viscosity versus shear rate/stress
  - Yield stress – why orange juice has no phase separation?

Eye drop: Shear thinning

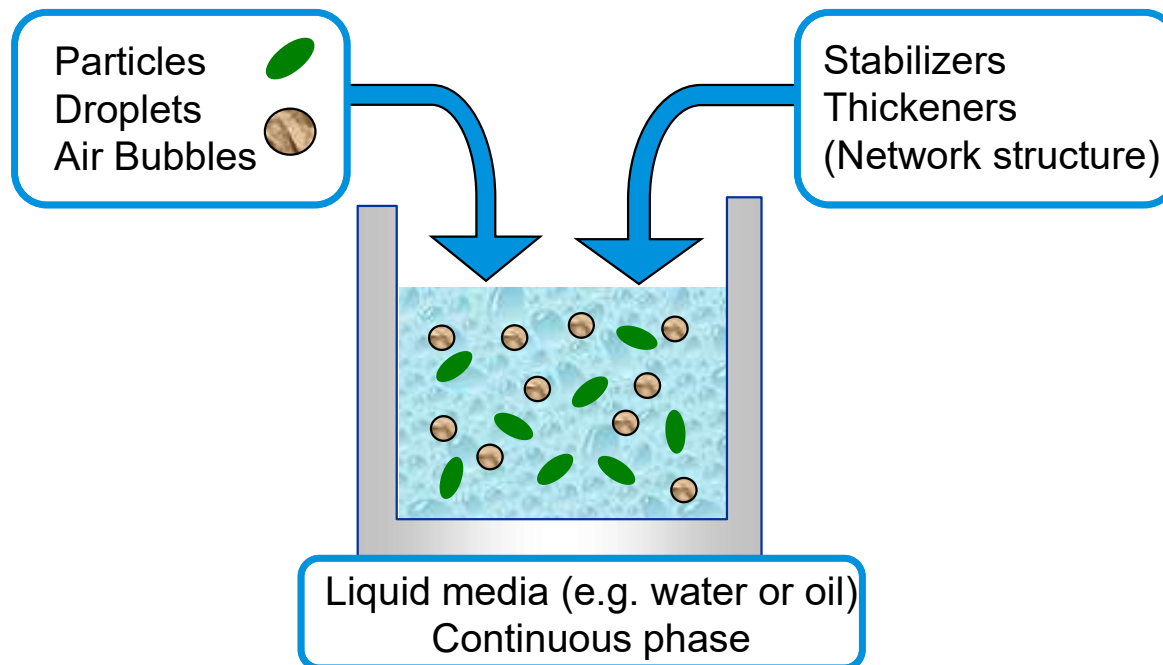


Orange Juice: Yield



# Structured Fluids

- A multiphase complex system consists of a continuous phase (e.g. water or oil) and a dispersed phase (solid, fluid, gas)
- Stabilizers or thickeners are added to form a weak three-dimensional network structure



# Types of Structured Fluids

- Three categories

- Suspension      Solid particles in a Newtonian fluid
- Emulsion      Fluid in a fluid
- Foam            Gas in a fluid (or solid)

- Examples are:

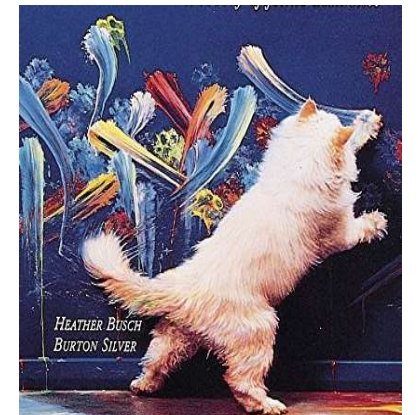
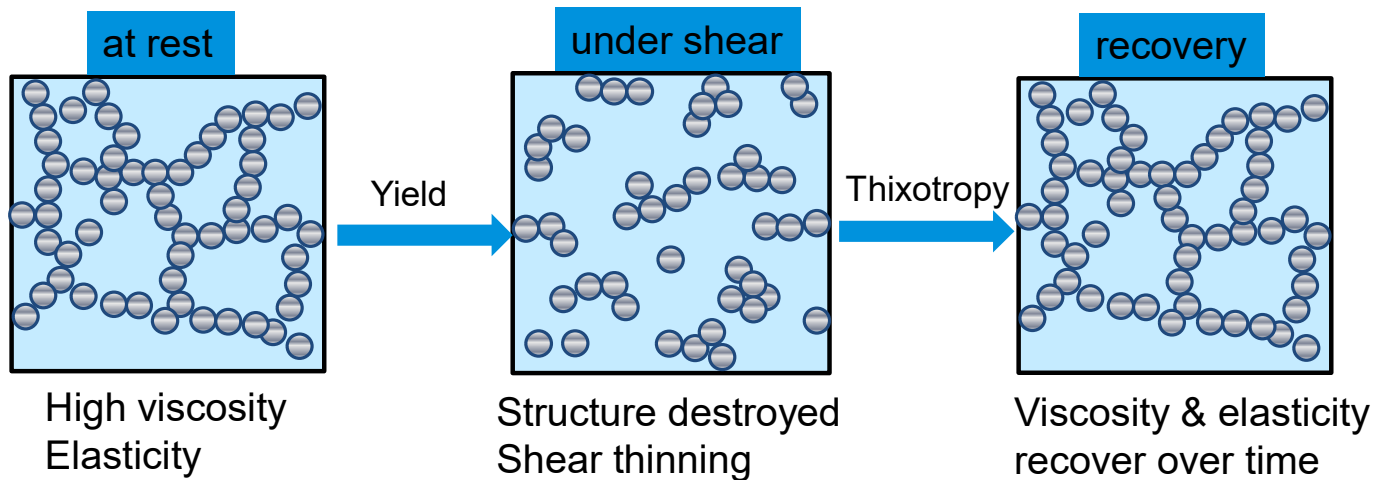
- Paints
- Coatings
- Inks
- Adhesives
- Personal Care Products
- Cosmetics
- Foods





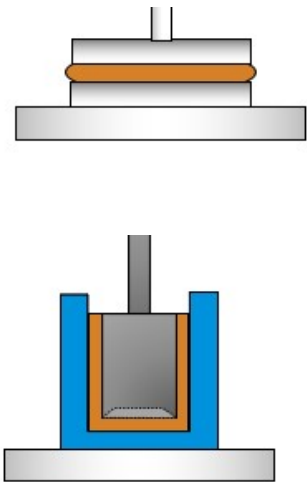
# Properties of Structured Fluids

- Structured fluid properties
  - Non-Newtonian
  - Yield stress
  - Thixotropic
  - Viscoelasticity

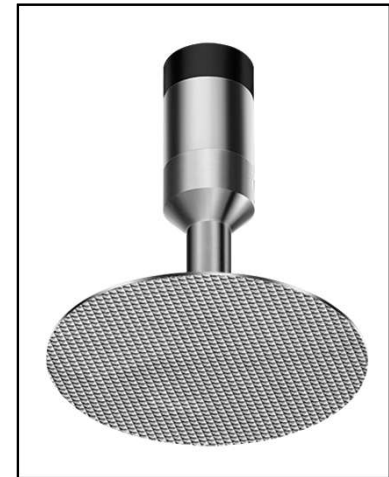


## What Geometry to Use?

- Parallel plate (e.g. 40mm, 25mm, 20mm)
- Roughen surface parallel plate (e.g. crosshatched, sandblasted)
- Concentric cylinder cup with vane or helical rotor

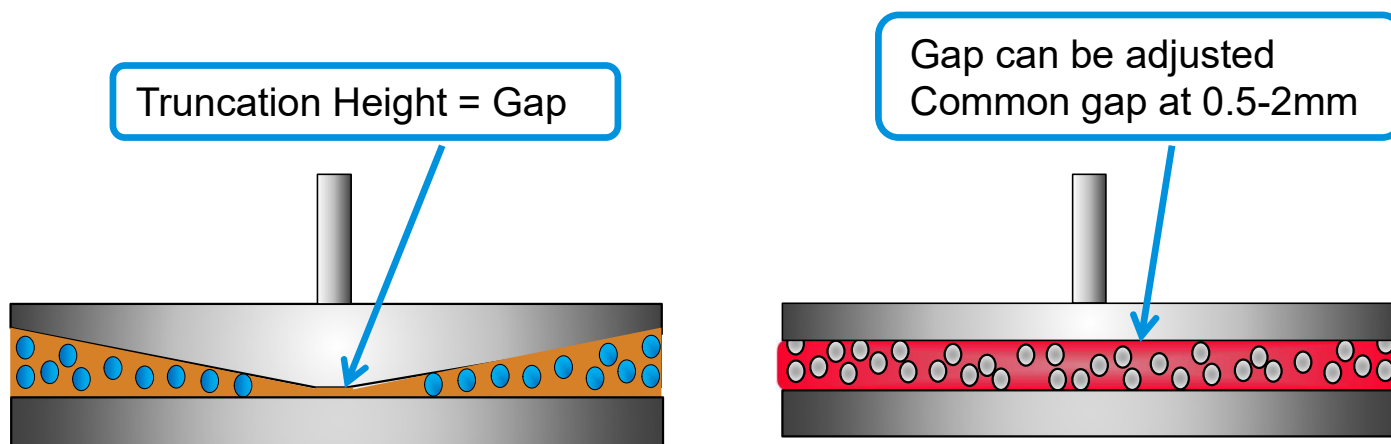


Avoid slippage

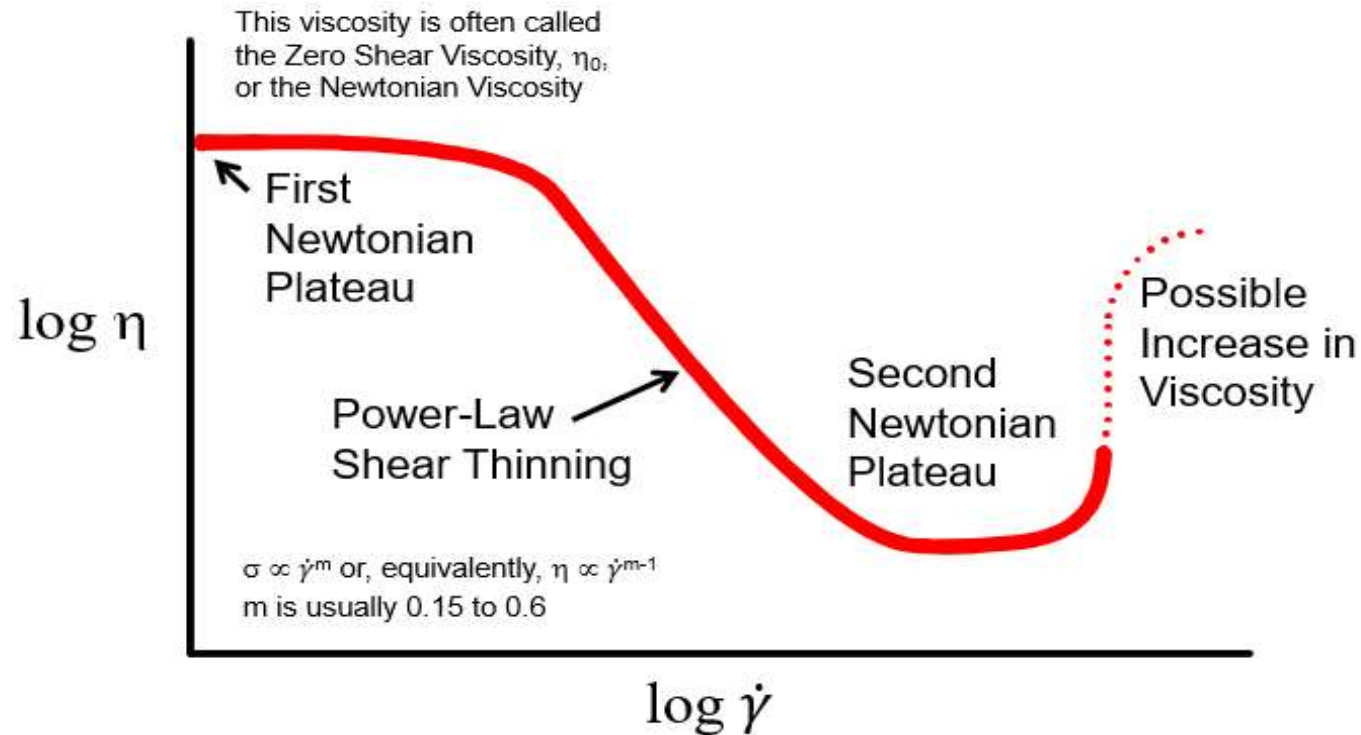


## Be Careful When Using a Cone and Plate

- Most structured fluids contain particles with size in the micrometer range
- Depending on the cone angle, the truncation gap of a cone geometry will be between 10 and 120  $\mu\text{m}$
- Parallel plate geometry is recommended

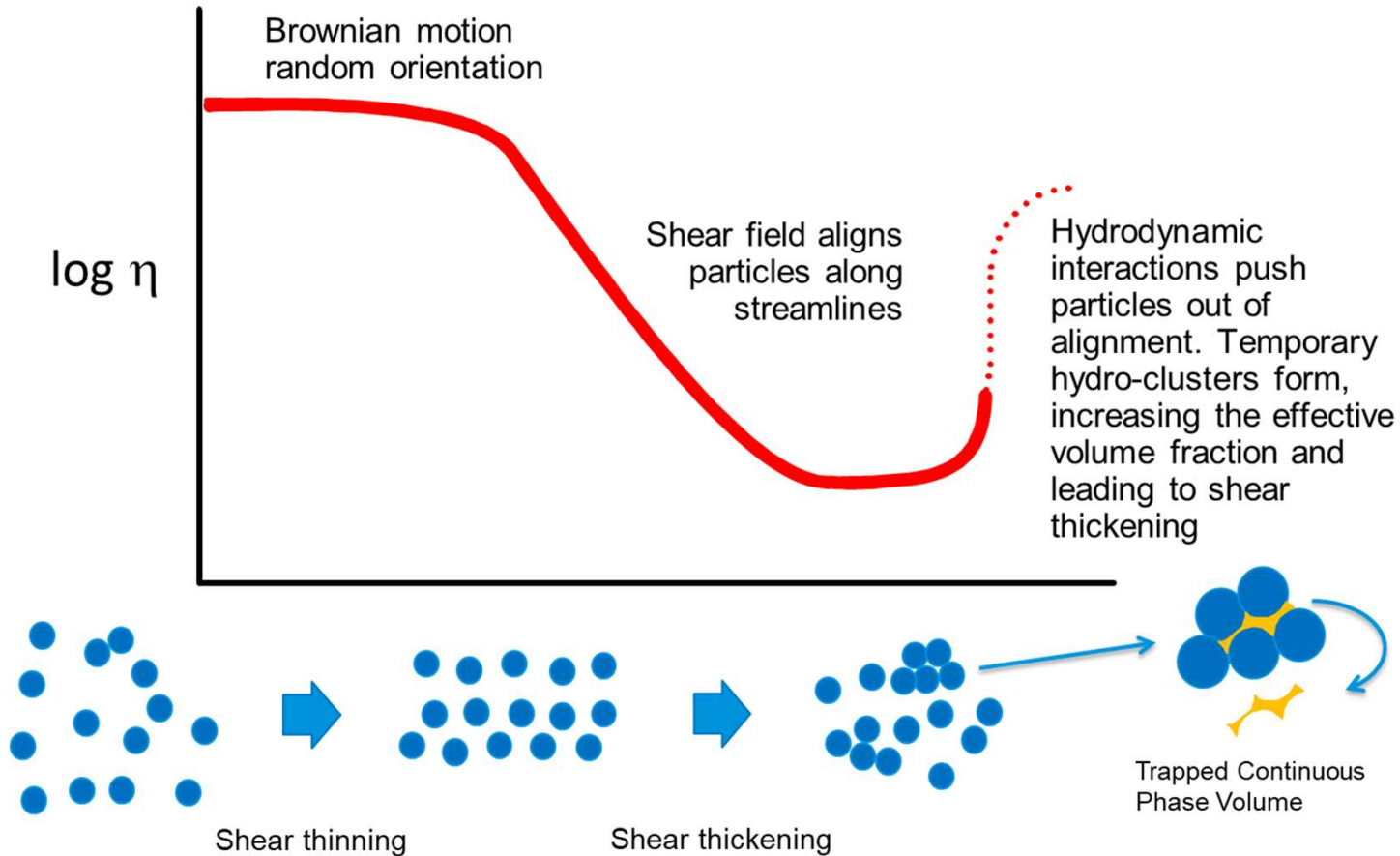


# General Viscosity Curve for Suspensions



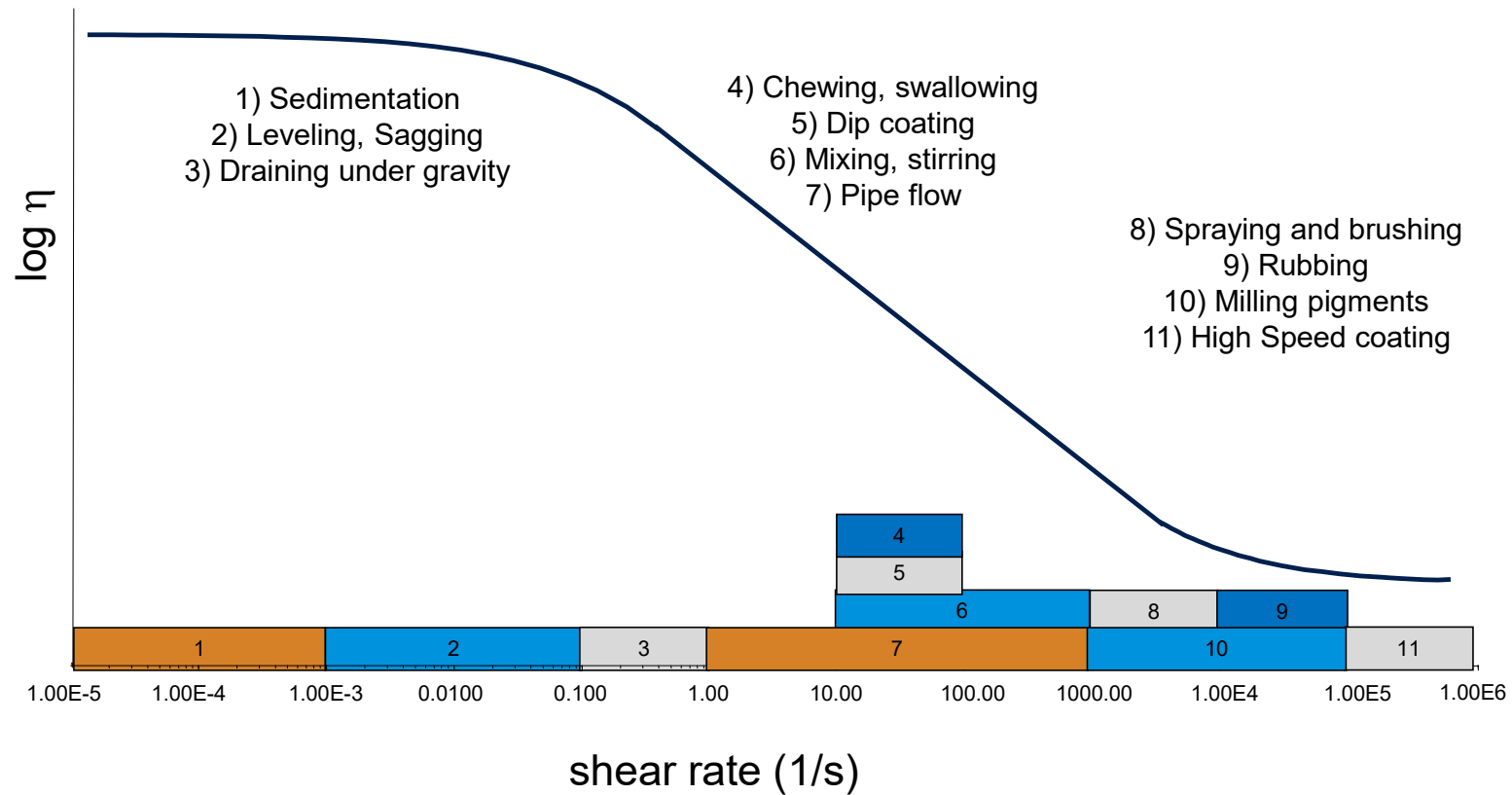
Reference: Barnes, H.A., Hutton, J.F., and Walters, K., An Introduction to Rheology, Elsevier Science B.V., 1989. ISBN 0-444-87469-0

# Reason for Shape of General Flow Curve

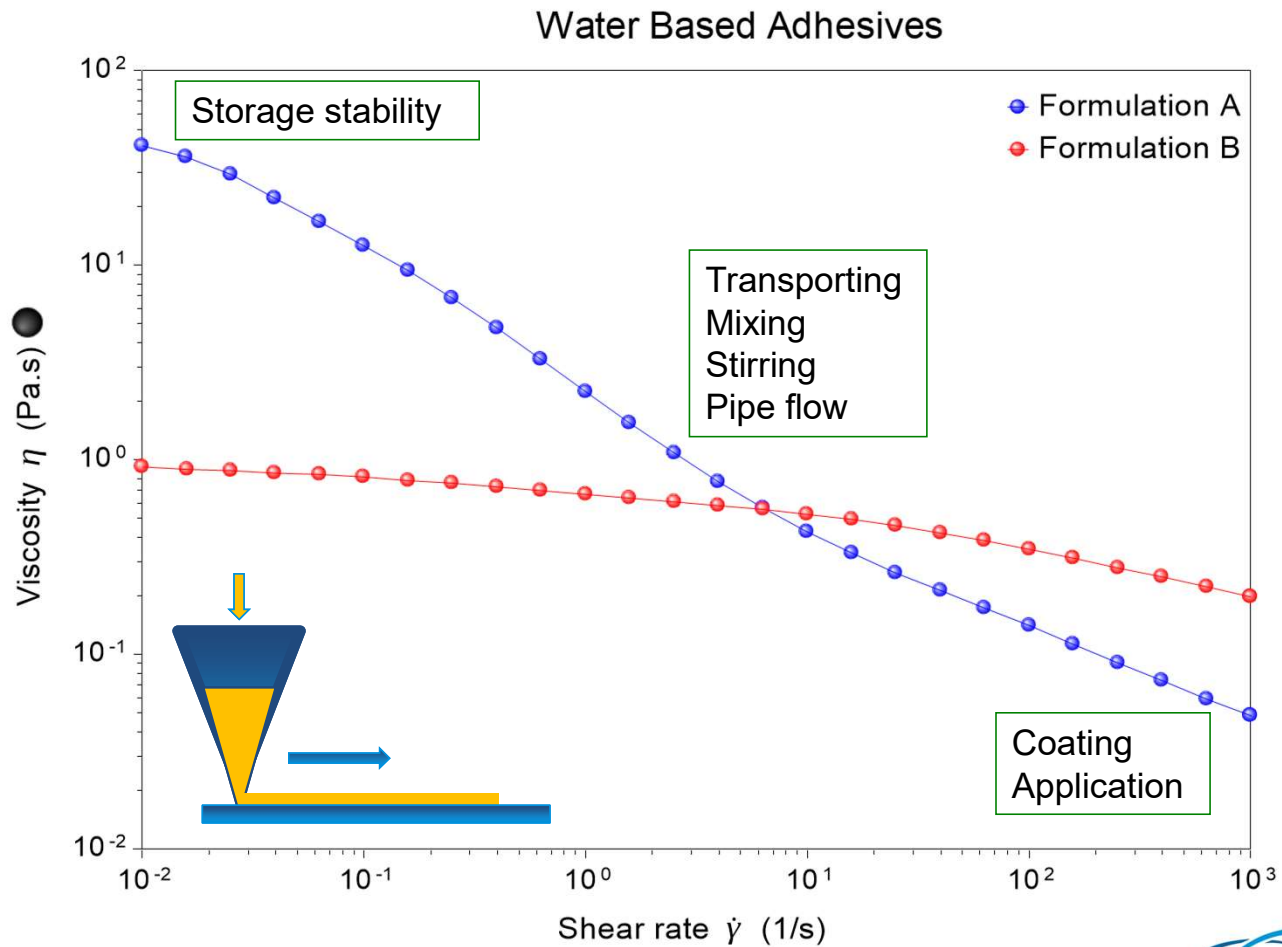


# Viscosity vs. Shear Rate and Properties

- What shear rate?



