RSA-G2

DMA 850

DMA 3200

Dynamic Mechanical Analysis
Basic Theory & Applications Training

TA Instruments – Waters LLC

Course Outline

- Basic Theories of Dynamic Mechanical Analysis
- DMA Instrumentation and Clamps
- DMA Experiments
  - Dynamic tests
  - Transient tests
- DMA Applications and Data Interpretation
- Troubleshooting Experimental Issues

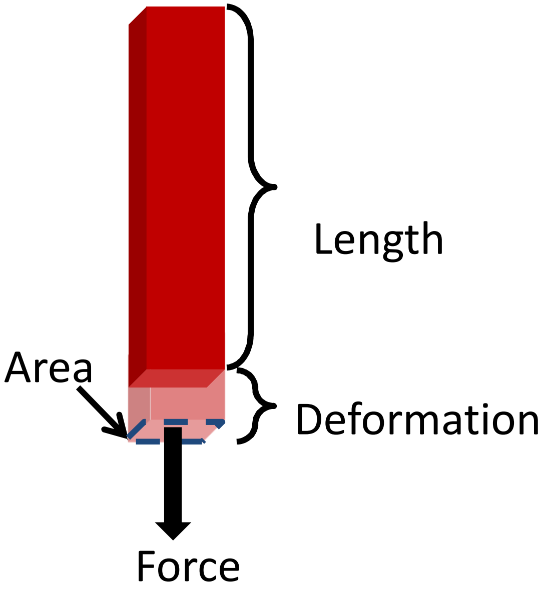
Basic Theories of Dynamic Mechanical Analysis

DMA Definitions

- What is a DMA?
  - Dynamic Mechanical Analyzer/ Dynamic Mechanical Analysis
- What does a DMA do?
  - A DMA measures the mechanical/rheological properties of a material as a function of time, frequency, temperature, stress and strain
- What are the typical samples a DMA can handle?
  - Thermal plastic and thermosets
  - Elastomers/ rubbers
  - Gels
  - Foams
  - More….

How Does a DMA Work?

- Apply a force or a deformation to a sample, then measure sample's response, which will be a deformation or a force.
- All mechanical parameters (stress, strain, modulus, stiffness et al) are calculated from these 2 raw signals



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

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

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

What Does a DMA Measure?

- DMA measures the **viscoelastic properties** (stiffness and damping) of a material as a function of time and temperature. These are reported as
  - Modulus (E and G) / Compliance (J)
  - Damping factor (tan δ)
  - Transition temperatures (e.g. T_g)

Viscoelasticity Defined

- Most of the materials in the world have both elastic and viscous behavior. Therefore, they are viscoelastic

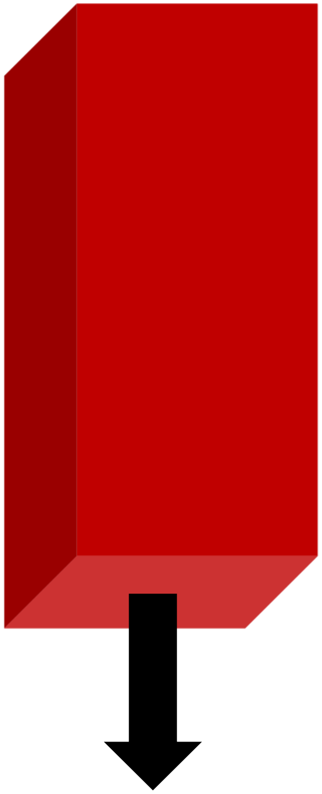
Range of Material Behavior

Ideal Liquid ----- Most Materials ----- Ideal Solid

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

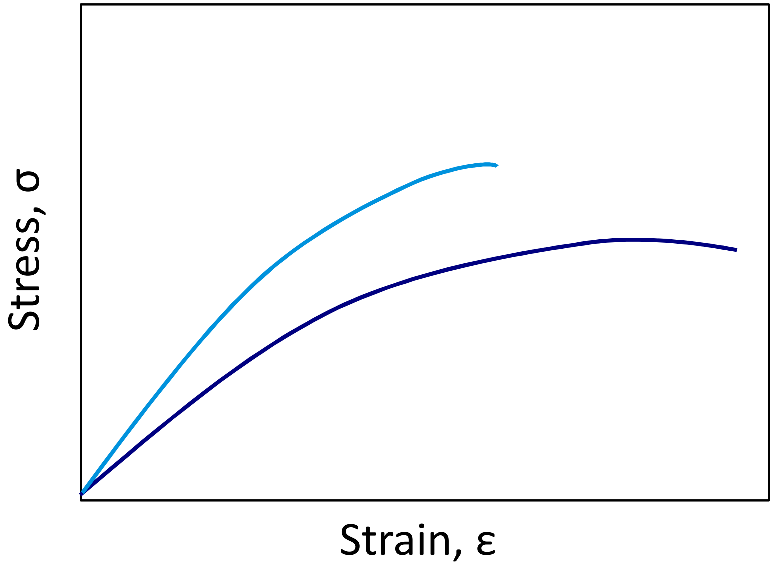
Viscoelasticity: Having both viscous and elastic properties

Mechanical Property Becomes Time Dependent



- 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*

$$\sigma = E^*\varepsilon + \eta^* d\varepsilon/dt$$



Time-Dependent Viscoelastic Behavior

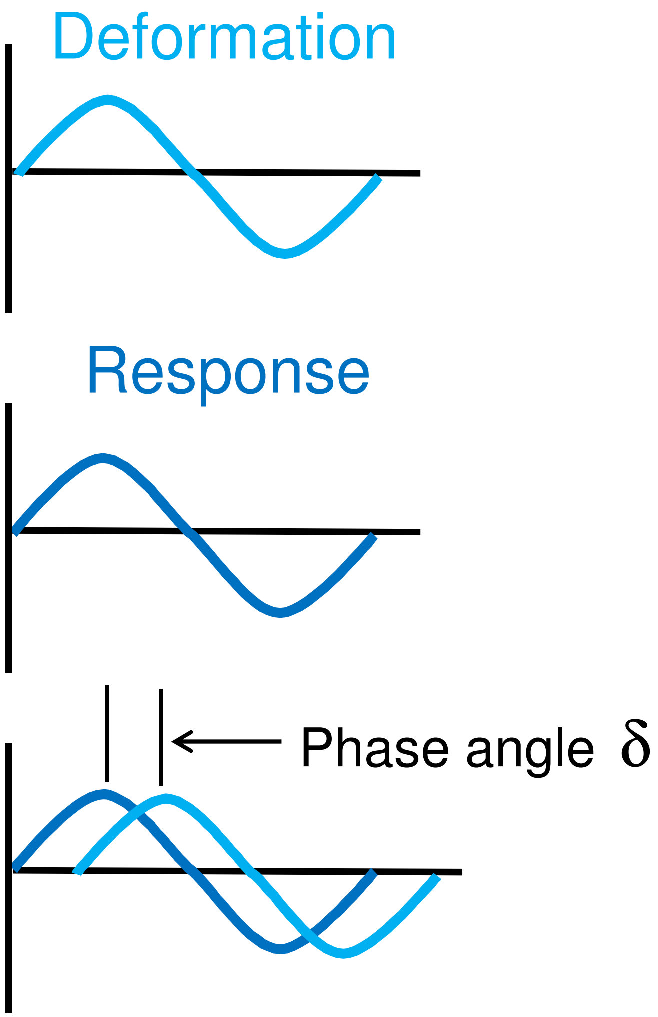
- Short deformation time: pitch behaves like a solid
- Long deformation time: pitch behaves like a highly viscous liquid
  - 9th drop fell July 2013

Started in 1927 by Thomas Parnell in Queensland, Australia

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

Dynamic Mechanical Testing

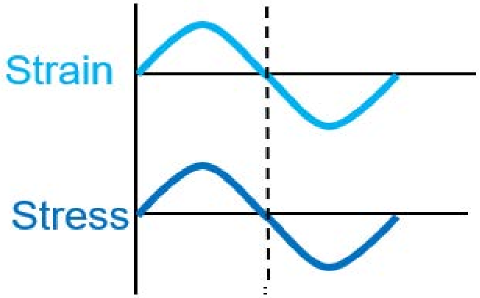
- An oscillatory (sinusoidal) deformation (stress or strain) is applied to a sample.
- The material response (strain or stress) is measured.
- The phase angle δ, or phase shift, between the deformation and response is measured.



Phase Angles

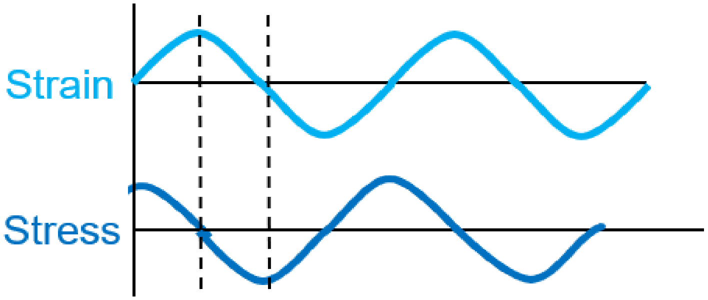
Purely Elastic Response
(Hookean Solid)

$\delta = 0°$



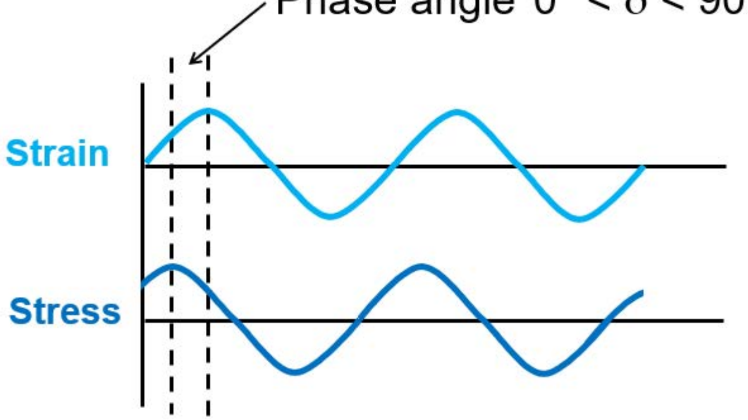
Purely Viscous Response
(Newtonian Liquid)

$\delta = 90°$



Viscoelastic Response
(Most materials)

Phase angle $0° < \delta < 90°$



DMA Viscoelastic Parameters

The Modulus: Measure of materials overall resistance to deformation.

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

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

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

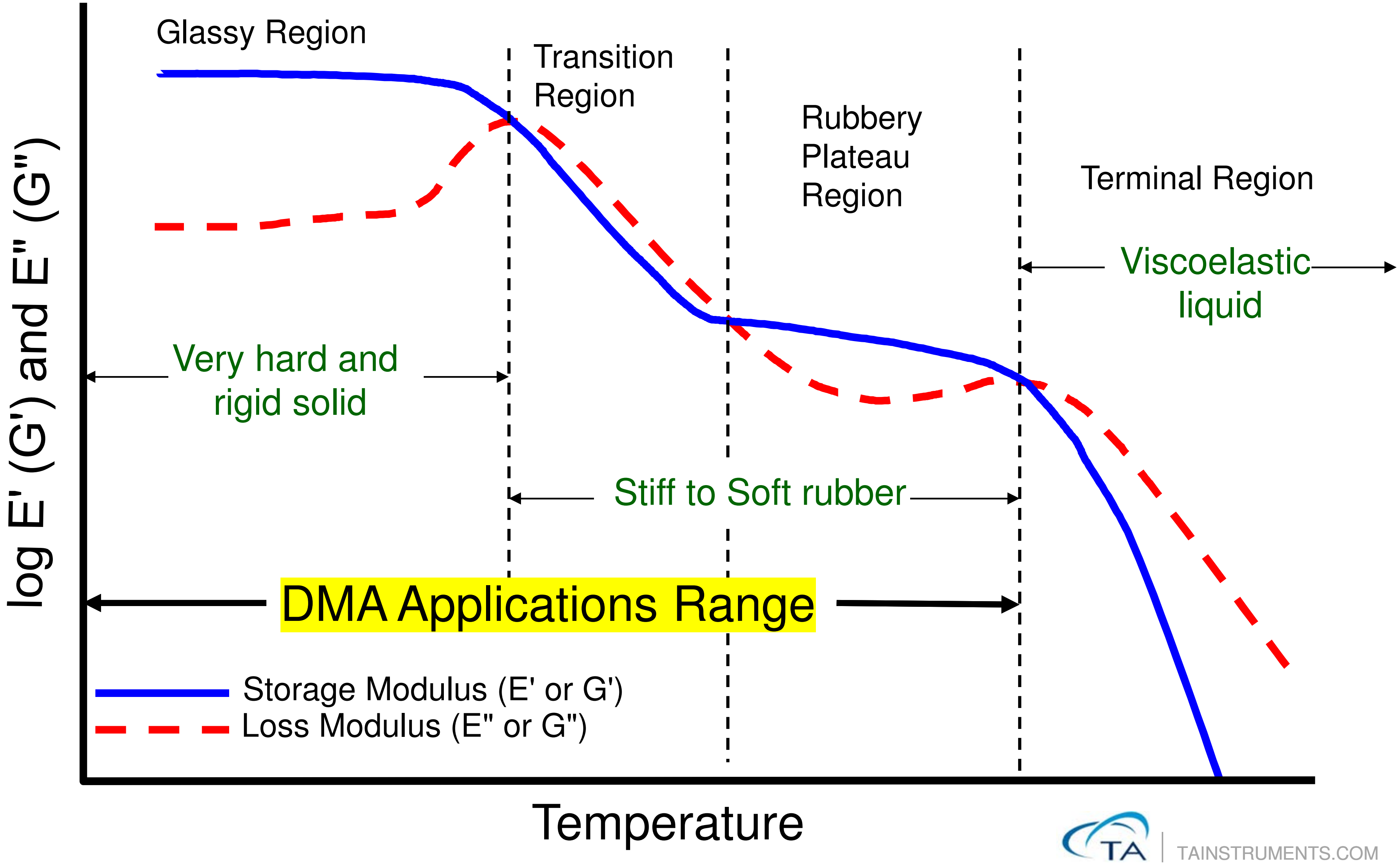
The Viscous (loss) Modulus: The ability of the material to dissipate energy. Energy lost as heat.

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

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

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

Viscoelastic Spectrum for a Typical Amorphous Polymer



DMA Instrumentation and Clamps

DMAs from TA Instruments

RSA G2

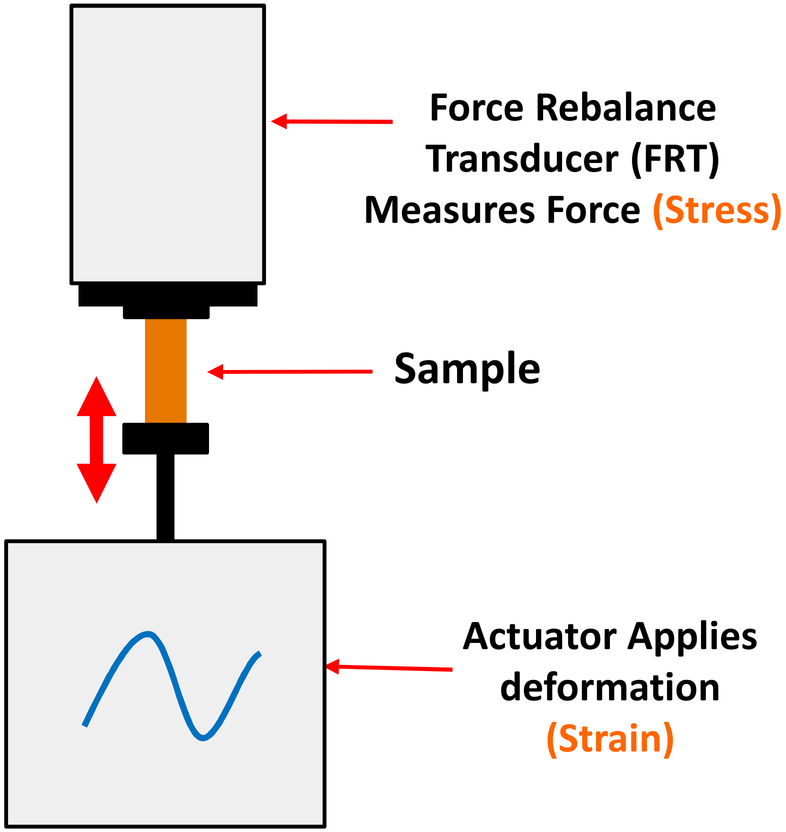
Discovery DMA850

Q800

DMAs from TA Instruments

RSA G2

Separate Motor & Transducer



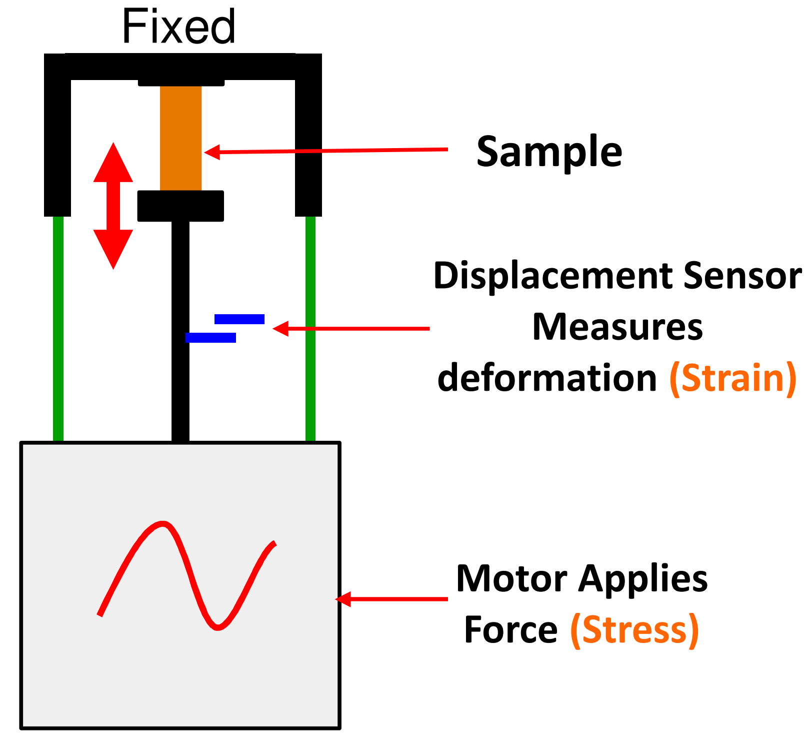
Force Rebalance Transducer (FRT) Measures Force (Stress)

Sample

Actuator Applies deformation (Strain)

DMA850 and Q800

Combined Motor & Transducer



Fixed

Sample

Displacement Sensor Measures deformation (Strain)

Motor Applies Force (Stress)

RSA G2: Schematic Dual Head Design

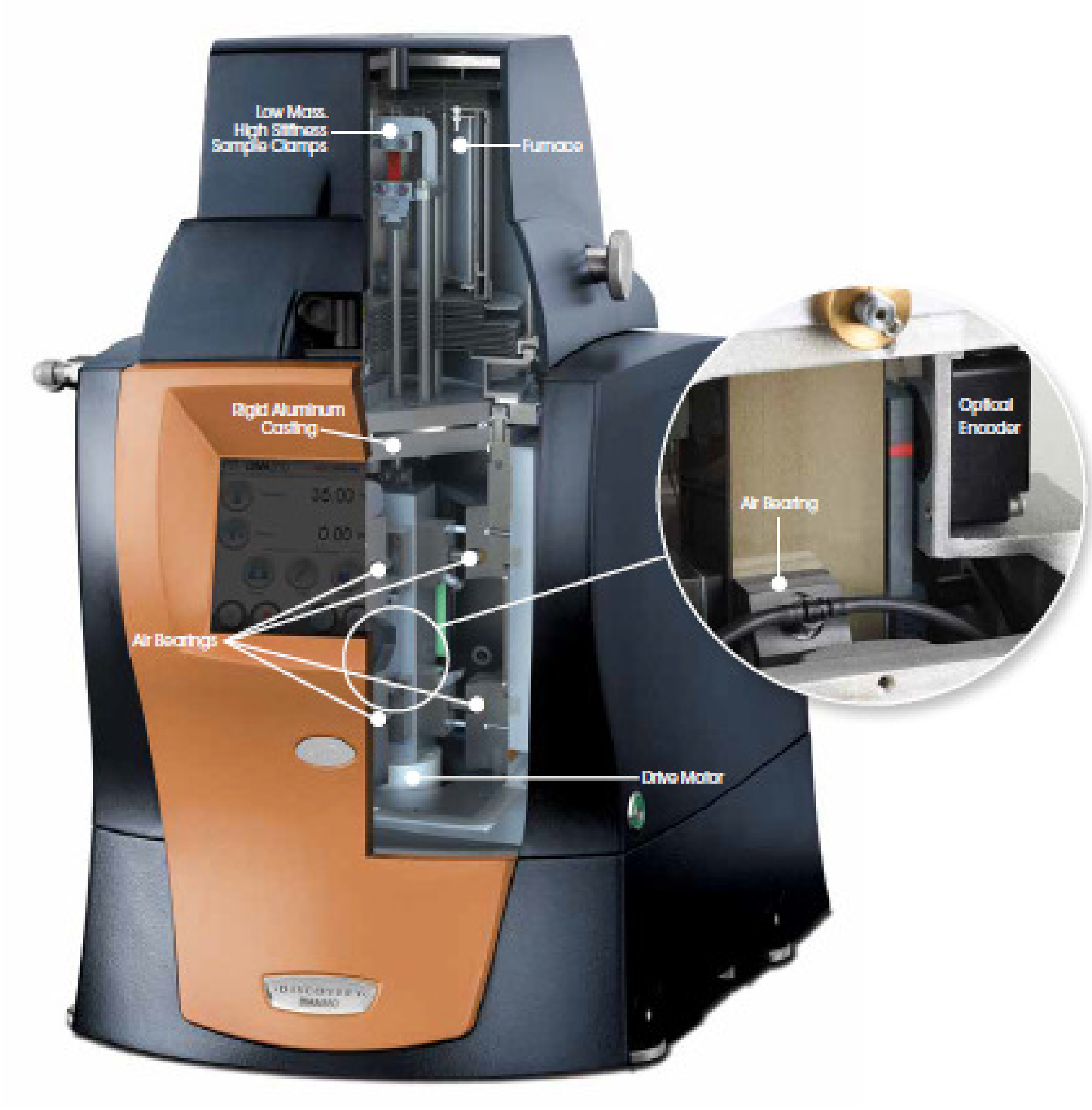
Transducer

Upper Geometry Mount

Lower Geometry Mount

Motor

DMA850: Schematic



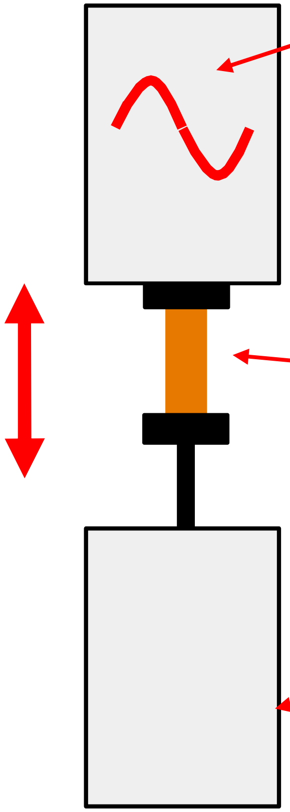
DMA Specifications

	RSA G2	DMA850	Q800
Max Force	35 N	18 N	18 N
Min Force	0.0005 N	0.0001 N	0.0001 N
Displacement Resolution	1 nm	0.1 nm	1 nm
Frequency Range	2 x 10^{-6} to 100 Hz	1 x 10^{-4} to 200 Hz	1 x 10^{-2} to 200 Hz
Dynamic Deformation Range	± 5 x 10^{-5} to 1.5 mm	± 5 x 10^{-6} to 10 mm	± 5 x 10^{-4} to 10 mm
Temperature range	-150 to 600 ℃	-150 to 600 ℃	-150 to 600 ℃
Isothermal Stability	± 0.1	± 0.1	± 0.1
Heating Rate	0.1°C to 60°C/min	0.1°C to 20°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	0.1°C to 10°C/min

DMA Mode on DHR and ARES-G2

ARES G2 and DHR DMA Mode

Strain control & dynamic test only



Force Rebalance Transducer (FRT)
(Measures Stress)

Servo control on Null position
(Strain)

Sample

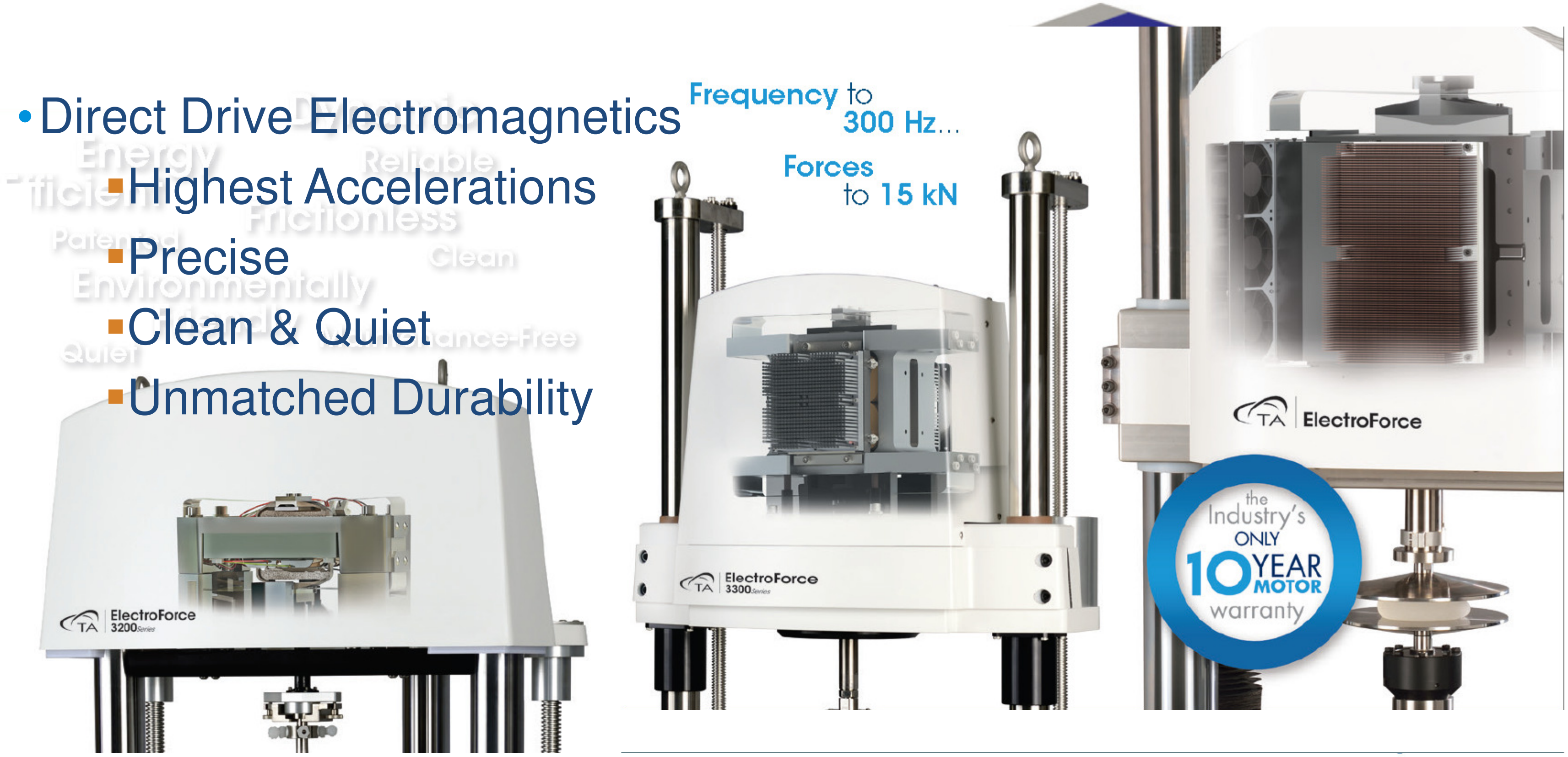
For the ARES-G2, the bottom Actuator remains locked during DMA function

Specifications of the DHR-DMA and the ARES-G2 DMA

- Dynamic test only

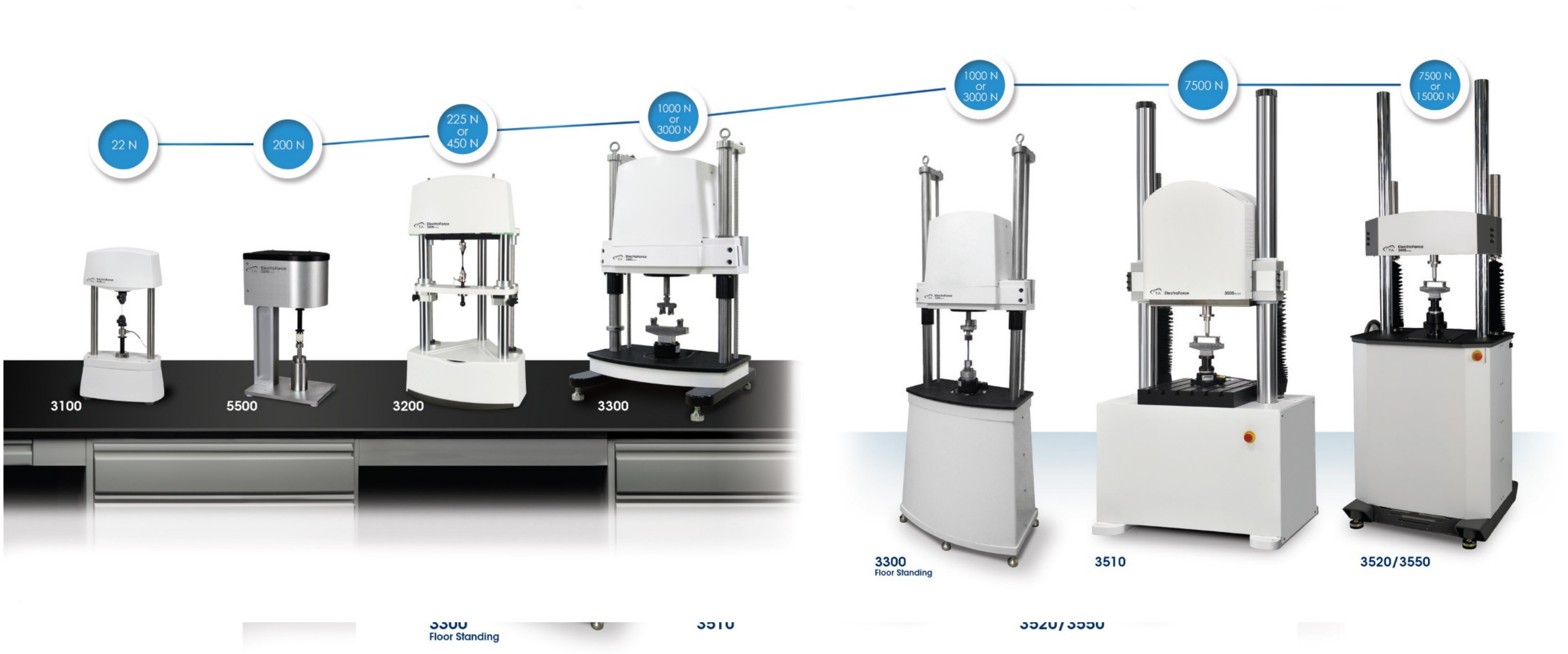
	DHR – DMA mode	ARES-G2 DMA mode
Motor Control	FRT	FRT
Minimum Force (N) Oscillation	0.1	0.001
Maximum Axial Force (N)	50	20
Minimum Displacement (µm) Oscillation	1.0	0.5
Maximum Displacement (µm) Oscillation	100	50
Displacement Resolution (nm)	10	10
Axial Frequency Range (Hz)	1 x 10^{-5} to 16	1 x 10^{-5} to 16

