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Philadelphia Short Course: Day II

Section IV: DMA Theory and Instrumentation

Terri Chen, PhD

Principal Application Scientist

TA Instruments – Waters LLC

DMA: An introduction

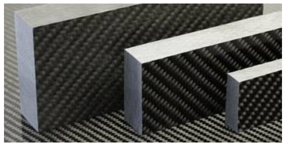
A Dynamic Mechanical Analyzer (DMA) measures the mechanical/rheological properties of a material as a function of time, frequency, temperature, stress, and strain.

Typical materials tested on a DMA - Solids

- Thermoplastic and thermosets
- Elastomers/rubbers
- Gels
- Foams
- More….

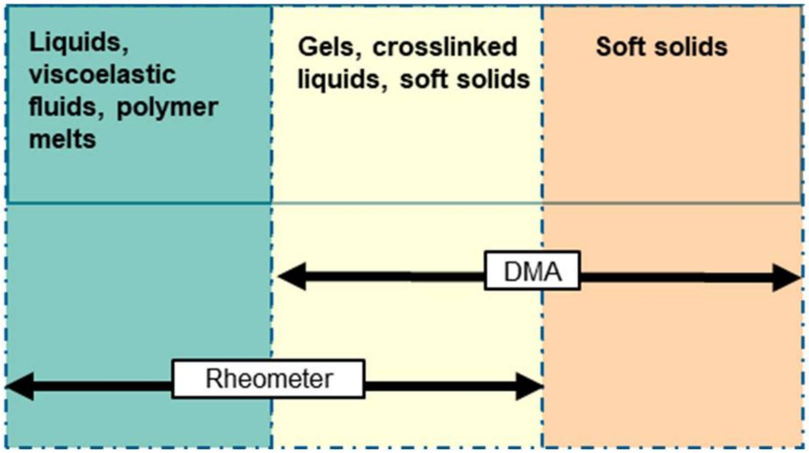






Rheology and DMA are complimentary

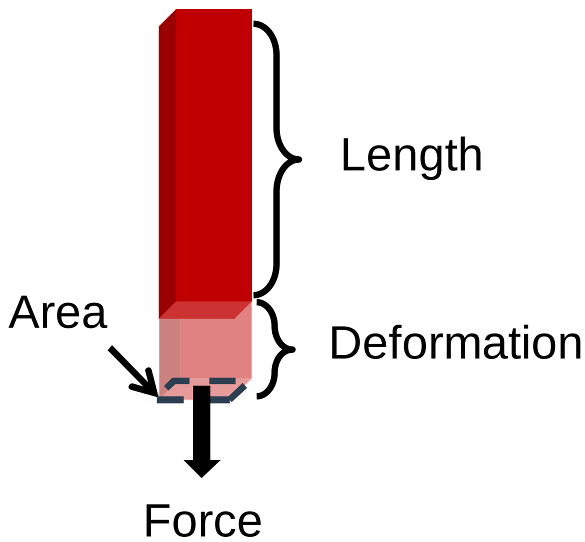
<u>DHR Rheometers can do both</u>



Working principle of DMA

Apply a force or a deformation to a sample, then measure the sample's response, which will be a deformation or a force.

All mechanical parameters (stress, strain, modulus, stiffness) are calculated from these 2 raw signals.



$$\text{Stress (Pa)} = \frac{\text{Force(N)}}{\text{Area(m}^2\text{)}}$$

$$\text{Strain} = \frac{\text{Deformation (m)}}{\text{Length (m)}}$$

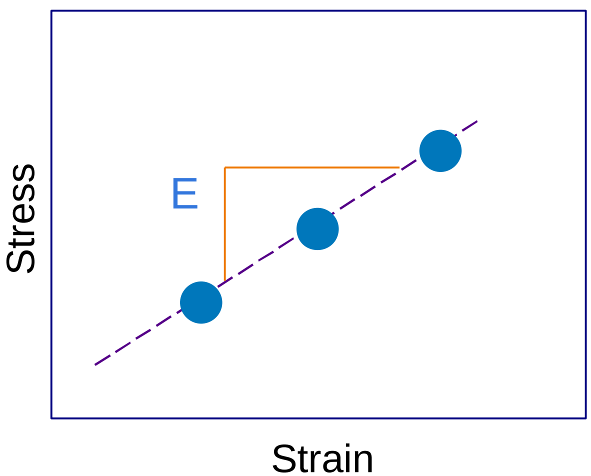
$$\text{Modulus (Pa)} = \frac{\text{Stress (Pa)}}{\text{Strain}}$$

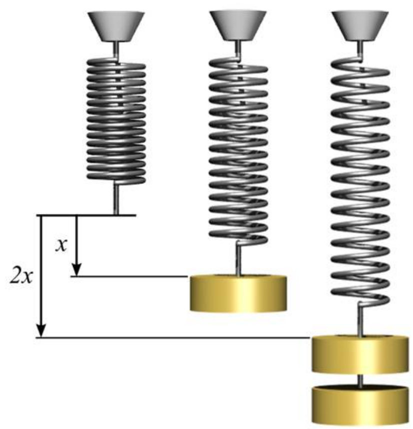
Hook’s law of elasticity, Newton’s law of viscosity

For a purely Elastic Solid, Stress and Strain have a constant proportionality

The slope of stress over strain is the Young’s modulus of the material

$$\sigma = E^* \varepsilon$$

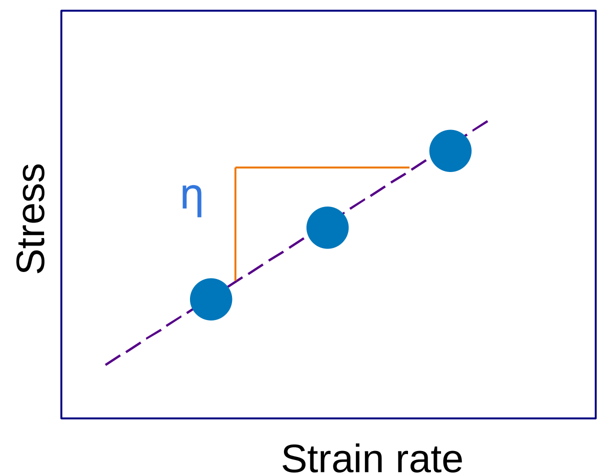


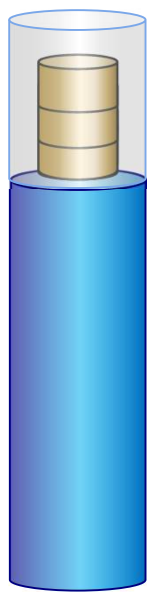


For a purely Viscous Liquid, Stress is proportional to Strain Rate dε/dt

The slope of stress over strain rate is the viscosity of the material

$$\sigma = \eta^* \frac{d\varepsilon}{dt}$$

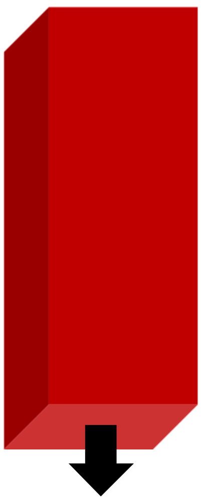


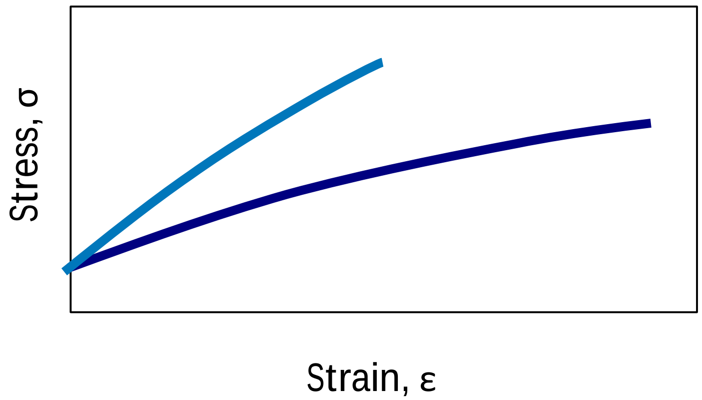


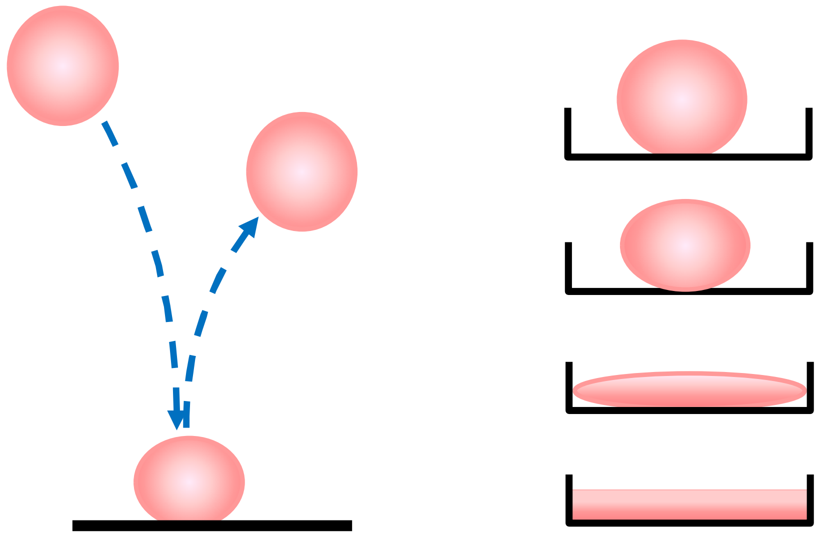
Time dependency of viscoelastic materials

- In tensile testing of viscoelastic materials, the rate of extension will give different results
- the stress depends on both the strain, and the strain rate

$$\sigma = E\,\varepsilon + \eta\frac{d\varepsilon}{dt}$$



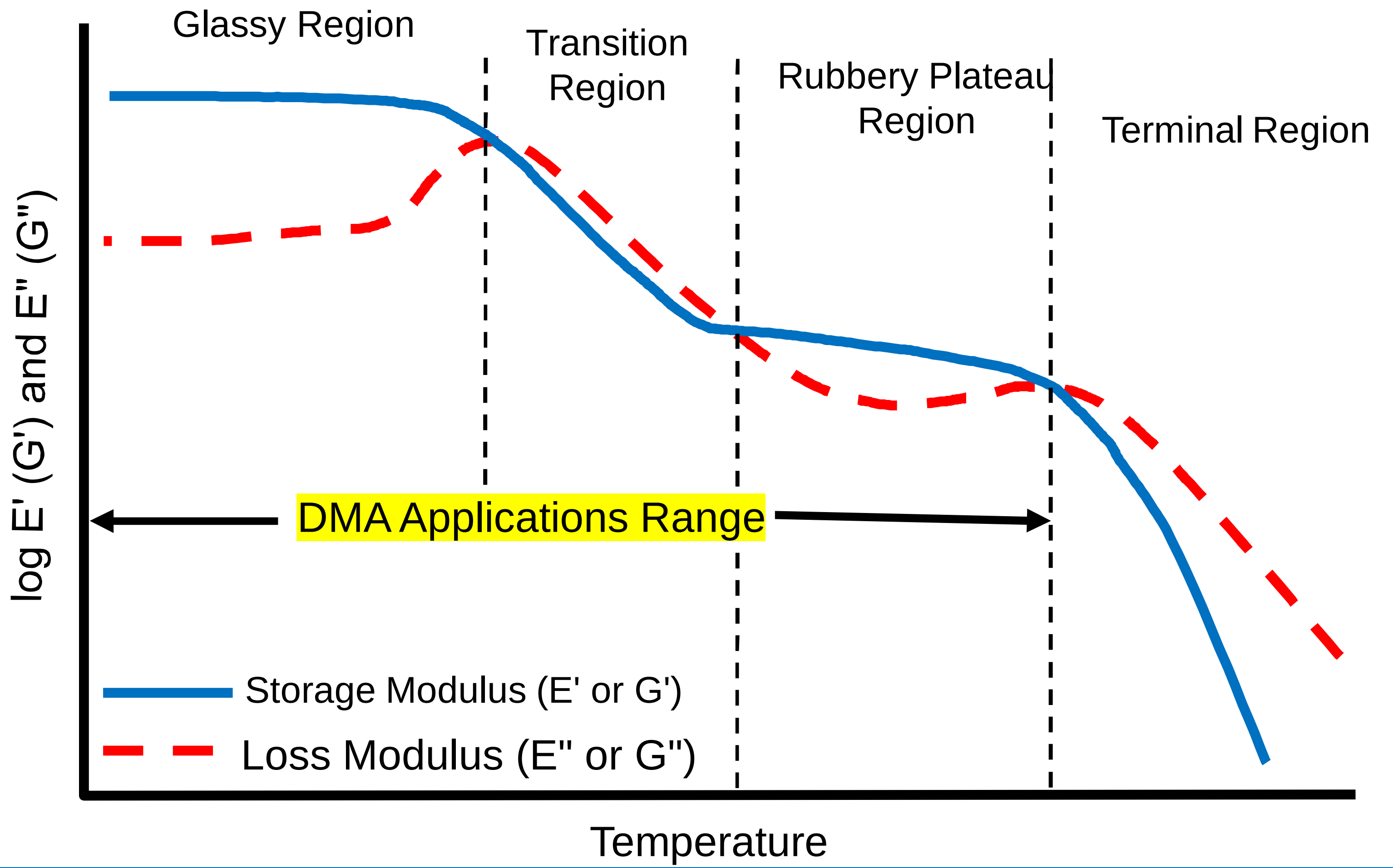




Fast deformation
(high frequency)

Slow deformation
(low frequency)

Viscoelastic spectrum for an amorphous polymer



DMA instrumentation

Discovery DMA850

RSA G2

Electroforce series

Standalone DMA

HR series

ARES G2

Rheometers with DMA mode

DMA instrumentation – Load Cell and Sensitivity

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Discovery DMA850	RSA G2 & ARES G2	HR 20 & 30 + DMA Mode	Electroforce series (high load frame, fatigue)
 18N	 35N  20N	 50N	 300N

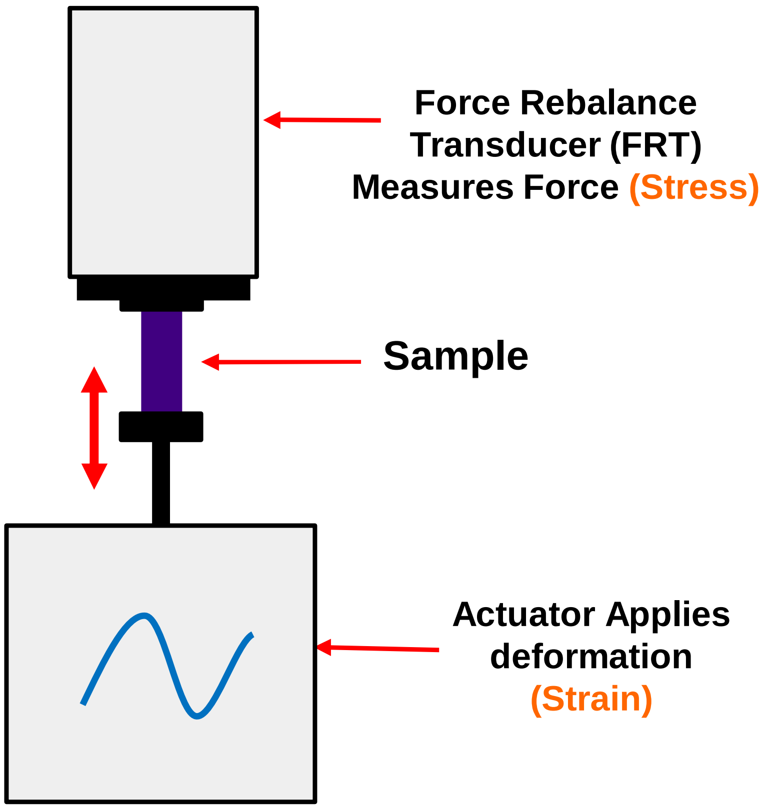
Load Cell Size (Maximum Force)

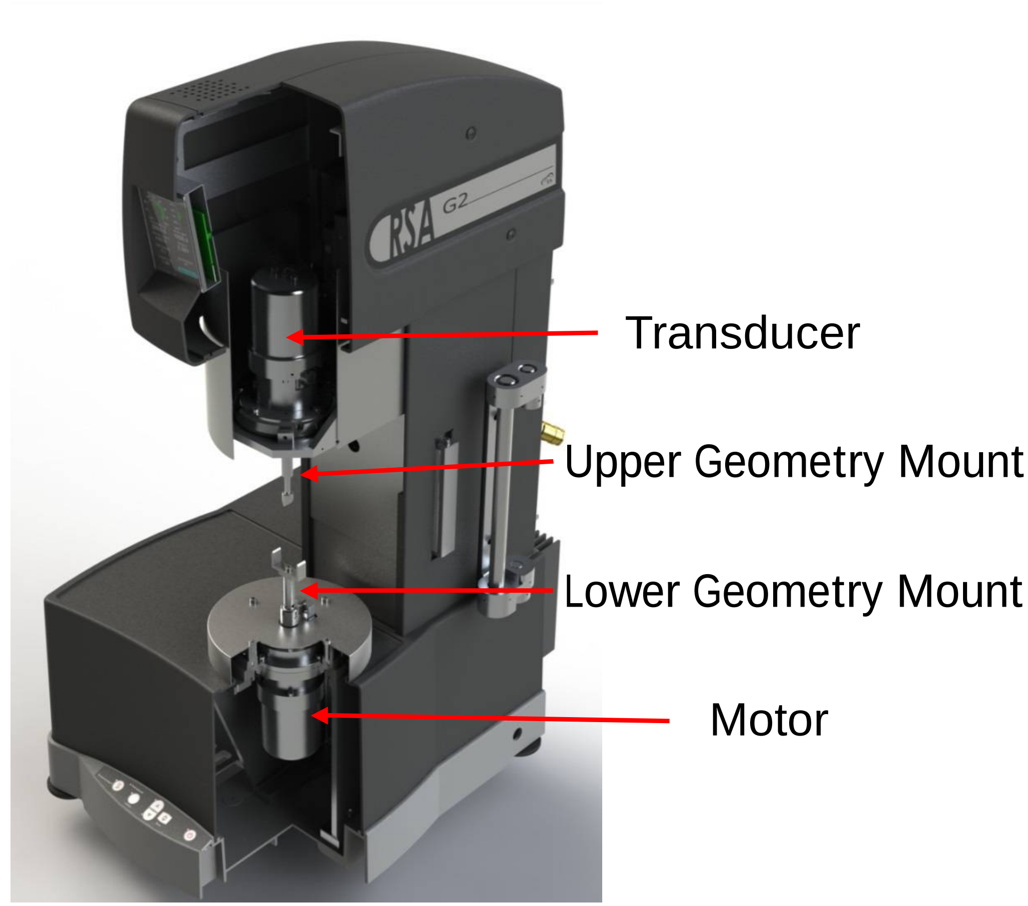
Load Cell Sensitivity (Force resolution & minimum force)

Separate motor and transducer

RSA G2

Separate Motor & Transducer

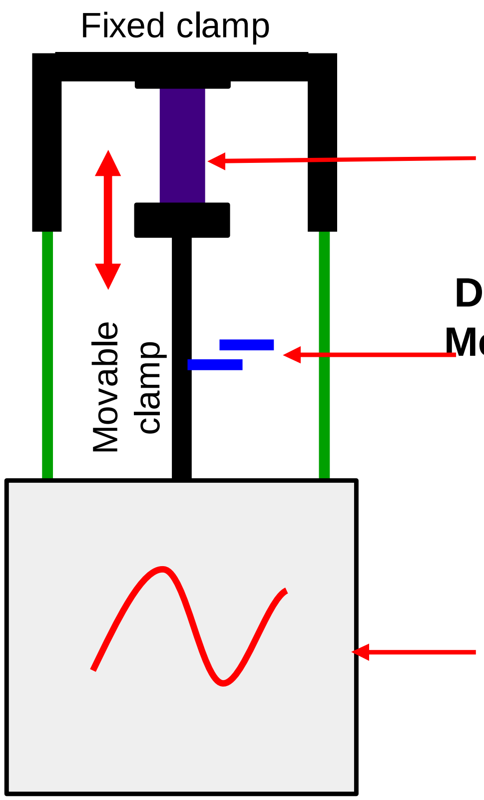




Combined motor and transducer

DMA850

Combined Motor & Transducer



Sample

Displacement Sensor Measures deformation (Strain)

Motor Applies Force (Stress)

Instrument specifications

	RSA G2	DMA850
Max Force	35 N	18 N
Min Force	0.0005 N	0.0001 N
Displacement Resolution	1 nm	0.1 nm
Frequency Range	2×10^{-6} to 100 Hz	1×10^{-4} to 200 Hz
Dynamic Deformation Range	$\pm 5 \times 10^{-5}$ to 1.5 mm	$\pm 5 \times 10^{-6}$ to 10 mm
Temperature range	-150 to 600°C	-150 to 600°C
Isothermal Stability	± 0.1	± 0.1
Heating Rate	0.1°C to 60°C/min	0.1°C to 20°C/min
Cooling Rate	0.1°C to 60°C/min	0.1°C to 10°C/min

DMA on TA rheometers

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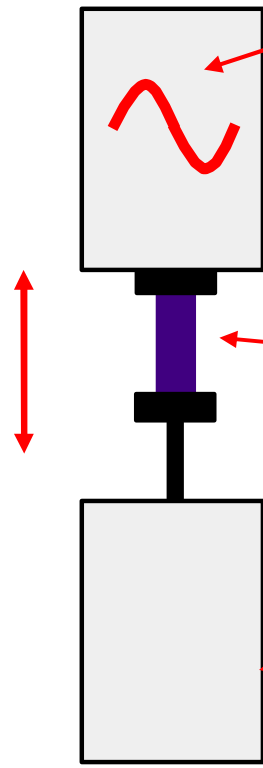
ARES-G2

HR 20/30



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

Specifications of HR and ARES-G2 DMA mode

Parameter	HR20/30 DMA mode	ARES-G2 DMA mode
Motor Control	FRT	FRT
Minimum Force (N) Oscillation	0.003	0.001
Maximum Axial Force (N)	50	20
Minimum Displacement (μm) Oscillation	0.01	0.5
Maximum Displacement (μm) Oscillation	100	50
Axial Frequency Range (Hz)	1×10^{-5} to 16	1×10^{-5} to 16

Samples tested on DMA

By changing the clamp, we can test a range of different materials

Elastomers

Films

Fibers

Gels

Plastics

Foams

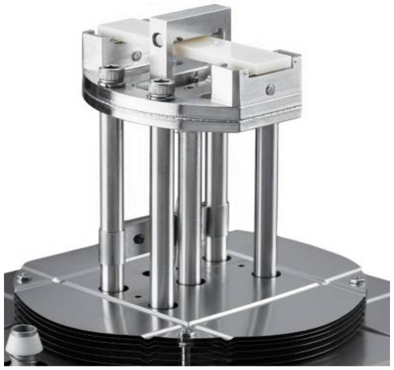
Composites

Popular DMA850 clamps

S/D Cantilever

Film/Fiber Tension

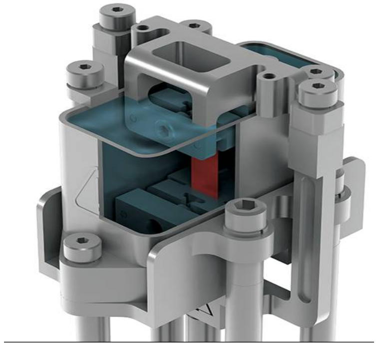
3-Point Bending



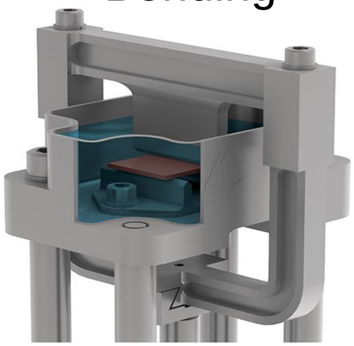
Compression

Shear Sandwich

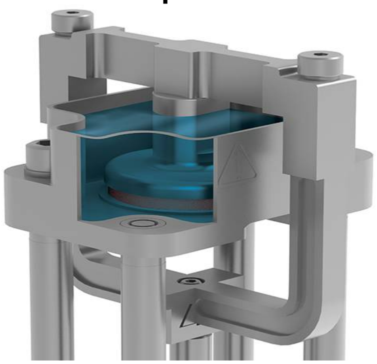
Submersible Tension



Submersible Bending

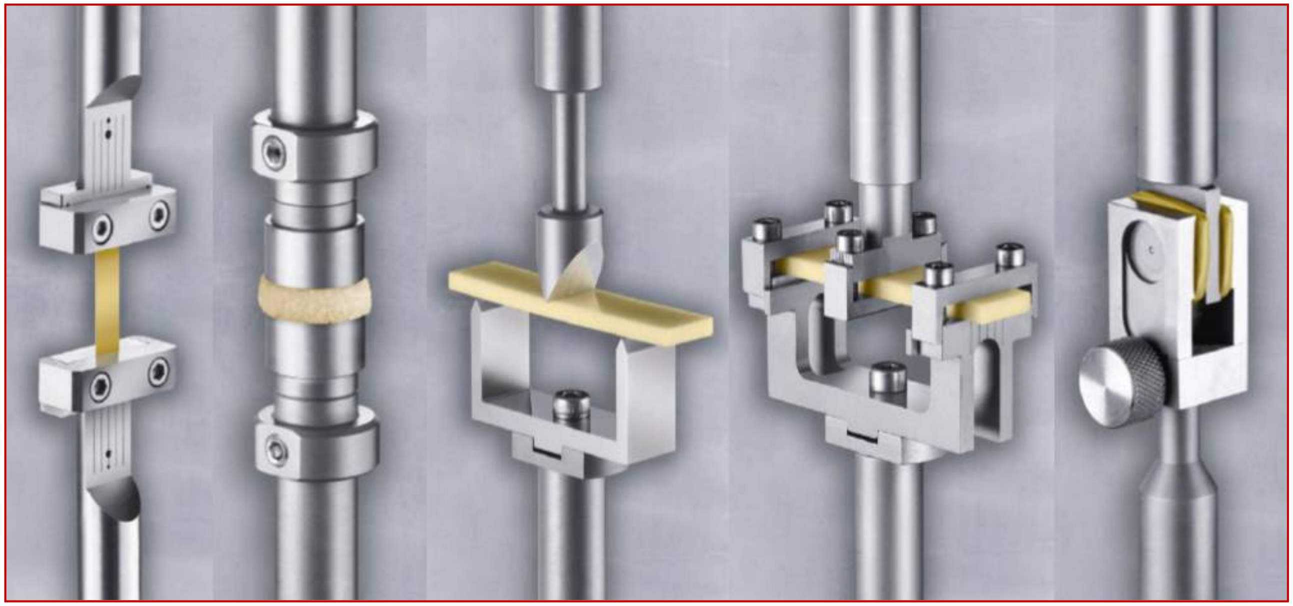


Submersible Compression



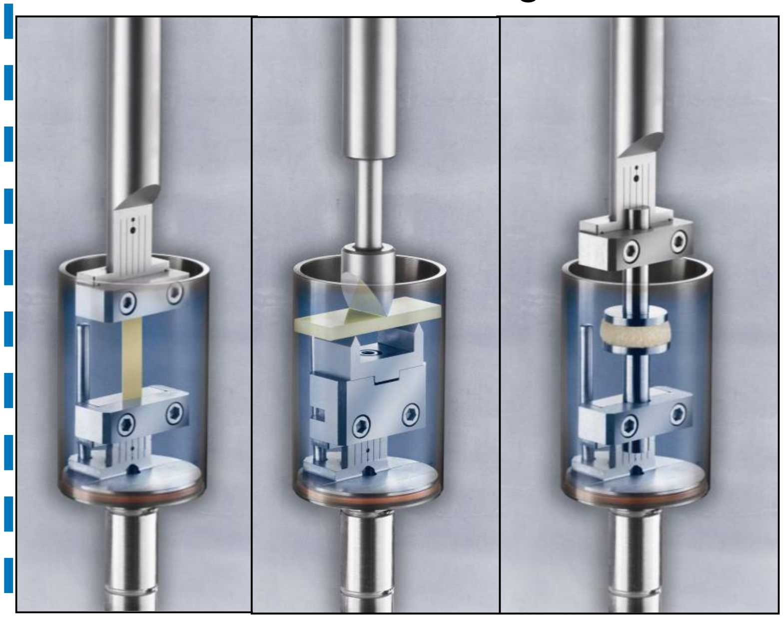
Popular RSA G2 clamps

Tension 3-Point Bending Shear Sandwich



Compression S/D Cantilever

3 Point Bending



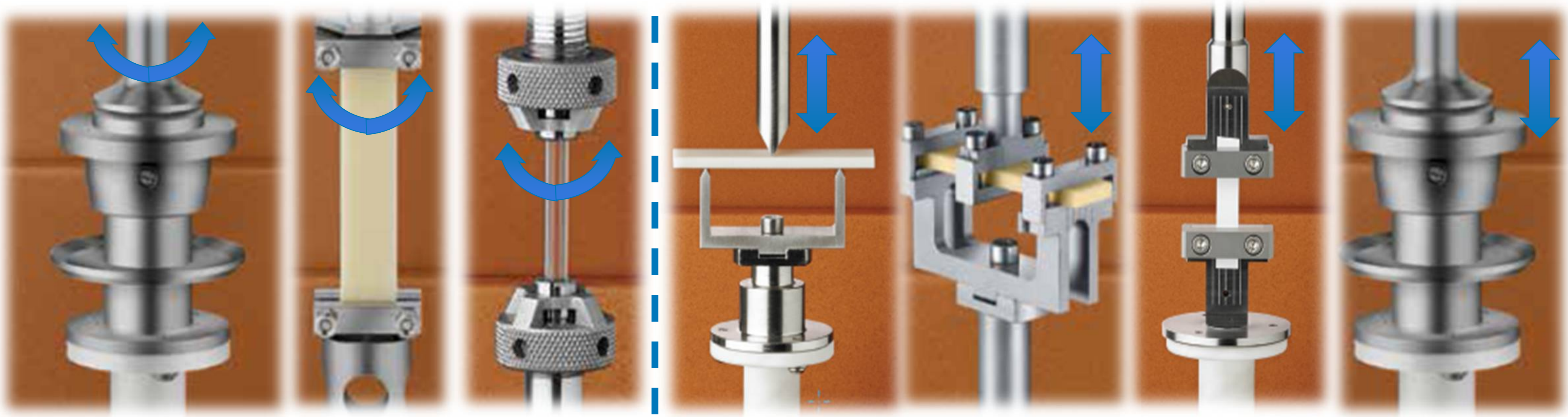
Tension Compression

Popular HR solid testing clamps

Torsion (rotational) and DMA (axial) geometries allow solid samples to be characterized in a temperature-controlled environment.

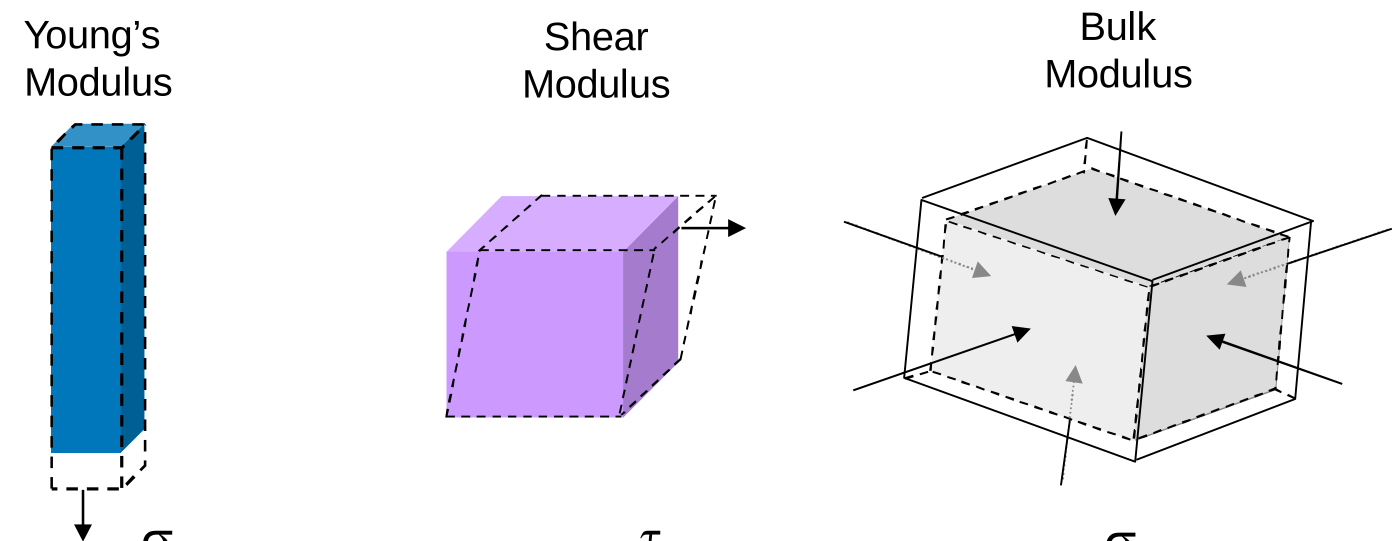
Shear Modulus: G', G'', G^*

Young's Modulus: E', E'', E^*



Parallel plate | Rectangular and cylindrical torsion | 3-point bending | Cantilever | Tension | Compression

Three fundamental modes of deformation



$$E = \frac{\sigma}{\varepsilon} \qquad G = \frac{\tau}{\gamma} \qquad B = \frac{\sigma_{hyd}}{\Delta V/V_o}$$

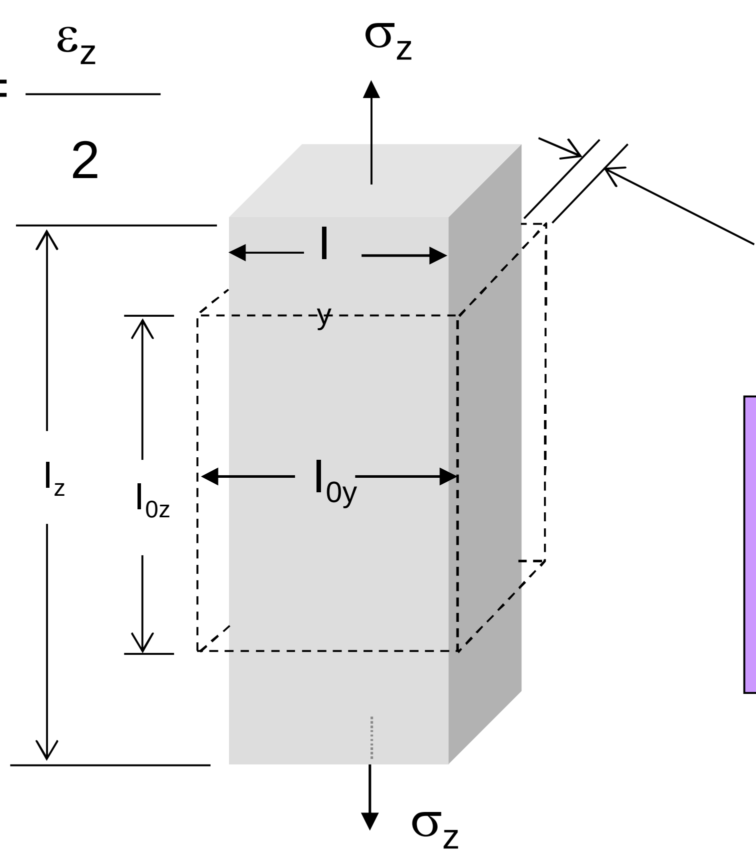
Where dashed lines indicate initial stressed state

- $\boldsymbol{\sigma}$ = uniaxial tensile or compressive stress
- $\boldsymbol{\tau}$ = shear stress
- $\boldsymbol{\sigma_{hyd}}$ = hydrostatic tensile or compressive stress
- $\boldsymbol{\varepsilon}$ = normal strain
- $\boldsymbol{\gamma}$ = shear strain
- $\boldsymbol{\Delta V/V_o}$ = fractional volume expansion or contraction

Poisson's Ratio

- Poisson's ratio, ν, is the ratio of transverse to axial strain

$$\frac{l_z - l_{0z}}{2} = \frac{\varepsilon_z}{2}$$



$$\frac{l_y - l_{0y}}{2} = \frac{-\varepsilon_y}{2}$$

Poisson's Ratio

$$\nu = \frac{-\varepsilon_y}{\varepsilon_z}$$

Relationship between moduli and Poisson’s ratio for an elastic isotropic materials

- Elastic Isotropic materials are materials in which properties at a point are the same in all directions. Some examples of isotropic materials are unoriented amorphous polymers and annealed glasses [1].
- If any of the two elastic constants of a homogenous (in which properties do not vary from point to point) isotropic material, the other two may be calculated [2].
- If the volume of the specimen remains constant when deformed (e.g., liquids or rubber) , then $\nu = 0.5$.
- In general, there is an increase in volume given by $DV/V_o = (1 - 2n)e$ where DV = increase in initial volume V_o caused by straining the sample.

$$E = 2G(1 + \nu) = 3B(1 + 2\nu)$$

1. Nielsen, Lawrence E., Mechanical Properties of Polymers and Composites, Marcel Dekker, Inc., New York, 1974, p. 1.

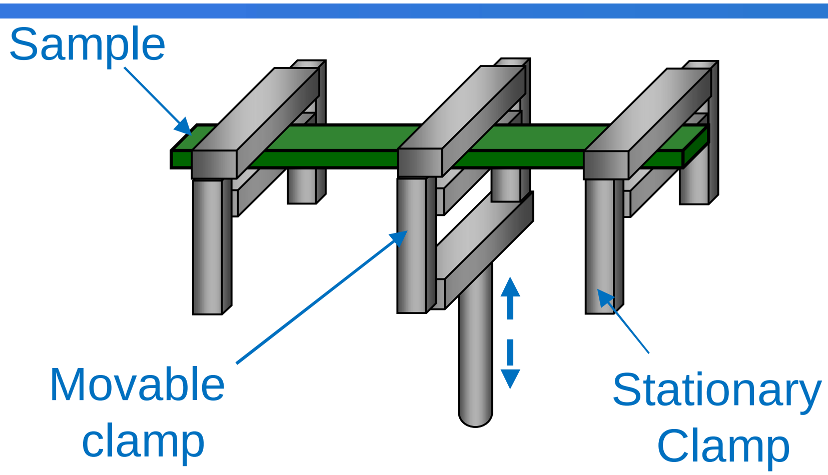
2. Hayden, H. W., Moffatt, W.G., and Wulff, J., The structure and Properties of Materials, Volume III, Mechanical Behavior, John Wiley & Sons, Inc, New York, 1965, p.26.