# Adhesive Coating Process: Viscosity Scan



# What is Yield?

- Yield stress is a time dependent characteristic that is associated with many structured fluids such as Mayonnaise, Ketchup, hand lotion, hair gels, paints etc.
- A material that has yield does not flow unless the applied stress exceeds a certain value – yield point
- Yield stress is created in formulation by adding additional thickeners
- Yield helps stabilize complex fluids
  - Avoid sedimentation and increase shelf life
  - Reduce flow under gravity
  - Stabilize a fluid against vibration





# How to Measure Yield

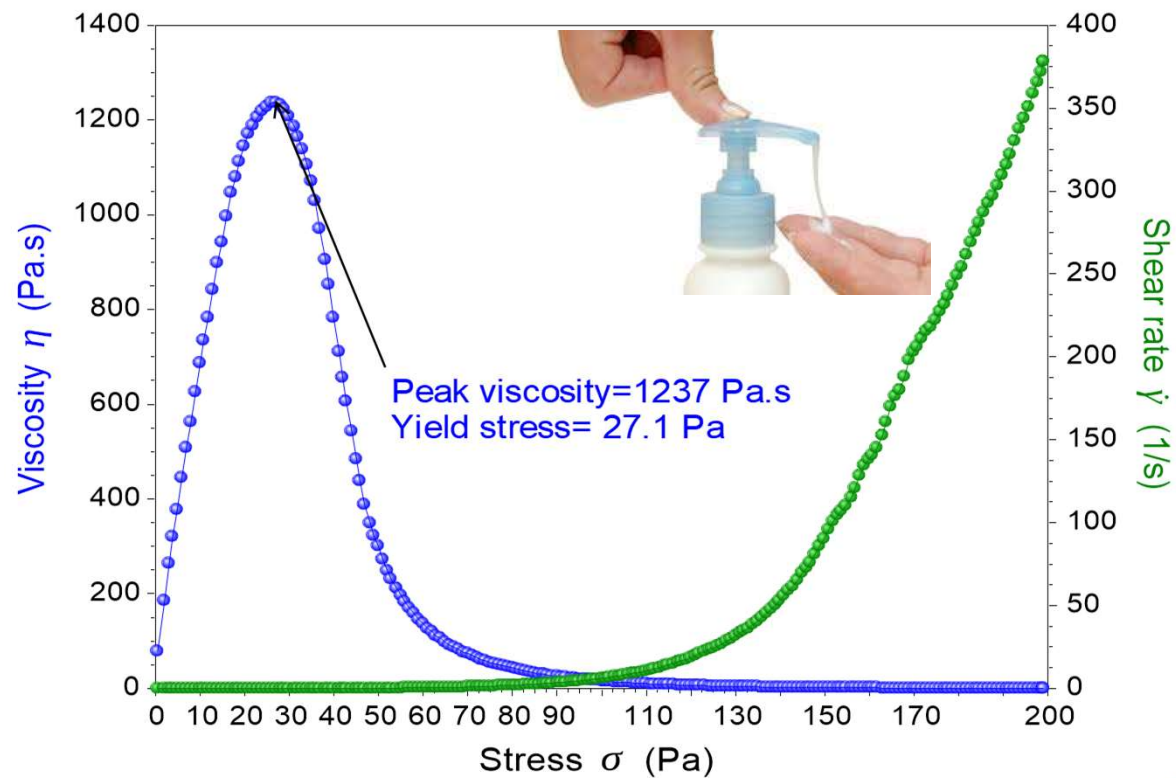
- Yield can be quantitatively measured on a rotational rheometer
- Common methods
  - Stress ramp
  - Stress sweep
  - Shear rate ramp
  - Dynamic stress/strain sweep

Note:

Yield behavior is a time dependent characteristic. Measured yield stress values will vary depending on experimental parameters

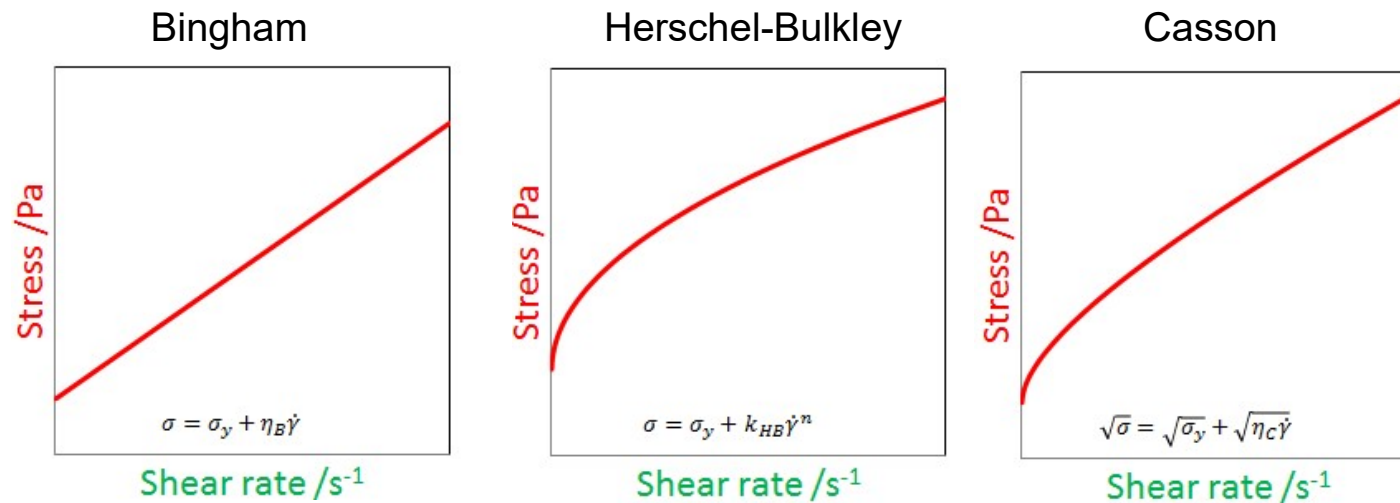
# Yield Stress of a Body Lotion

- Stress ramp from 0 to 200 Pa in 60 seconds
- Yield is determined at the point where viscosity shows a peak



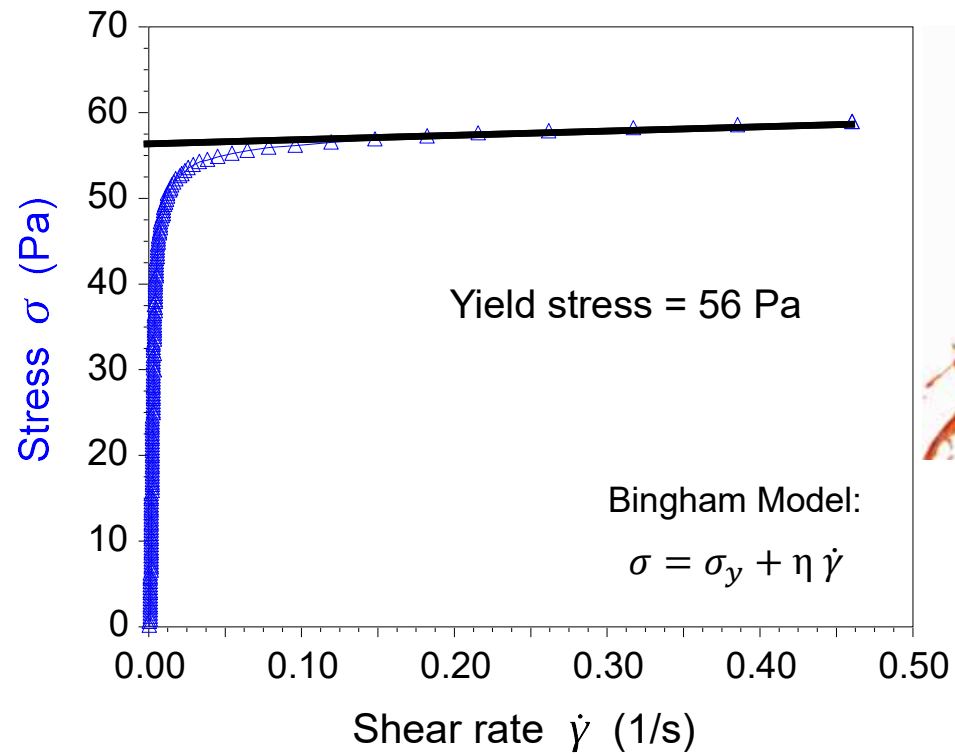
## Fit Results with a Flow Models

- Fit the stress ramp curves with a mathematical flow model
- Three flow models to describe the yield behavior



# Yield Stress of Ketchup

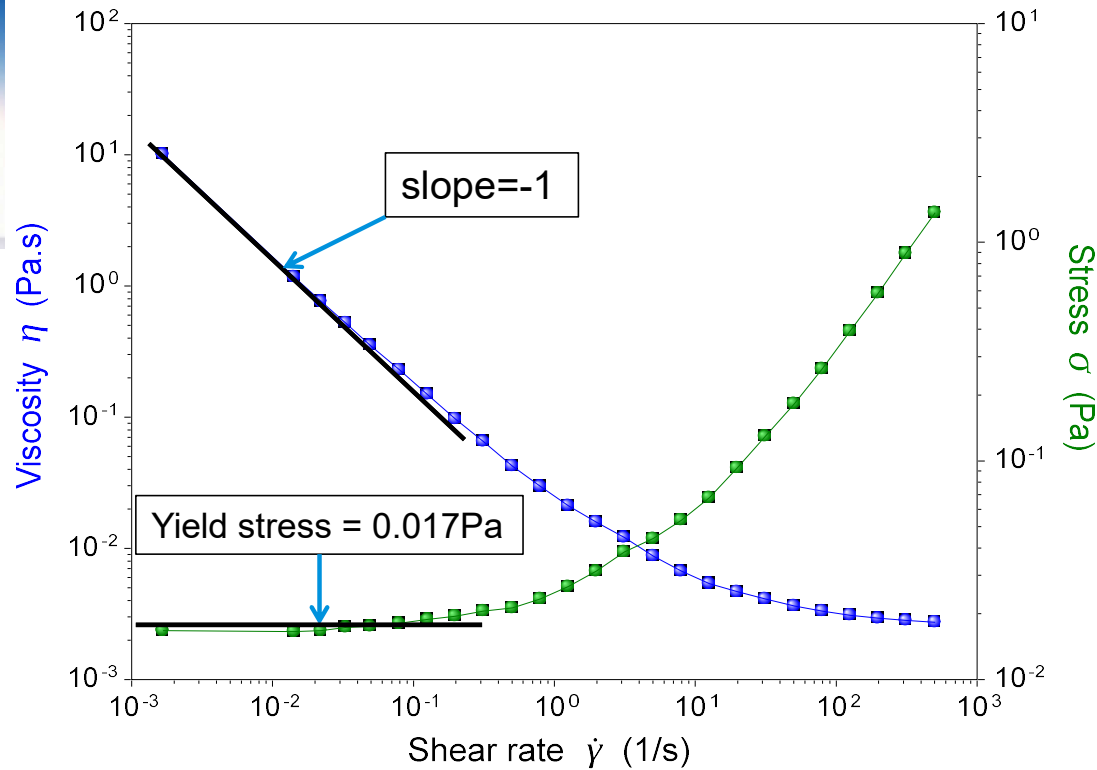
- Stress ramp test on Ketchup
- Yield is computed by fitting the flow curve with a mathematical model



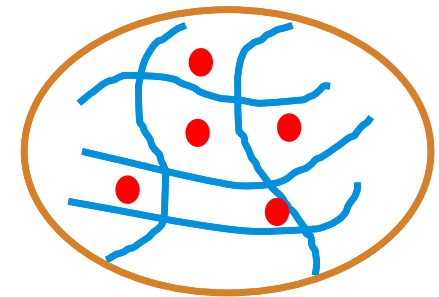
# Yield Stress of Orange Juice



- Shear rate ramp down from 500 to 0.001 1/s
- Yield is identified by the stress plateau

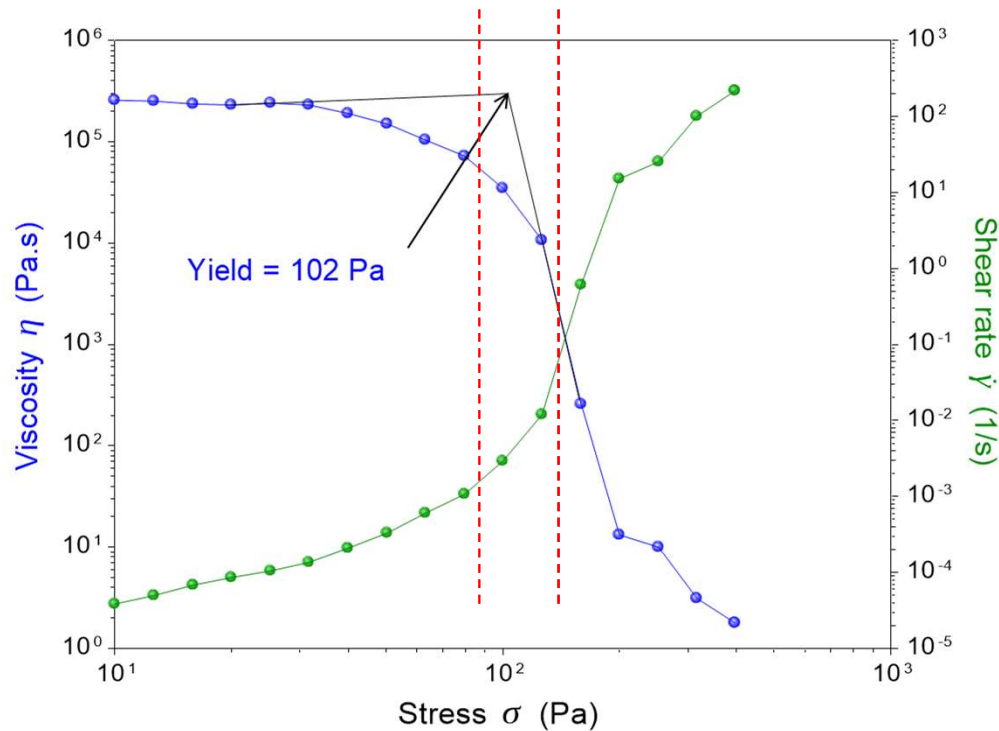


No settling?!



# Yield Stress of a Toothpaste

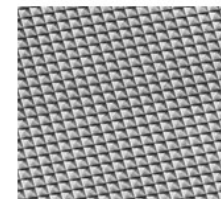
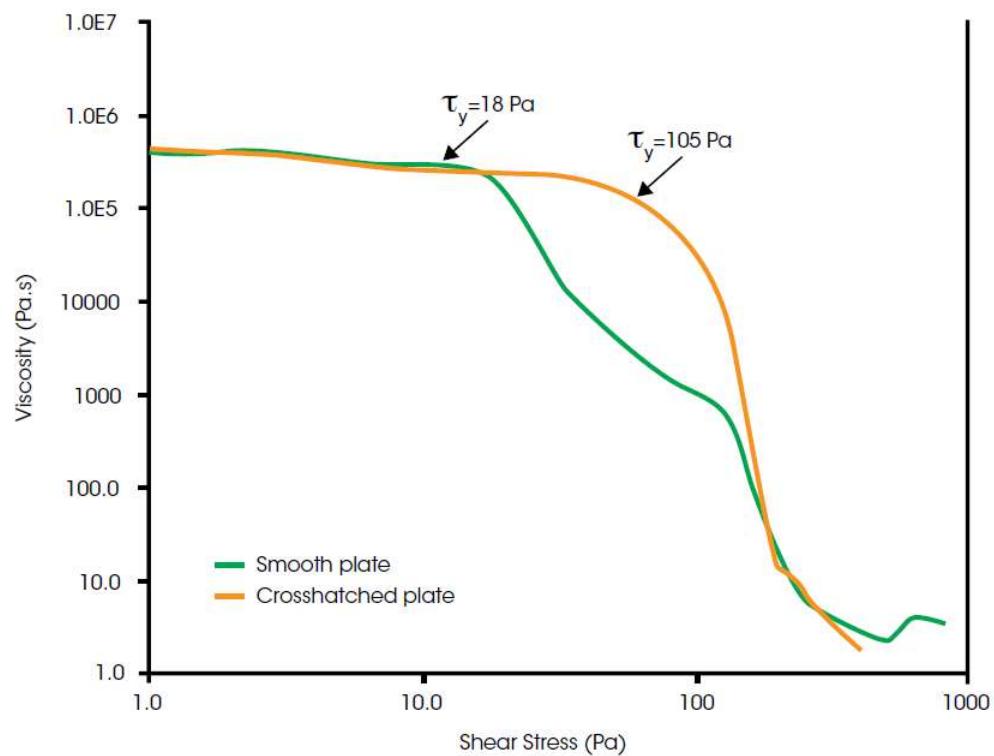
- Steady state stress sweep from 10 Pa to 500 Pa
- Yield stress is determined by a sharp decrease in viscosity over a narrow range of applied shear stress
- Take the onset of viscosity vs. stress curve



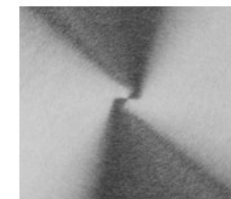
# Wall Slip – Artifact Yield

- Incidence of wall slip is often observed when testing structured fluids
- Wall slip shows artifact yield

Yield Stress Measurements on Toothpaste



crosshatched plate

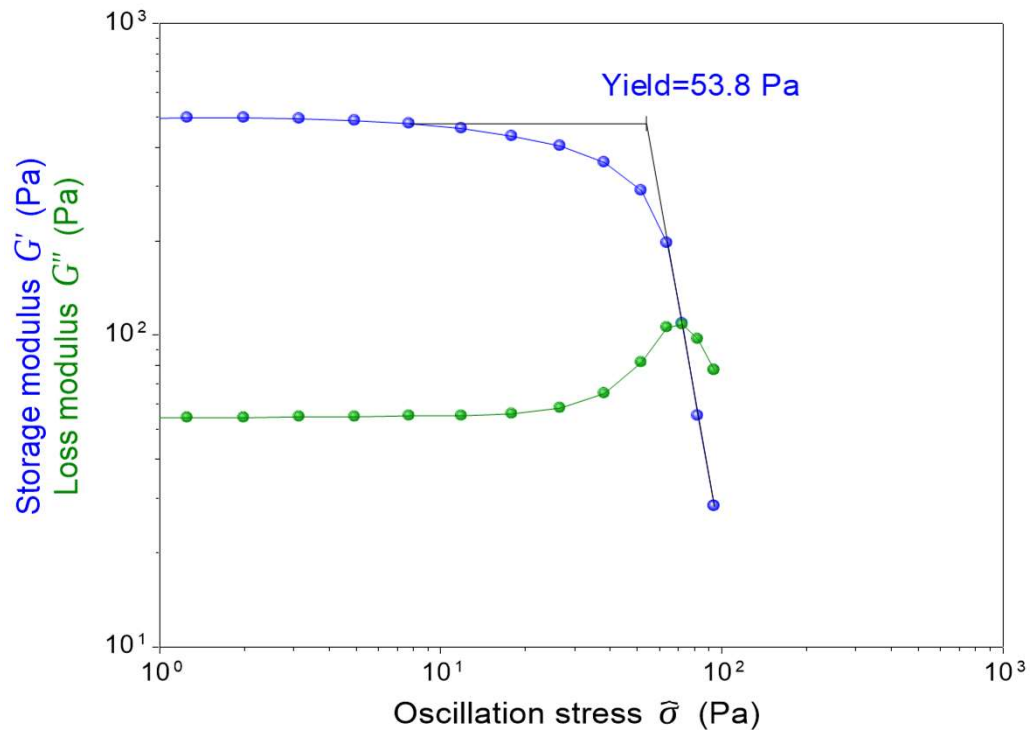


smooth plate



# Yield Stress of Mayonnaise

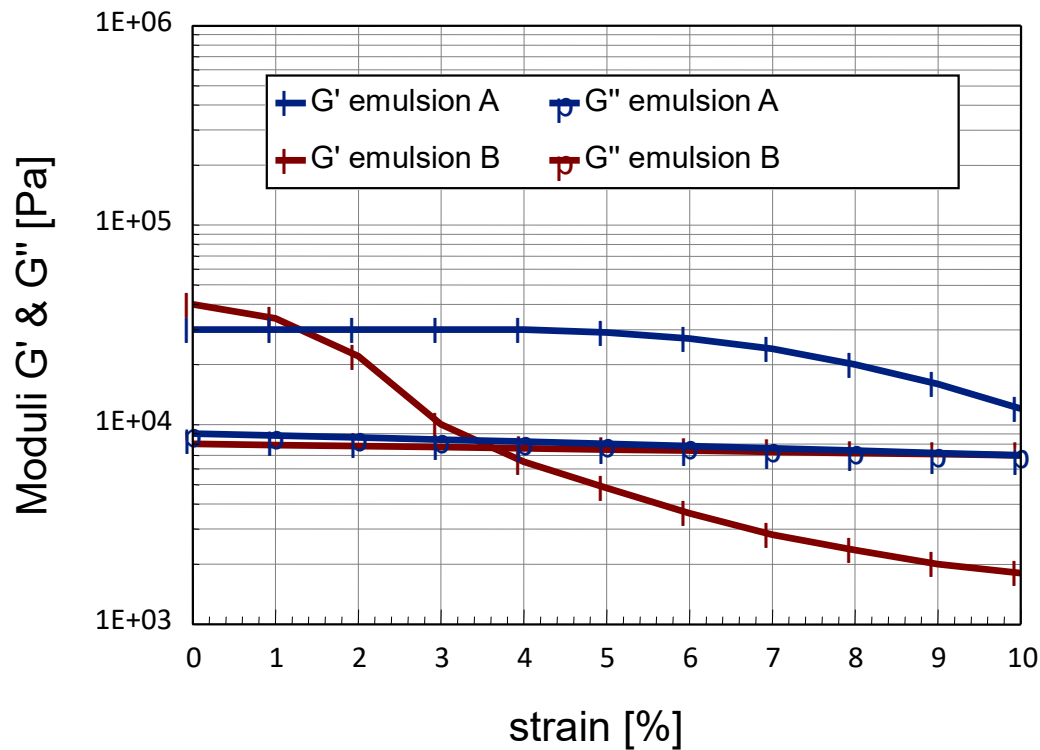
- Dynamic stress/strain sweep test on Mayonnaise
- Yield stress is signified at the onset of  $G'$  vs. stress curve
- Yield determined by this method indicates the critical stress at which irreversible plastic deformation occurs





# Creams/Lotions: Predict Stability

## Stability, phase separation of a cosmetic cream



# What is Thixotropy?

- Thixotropy is a time-dependent shear thinning property, which is used to characterize structure change reversibility
- A thixotropic fluid takes a finite time to attain equilibrium viscosity when introduced to a step change in shear rate
- Thixotropy is a desired property for many applications such as:
  - Control sagging and levelling of paints
  - Start up of pipeline flow after rest



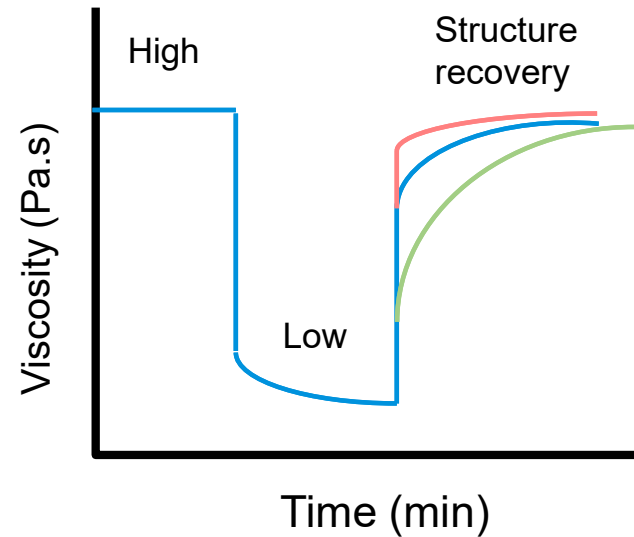
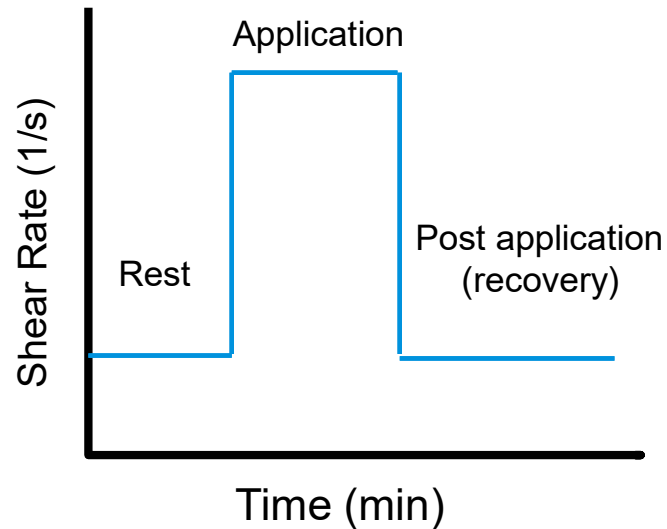
# How to Measure Thixotropy

- Thixotropy can be quantitatively measured on a rotational rheometer
- Common methods
  - Stepped flow method
  - Stepped dynamic method
  - Stress ramp up and down method (Thixotropic loop)
  - Dynamic time sweep after pre-shear method

**Note:**

Thixotropic behavior is a time dependent characteristic. Measured thixotropy will vary depending on experimental parameters.