Electroforce DMA3200: Linear Motor Technology



- Direct Drive Electromagnetics
  - Highest Accelerations
  - Precise
  - Clean & Quiet
  - Unmatched Durability

Load Frame Instruments



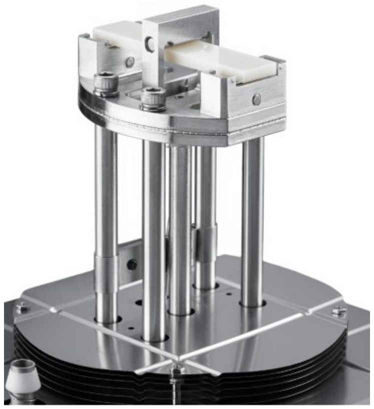
TestBench Instruments

Clamps for DMA850 and Q800

S/D Cantilever

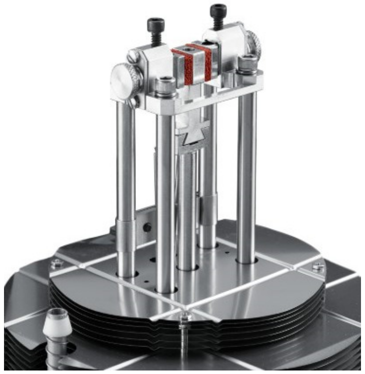
Film/Fiber Tension

3-Point Bending

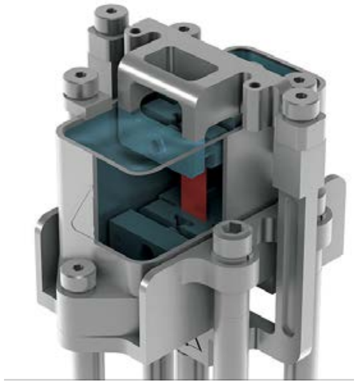


Compression

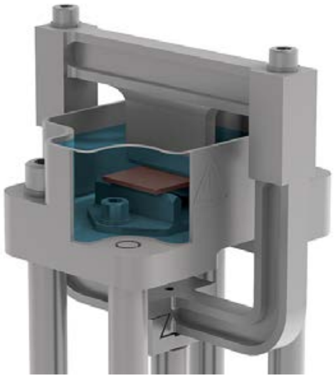
Shear Sandwich



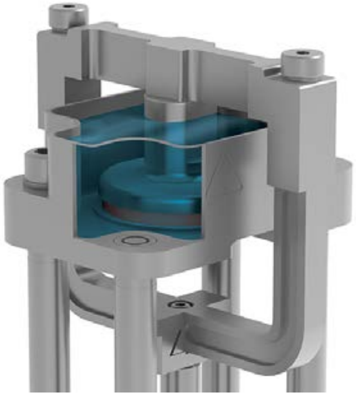
Submersible Tension



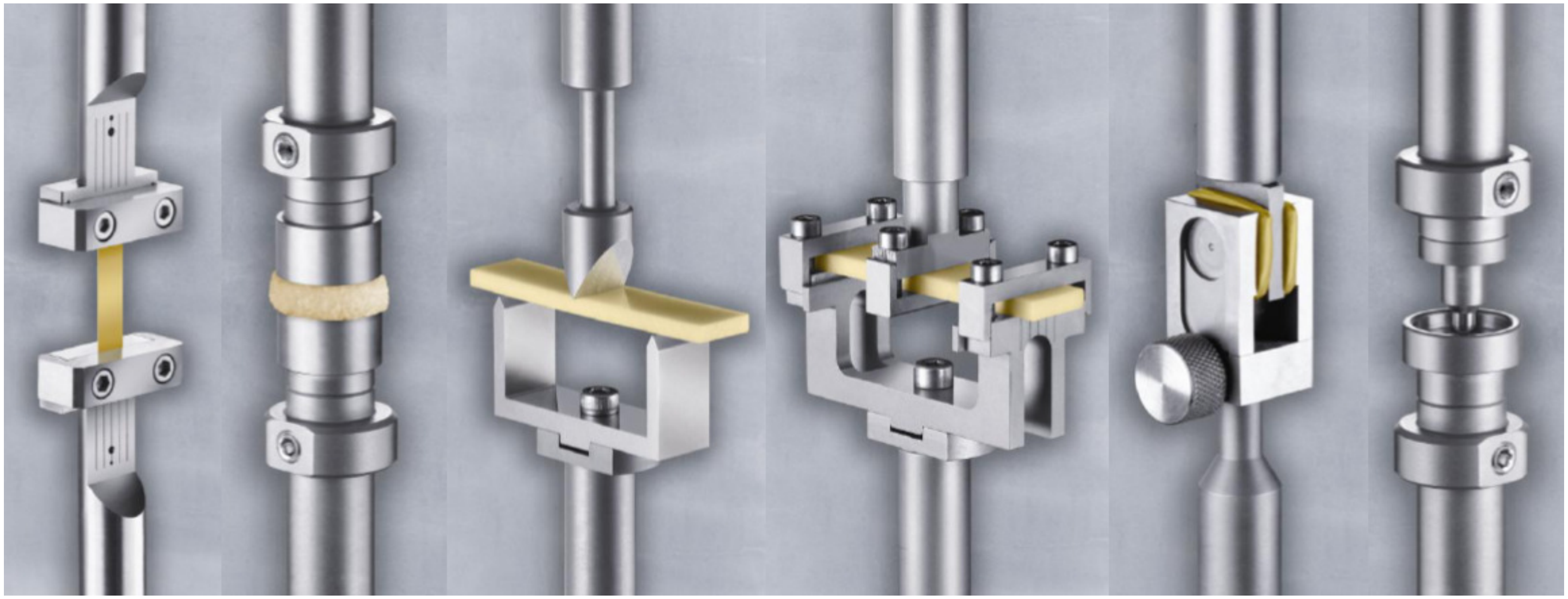
Submersible Bending



Submersible Compression



Clamps for RSA G2

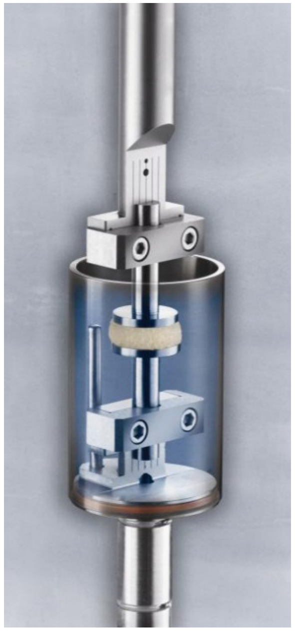


RSA G2 Immersion Clamps

- Immersion clamp kit offers 3 geometries with temperature control from -10 to 200 °C in the FCO.

Tension

Compression



3 Point Bending

Tension: Up to 25 mm long, 12.5 mm wide and 1.5 mm thick.
Compression: 15 mm in diameter; maximum sample thickness is 10 mm.
Three Point Bending: includes interchangeable spans for lengths of 10, 15, and 20 mm. Maximum sample width is 12.5 mm and maximum thickness is 5 mm.

How DMA Calculate Modulus?

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 = Force x $K\sigma$ Strain = Displacement x $K\nu$ Modulus (E) = Stress / Strain $K\sigma$: Stress constant $K\nu$: Strain constant Clamp dependent Can be found in online help manual

$$GF = K\sigma / K\nu$$

Choose the Correct Clamp for Testing

Sample Dimension

- Films and fibers: tension clamps
- Bars and cylinders: bending clamps
- O-rings and tablets: compression and/or shear

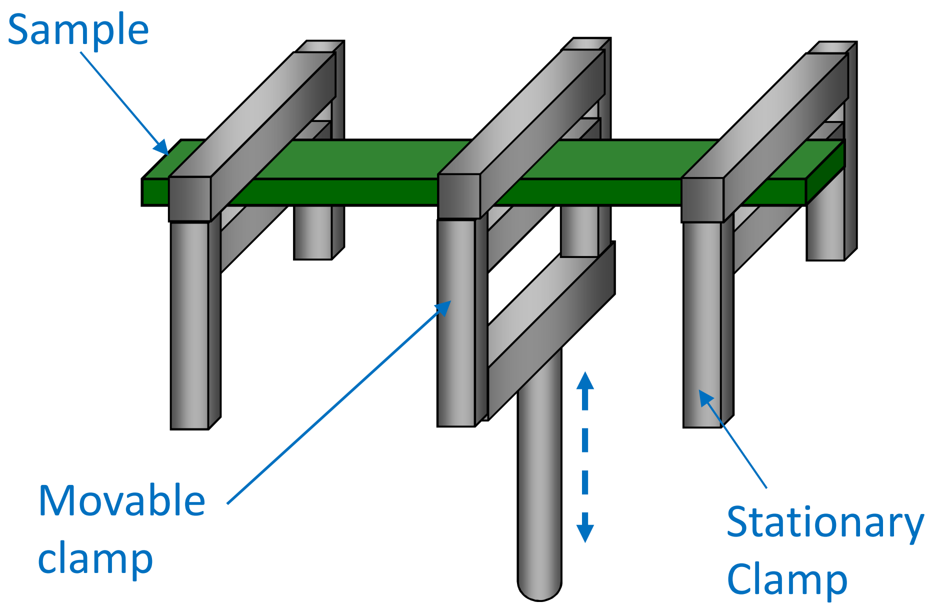
Deformation Mode:

- E [tension, compression and bending]
- G [shear]

Sample Stiffness:

- Machine range fixed: **100 - 10, 000,000 N/m**. Stiffness of sample related to its dimensions [L, w, t]. Stiffness may limit sample size to below clamp maximum.

DMA: Dual Cantilever Clamp



- Highly damped materials can be measured
- Best mode for evaluating the cure of supported materials

Geometry Factor - Dual Cantilever Clamp

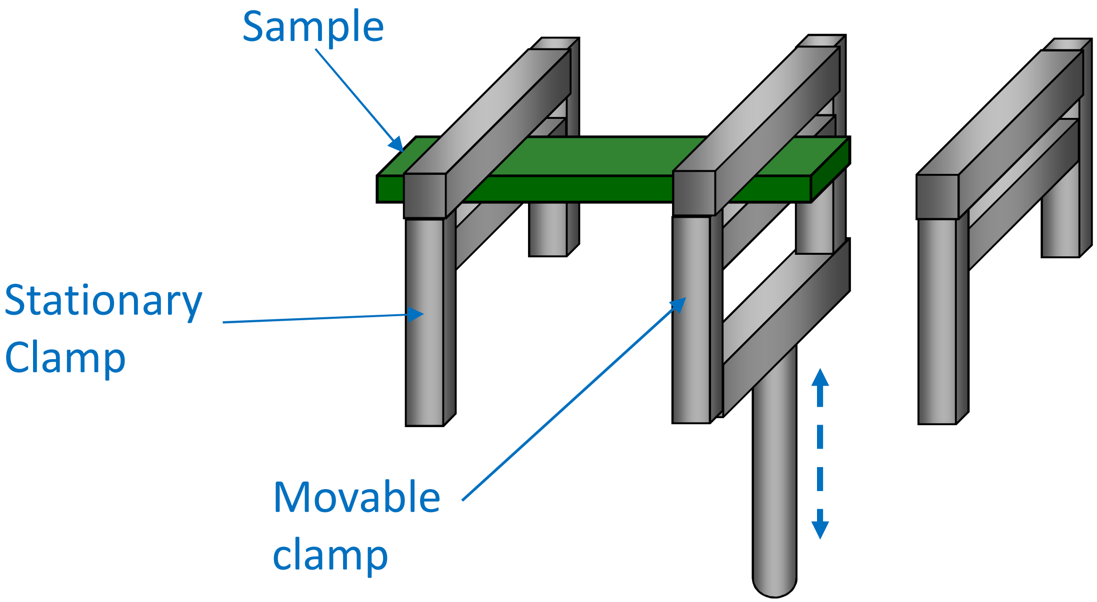
Modulus = Stiffness × Geometry Factor

If length/thickness > 10, Poisson's Ratio term is dropped

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

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

DMA: Single Cantilever Clamp



- Best general purpose mode (thermoplastics)
- Preferred mode over dual cantilever for most neat thermoplastics (unreinforced), except elastomers
- Clamping torque is important

Geometry Factor - Single Cantilever Clamp

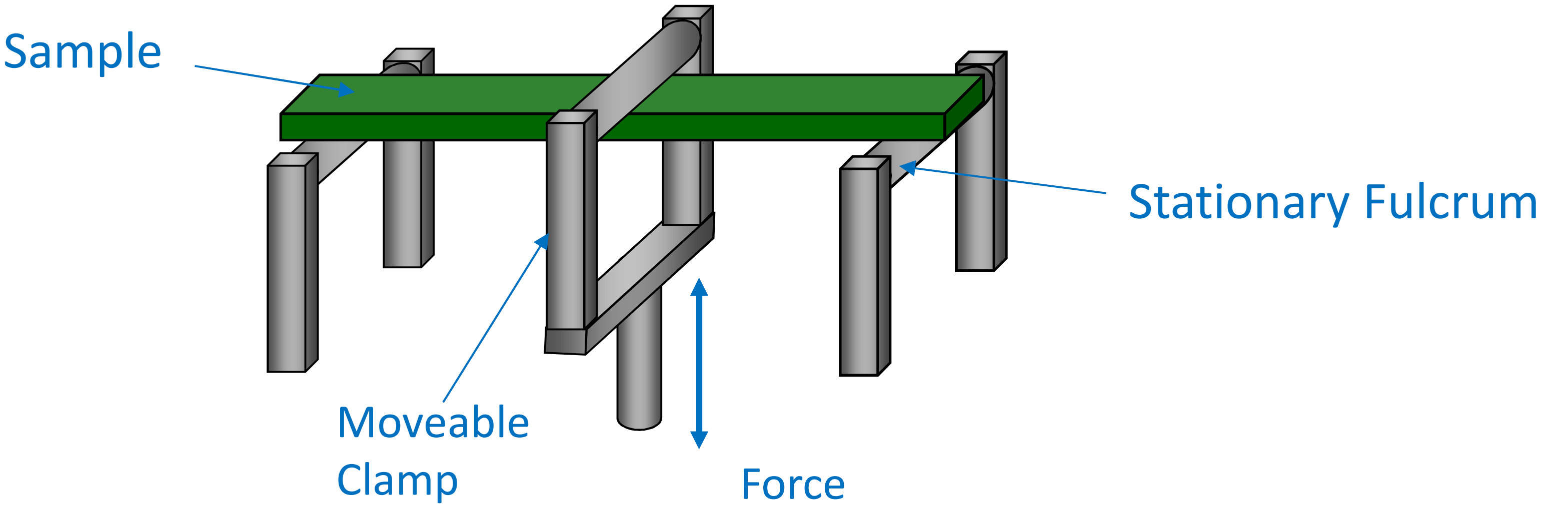
Modulus = Stiffness × Geometry Factor

If length/thickness > 10, Poisson's Ratio term is dropped

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

$$GF_{SC} = \frac{l^3}{wt^3}$$

DMA: 3 Point Bend Clamp



- Best mode for measuring medium to high modulus materials
- Conforms with ASTM standard test method for bending
- Purest deformation mode since clamping effects are eliminated

Geometry Factor - 3 Point Bending Clamp

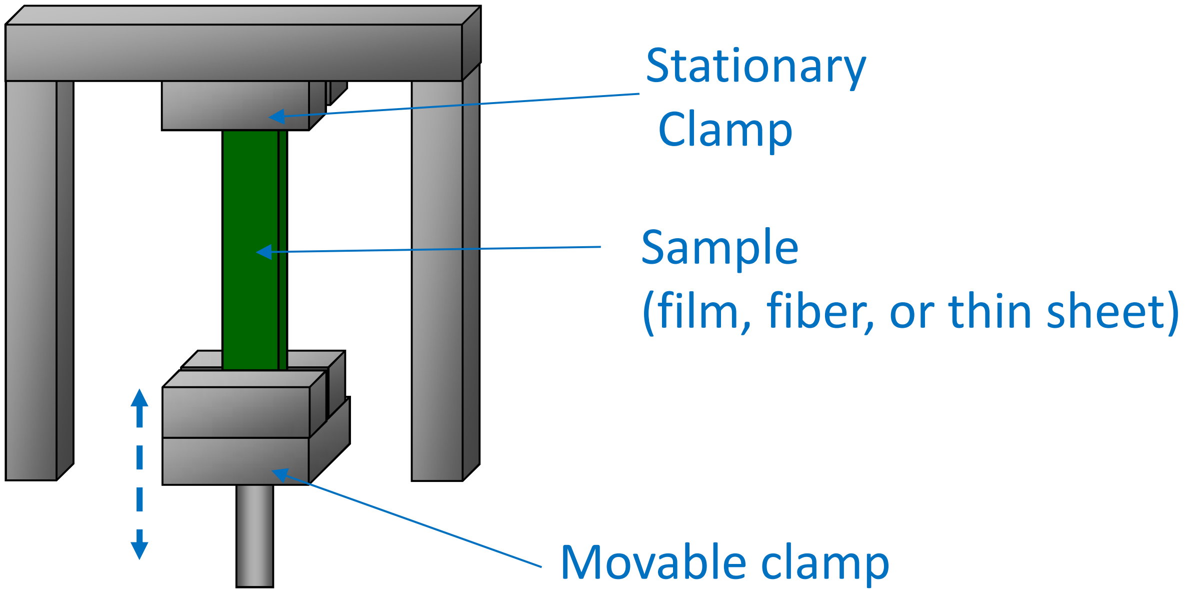
Modulus = Stiffness × Geometry Factor

If length/thickness > 10, Poisson's Ratio term is dropped

$$GF_{3PB} = \frac{\cancel{3}l^3\left[1+\frac{6}{10}\cancel{(1+\nu)\left(\frac{2t}{l}\right)^2}\right]}{4\,\cancel{12}wt^3}$$

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

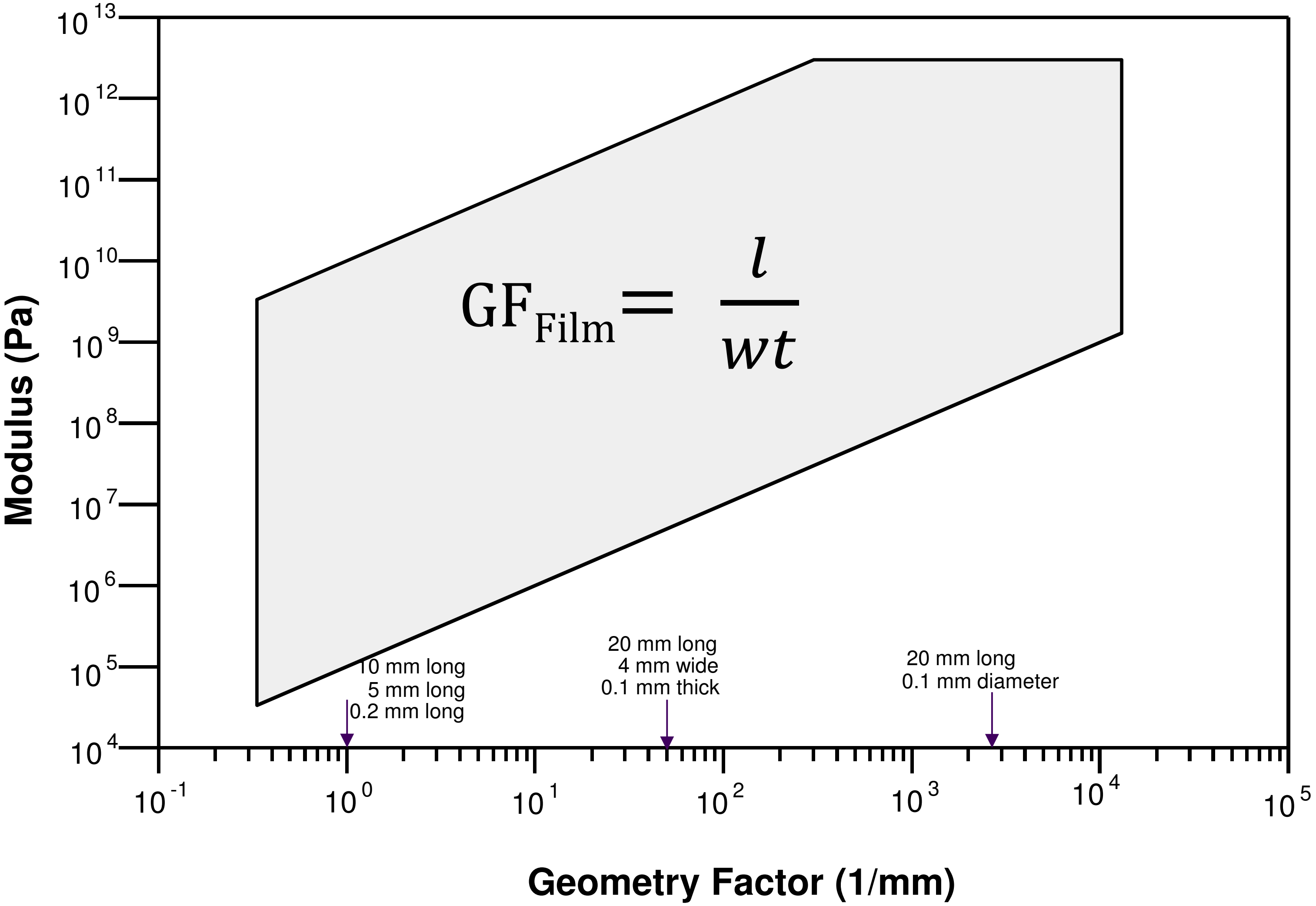
DMA: Film and Fiber Tension Clamp



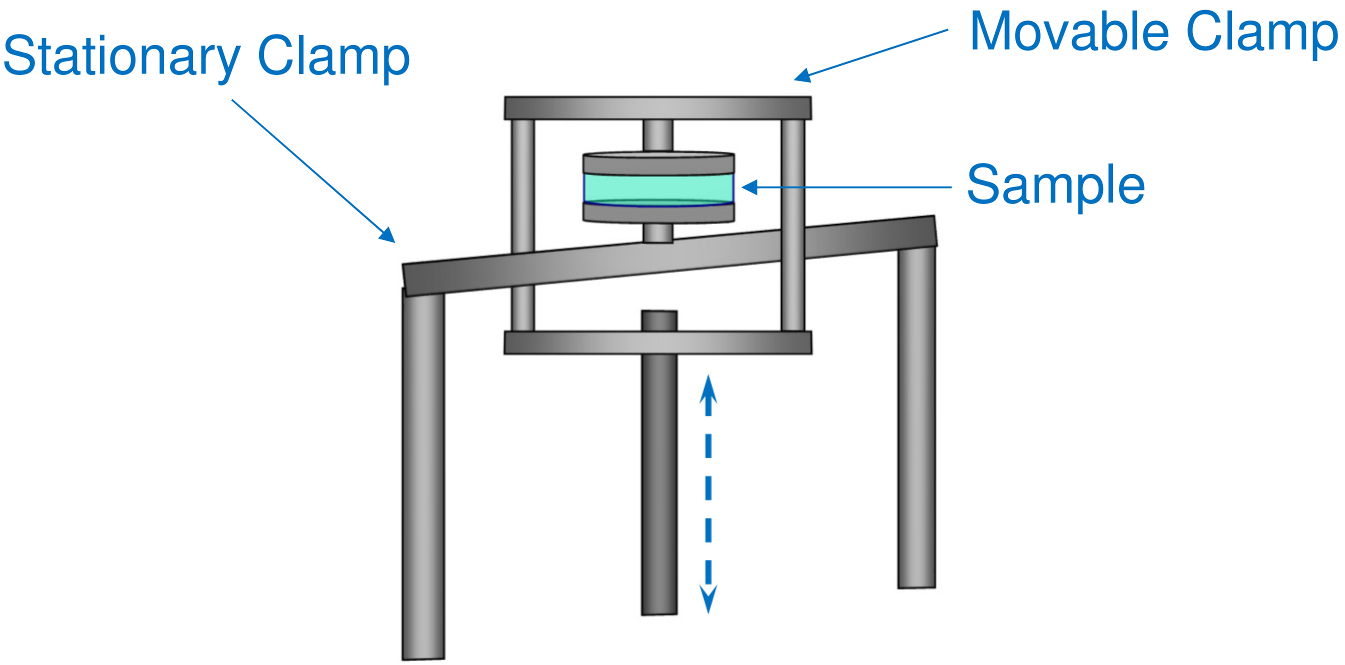
- Best mode for evaluation of thin films and fibers
  - bundle or single filaments
- Small samples of high modulus materials can be measured
- TMA-like constant force and force ramp measurements
  - aka. mini-tensile tester
- Force track and constant force control

Operating Range of the Film/Fiber Tension Clamp

Modulus = Stiffness × Geometry Factor



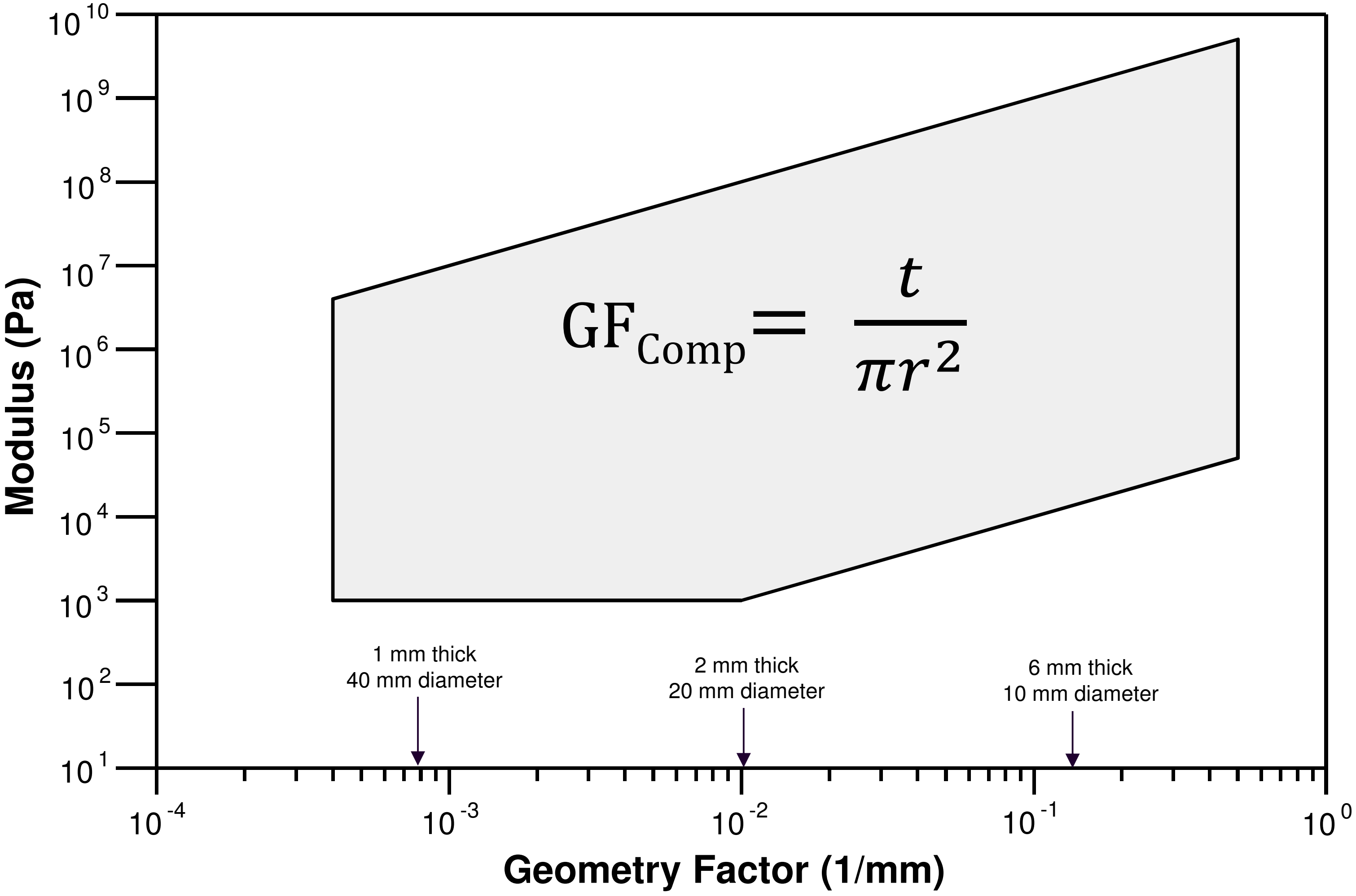
DMA: Compression Clamp



- Good mode for low to medium modulus materials (gels,elastomers)
- Materials must provide restoring force (support necessary static load)
- Options for expansion & penetration measurements
- Typically shear component is significant

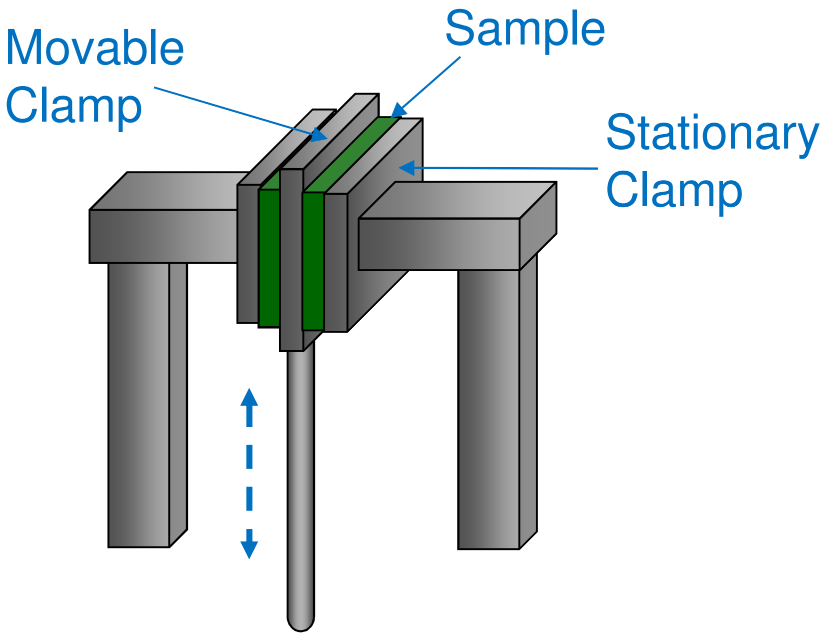
Operating Range of the Compression Clamp

Modulus = Stiffness × Geometry Factor



$$GF_{Comp} = \frac{t}{\pi r^2}$$

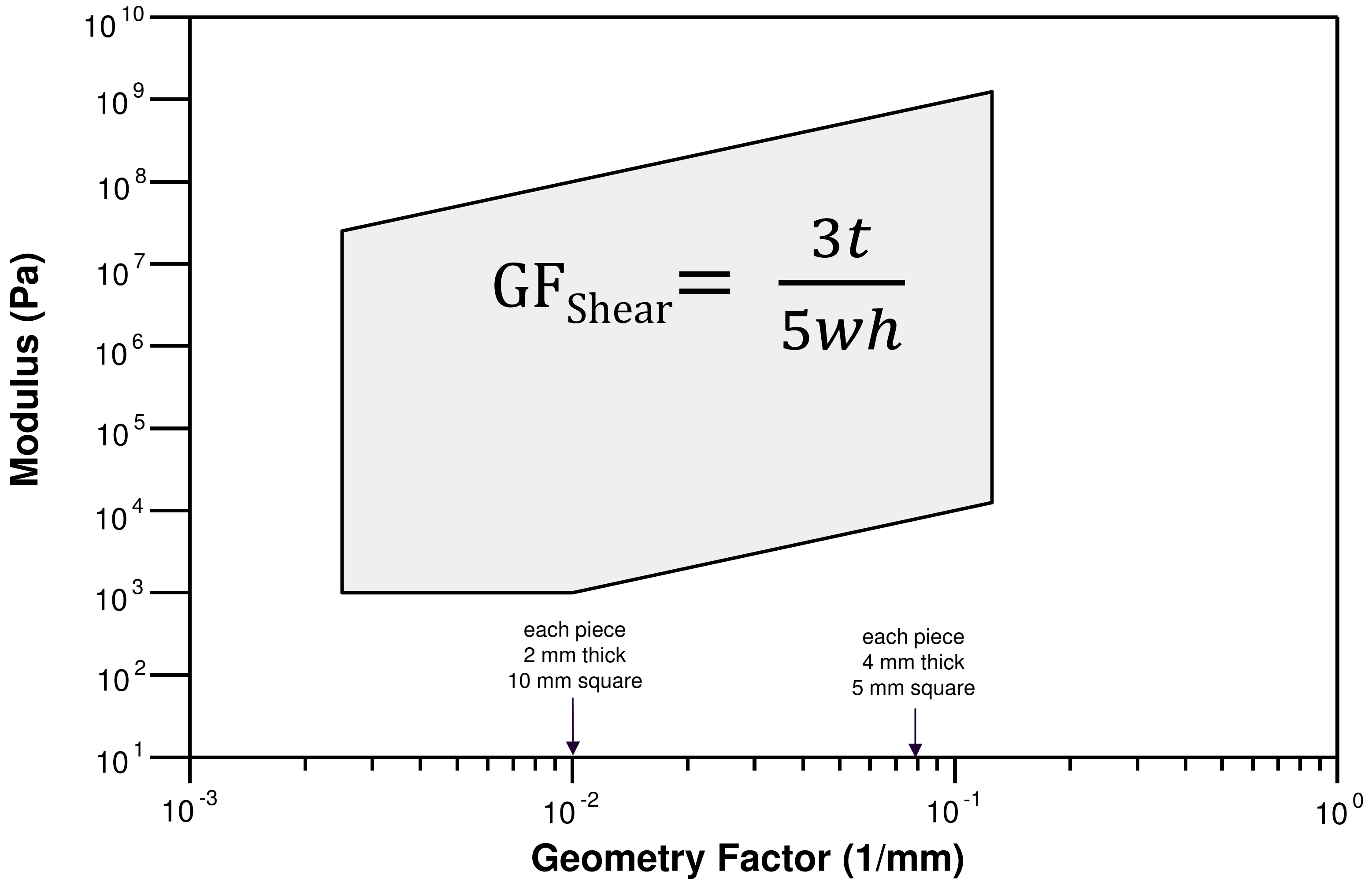
DMA: Shear Sandwich Clamp



- Square sample configuration provides pure shear deformation
- Provides *Shear Moduli: G*, G', G" & G(t)*
- Good for evaluating highly damped soft solids such as gels and adhesives & elastomers > T_g

Operating Range of the Shear Sandwich Clamp

Modulus = Stiffness × Geometry Factor



Changing Sample Stiffness

Clamp Type	To Increase Stiffness…	To Decrease Stiffness…
Tension Film	Decrease length or increase width. If possible increase thickness.	Increase length or decrease width. If possible decrease thickness.
Tension Fiber	Decrease length or increase diameter if possible.	Increase length or decrease diameter if possible.
Dual/Single 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
Three Point Bending	Decrease length or increase width. If possible increase thickness.	Increase length or decrease width. If possible decrease thickness.
Compression – circular sample	Decrease thickness or Increase diameter.	Increase thickness or decrease diameter.
Shear Sandwich	Decrease thickness or Increase length and width.	Increase thickness or decrease length and width.