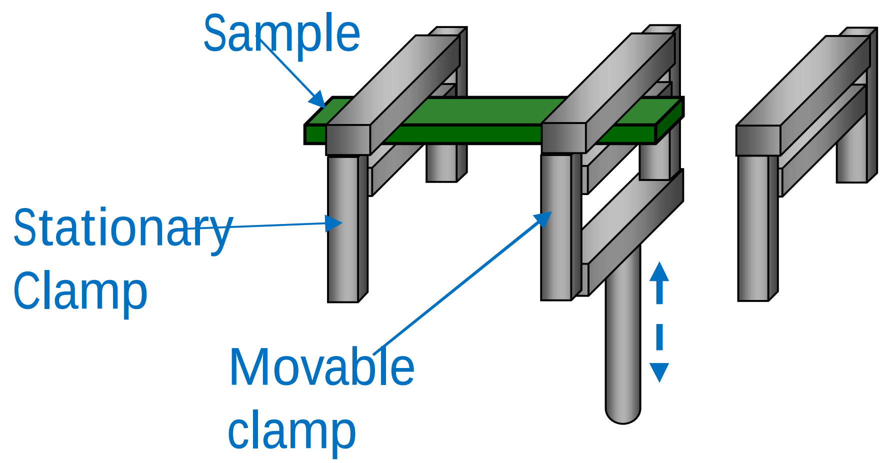
Modulus calculations in DMA

DMA850 and Q800	RSA G2
Stiffness (K) = Force / Displacement Modulus (E) = K x GF GF: Geometry factor. Clamp dependent Can be found in online help manual	Stress (σ) = Force x K_σ Strain (γ)= Displacement x K_γ Modulus (E) = σ / γ K_σ : Stress constant K_γ : Strain constant Clamp dependent Can be found in online help manual

$$GF = K_\sigma / K_\gamma$$

Cantilever clamps





Stiff samples with well-defined sample dimensions can be measured accurately.

- Soft samples (with Tg < RT) such as elastomers may get pinched during clamping and cause errors in measurement.
- Samples with high CTE can expand between the clamp faces and buckle, causing significant errors in measurement

Tracking cure of thermosets/composites, mechanical properties, secondary transitions and T_g of polymers (thermoplastics/thermosets)

Measurement of modulus and tan δ

Dual cantilever clamp governing equations

Modulus = Stiffness × Geometry Factor (GF)

$$GF_{DC} = \frac{12 \cdot l^3 \cancel{\left[1 + \frac{12}{5}(1+\nu)\left(\frac{t}{l}\right)^2\right]}}{24wt^3}$$

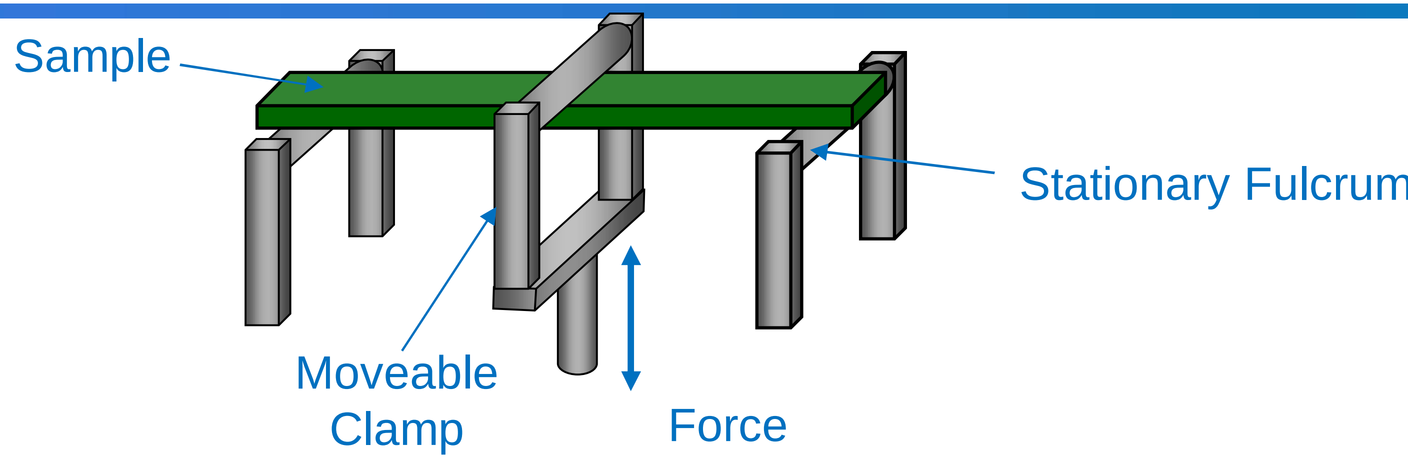
$$GF_{DC} = \frac{l^3}{2wt^3}$$

If length/thickness > 10, the contribution of the term containing the Poisson's Ratio can be approximated to be negligible

w = sample width
l = sample length
t = sample thickness

	To increase stiffness	To decrease stiffness
Dual cantilever	Decrease length or increase width. If possible, increase thickness. Note: L/T ≥ 10	Increase length or decrease width If possible, decrease thickness. Note: L/T ≥ 10

3-point bend clamp



Conforms with ASTM standard test method for bending

Purest deformation mode since clamping effects are eliminated

Stiff samples with well-defined sample dimensions can be measured accurately.

- Samples that get soft around T_g (typically unfilled thermoplastics) can sag and introduce errors in modulus measurements.

Tracking cure of thermosets/composites, mechanical properties and T_g of polymers that are stiff past the glass transition (filled thermoplastics/thermosets/elastomers)

Measurement of modulus and tan δ

3-point bend clamp governing equations

Modulus = Stiffness × Geometry Factor (GF)

$$GF_{3PB} = \frac{3l^3\left[1+\cancel{\frac{6}{10}(1+\nu)\left(\frac{2t}{l}\right)^2}\right]}{12wt^3}$$

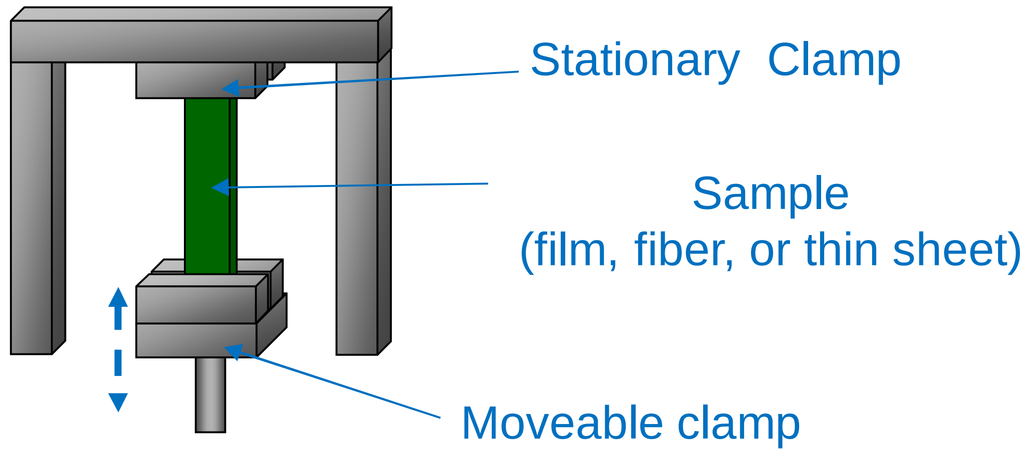
$$GF_{DC} = \frac{l^3}{4wt^3}$$

If length/thickness > 10, the contribution of the term containing the Poisson's Ratio can be approximated to be negligible

w = sample width
l = sample length
t = sample thickness

	To increase stiffness	To decrease stiffness
3-point bend	Decrease length or increase width. If possible, increase thickness. Note: L/T ≥ 10	Increase length or decrease width If possible, decrease thickness. Note: L/T ≥ 10

Tension clamp



Films and fibers with well-defined sample dimensions can be measured accurately. Sample length is calculated automatically by the instrument.

Applications

- Mechanical properties, Tg, secondary transitions (modulus and tan d)
- Creep and stress relaxation
- Temperature-controlled constant force or displacement tests to understand processing effects and shrinkage
- Generation of stress-strain curves

Tension clamp governing equations

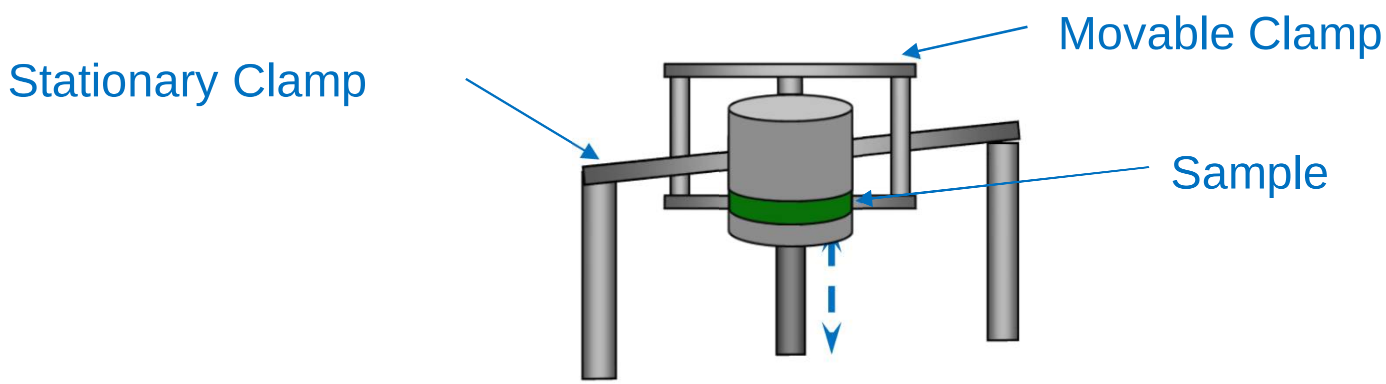
Modulus = Stiffness × Geometry Factor (GF)

$$GF_{Film} = \frac{l}{wt}$$

w = sample width
l = sample length
t = sample thickness

	To increase stiffness	To decrease stiffness
Tension	Decrease length or increase width. If possible, increase thickness.	Increase length or decrease width If possible, decrease thickness.

Compression clamp



Good mode for low to medium modulus materials (gels, elastomers) which are compressible throughout the test temperature range

- Samples that are incompressible (typically below the Tg) are difficult to test under compression
- Samples that are too soft and cannot support the load of the clamp need alterations in sample dimensions to get meaningful measurements

Applications:

- Mechanical properties, Tg, secondary transitions (modulus and tan δ)
- Creep and stress relaxation
- Temperature controlled constant force or displacement tests to understand processing effects

Compression clamp governing equations

Modulus = Stiffness × Geometry Factor (GF)

$$GF_{Comp} = \frac{thickness}{sample\ surface\ area} = \frac{t}{\pi r^2}$$

r = sample radius
t = sample thickness, between clamp faces

	To increase stiffness	To decrease stiffness
Compression	Decrease thickness. If possible, increase radius.	Increase thickness. If possible, decrease radius.

Dynamic (Oscillatory) Testing

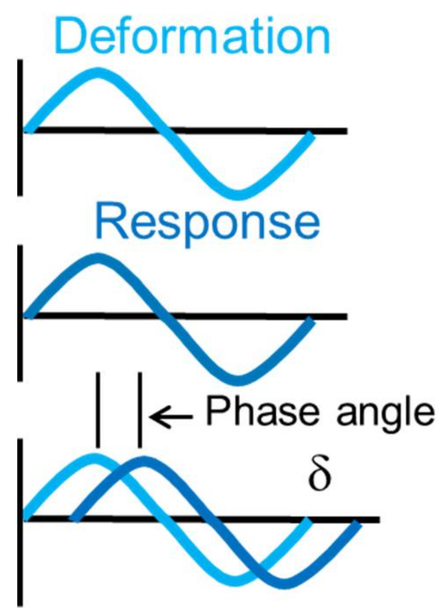
Available oscillatory test modes

- Strain (stress) Sweep
- Time Sweep
- Frequency Sweep
- Temperature Ramp
- Temperature Step (Sweep) (TTS)

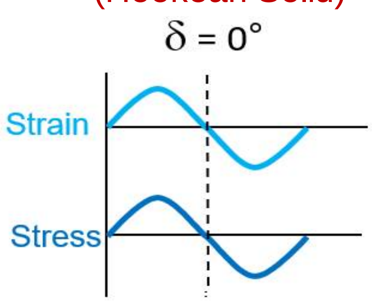
https://www.tainstruments.com/recorded-theory-applications-training/

Dynamic testing and phase angle

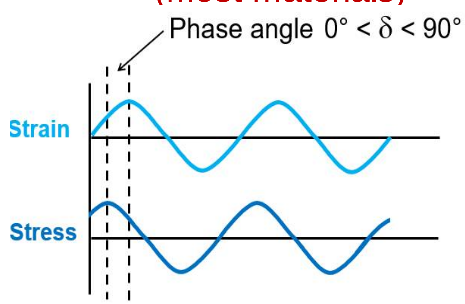
- An oscillatory (sinusoidal) deformation (stress or strain) is applied to a sample.
- The material response (strain or stress) is measured.
- The phase angle δ, or phase shift, between the deformation and response is also measured.



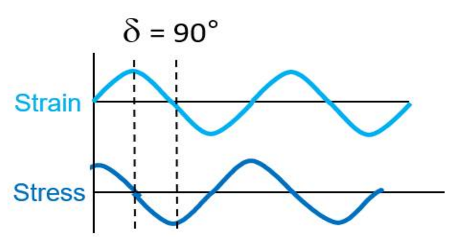
Purely Elastic Response
(Hookean Solid)



Viscoelastic Response
(Most materials)



Purely Viscous Response
(Newtonian Liquid)



Viscoelastic parameters

- Complex Modulus:

$$E^* = \frac{\sigma}{\gamma}$$

Measure of materials overall resistance to deformation.

- The Elastic (storage) Modulus:

$$E' = \left(\frac{\sigma}{\gamma}\right)\cos\delta$$

Measure of elasticity of material. The ability of the material to store energy.

- The Viscous (loss) Modulus:

$$E'' = \left(\frac{\sigma}{\gamma}\right)\sin\delta$$

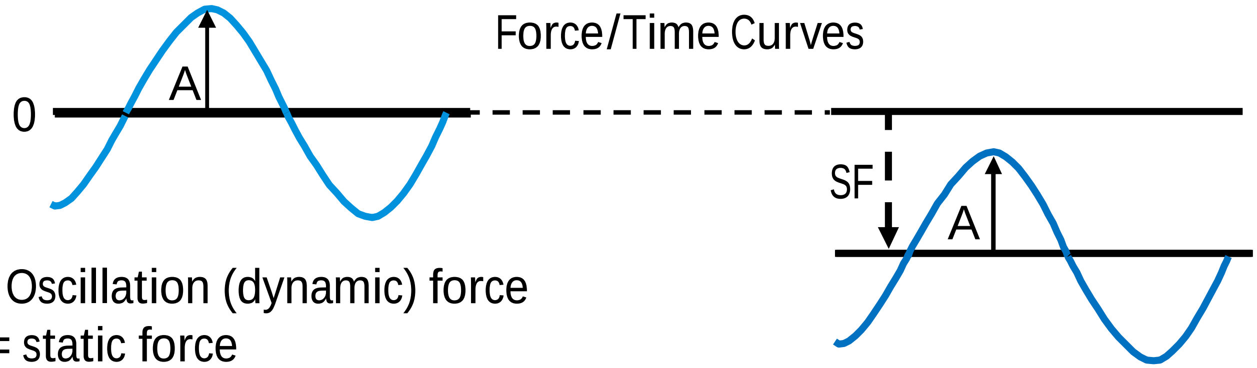
The ability of the material to dissipate energy. Energy lost as heat.

- Tan Delta:

$$\tan\delta = \frac{E''}{E'}$$

Measure of material damping. Increasing tan d implies a greater potential for energy dissipation and lower elasticity, and vice-versa. Measure of viscous property while having the appropriate level of stiffness.

Some Clamps Require Offset (static) Force!



A = Oscillation (dynamic) force
SF = static force

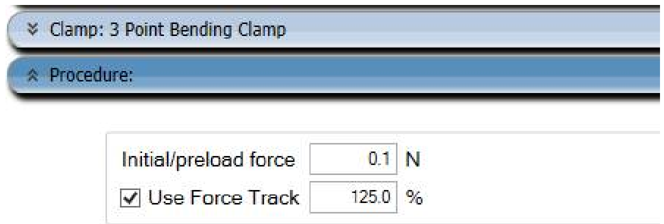
<u>Clamps **without** static force:</u>
- Single Cantilever
- Dual Cantilever
- Shear Sandwich

<u>Clamps **with** static force:</u>
- Tension Film
- Tension: Fiber
- 3-Point Bend
- Compression
- Penetration

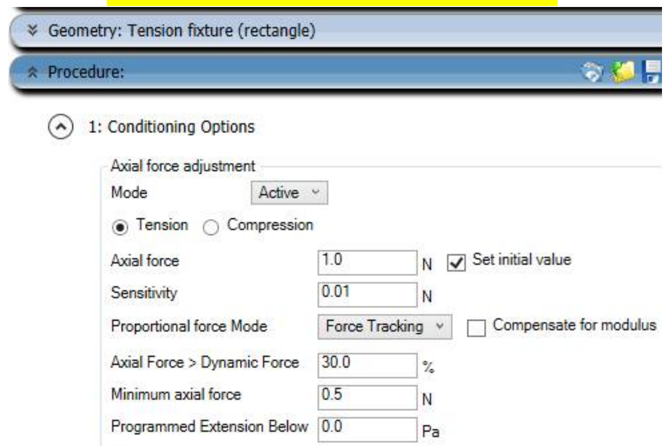
How to Setup Force Track?

- **Recap: Desired situation for all clamps is that F_{static} > F_{osc}**
- Force track = $\frac{F_{static}}{F_{osc}}$
- If $\frac{F_{static}}{F_{osc}}$ > 1, then $\mathbf{F_{static} > F_{osc}}$
- Force track ratio is expressed as a percentage
  - On 850 and 800, Force track = $\frac{F_{static}}{F_{osc}}$ x 100%
  - On RSA-G2, Force track = ($\frac{F_{static}}{F_{osc}}$ - 1) x 100%

DMA850

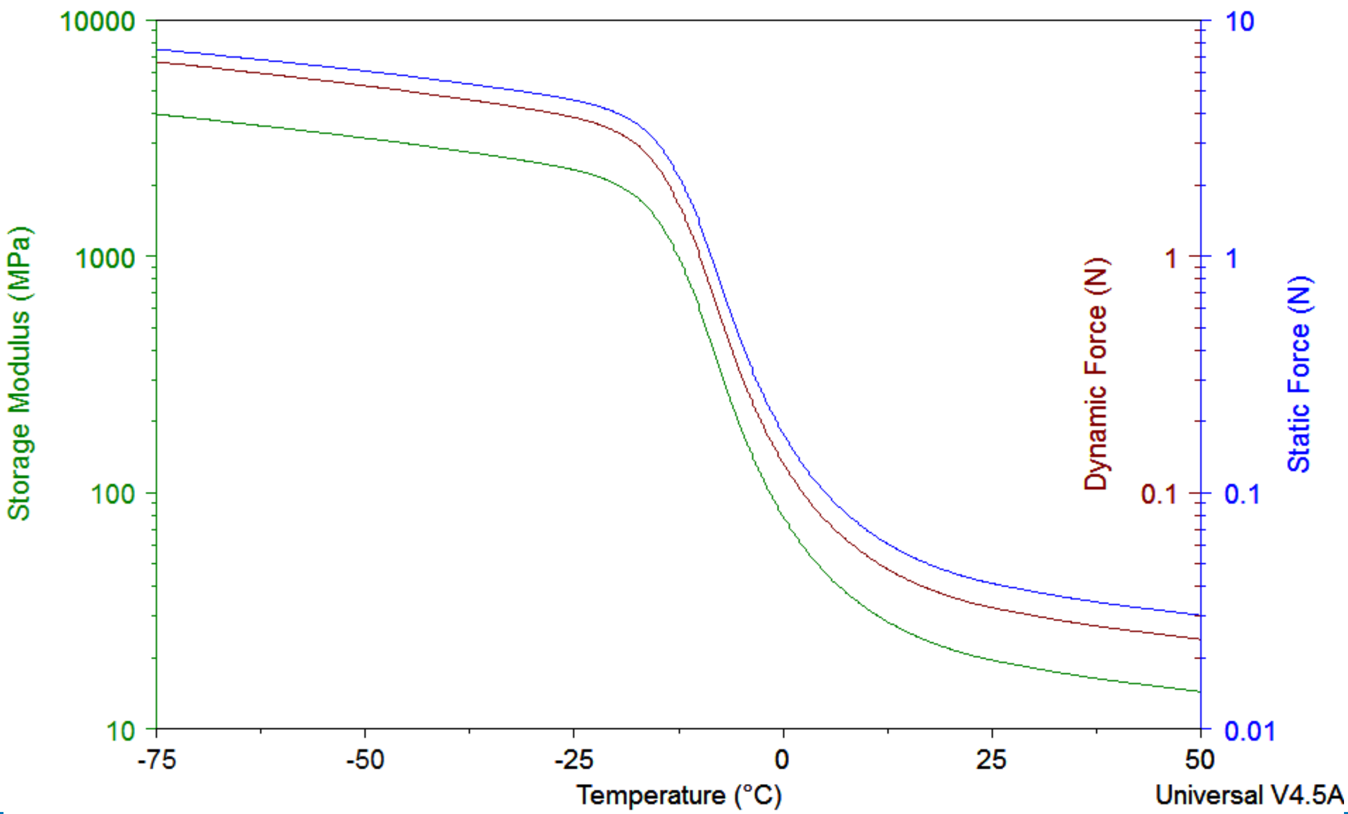


RSA G2 or rheometer

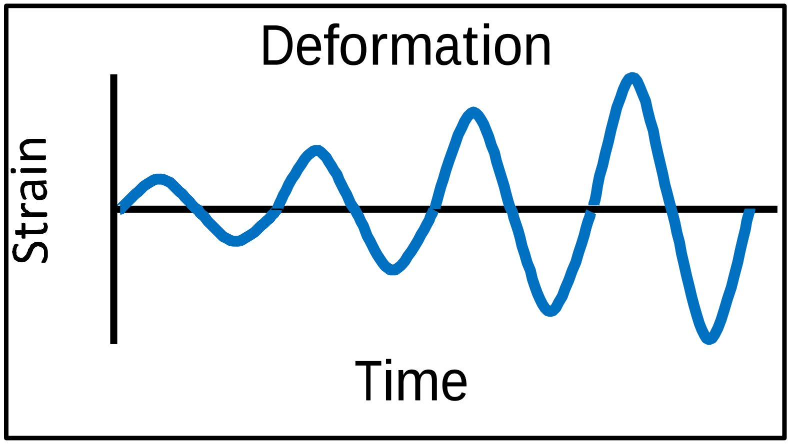


Temperature Ramp with Force Track

- Static Force tracks Dynamic Force throughout Temperature Ramp to prevent over-stretching



Dynamic Strain (Stress) Sweep

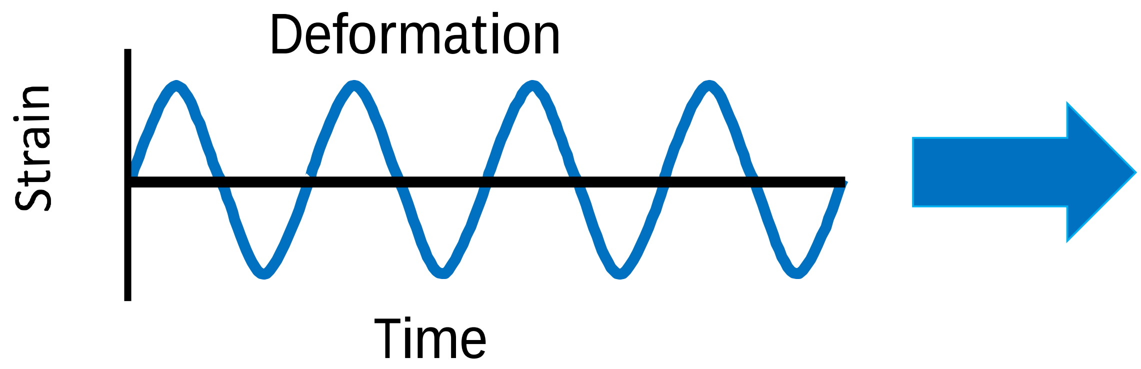


The material response to increasing deformation amplitude is monitored at a constant frequency and temperature.

USES

- Identify Linear Viscoelastic Region
- Payne effect analysis for elastomers

Dynamic Time Sweep

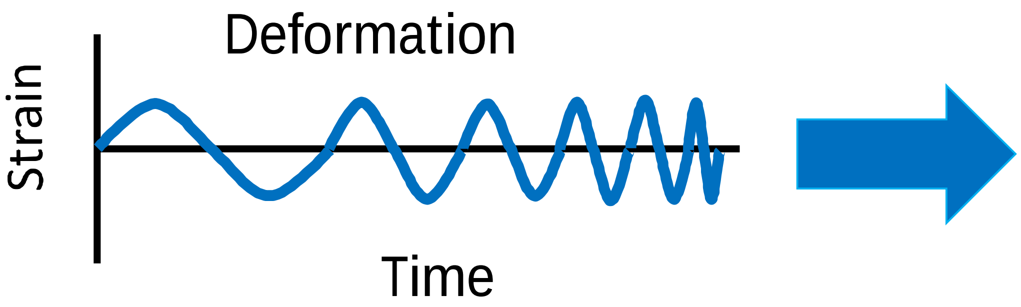


The material response is monitored at a constant frequency, amplitude and temperature.

USES

- Curing studies
- Fatigue tests
- Stability against thermal degradation

Frequency Sweep



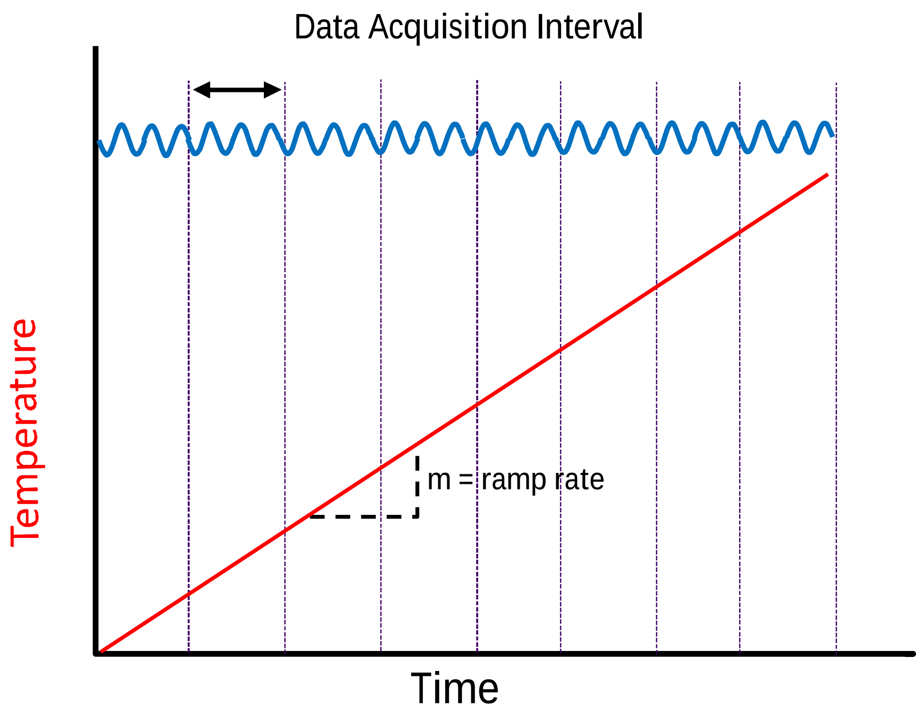
- The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude and temperature.

<u>USES</u>

- Quick comparison on modulus and elasticity on solids
- Study polymer melt processing (shear sandwich).
- Estimate long term properties with extended frequency (time) range using TTS

Dynamic Temperature Ramp

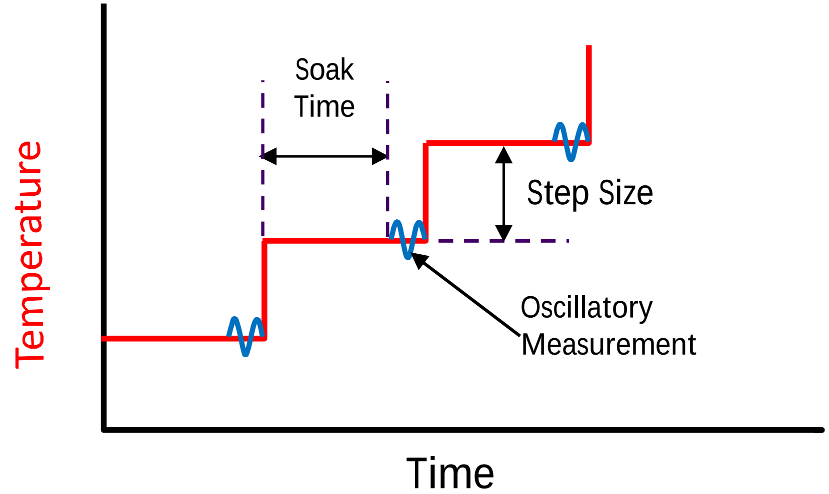
- A linear heating rate is applied. The material response is monitored at a constant frequency and constant amplitude of deformation. Data is taken at user defined time intervals.

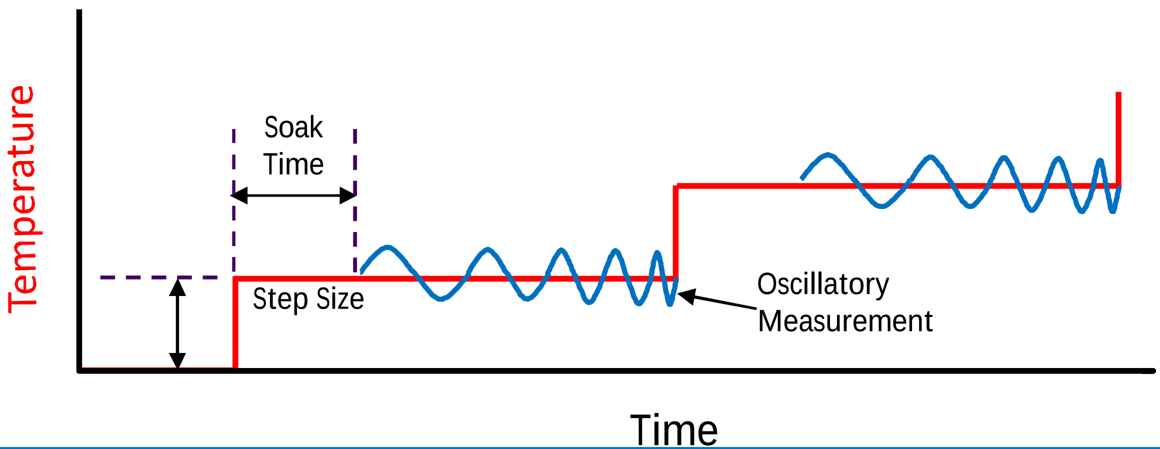


Recommend ramp rate for polymer testing: 1-5˚C/min.

Temperature Step & Hold- Single /Multi-Frequency

- A step and hold temperature profile is applied. The material response is monitored at one, or over a range of frequencies, at constant amplitude of deformation





Transient Testing

Available transient test modes

- Creep-Recovery
- Stress Relaxation
- Iso-strain Temperature Ramp
- Iso-force Temperature Ramp
- Stress-Strain Rate Tests

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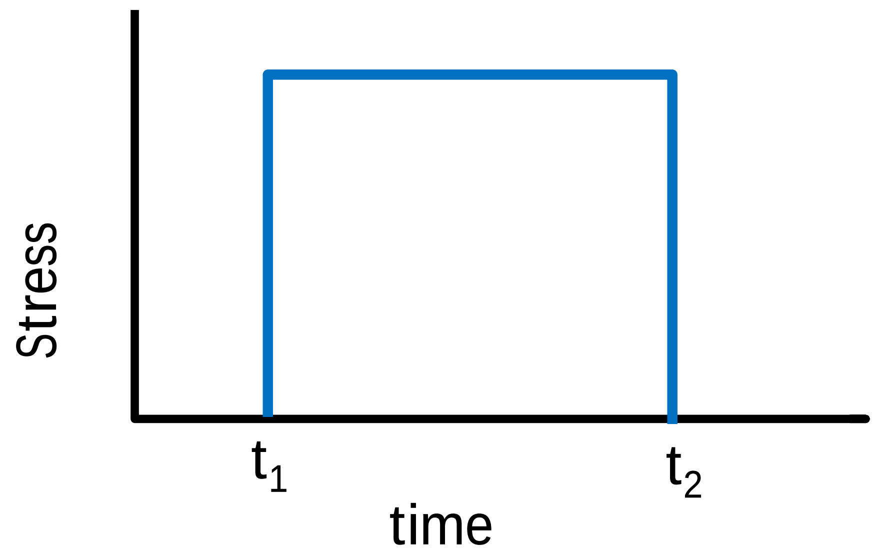
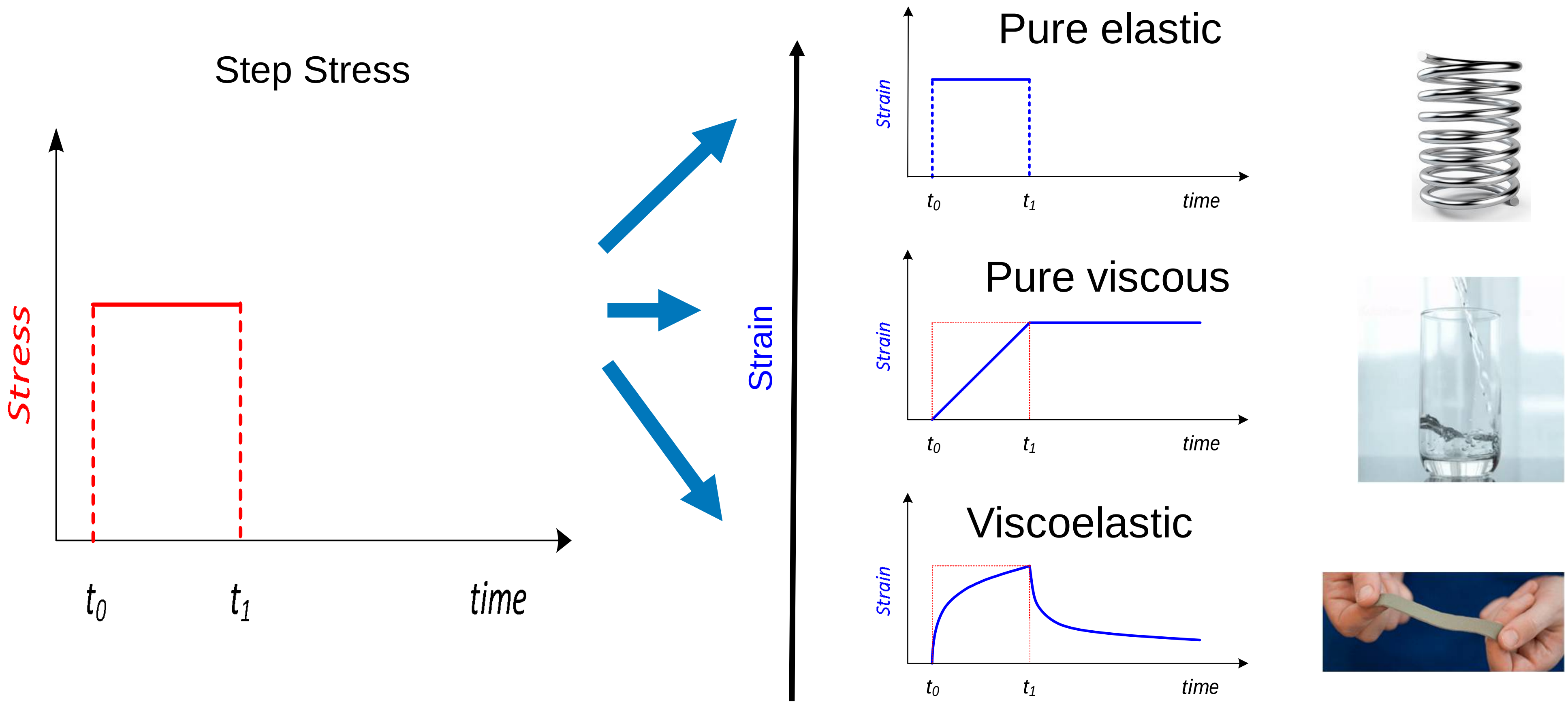
Creep Recovery Experiment

- A stress is applied to sample instantaneously at t_1 and held constant for a specific period of time. The strain is monitored as a function of time (γ(t) or ε(t)).