# Stepped Flow Method



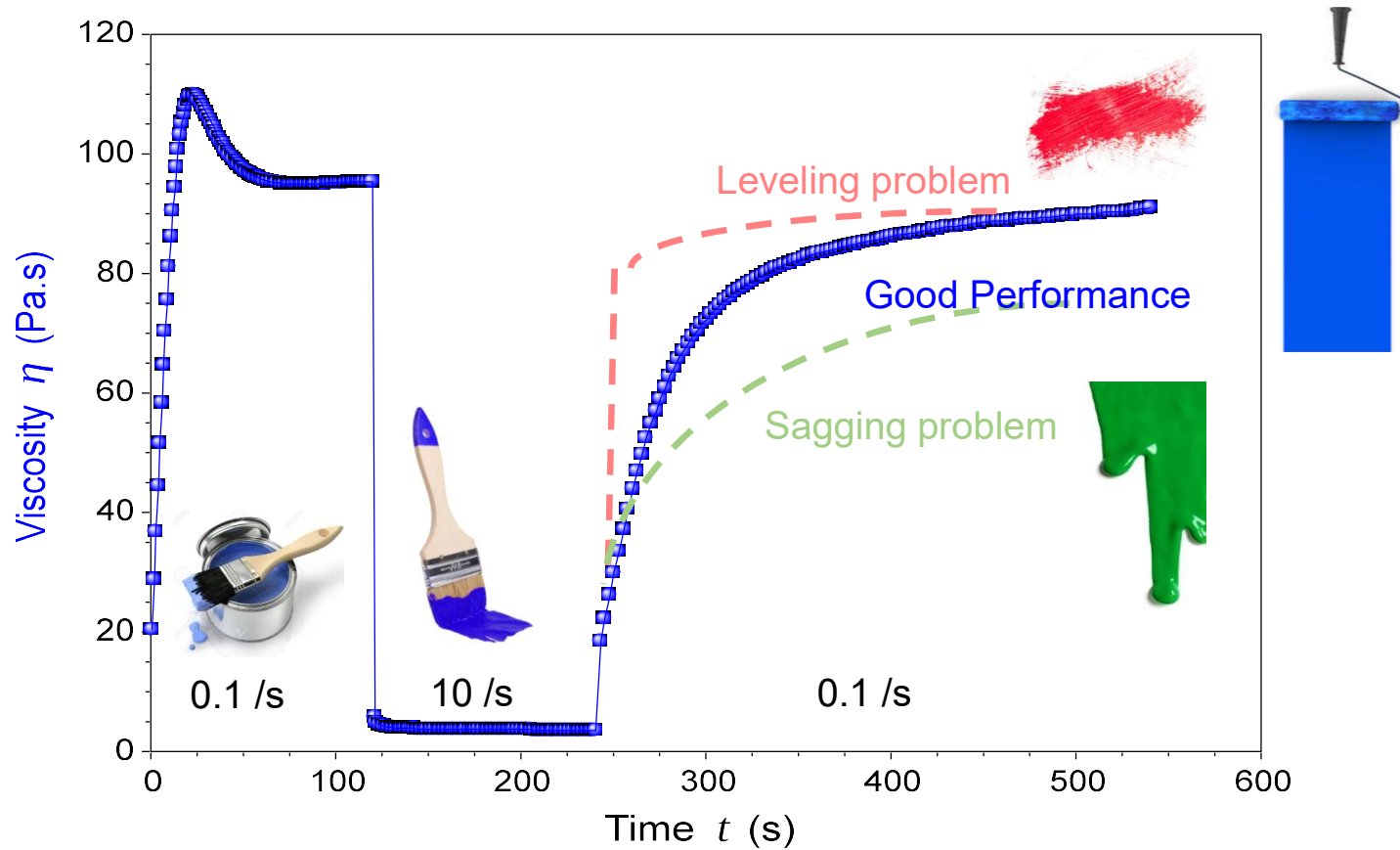
Experimental:

Step 1: Low Shear (e.g. 0.1 1/s), state of rest

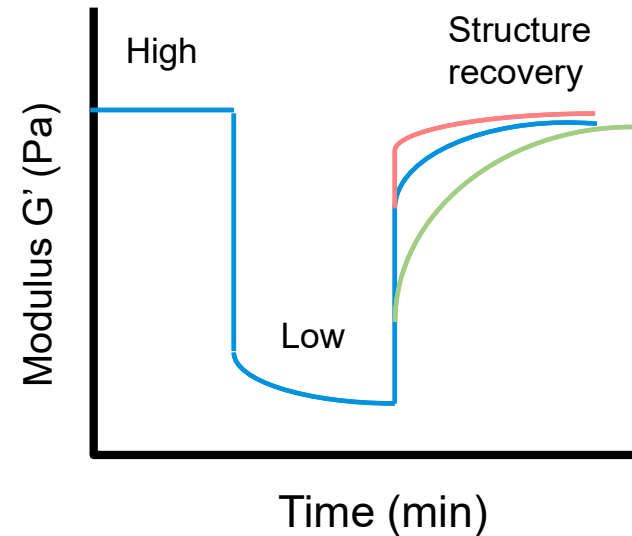
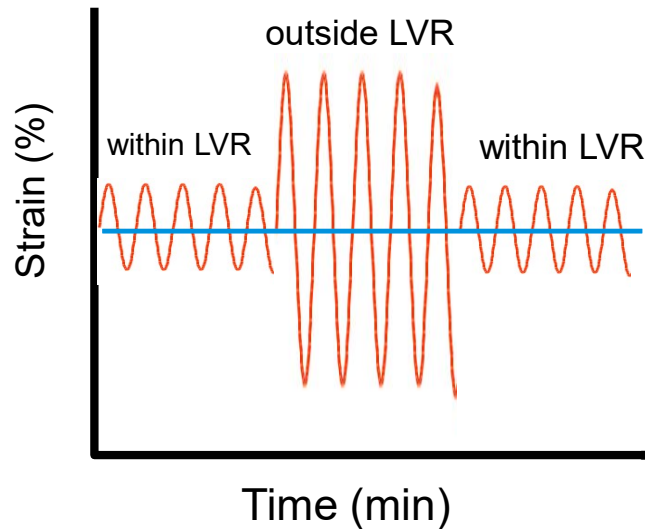
Step 2: High Shear (e.g. 10 1/s), structural destruction

Step 3: Low Shear (e.g. 0.1 1/s), structural regeneration

# Thixotropic Analysis of a Blue Paint



# Stepped Dynamic Method



Experimental:

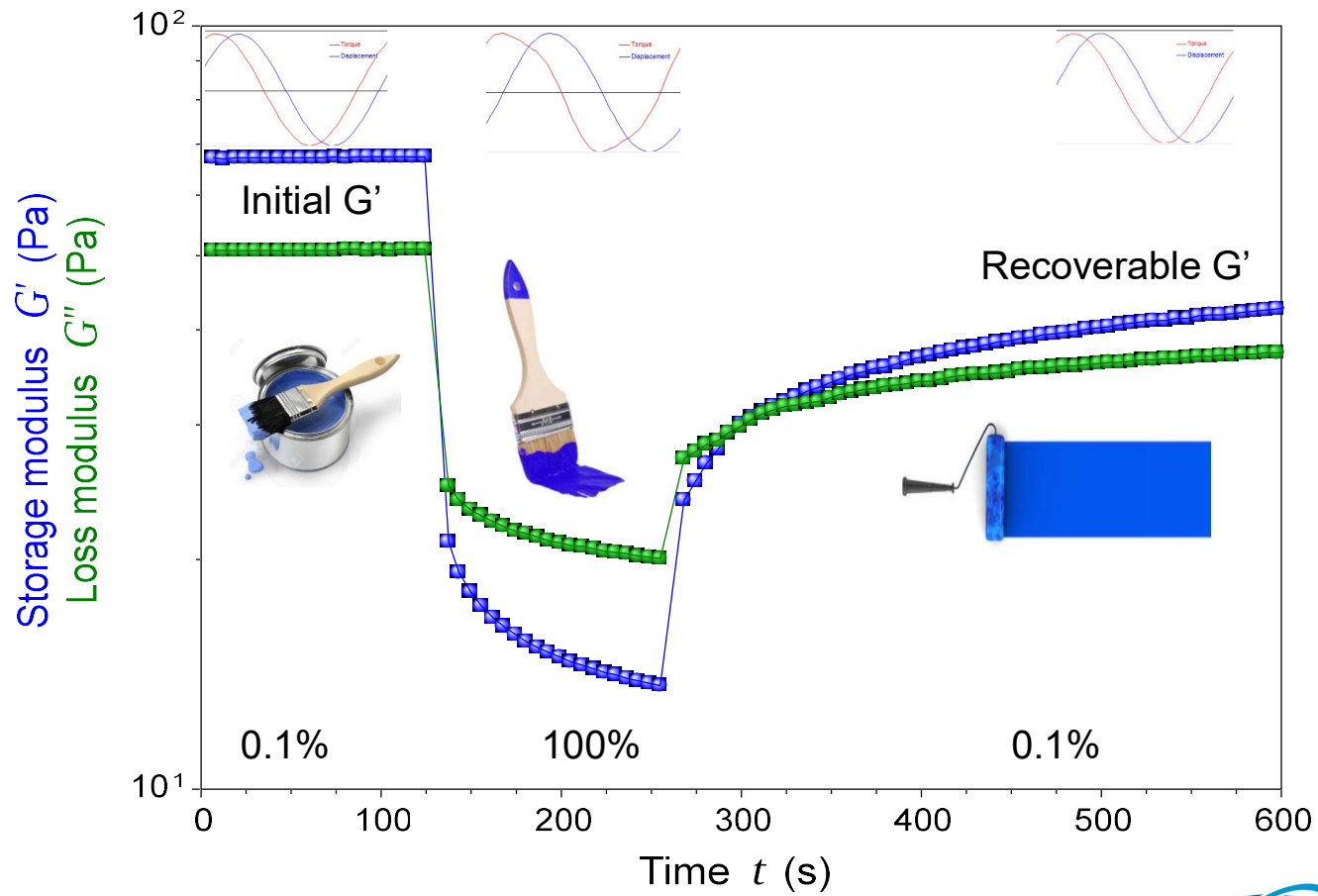
Step 1: Dynamic time sweep within LVR, structure at rest

Step 2: Dynamic time sweep outside LVR, structural destruction

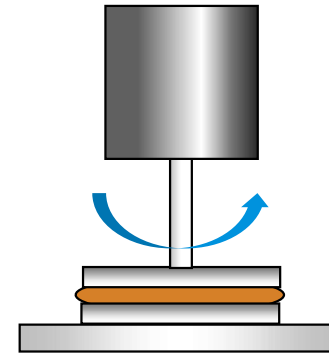
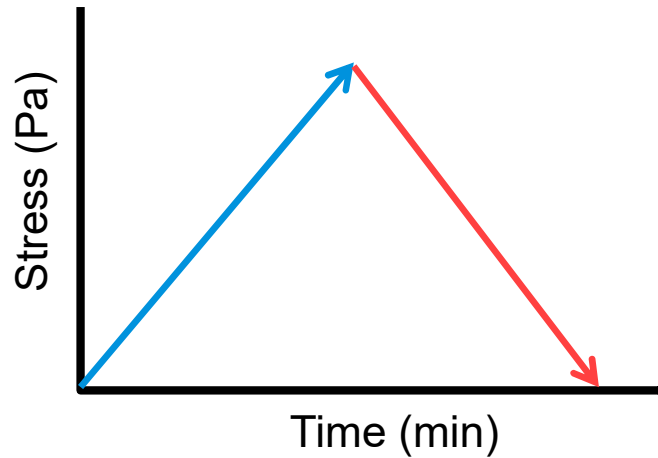
Step 3: Dynamic time sweep within LVR, structural regeneration

Good for measuring high viscosity samples

# Blue Paint: Stepped Time Sweep



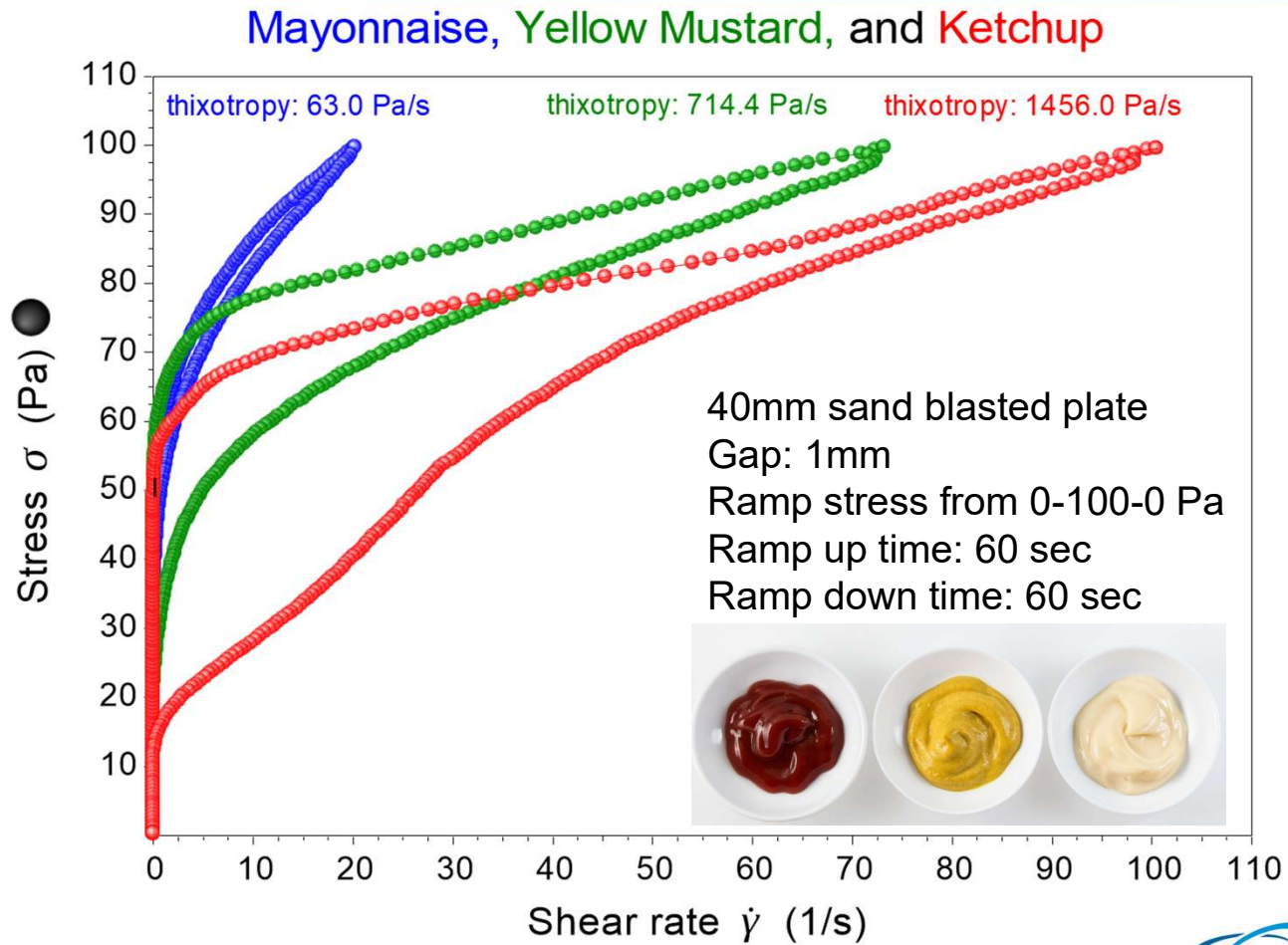
# Stress/Rate Ramp Up and Down Method



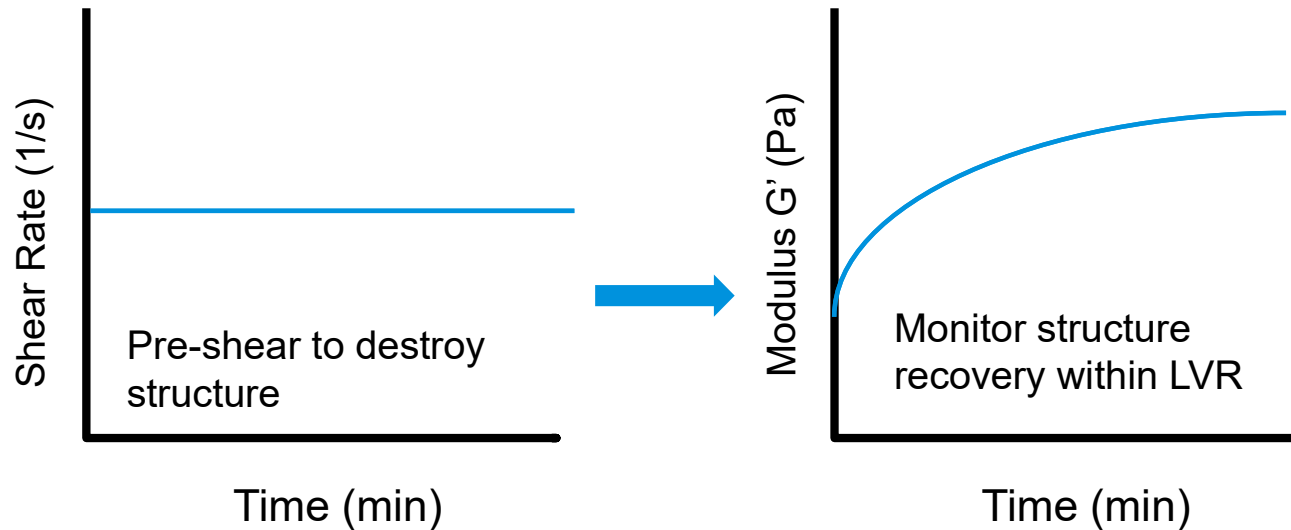
- Ramp shear stress linearly from zero up until sample flows, then ramp stress back down to zero
- Thixotropic index is measured by taking the area between the up and down stress curves
- TA Tech Tip: <https://www.youtube.com/watch?v=8lZangOp1SY>



# Thixotropic Loop Testing on Foods



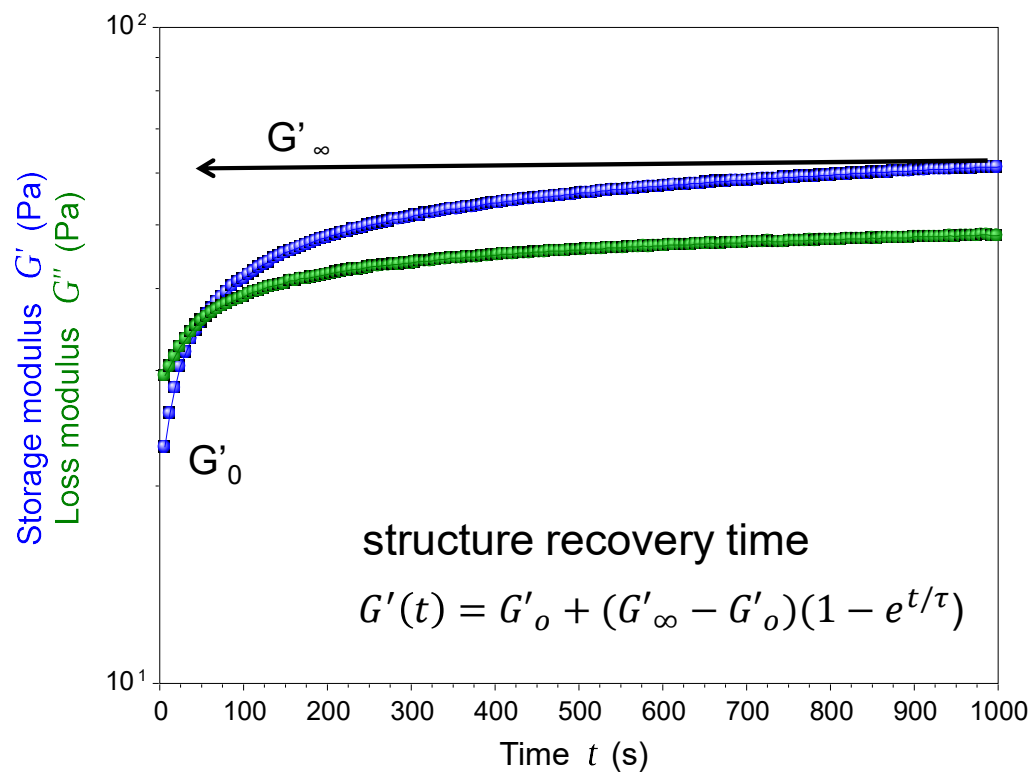
## Time Sweep After Pre-shear Method



- Apply a constant shear (e.g. 10 or 100 1/s) for a certain time (e.g. 1 min.) to break down structure
- Immediately start a time sweep within the linear region of the material to monitor structure recovery

# Blue Paint: Time Sweep After Pre-shear

- Monitor the increase of the  $G'$  as a function of time.
- Thixotropic recovery is described by measuring the recovery time ( $\tau$ )



# TA Practical Series Training Course

<https://www.tainstruments.com/a-practical-approach-to-rheology/>

- How to measure Yield stress
- How to measure Thixotropy
- How to avoid wall slip and edge fracture
- How to fit flow curves with models



## Viscosity Measurements on Liquids

The second chapter this four part series on rheology will cover viscous behaviors of liquids.

[View Archive](#)



## Yield and Thixotropy Measurements

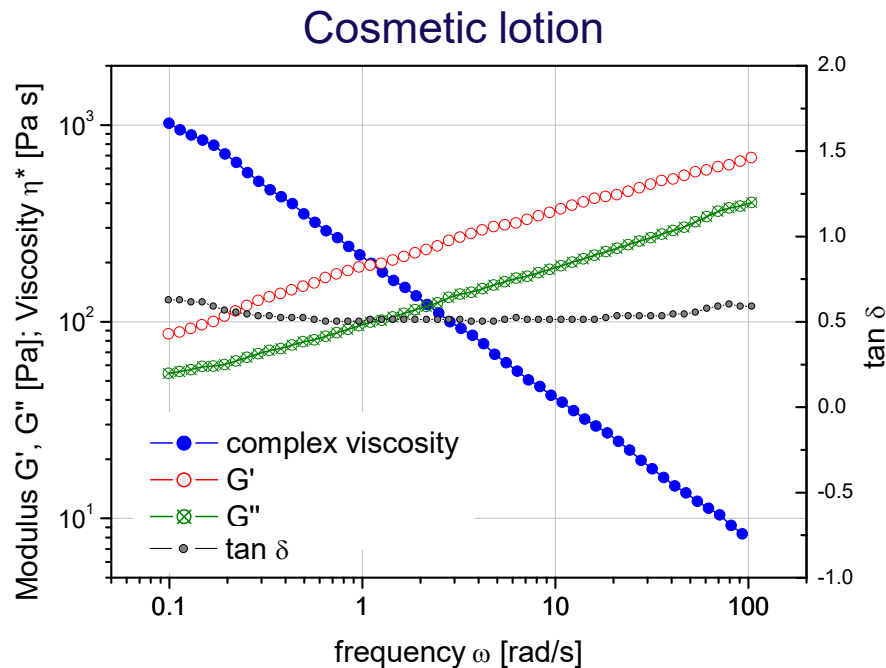
Beyond viscous behavior, complex fluids can exhibit other important flow characteristics, most notably yield stresses and thixotropy. In this third part, we will explore effective ways to quantify these behaviors.

# Elasticity Measurement

The elasticity characterizes the mechanical energy stored (recoverable) during deformation and is a measure of the structure in a material

- Three test methods are commonly used to determine the elastic contribution:
  - Oscillation test – frequency sweep (most common)
  - Creep Recovery test
  - Normal stress measurement

# Elasticity: Oscillation Frequency Sweep

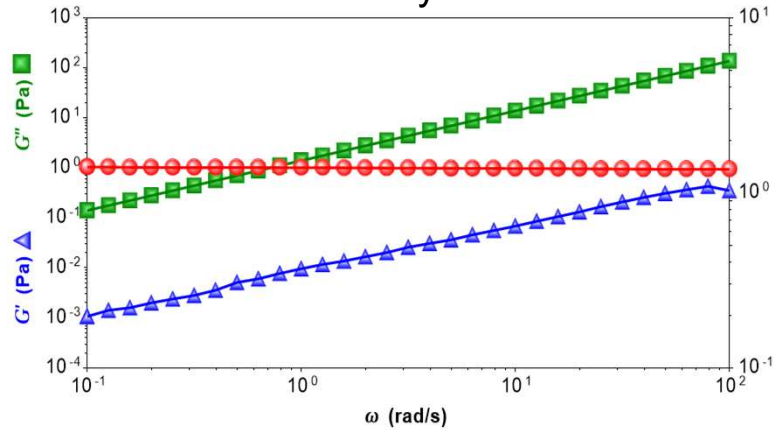


- Many dispersions exhibit solid like behavior at rest
- The frequency dependence and the absolute value of  $\tan \delta$  correlate with long time stability

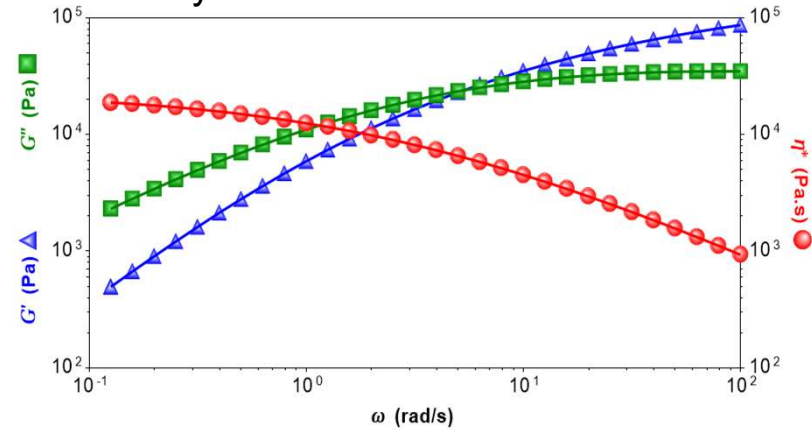
- Note: strain amplitude has to be in the linear region