DMA Clamping Guide

Sample	Clamp	Sample Dimensions
High modulus metals or composites	3-point Bend Dual Cantilever Single Cantilever	L/T> 10 if possible
Unreinforced thermoplastics or thermosets	Single Cantilever	L/T >10 if possible
Brittle solid (ceramics)	3-point Bend Dual Cantilever	L/T>10 if possible
Elastomers	Dual Cantilever Single Cantilever Shear Sandwich Tension	L/T>20 for T<Tg L/T>10 for T<Tg (only for T> Tg) T<2 mm W<5 mm
Films/Fibers	Tension	L 10-20 mm T<2 mm
Supported Systems	8 mm Dual Cantilever	minimize sample, put foil on clamps

Available DMA Experiments

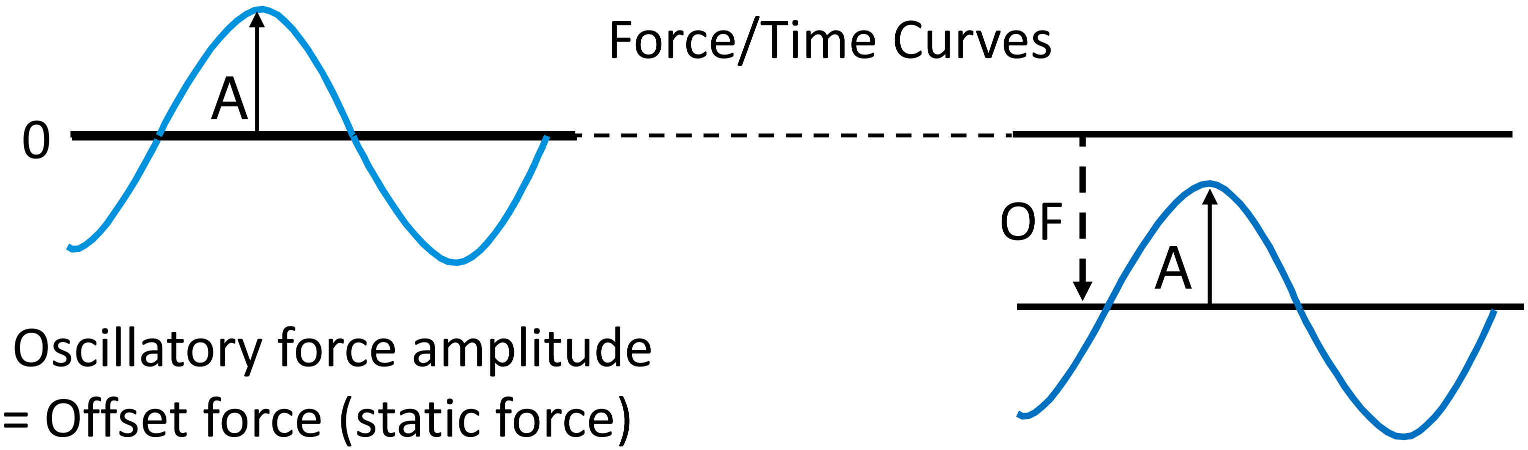
(1) Dynamic Tests

Dynamic (Oscillatory) Testing

Available oscillatory test modes

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

Some Clamps Require Offset (static) Force!



Force/Time Curves

A = Oscillatory force amplitude
OF = Offset force (static force)

Clamps **without** offset force:

- Single Cantilever
- Dual Cantilever
- Shear Sandwich

Clamps **with** offset force:

- Tension Film
- Tension: Fiber
- 3-Point Bend
- Compression
- Penetration

Offset (Static) Force

Static force [General]

- Used in tensioning clamps to prevent sample buckling [tension], or loss of contact with the probe [compression] during the test. Static force must exceed dynamic force at all times during experiment
- Applied before dynamic oscillation to automatically measure sample length

Constant Force

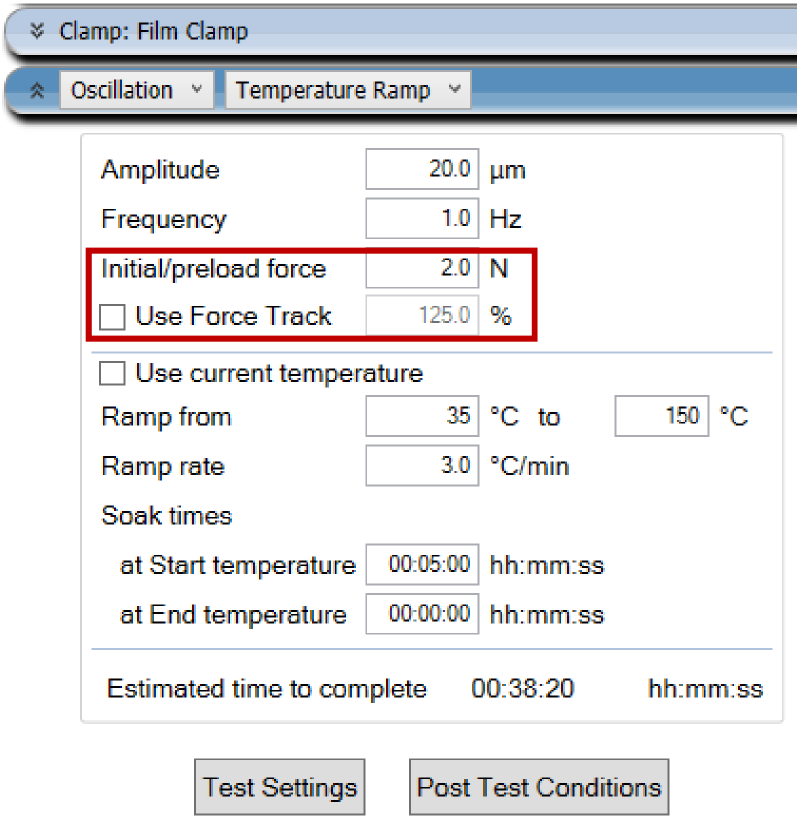
- Applies same static force throughout experiment
- Can be used with highly crystalline or cross-linked materials
  to measure displacement at constant force for quant. expansion

Force Track

- Applies Static Force in Proportion to Sample Modulus. Used in "Tensioning" Clamps to reduce stretching as specimen weakens
- Ratio of static to dynamic force:
  - **Static Force = (Force Track %/100) x (Stiffness x Amplitude)**
  - where stiffness = Force applied to sample/amplitude of deformation
- Values from 125-150% work well for most samples

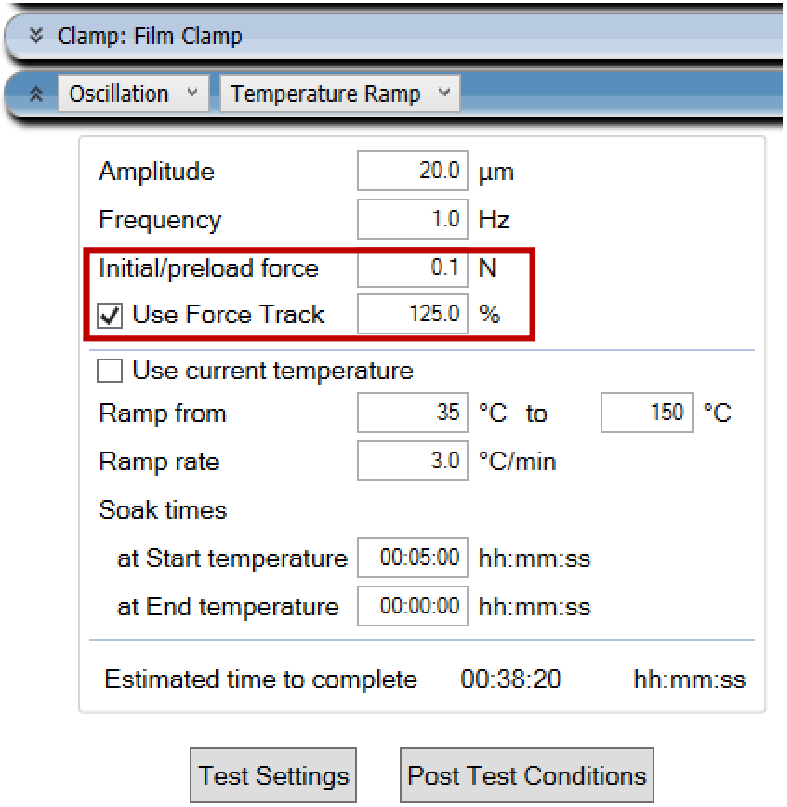
Offset Force on DMA850

- Constant static force



Amplitude 20.0 µm
Frequency 1.0 Hz
Initial/preload force 2.0 N
☐ Use Force Track 125.0 %
☐ Use current temperature
Ramp from 35 °C to 150 °C
Ramp rate 3.0 °C/min
Soak times
at Start temperature 00:05:00 hh:mm:ss
at End temperature 00:00:00 hh:mm:ss
Estimated time to complete 00:38:20 hh:mm:ss

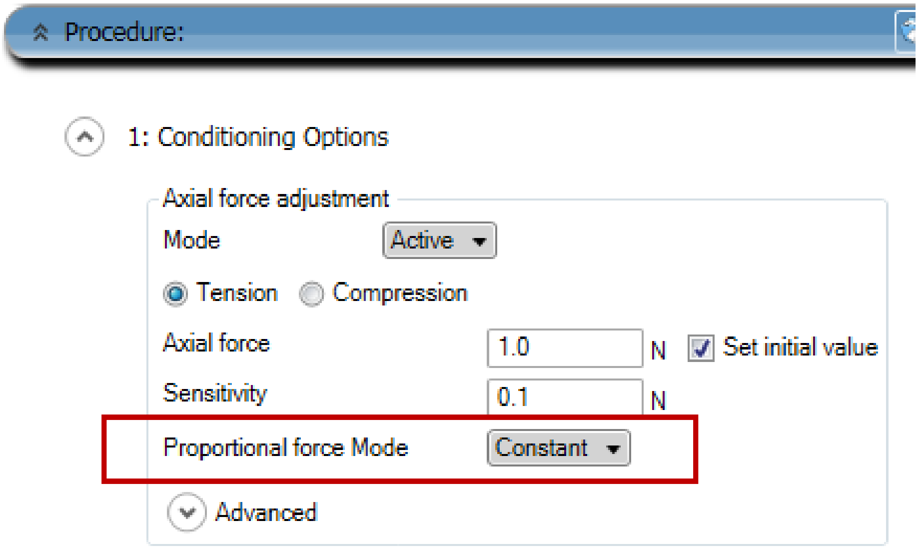
- Force track



Amplitude 20.0 µm
Frequency 1.0 Hz
Initial/preload force 0.1 N
☑ Use Force Track 125.0 %
☐ Use current temperature
Ramp from 35 °C to 150 °C
Ramp rate 3.0 °C/min
Soak times
at Start temperature 00:05:00 hh:mm:ss
at End temperature 00:00:00 hh:mm:ss
Estimated time to complete 00:38:20 hh:mm:ss

Offset Force on RSA G2

- Constant static force



Procedure:

1: Conditioning Options

Axial force adjustment

Mode: Active

● Tension ○ Compression

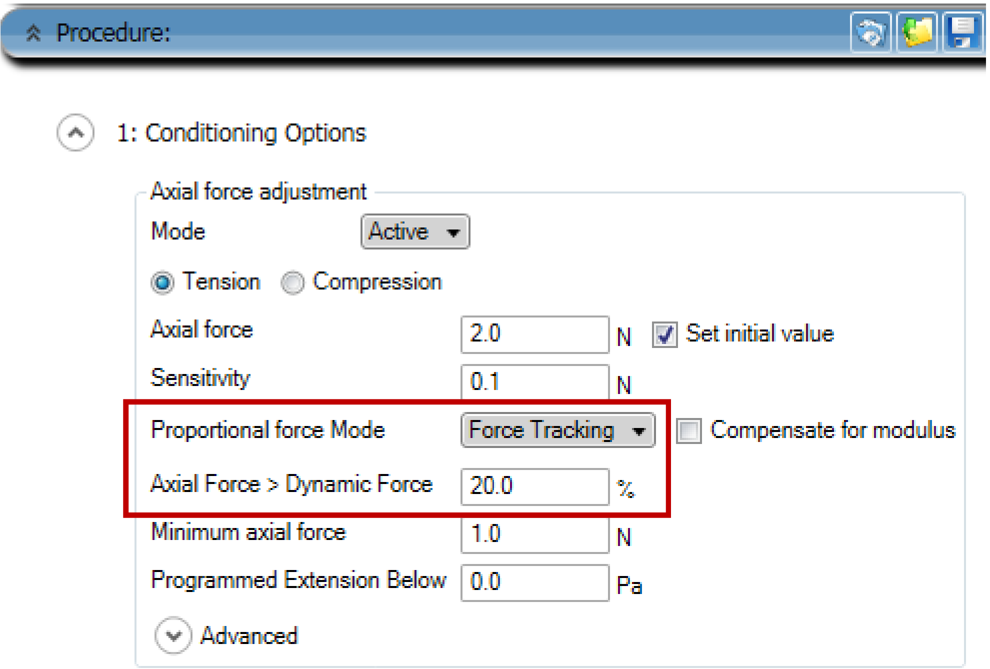
Axial force: 1.0 N ☑ Set initial value

Sensitivity: 0.1 N

Proportional force Mode: Constant

Advanced

- Force track



Procedure:

1: Conditioning Options

Axial force adjustment

Mode: Active

● Tension ○ Compression

Axial force: 2.0 N ☑ Set initial value

Sensitivity: 0.1 N

Proportional force Mode: Force Tracking ☐ Compensate for modulus

Axial Force > Dynamic Force: 20.0 %

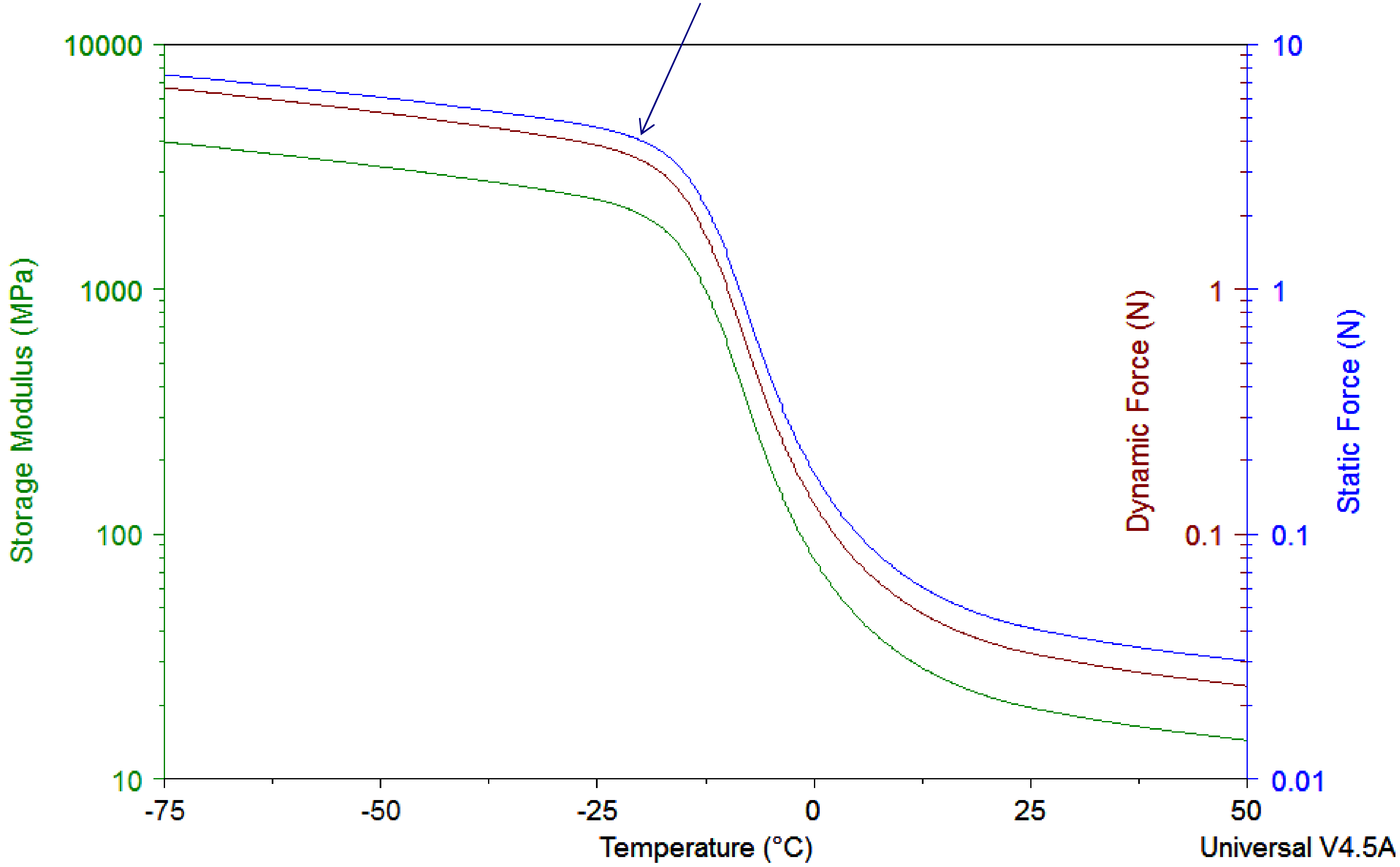
Minimum axial force: 1.0 N

Programmed Extension Below: 0.0 Pa

Advanced

Temperature Ramp with Force Track

- Static Force tracks Dynamic Force throughout Temperature Ramp



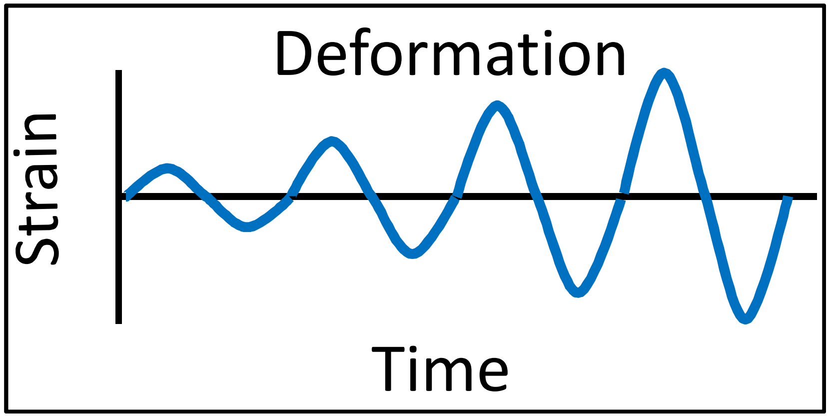
Choosing Force Track Parameters

Initial static force before testing

Clamp Type	Static Force	Force Track
Tension Film	0.01 N	120 to 150%
Tension Fiber	0.001 N	120%
Compression	0.001 to 0.01 N	125%
Three Point Bending Thermoplastic Sample	1 N	125 to 150%
Three Point Bending Stiff Thermoset Sample	1 N	150 to 200% Can use constant static force

Note: Constant (or static) force can be used as long as static force > dynamic force through out the entire experiment.

Dynamic Strain (Stress) Sweep

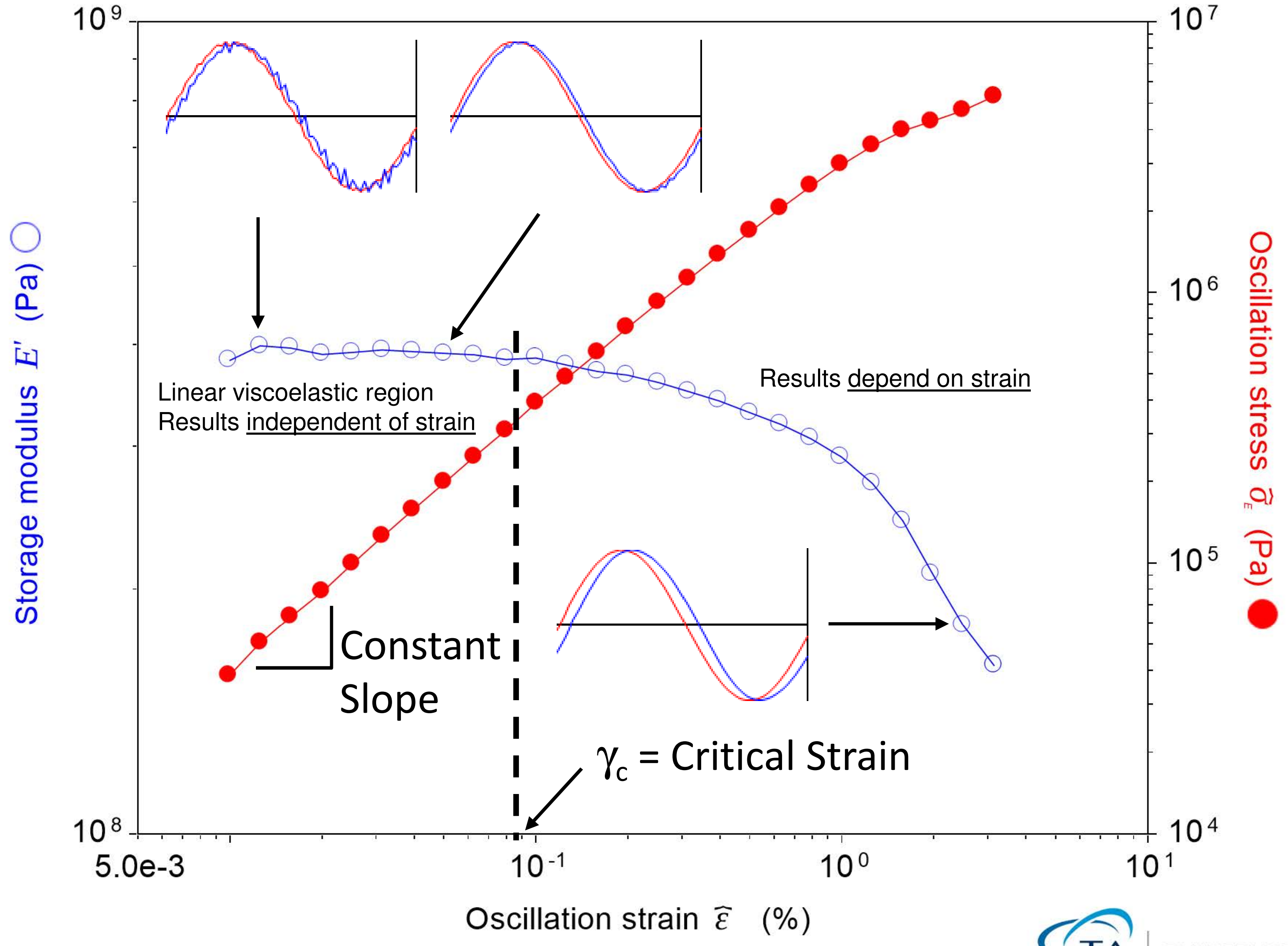


- The material response to increasing deformation amplitude is monitored at a constant frequency and temperature.

USES

- Identify Linear Viscoelastic Region
- Resilience/elasticity

Dynamic Strain Sweep: Material Response



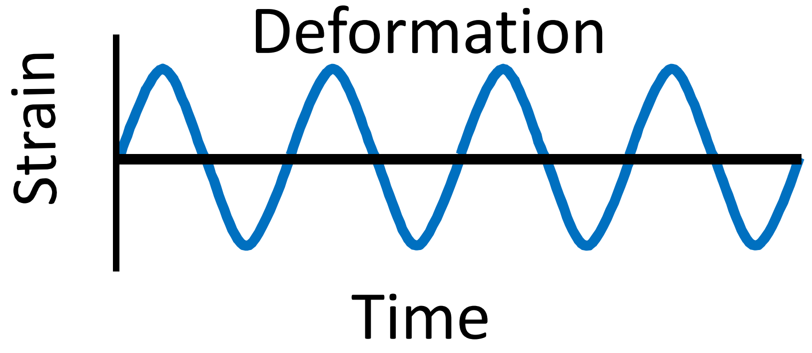
Linear viscoelastic region
Results independent of strain

Results depend on strain

Constant Slope

γ_c = Critical Strain

Dynamic Time Sweep

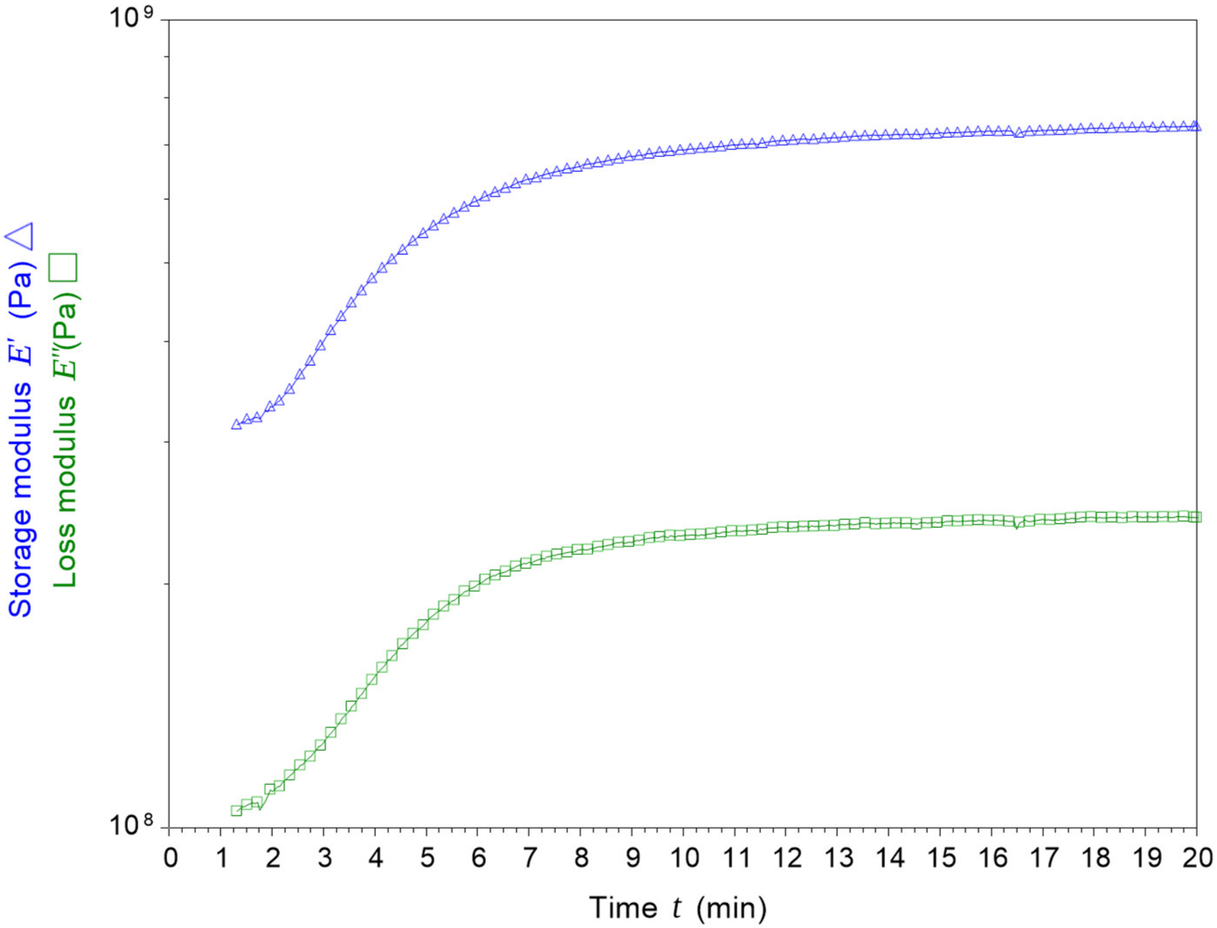


- The material response is monitored at a constant frequency, amplitude and temperature.