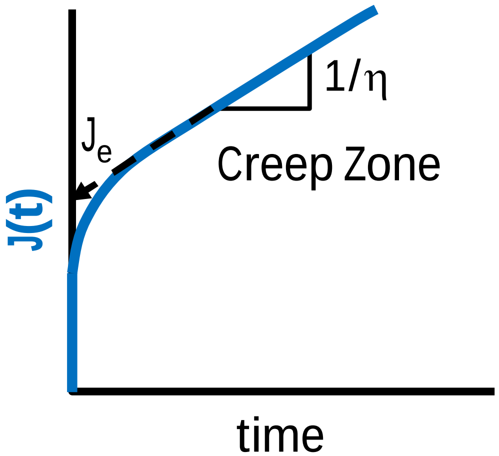
- The stress is reduced to zero at t_2 and the strain is monitored as a function of time (γ(t) or ε(t)).

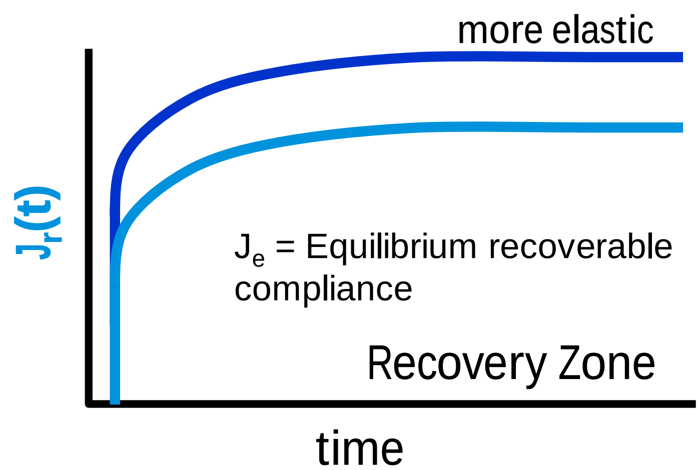


Creep-recovery: Material response



Creep and Recoverable Compliance





<u>Creep Compliance</u>

$$J(t) = \frac{\gamma(t)}{\sigma}$$

Creep experiments report the material property *Compliance* which is in a sense the inverse of Modulus

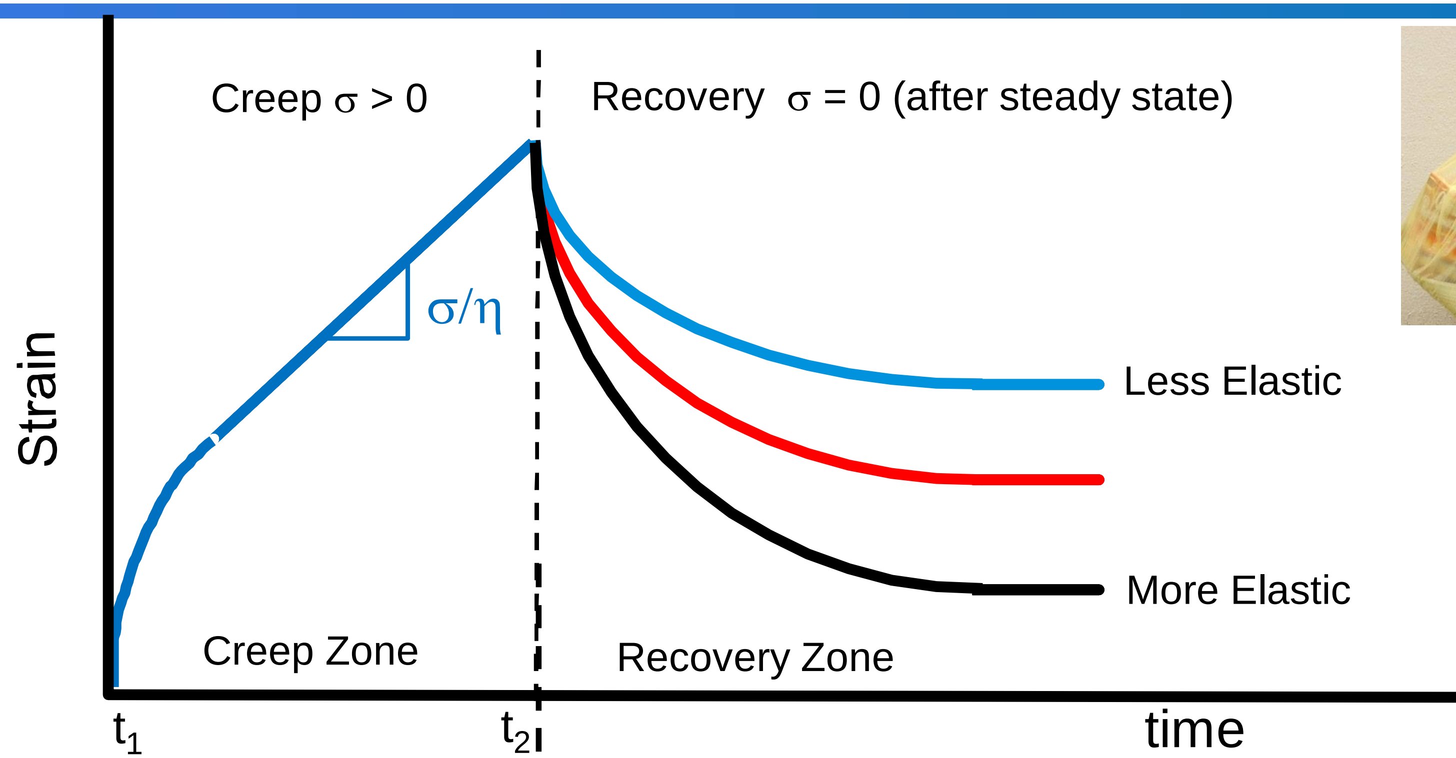
<u>Recoverable Compliance</u>

$$J_r(t) = \frac{[\gamma_u - \gamma(t)]}{\sigma}$$

Where γ_u = Strain at unloading
$\gamma(t)$ = time dependent recoverable strain

Mark, J., et. al., <u>Physical Properties of Polymers</u>, American Chemical Society, 1984, p. 102.

Creep-recovery: Viscoelastic fingerprint



Strain rate decreases with time in the creep zone until finally reaching a steady state

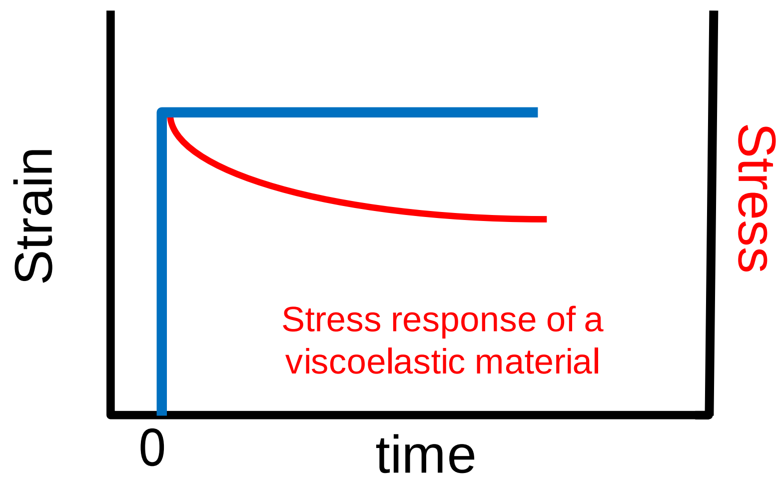
In the recovery zone, the viscoelastic fluid recoils, eventually reaching an equilibrium at some small total strain relative to the strain at unloading.

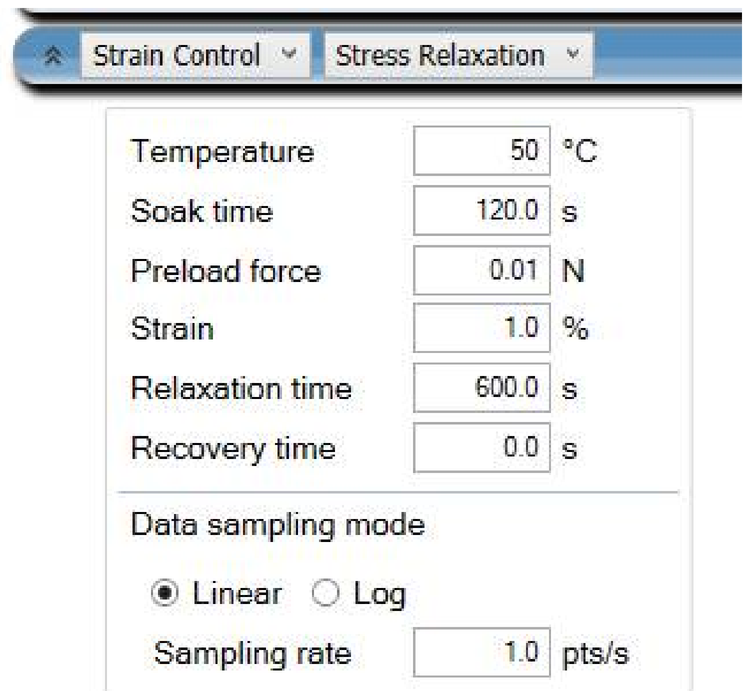
Mark, J., et. al., Physical Properties of Polymers, American Chemical Society, 1984, p. 102.

Stress relaxation

Strain is applied to the sample instantaneously (in principle) and held constant with time

Stress is monitored as a function of time σ(t)

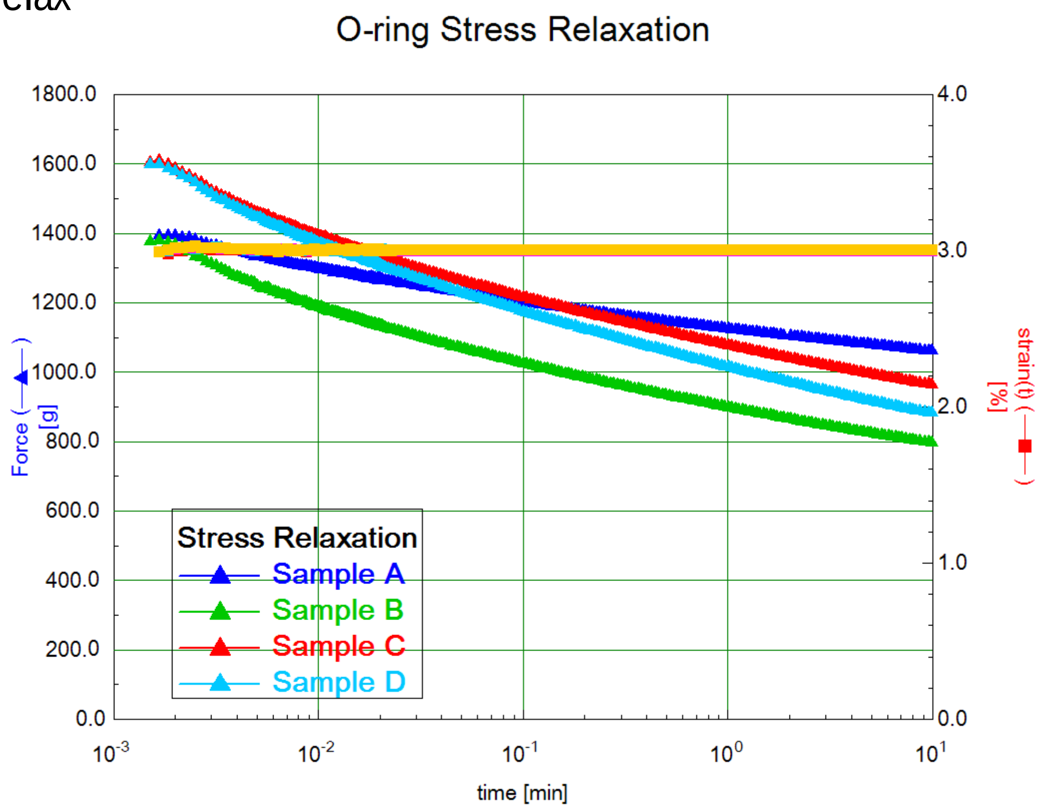




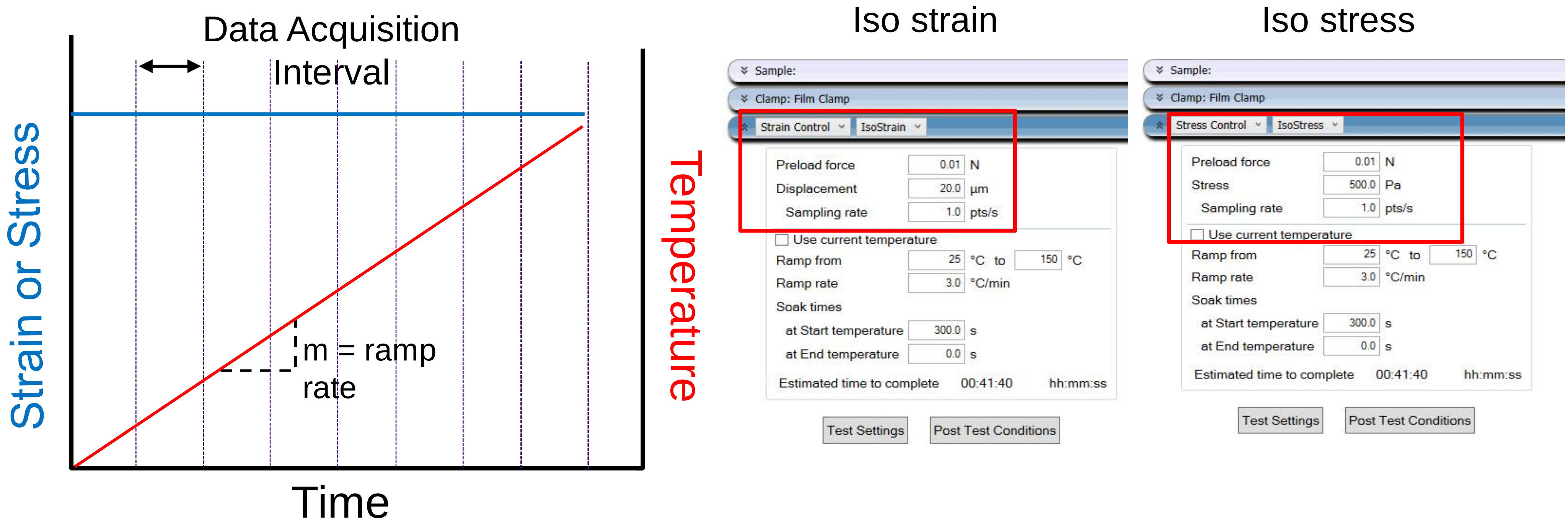
$$Relaxation\ modulus = \frac{stress}{strain}$$

O-rings: Stress Relaxation

- Squeeze the O-ring to a certain strain. Hold it constant, then measure how long it takes for the force to relax



Iso strain/stress temperature ramp



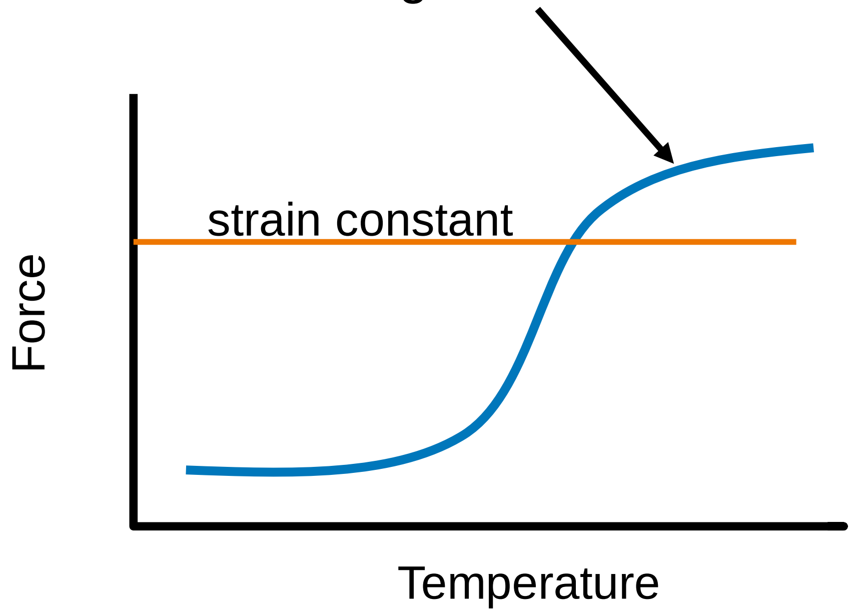
The strain or stress is held at a constant value and a linear heating rate is applied.

Assessing mechanical behavior under conditions of confined or fixed load (stress) or deformation (strain).

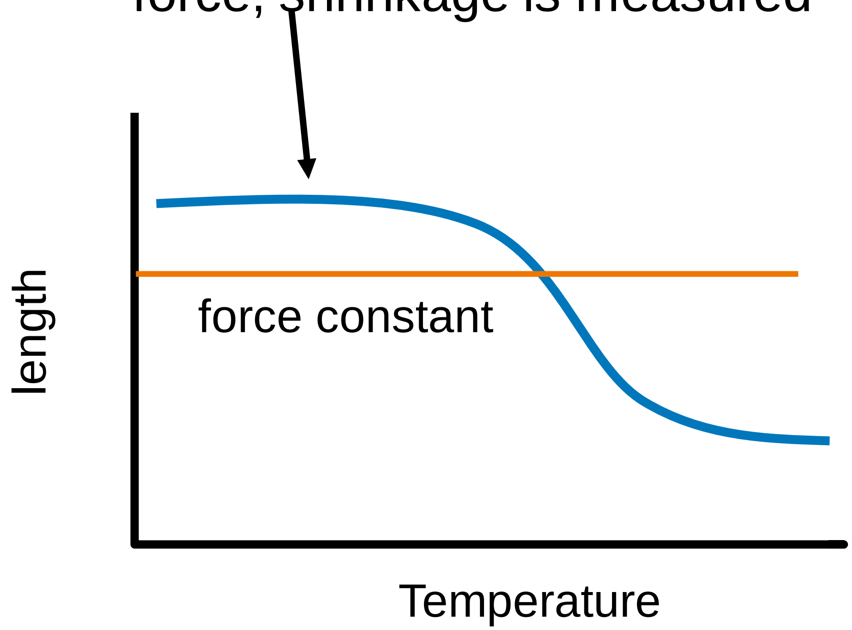
Example: Measure sample shrinkage

Iso strain/stress temperature ramp

Sample is held at a constant length; shrinkage force is measured



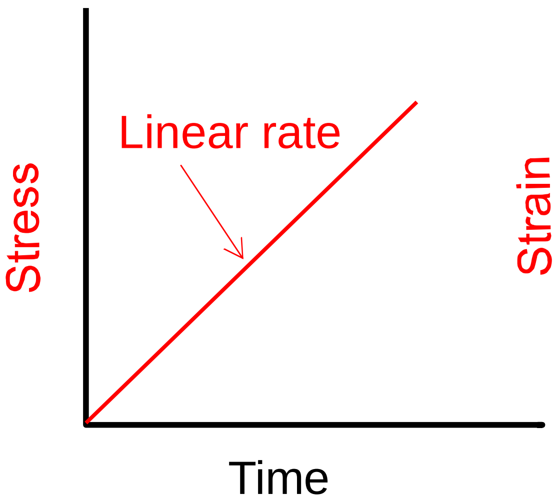
Sample is held at a constant force; shrinkage is measured

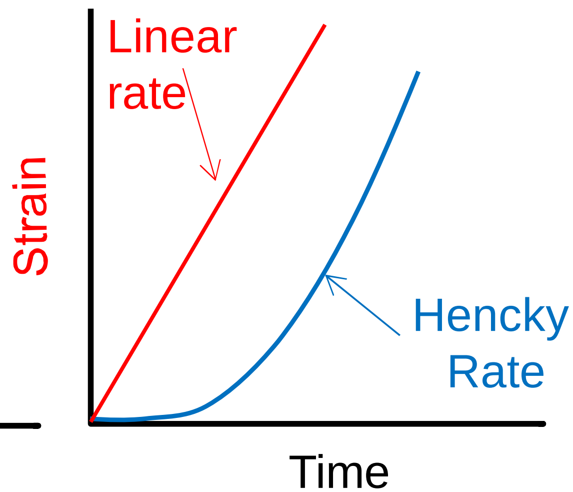


Stress-strain test

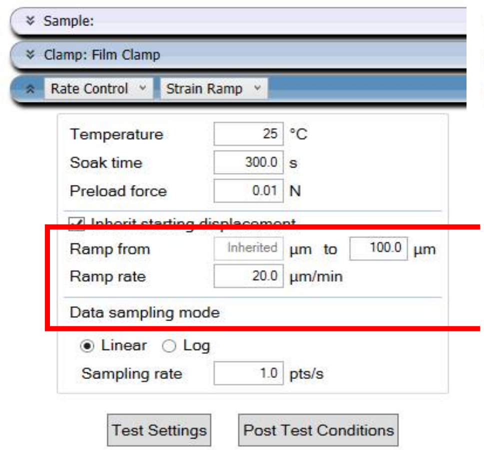
Sample is deformed under a constant linear strain rate, Hencky strain rate, force, or stress for generating more traditional stress-strain curves.

Measure sample's Young's modulus, yield stress, strain hardening effect and sample fracture

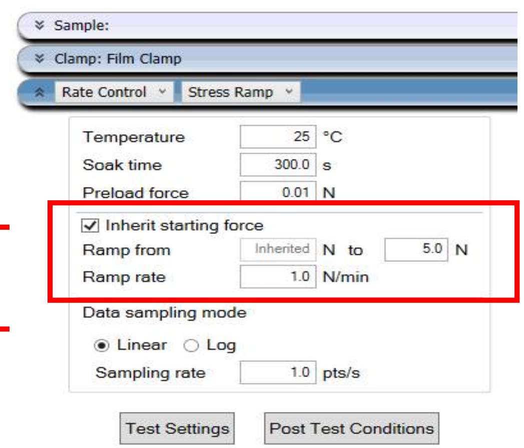




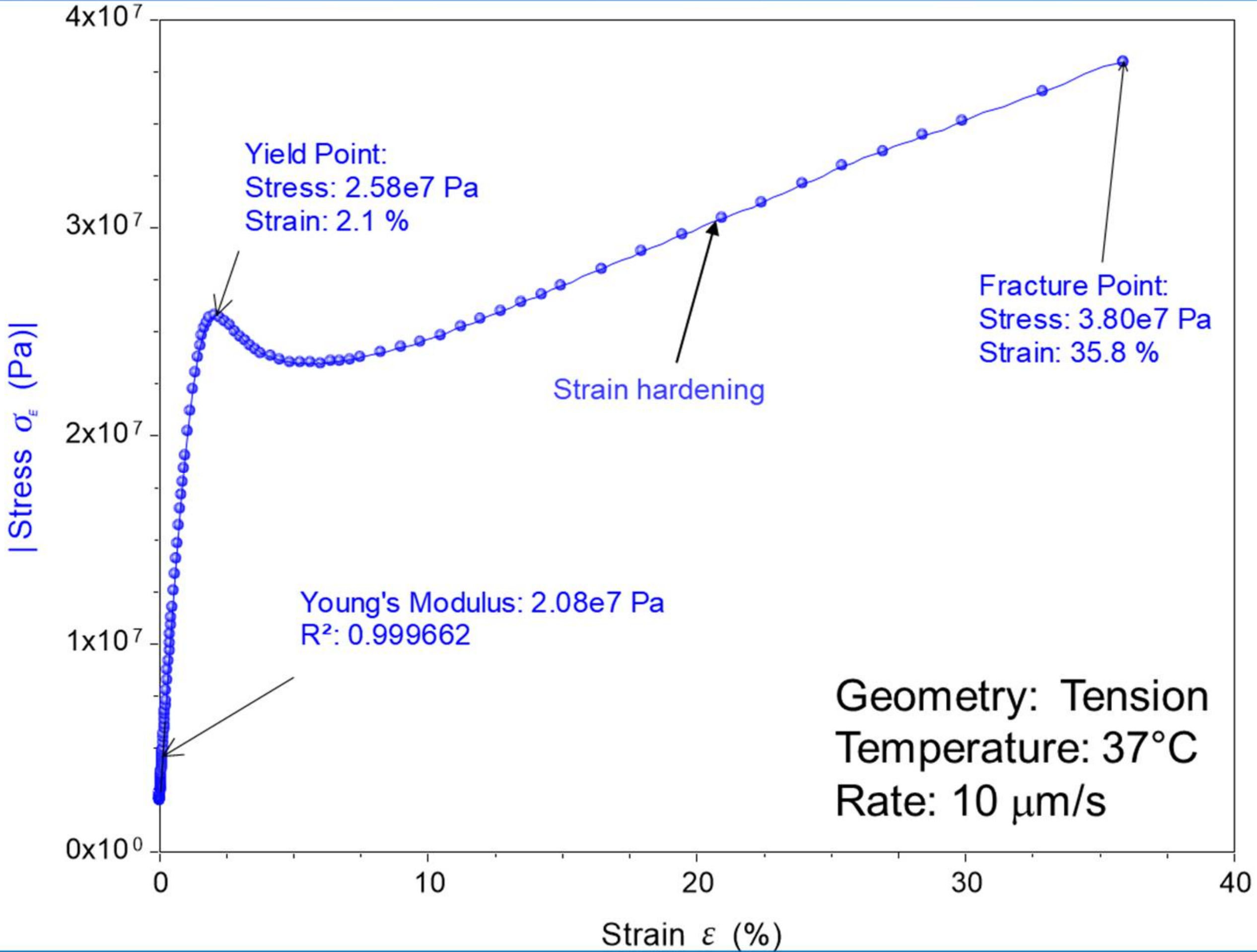
Strain Ramp

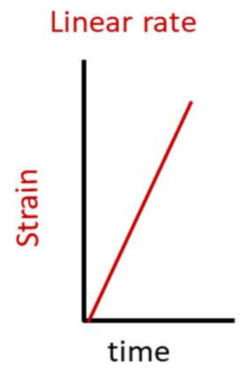


Stress Ramp



A typical stress-strain curve





Summary

Dynamic tests

- Strain/amplitude sweep
- Time sweep
- Frequency sweep
- Temperature ramp
- Temperature sweep

Transient tests

- Creep-recovery
- Stress-relaxation
- Iso-strain temperature ramp
- Iso-stress temperature ramp
- Stress-strain tests

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Philadelphia Short Course: Day II

Section V: DMA Applications

Terri Chen, PhD
Principal Application Scientist
TA Instruments – Waters LLC

The DMA Results Can Correlate To…

DMA Results:

E, G, J
Tan δ
Tg, Tβ, Tγ

Molecular structures
- MW and MWD
- Branching
- Crystallinity
- Crosslinking
- Phase
- Relaxation

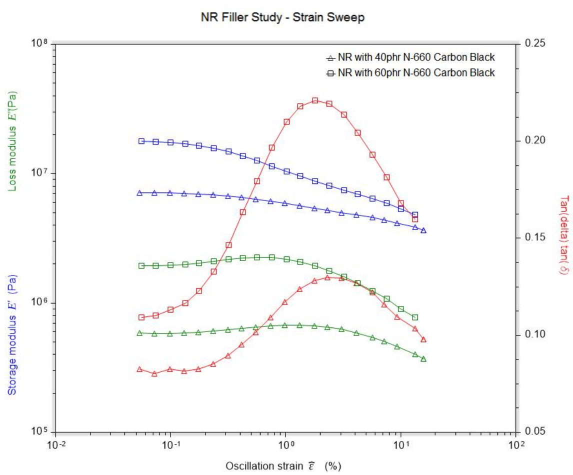
Processing:
- Heat history
- Residual stress
- Shear or orientation
- Temperature
- Fillers

Product properties
- Transition temperatures (Tg, Tβ, Tγ)
- Environmental resistance
- Impact strength
- Long term behavior, aging
- Adhesion

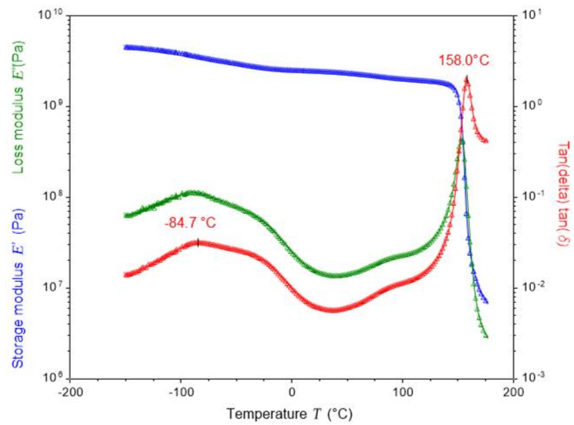
Most common DMA methods

Most common DMA methods

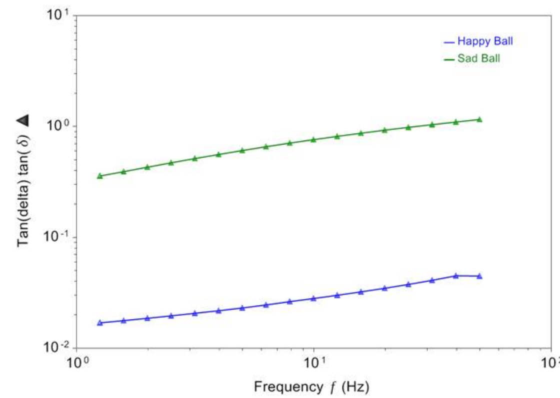
- Amplitude sweep
- Temperature ramp
- Frequency Sweep and TTS



Amplitude Sweeps
(Linear viscoelastic Region)



Temperature Ramp
(Transitions and viscoelasticity across temperature)



Frequency Sweep
(viscoelasticity across time scales of deformation)

Amplitude sweep: identify LVR

Common DMA methods

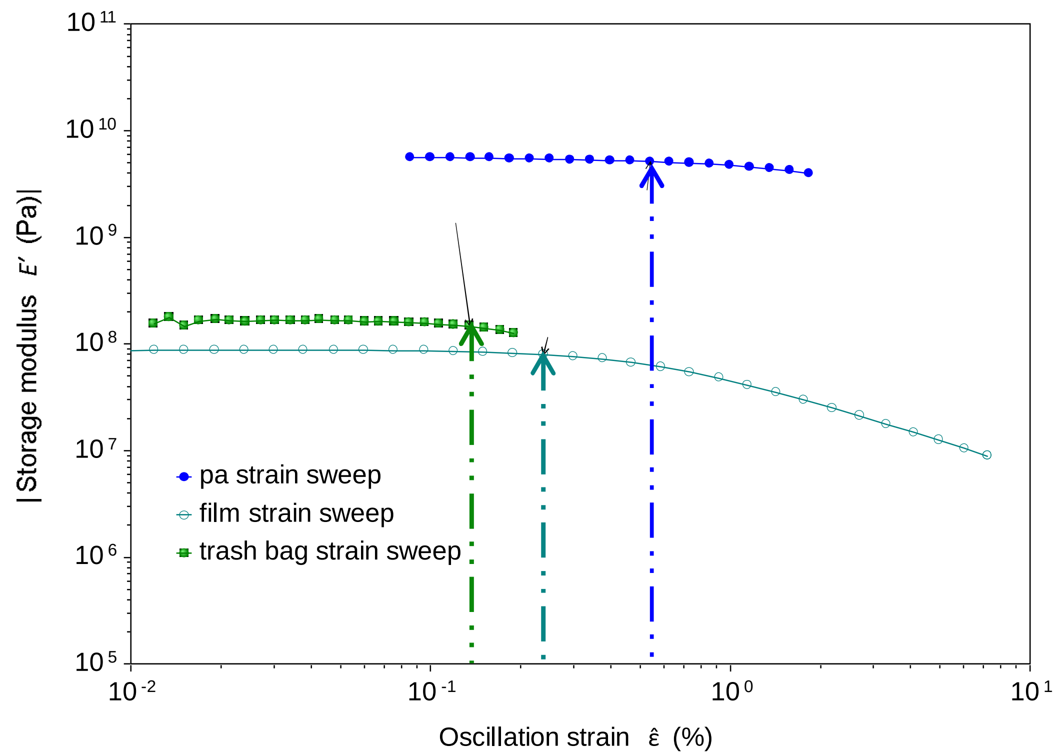
- Amplitude Sweep

From an amplitude sweep:

Obtain the Linear Viscoelastic Region (range of strain values where modulus is independent) at a given frequency

When performing nondestructive experiments (frequency sweep, temperature ramp, time sweep) a strain within the LVR must be chosen

Solid samples typically have an LVR that ends ≤1%



LVR dependence on frequency

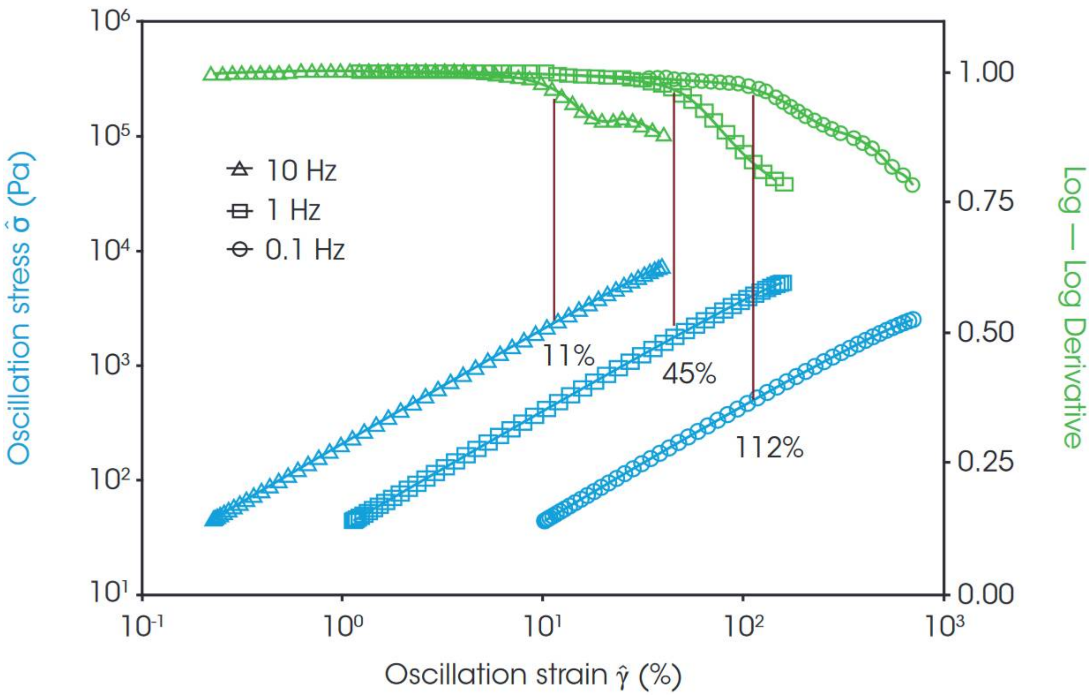
Common DMA methods

- Amplitude Sweep

From an amplitude sweep:

Obtain the Linear viscoelastic region (LVR - range of strain values where modulus is independent) at a given frequency

Frequency dependence of LVR – LVR is shorter at higher frequencies, molecules are more stiff