# Differences in elasticity using frequency sweep

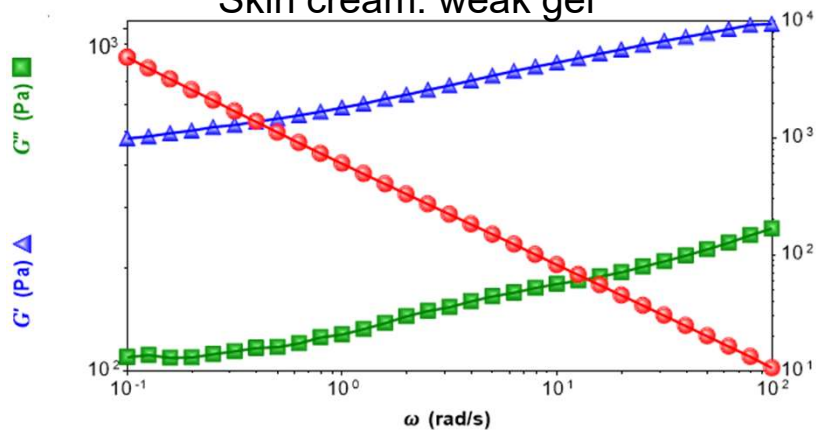
Mineral oil: Mostly Newtonian



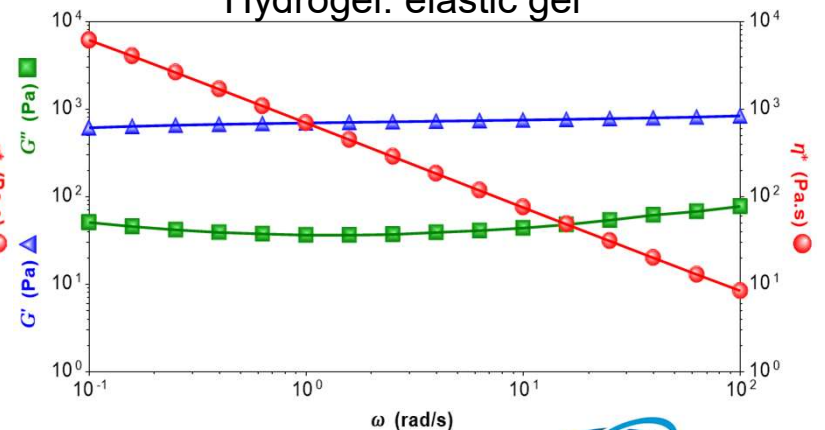
Polymer melts: viscoelastic



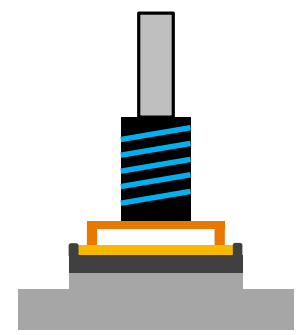
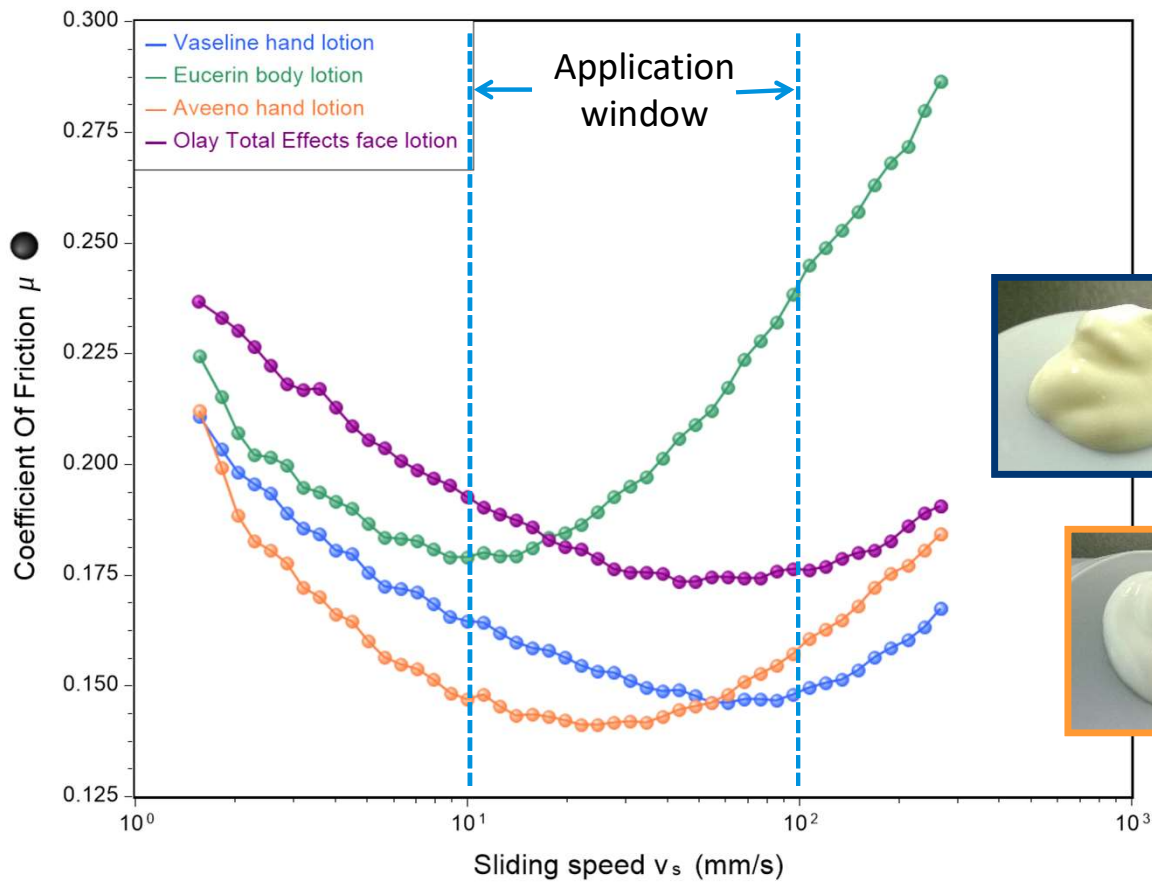
Skin cream: weak gel



Hydrogel: elastic gel



# Lotions: Coefficient of Friction



37°C, 3 N load  
TransPore™

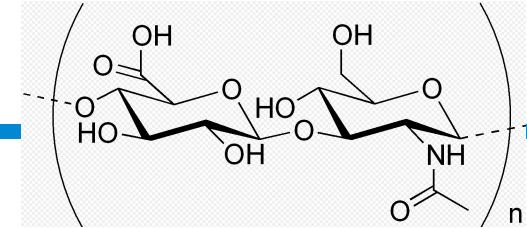


# Hydrogels

- Hydrogels and creams are used in a wide variety of applications including tissue engineering, wound patch, drug delivery, contact lenses and superabsorbent materials
- Rheology can provide key information on gel formation and gel strength on different formulations
- Related applications Notes: AAN033; EF014; EF015; EF016; TA384; TA410



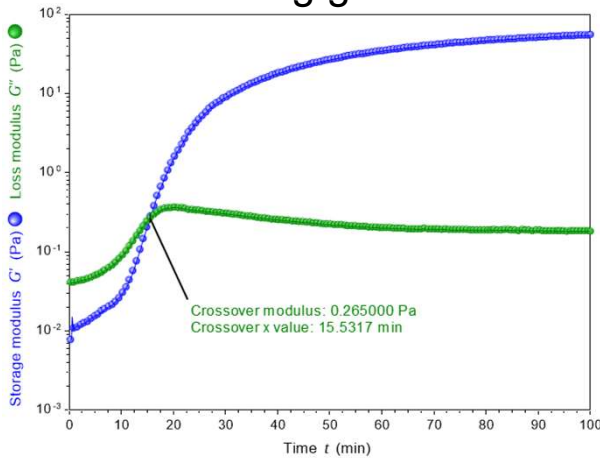
# Natural Polymer: Hyaluronic Acid



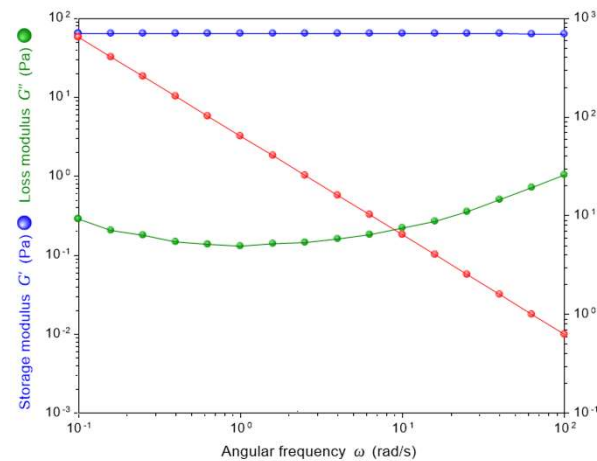
- Hyaluronic acid is a natural polysaccharide, which is commonly used in pharmaceutical, biomedical and personal care
- Rheology can evaluate the visco-elastic properties as function of concentration, ionic strength, Mw, degree of crosslinking, formulations etc.



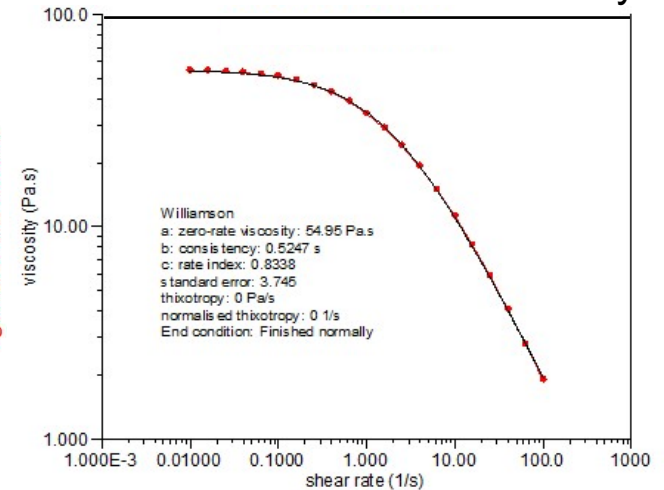
Monitoring gelation



Measure gel strength

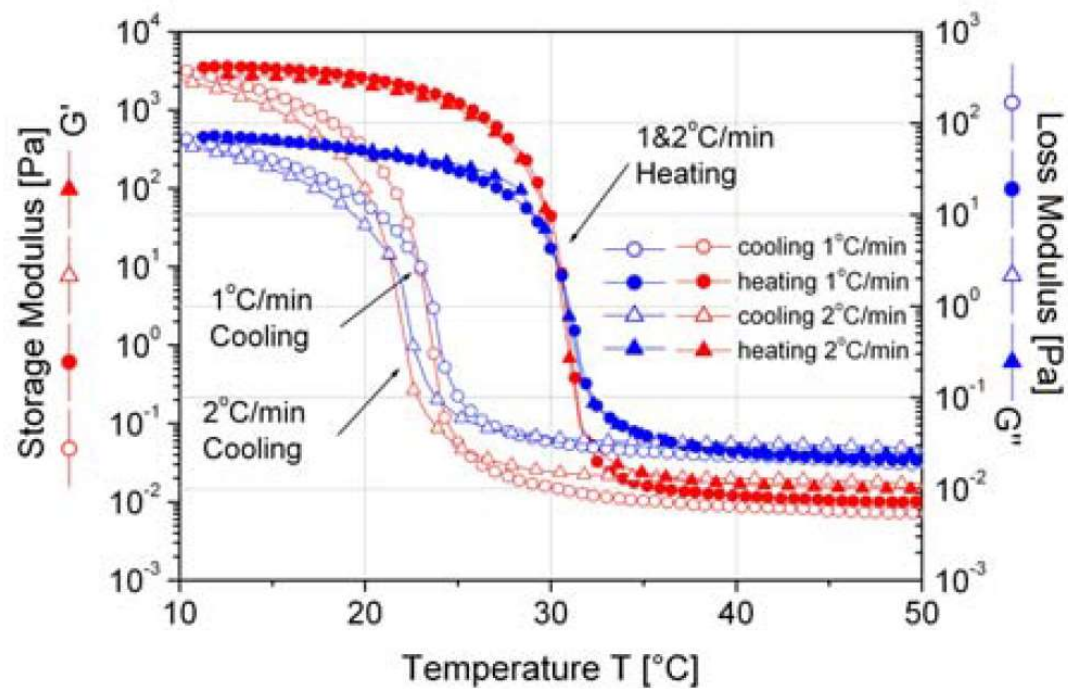


Measure zero shear viscosity



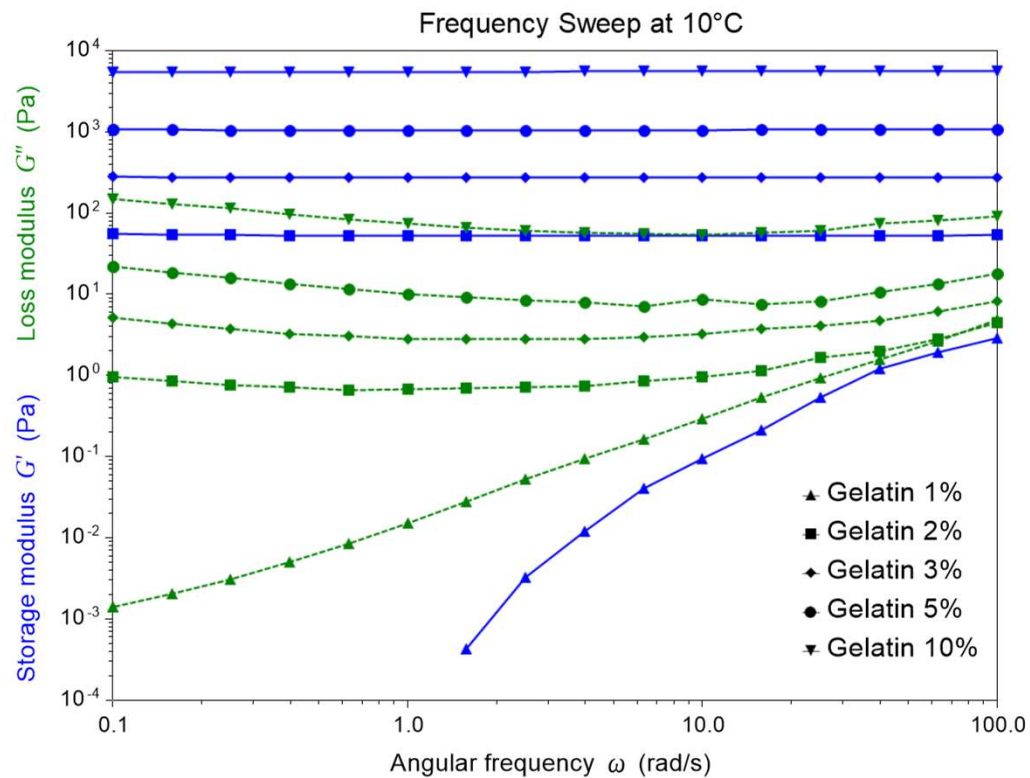
# Gelatin: Gelation vs. Temperature

- Thermal reversible gelatin gels:
  - Measure gelation and gel melt



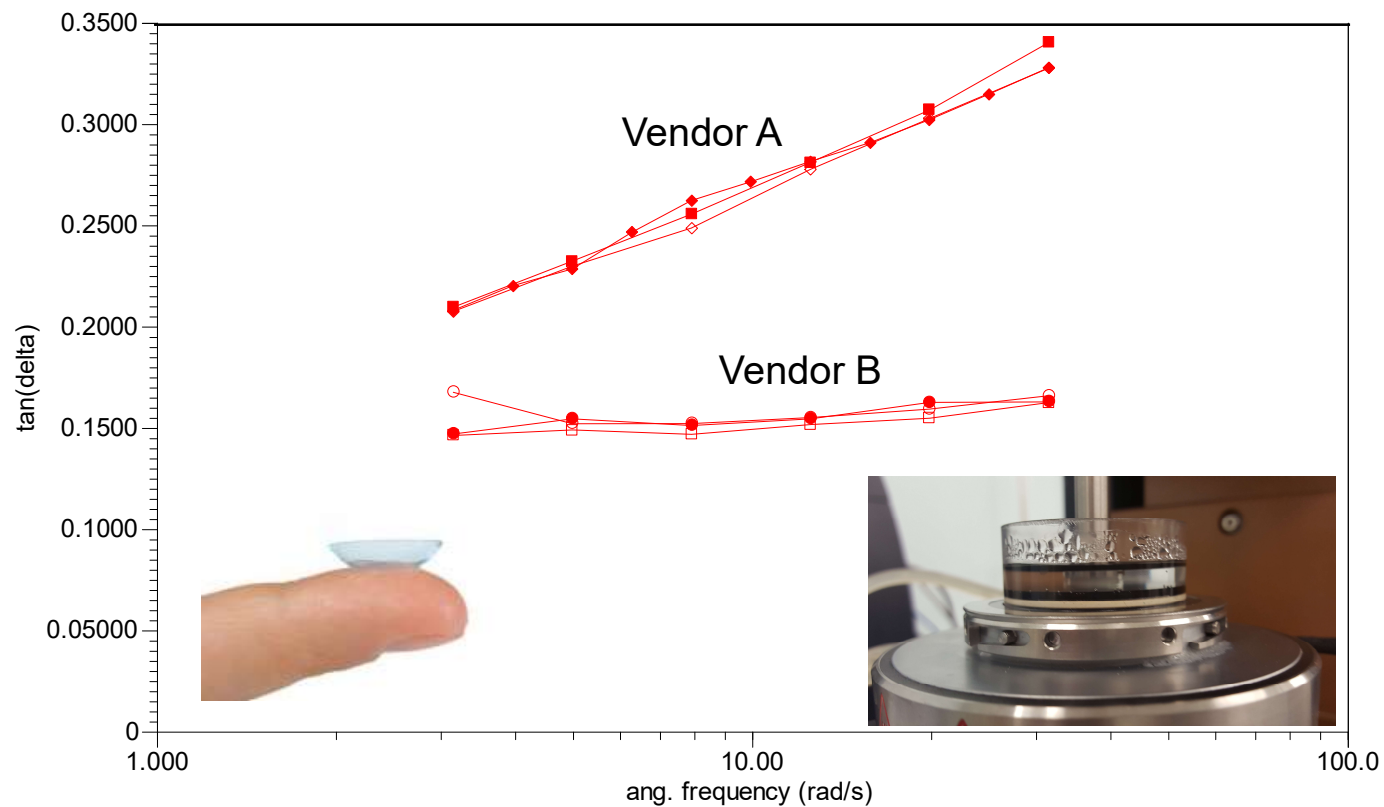
# Gelatin Gel Strength at Different Concentration

- A dynamic frequency sweep test can be used to compare gel strength at applications temperature



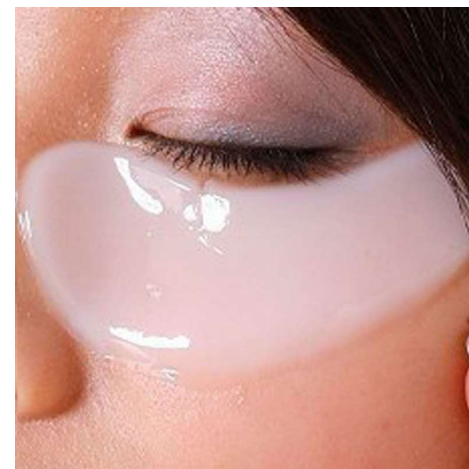
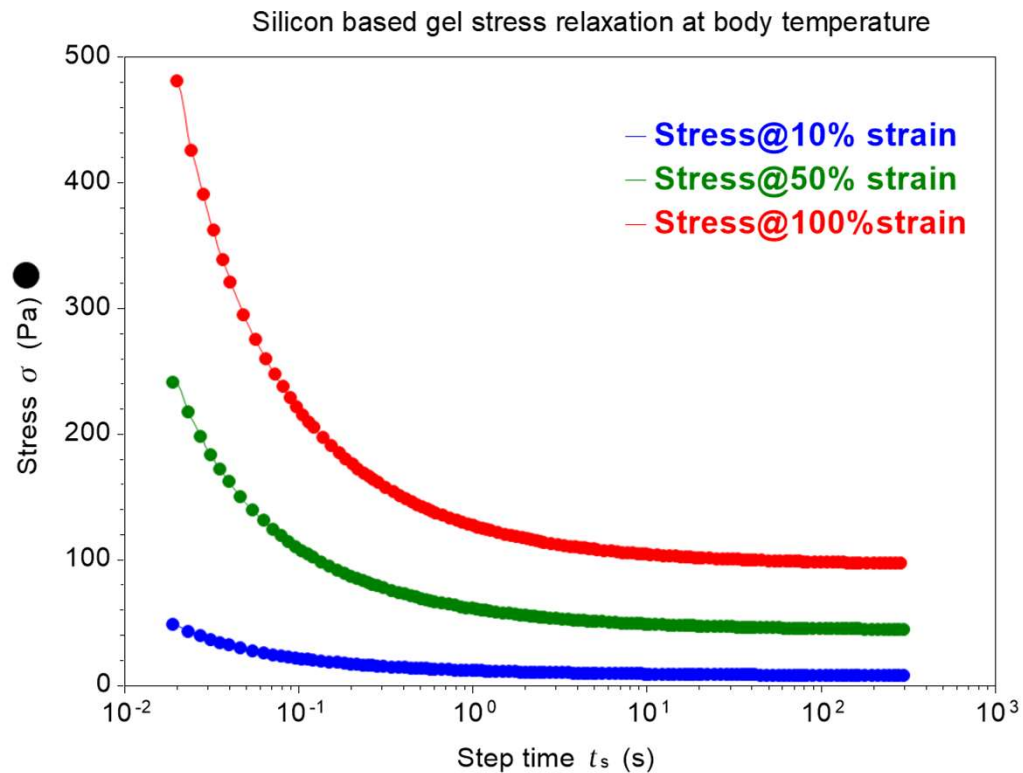
# Contact Lens Visco-elasticity

- Compare frequency dependency of contact lens' elasticity



# Eye Patch Gel: Stress Relaxation

- A stress relaxation test can measure how much stress a gel can hold at a given deformation



# Rheology Applications

## 2. Polymers



# Available Polymer Applications Notes on TA Website

Products ▾ Videos ▾ **Support ▾** Training ▾ News & Events ▾ Sales Promos Careers ▾ About TA ▾ Contact ▾

Applications Notes Library

## Applications Notes Library

Our instruments are used in a variety of products, in multiple industries. The application notes below provide more detail on specific potential applications. You can search for specific app notes with the search field.

Title	Product Category	Ref#	Link
Application of Rheology of Polymers	Rheology	AAN009	<a href="#">Download Note</a>
Understanding Rheology of Thermoplastic Polymers	Rheology	AAN013	<a href="#">Download Note</a>
Creep Recovery Measurements of Polymers	Rheology	AAN022	<a href="#">Download Note</a>
Introduction to Polymer Blends and Alloys	Rheology	AAN023	<a href="#">Download Note</a>
The ARES-EVF: Option for Extensional Viscosity of Polymer Melts	Rheology	APN002	<a href="#">Download Note</a>
Automotive Fatigue Life and Dynamic Mechanical Analysis of a Matrix Polymer	ElectroForce Mechanical Testing	EF026	<a href="#">Download Note</a>
Use of Reology to Determine Molecular Weight Distribution of Polymers	Rheology	L2092	<a href="#">Download Note</a>
Efficiency of Stabilisers in Polymers Measured by Microcalorimetry	Microcalorimetry	M139	<a href="#">Download Note</a>
Oxidation of Polymers Studied by Microcalorimetry	Microcalorimetry	M22033	<a href="#">Download Note</a>
Multisample Stability Testing of Polymers	Microcalorimetry	M22037	<a href="#">Download Note</a>
Mixing Rules for Complex Polymer Systems	Rheology	RH095	<a href="#">Download Note</a>

RS25 Polymer Mw...pdf ^



# Purpose of a Rheological Measurement

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Three main reasons for rheological testing:

- **Characterization**

MW, MWD, formulation, state of flocculation, etc.

- **Process performance**

Extrusion, blow molding, pumping, leveling, etc.

- **Product performance**

Strength, use temperature, dimensional stability, settling stability, etc.