<u>USES</u>

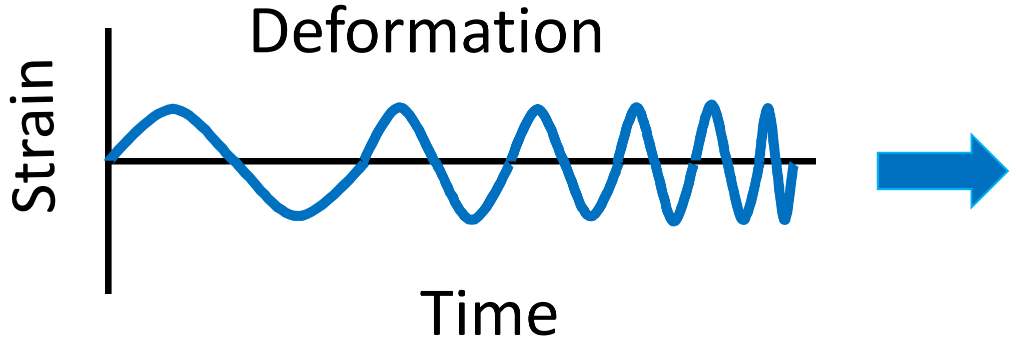
- Curing studies
- Fatigue tests
- Stability against thermal degradation

Epoxy Curing on Glass Braid



Instrument: DMA850
Clamp: Dual cantilever
Sample: Epoxy coated on glass braid
Dynamic time sweep
Temperature: 35℃
Frequency: 1 Hz
Amplitude: 10 µm

Frequency Sweep

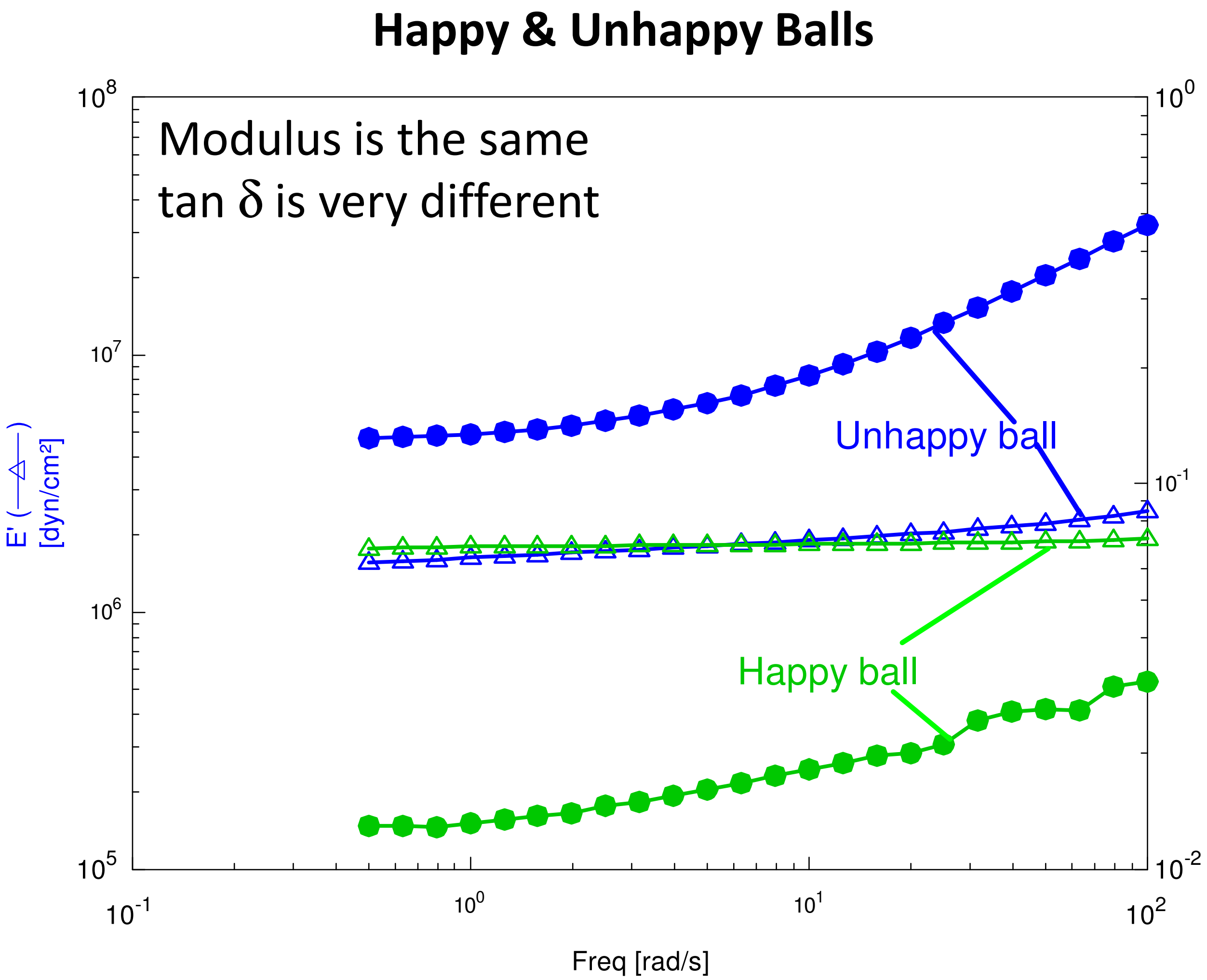


- The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude and temperature.

USES

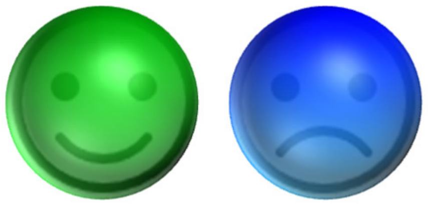
- Quick comparison on modulus and elasticity on solids
- Study polymer melt processing (shear sandwich).
- Estimate long term properties with extended frequency (time) range using TTS

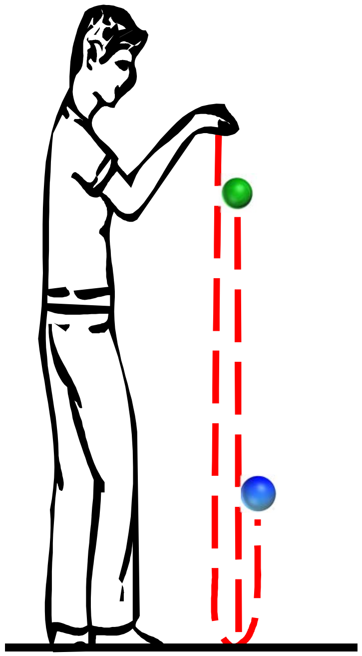
Happy & Unhappy Balls



Modulus is the same

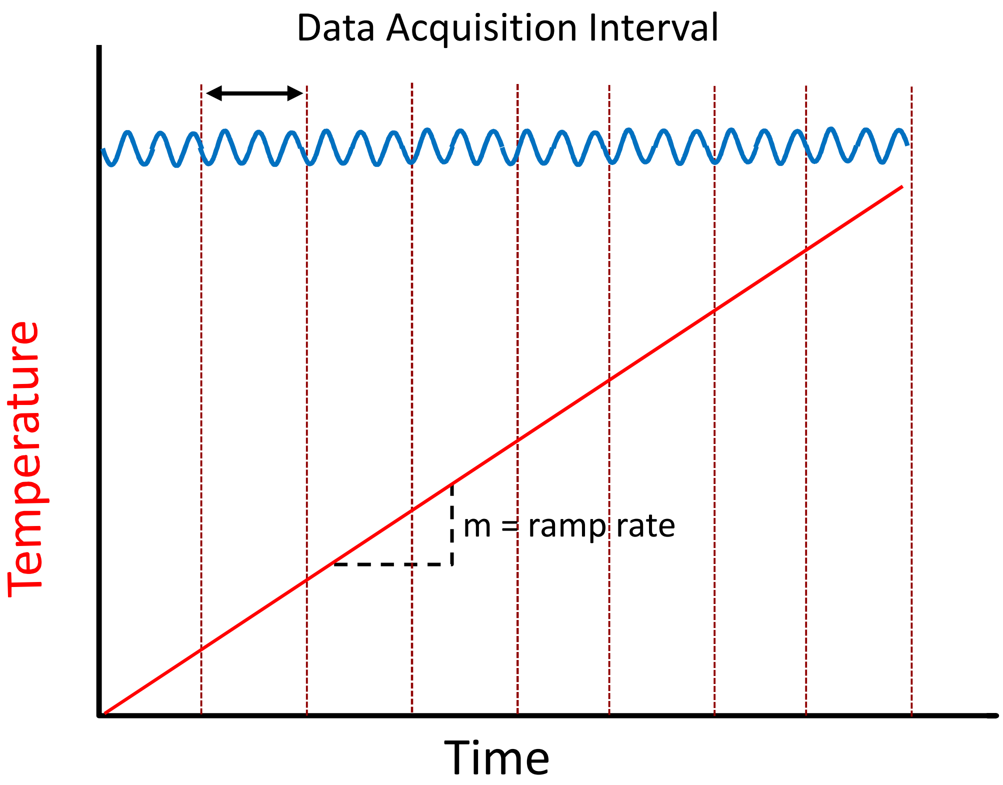
tan δ is very different





Dynamic Temperature Ramp

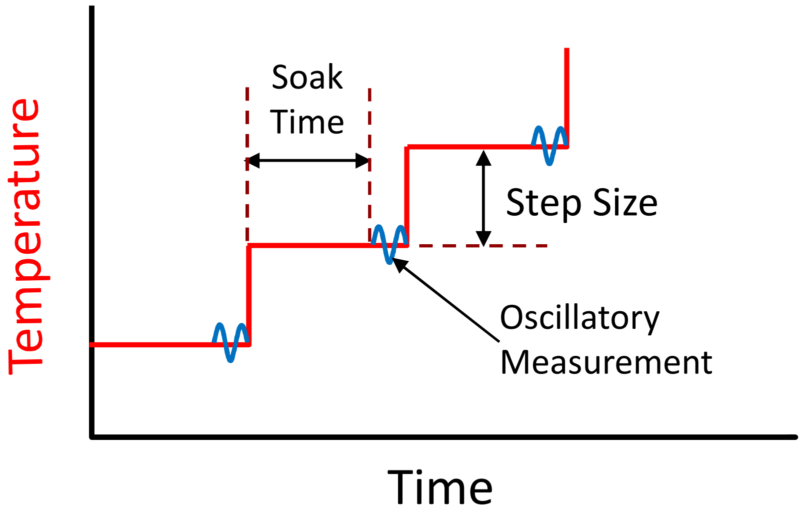
- A linear heating rate is applied. The material response is monitored at a constant frequency and constant amplitude of deformation. Data is taken at user defined time intervals.

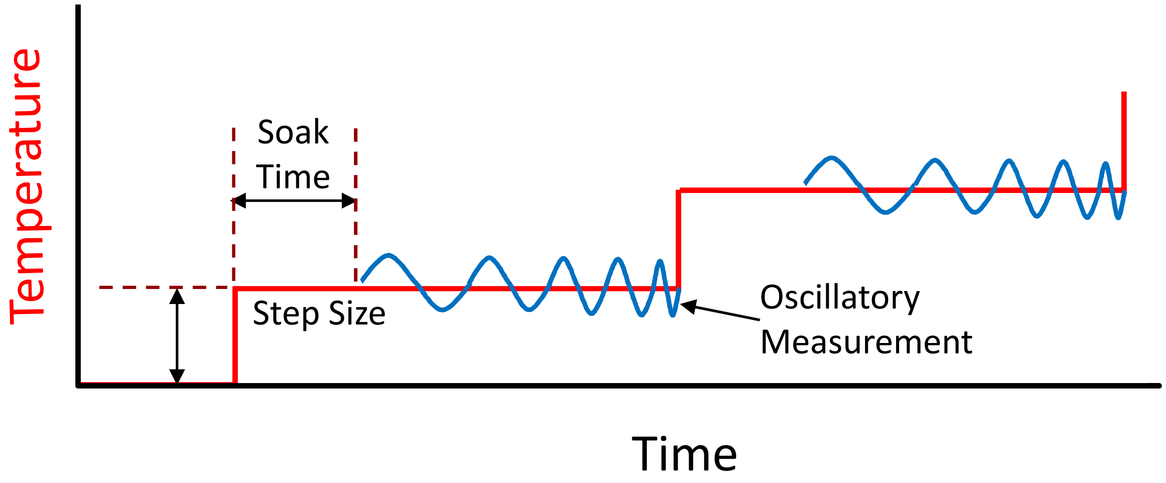


Recommend ramp rate for polymer testing: 1-5˚C/min.

Temperature Step & Hold- Single /Multi-Frequency

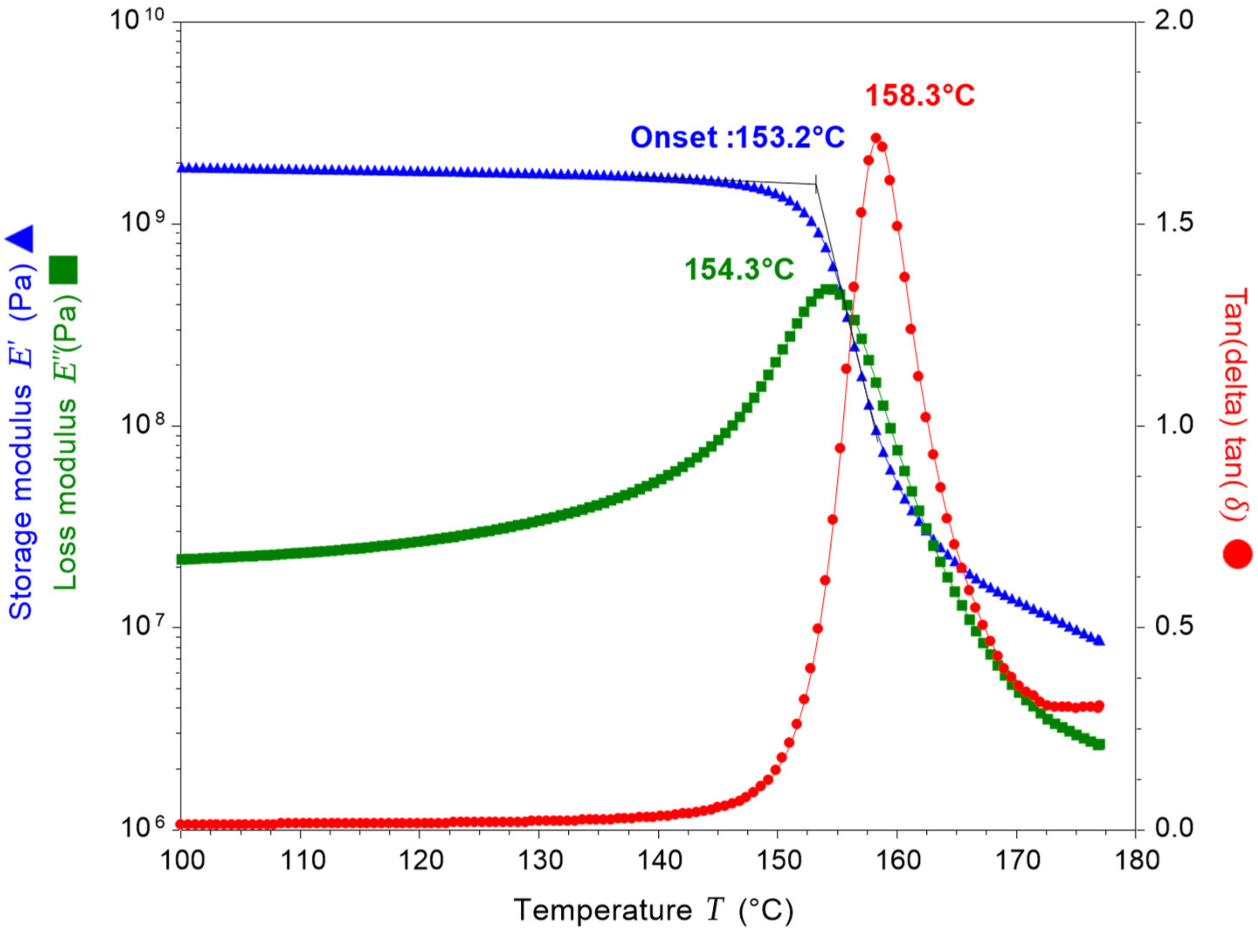
- A step and hold temperature profile is applied. The material response is monitored at one, or over a range of frequencies, at constant amplitude of deformation



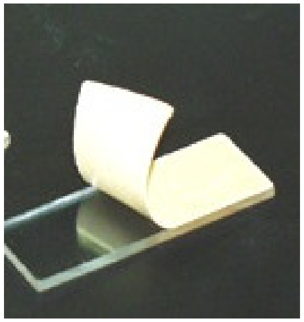


Temp Ramp on Polycarbonate

- Available from TA for Instrument verification



PC sample



p/n: 982165.903

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

Available DMA Experiments

(2) Transient Tests

Transient Testing

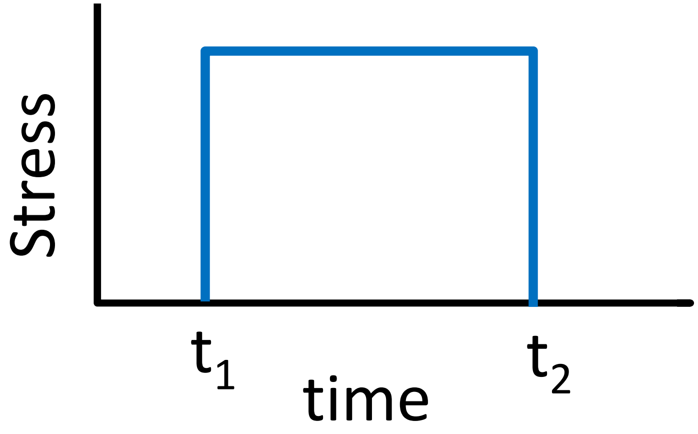
Available transient test modes

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

Creep Recovery Experiment

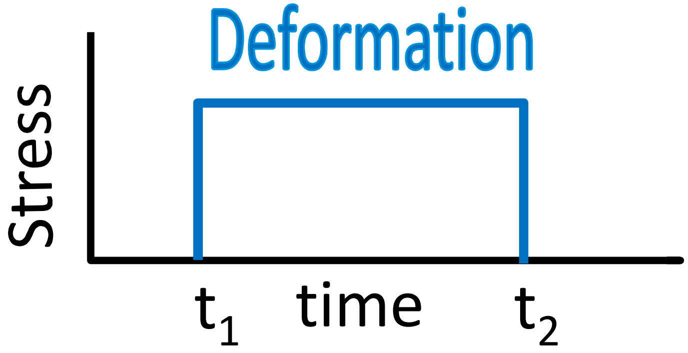
- A stress is applied to sample instantaneously at t_1 and held constant for a specific period of time. The strain is monitored as a function of time ($\gamma(t)$ or $\varepsilon(t)$).

- The stress is reduced to zero at t_2 and the strain is monitored as a function of time ($\gamma(t)$ or $\varepsilon(t)$).



Creep Recovery Experiment

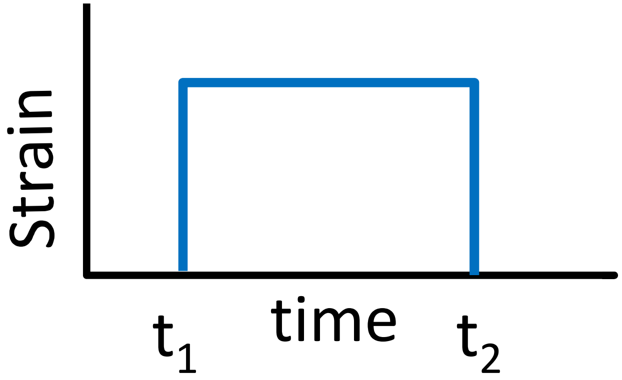
Deformation



Response of Classical Extremes

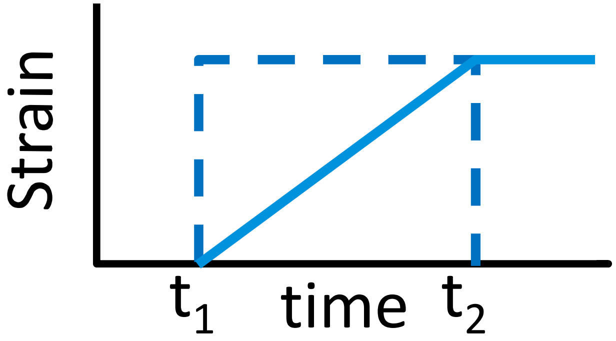
Elastic

- Stain for t>t1 is constant
- Strain for t >t2 is 0

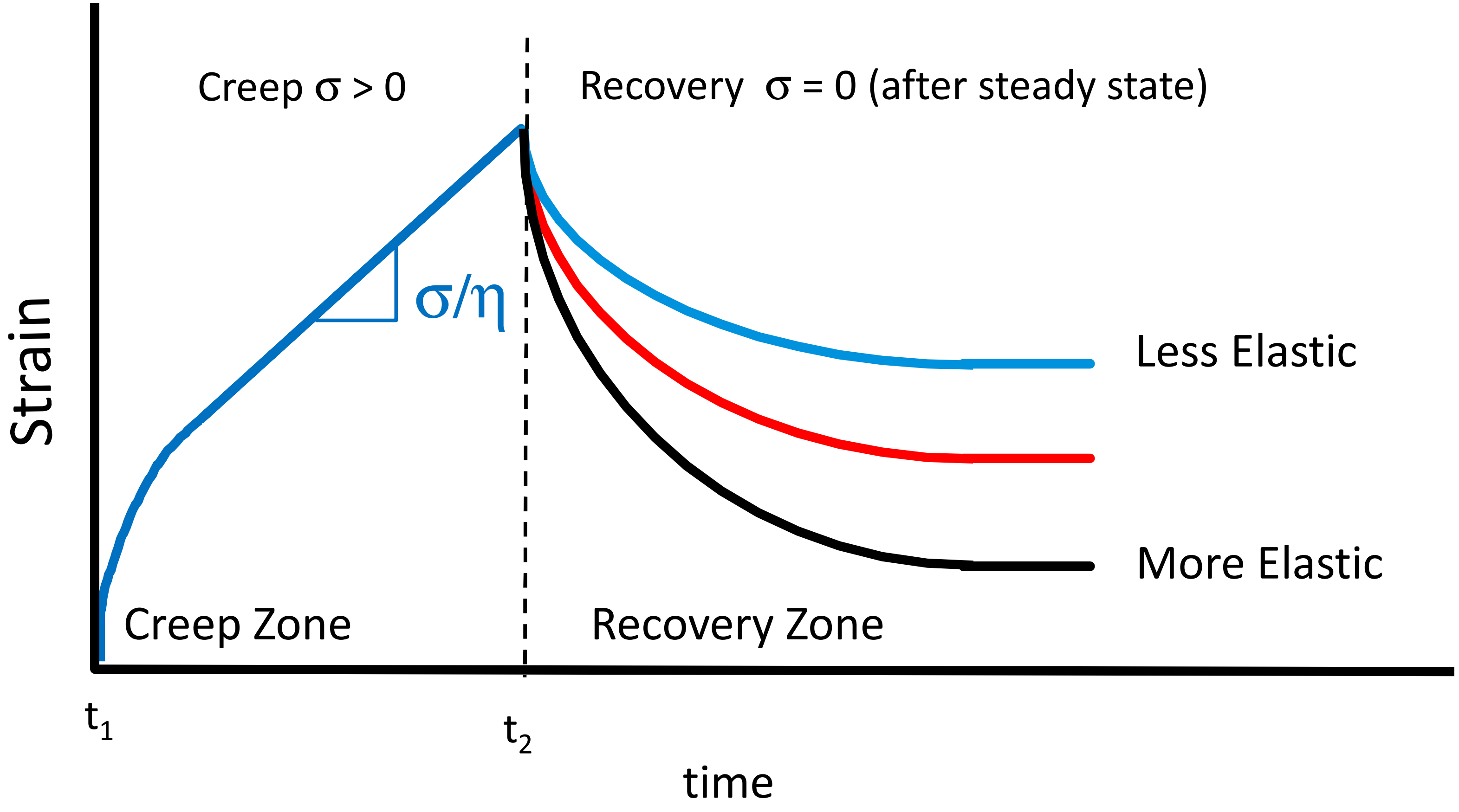


Viscous

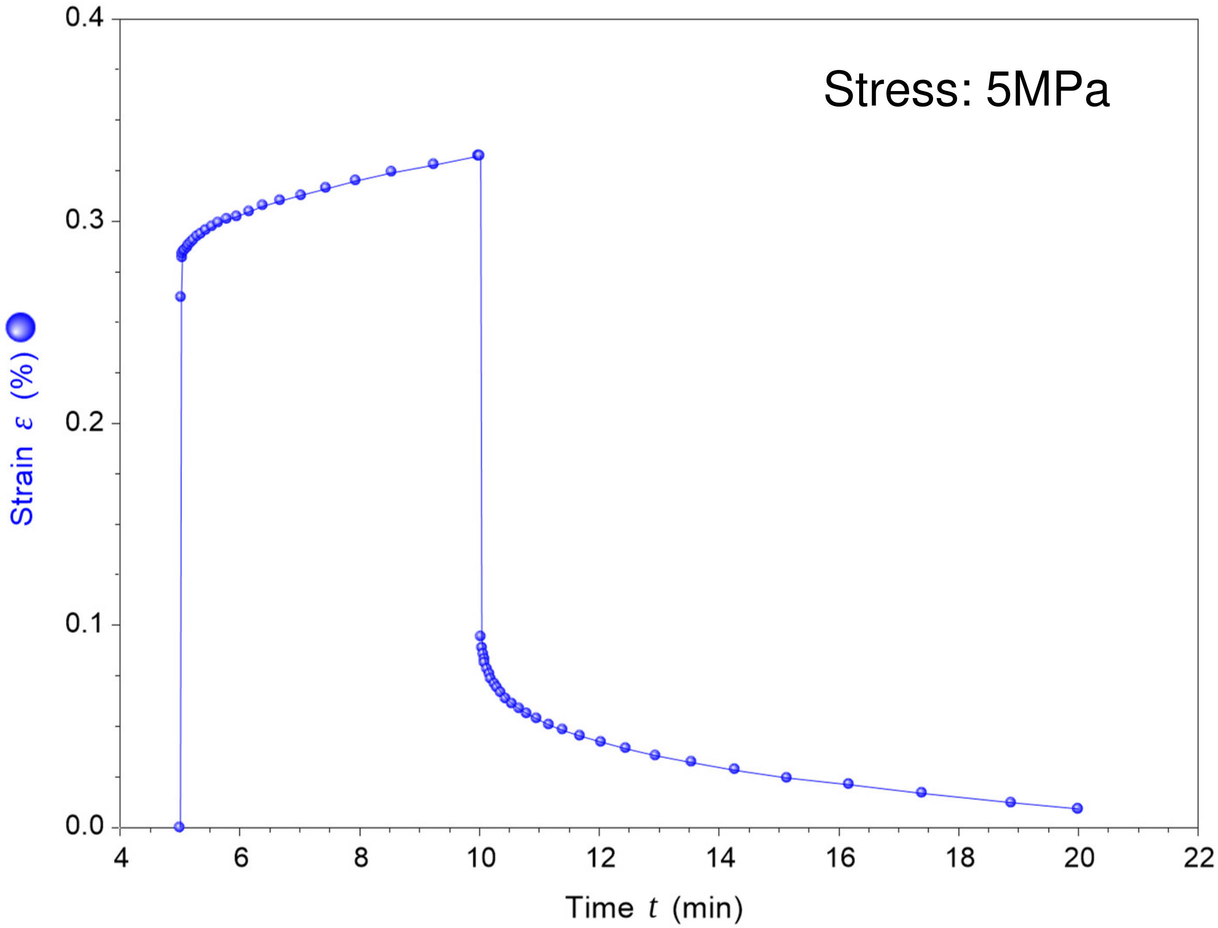
- Stain rate for t>t1 is constant
- Strain for t>t1 increase with time
- Strain rate for t >t2 is 0