LVR dependence on temperature

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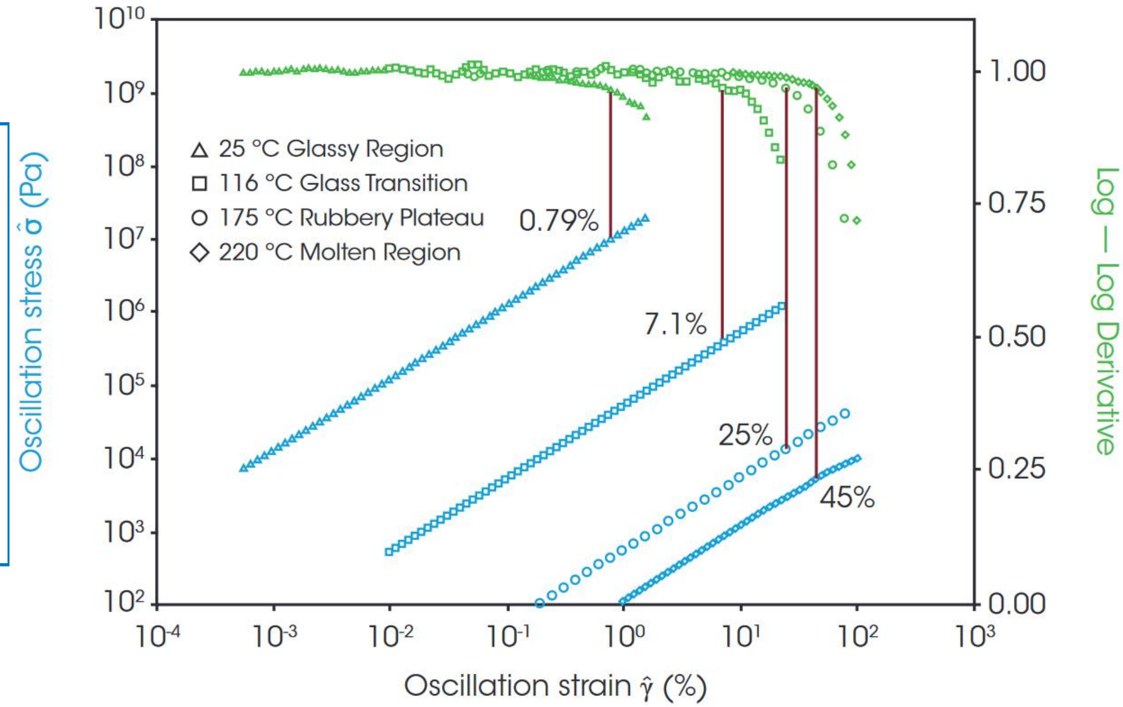
Common DMA methods

o Amplitude Sweep

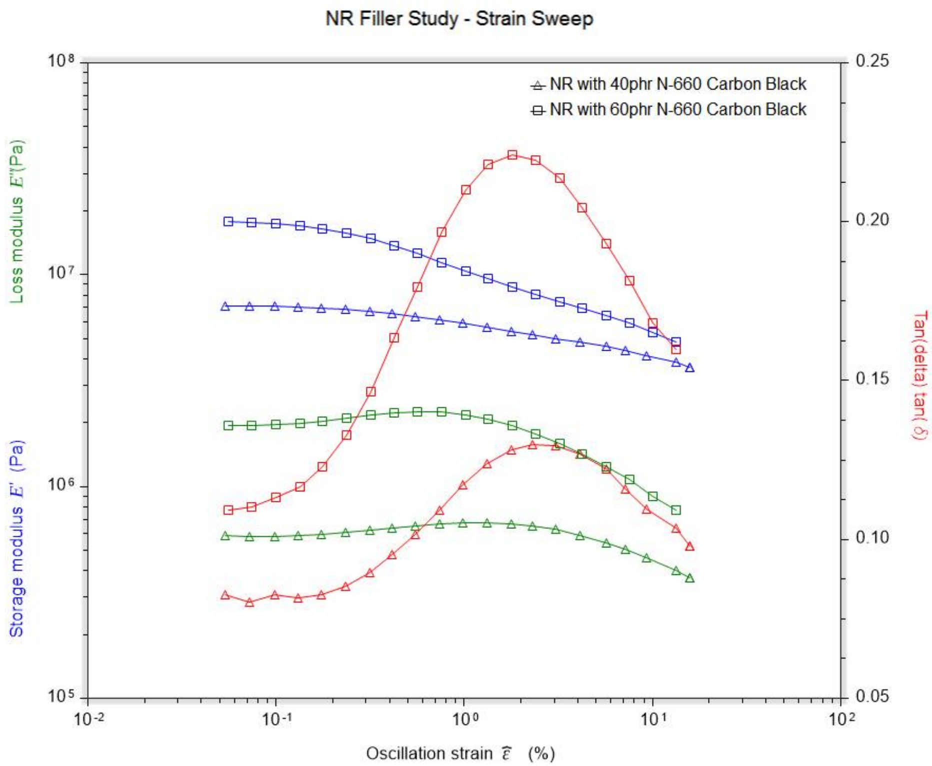
From an amplitude sweep:

Obtain the Linear viscoelastic region (LVR - range of strain values where modulus is independent) at a given frequency

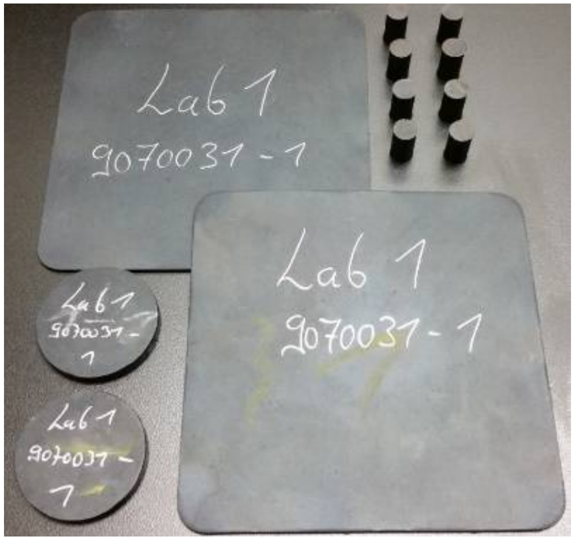
Temperature dependence of LVR – LVR is shorter at lower temperatures, molecules are more stiff



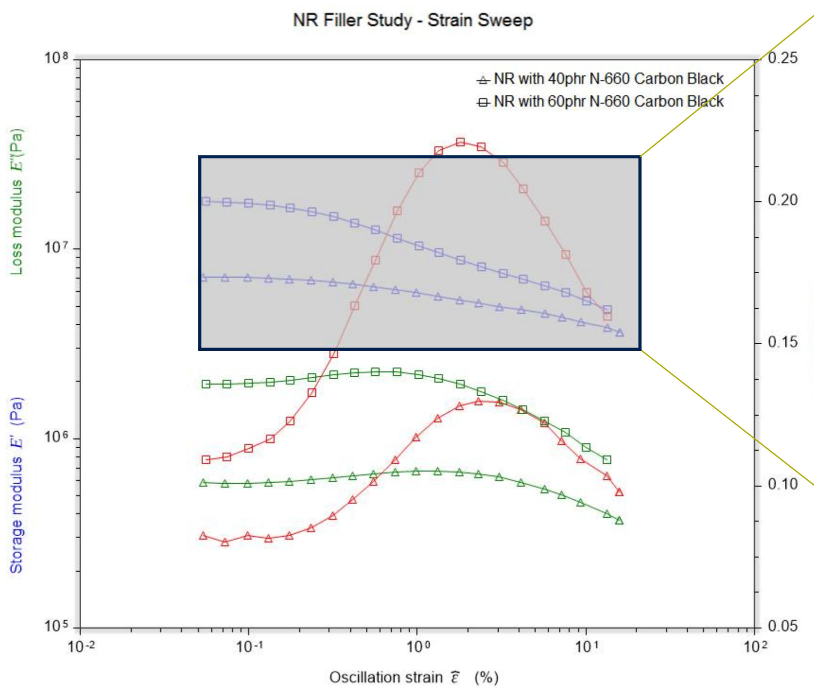
Rubber: Effect of Filler Content in Tire Rubber (NR)

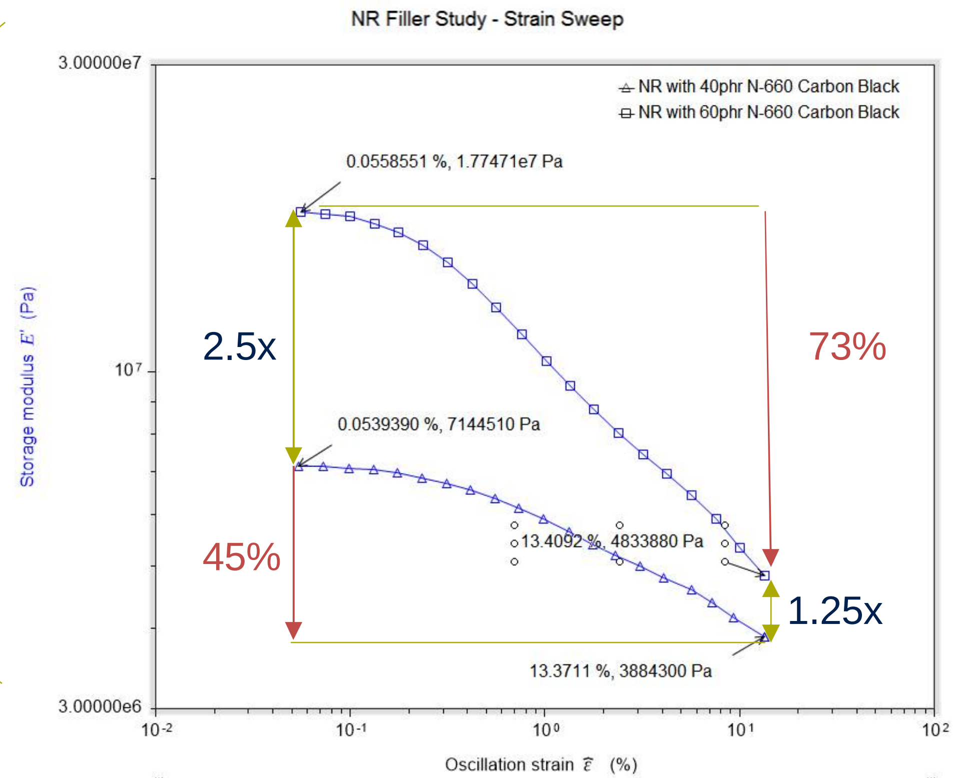


Study on DMA3200
High Force DMA example:
Larger rubber samples where rubber samples are difficult to cut small and precisely enough for conventional DMA tests



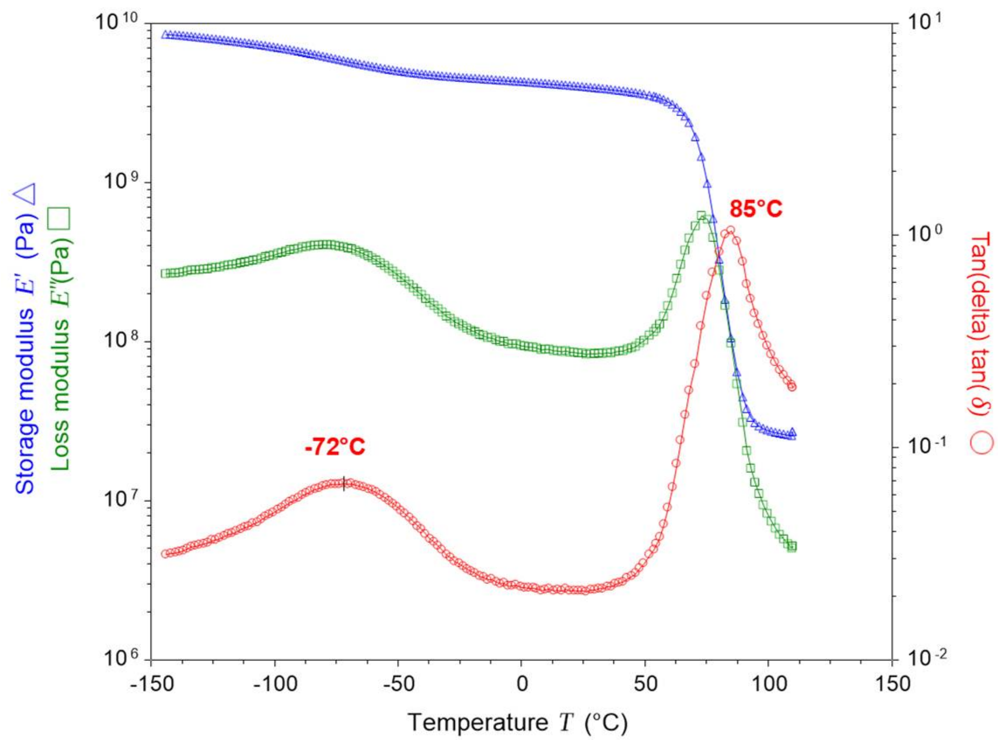
Rubber: Effect of Filler Content in Tire Rubber (NR)





DMA temperature ramp

PET film: Tested in tension



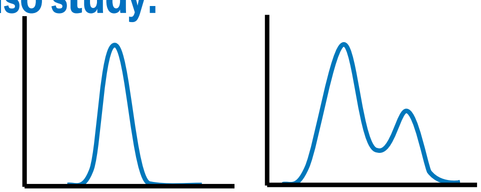
Glass Transition (T_g): Cooperative motion among a **large number** of chain segments

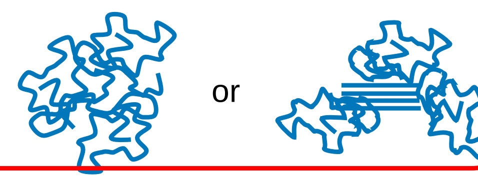
Secondary Transitions (T_β, T_γ): Local or side group motion

Rheology/DMA is 100-1000× more sensitive than DSC for identifying weak amorphous transitions

DMA temp ramp can also study:

- Crystallinity
- Crosslinking density
- Blend Miscibility





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Primary and secondary transitions in PC

Common DMA methods

- Temperature Ramp

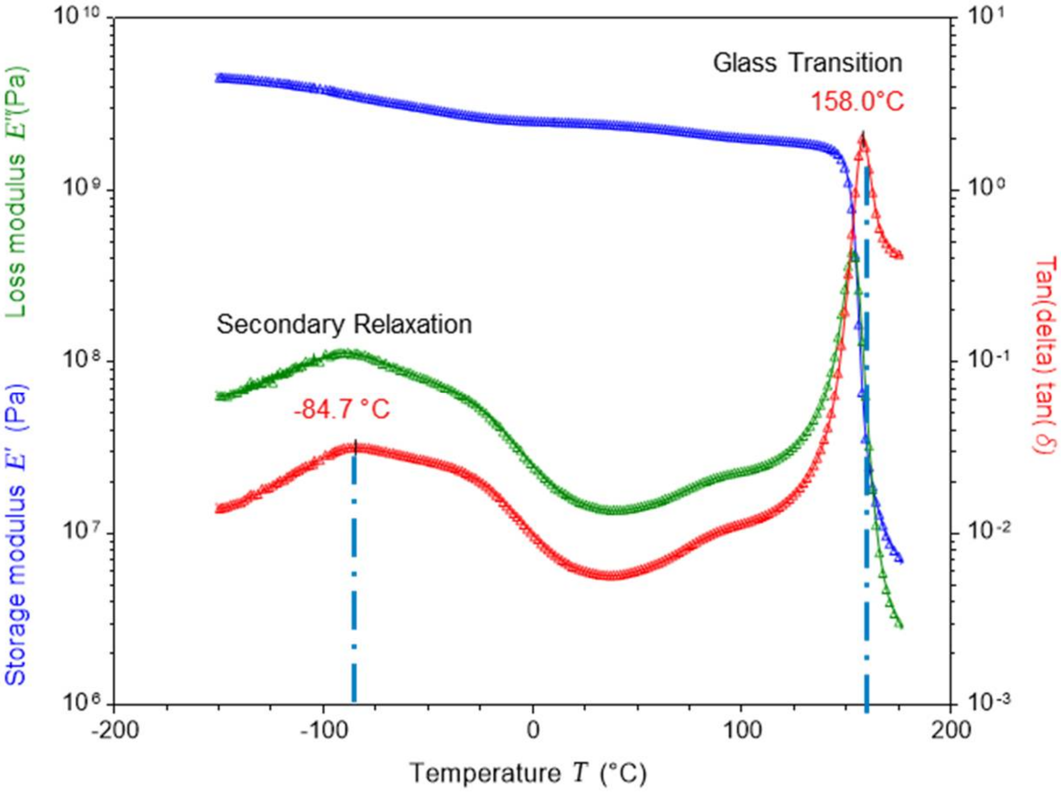
From temperature ramp:

Material glass transition
Local Main-Chain Motion – intra-molecular rotational motion of main chain segments four to six atoms in length

Secondary transitions
Side group motion with some cooperative motion from the main chain

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

- Polycarbonate



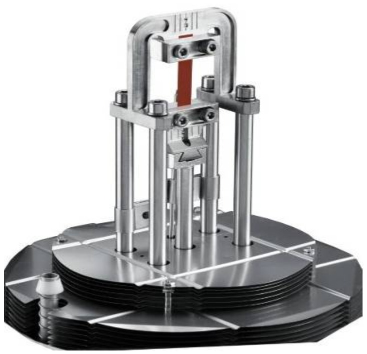
Effect of frequency on Tg: PET film

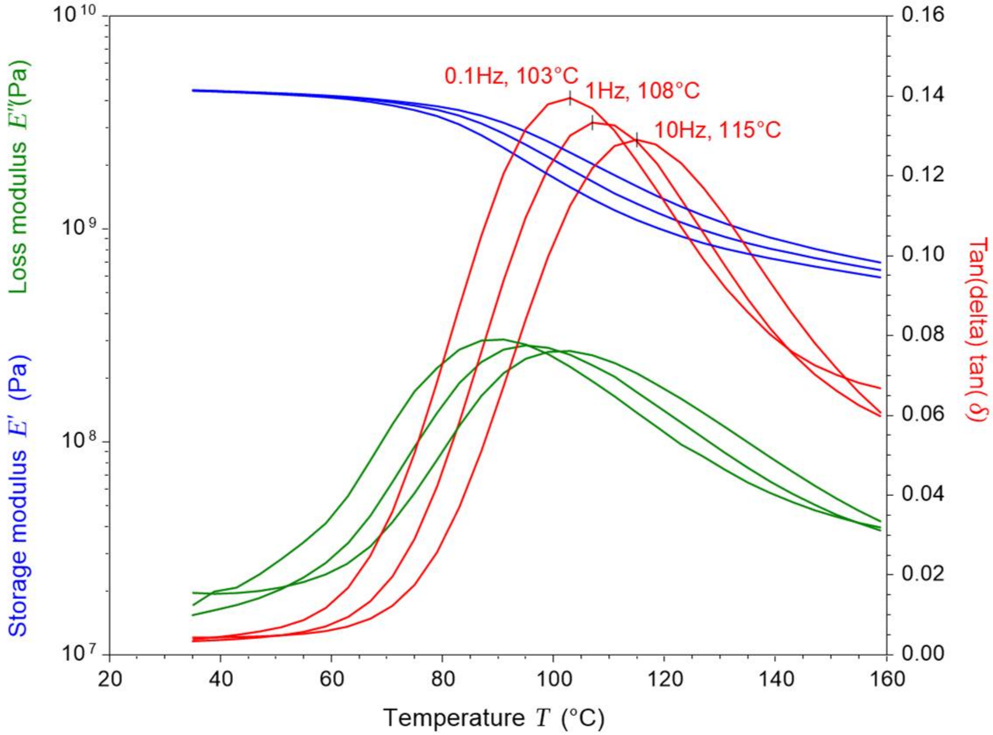
Common DMA methods

- Temperature Ramp

From temperature ramp:

Observe effect of frequency on the glass transition – higher frequency generally increases Tg, the molecules become more stiff

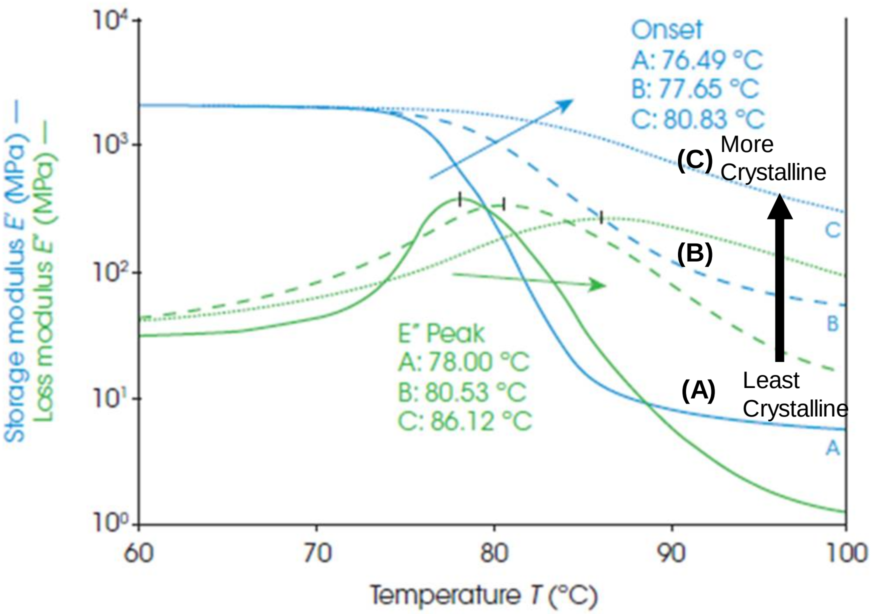


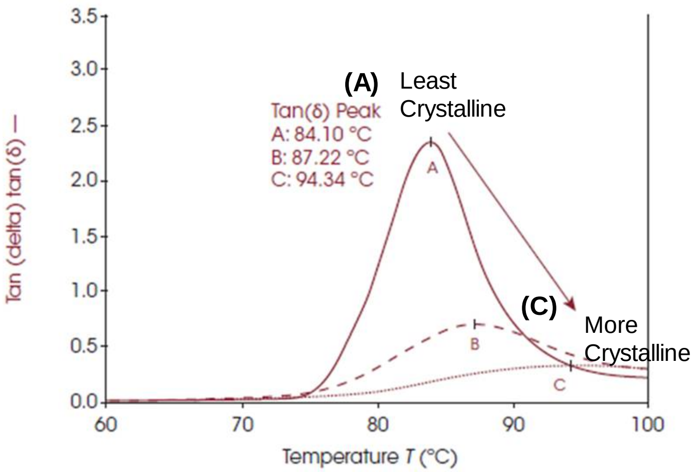


Effect of crystallinity on E’ and tanδ: PET

Common DMA methods

- Temperature Ramp





From temperature ramp:

Observe effect of crystallinity on the storage modulus (Left) and the glass transition temperature (Right)

Effect of crosslinking on E' and Tg

Common DMA methods

- Temperature Ramp

From temperature ramp:

Observe effect of crosslinking on the storage modulus and the glass transition temperature

Increasing crosslinking :

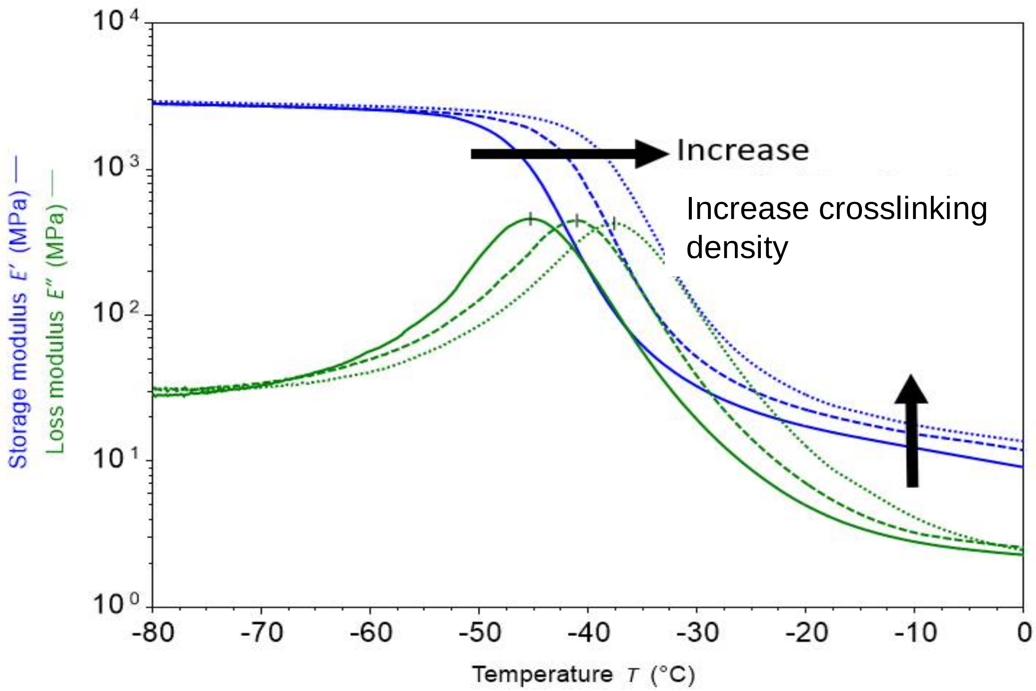
Tg shifted to higher temperatures

Transition becomes broader and weaker (tan δ decreases)

Rubbery plateau modulus increases

Calculating crosslinking density:

$$M_c = \frac{3RTd}{E'_{rubbery}} \qquad q = \frac{Mw}{Mc}$$



TA Applications note: RH100 Measurement of Glass Transition Temperatures by Dynamic Mechanical Analysis and Rheology, https://www.tainstruments.com/pdf/literature/RH100.pdf

Effect of aging over time: O-ring

Common DMA methods

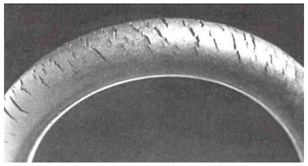
- Temperature Ramp

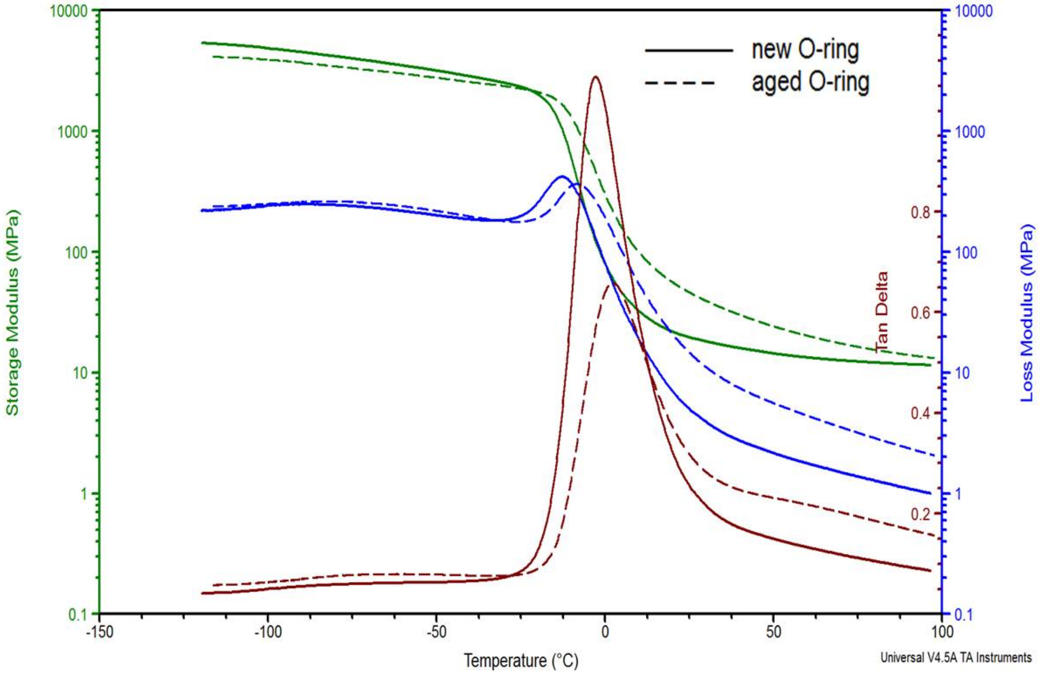
From temperature ramp:

Observe effect of aging on a rubber sample - aged O-ring has higher Tg and increased storage modulus at rubbery plateau

New

Aged





Effect of plasticizer on vinyl flooring Tg

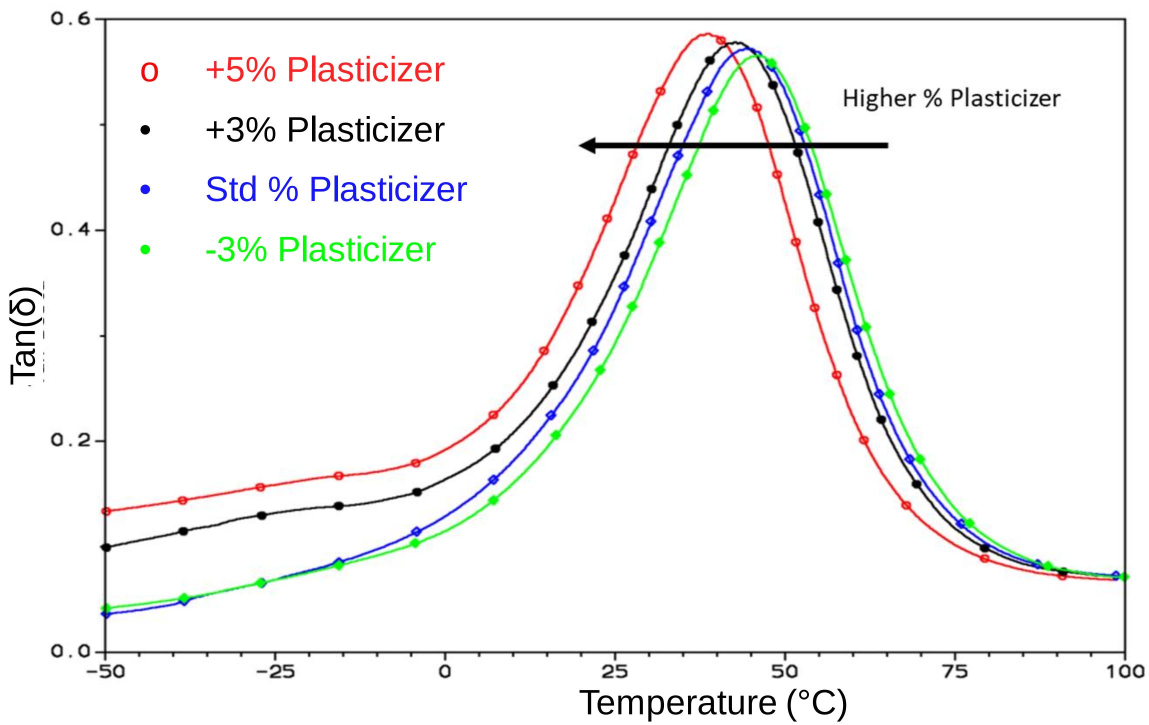
Common DMA methods

- Temperature Ramp

From temperature ramp:

Observe effect of increased plasticizer loading

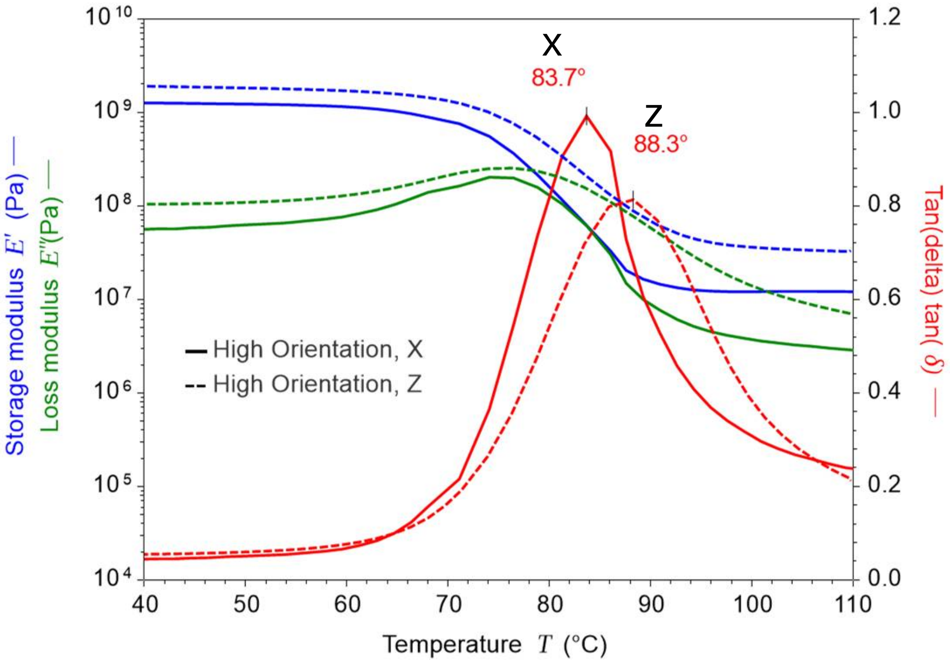
Plasticizers shield molecular interactions of matrix, thereby decreasing the glass transition, and softening the material



Effect of orientation on mechanical properties

Common DMA methods

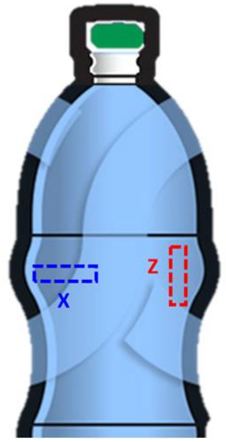
- Temperature Ramp



From temperature ramp:

Observe effect of orientation on storage modulus and glass transition temperature

Bottle is stronger in "Z" direction, and this makes sense considering the application



Polymer blends - miscibility

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Common DMA methods

- <u>Temperature Ramp</u>

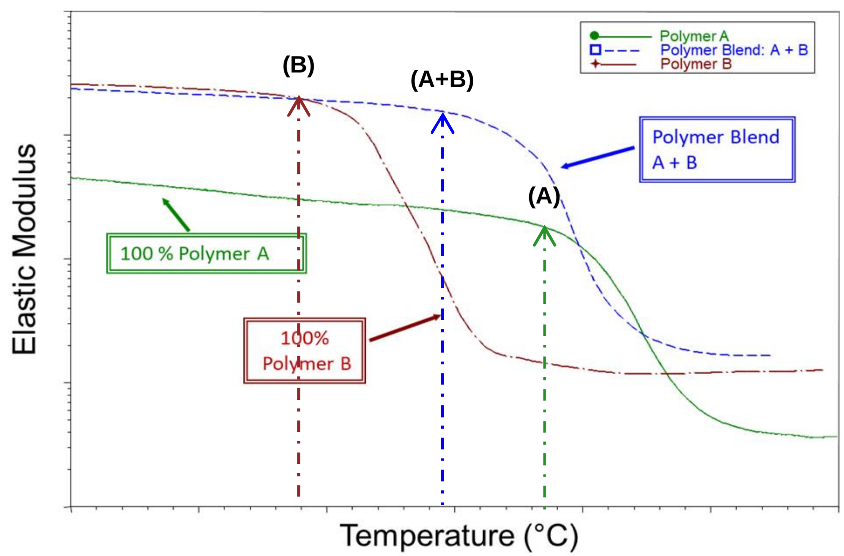
From temperature ramp:

<u>Observe blend compatibility</u>

<u>Miscible Blend</u>

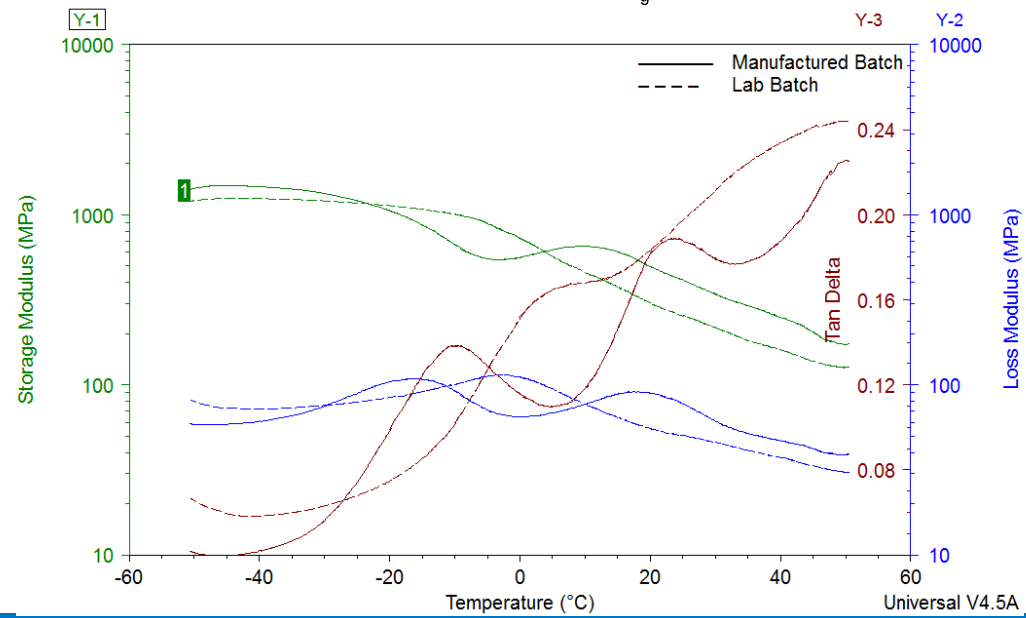
Pure components have unique T_g's

Blend has one T_g

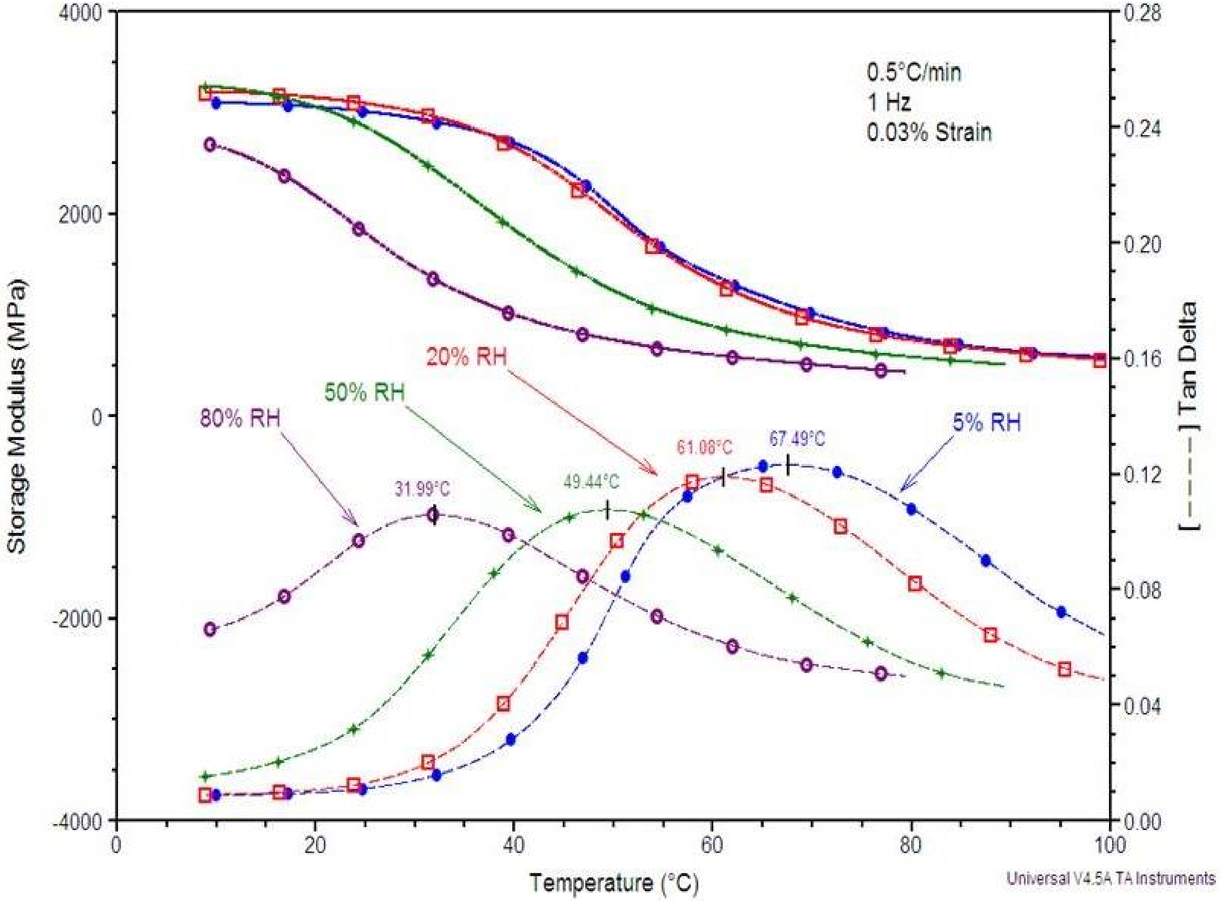


<u>Immiscible Blend</u>

Blend has two T_g's

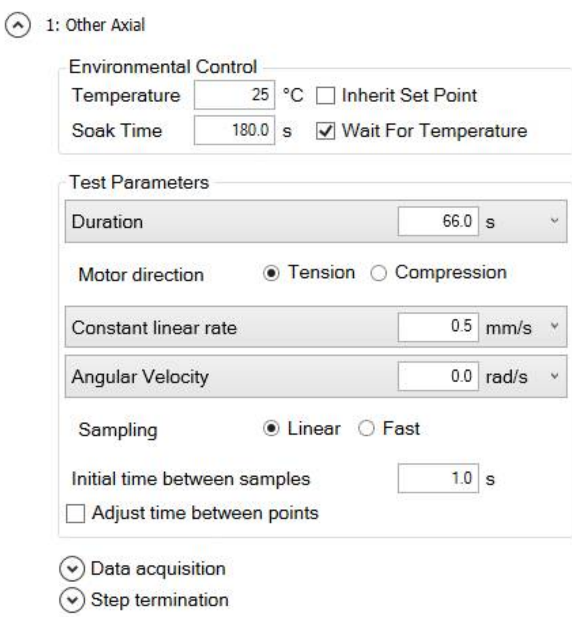


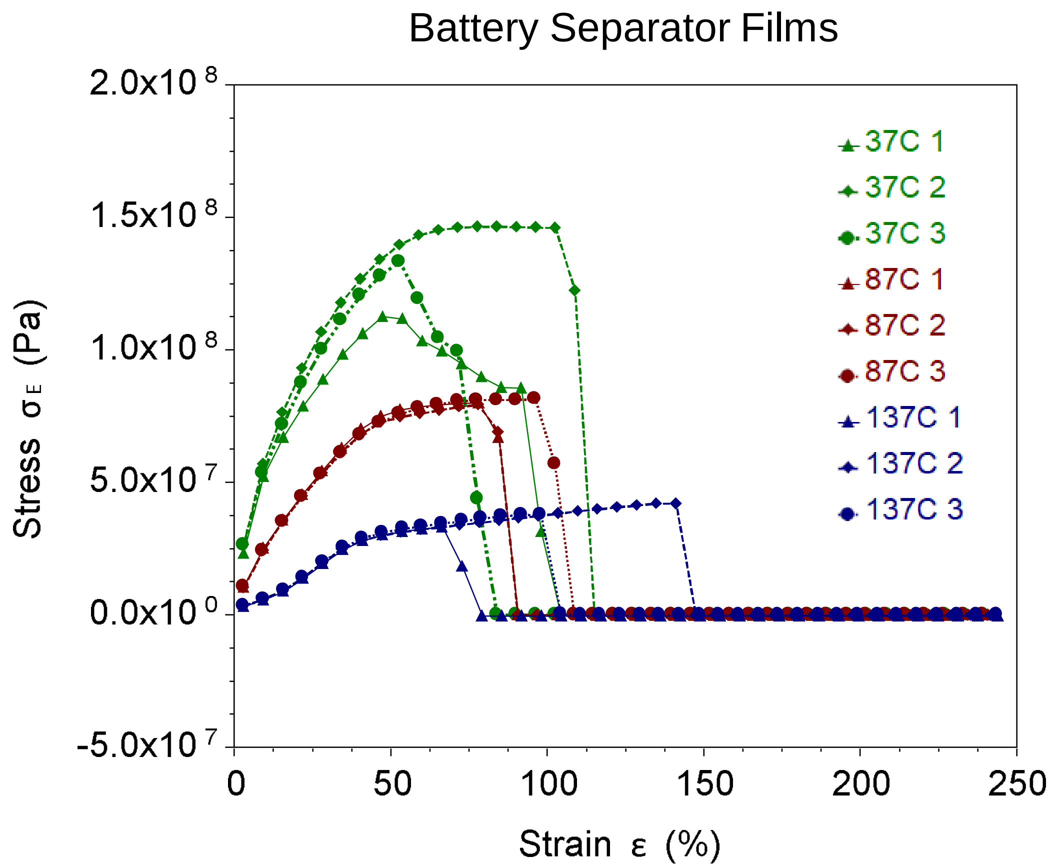
Humidity Influence: Nylon Film



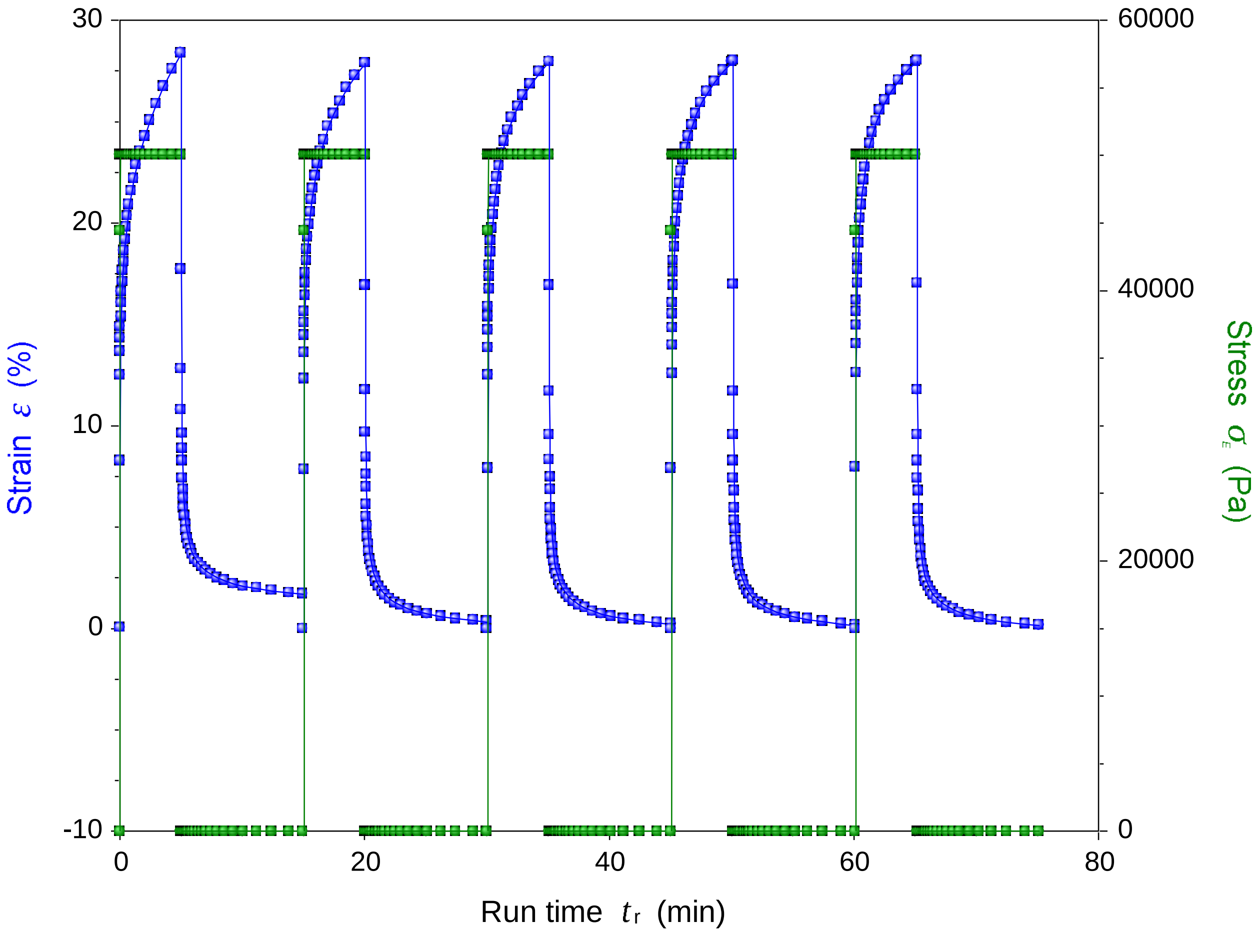
DMA mechanical stress-strain test

- Pull sample at one rate
- Generate Stress vs Strain plot





Multi-step creep recovery: memory foam

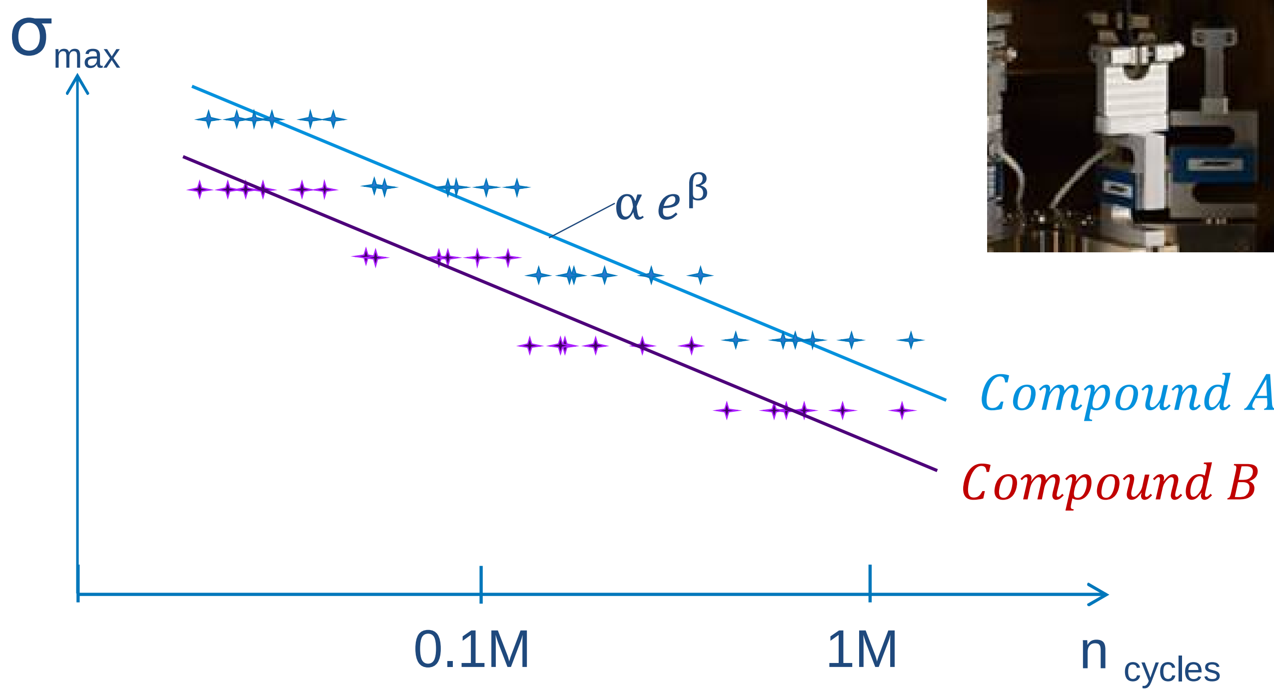


Tensile fatigue test – Time sweep

BR Rubber (Tire Rubber) Example

- High force DMA for rubber tire fatigue test
- Compound B has a lower life than A because it typically fails at less number of cycles when subjected to the same stress.

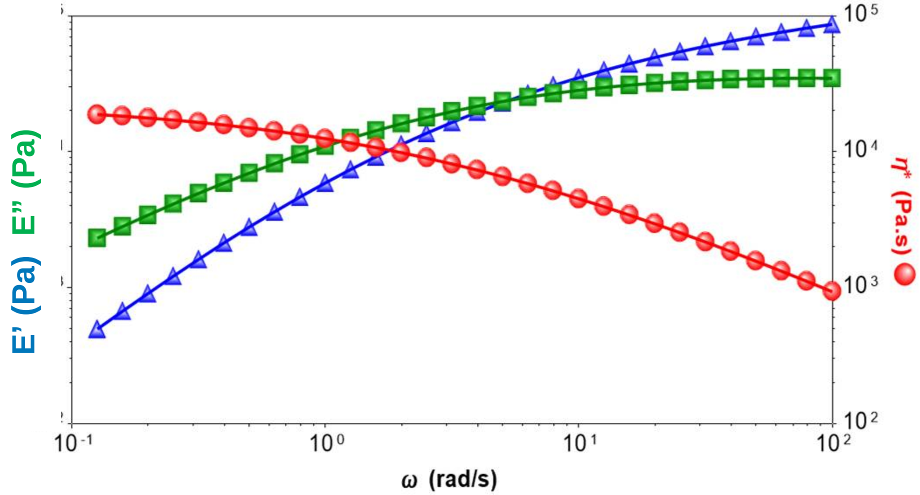
- Time sweep to obtain Stress-Number of cycle (SN) points
- Data is fit to exponential equation (line on plot)
- Data and exponential fit is used to compare materials

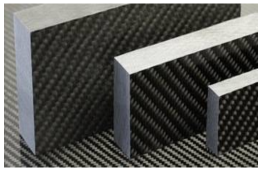


DMA frequency sweep test

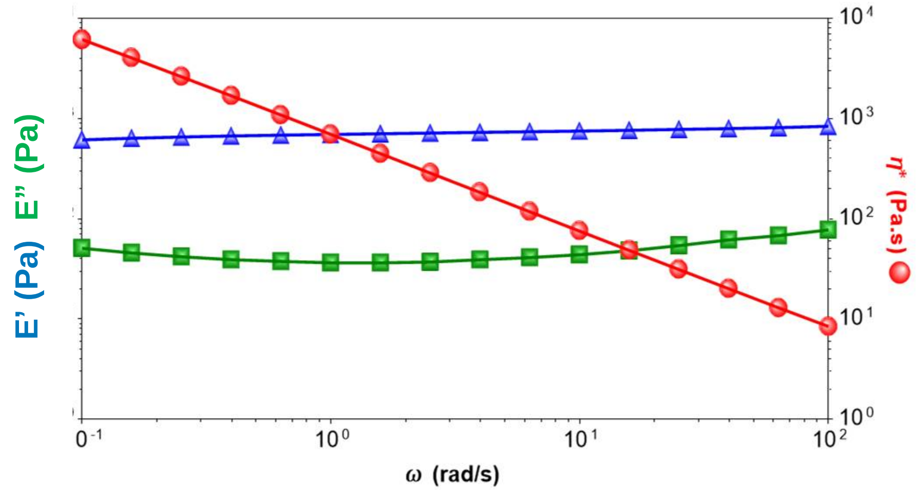
- Maximum frequency in a single test: 100-200Hz

Viscoelastic solids





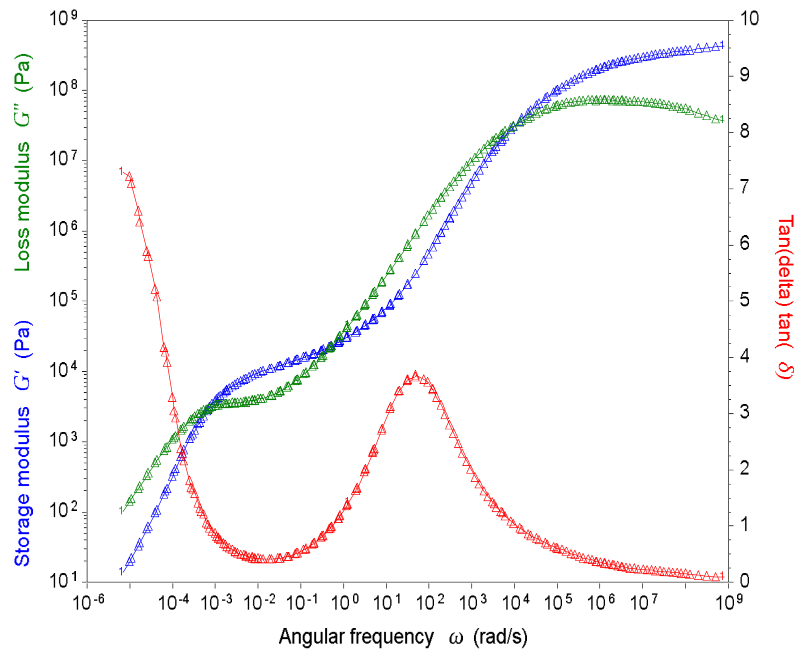
Elastic solids



Time-Temperature Superposition (TTS)

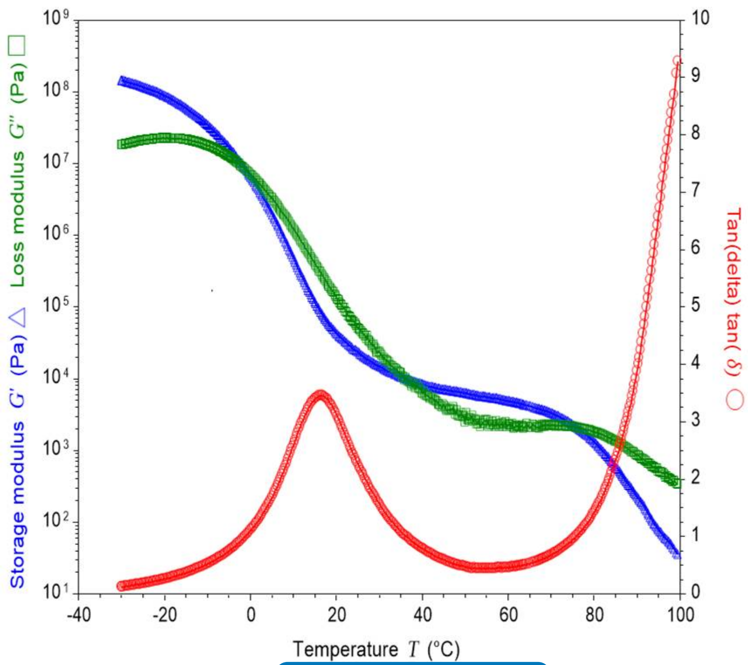
- The viscoelastic properties of an amorphous polymer as a function of temperature is mirror imaged as its properties as a function of time (frequency)

TTS master curve generated at 20°C



Time

Dynamic temperature ramp



Temperature

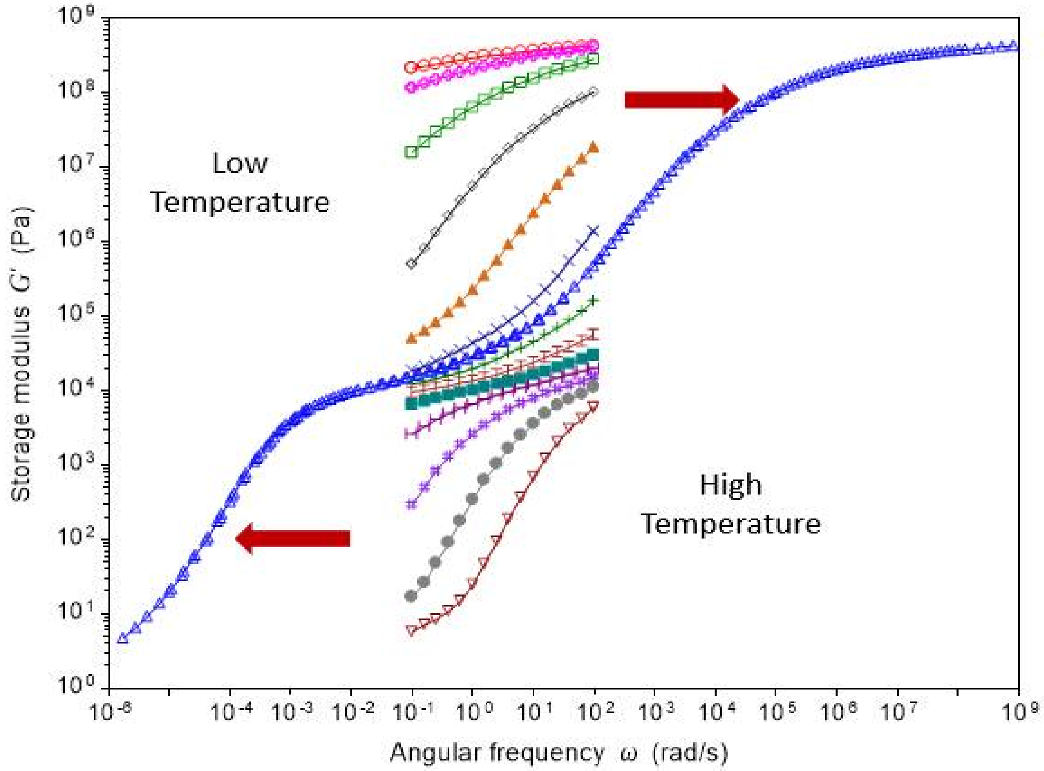
Benefit of TTS

- TTS can be used to extend the frequency beyond the instrument's range.
- Low frequency data predicts material behavior over longer timescales that cannot be practically measured on a laboratory instrument.
- High frequency data predicts material behavior at short timescales (high-speed impact, mechanical vibrations, acoustics) that are challenging to measure accurately using an analytical instrument.
- Creep or Stress Relaxation TTS can predict behavior over longer times under static load/deformation.

- Dealy J, Plazek D. *Time-Temperature Superposition – A Users Guide.* Rheology Bulletin 2009; 78**:** 16
- van Gurp M, Palmen J. *Time-temperature superposition for polymeric blends.* Rheology Bulletin 1998; 67: 5.
- Cox WP and Merz EH. *Correlation of dynamic and steady flow viscosities.* Journal of Polymer Science 1958; 28: 619

How to perform TTS analysis

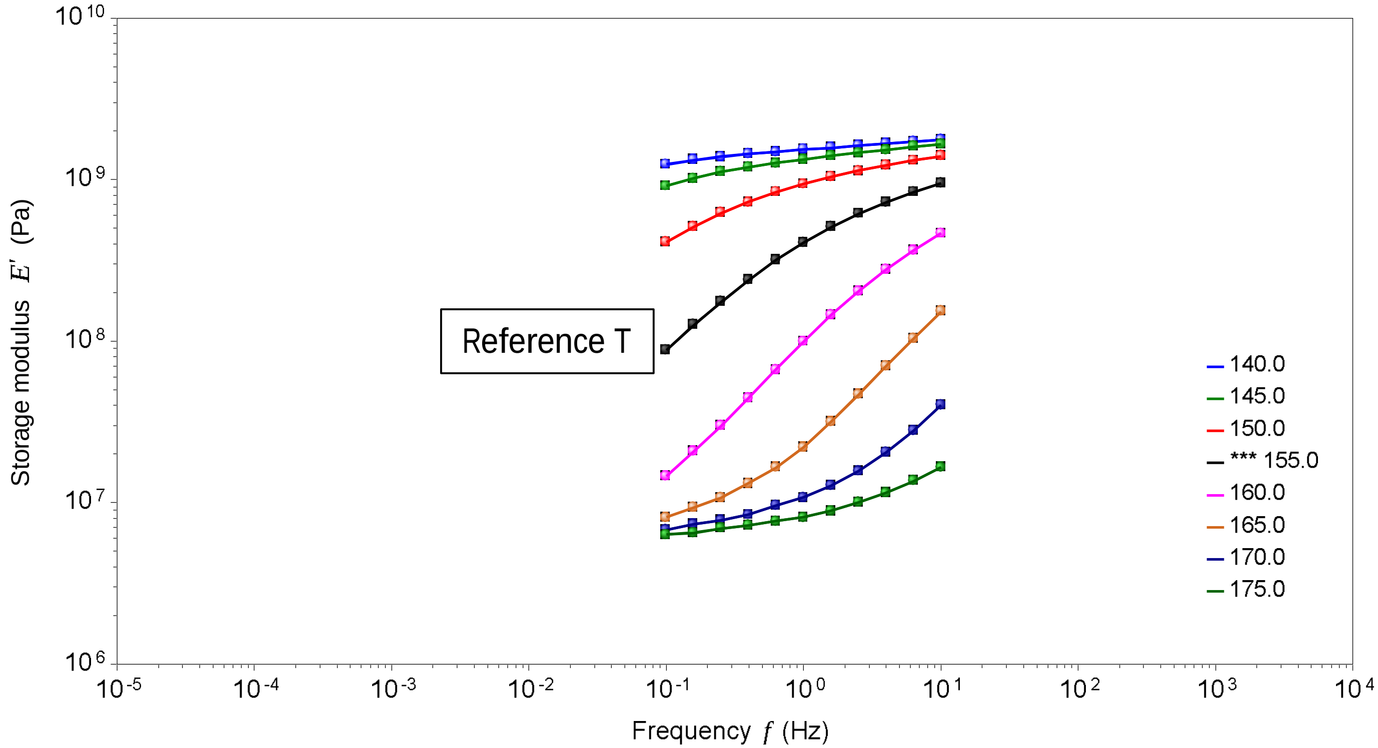
- Perform frequency sweeps at different temperature
- Extrapolates properties to time scales outside the instrumental range



- Frequency sweep data collected under different temperature steps can be shifted along the x-axis.
- Access to a wide range of frequency or time scales
- Predict properties outside of instrument capability
- TTS can be applied to both dynamic and transient measurements

TTS example: shifting of individual curves

- Generating frequency sweep data at different temperature steps
- Select your reference temperature (e.g. 155°C)

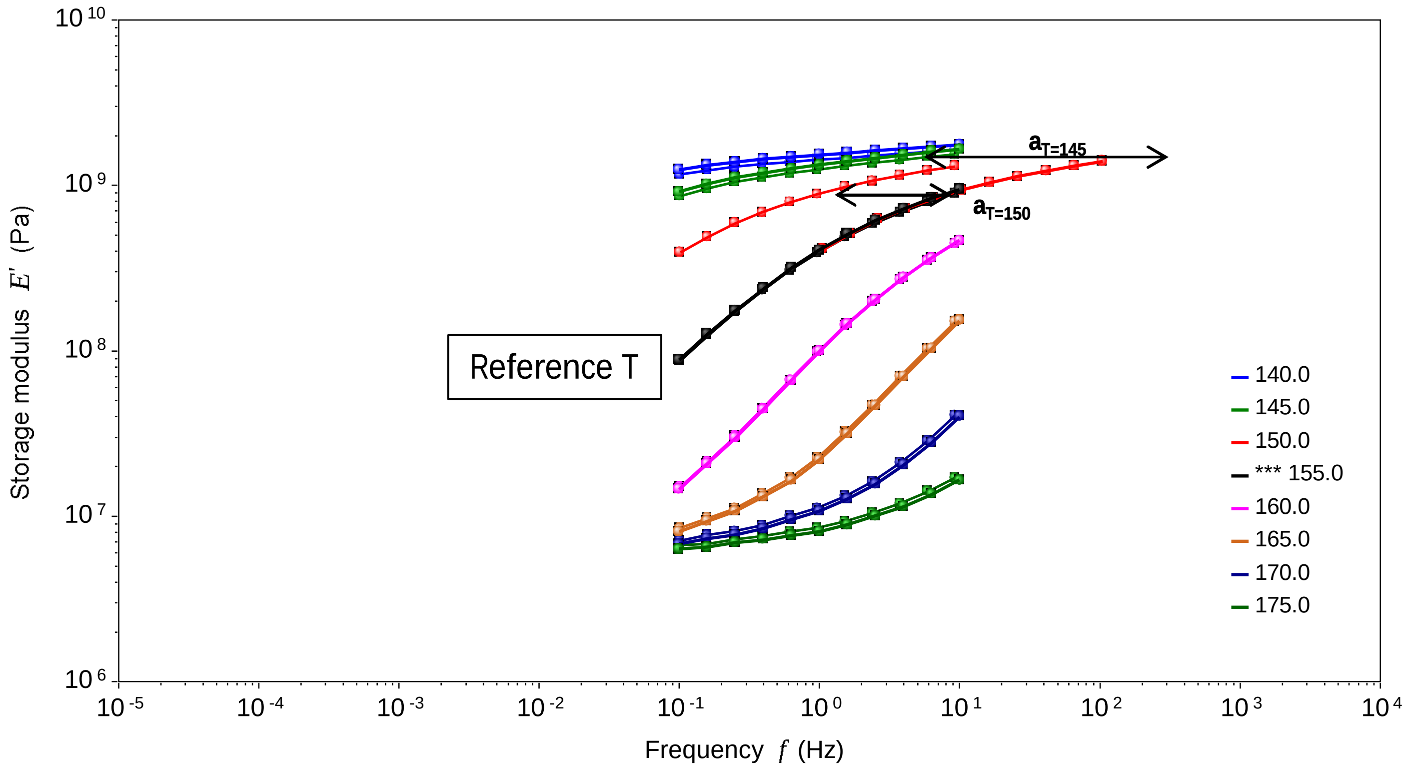


- Shifts can be performed automatically in TRIOS.