# Most Common Experiments on Polymers

## • Oscillation/Dynamic

- **Time Sweep**
  - Degradation studies, stability for subsequent testing
- Strain Sweep – Find LVR
- **Frequency Sweep –  $G'$ ,  $G''$ ,  $\eta^*$** 
  - Sensitive to MW/MWD differences melt flow can not see
- **Temperature Ramp/Temperature Step**
  - Transitions, end product performance
- TTS Studies

## • Flow/Steady Shear

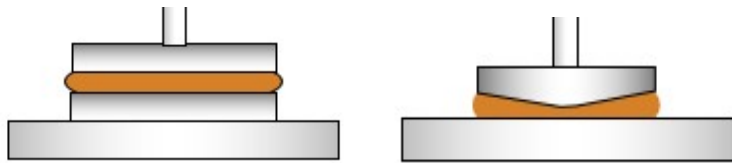
- Viscosity vs. Shear Rate, mimic processing
- Find Zero Shear Viscosity
- Low shear information is sensitive to MW/MWD differences melt flow can not see

## • Creep and Recovery

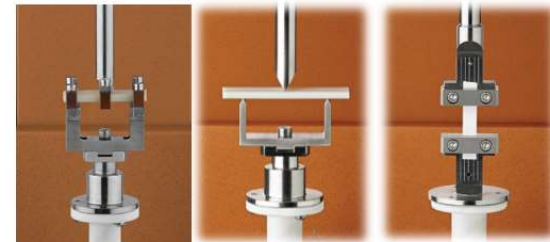
- Creep Compliance/Recoverable Compliance are sensitive to long chain entanglement, elasticity

# Most Common Geometries

- Polymer melts:
  - 25mm and 8mm parallel plates, and disposable plates (cure)
  - Cone-plate (normal force measurement)
  - Cone partitioned plate (avoid edge fracture, LAOS)
- Polymer solids:
  - Torsion rectangular and cylindrical geometry
  - DMA clamps (tension, bending, cantilever, compression)



Torsion rectangular and cylindrical clamps

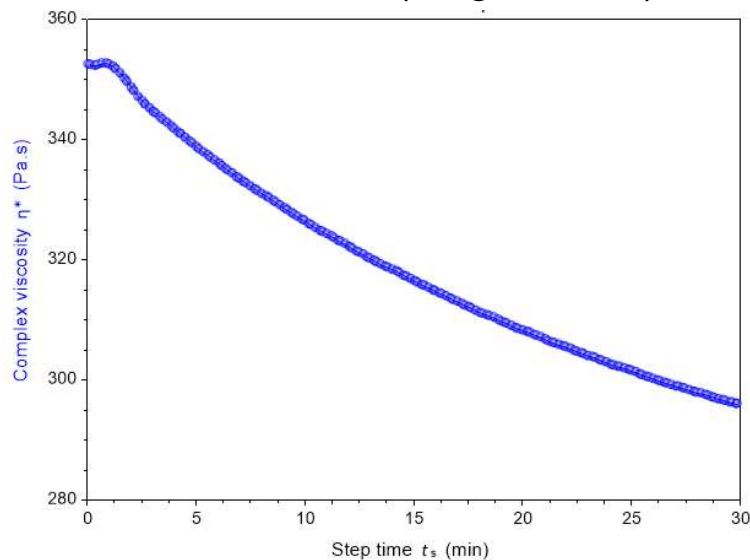


DMA cantilever, 3-point bending and tension clamps

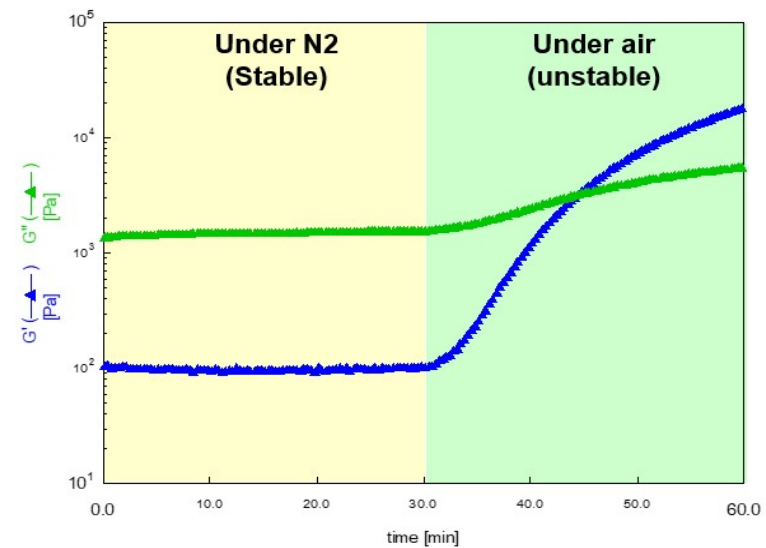
# Polymer Melt Thermal Stability

- Determines if properties are changing over the time of testing
  - Degradation
  - Molecular weight building, crosslinking

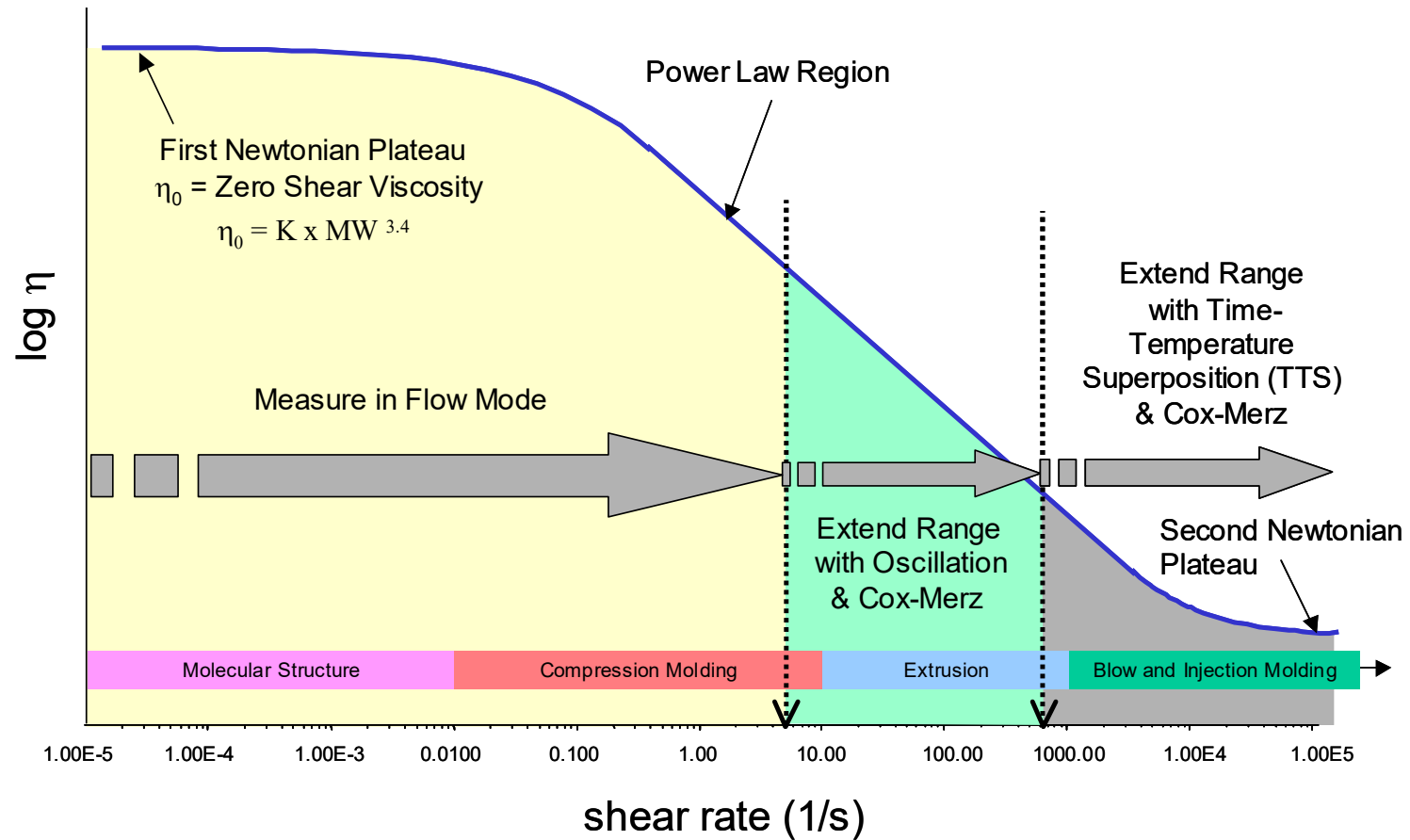
PP at 230°C ( degradation)



PEEK at 400°C ( crosslinking)



# Idealized Flow Curve – Polymer Melts



# Melt Flow Testing Considerations

- Edge Fracture:  
Sample leaves gap because of normal forces
- Cox-Merz Rule  
An empirical relationship between a dynamic complex viscosity and steady shear viscosity. It has been observed working with many polymer melt systems

$$\eta = \sigma / \dot{\gamma}$$
$$\eta^* = G^* / \omega$$
$$\eta(\dot{\gamma}) \equiv \eta^*(\omega)$$

<https://www.youtube.com/watch?v=urGKnj5Qmhc>

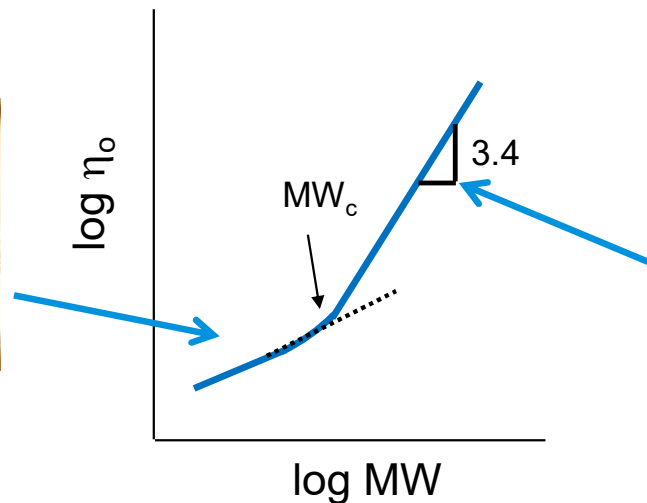


# Melt Rheology: MW Effect on Zero Shear Viscosity

- Sensitive to Molecular Weight, Mw
- For Low MW (no Entanglements)  $\eta_0$  is proportional to Mw
- For MW > Critical Mw<sub>c</sub>,  $\eta_0$  is proportional to Mw<sup>3.4</sup>



$$\eta_0 = K \cdot Mw$$

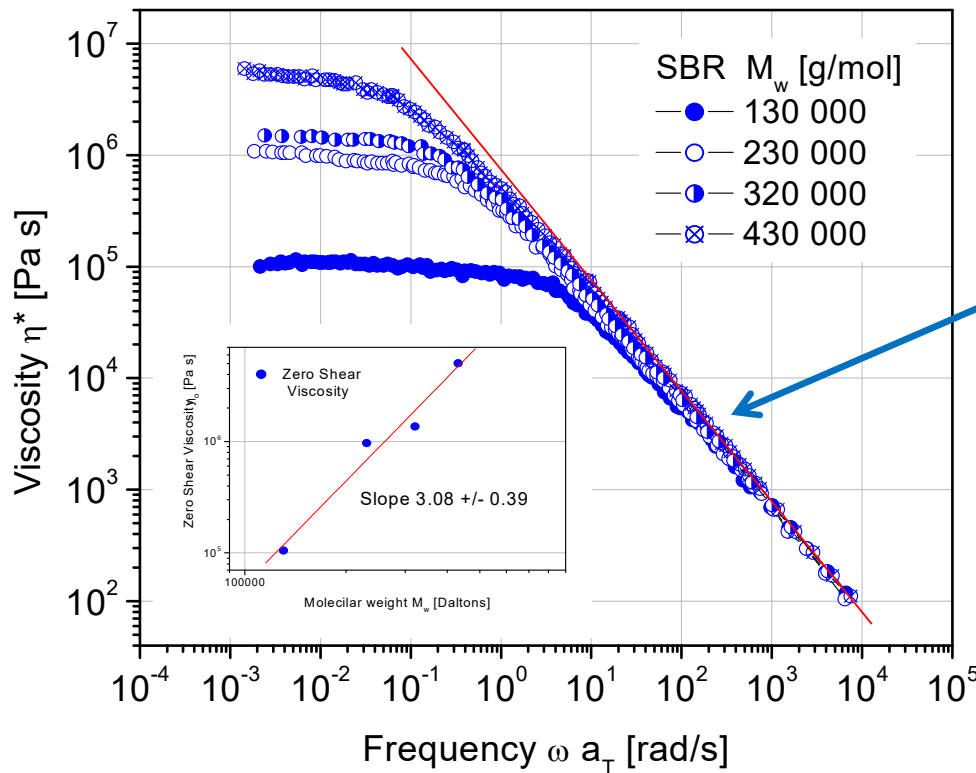


$$\eta_0 = K \cdot Mw^{3.4}$$

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

# Influence of MW on Viscosity

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

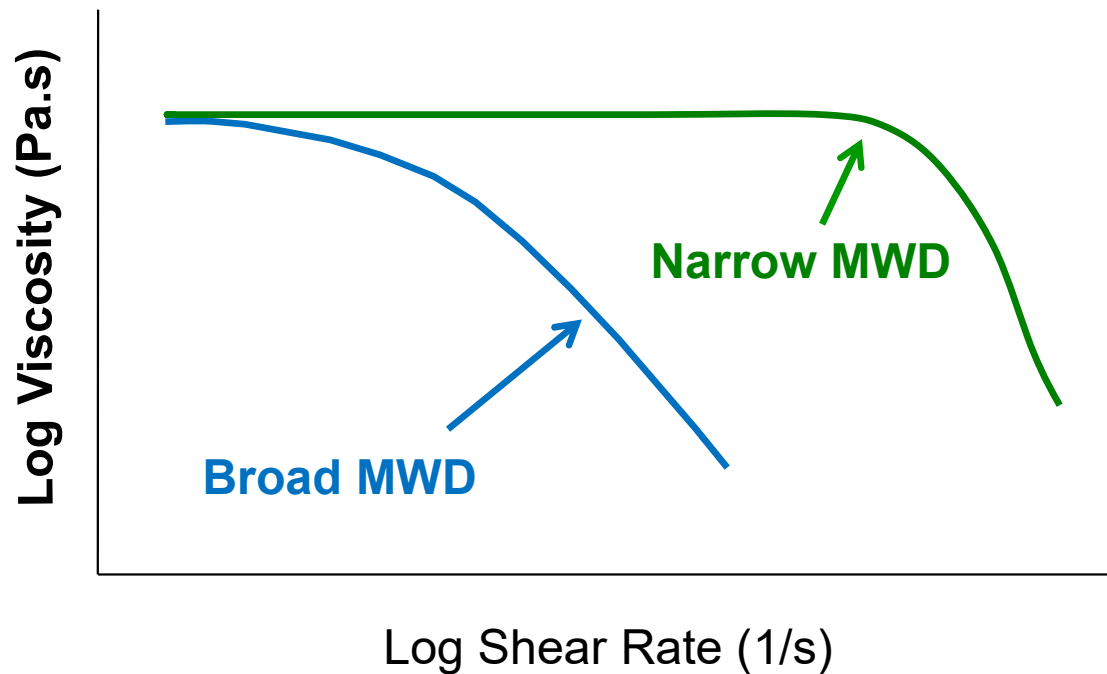


The high frequency behavior (slope -1) is independent of the molecular weight



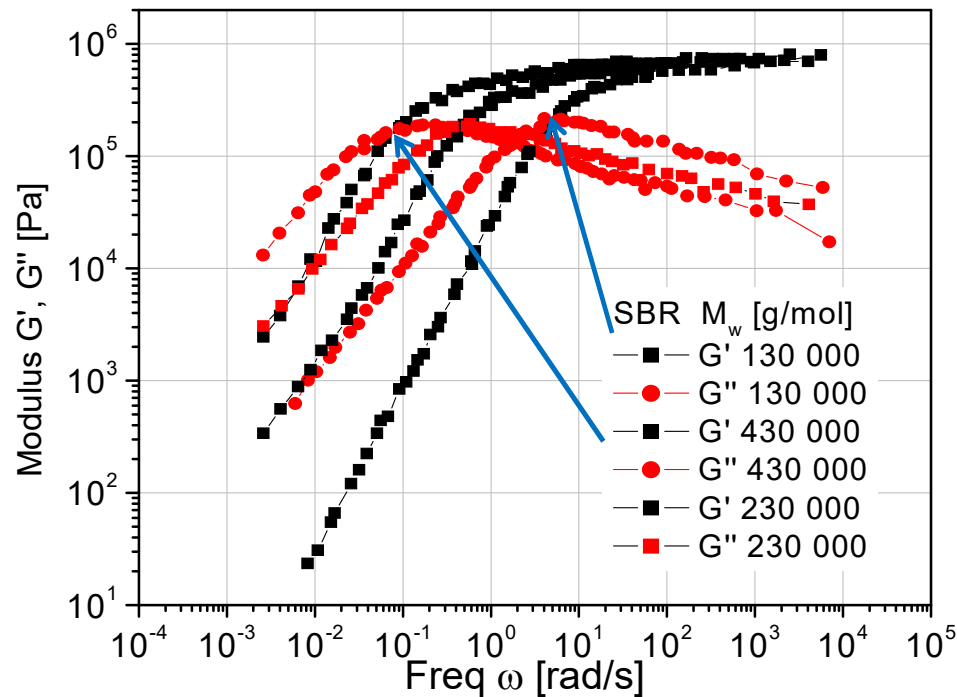
## Influence of MWD on Viscosity

- A Polymer with a broad MWD exhibits non-Newtonian flow at a lower rate of shear than a polymer with the same  $\eta_0$ , but has a narrow MWD.



## Influence of MW on $G'$ and $G''$

- The  $G'$  and  $G''$  curves are shifted to lower frequency with increasing molecular weight.



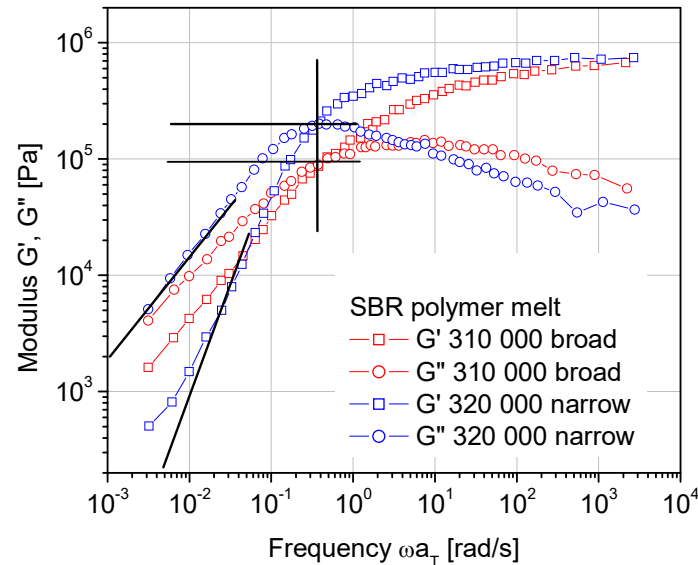
TA Instruments Webinar



TA WEBINARS

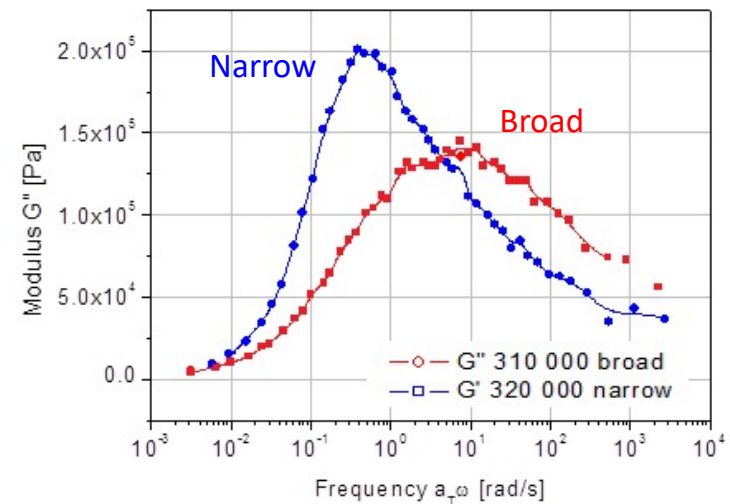
Professor Chris Macosko  
– Analyzing Molecular  
Weight Distribution w/  
Rheology

# Influence of MWD on $G'$ and $G''$



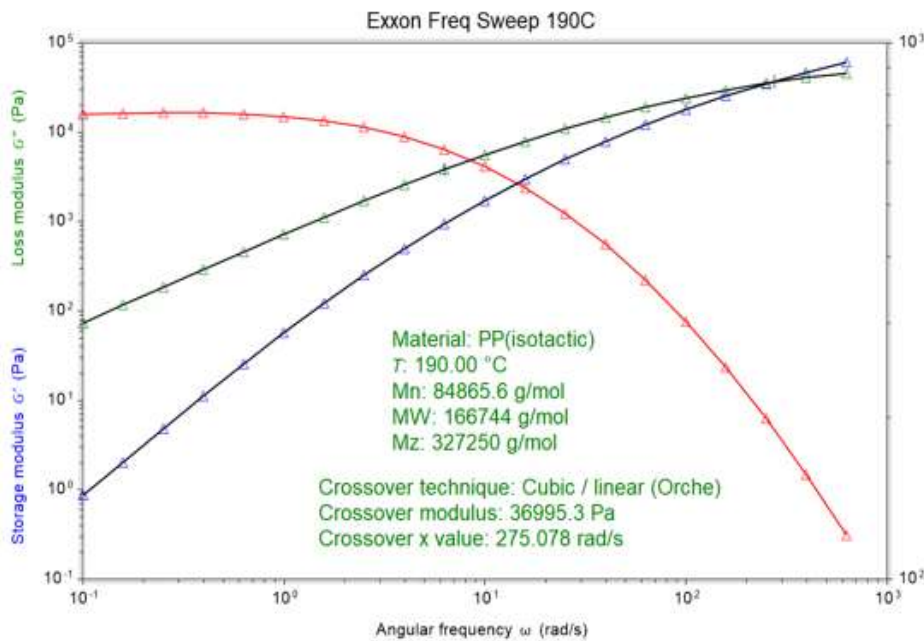
Higher crossover frequency : lower  $M_w$   
 Higher crossover Modulus: narrower MWD  
 (note also the slope of  $G''$  at low frequencies – narrow MWD steeper slope)

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



# Frequency Sweep – Mw and MWD

- Using rheological measurements to quantify molecular weight and molecular weight distribution



Molecular Weight Distribution Calculation Iteration 5

Material  
 Polymer Type: PP(isotactic) Edit...  
 Data Temperature: 190.00 [°C]

Molecular Weight and Distribution  
 Unimodal  Bimodal  N-modal

Distribution Type: Log-Normal

Weight Average Mw: 1.67e+05  
 Mw/Mn: 1.9651

Data Clipboard: Copy Paste

Advanced Options  
 Mixing Rule:  Double Reptation  Wt Average  
 Add Rouse motions:   
 Doi-Edwards terms: 1 Settings

Calculation Results

Mn	84866	Mw	1.67e+05
Mz	3.27e+05	Mw/Mn	1.9648
Mz+1	6.35e+05	Error	0.1088

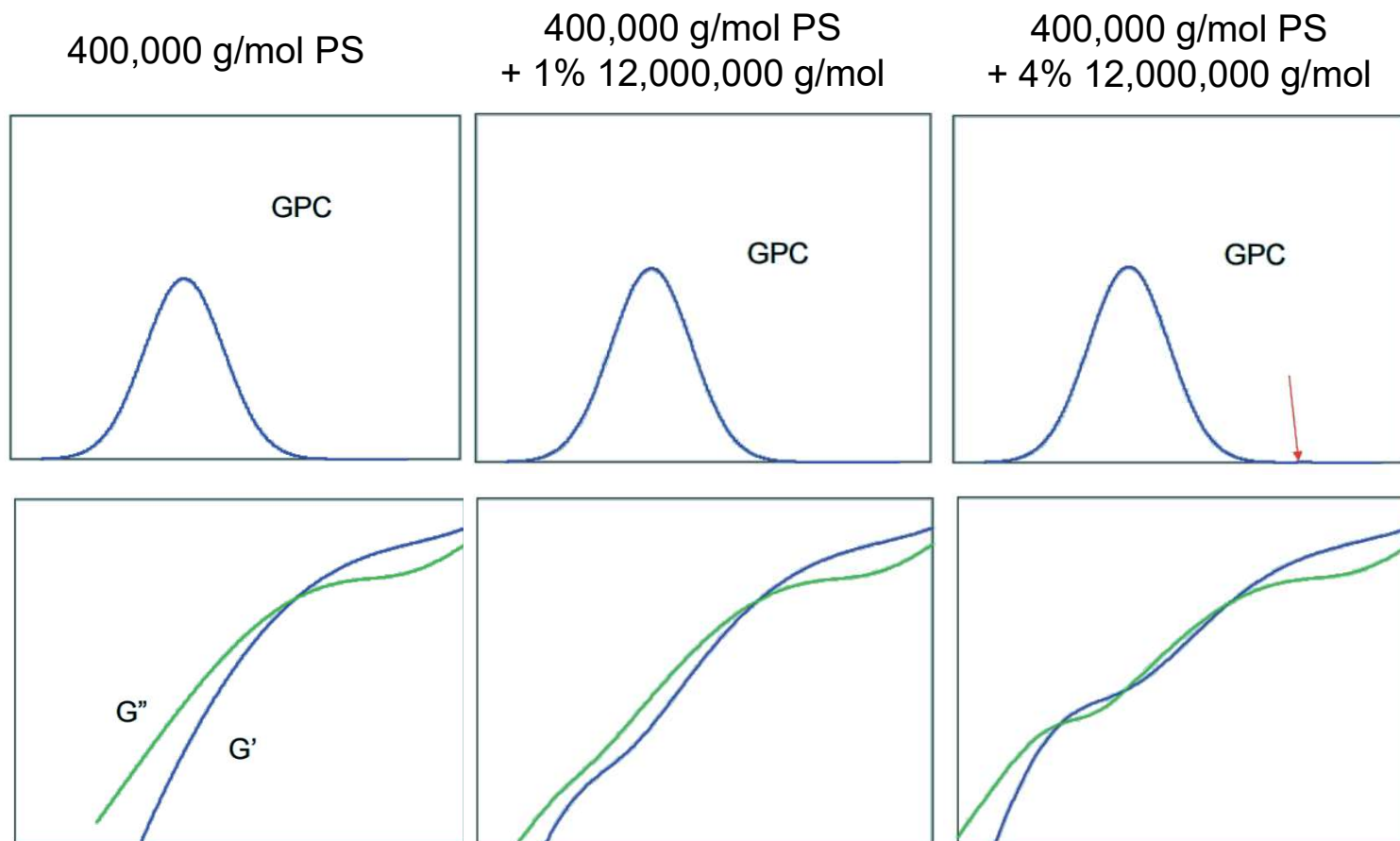
Plot Format  
 Dynamic Data (G', G'')  MWD (w(Mw))  MWD (w(Mw) \* Mw)

Auto Solution Update:

Calculate Optimize Help Exit

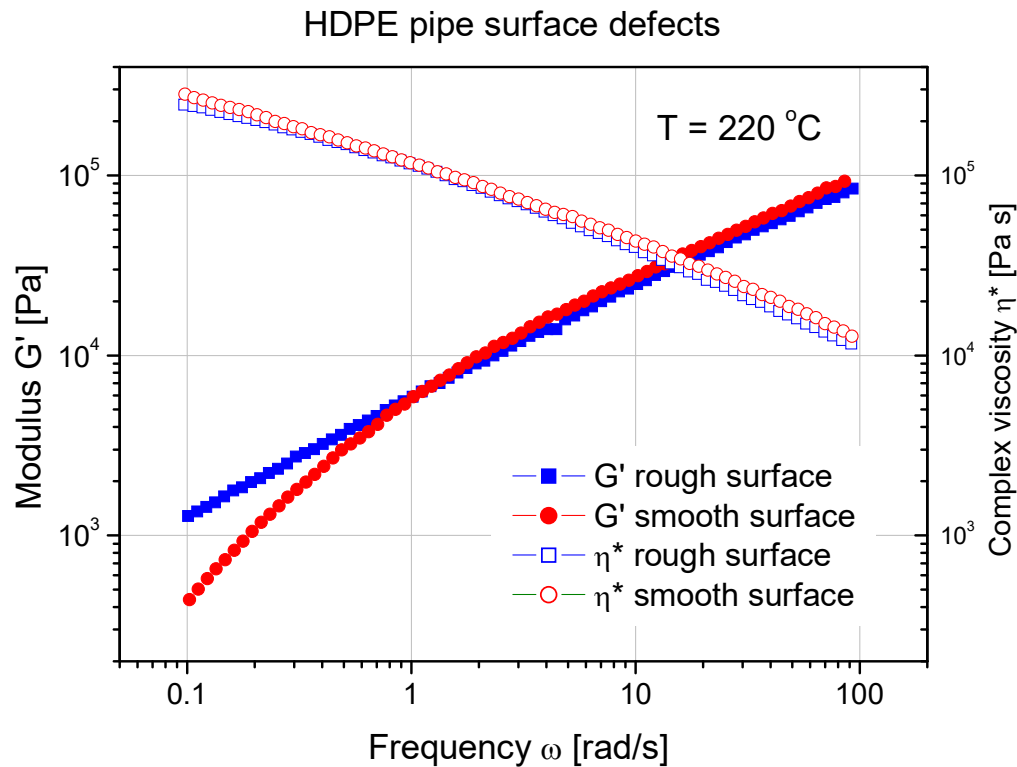
[João Maia: The Role of Interfacial Elasticity on the Rheological Behavior of Polymer Blends](#)  
[Chris Macosko: Analyzing Molecular Weight Distribution w/ Rheology](#)