Creep Recovery Experiment



Creep-Recovery Test on PET Film

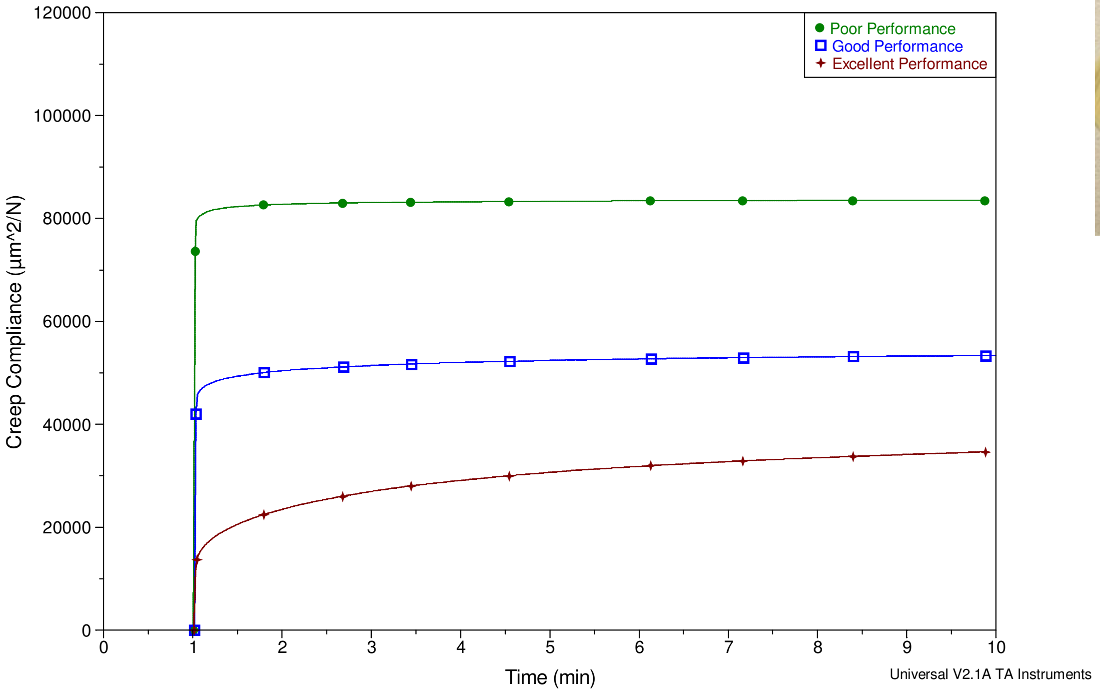


p/n: 984309.901

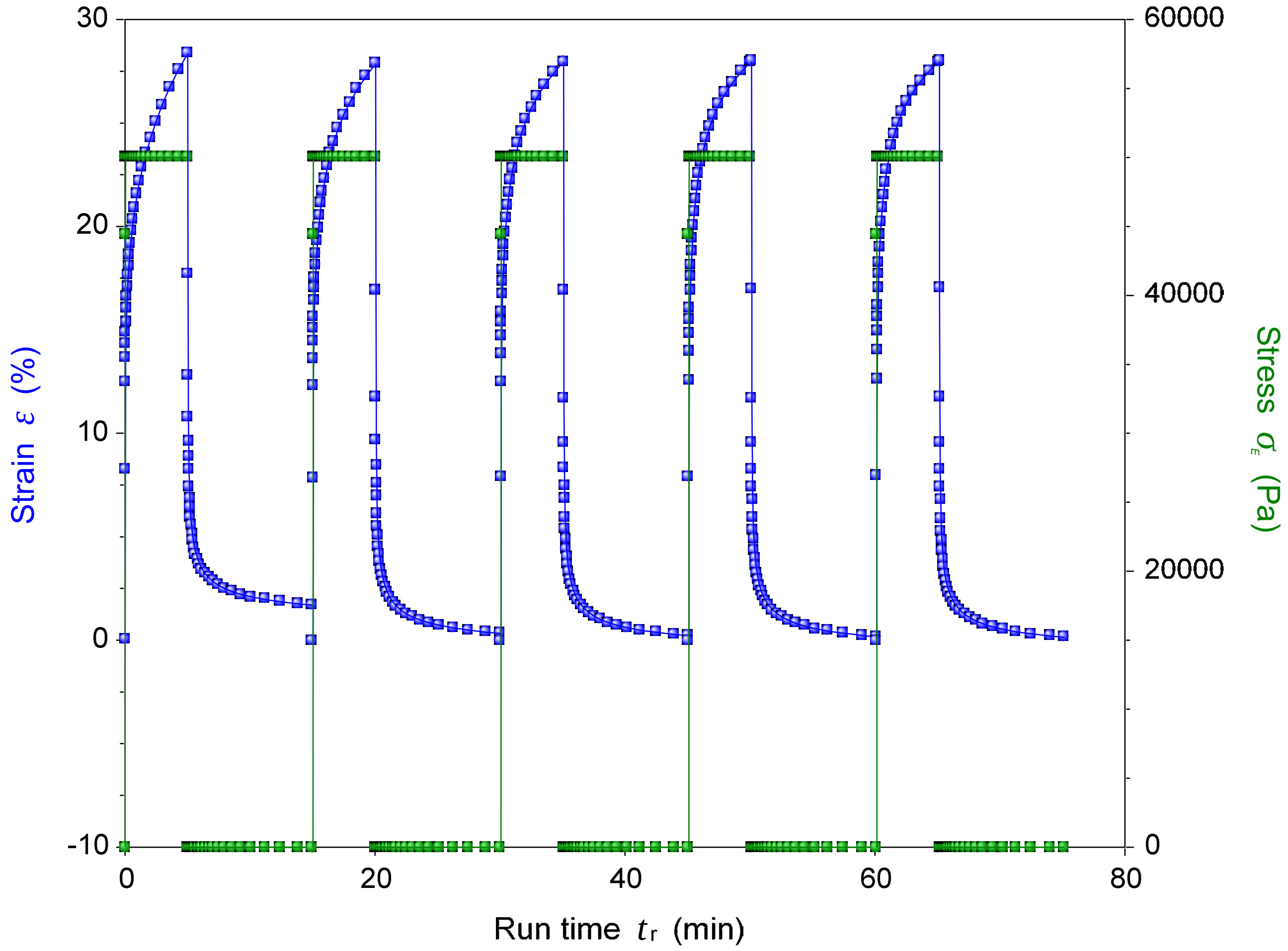
Instrument: Q800
Clamp: Tension
Temperature: 75℃
Stress: 5MPa

Creep Tests on Packaging Bags

- Apply a load force, then measure how much the bag is stretched

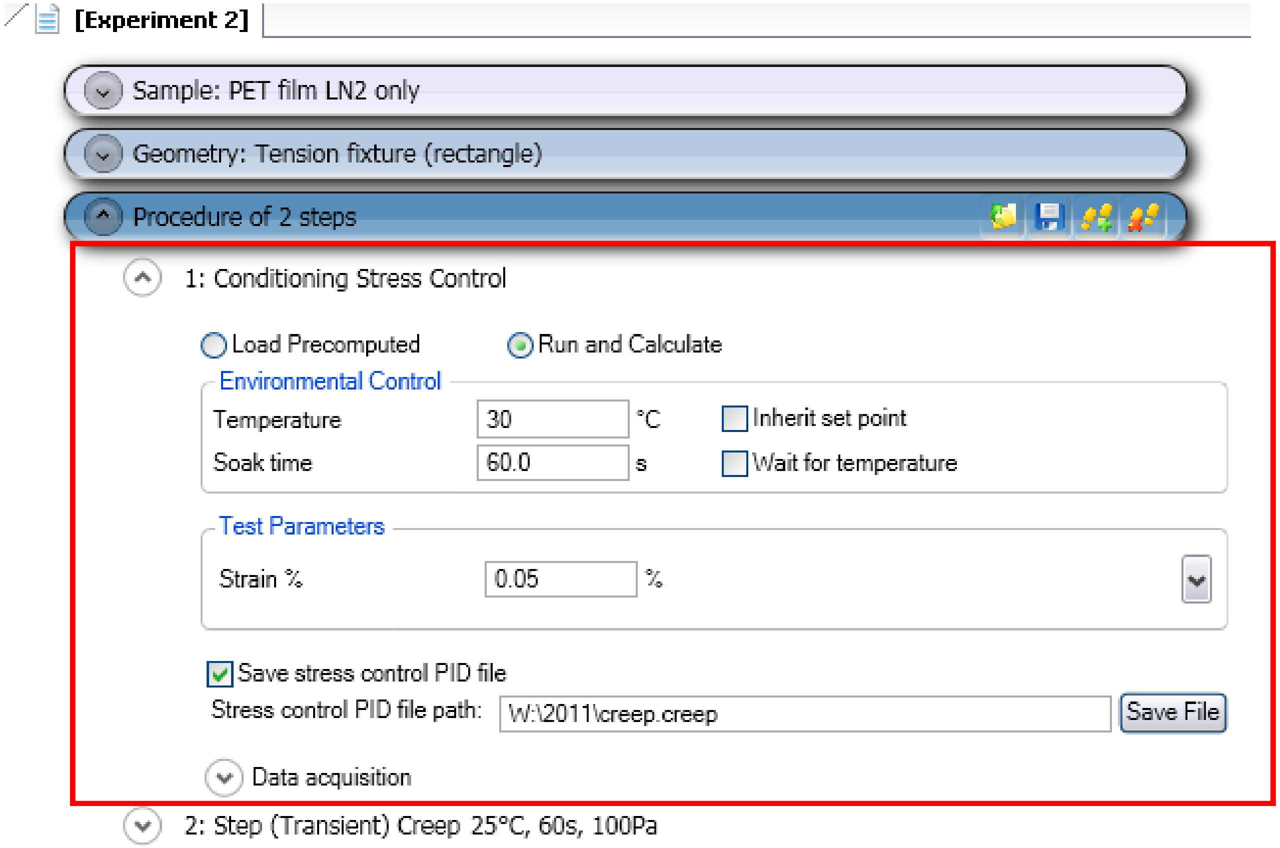


Memory Foam: Multi-Step Creep Recovery



Programming Creep Recovery on a RSA-G2

- A pre-test is required to obtain sample information for the feedback loop
- Stress Control Pre-test: frequency sweep within LVR



[Experiment 2]

Sample: PET film LN2 only

Geometry: Tension fixture (rectangle)

Procedure of 2 steps

1: Conditioning Stress Control

○ Load Precomputed ● Run and Calculate

Environmental Control

Temperature 30 °C ☐ Inherit set point

Soak time 60.0 s ☐ Wait for temperature

Test Parameters

Strain % 0.05 %

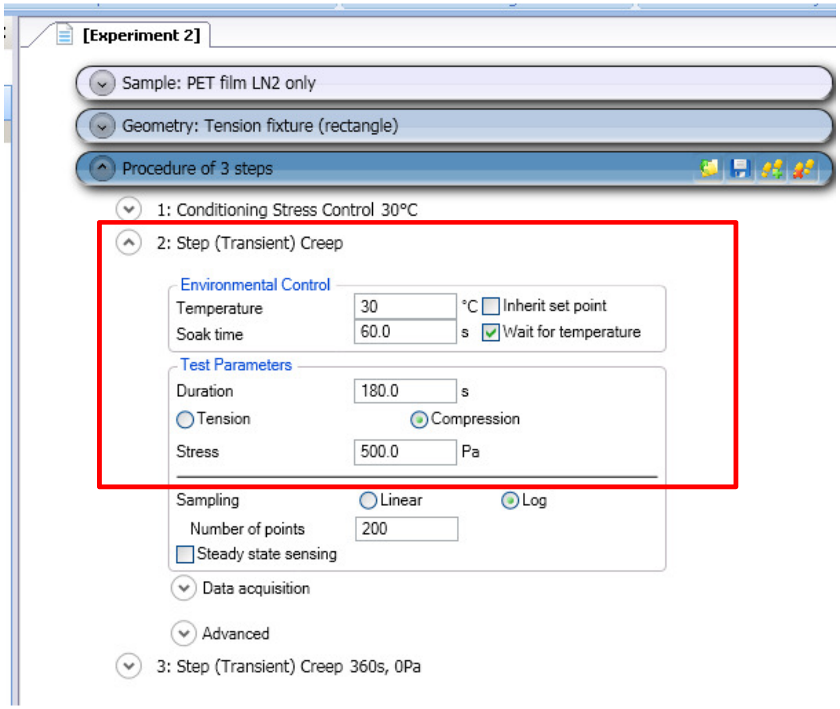
☑ Save stress control PID file

Stress control PID file path: W:\2011\creep.creep

2: Step (Transient) Creep 25°C, 60s, 100Pa

Programming Creep Recovery on a RSA-G2

Creep



[Experiment 2]

Sample: PET film LN2 only

Geometry: Tension fixture (rectangle)

Procedure of 3 steps

1: Conditioning Stress Control 30°C

2: Step (Transient) Creep

Environmental Control

Temperature 30 °C ☐ Inherit set point

Soak time 60.0 s ☑ Wait for temperature

Test Parameters

Duration 180.0 s

○ Tension ● Compression

Stress 500.0 Pa

Sampling ○ Linear ● Log

Number of points 200

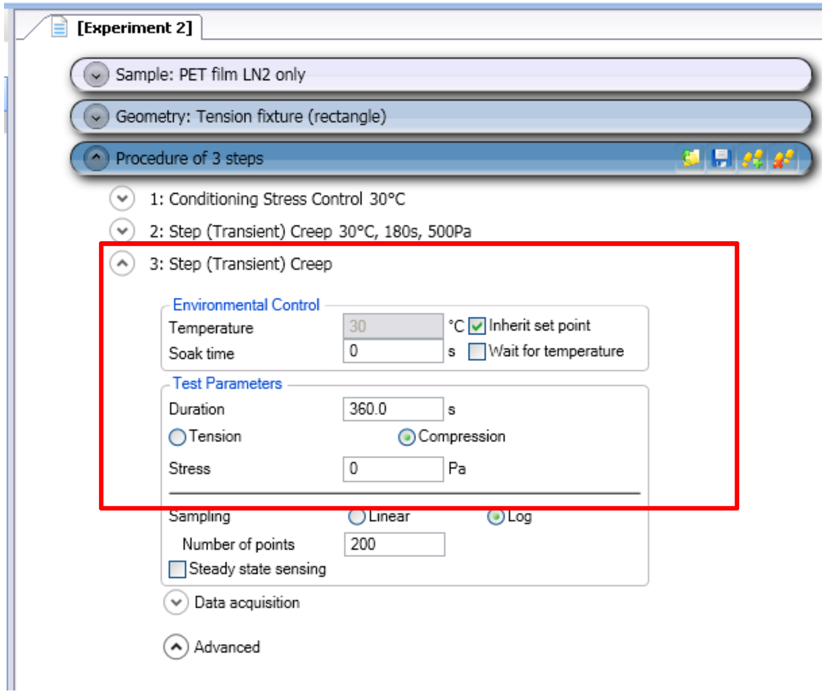
☐ Steady state sensing

Data acquisition

Advanced

3: Step (Transient) Creep 360s, 0Pa

Recovery



[Experiment 2]

Sample: PET film LN2 only

Geometry: Tension fixture (rectangle)

Procedure of 3 steps

1: Conditioning Stress Control 30°C

2: Step (Transient) Creep 30°C, 180s, 500Pa

3: Step (Transient) Creep

Environmental Control

Temperature 30 °C ☑ Inherit set point

Soak time 0 s ☐ Wait for temperature

Test Parameters

Duration 360.0 s

○ Tension ● Compression

Stress 0 Pa

Sampling ○ Linear ● Log

Number of points 200

☐ Steady state sensing

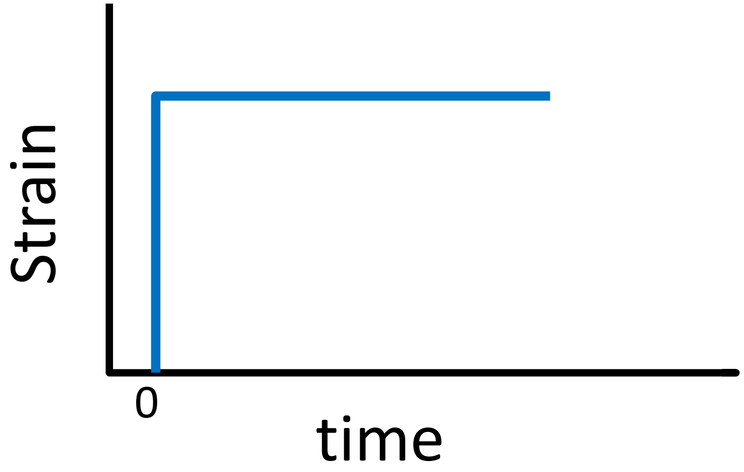
Data acquisition

Advanced

- Stress: needs to be in the linear region
- Creep time: until it reaches steady state
- Recovery time: until the compliance and strain reach plateau

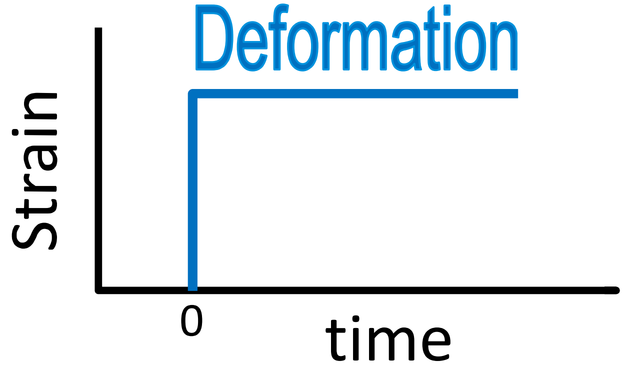
Stress Relaxation Experiment

- Strain is applied to sample instantaneously (in principle) and held constant with time.
- Stress is monitored as a function of time $\sigma(t)$.



Stress Relaxation Experiment

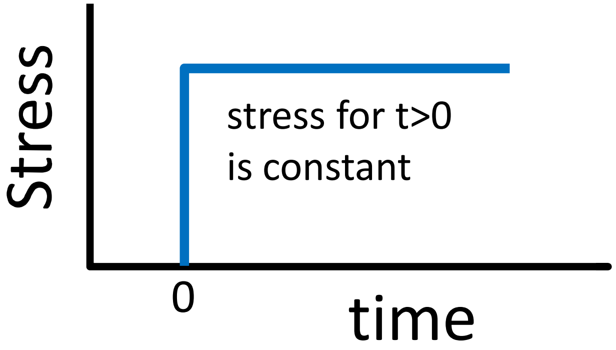
Deformation



Response of Classical Extremes

Elastic

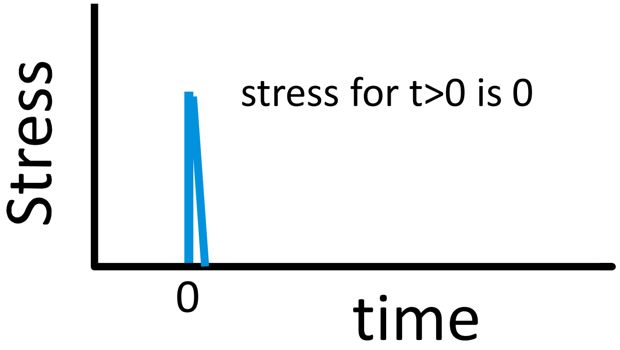
Hookean Solid



stress for t>0
is constant

Viscous

Newtonian Fluid

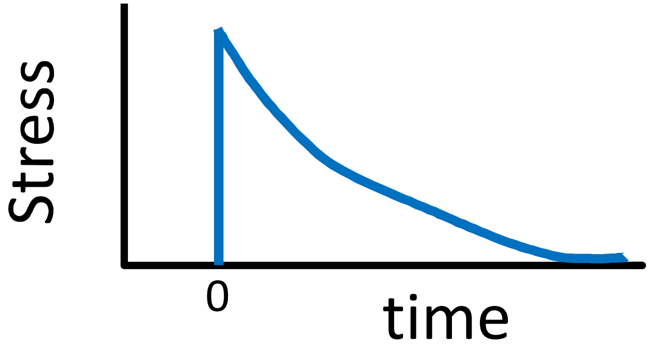


stress for t>0 is 0

Stress Relaxation Experiment

Response of ViscoElastic Material

Stress decreases with time starting at some high value and decreasing to zero.

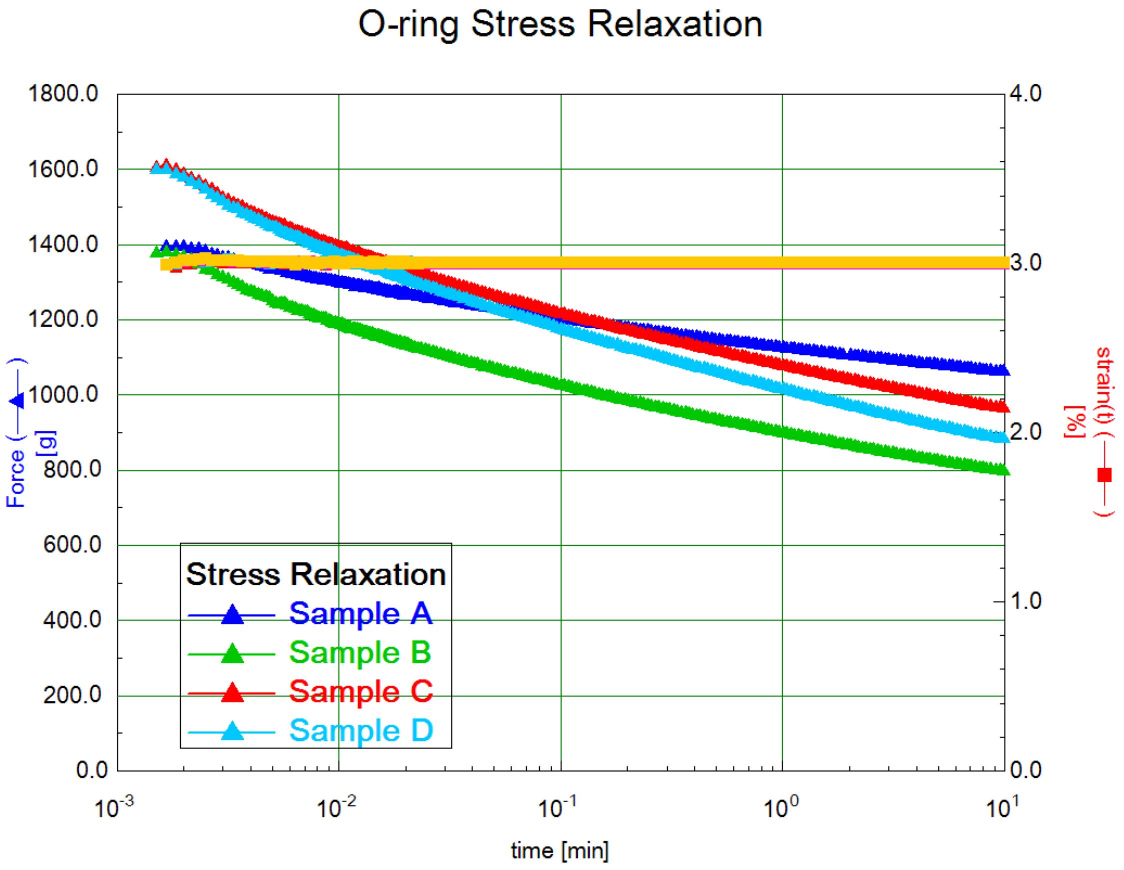


- For small deformations (strains within the linear region) the ratio of stress to strain is a function of time only.
- This function is a material property known as the STRESS RELAXATION MODULUS, E(t)

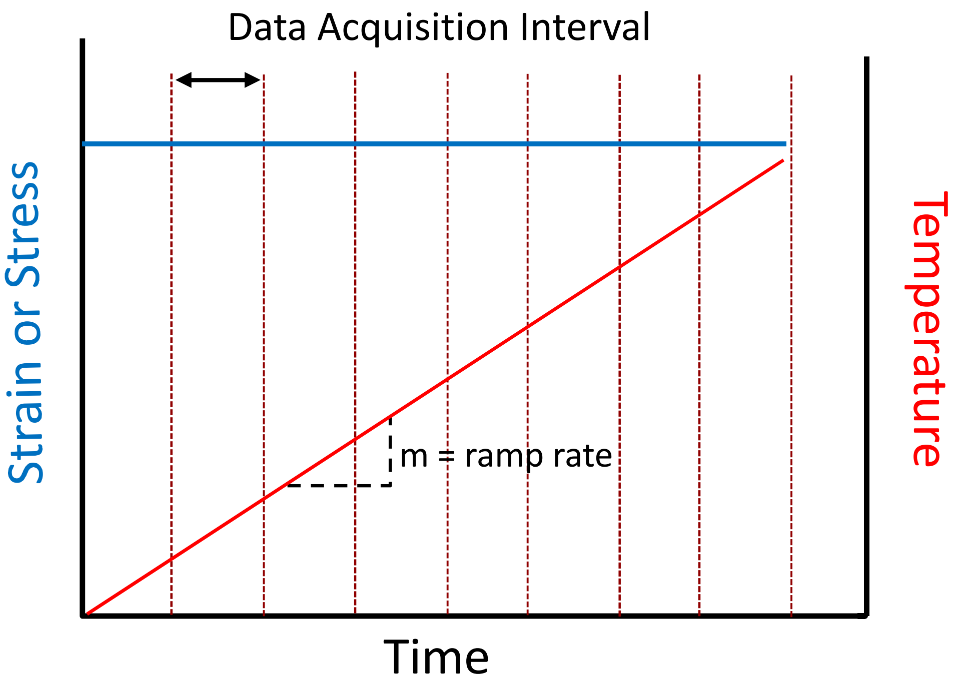
$$E(t) = \sigma(t)/\gamma$$

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/Iso-stress Temperature Ramp

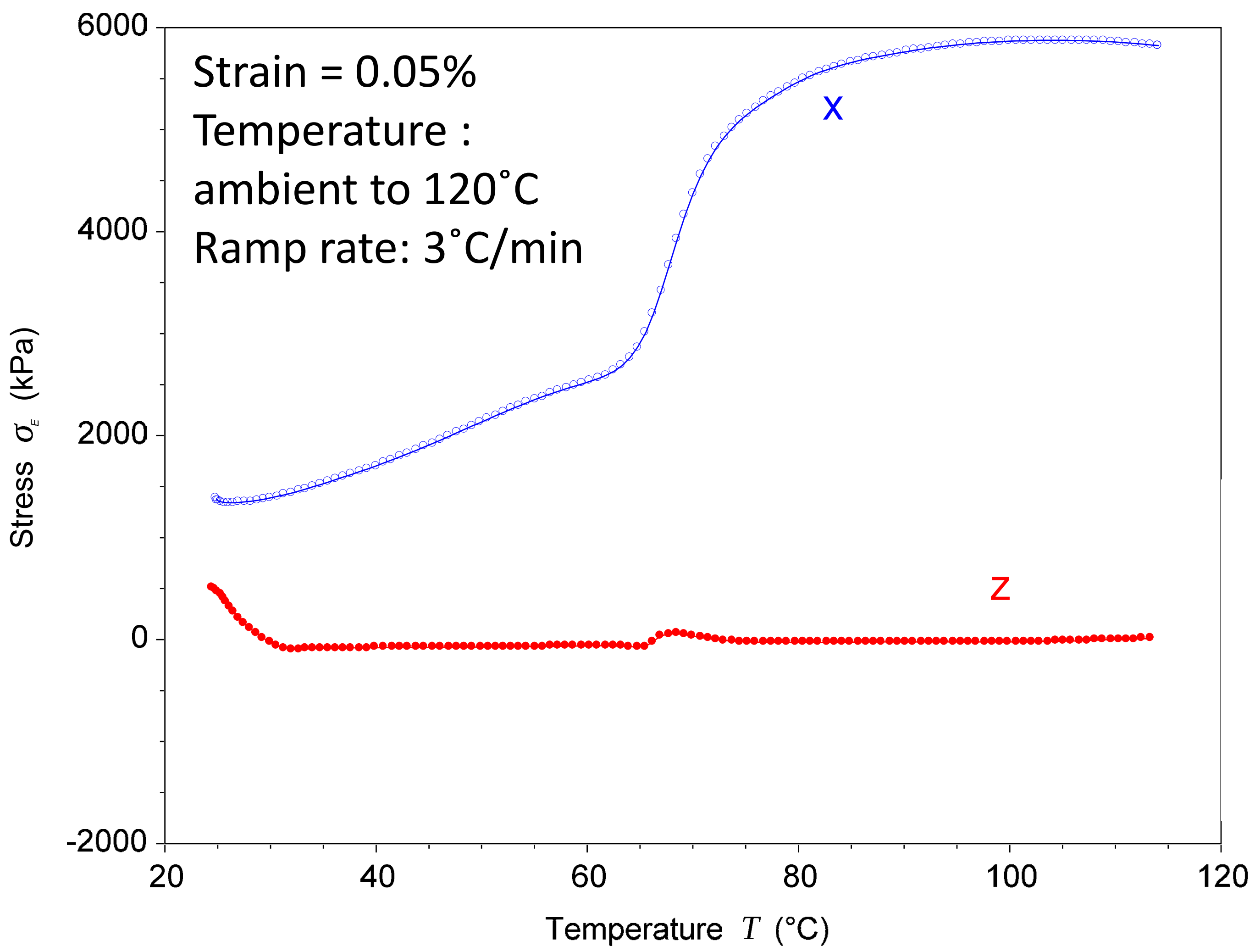


- The strain or stress is held at a constant value and a linear heating rate is applied.

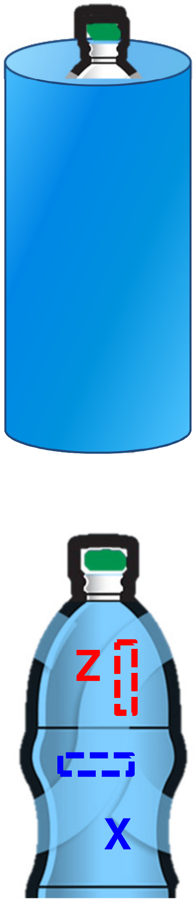
- Valuable for assessing mechanical behavior under conditions of confined or fixed load (stress) or deformation (strain).