Refer to http://www.tainstruments.com/tts-and-trios-software/

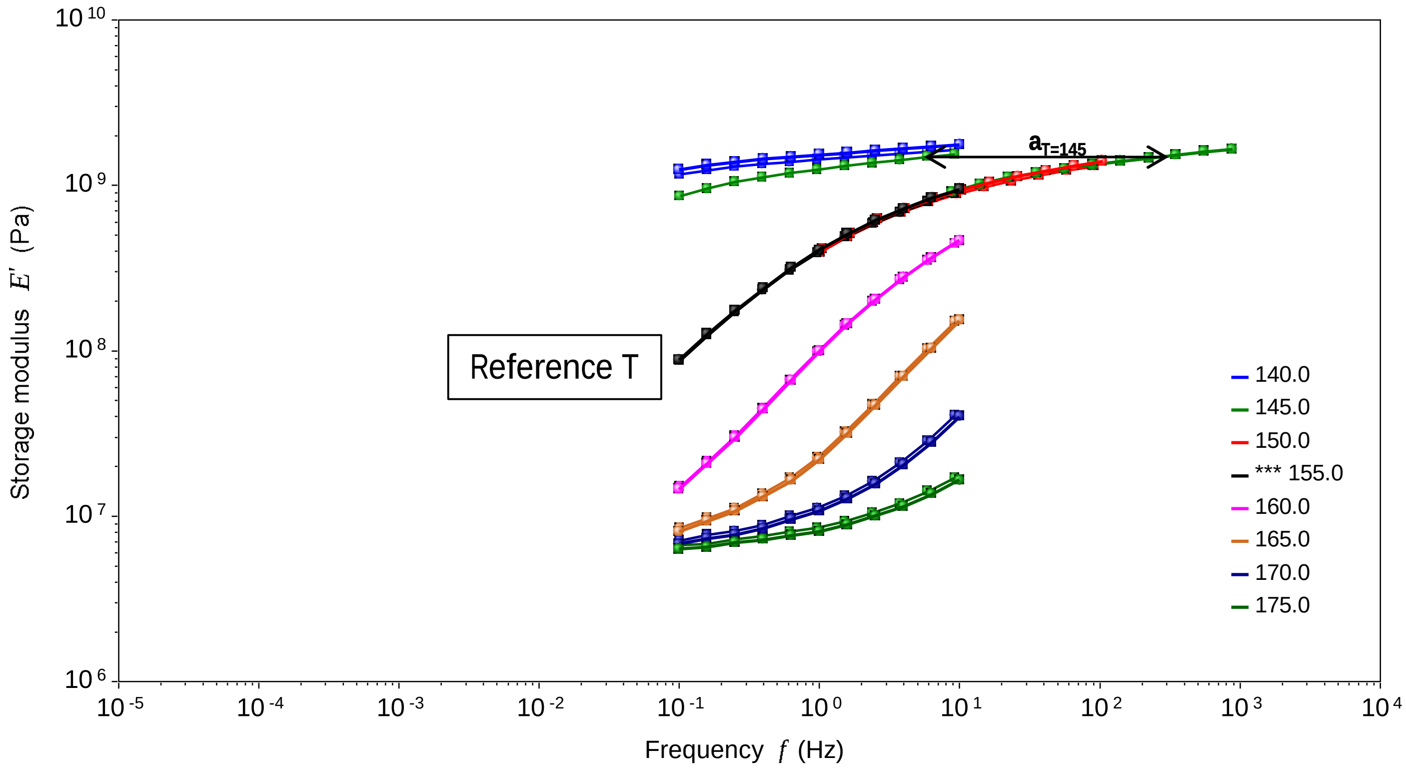
TTS example: shifting of individual curves

- Low temperature data shift to higher frequencies



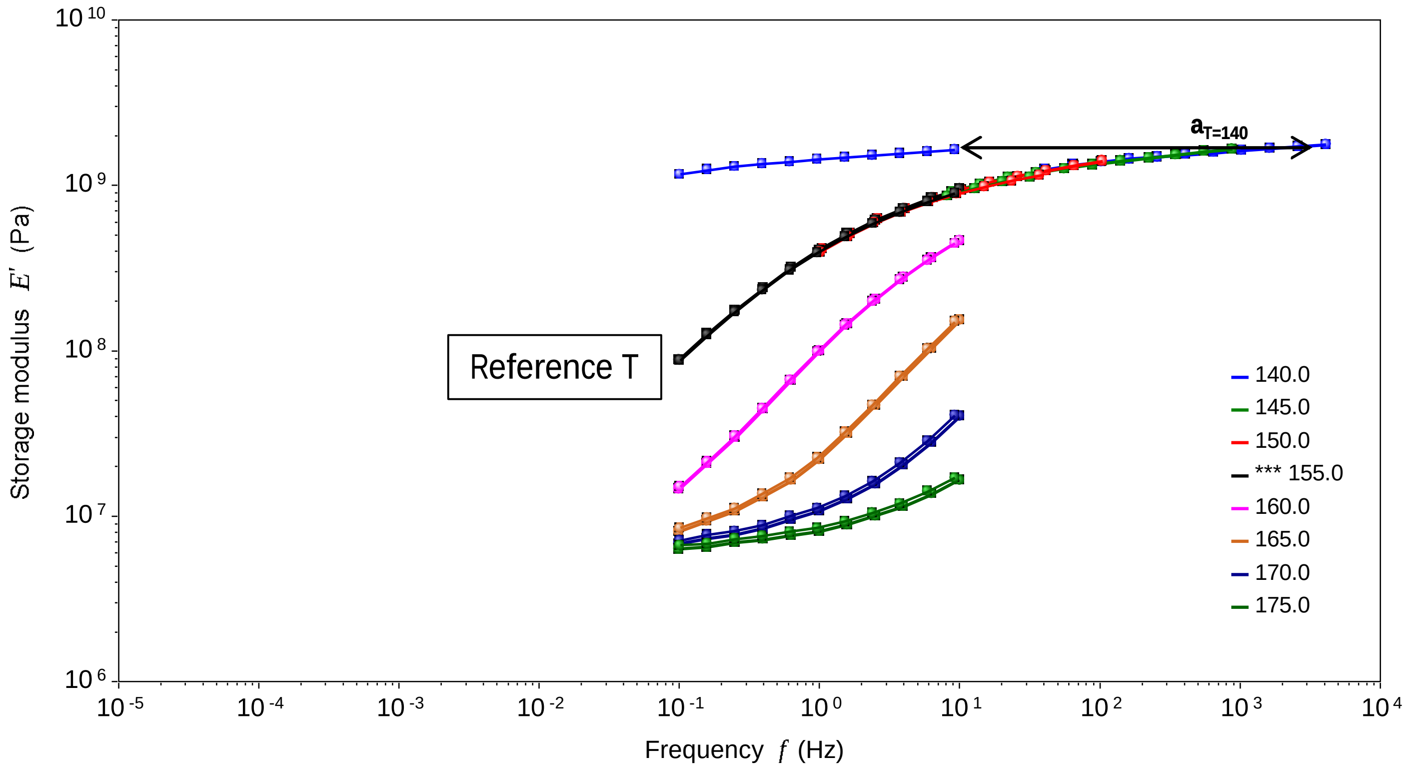
TTS example: shifting of individual curves

- Low temperature data shift to higher frequencies



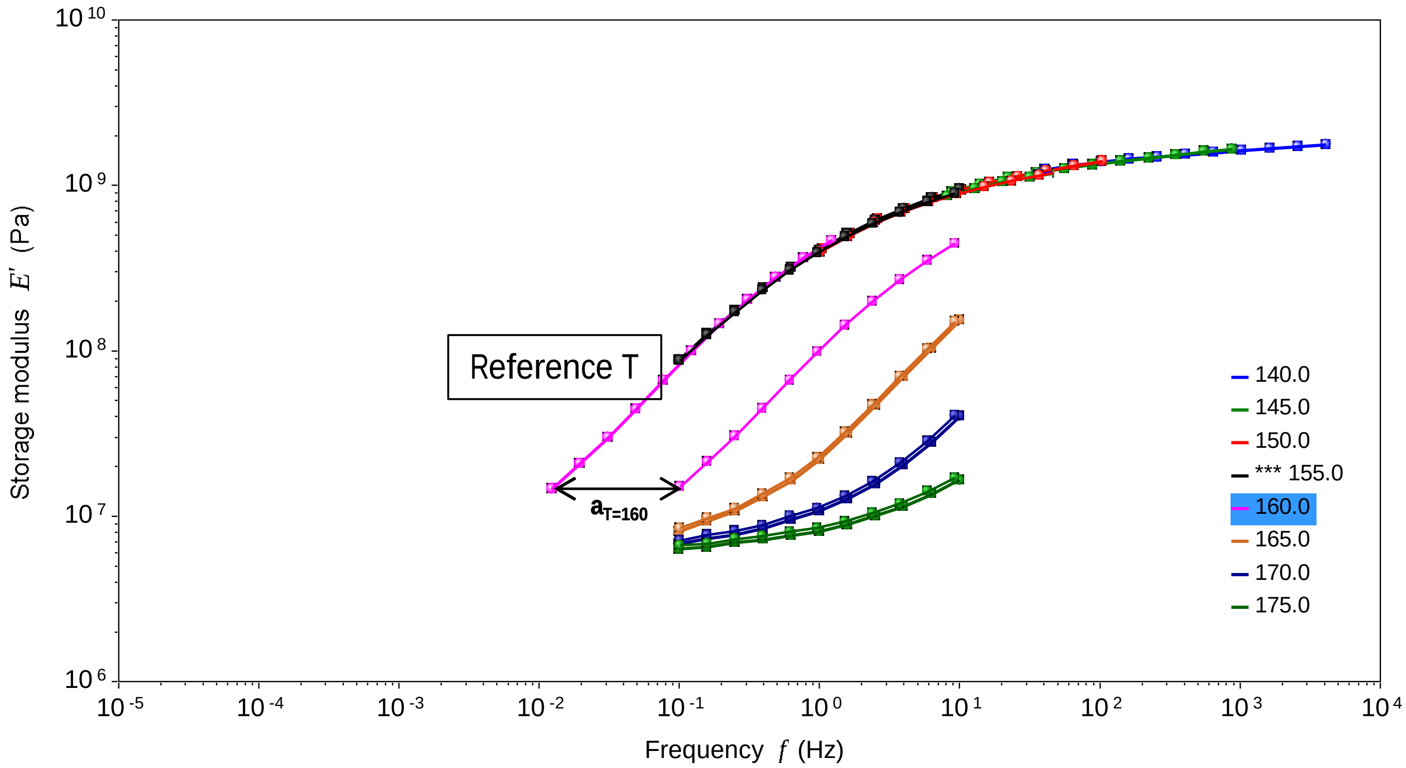
TTS example: shifting of individual curves

- Low temperature data shift to higher frequencies



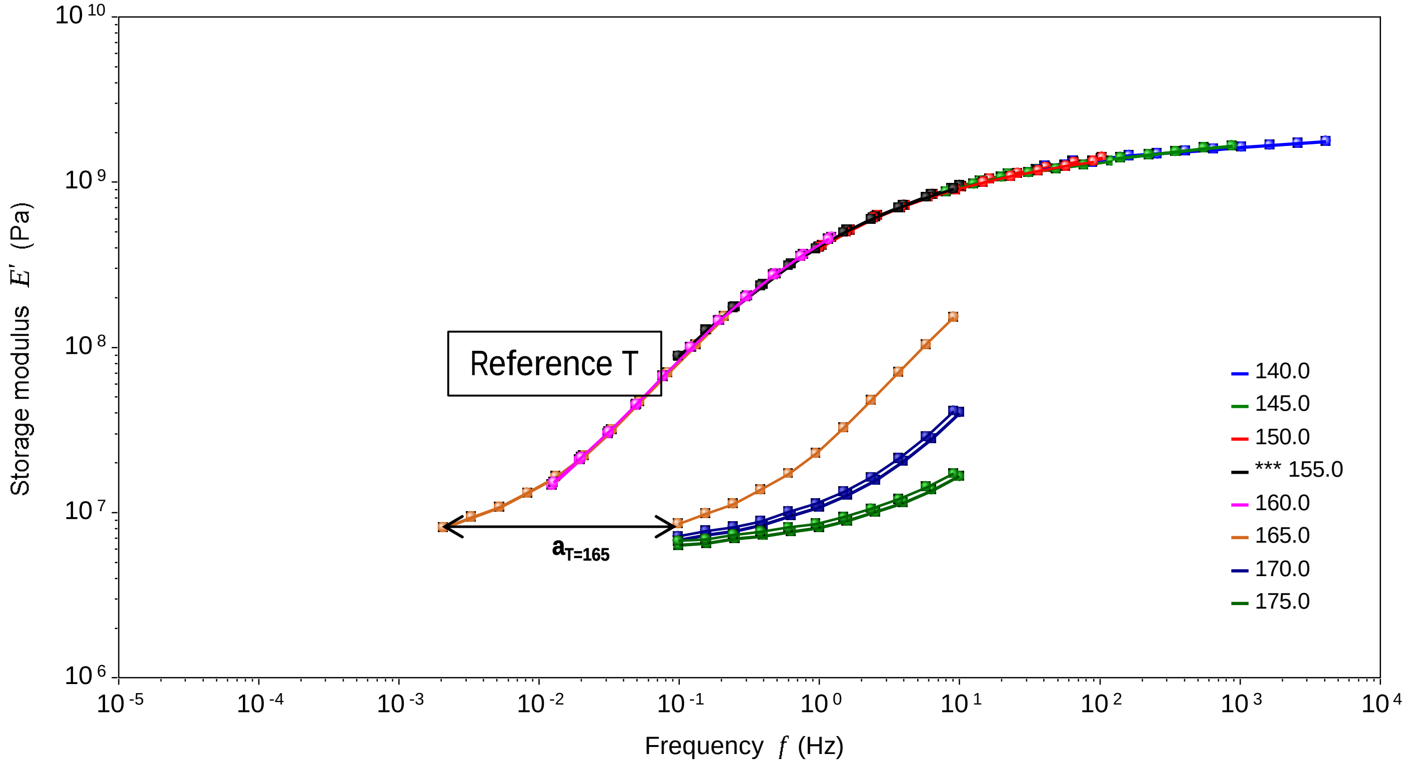
TTS example: shifting of individual curves

- High temperature data shift to lower frequencies



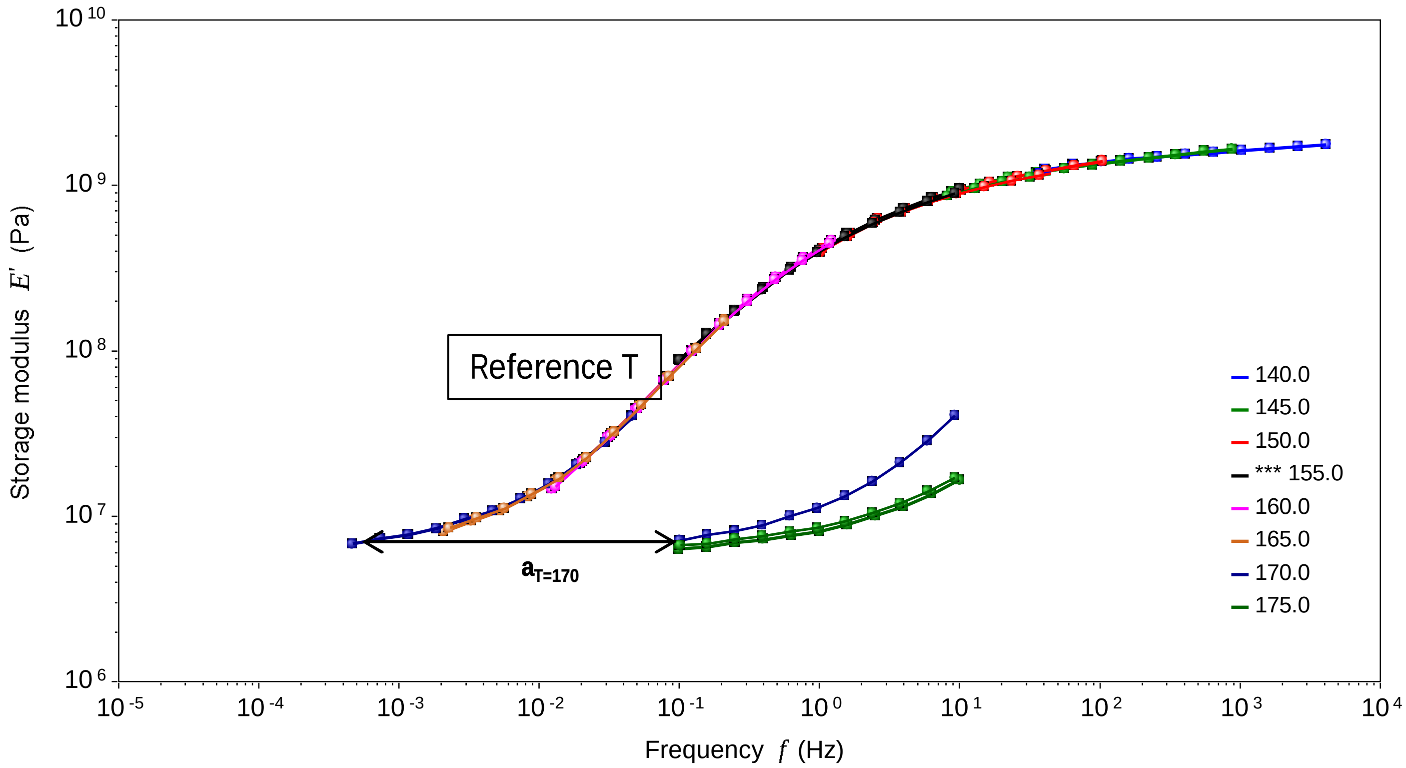
TTS example: shifting of individual curves

- High temperature data shift to lower frequencies



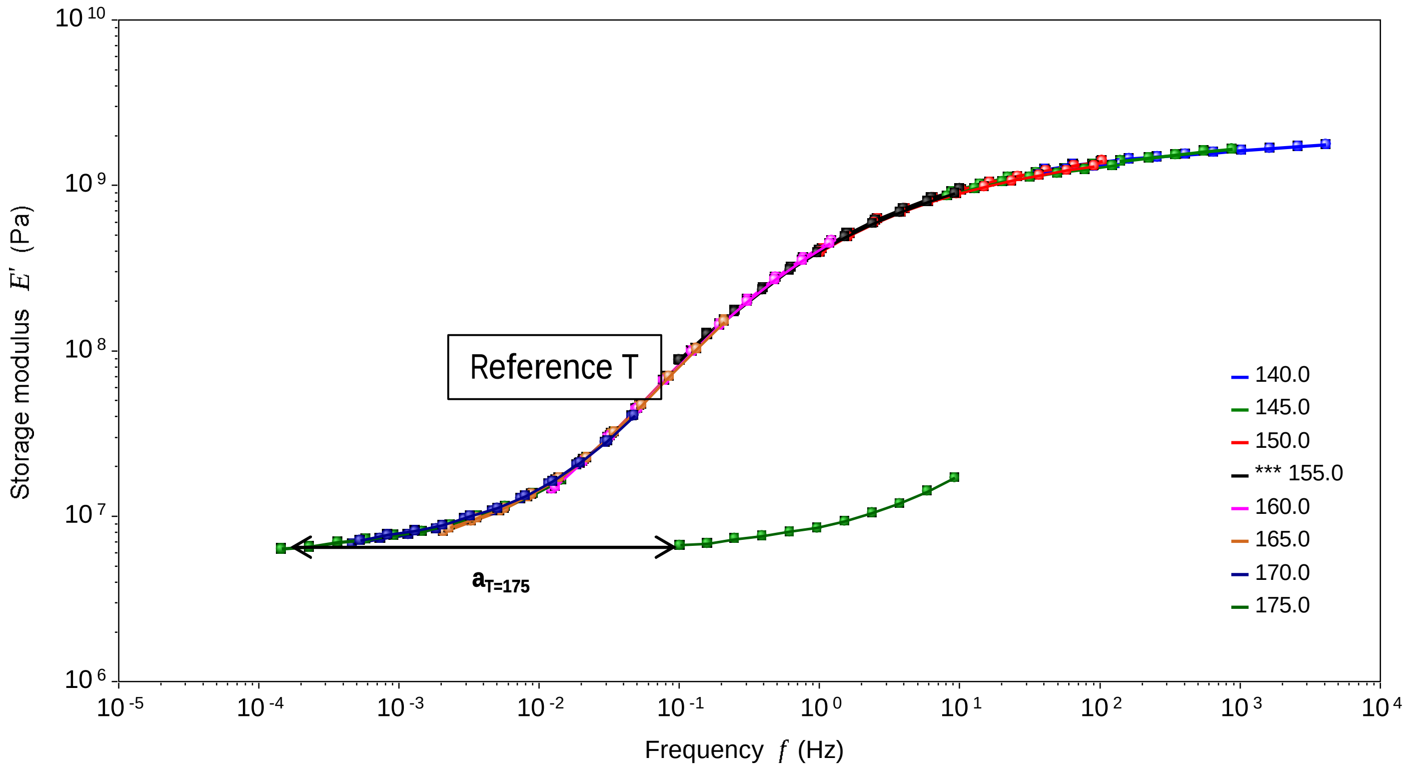
TTS example: shifting of individual curves

- High temperature data shift to lower frequencies



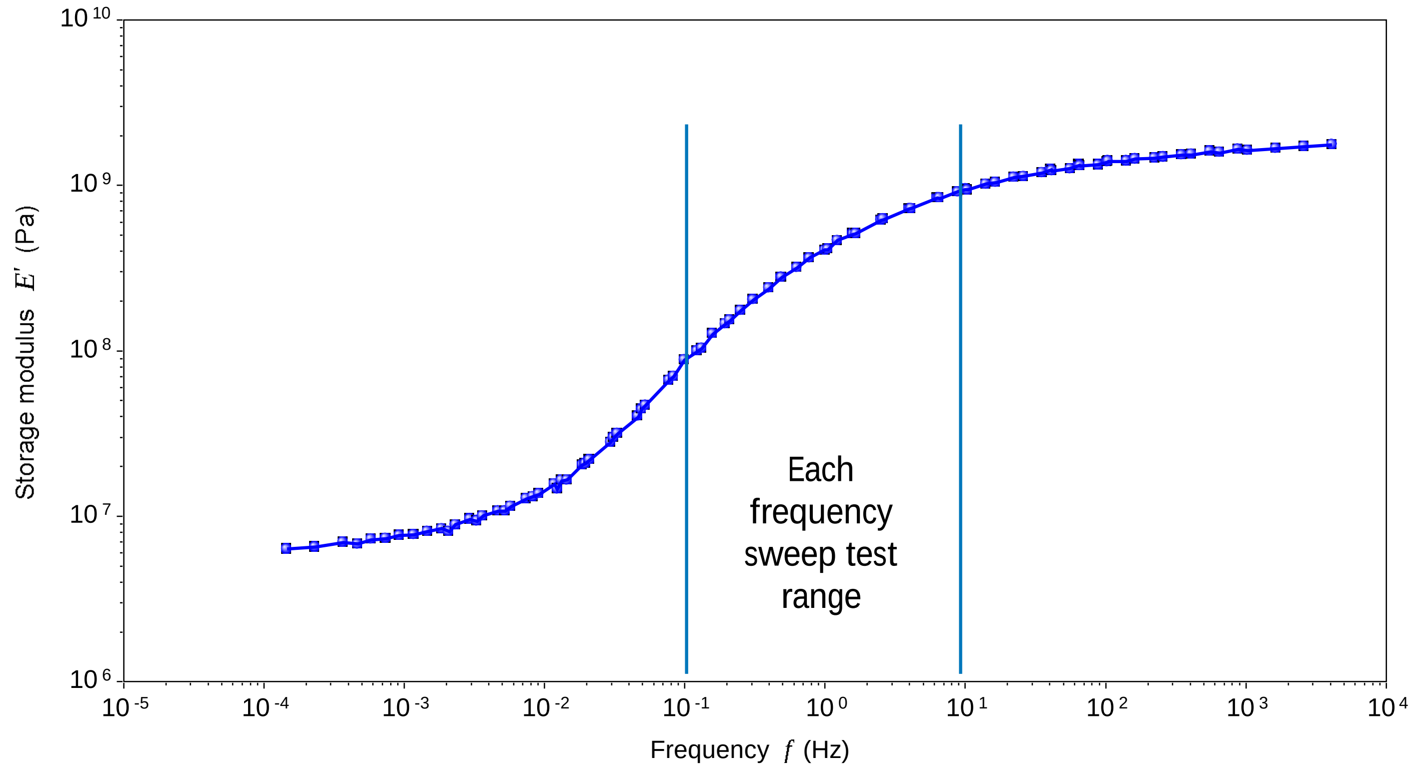
TTS example: shifting of individual curves

- High temperature data shift to lower frequencies

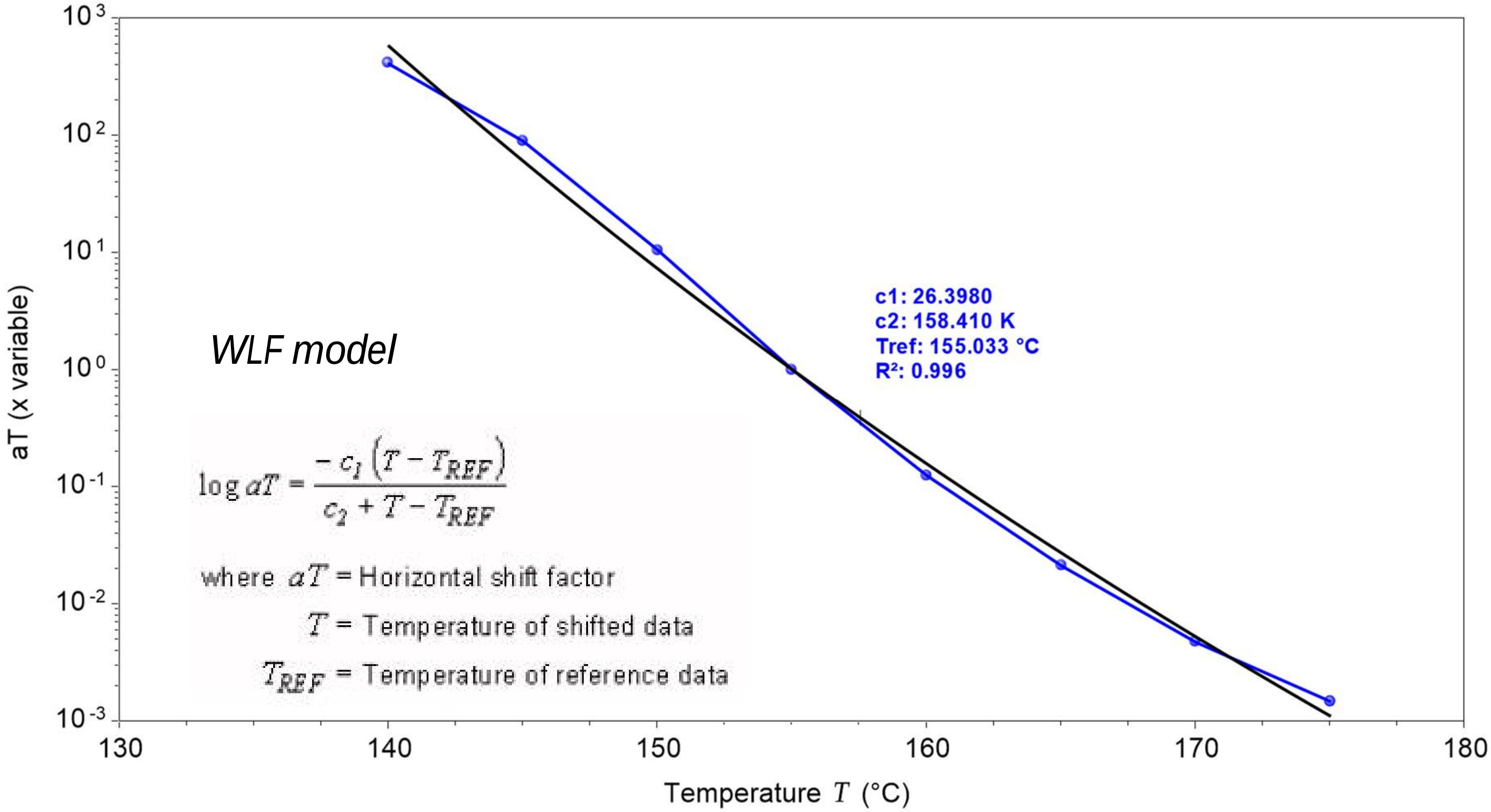


TTS example: shifting of individual curves

- TTS Master Curve using 155°C as reference



Shift Factors aT vs. Temperature



$$\log aT = \frac{-c_1 (T - T_{REF})}{c_2 + T - T_{REF}}$$

where aT = Horizontal shift factor

T = Temperature of shifted data

T_{REF} = Temperature of reference data

WLF or Arrhenius Equations

- Master Curves can be generated using shift factors derived from the Williams, Landel, Ferry (WLF) model

$$\log a_T = -c_1(T-T_0)/(c_2+(T-T_0))$$

a_T = temperature shift factor T_0 = reference temperature

c_1 & c_2 = constants from curve fitting

Generally, c_1=17.44 & c_2=51.6 when $T_0 = T_g$

- The Arrhenius model works better if
  - $T > T_g$+100°C; or $T < T_g$ and polymer is not elastomeric
  - temperature range is small, then c_1 & c_2 cannot be calculated precisely

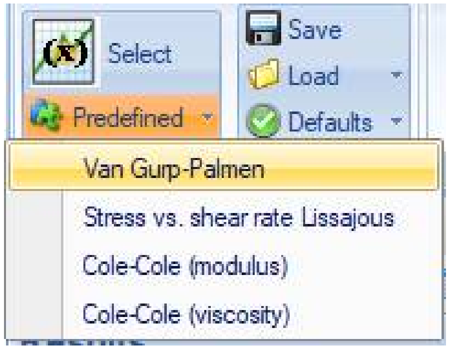
$$\ln a_T = (E_a/R)(1/T-1/T_0)$$

a_T = temperature shift factor E_a = Apparent activation energy

T_0 = reference temperature R = gas constant

How do I know if TTS works for my sample?

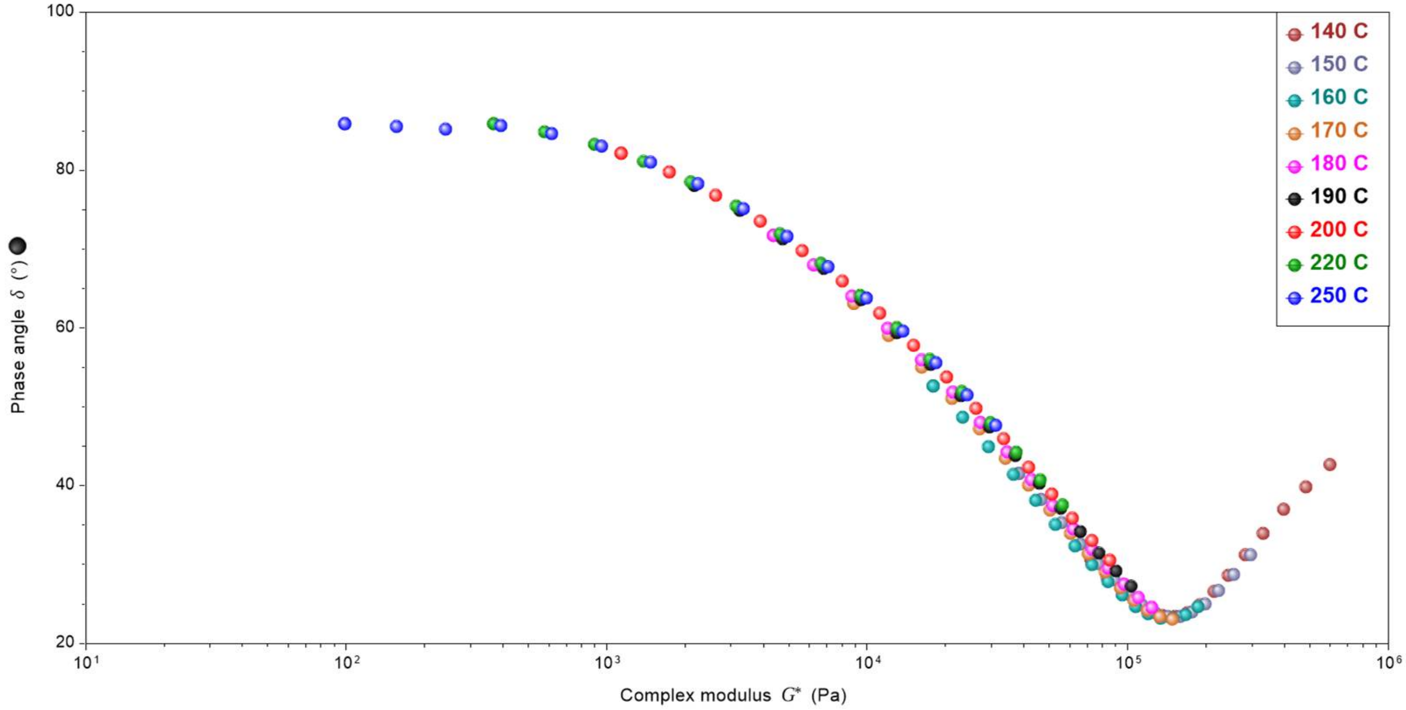
- TTS does not applicable for any materials.
- Check validity of TTS
  - ✓Van-Gurp Palmen plot should be a smooth curve
  - ✓Cole-Cole plot should be a smooth curve
  - ✓Shift factor (a_T) should fit either WLF or Arrhenius equation

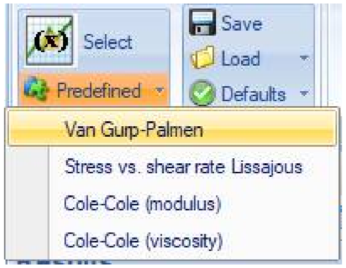


If any one of the above criteria are not met, TTS may not be applicable for your material.

1. van Gurp-Palmen plot to Validate TTS

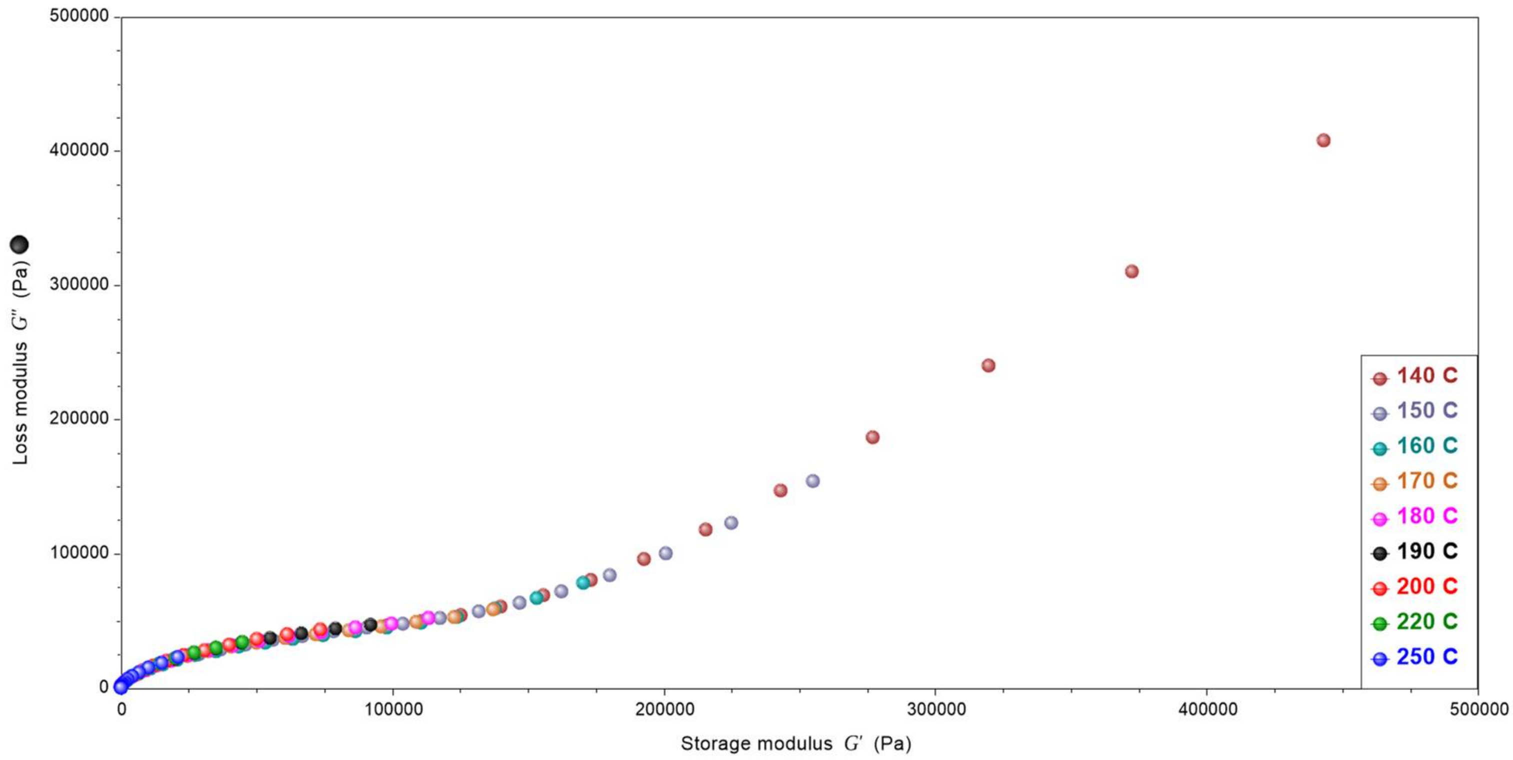
- The van Gurp-Palmen plot can be directly plotted in TRIOS to validate the application of (TTS).

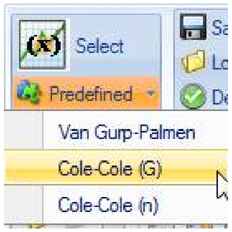




2. Cole-Cole plot to Validate TTS

- The Cole-Cole plot can be directly plotted in TRIOS to validate the application of (TTS).