# High MW Contributions



Macosko, TA Instruments Users' Meeting, 2015

# Surface Defects during Pipe Extrusion

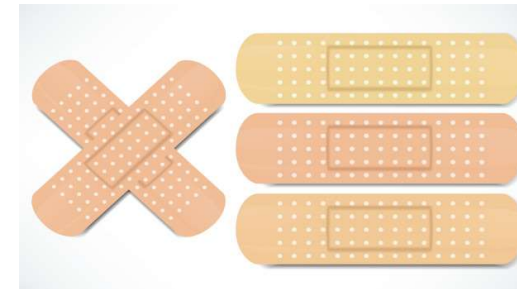
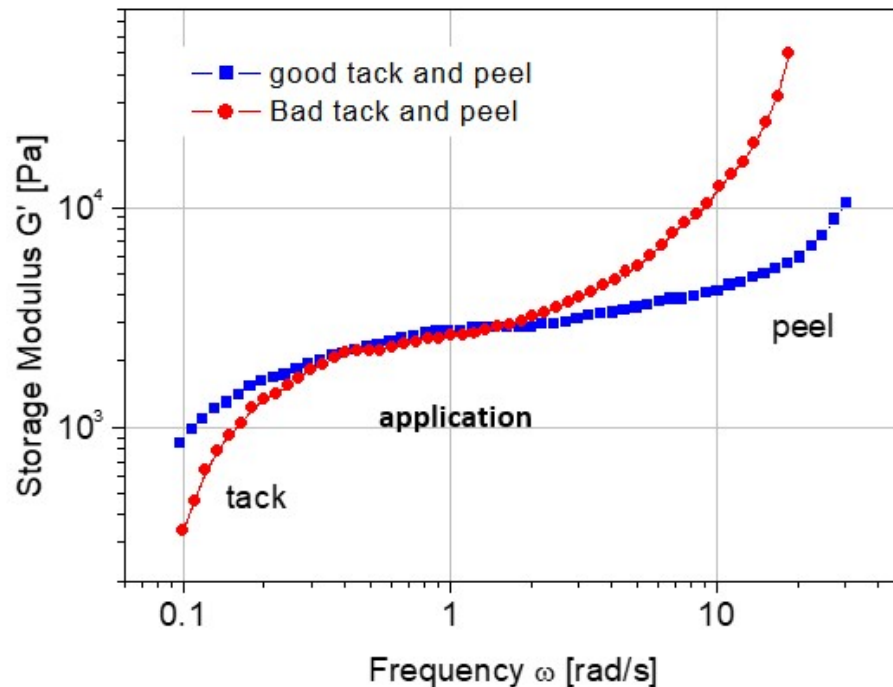


- Surface roughness correlates with  $G'$  or elasticity  $\rightarrow$  broader MWD or tiny amounts of a high MW component
- Blue-labeled sample shows a rough surface after extrusion

# Frequency Sweep – Tack and Peel of Adhesives

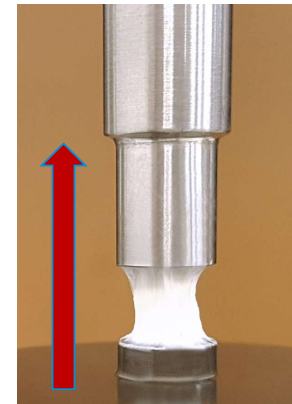
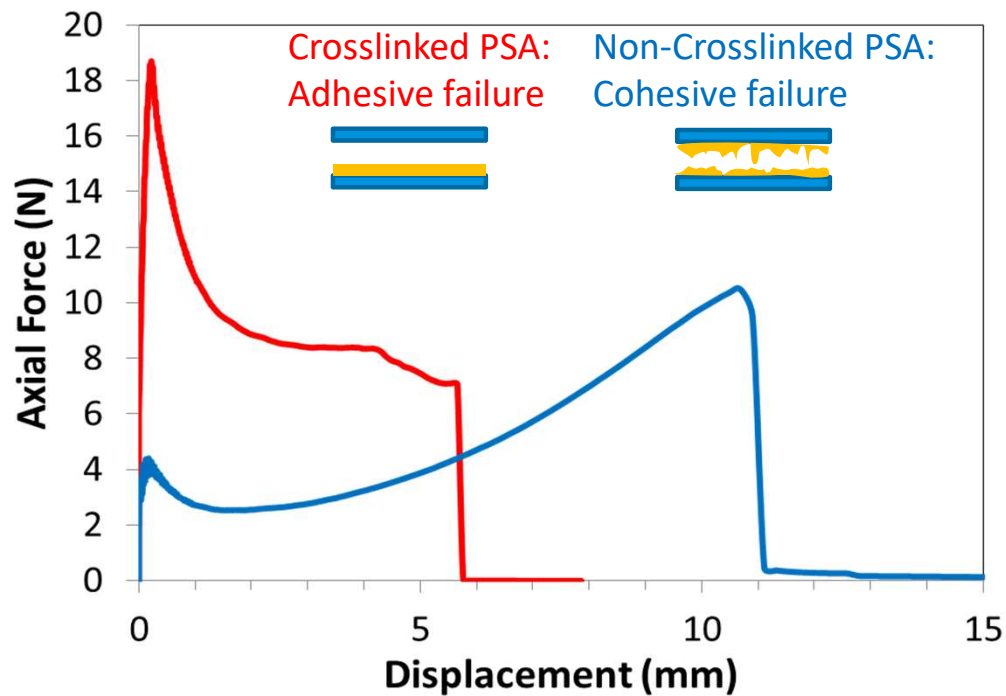
- A dynamic frequency sweep test results can correlate to tack and peel performance
- One single frequency sweep test cannot cover the entire frequency range of interest. Use Time-Temperature Superposition (TTS).

Tack and Peel performance of a PSA



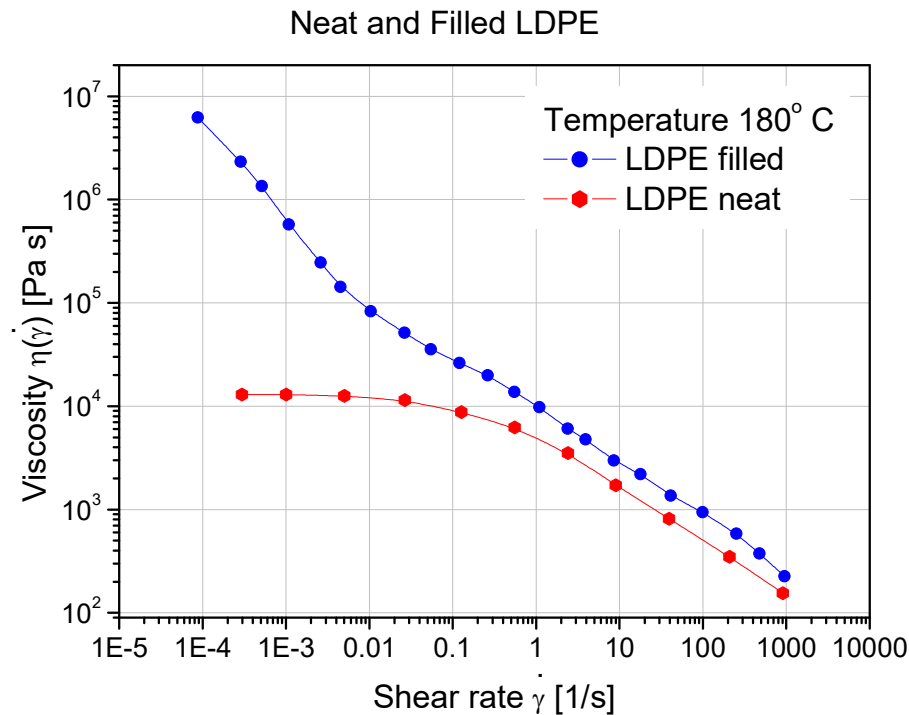
# Adhesive Tack Testing

- Tack testing method: ASTM D2979
- Use 8mm parallel plate, axial tensile at 0.1mm/sec
- The maximum force required to pull the plate away is defined as the sample's tackiness.





# Effect of Filler on Melt Viscosity

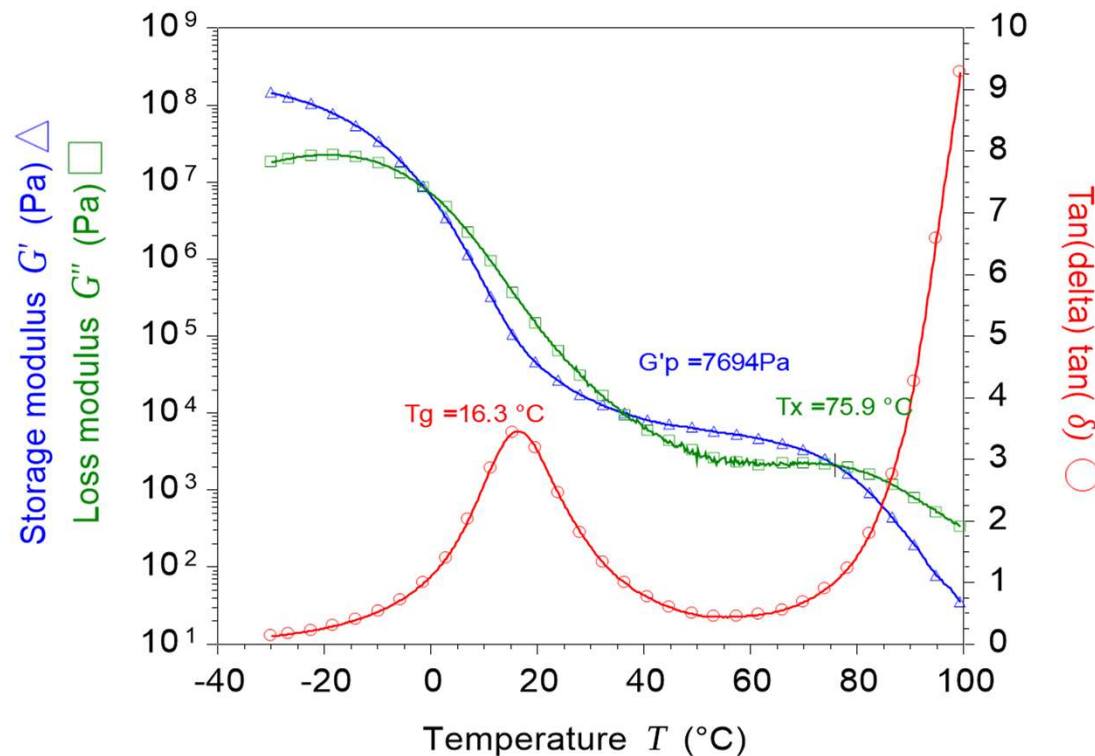


- Fillers increase the melt viscosity
- Due to inter-particle interactions, the non-Newtonian range is extended to low shear rates and the zero shear viscosity increases dramatically

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

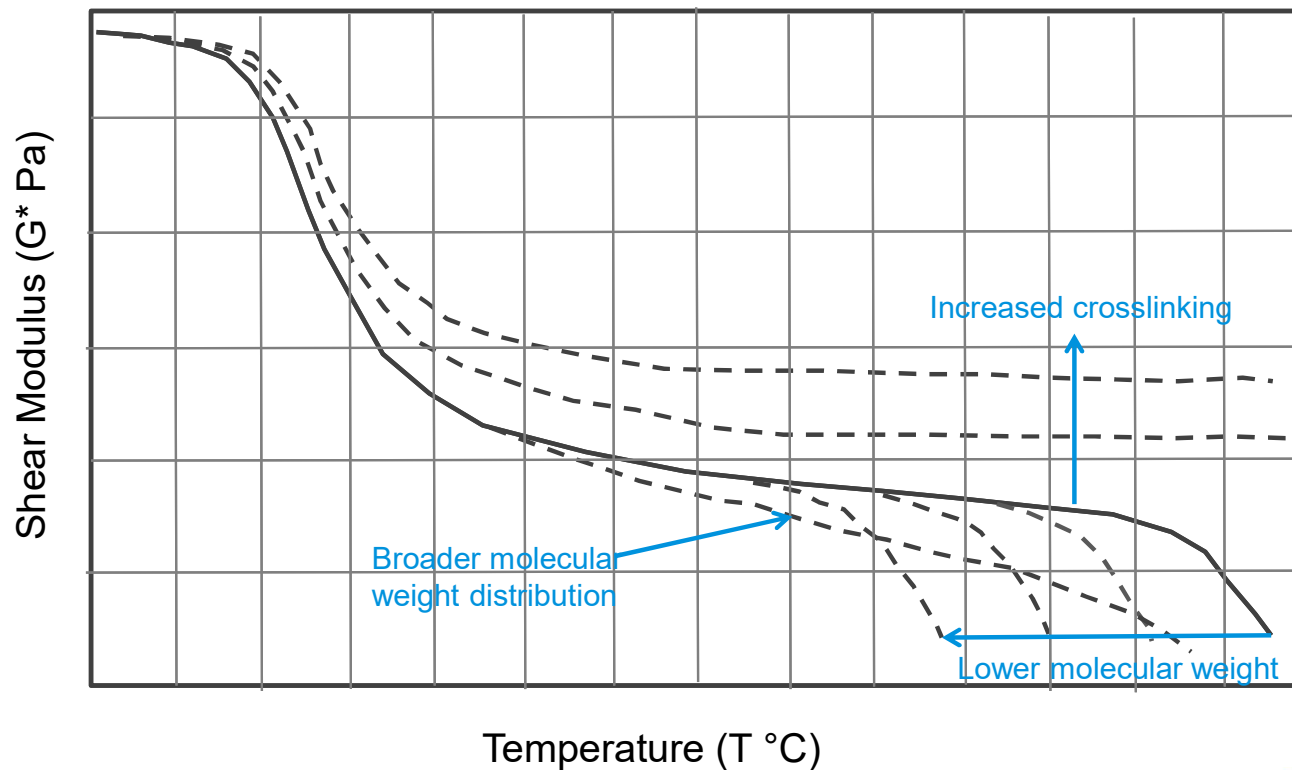
# Dynamic Temp Ramp Test on Adhesives

- Most popular test for PSA evaluations
- Results correlate to the PSA performance with temperature



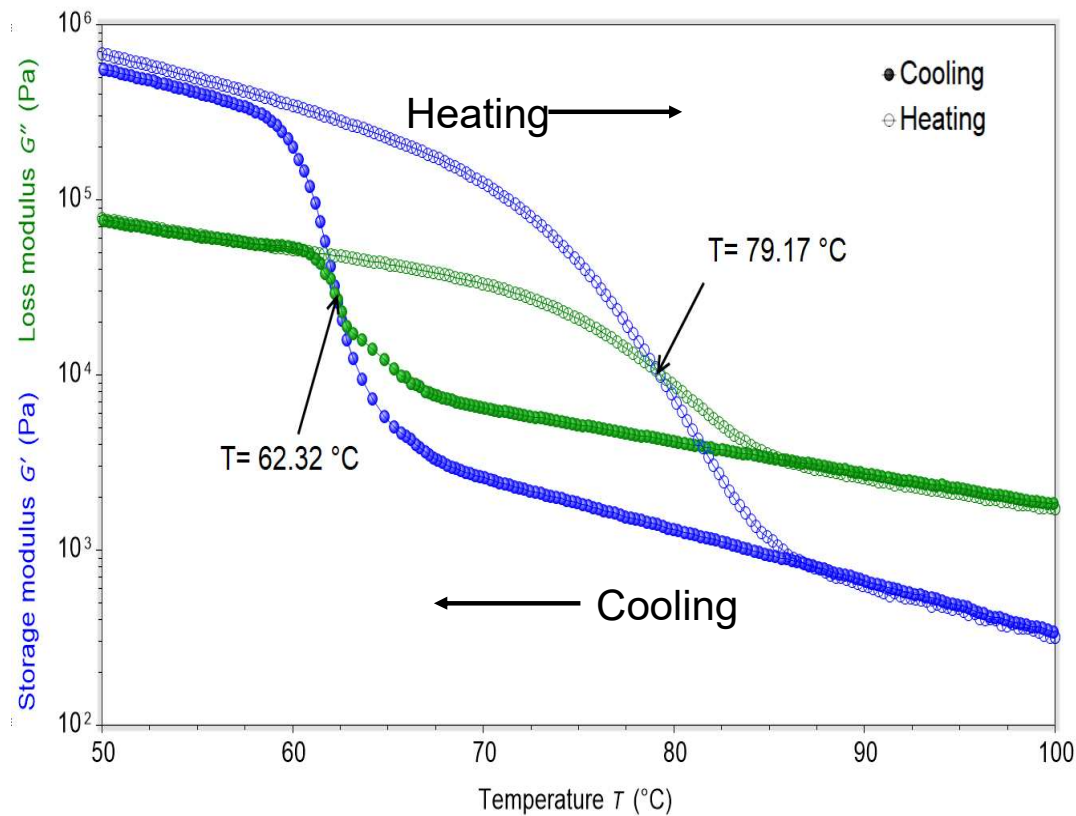
# What do We Learn from a Temp Ramp Test?

- Correlates with polymer molecular structure:  
Mw, MWD, and crosslinking



# Hot Melt Adhesive – Operation Temperature Window

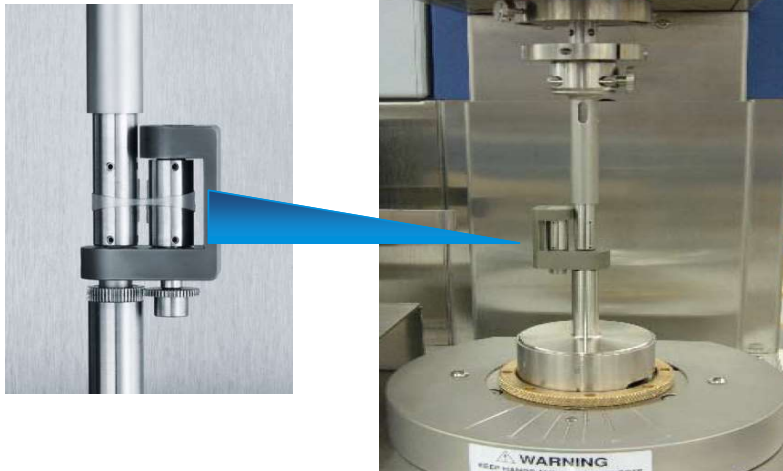
- Operation temperature window: 62°C to 79°C
- Oscillation temperature ramp at 3°C/min



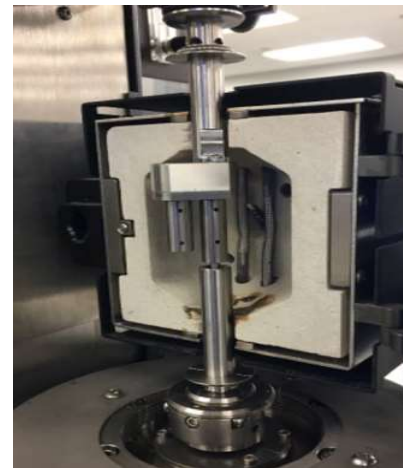
# Extensional Viscosity Measurements

- Nonlinear elongation flow is more sensitive for some structure elements (e.g. branching ) than shear flows
- Many processing flows are elongation flows. Extensional viscosity measurements can be used to help predict processability

ARES G2 - EVF



ARES G2 - EVA



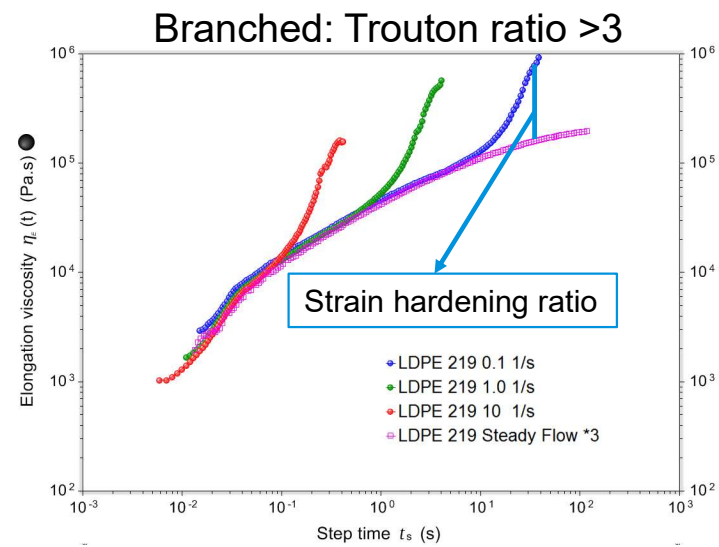
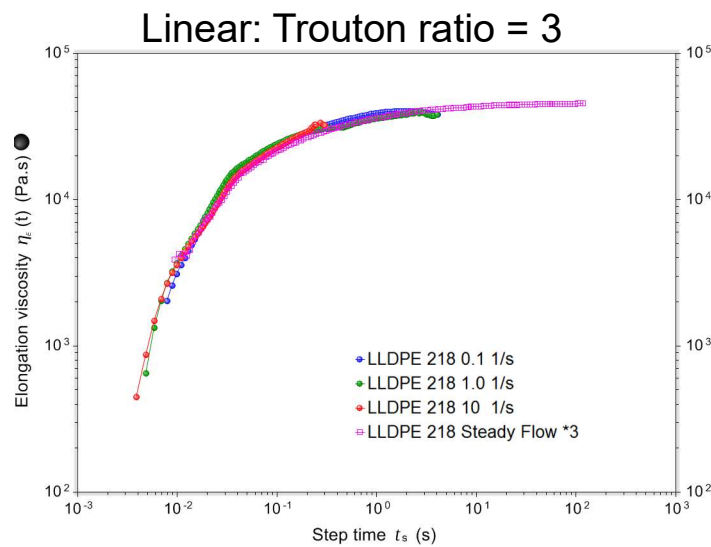
DHR/HR - EVA



# Extensional Viscosity

- Extensional rheology is very sensitive to polymer chain entanglement. Therefore it is sensitive to LCB
- The measured extensional viscosity is 3 times the steady shear viscosity
- LCB polymer shows the strain hardening effect – Trouton ratio

$$\text{Trouton Ratio} = \eta_E(t, \dot{\epsilon}) / \eta_0(t)$$



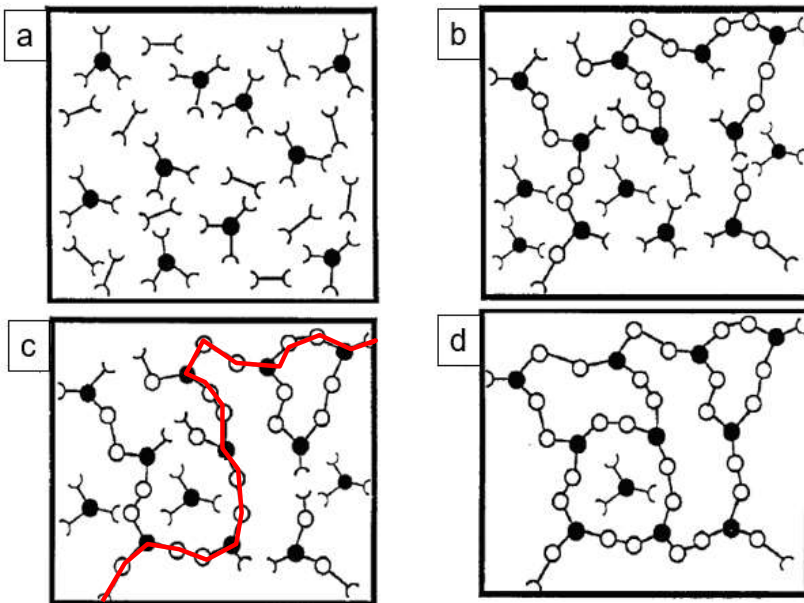
# Thermosetting Polymers Analysis

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

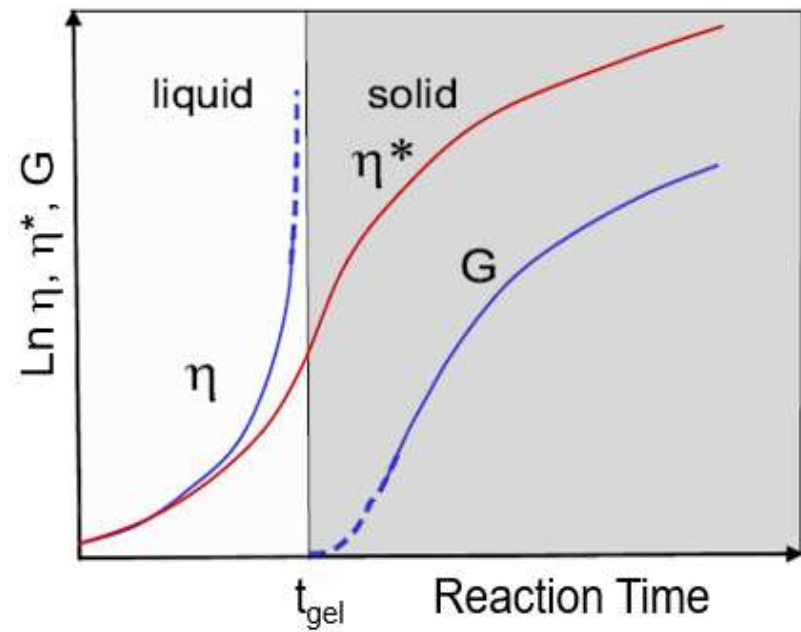


# Thermoset Curing Process

## Gelation and Vitrification



## What Rheology Measures

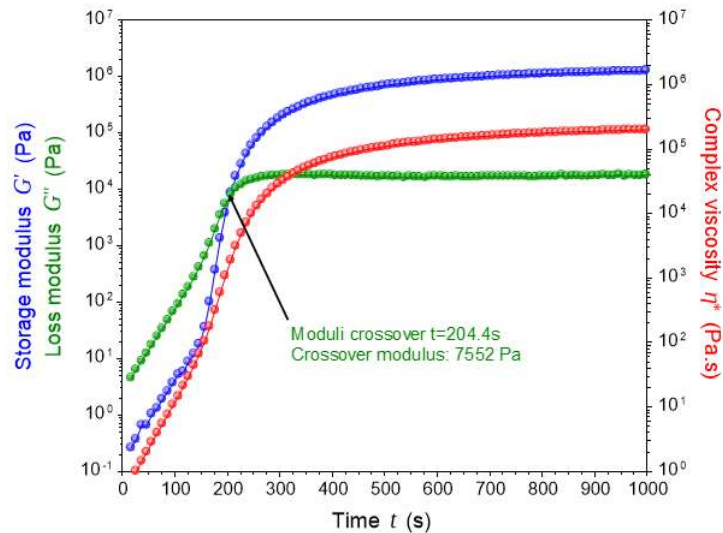




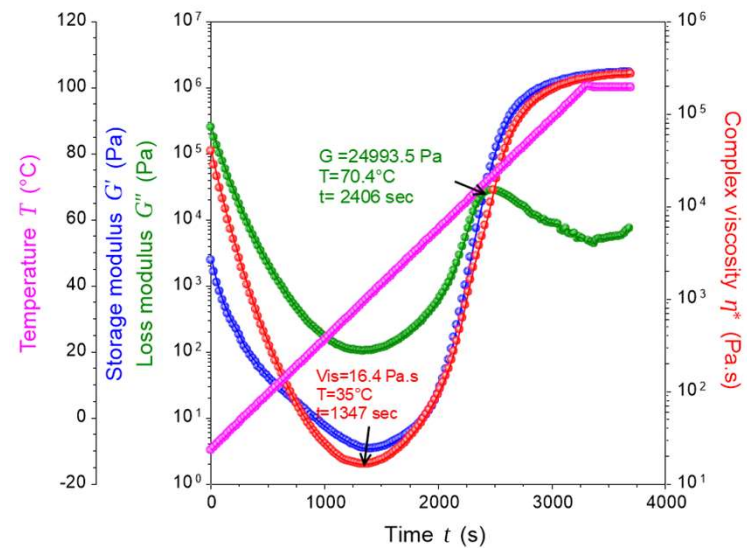
# Rheology for Thermoset Characterization