- Example: Measure sample shrinkage (length shrinkage or shrinking force)

Iso-strain Temp Ramp: measure shrinking force

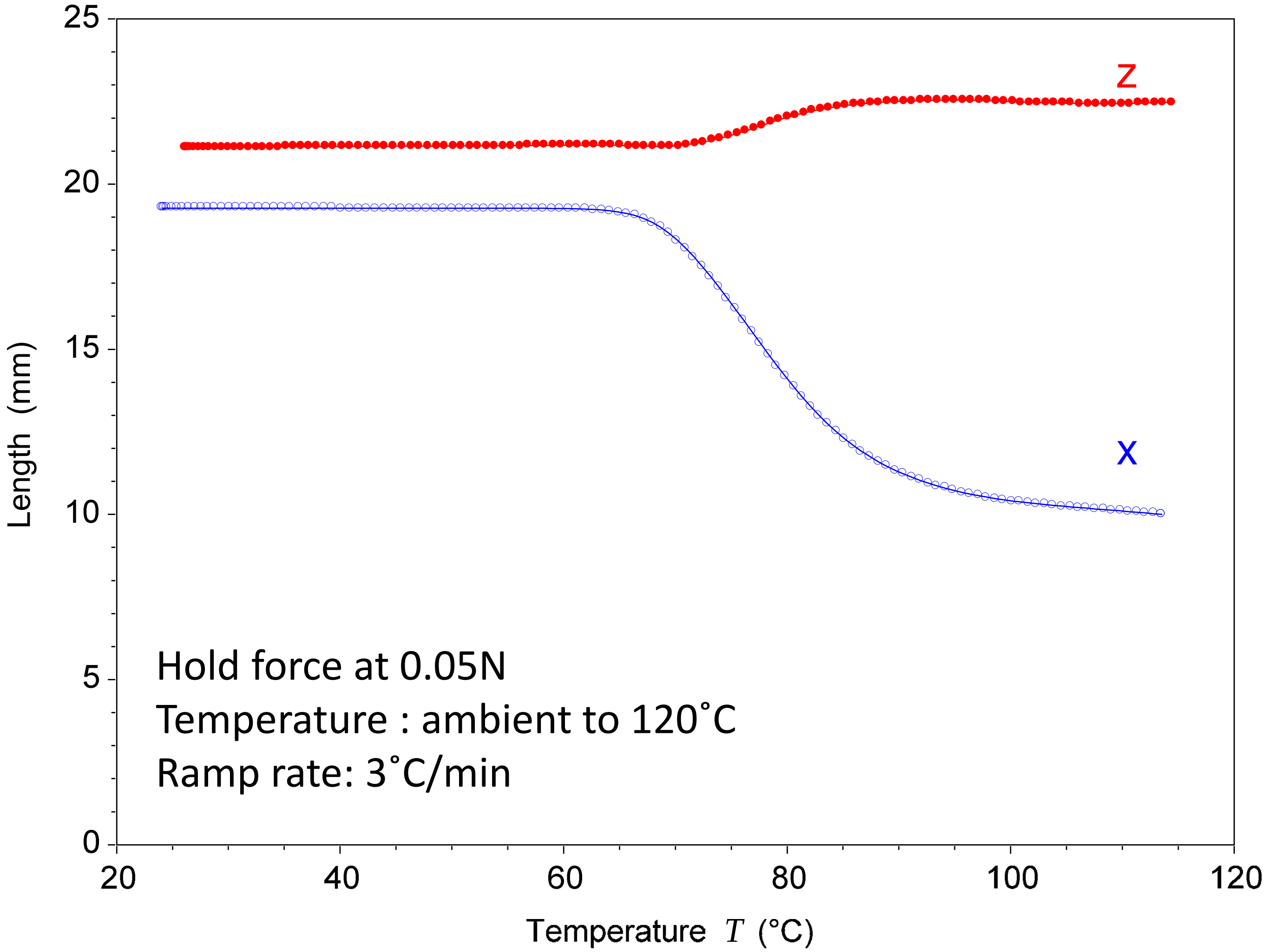


Strain = 0.05%
Temperature :
ambient to 120˚C
Ramp rate: 3˚C/min

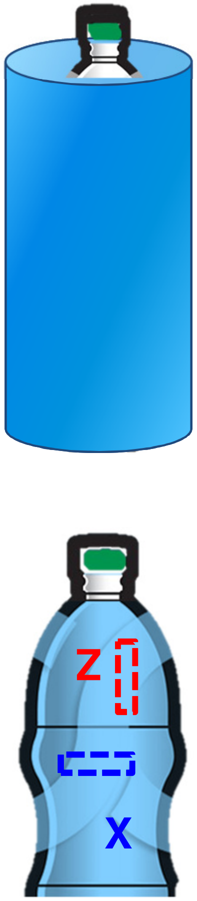


Sample is held at a constant length; shrinkage force is measured

Iso-force Temp Ramp: measure shrinkage



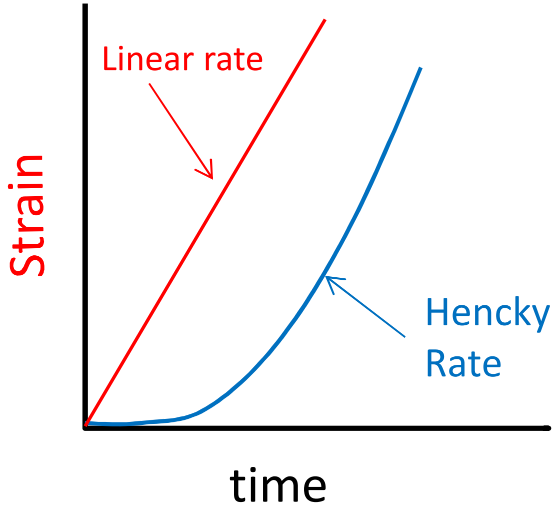
Hold force at 0.05N
Temperature : ambient to 120˚C
Ramp rate: 3˚C/min

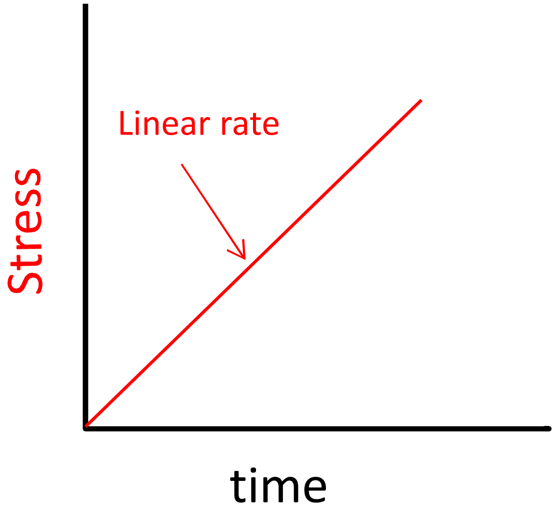


Sample is held at a constant force; shrinkage is measured

Stress-Strain Testing

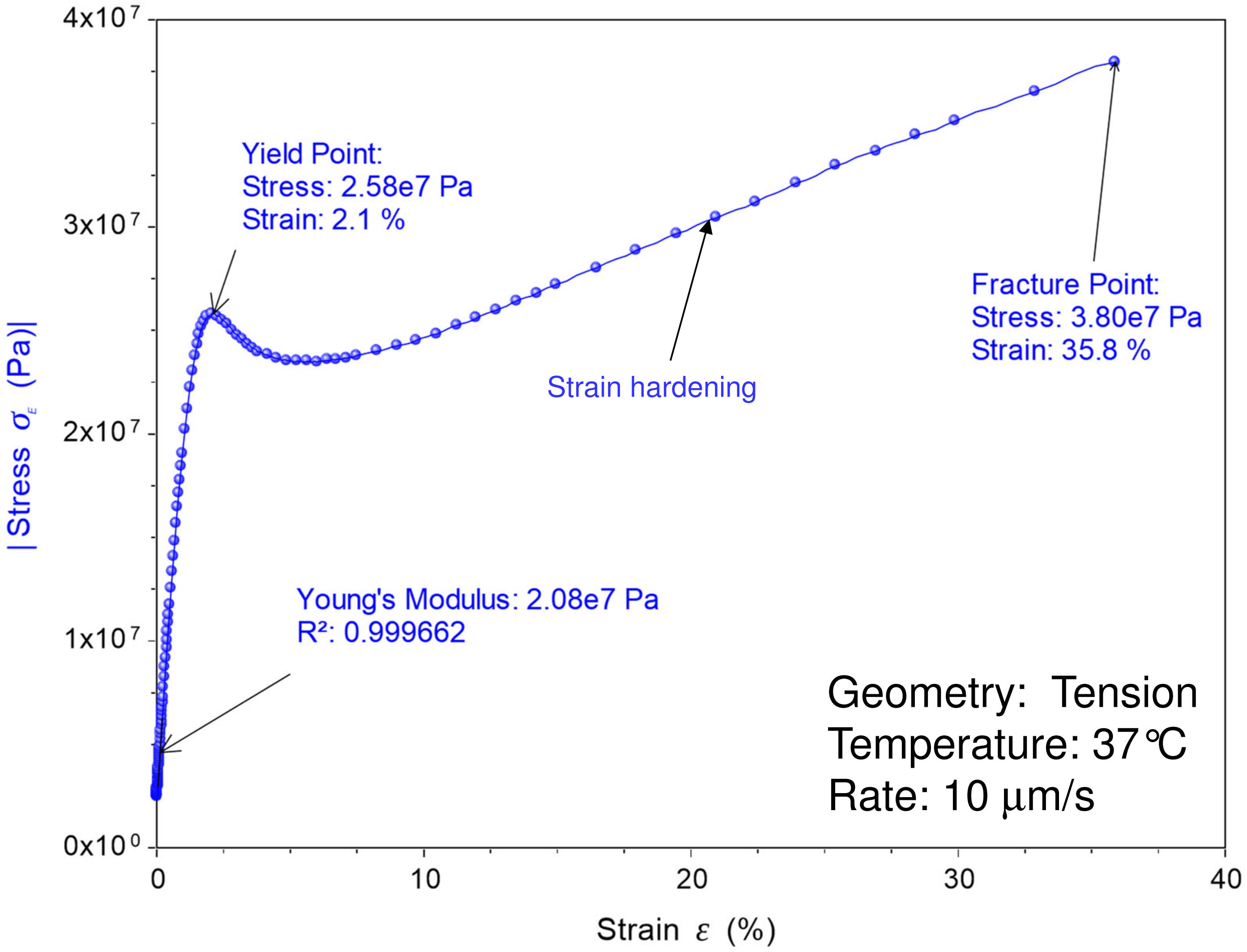
Axial Test: Strain Rate Controlled





- 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

Polysaccharide Film Stress-Strain Test



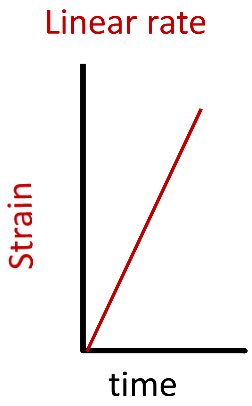
Yield Point:
Stress: 2.58e7 Pa
Strain: 2.1 %

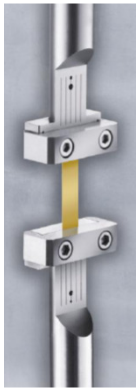
Strain hardening

Fracture Point:
Stress: 3.80e7 Pa
Strain: 35.8 %

Young's Modulus: 2.08e7 Pa
R^2: 0.999662

Geometry: Tension
Temperature: 37℃
Rate: 10 μm/s

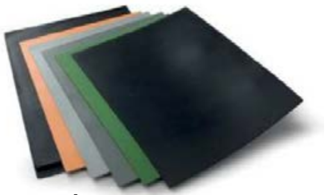




DMA Applications and Data Interpretation

What Samples Can DMA Measure?

- By changing the clamp, we can test a range of different materials: solid bars, elastomers, soft foams, thin films and fibers


Elastomers


Films


Fibers

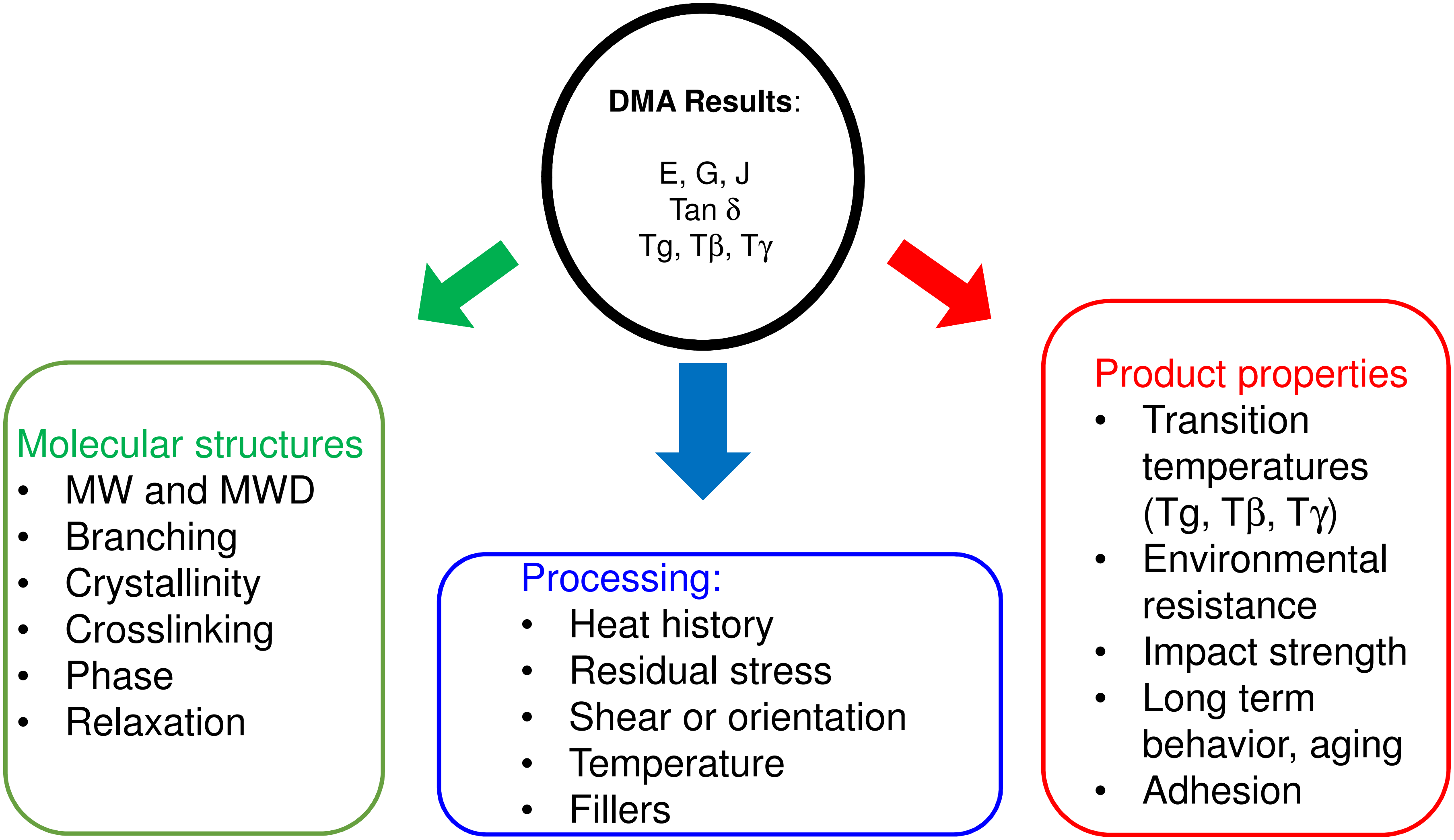

Gels


Solid Polymers


Foams


Composites

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:

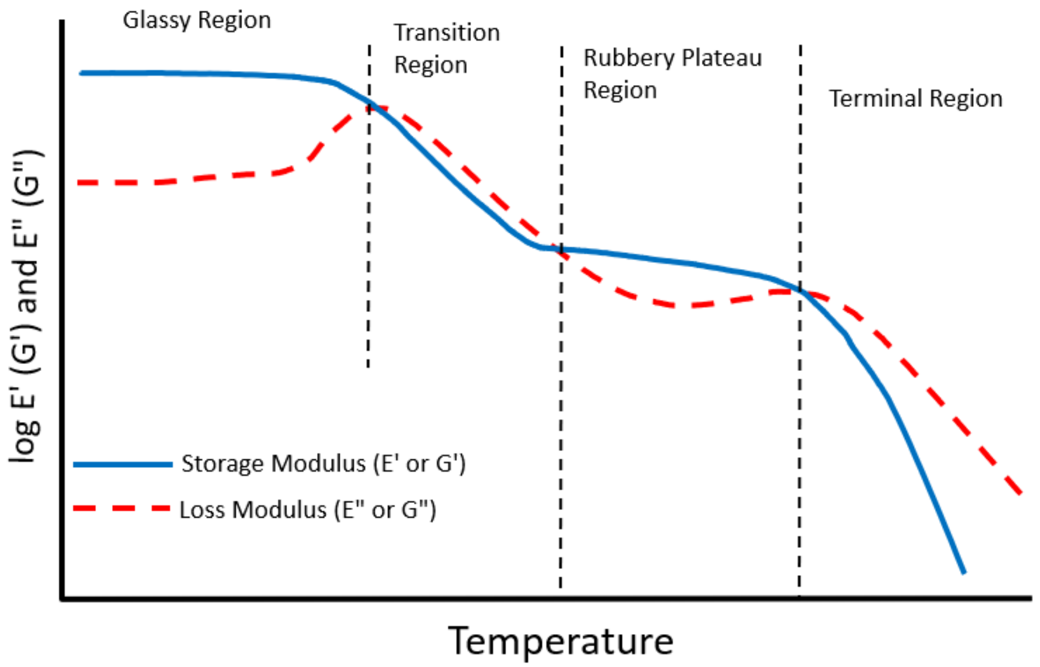
- Heat history
- Residual stress
- Shear or orientation
- Temperature
- Fillers

Product properties

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

Most Common DMA Test – Temp Ramp

- The most Common DMA measurement is a dynamic temperature ramp
- The test results report modulus (E*, E', E"), damping factor (Tan δ) and transition temperatures (T_g)
- Provide information to polymer's structure-property relationship



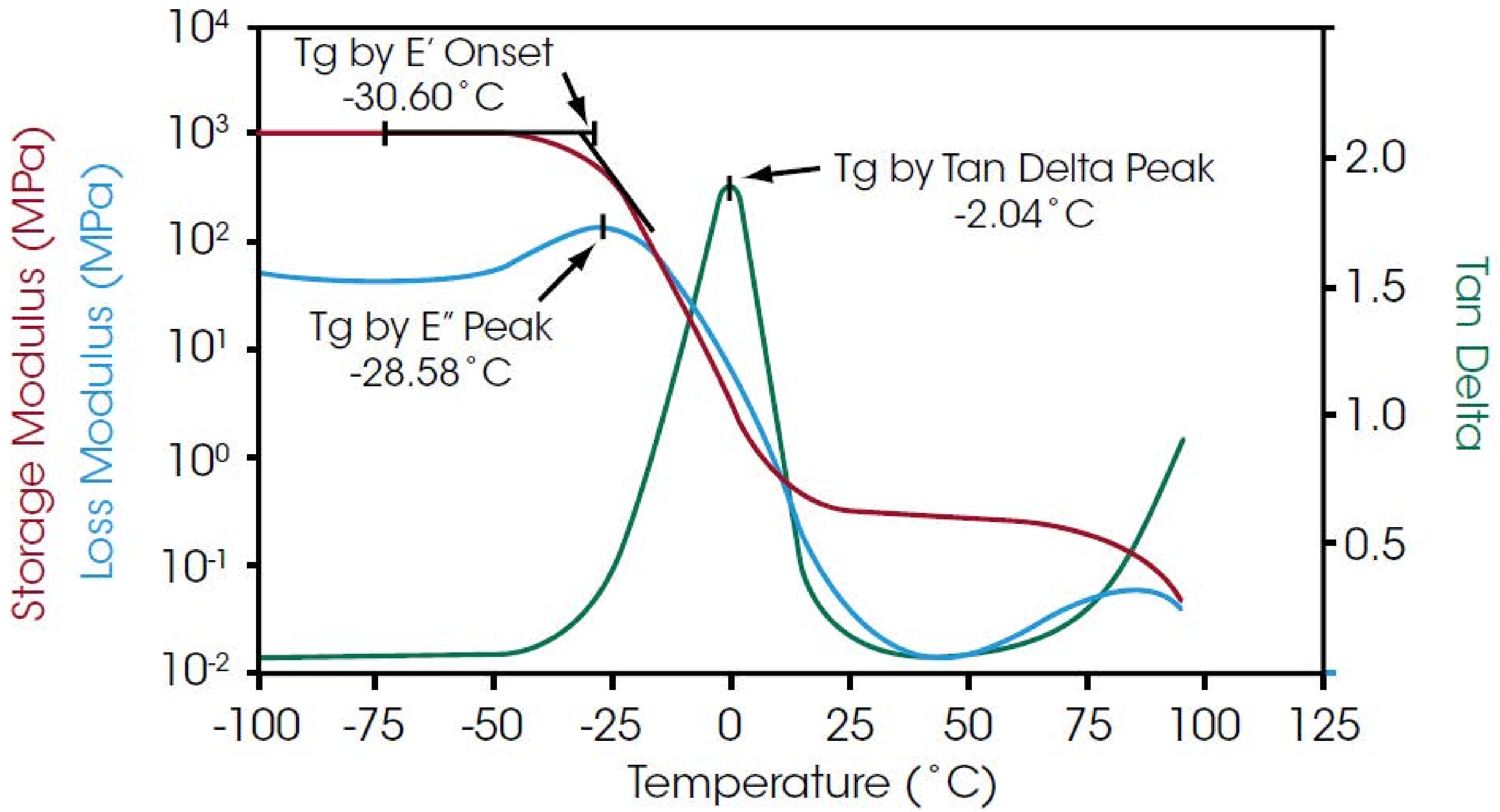
The Glass Transition

- "The glass transition is associated with the onset of long-range cooperative segmental mobility in the amorphous phase, in either an amorphous or semi-crystalline polymer."
- Any factor that affects segmental mobility will affect T_g, including…
  - the nature of the *moving segment*,
  - chain stiffness or steric hindrance
  - the free volume available for segmental motion

Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 508.

How to Define T_g in DMA?

Onset of E' **Peak of E"** **Peak of Tan δ**



Secondary Transitions

Glass Transition (T_g)

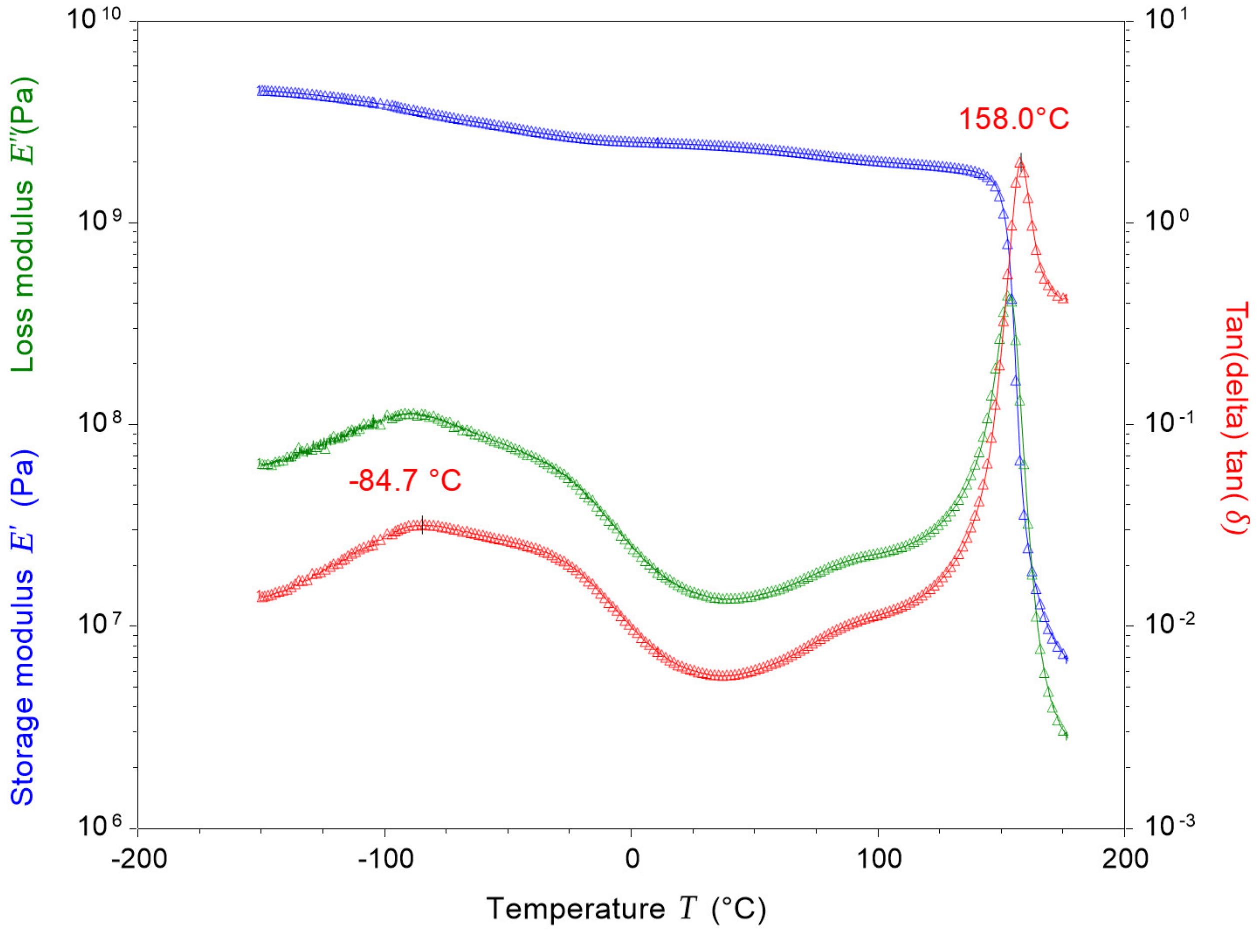
- Cooperative motion among a **large number** of chain segments, including those from neighboring polymer chains

Secondary Transitions (T_β, T_γ)

- Local Main-Chain Motion – intra-molecular 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 (eg. plasticizer.)

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

Primary and Secondary Transitions in PC



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

What Will Affect T_g and Modulus?

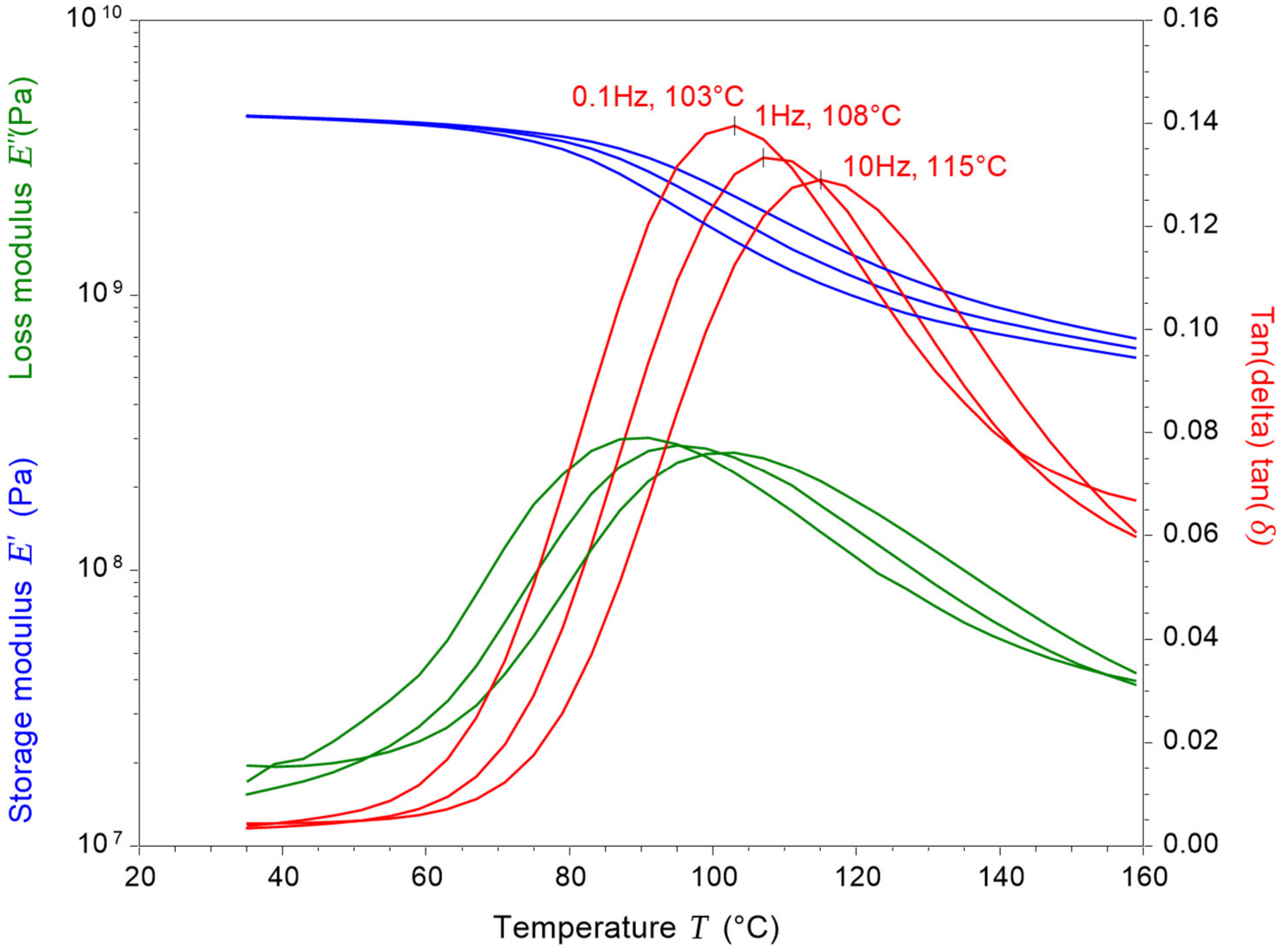
- Heating rate
  - Thermal lag

- Test frequency

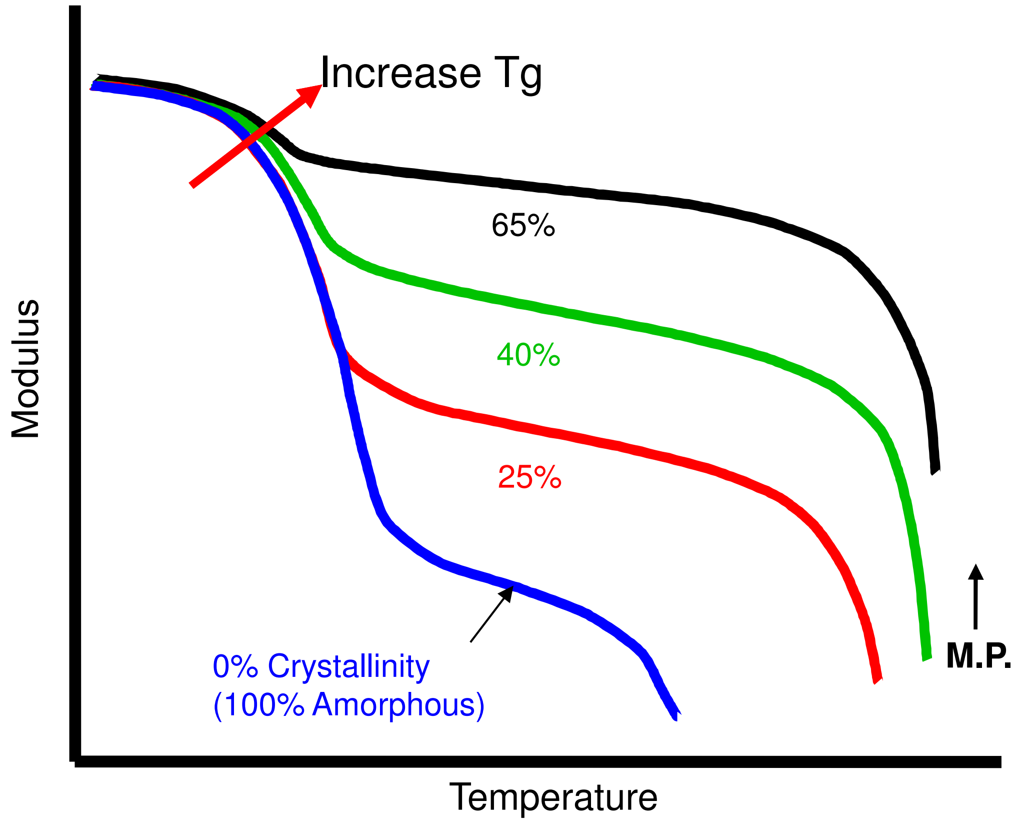
- Polymer structures
  - Rigid polymer chain shows higher T_g (e.g. PS)
  - Flexible polymer chain shows lower T_g (e.g. PE)
  - Crystallization
  - Degree of crosslinking