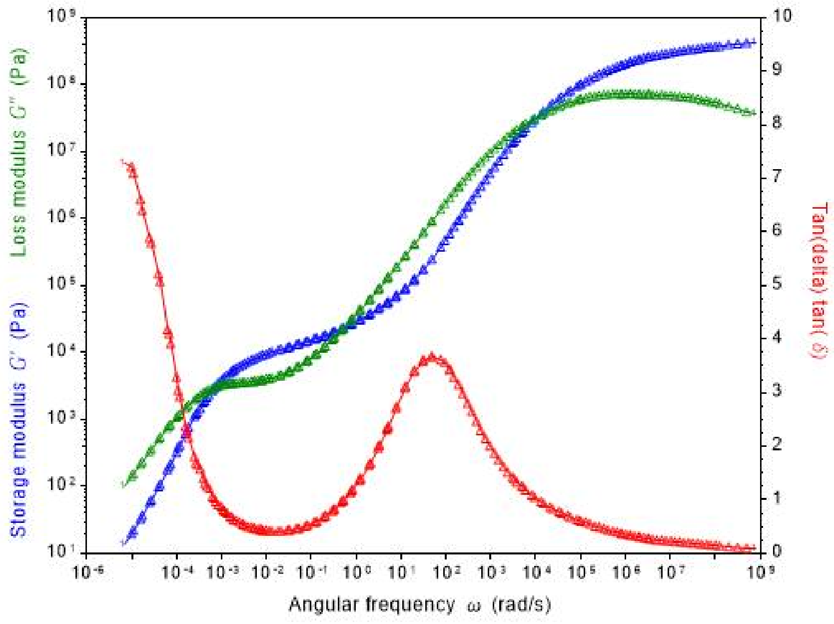




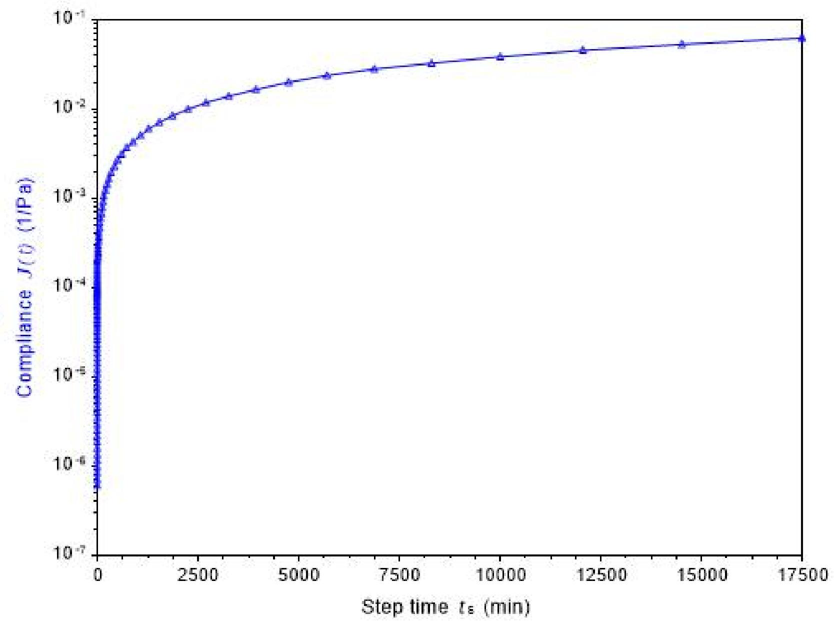
Transformation within Linear Viscoelastic Region

- TTS analysis can be applied to both dynamic and transient (creep and stress relaxation) measurements
- Within the linear viscoelastic region, the dynamic and transient data are inter-convertible

Dynamic master curve



Creep master curve



Philadelphia Short Course: Day II

Section VI: DMA Troubleshooting

Terri Chen, PhD
Principal Application Scientist
TA Instruments – Waters LLC

Factors that influence measurement results

Primary measurements
- Force
- Displacement
- Temperature

<u>Check list</u>
- Instrument calibrations
- Thermocouple position

Geometry
- Clamp
- Sample size
- Sample loading
- Sample integrity

<u>Check list</u>
- Clamp calibrations
- Proper loading torque/force
- Sample uniformity and thermal stability
- Bad contact or sample bending and twisting

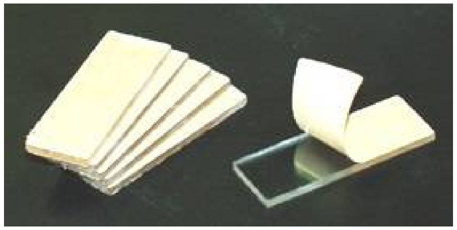
Test Parameters

<u>Check list</u>
- Loading force
- Proper force track
- Equilibration time
- Heating rates
- Amplitude
- Frequency

Instrument and clamp

- Periodically calibrate the instrument following the online help manual
- Perform clamp calibration every time when attaching a new clamp on the instrument
  - http://www.youtube.com/user/TATechTips
- Perform confidence verification check using polycarbonate provided by TA Instruments

p/n: 984309.901

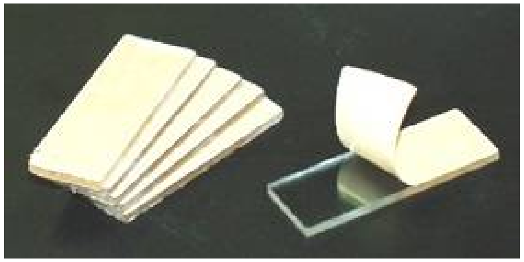


p/n: 982165.903

DMA confidence check - polycarbonate

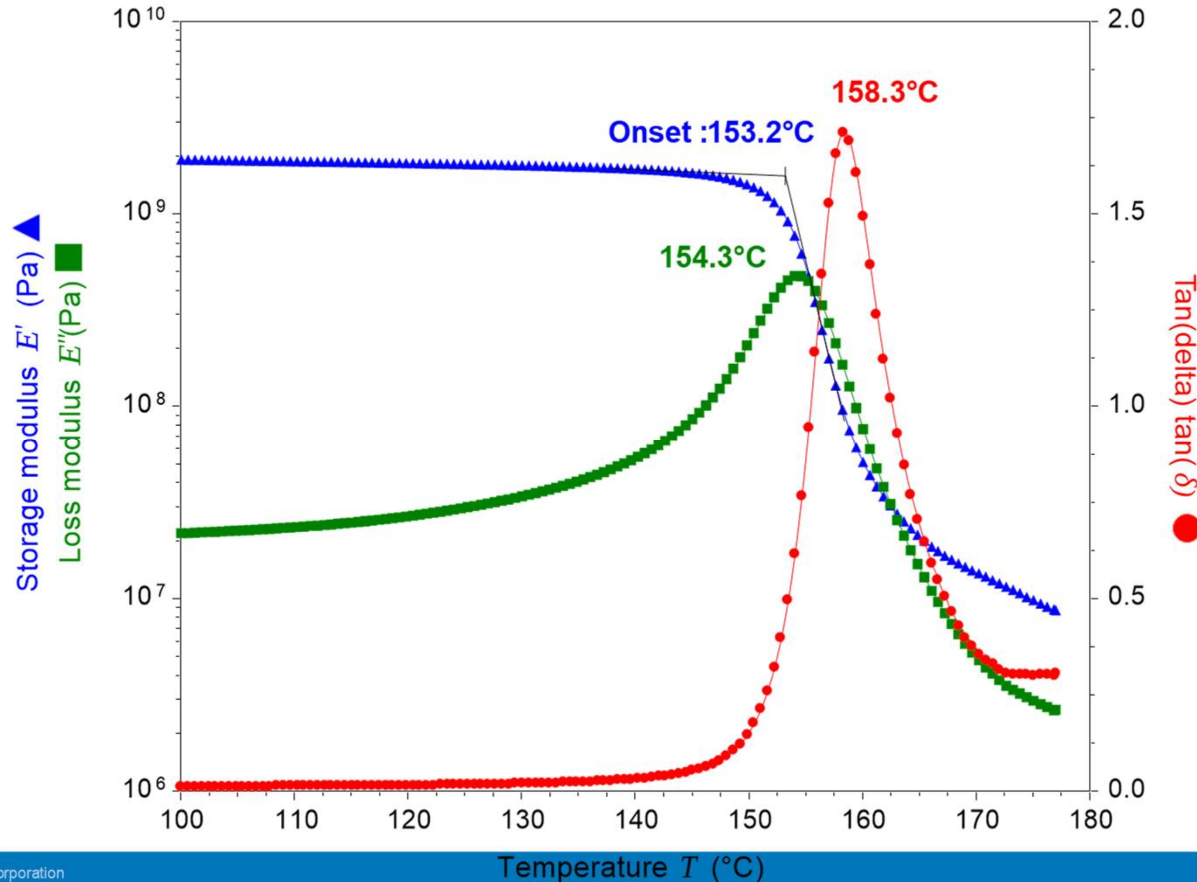
- Load Polycarbonate (L ≈ 17.5, w ≈ 12.85, t ≈ 1.6mm)
- Use Single Cantilever Clamp
  - 20-30 micrometer amplitude
  - 1 Hz frequency
- Storage Modulus at Room Temperature
  E' = 2.35 GPa (2350 MPa) +/- 5%
- Tan Delta at Room Temperature
  Tan δ < 0.01
- Transition Temperature
  Tan δ peak between 155-160°C @ 1Hz, 3-5°C/min
  E" peak will be about 5°C lower

p/n: 982165.903

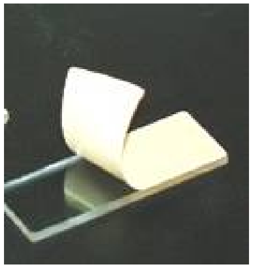


Temp ramp on polycarbonate

- **Available from TA for Instrument verification**



PC sample

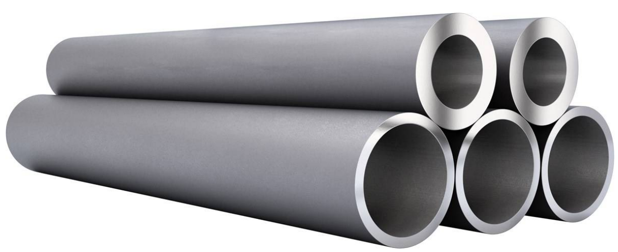


p/n: 982165.903

Clamp:
single cantilever
Temperature:
ambient to 180°C
Heating rate: 3°C/min
Frequency: 1 Hz
Amplitude: 20 μm

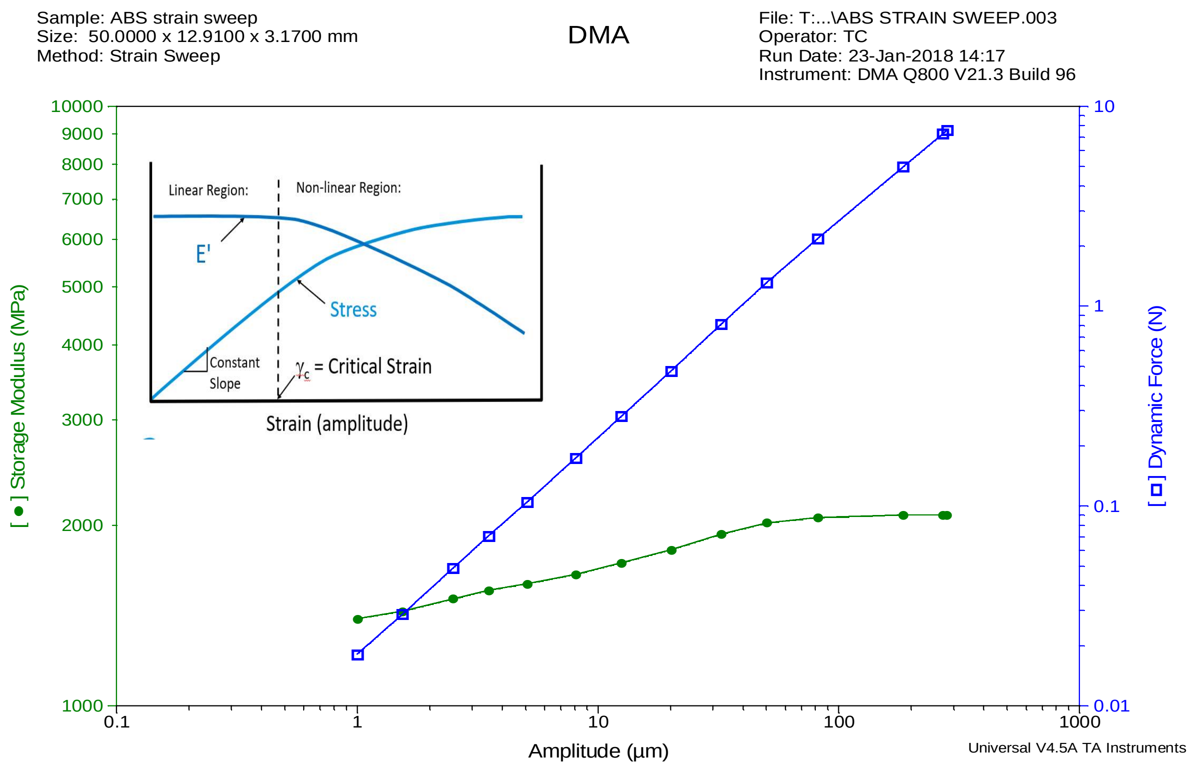
Sample preparation – the key to get good data

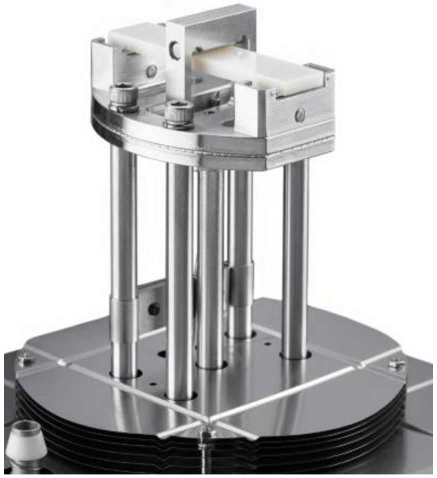
- DMA measurement results are highly depending on the quality of sample preparation
- Sample flatness and uniformity have big influence on the accuracy of the test results



E’ Increase in a strain sweep

Why does E’ increase with increasing amplitude?
How to verify linear viscoelastic region?

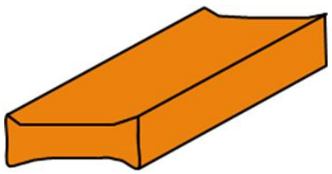


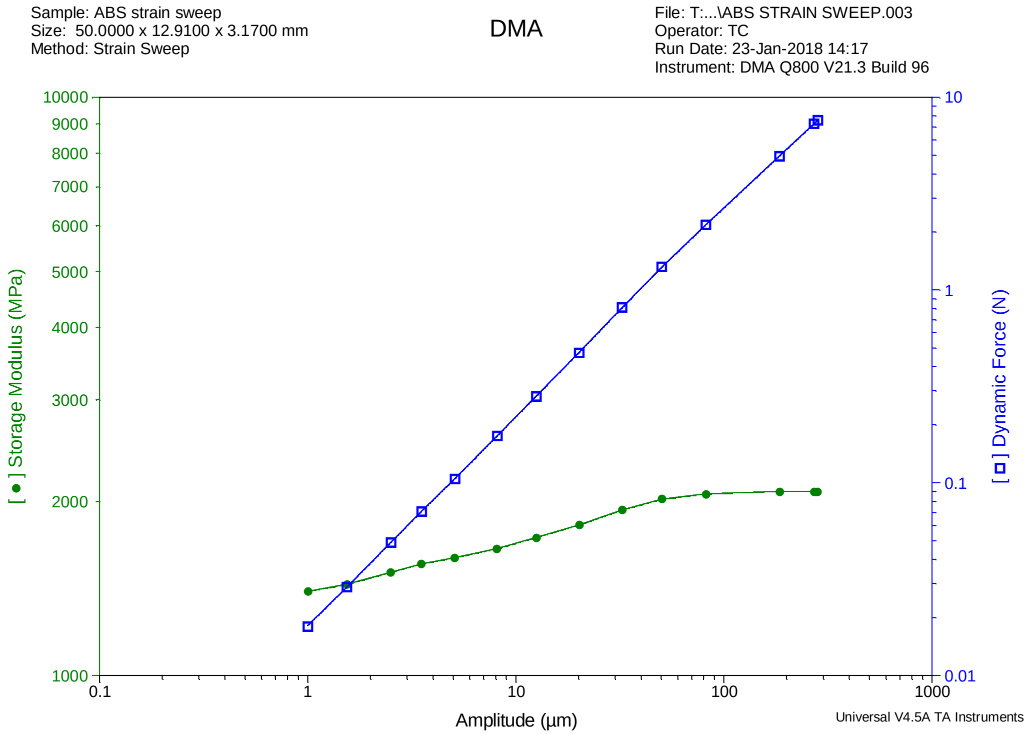


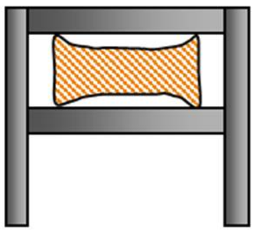
Instrument: DMA
Clamp: 3-p bending
Temperature: ambient
Amplitude: 1-500 μm
Frequency: 1Hz

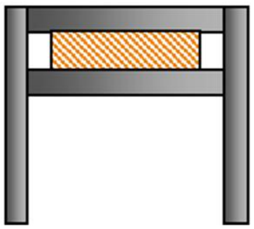
E' Increase in a strain sweep

The sample is not flat and not in full contact with the clamp face.
Solutions: (1) Prepare a flat sample
(2) Increase force track or increase static force



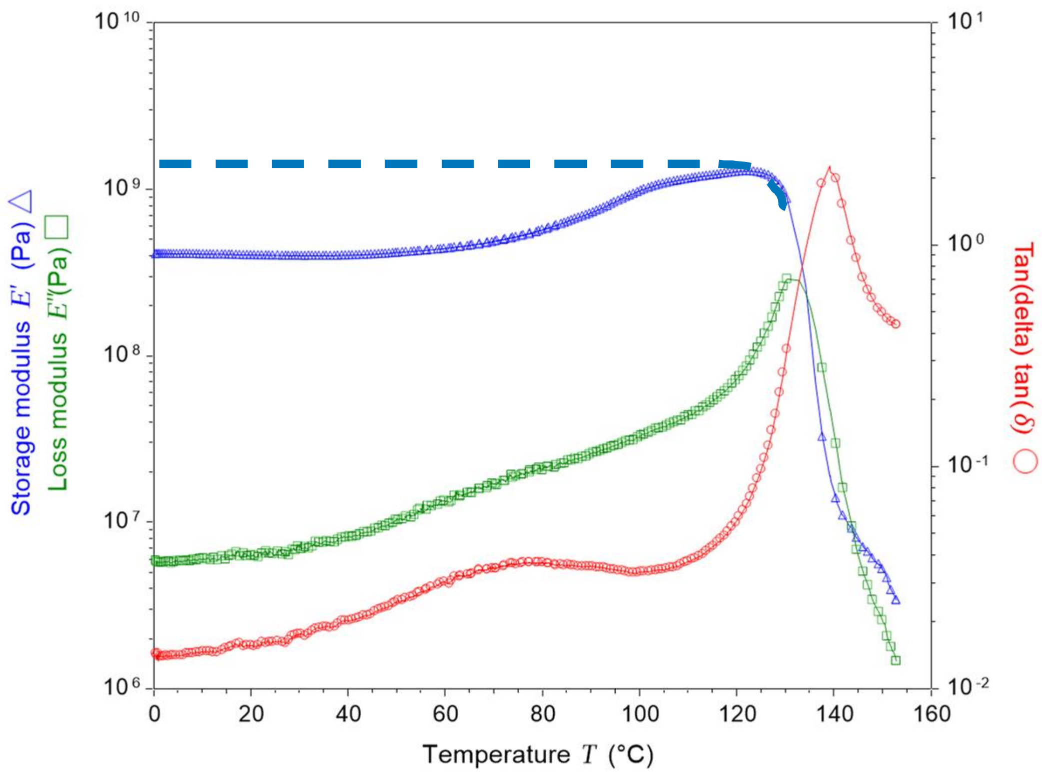






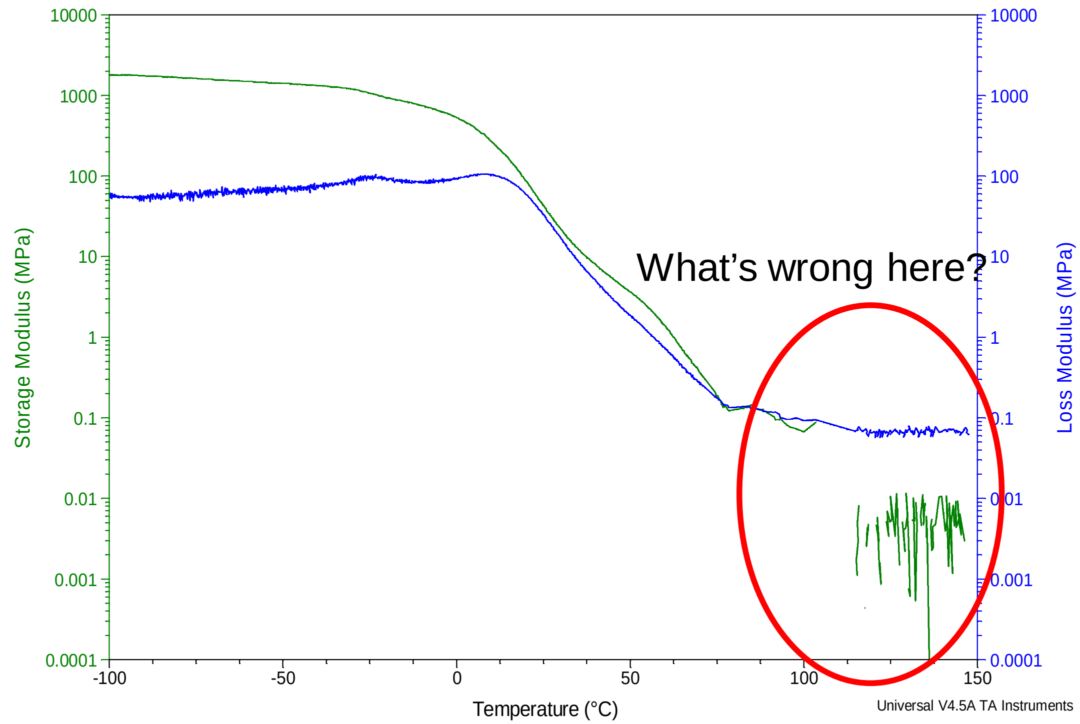
E’ increase in a temp ramp

- The E’ of a material should not increase with temperature unless it is crystalized or crosslinked



Noisy modulus after Tg

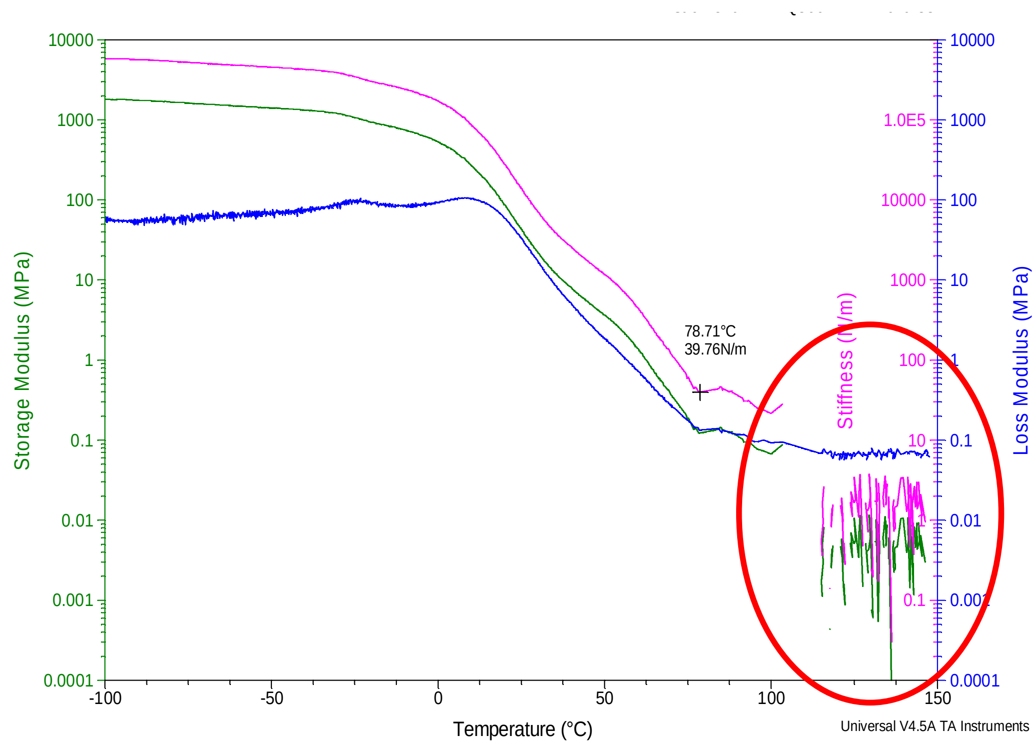
What is the problem with this data collected after T_g?



Instrument: DMA
Clamp: tension
Temperature:
-100°C to 150°C
Heating rate: 3°C/min
Frequency: 1Hz
Amplitude: 10 μm

Noisy modulus after Tg

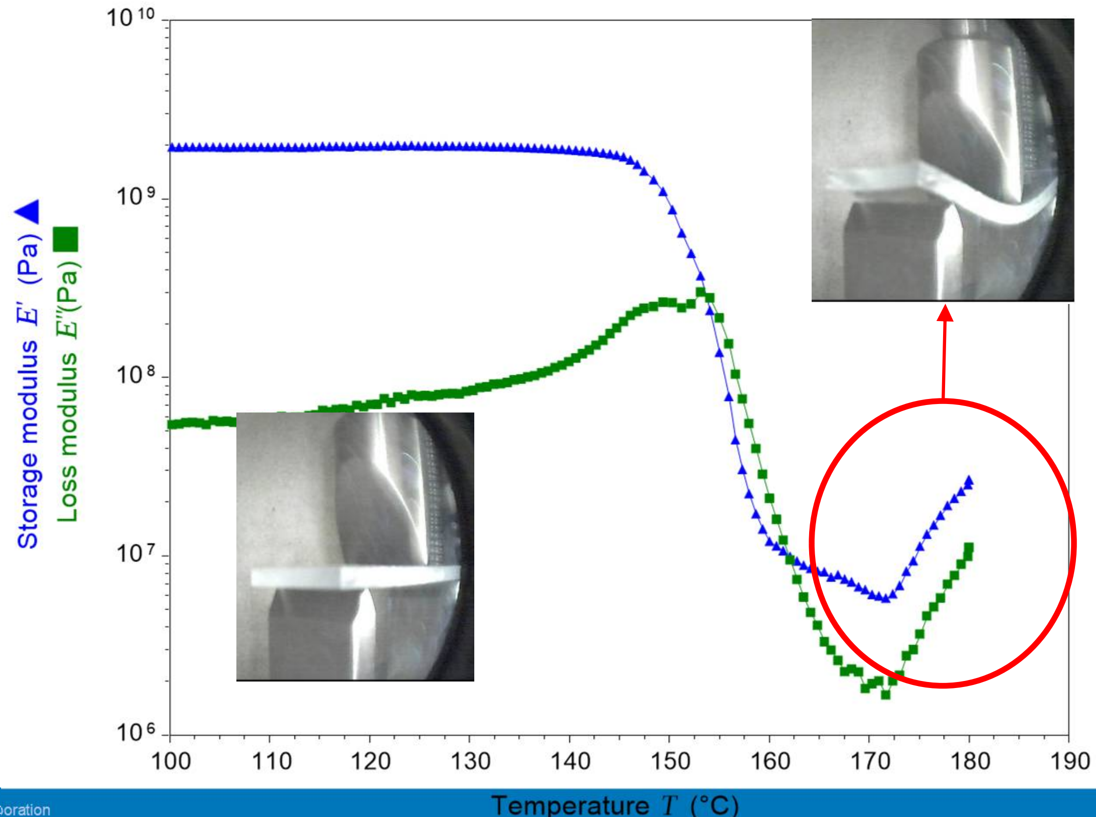
What is the problem with this data collected after T_g?



Instrument: DMA
Clamp: tension
Temperature:
-100°C to 150°C
Heating rate: 3°C/min
Frequency: 1Hz
Amplitude: 10 μm

Sample sagging

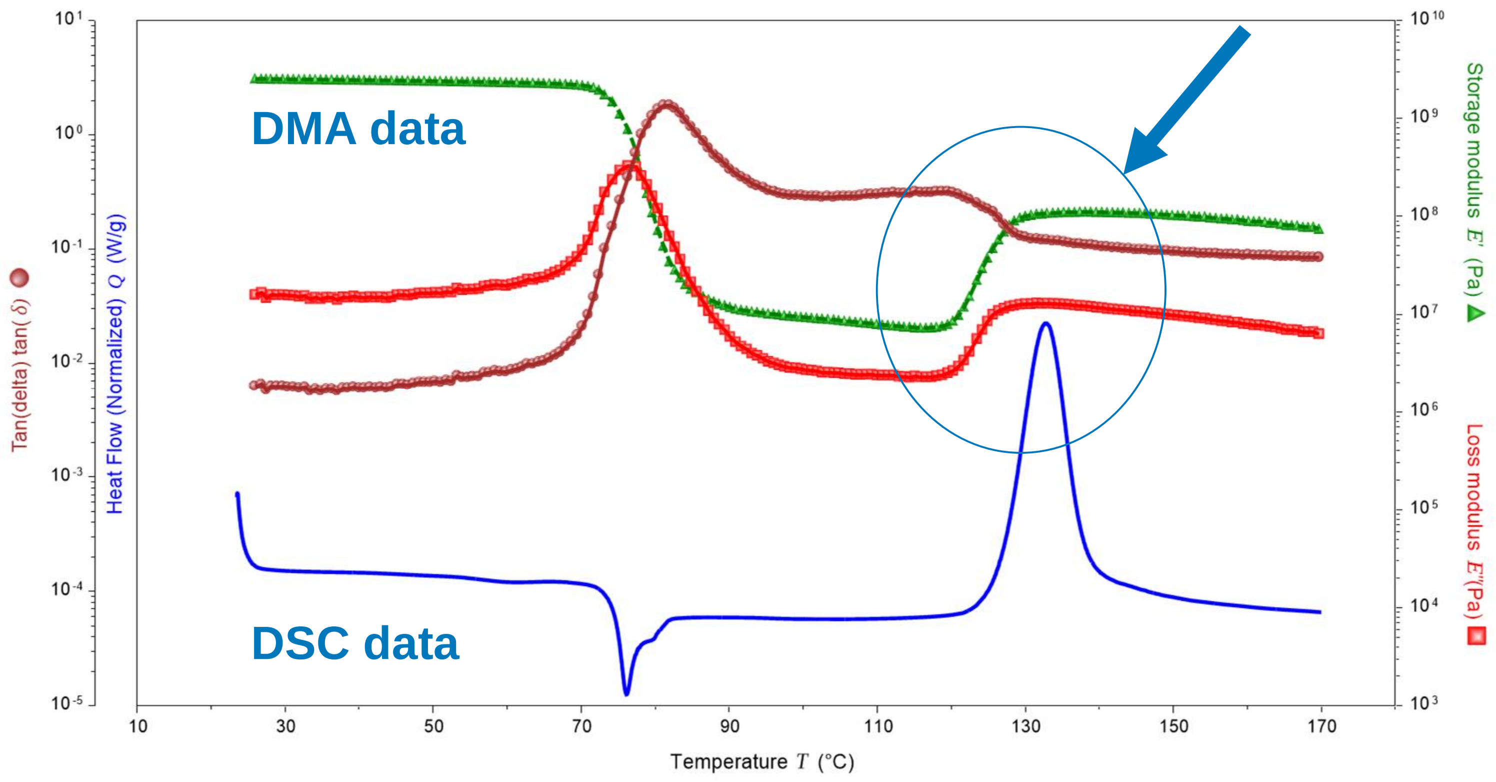
- Sample sagging after T_g
- Solution: use cantilever clamp instead of 3-p bending



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

Cold crystallization after Tg - PLA

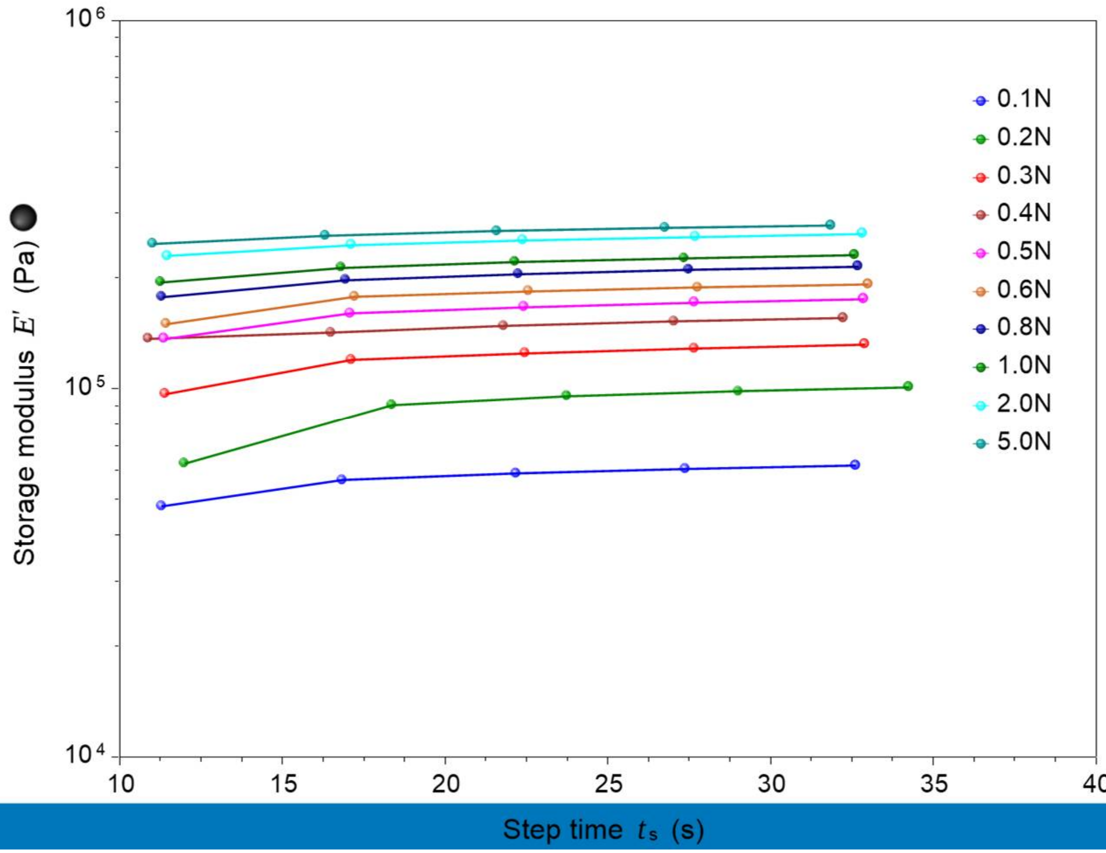
- What causes the E' to increase after Tg?

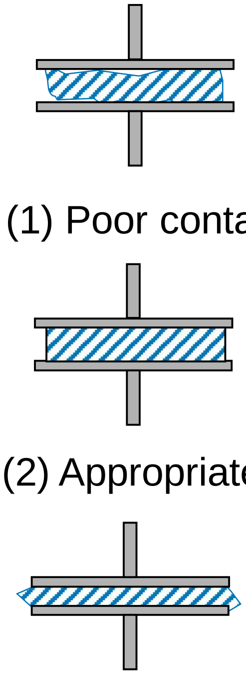


Compression testing on foam/rubber

Question: How to measure correct modulus?