- Measure viscosity change before crosslinking
- Monitor gelation and measure the gel point
- Monitor sample viscoelastic property change ( $G'$  and  $G''$ ) during curing
- Evaluate the mechanical properties of the end-use product

## Isothermal Curing



## Temperature Ramp Curing



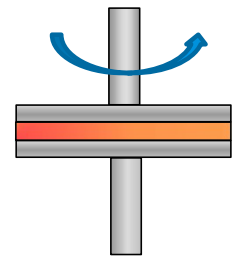
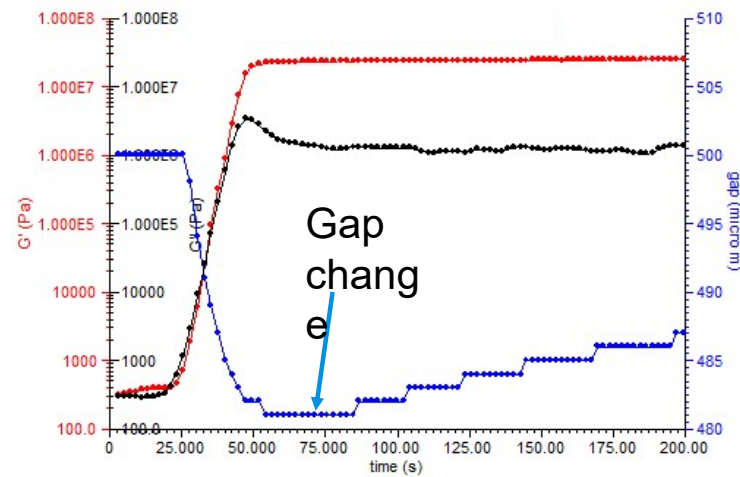
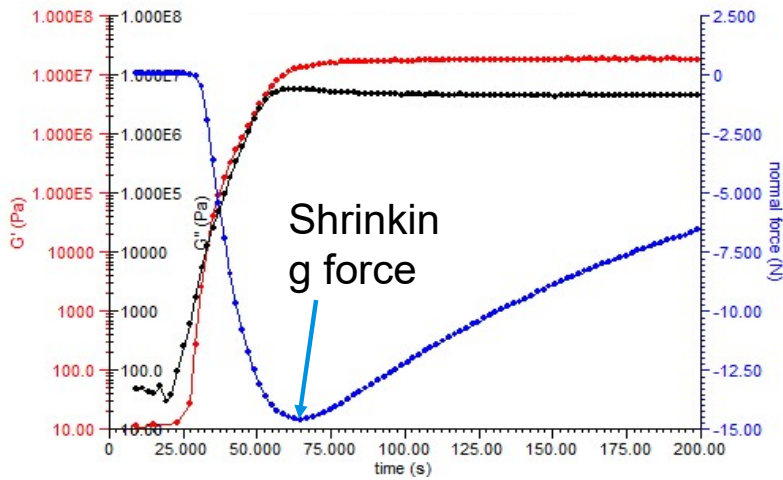
# Monitoring Shrinkage



- Thermoset material shrinks during curing
- The amount of shrinkage could cause cracking or failure to the end products

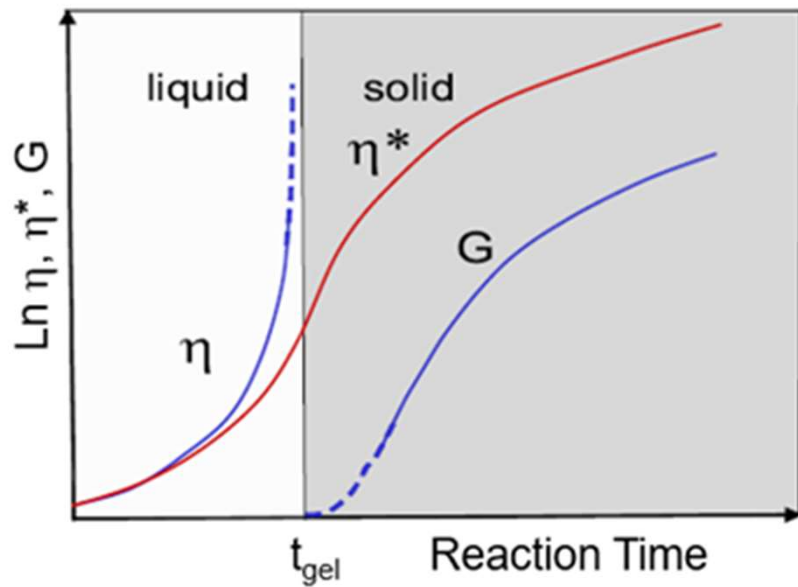
(1) Set Gap Constant  
monitor shrinking force

(2) Set Axial Force = 0  
monitor dimension(gap) change



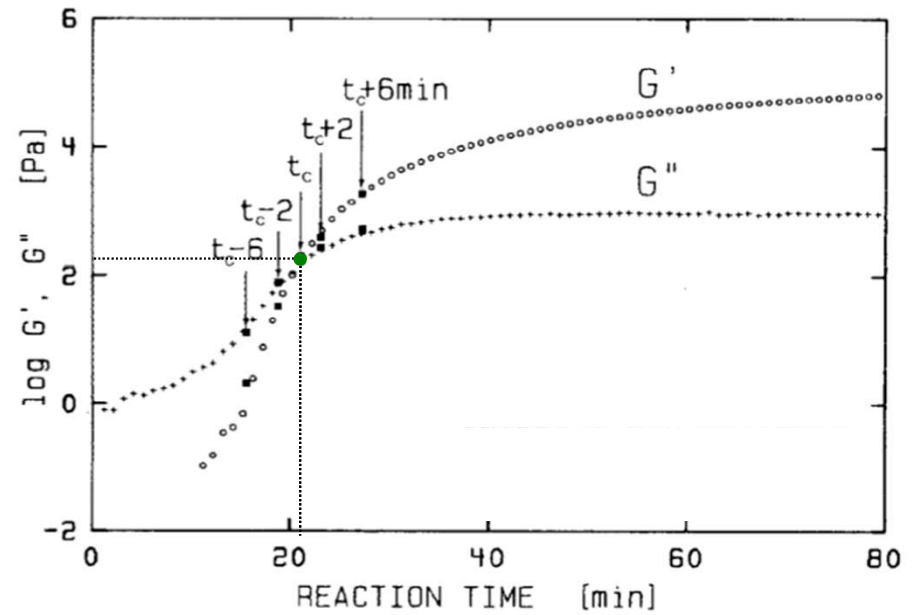
# Measure Gel Point

- Viscosity goes to infinity
- System loses solubility
- Molecular weight  $M_w$  goes to infinity



Empiricism of Y. M. Tung and P. J. Dynes (1982)

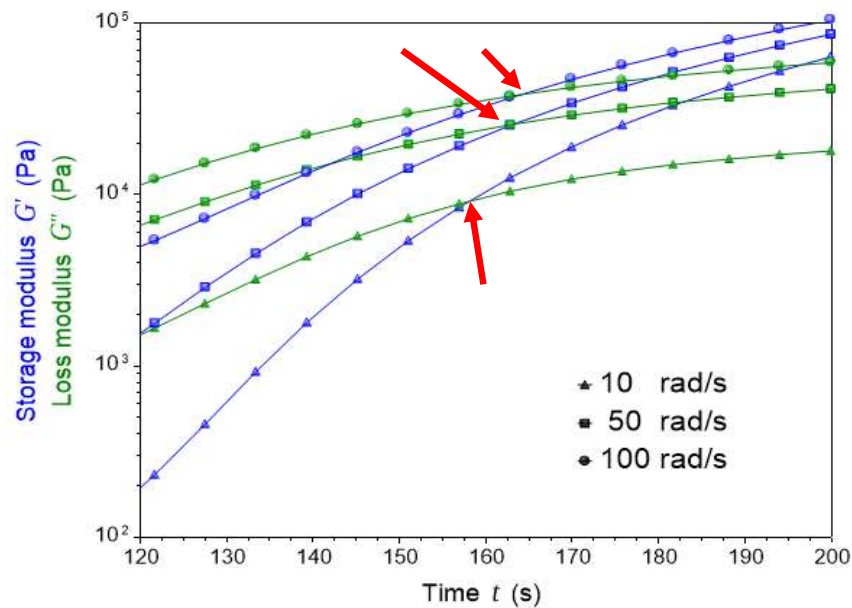
When  $G' = G''$  and  $\tan \delta = 1$



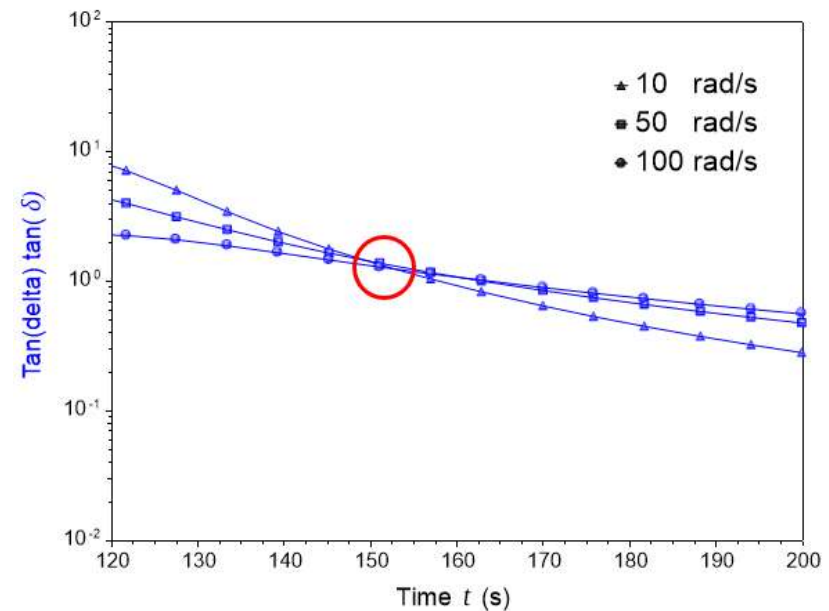
F. Chambon and H. H. Winter (1985)

# The “True Gel Point”

G'/G'' crossover: frequency dependent



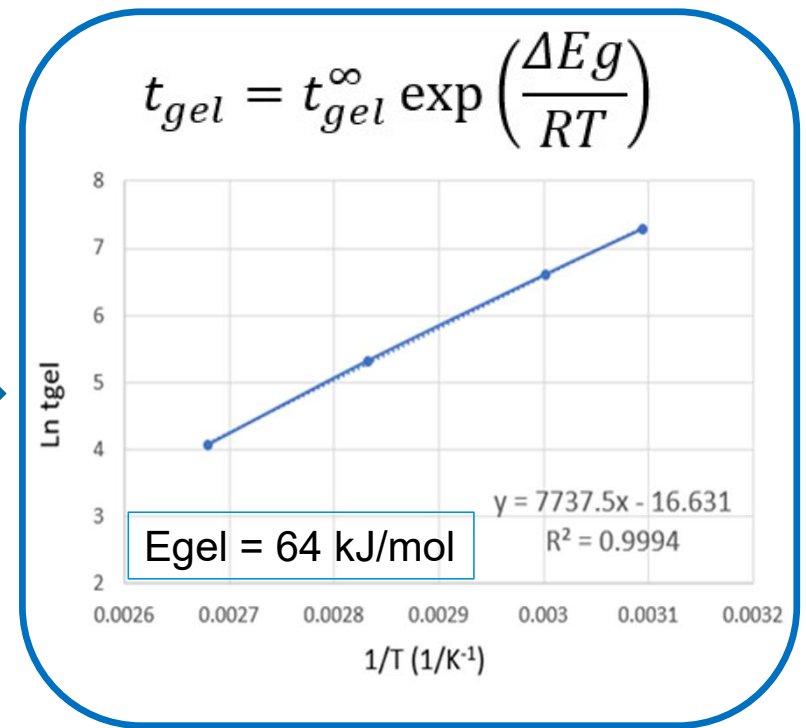
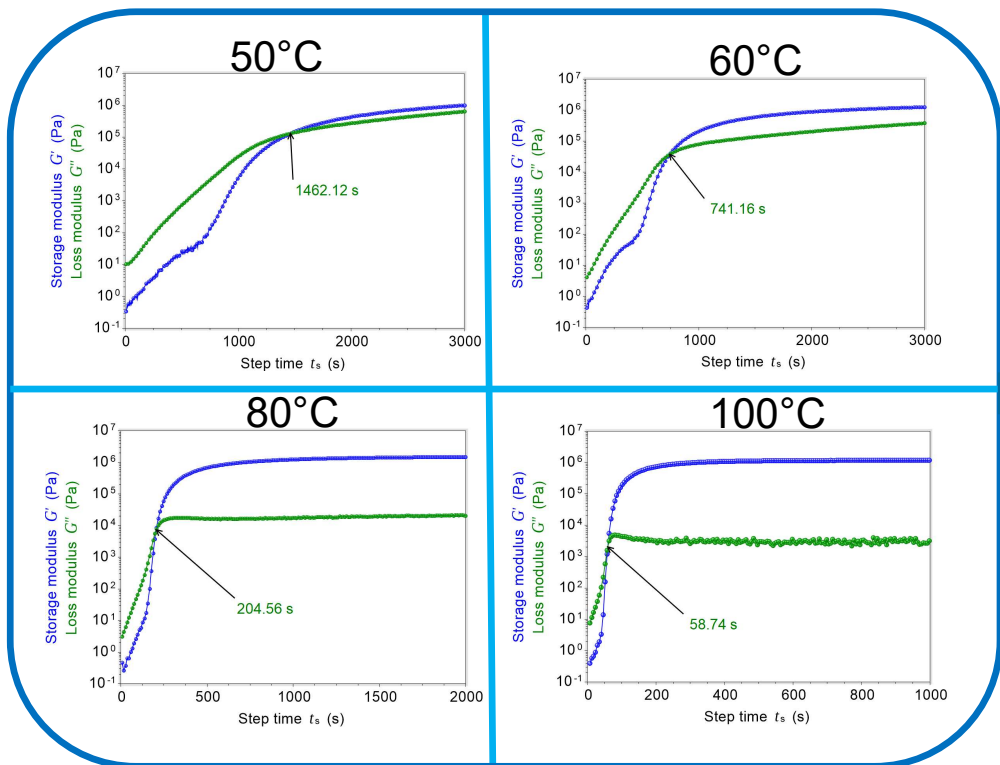
Gel Point:  $\tan \delta$  crossover point



G. Kamykowski; T. Chen, **The Use of Multi-wave Oscillation to Expedite Testing and Provide Key Rheological Information. ANTEC, 2020**

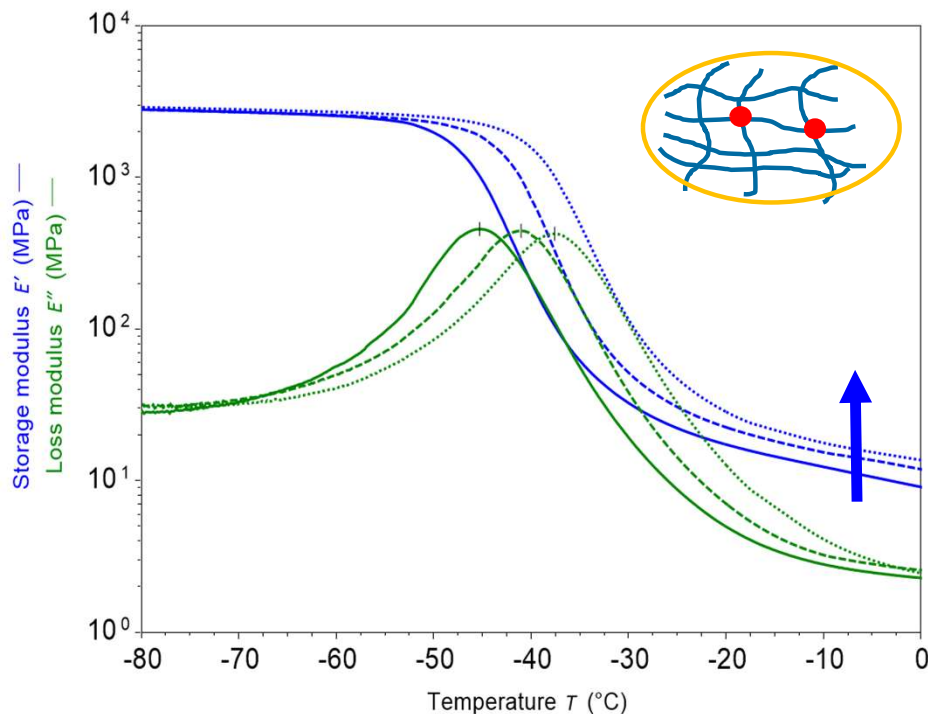
# Gelation Kinetics

- The gelation kinetics can be described using the empirical Arrhenius model
- Perform isothermal curing at different temperatures



# Quantify Crosslinking Density

- For unfilled polymers, crosslinking density can be quantitatively measured using rheology
- Calculation uses storage modulus in rubber plateau region ( $G'_{\text{rubbery}}$  or  $E'_{\text{rubbery}}$ )



$$M_c = \frac{3RTd}{E'_{\text{rubbery}}} \quad \text{or} \quad M_c = \frac{RTd}{G'_{\text{rubbery}}}$$

$M_c$  = Molecular weight between crosslinks  
 R = Universal gas constant  
 T = Absolute temperature (K)  
 d = Polymer density

$$\text{Crosslinking density, } q = \frac{Mw}{M_c}$$

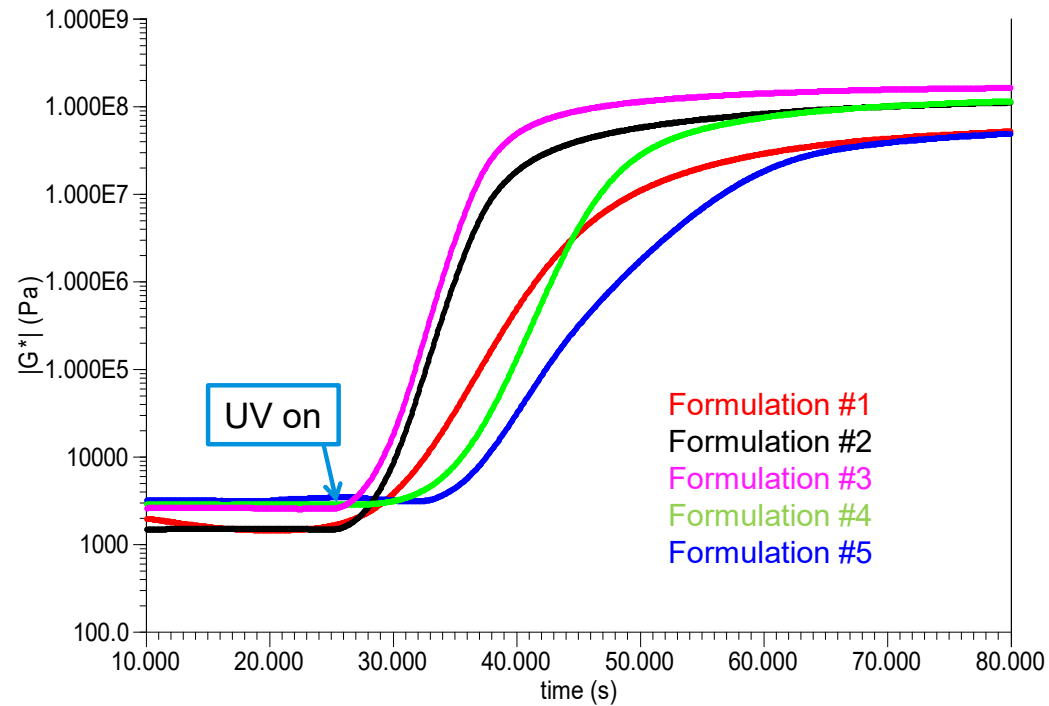
Mw = Molecular weight of the monomer

M. Barszczewska-Rybarak et al; Acta of Bioengineering and Biomechanics, vol 19, 1, 2017.

M. H. Abd-El Salam, J of Applied Polymer Sci, vol 90, 1539-1544, 2003.

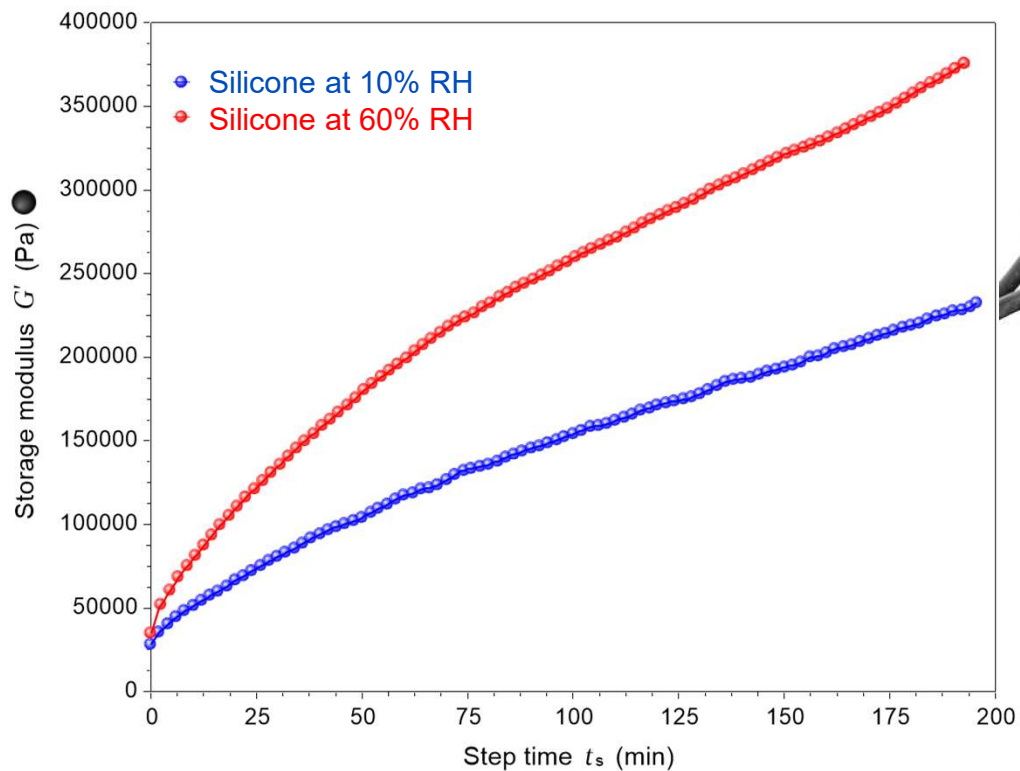
# UV Curing

- Monitor UV curing: Dynamic time sweep
- Measure curing time with different formulations, UV intensity and temperature
- Measure cured adhesive modulus



# Curing with Controlled Humidity

- Silicone adhesive curing under 25°C and 10%; 60% relative humidity
- Higher humidity, faster curing