PET Film: Effect of Frequency on T_g

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



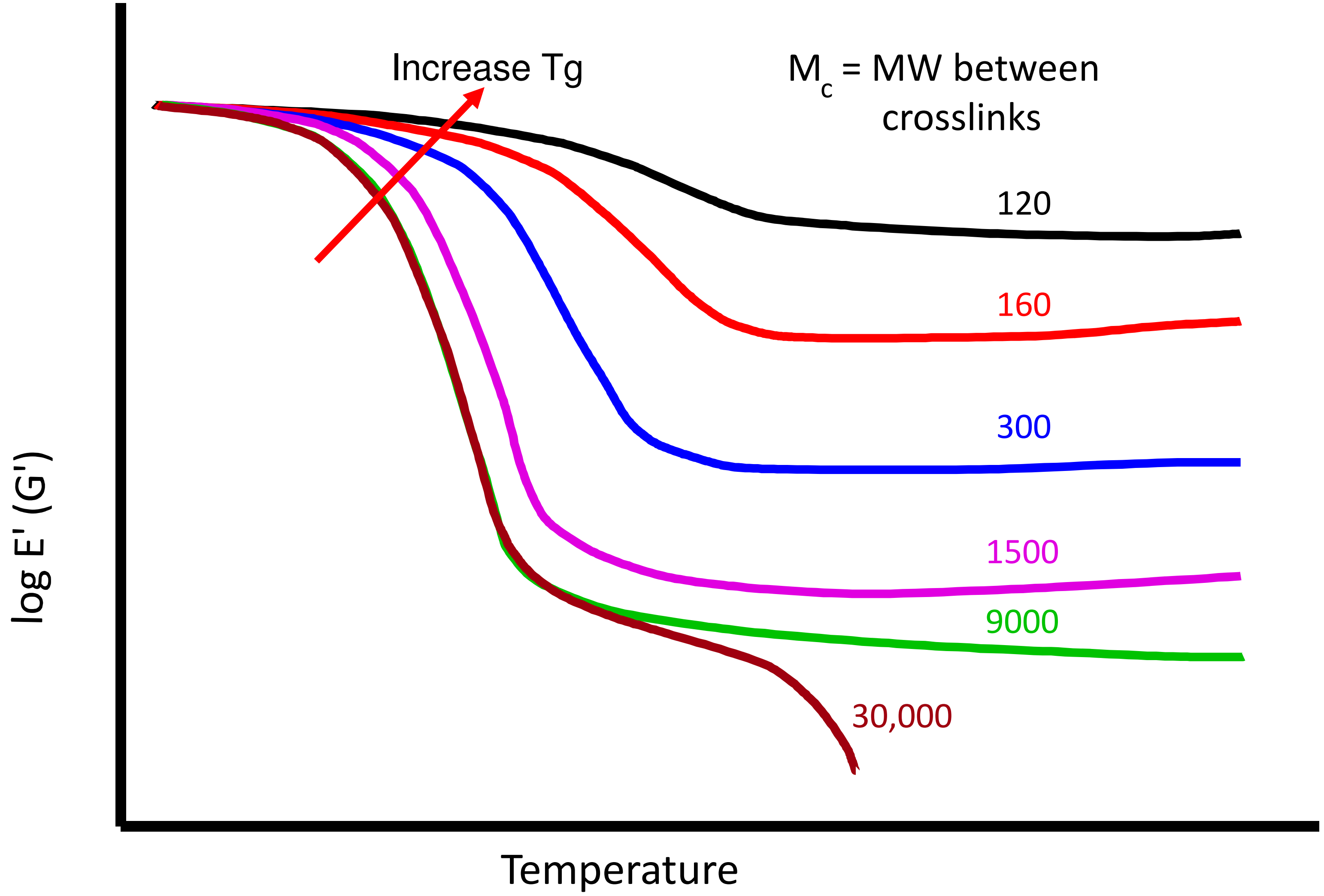
Effect of Crystallinity on Modulus



- Crystallinity mostly affects the sample at $T_g < T < T_m$,
- Below T_g the effect on the modulus is small
- The modulus at $T > T_g$ of a semi-crystalline polymer is directly proportional to the degree of crystallinity
- Remains independent of temperature if the amount of crystalline order remains unchanged

Cowie, J.M.G., Polymers: Chemistry & Physics of Modern Materials, 2nd Edition, Blackie academic & Professional, and imprint of Chapman & HallBishopbriggs, Glasgow, 1991p. 330-332. ISBN 0 7514 0134 X

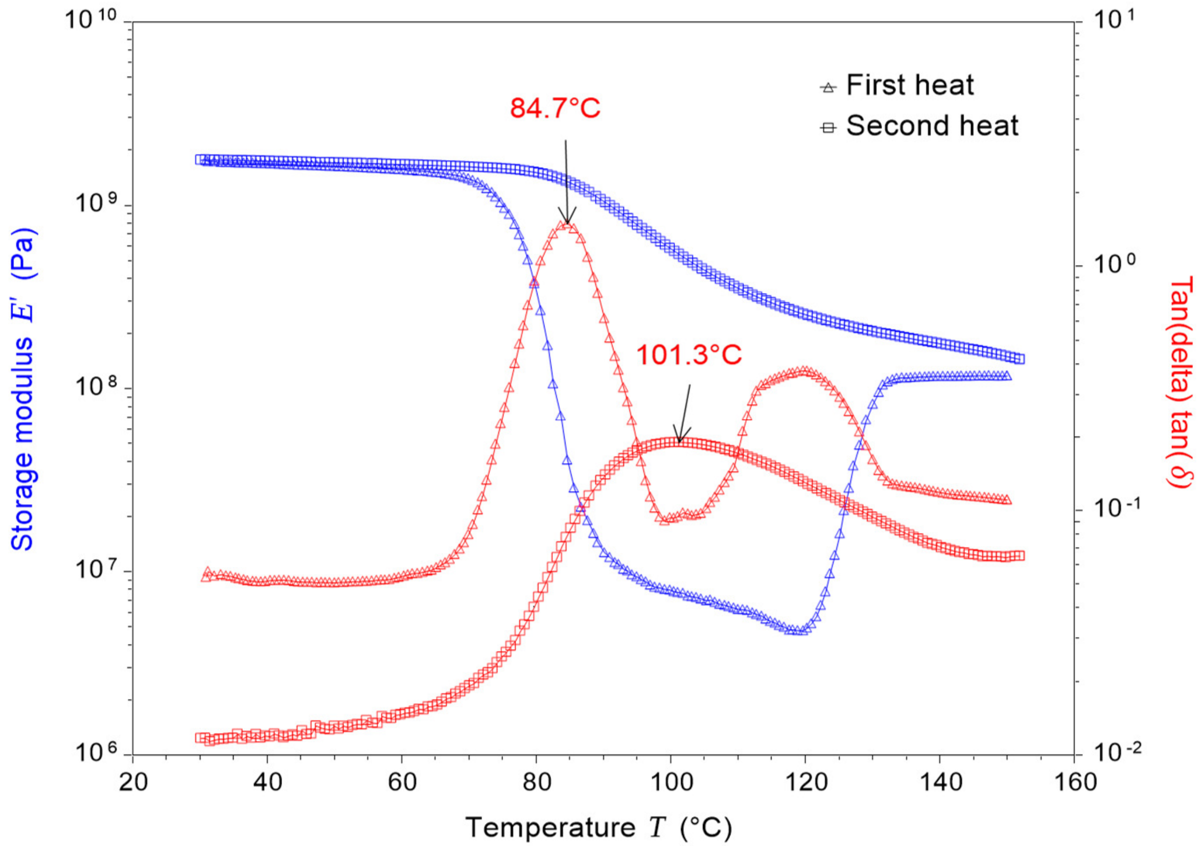
Effect of Crosslinking

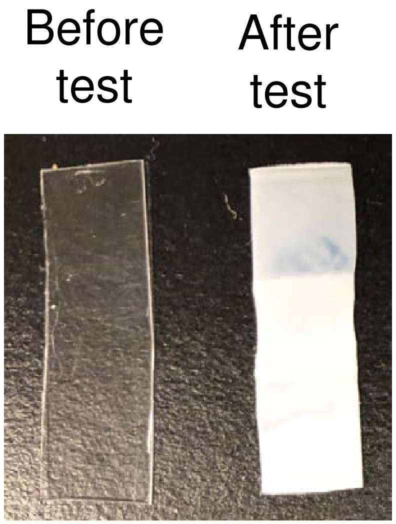


PET: Heat-Cool-Heat Test

In second heat:

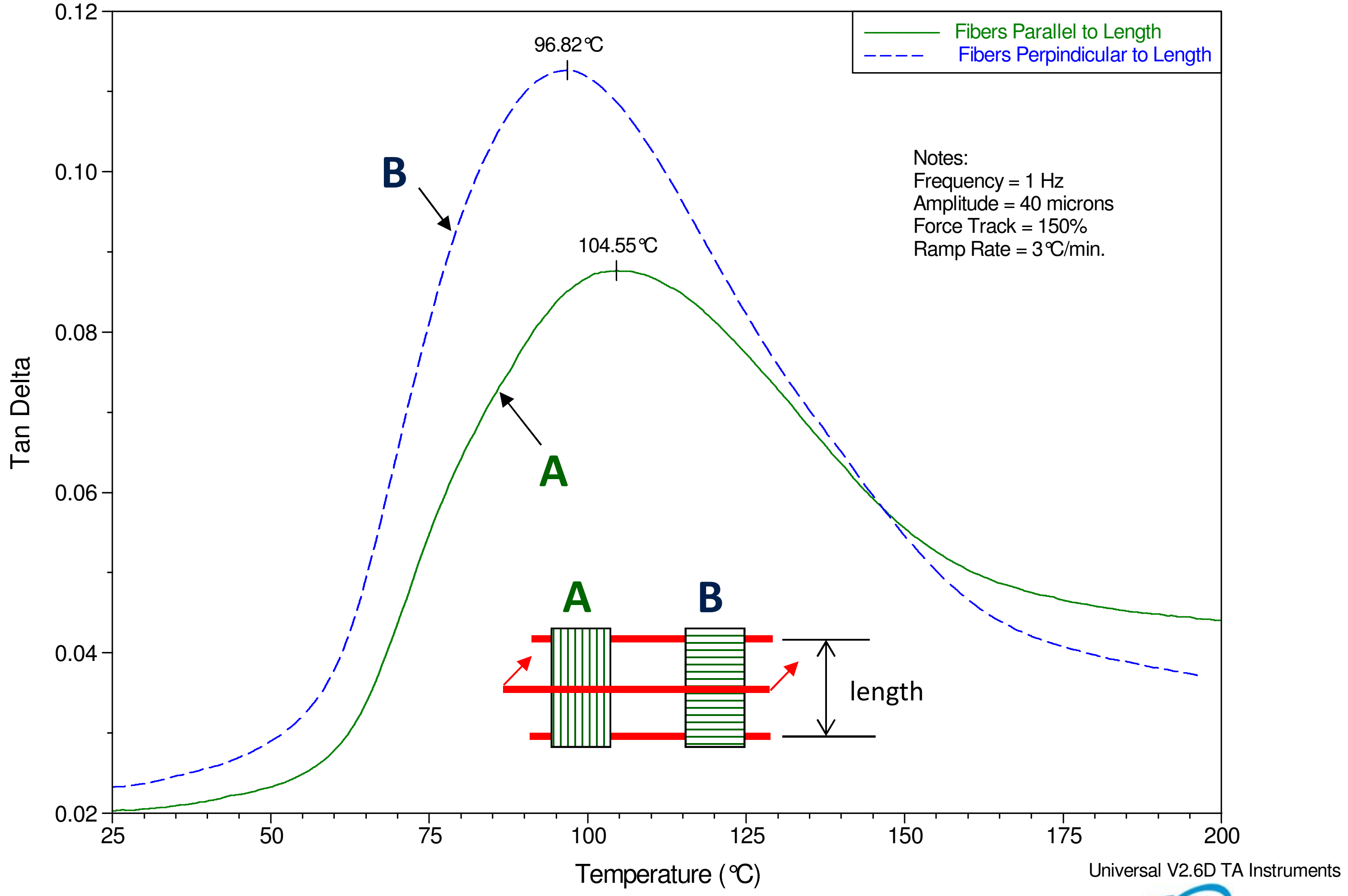
- Tg shifted to higher temperature
- Transition becomes much broader and weaker
- Rubbery plateau modulus increased more than one decade



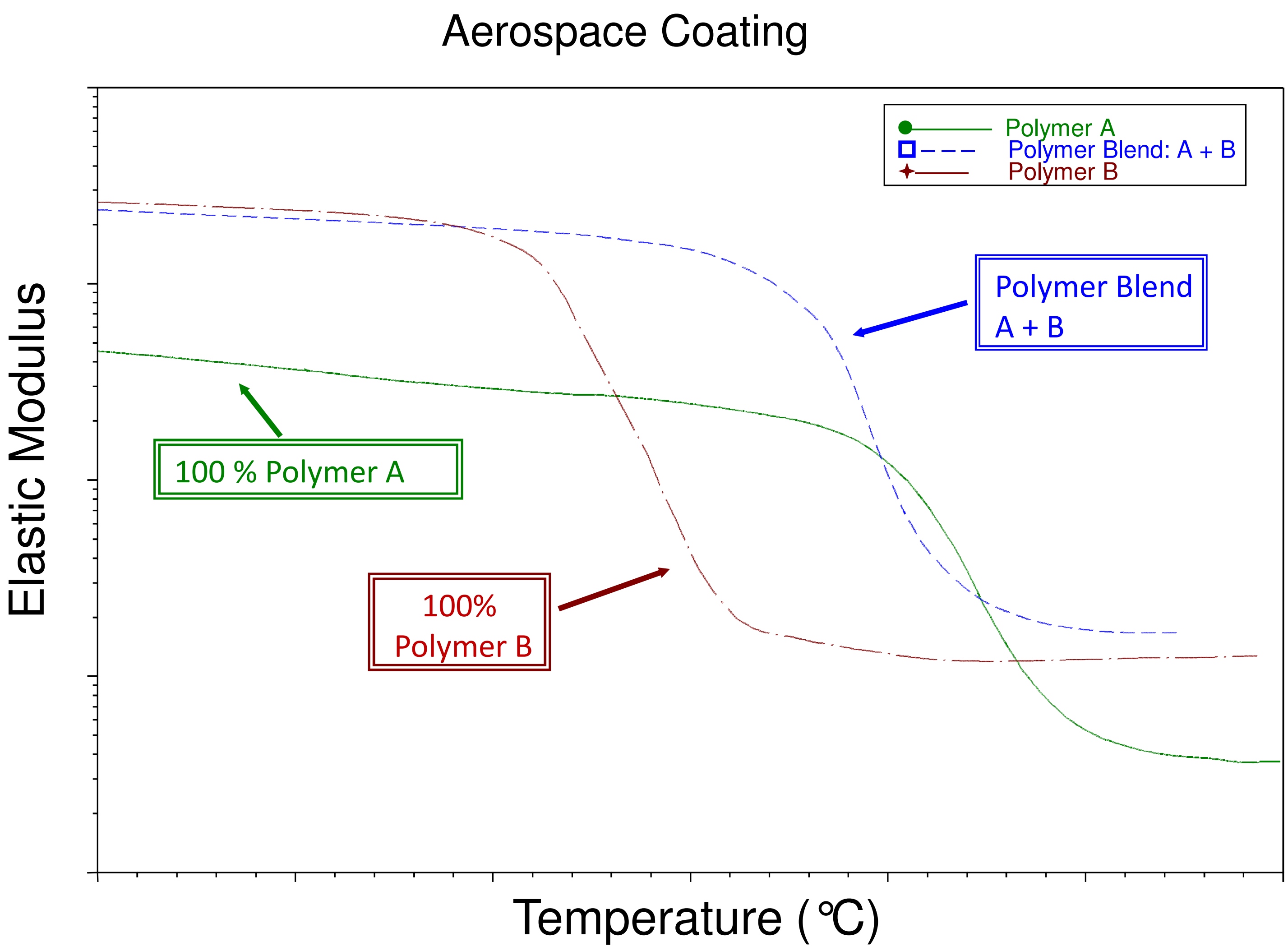


Anisotropic Material

- Polyester/Glass Fiber Reinforced Composite



Polymer Blend – Miscible Case



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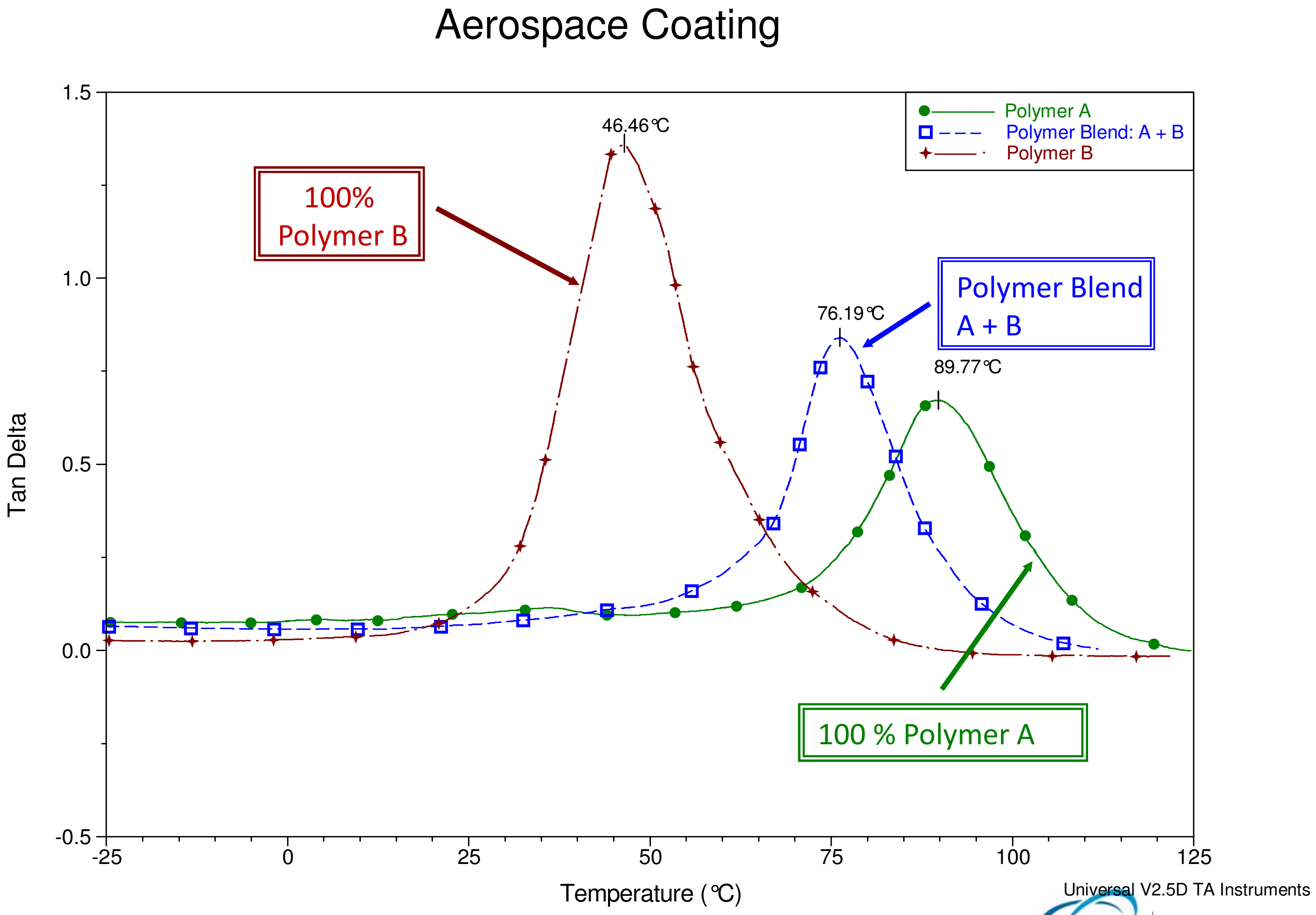
Polymer Blend – Miscible Case



100%
Polymer B

Polymer Blend
A + B

100 % Polymer A

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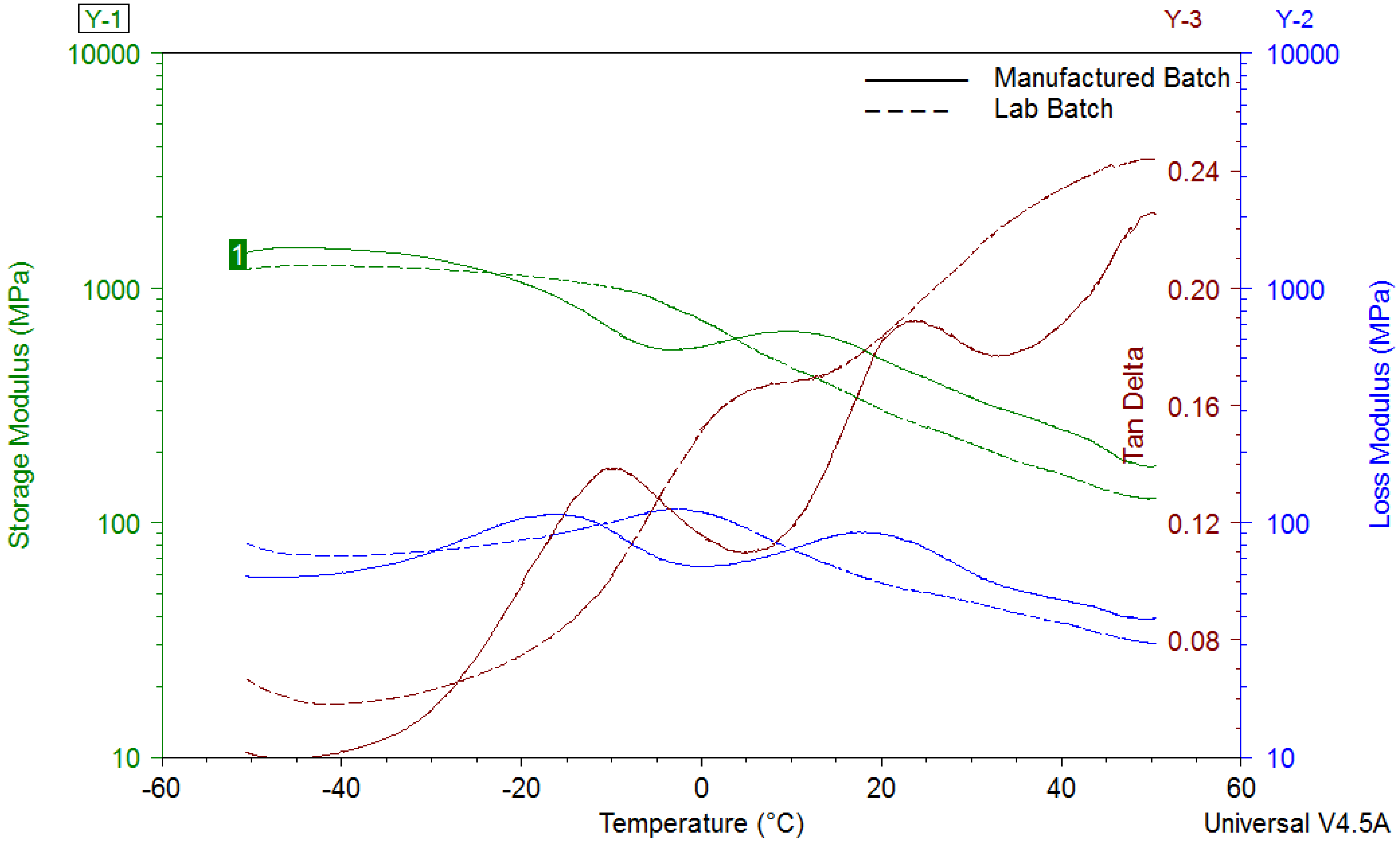
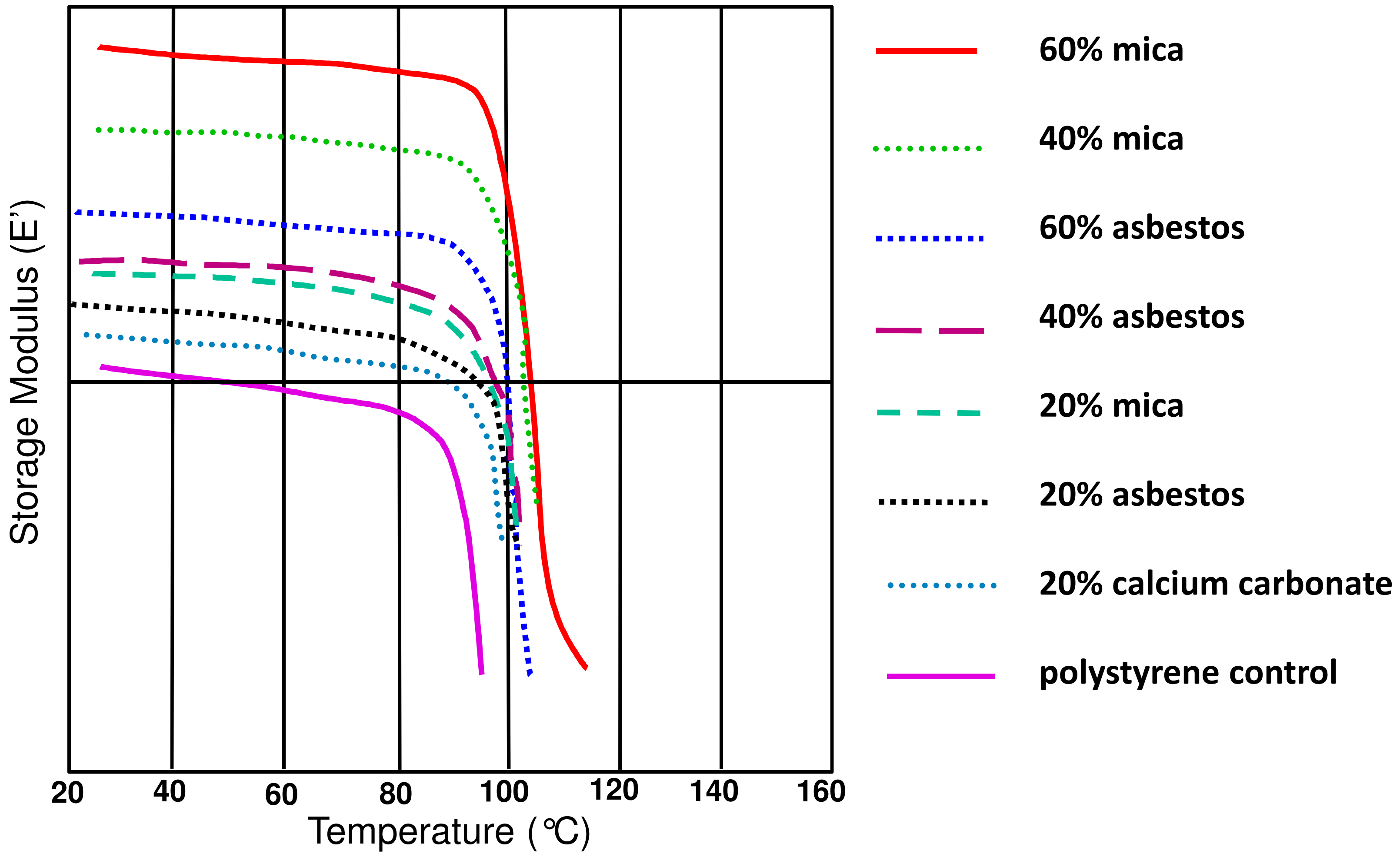
Using Glass Transition to Evaluate Blending

- Investigating manufacturing blend uniformity

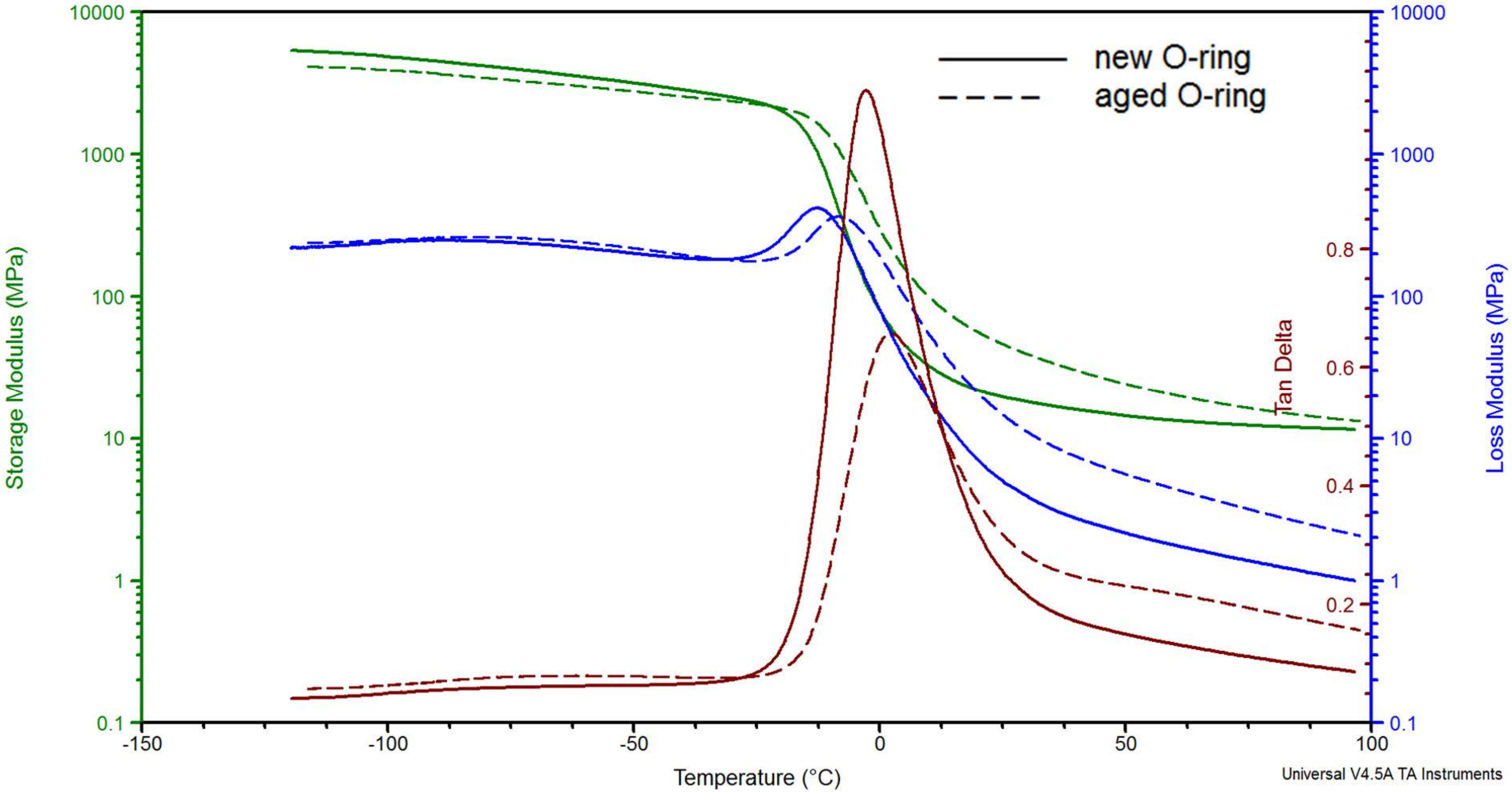


Effect of Filler on Modulus

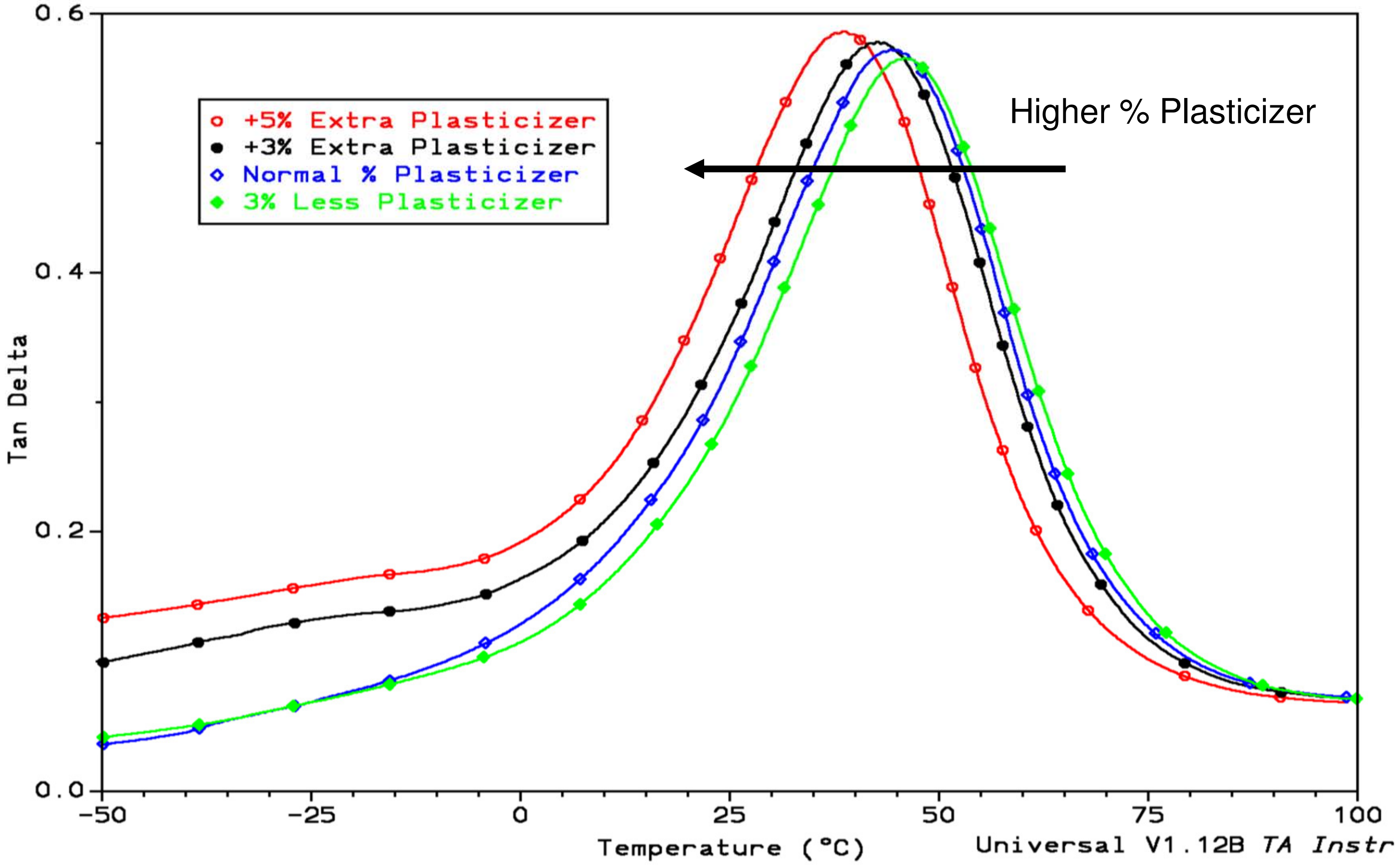


Nielson, L. E., Wall, R. A., and Richmond, P. G., **Soc. Plastics Eng. J.**, **11**, 22 (1966)