Answer: (1) Prepare regular sample (2) Apply appropriate static force





Philadelphia Short Course: Day II

Introduction to New Rheology Accessories

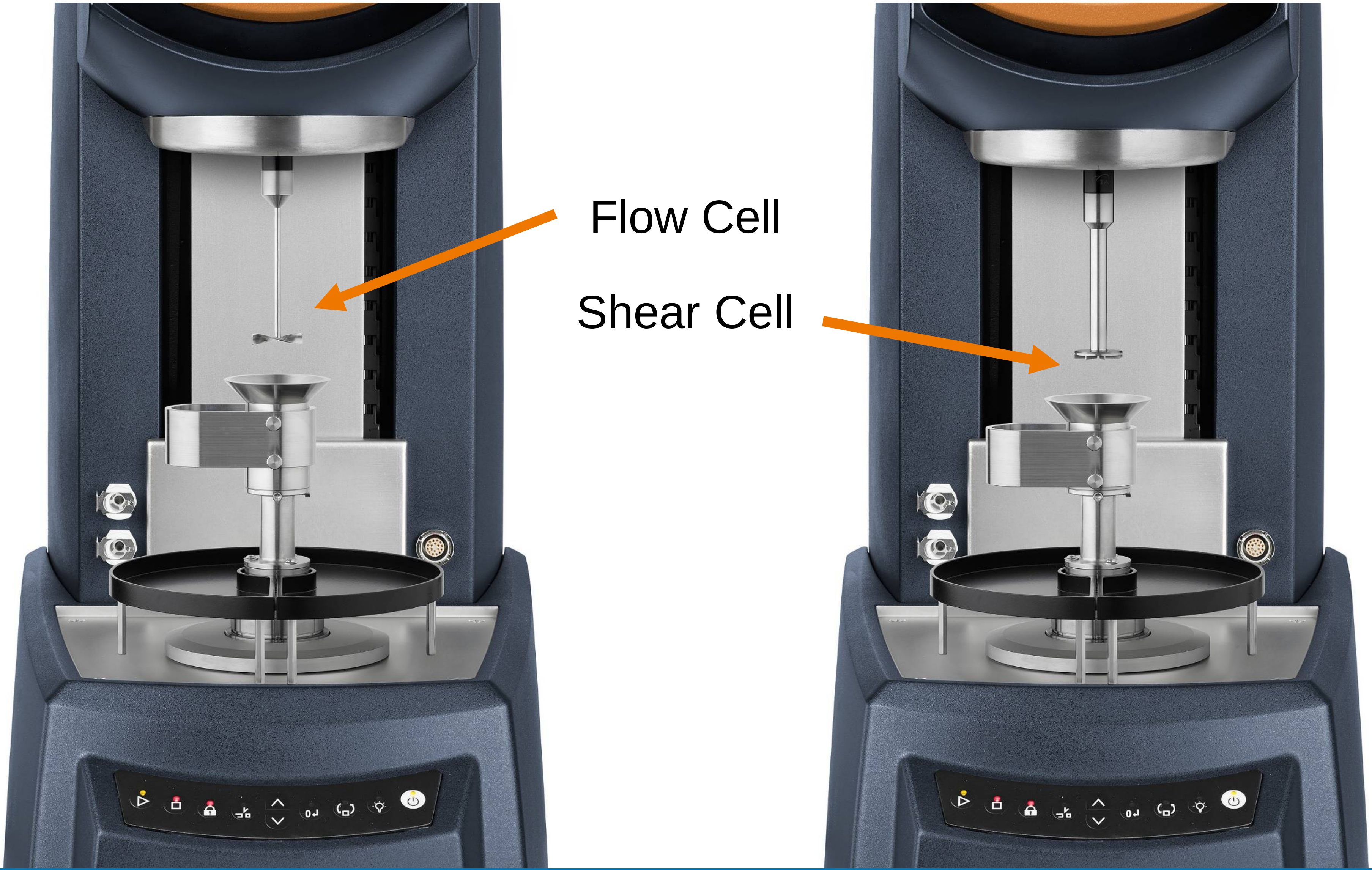
Terri Chen, PhD

Principal Application Scientist

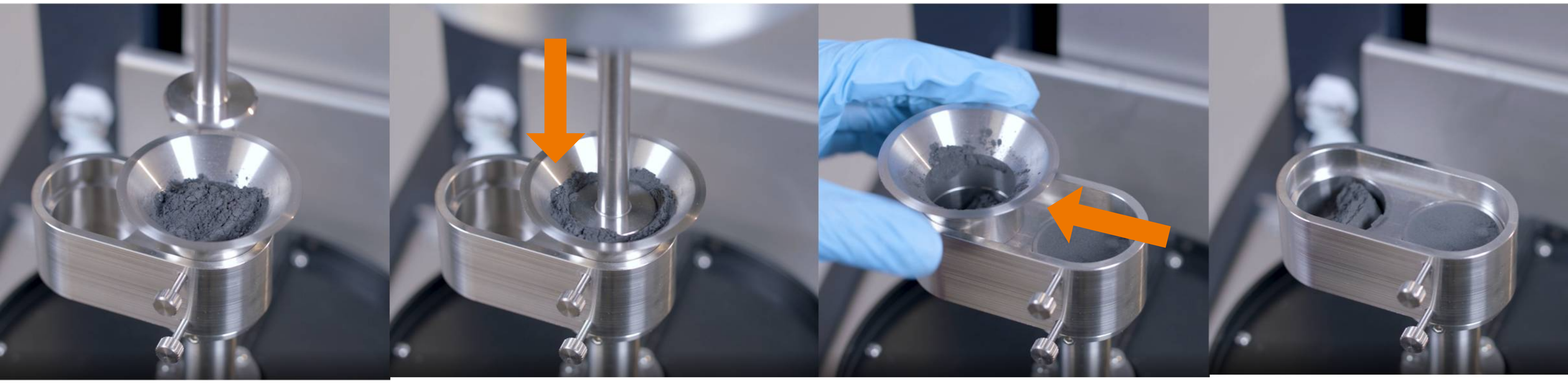
TA Instruments – Waters LLC

HR x0 Powder Rheology Accessory

- Available on HR 10, HR20 and HR30 rheometer. Powder solution offers comprehensive powder flow analysis
    - Flowability
    - Shear
    - Wall friction (2023)
    - Compressibility (2023)
- Excellent repeatability (within 5%)
- Easy sample preparation: loading and trimming
- Integrated Smart Swap design. Accessory change in less than 10 seconds
- One click data analysis package in Trios


Flow Cell
Shear Cell

Powder Shear Cell sample preparation



Load Sample

>15 mL

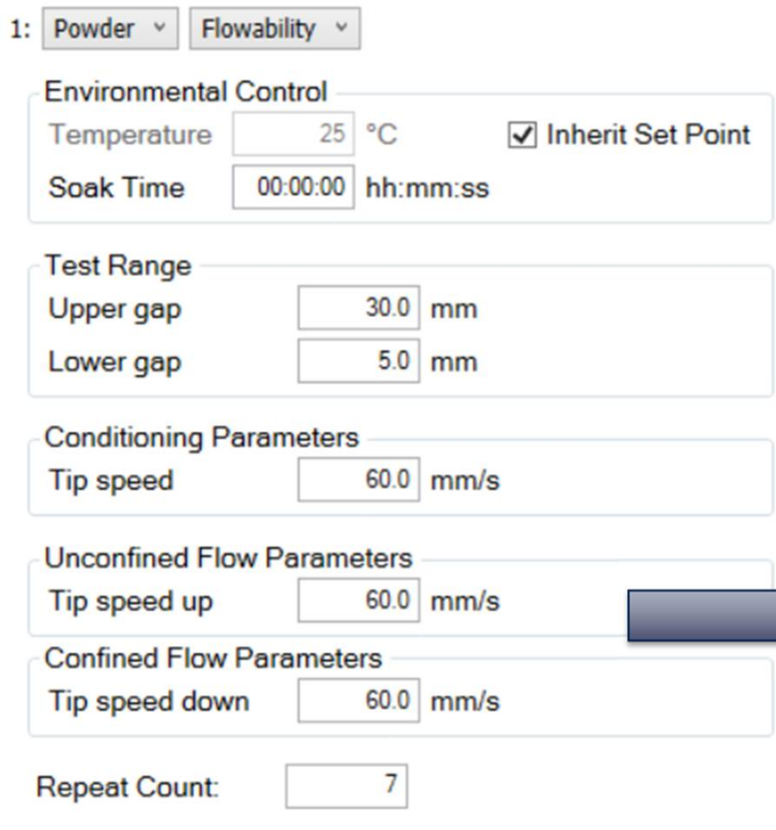
Sample Consolidation

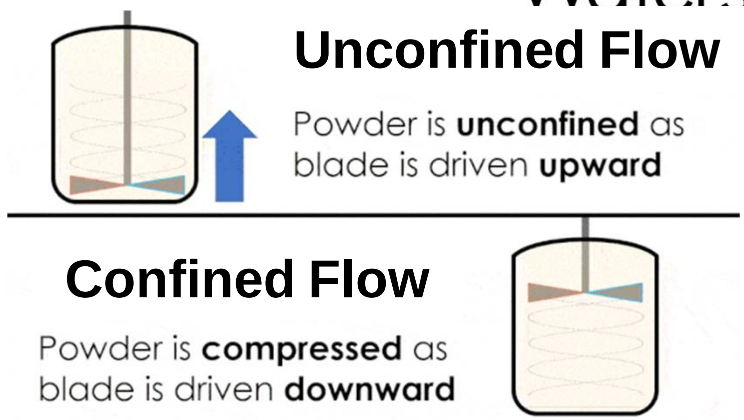
Trim Sample

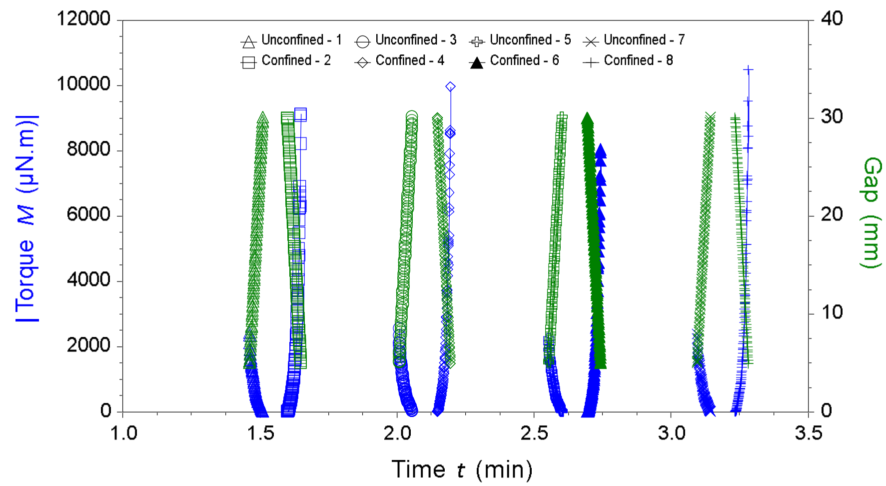
User prompt from the touchscreen

Start the Test

TRIOS simplifies Powder Flowability test





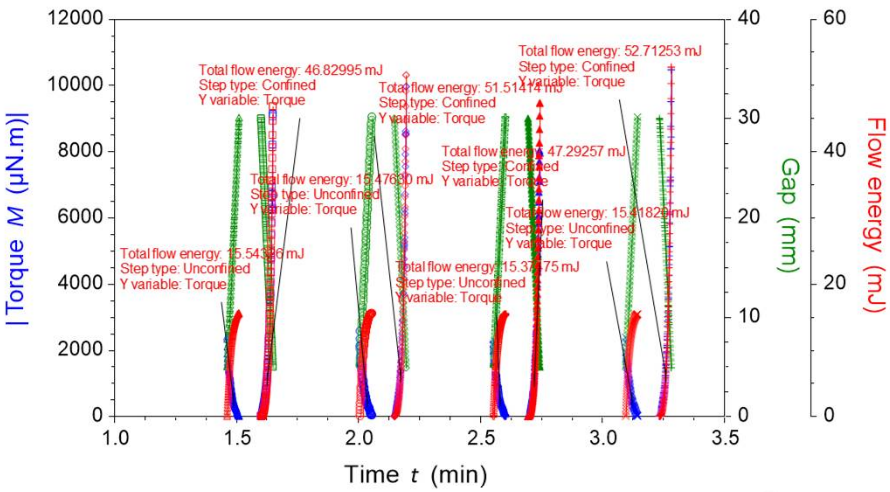


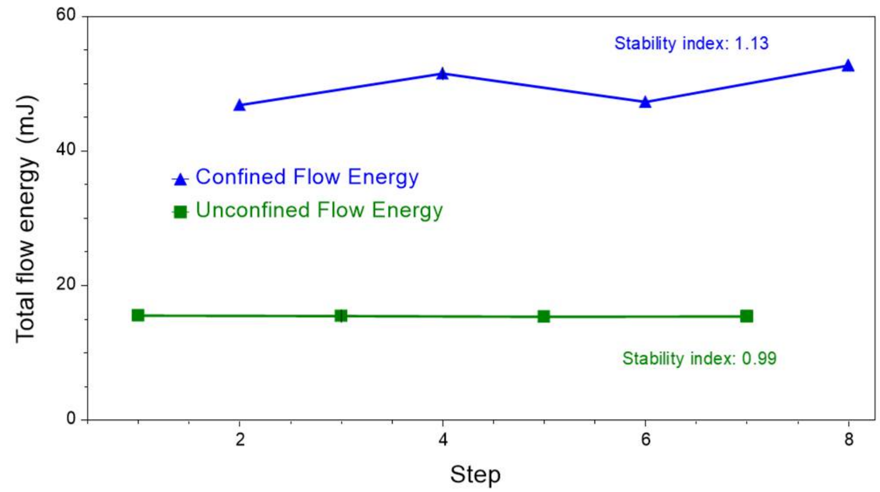
- Repeat steps – Stability Index
- Vary Tip Speed – Flow Rate Index

Powder Analysis Key automates Flowability calculation

TRIOS Powder Analysis Software key (optional)

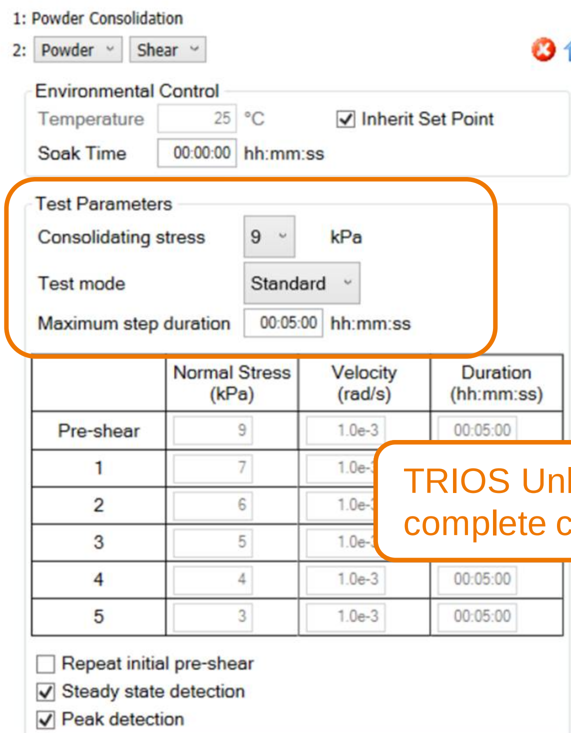
- Powder Key Performance Indicators are ***One Click away***
- Automated process saves user from complicated mathematical analysis
- Quantitative, relevant, repeatable results





$$\text{Flow Energy} = \underbrace{\int T * d\theta}_{\text{Torque energy}} + \underbrace{\int N * dh}_{\text{Force energy}}$$

TRIOS simplifies Powder Shear Test



1: Powder Consolidation
2: Powder Shear

Environmental Control
Temperature 25 °C ☑ Inherit Set Point
Soak Time 00:00:00 hh:mm:ss

Test Parameters
Consolidating stress 9 kPa
Test mode Standard
Maximum step duration 00:05:00 hh:mm:ss

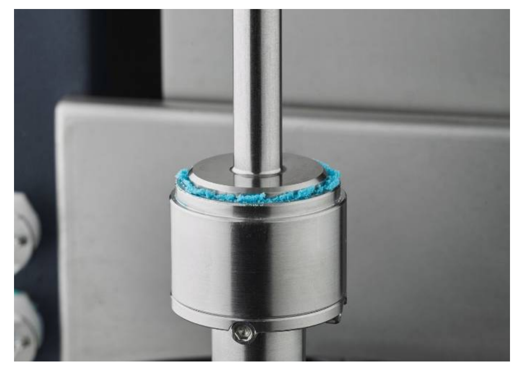
	Normal Stress (kPa)	Velocity (rad/s)	Duration (hh:mm:ss)
Pre-shear	9	1.0e-3	00:05:00
1	7	1.0e-	
2	6	1.0e-	
3	5	1.0e-	
4	4	1.0e-3	00:05:00
5	3	1.0e-3	00:05:00

☐ Repeat initial pre-shear
☑ Steady state detection
☑ Peak detection

TRIOS Unlimited:
complete customizability

TRIOS Powder-Shear test form performs ASTM D7891 measurement

- “Pre-Shear”: Apply consolidating normal stress (9 kPa), pre-shear until steady state
- “Shear” Reduce normal stress, shear until yield
- Repeat consolidating pre-shear
- Repeat shear with decreasing normal stress



TRIOS simplifies Powder Shear Test

Waters™ | TA Instruments

1: Powder Consolidation

2: Powder | Shear

Environmental Control

Temperature 25 °C ☑ Inherit Set Point

Soak Time 00:00:00 hh:mm:ss

Test Parameters

Consolidating stress 9 kPa

Test mode Standard

Maximum step duration 00:05:00 hh:mm:ss

	Normal Stress (kPa)	Velocity (rad/s)	Duration (hh:mm:ss)
Pre-shear	9	1.0e-3	00:05:00
1	7	1.0e-3	00:05:00
2	6	1.0e-3	00:05:00
3	5	1.0e-3	00:05:00
4	4	1.0e-3	00:05:00
5	3	1.0e-3	00:05:00

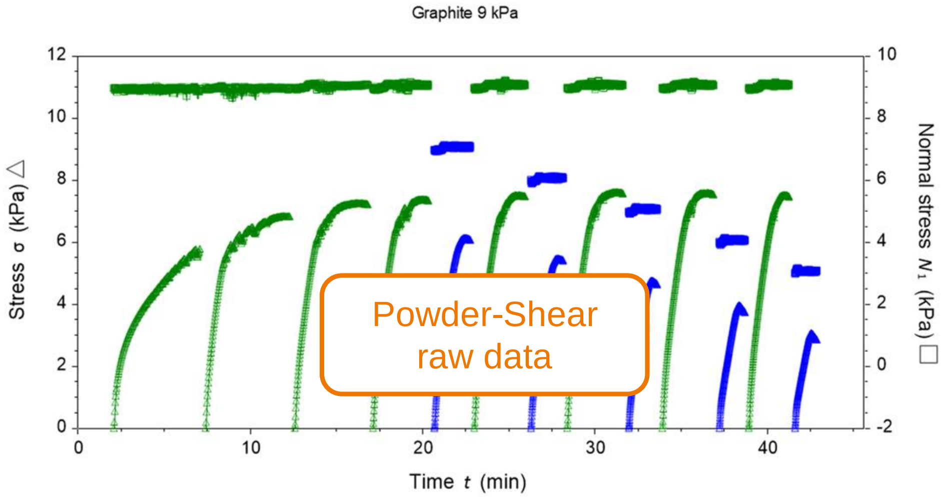
☐ Repeat initial pre-shear

☑ Steady state detection

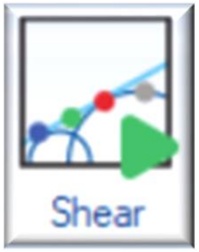
☑ Peak detection

TRIOS Powder – Shear test form performs measurement per **ASTM D7891**

- "Pre-Shear": Apply consolidating normal stress (9 kPa), pre-shear until steady state
- "Shear" Reduce normal stress, shear until yield
- Repeat consolidating pre-shear
- Repeat shear with decreasing normal stress

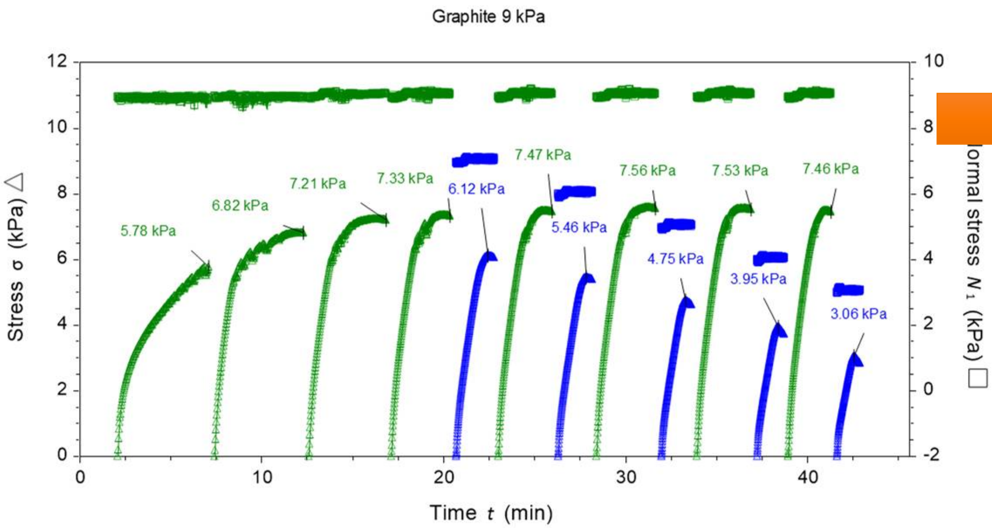


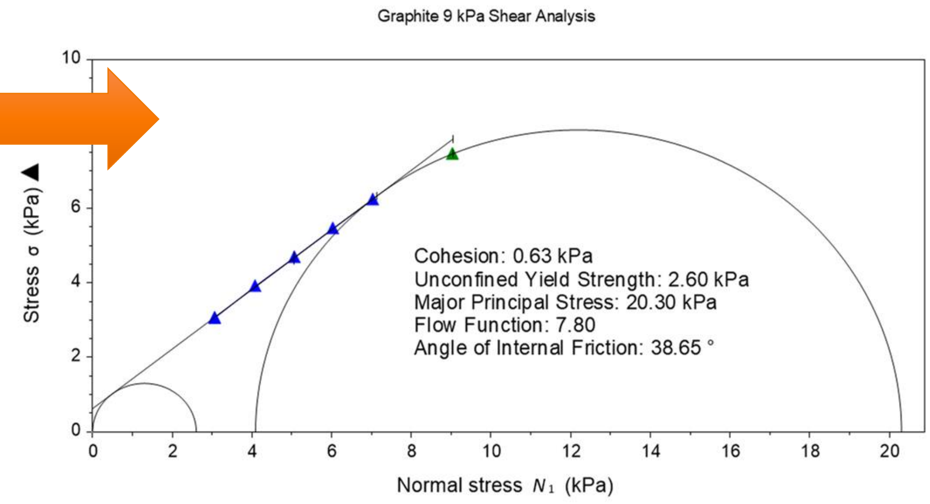
Powder Analysis Key automates Shear calculations



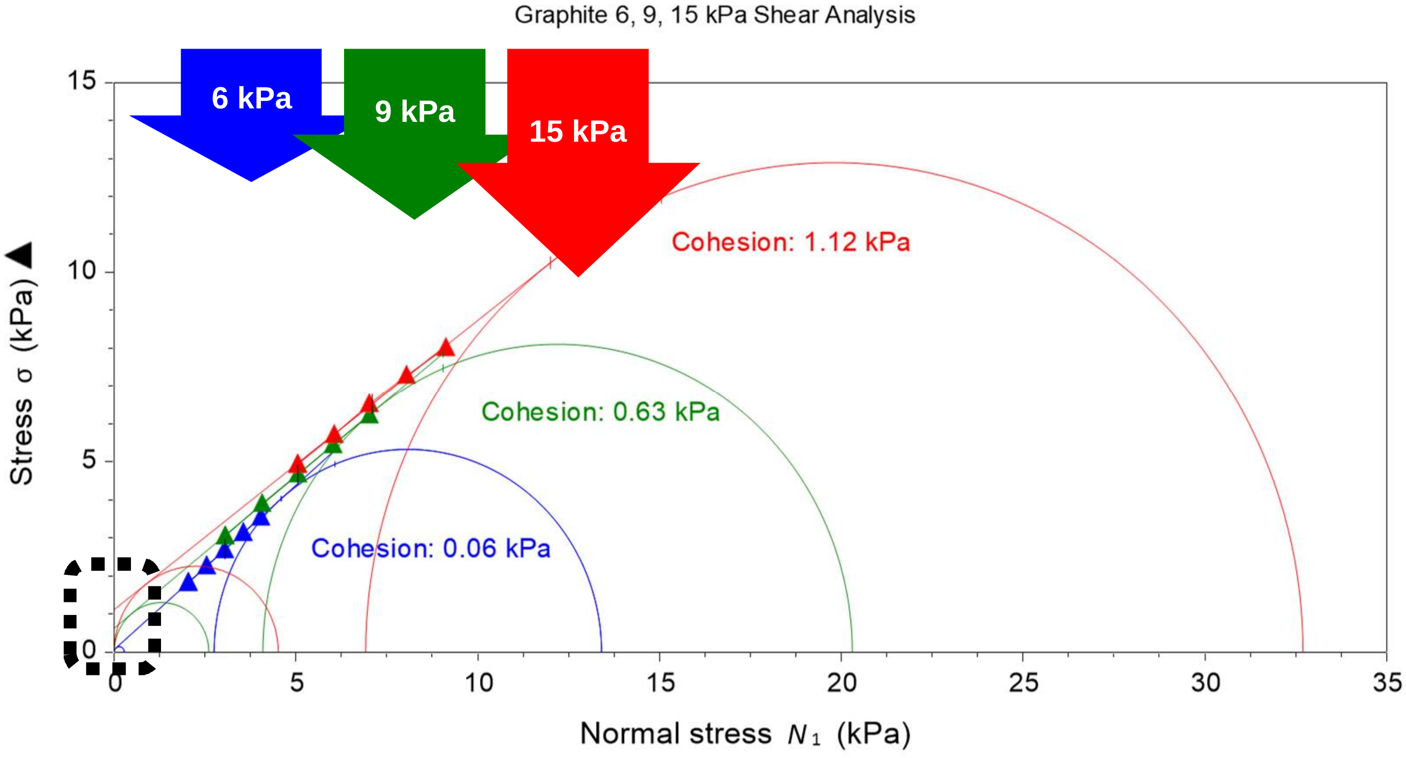
TRIOS Powder Analysis Software key (optional)

- Powder Key Performance Indicators are ***One Click away***
- Automated process saves user from complicated mathematical analysis
- Quantitative, relevant, repeatable results

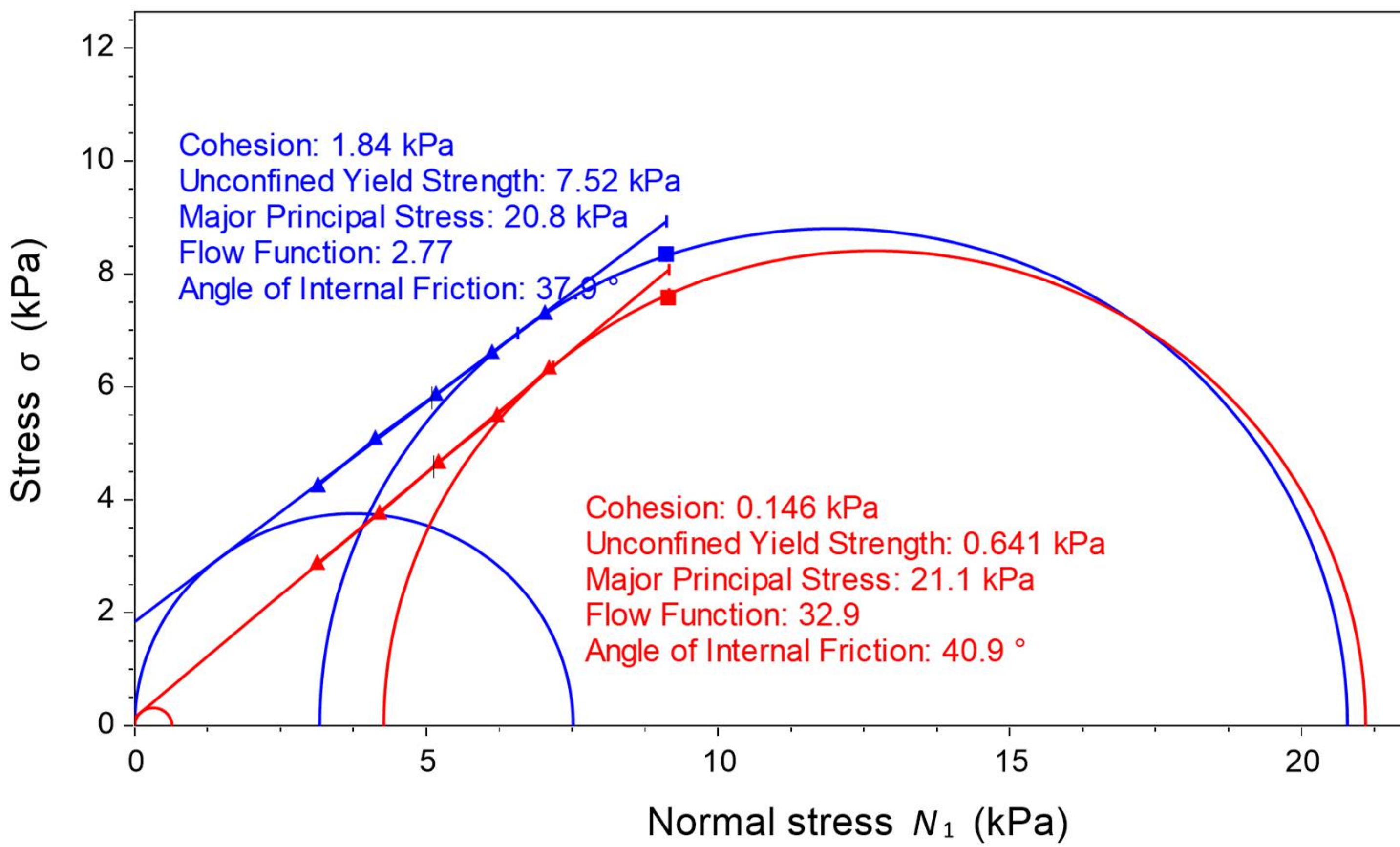




How do powder properties change with increasing consolidation?



How do powder properties change with added ingredients?



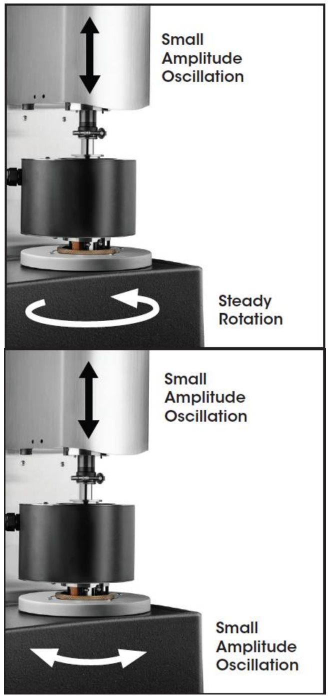
Sand

Sand + 5% S60 oil

OSP Features and Benefits

- Available on both Discovery HR rheometer and ARES G2
- Ensure accuracy in both rotational and axial measurements, avoiding artifacts from pumping effects and surface tension with the specially designed OSP double-gap cup and rotor
- OSP and 2D-SAOS experiments fully programmable from TRIOS Software. Simultaneous measurements in two directions
- Monitor temperature-dependent changes and replicate real-world processing conditions with optional temperature control through the Environmental Test Chamber (-10 °C to 150 °C)

ARES G2 Rheometer



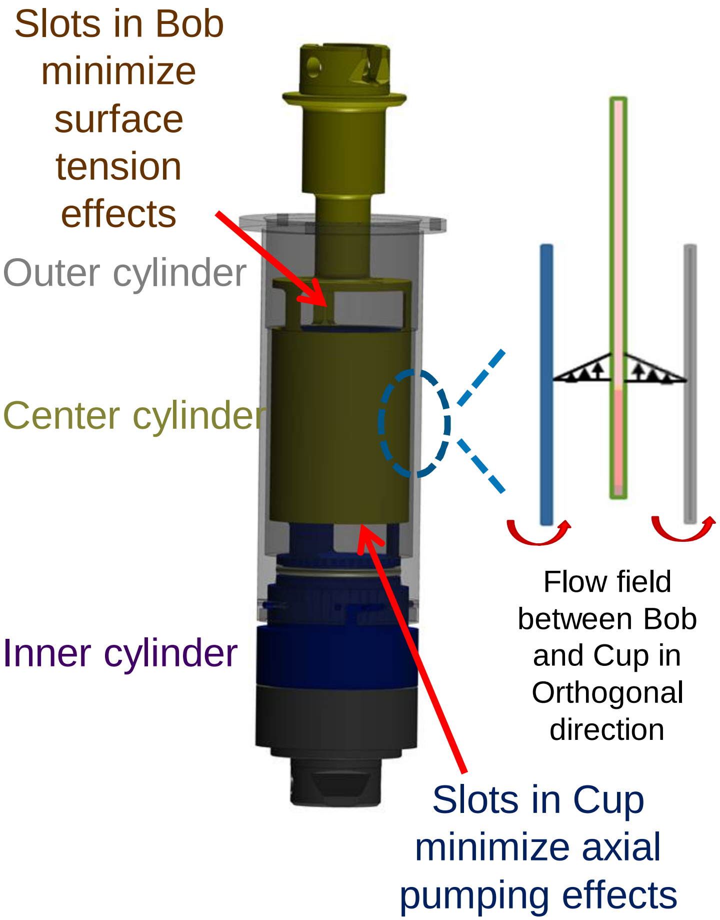
HRx0 Rheometer

OSP Geometry

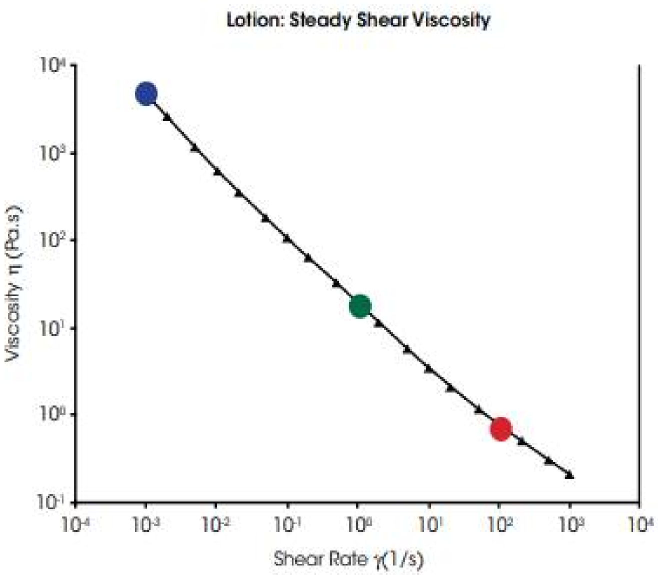
Outer Double Gap Cup

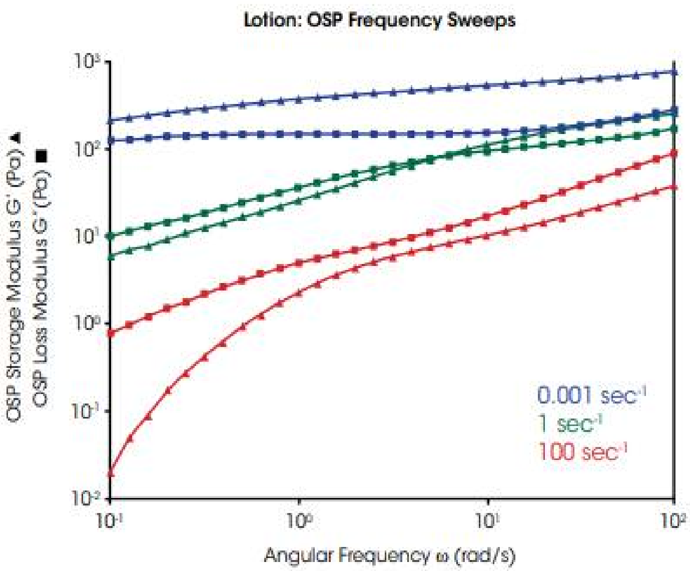
Inner Double Gap Cup with Slots

Bob with Slots



Example of Orthogonal Superposition analysis on Lotion

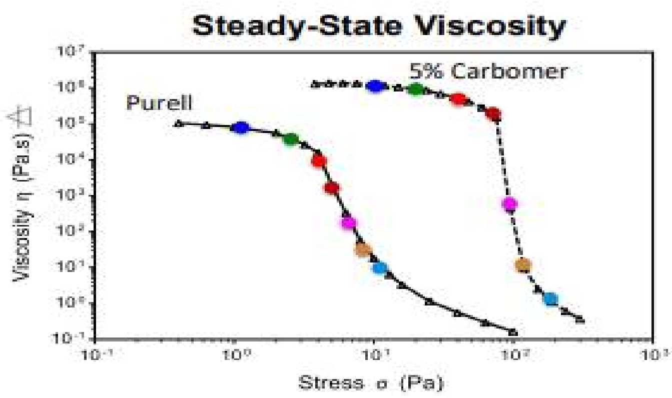




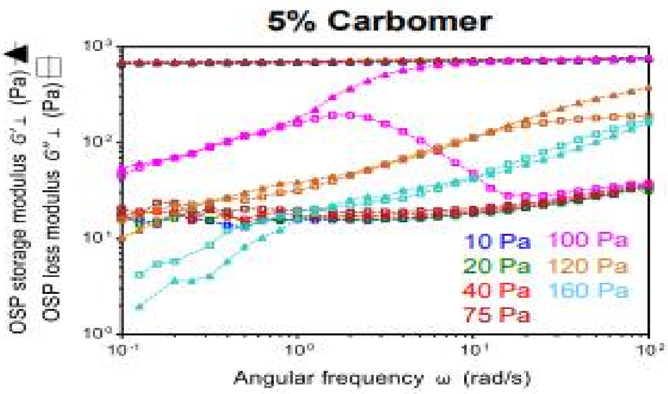
Change in viscoelasticity during yield

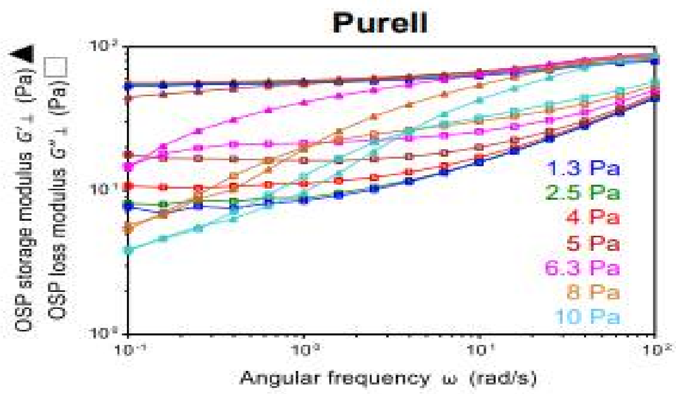
Materials: 5% Carbopol 940 NF   Purell hand sanitizer

Shear Rheology:
- Testing Method:
  - Discovery HR-30 rheometer
  - OSP geometry (rotation only)
  - Steady-state flow sweep, stress-controlled
- Both show similar viscosity profile:
  - Plateau decreasing with stress
  - Sharp drop at critical yield stress (σ_y)
  - Newtonian at $\sigma > \sigma_y$



OSP Frequency Sweeps under Shear Stress





Rheo-Raman system

Features and Benefits

- Integrated operation with Thermo Fisher™ iXR Raman spectrometer
- Choice of different lasers for maximum versatility
  - 432 nm, 532 nm and 785 nm (high brightness, high power options)
  - User installable laser sets — quick and easy to switch lasers
- Multiple interlocks for class 1 laser classification
- Safe under all conditions of normal use
- Free space coupling maximizes laser intensity at sample
- Software integration provides seamless Rheo-Raman experiments
  - Synchronized data collection between TRIOS and Thermo Scientific™ OMNIC™ software
  - Rheo-Raman data analysis performed in OMNIC software
- Temperature control up to 100 °C using Upper Heated Plate (UHP)
- Optical table provides excellent stability, alignment, and vibration free measurements
- Micrometer driven access to any radial positions
- Fine axial adjustment for focusing inside the sample
- Quartz plates minimize fluorescence artefacts

Rheo-optics system: Modular Microscope Accessory (MMA)

- Available on Discovery HR rheoemters.
- Compact, modular design, that mounts on instrument frame for easy alignment and minimum vibration
- Uses standard Nikon microscopy objectives. Tested with 20× to 100×.
- Fast speed camera for image capture up to 90 fps
- X-Y-Z micrometer stage controls to select observation position
- Brightfield microscopy with cross-polarization
- Modular Options:
  - Counter-rotating plate for zero-velocity stagnation plane
  - Piezo-scanning stage for 100 µm depth profiling
  - Dichroic splitter for fluorescence microscopy
  - UHP for temperature control up to 100°C

Simultaneous Rheology-Dielectric Measurement

Agilent E4980A LCR meter

Grounded Geometries with Ceramic Insulator (standard or disposable)

Other Accessories

Small Angle Light

Interfacial Accessori

Magneto-Rheology

Electro-Rheology

Pressure Cell

Starch Pasting Cell

Immobilization Cell

Building material cell

Thank You!