# Testing Solids: Torsion and DMA

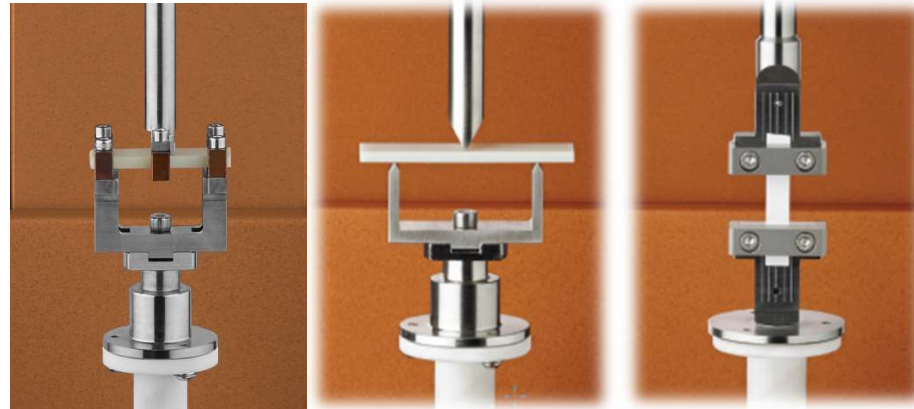
- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment
  - Torsion measures  $G'$ ,  $G''$ , and  $\tan \delta$
  - DMA measures  $E'$ ,  $E''$ , and  $\tan \delta$ 
    - DMA mode on ARES G2 (max 50  $\mu\text{m}$  amplitude)
    - DMA mode on DHR ( max 100  $\mu\text{m}$  amplitude)

$$E = 2G(1 + \nu)$$

$\nu$  : Poisson's ratio

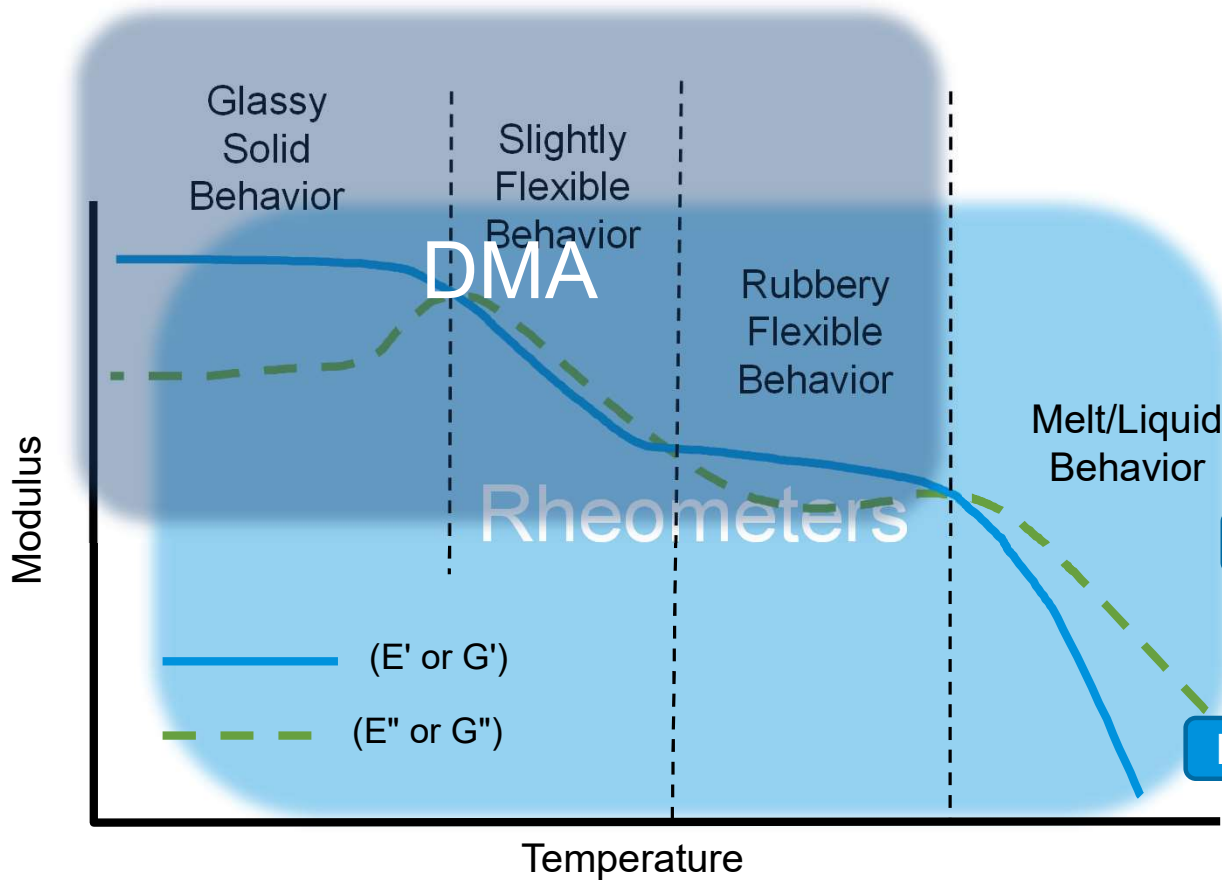


Torsion rectangular and cylindrical clamps

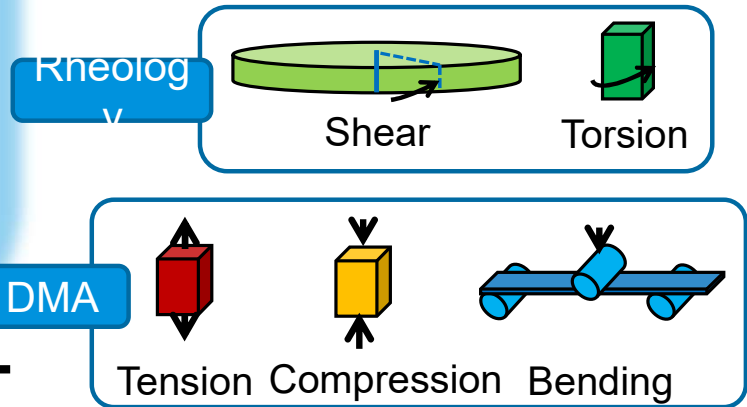


DMA cantilever, 3-point bending and tension clamps

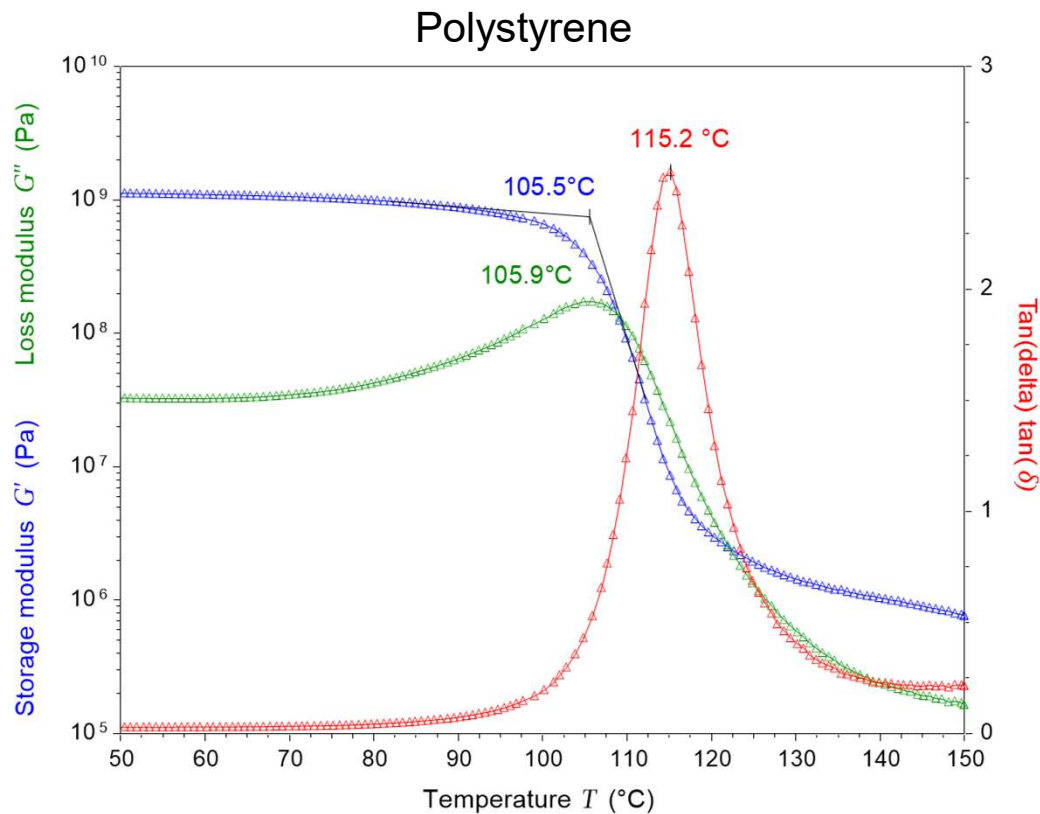
# DMA and Rheology Measurement Windows



$$E = 2G(1 + \nu)$$



# Dynamic Temp Ramp Test – Measure Tg



## How to define Tg in a Temp Ramp test:

- (1) **G' onset** - Occurs at lowest temperature
- (2) **G'' peak** - Occurs at middle temperature
- (3) **Tan delta peak** - Occurs at highest temperature - used historically in literature

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

# The Glass & Secondary Transitions

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

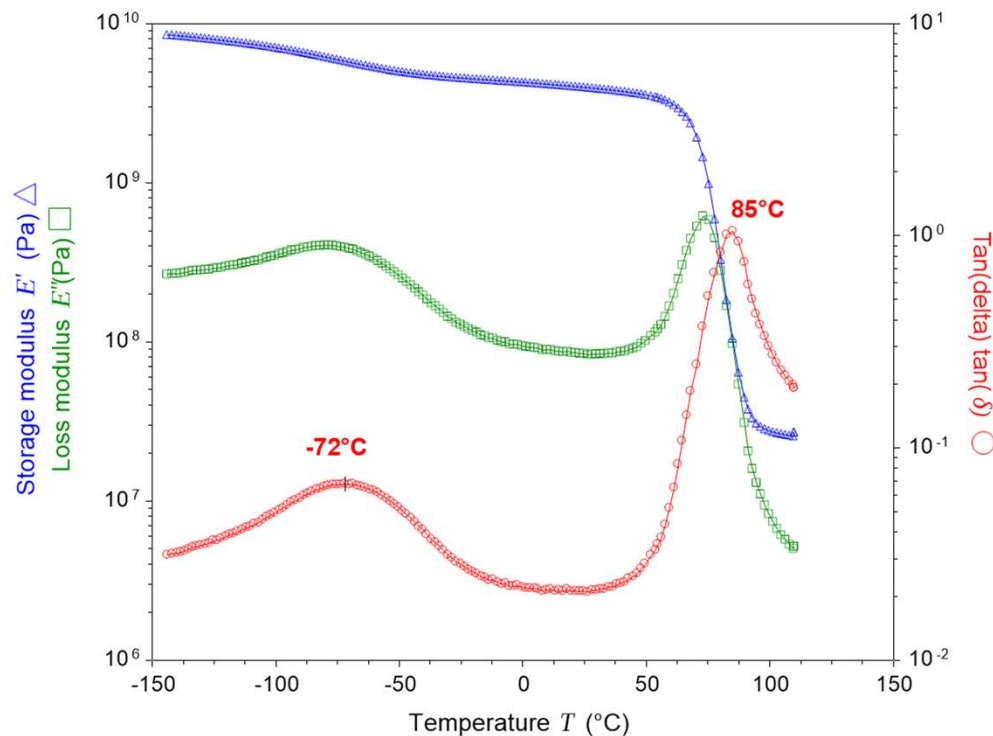
## **Secondary Transitions**

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

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

# Rheometers and DMAs are more sensitive to weak amorphous transitions than DSC

PET film: Tested in tension



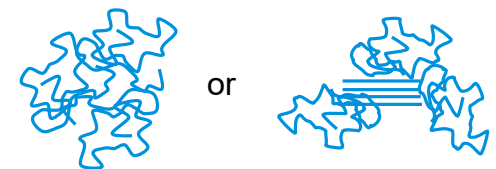
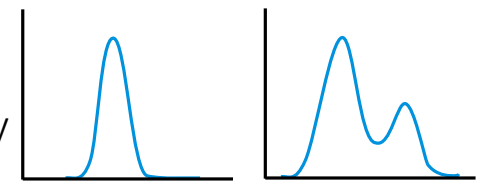
Glass Transition ( $T_g$ ): Cooperative motion among a large number of chain segments

Secondary Transitions ( $T_{\beta}$ ,  $T_{\gamma}$ ): Local or side group motion

DMA is 100-1000 $\times$  more sensitive than DSC for identifying weak amorphous transitions

Monitor  $T_g$  using DMA to study:

- Blend Miscibility
- Crystallinity
- Crosslinking density



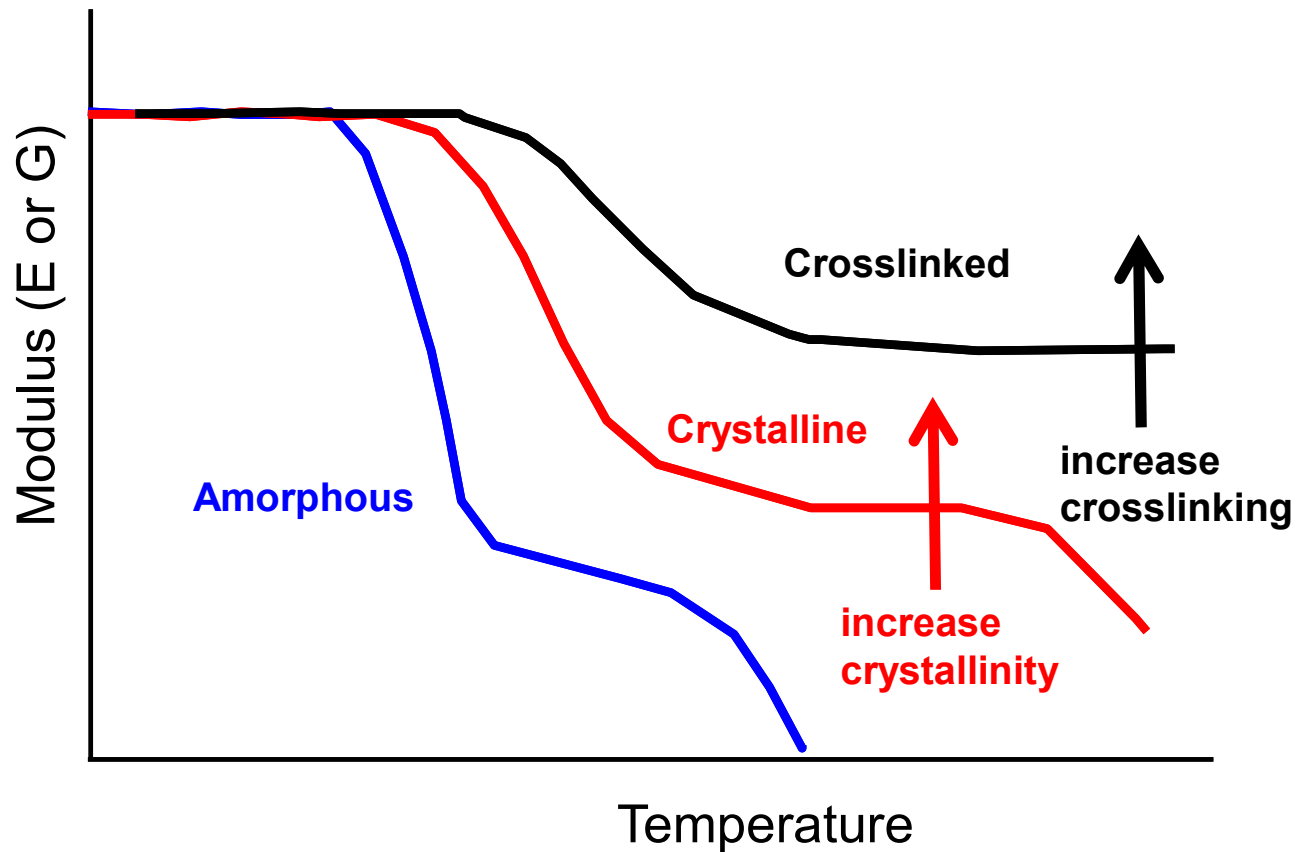
# Polymer Structure-Property Characterization

---

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

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

# Amorphous, Crystalline and Crosslinked Polymers



# Where to Find Help

## On your desktop



HR-DHR  
Manuals

### TA Instruments

#### HR/DHR Manuals

To view the desired manual using Acrobat Reader, click the name in the list below:

*TA Manual Supplement  
(Contains important information applicable to all manuals.)*

##### Instrument Documentation

HR/DHR Series Getting Started Guide - **UPDATED**  
AR-G2/AR2000ex/AR1500ex Rheometer Getting Started Guide

##### Accessory Documentation

Air Chiller System (ACS) Getting Started Guide  
Asphalt Submersion Cell Getting Started Guide  
Dielectric Accessory Getting Started Guide  
Electrically Heated Cylinder (EHC) Getting Started Guide  
Electrically Heated Plate (EHP) Getting Started Guide  
Electrorheological Accessory Getting Started Guide  
Environmental Testing Chamber (ETC) Getting Started Guide  
Gas Cooling Accessory Getting Started Guide  
High Sensitivity Pressure Cell Getting Started Guide  
Immobilization Cell Getting Started Guide  
Interfacial Subphase Exchange Cell Getting Started Guide  
MagnetoRheology Getting Started Guide  
Modular Microscopy Accessory Getting Started Guide  
Optics Plate Accessory Getting Started Guide  
Peltier Plate Concentric Cylinder Getting Started Guide  
Peltier Plate Getting Started Guide



ARES-G2  
Manuals

### TA Instruments

#### ARES-G2 Manuals

To view the desired manual using Acrobat Reader, click the name in the list below:

*TA Manual Supplement  
(Contains important information applicable to all manuals.)*

##### Instrument Documentation

ARES-G2 Getting Started Guide  
Accessory Documentation  
Air Chiller System (ACS) Getting Started Guide - **UPDATED!**  
Advanced Peltier System (APS) Getting Started Guide  
Chiller Panel Kit Installation Instructions  
Dielectric Accessory Getting Started Guide  
Electrorheological (ER) Accessory Getting Started Guide  
FCO Camera Kit Installation Guide  
High Sensitivity Pressure Cell Getting Started Guide - **NEW!**  
Interfacial Double Wall Ring (DWR) Getting Started Guide  
LN2 Kit Installation Guide  
Partitioned Plate Getting Started Guide  
Peltier Plate Kit Installation Instructions  
Sealed Fluid Bath Kit Installation Guide  
Sealed Fluid Bath Kit Upgrade Kit  
UV Curing Accessory Getting Started Guide

##### Software Documentation

What's New in TRIOS Software



## In TRIOS



Help

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Access Fund Applications SuccessFactors Log in Suggested Sites Link Site Gallery Log in to MyPage  
Search

Search by keywords

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You are here: Welcome to TRIOS

### Welcome to TRIOS Online Help for the HR/DHR Rheometers

TRIOS is TA Instruments' state-of-the-art software package that uses cutting-edge technology for instrument control, data collection, and data analysis of thermal and rheology instruments. The intuitive user interface allows you to simply and effectively program experiments and move easily between processing experiments and viewing and analyzing data. TRIOS software delivers a whole new experiment experience.

Before beginning, read our [Notices](#) and TA Instruments End-User License Agreement located in the [TA Manual Supplement](#). Find out what What's New in TRIOS Software by clicking [here](#).



# Web Based e-Training Courses

## 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.

<https://www.tainstruments.com/training/e-training-courses/>



# Practical Series Training Course

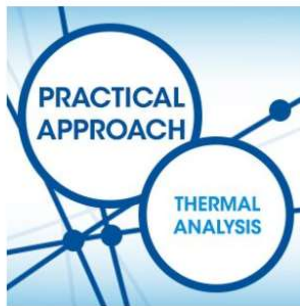
<https://www.tainstruments.com/practical-series-training-courses/>



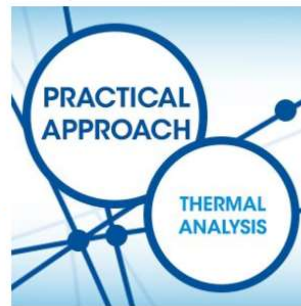
Sign up or log in for our free, on-demand practical series training courses here

Sign up

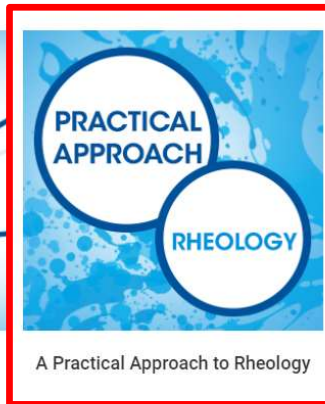
Log in



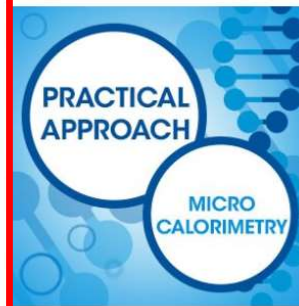
A Practical Approach to Thermal Analysis – Thermogravimetry



A Practical Approach to Thermal Analysis – Differential Scanning Calorimetry



A Practical Approach to Rheology



A Practical Approach to Microcalorimetry

# TA Webinars - Rheology

<https://www.tainstruments.com/support/webinars/>

View all Electroforce Dilatometry Microcalorimetry **Rheology** Rubber Thermal Analysis



TA WEBINARS

**Interfacial Rheology:  
Fundamental Overview  
and Applications**



TA WEBINARS

**Designing New  
Materials for Additive  
Manufacturing: Vat  
Photopolymerization**



TA WEBINARS

**Strategies for  
Rheological Evaluation  
of Adhesives**



TA WEBINARS

**An Introduction To High  
Pressure Rheology**



TA WEBINARS

**Randy H. Ewoldt:  
Experimental  
Challenges of Shear  
Rheology, How to Avoid  
Bad Data**



TA WEBINARS

**Norman J. Wagner: An  
Introduction to  
Colloidal Suspension  
Rheology**



TA WEBINARS

**Professor João Maia:  
The Role of Interfacial  
Elasticity on the  
Rheological Behavior  
of Polymer Blends**



TA WEBINARS

**Neil Cunningham:  
Essential tools for the  
new Rheologist**



TA WEBINARS

**Extensional Rheology  
in Polymer Processing**



TA WEBINARS

**An Introduction to  
Tribo-Rheometry:  
Quantifying Friction**



TA WEBINARS

**Rheo-Microscopy:  
Bridging Rheology,  
Microstructure &  
Dynamics**



TA WEBINARS

**Extensional Rheology &  
Analytics of Material  
Characterization**

# TA Website – Other Resources

## Tech Tips



Installation & Calibration of the Relative Humidity Accessory for the Discovery Hybrid Rheometer



Shear Sandwich Clamp Installation & Calibration for the Discovery DMA 850



Three Point Bend Clamp Installation & Calibration for the DMA850



Installation and Calibration for the UV Accessory on the Ares G2 Rheometer



Single Cantilever Installation & Calibration – DMA 850



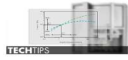
Dual Cantilever Installation & Calibration – DMA 850



Linear Film Tension Clamp for DMA using the ARES-G2



Loading the Powder Clamp on the Q800 DMA with 35mm Dual Cantilever Clamp



Frequency Sweep Tests for RPA Flex and RPA Elite



Improving Structured Fluid Measurements w/ Pre-Shearing



Measuring Thixotropy Of A Sample- TA TechTips



The Double Wall Ring & Interfacial Measurements – TA

## Applications Notes Library

### Applications Notes Library

Our instruments are used in a variety of products, in multiple industries. The application notes below provide more detail on specific potential applications. You can search for specific app notes with the search field.

261 item

Title	Product Category	Ref#	Link
Hot Melt Adhesives	Rheology	AAN001	<a href="#">Download Note</a>
Generating Mastercurves	Rheology	AAN005e	<a href="#">Download Note</a>
Analytical Rheology	Rheology	AAN006e	<a href="#">Download Note</a>
Normal Stresses in Shear Flow	Rheology	AAN007e	<a href="#">Download Note</a>
Mischungsregeln Komplexer Polysysteme	Rheology	AAN008d	<a href="#">Download Note</a>
Mixing Rules for Complex Polymer Systems	Rheology	AAN008e	<a href="#">Download Note</a>
Application of Rheology of Polymers	Rheology	AAN009	<a href="#">Download Note</a>
Synergy of the Combined Application of Thermal Analysis and Rheology Monitoring and Characterizing Changing Processes in Materials	Rheology	AAN010e	<a href="#">Download Note</a>

## Seminar Series: Instant Insights

### Seminars:

Thermal Analysis and Rheology

Medical Device and Biomaterials Testing

Elastomers and Rubber Compounds

TRIOS AutoPilot & TRIOS Guardian



### Thermal, Rheological and Mechanical Characterizations of Thermoset

*Tianhong (Terri) Chen, Ph.D.*

Thermosetting materials, such as epoxy, have been widely applied in many areas including automotive, aerospace and electronics industries in the form of surface coating, structural adhesives, advanced composites and packaging materials.

[View Archive](#)



### Advancements in the Characterization of Pharmaceuticals by DSC

*Jason Salenga, Ph.D.*

Differential Scanning Calorimetry is a simple, yet powerful technique to gain a broad understanding of the characteristics of pharmaceutical materials, from the crystalline structure that exists to the compatibility of a specific formulation.

[View Archive](#)



### Steady State & Flash Methods for Thermal Diffusivity and Thermal Conductivity Determination

*Justin Wynn*

In this presentation we will demonstrate accurate and high-throughput methods to measure the critical heat transfer properties of thermal diffusivity and thermal conductivity.

[View Archive](#)

- For additional questions:
- Email [rheologysupport@tainstruments.com](mailto:rheologysupport@tainstruments.com)
- Please put Online Training Questions in the subject line
- You can download this presentation from:
  - <https://www.tainstruments.com/online-training-course-downloads/>