Effect of Aging on Elastomer O Rings

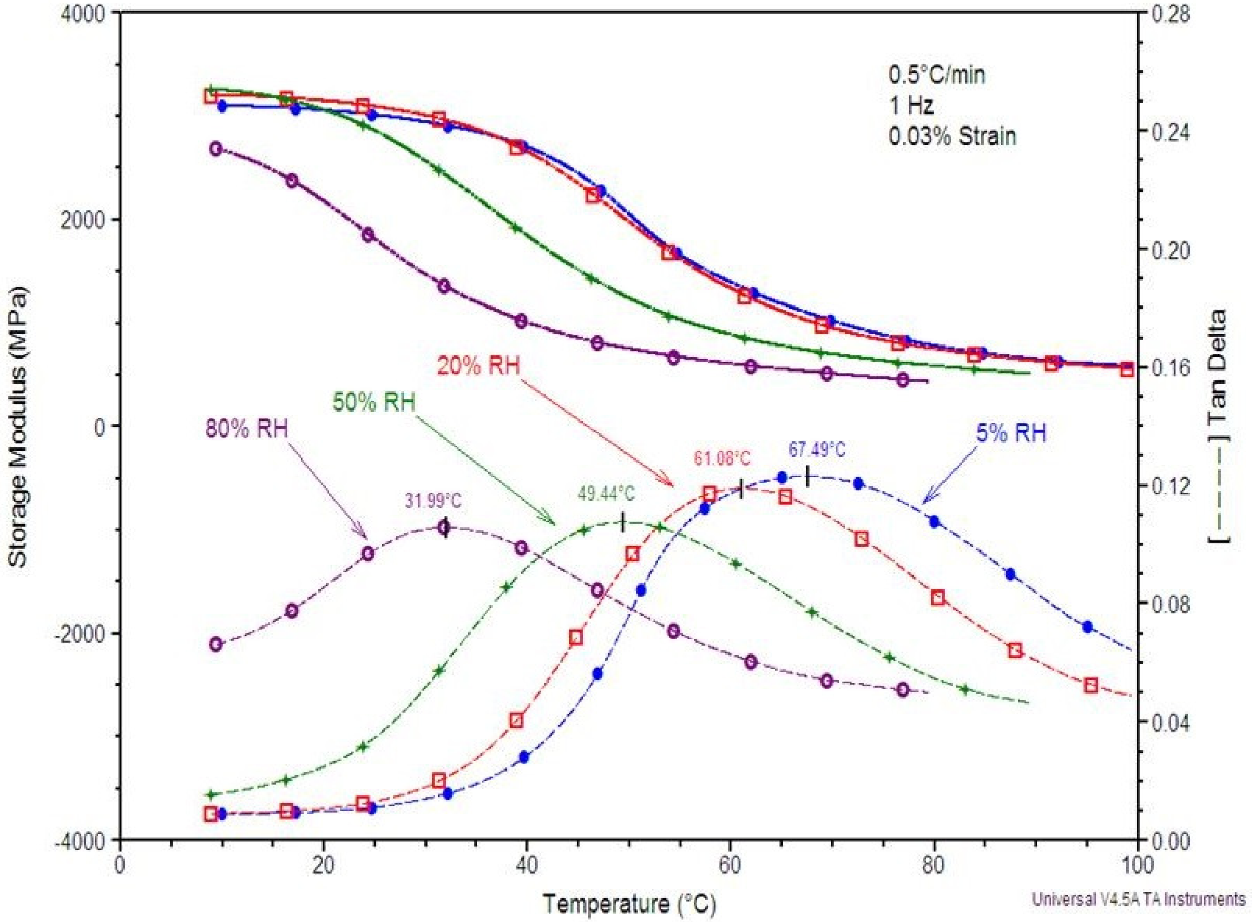


Effect of Plasticizer on Vinyl Flooring



Higher % Plasticizer

Humidity Influence: Nylon Film



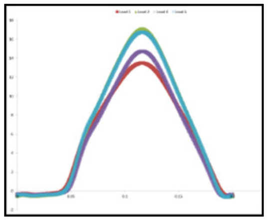
BR Rubber

Tension Fatigue

Purpose of Study

- Compare tensile fatigue of rubber compounds for tire beads
- Evaluate rubber lifetime at expected service temperatures

Test Method



- Pulse waveform
- 70°C Ambient
- 2.774Hz (30km/hr)
- Stress Ratio ~0.1

Material & Geometry

- Tension dog-bone samples
- Approx 2mm x 3mm mid-section x 10mm long

Instrument

- ElectroForce 3330 (3000 N)
- Temp Chamber
- Multi-Specimen Fixture

BR Rubber

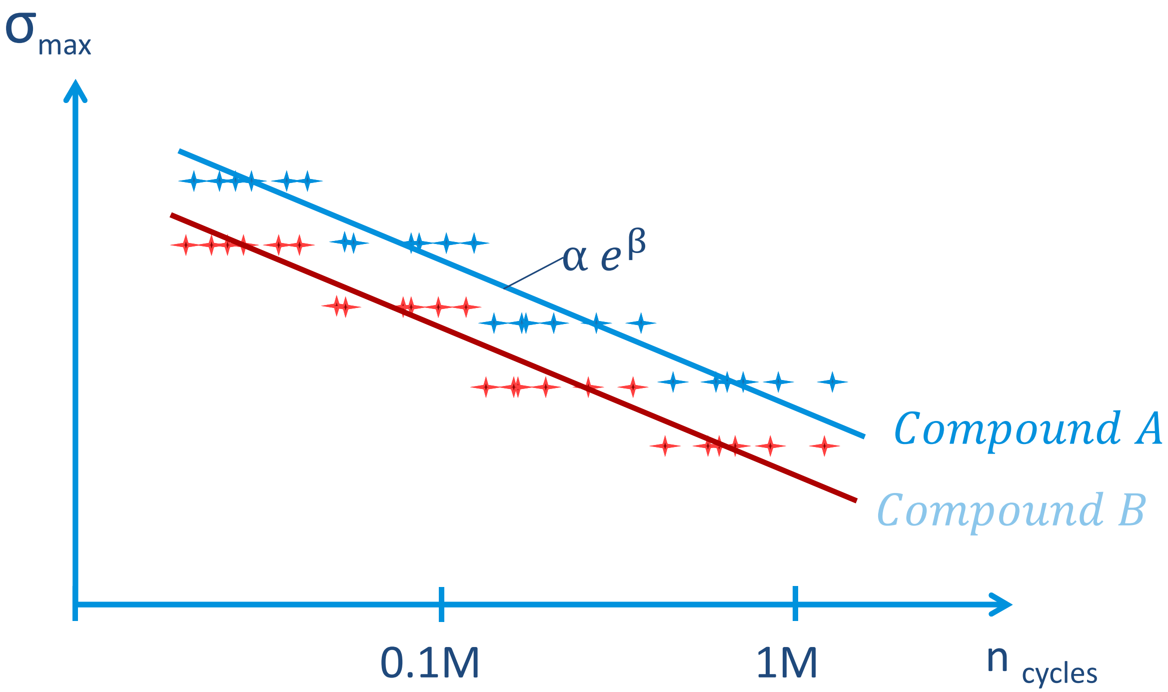
Tension Fatigue

6-Specimen Fixture
with Load Sensors

BR Rubber

Tension Fatigue

- Stress/Number of cycles (SN) curve obtained.
- Data is fit to exponential line
- Data and exponential fit is used to compare materials



Notice that there are 6 points in each grouping. This represents the 6 samples simultaneously loaded to a common strain level. So, the stress for each group is roughly the same. But, since samples vary, they fail at different times so we see the scatter as a line of points.

Troubleshooting

Experimental Issues

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

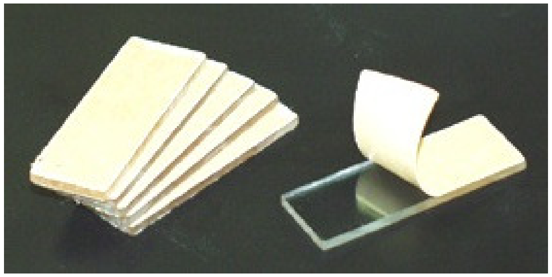
  E' = 2.35 GPa (2350 MPa) +/- 5%
- Tan Delta at Room Temperature

  Tan δ < 0.01
- Transition Temperature

  Tan δ peak between 155-160℃ @ 1Hz, 3-5℃/min

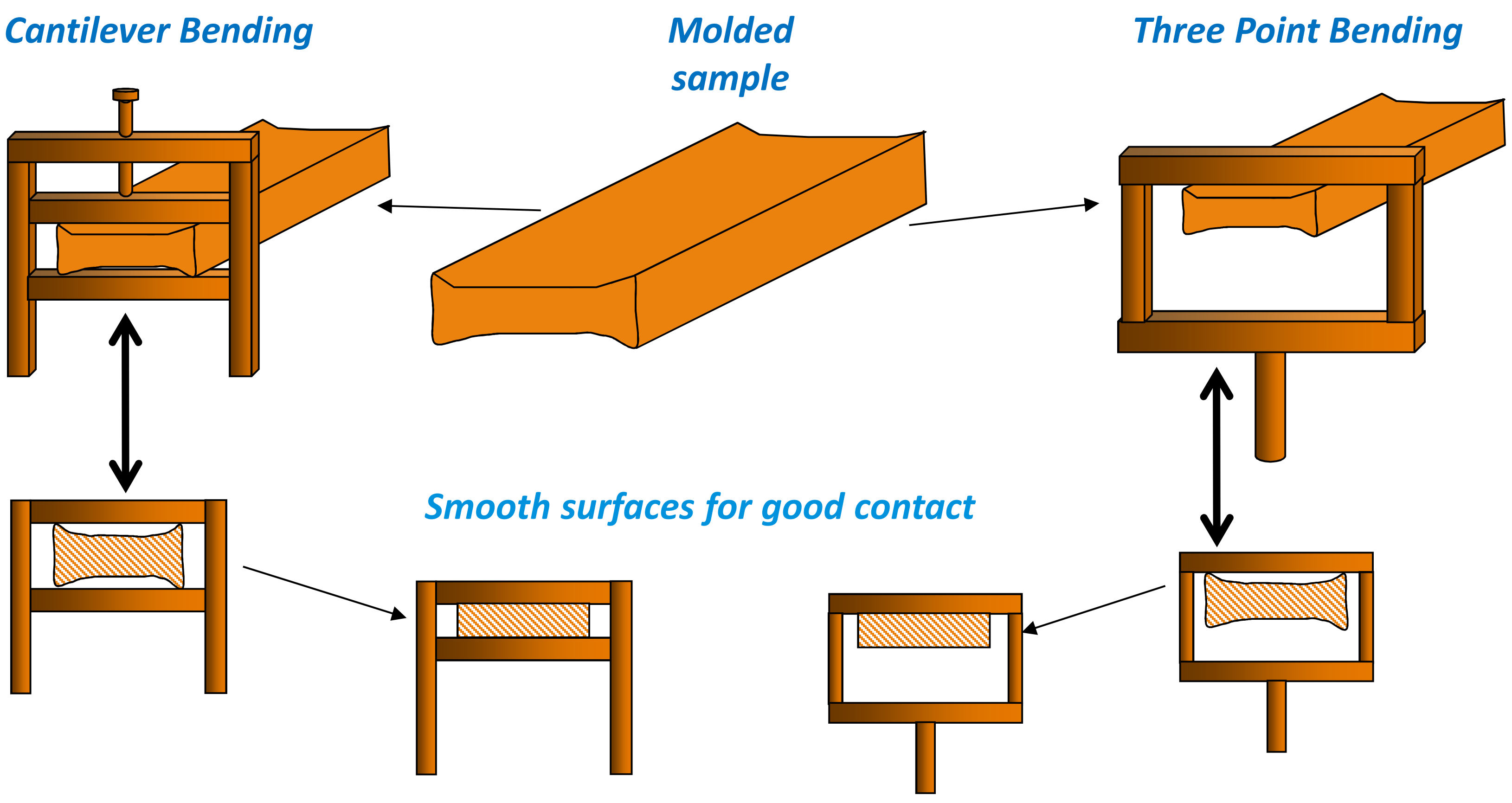
  E" peak will be about 5℃ lower

p/n: 982165.903

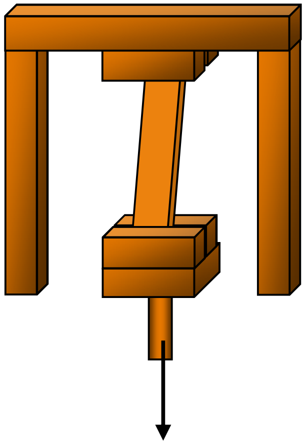


Preparing Samples – The Importance of Shape

Shape: Molded samples are often not flat. May lead to poor contact in Cantilever and Three Point Bend Clamps. Sand samples smooth.

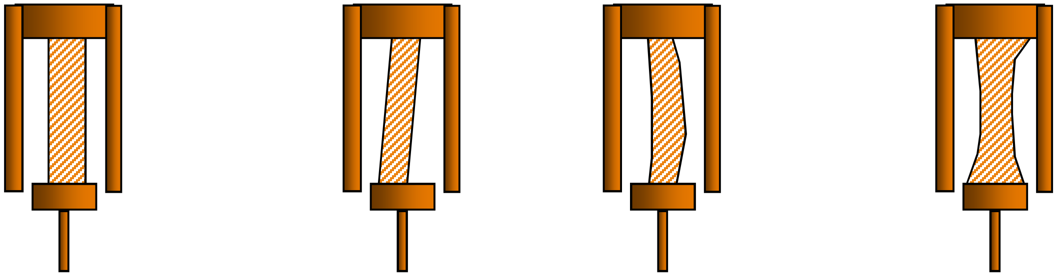


Alignment in Tension Mode



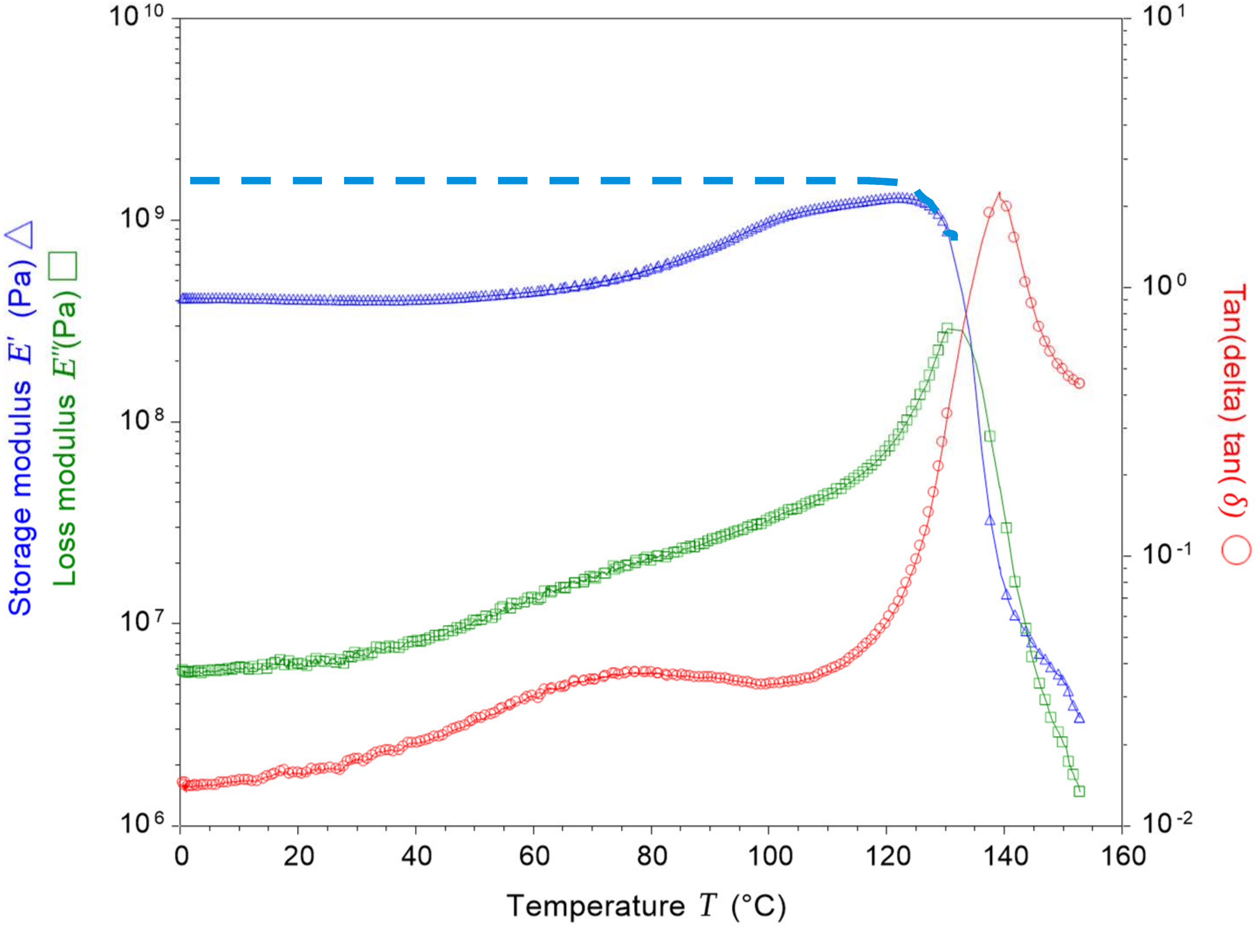
If sample buckles during Oscillation. Modulus will be artificially low.

- Buckling during loading causes serious errors as buckled areas do not “feel” the force or deformation
- Buckling can be the result of non-uniform stretching, or crooked loading of a film.
- Observe film from edge while oscillating to verify goodness of load.
- If sample is buckling, reload a new sample.



E’ Increase in a Temp Ramp

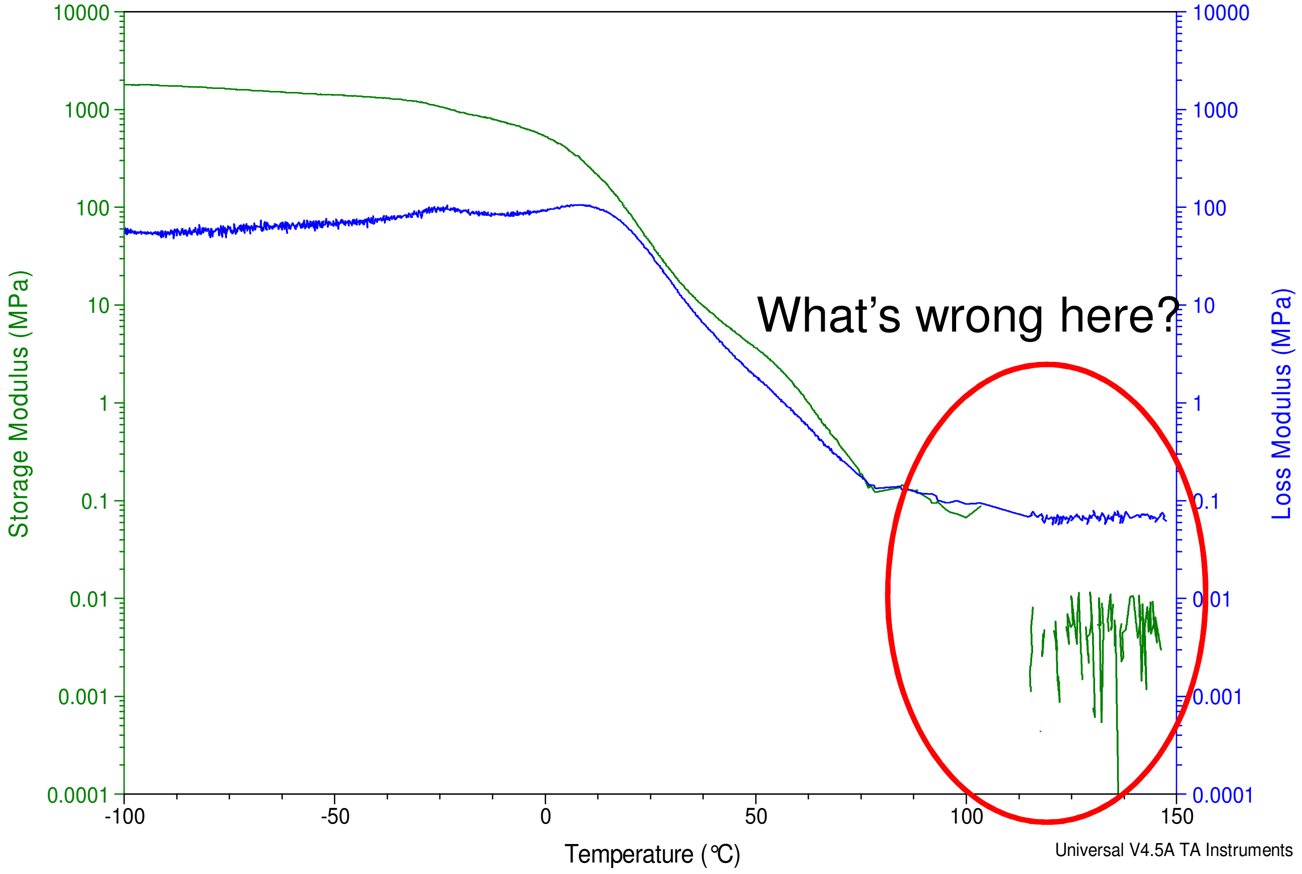
- The E’ of a material should not increase with temperature unless it is crystalized or crosslinked



Instrument: DMA850
Clamp: tension
Temperature:
0℃ to 180℃
Heating rate: 3℃/min
Frequency: 1Hz
Amplitude: 10 µm

Noisy Modulus After Tg

What is the problem with this data collected after T_g?

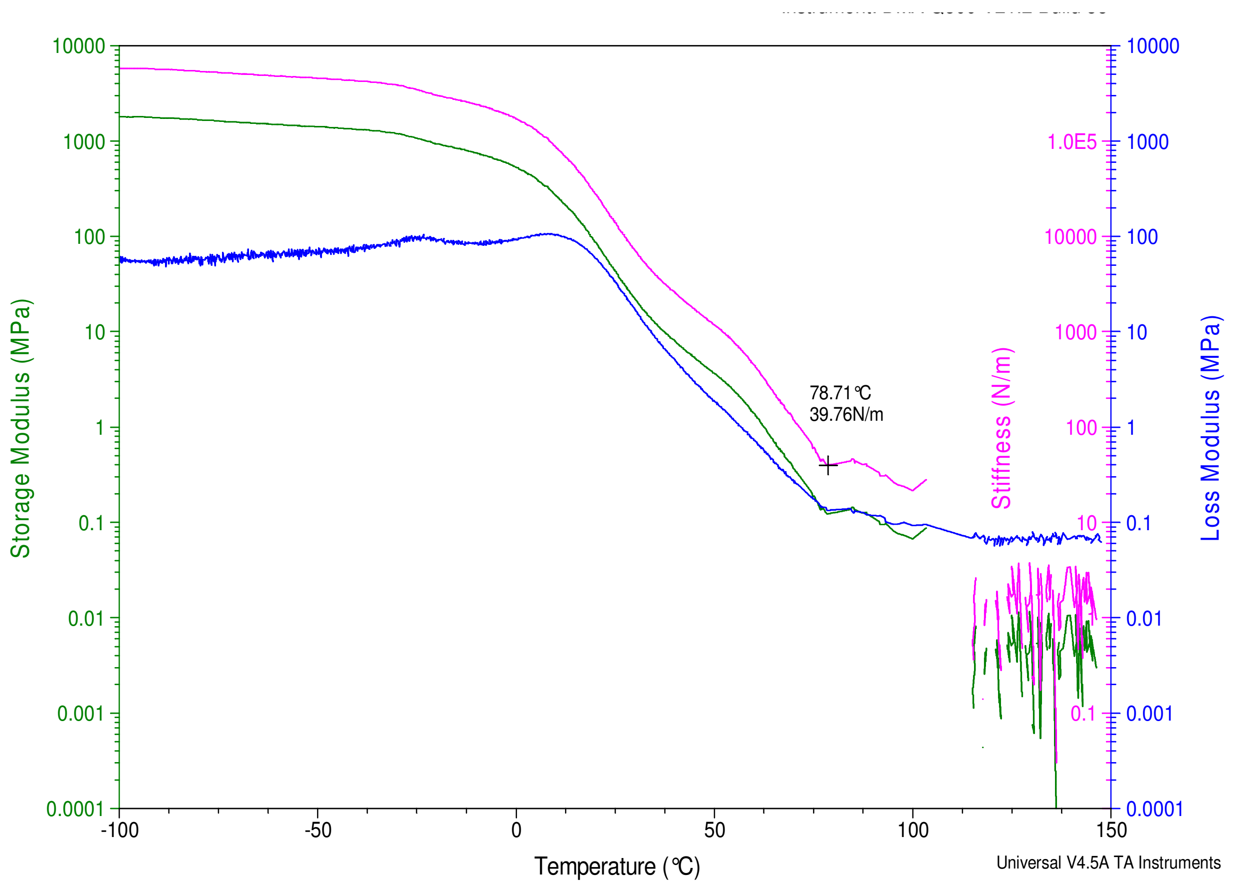


What's wrong here?

Instrument: Q800
Clamp: tension
Temperature:
-100℃ to 150℃
Heating rate: 3℃/min
Frequency: 1Hz
Amplitude: 10 µm

Noisy Modulus After Tg

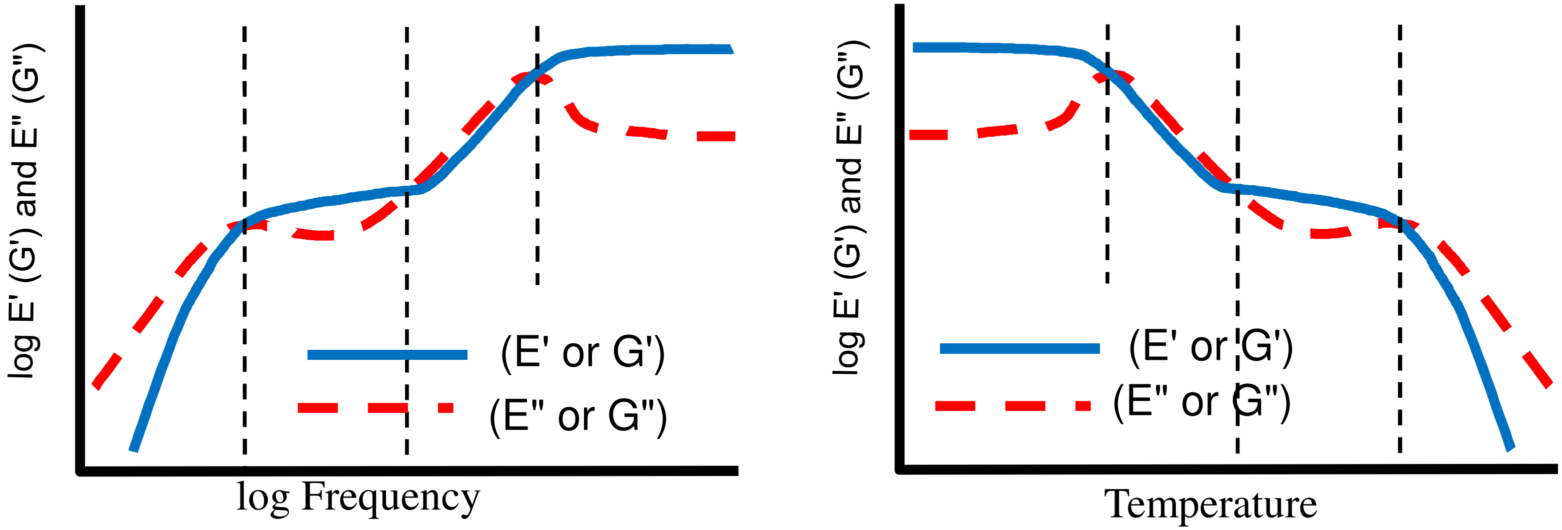
Sample stiffness is below the instrument spec. (100N/m)
Solution: Increase the sample stiffness (wider, thicker, shorter)



Instrument: Q800
Clamp: tension
Temperature:
-100℃ to 150℃
Heating rate: 3℃/min
Frequency: 1Hz
Amplitude: 10 µm

Time-Temperature Superposition (TTS)

Time and Temperature Relationship



- Linear viscoelastic properties are both time and temperature dependent
- Some materials show a time dependence that is proportional to the temperature dependence
  - Decreasing temperature has the same effect on viscoelastic properties as increasing the frequency, and vice versa
- For such materials, changes in temperature can be used to “re-scale” time, and predict behavior over time scales not easily measured

Time Temperature Superpositioning Benefits

- TTS applies to materials that are thermo-rheological simple. When all relaxation times have the same temperature dependence
- TTS can be used to extend the frequency beyond the instrument’s range. Frequency is correlate to time and shear
- Creep or Stress Relaxation TTS can predict behavior over longer times that cannot be practically measured

TTS Limitations

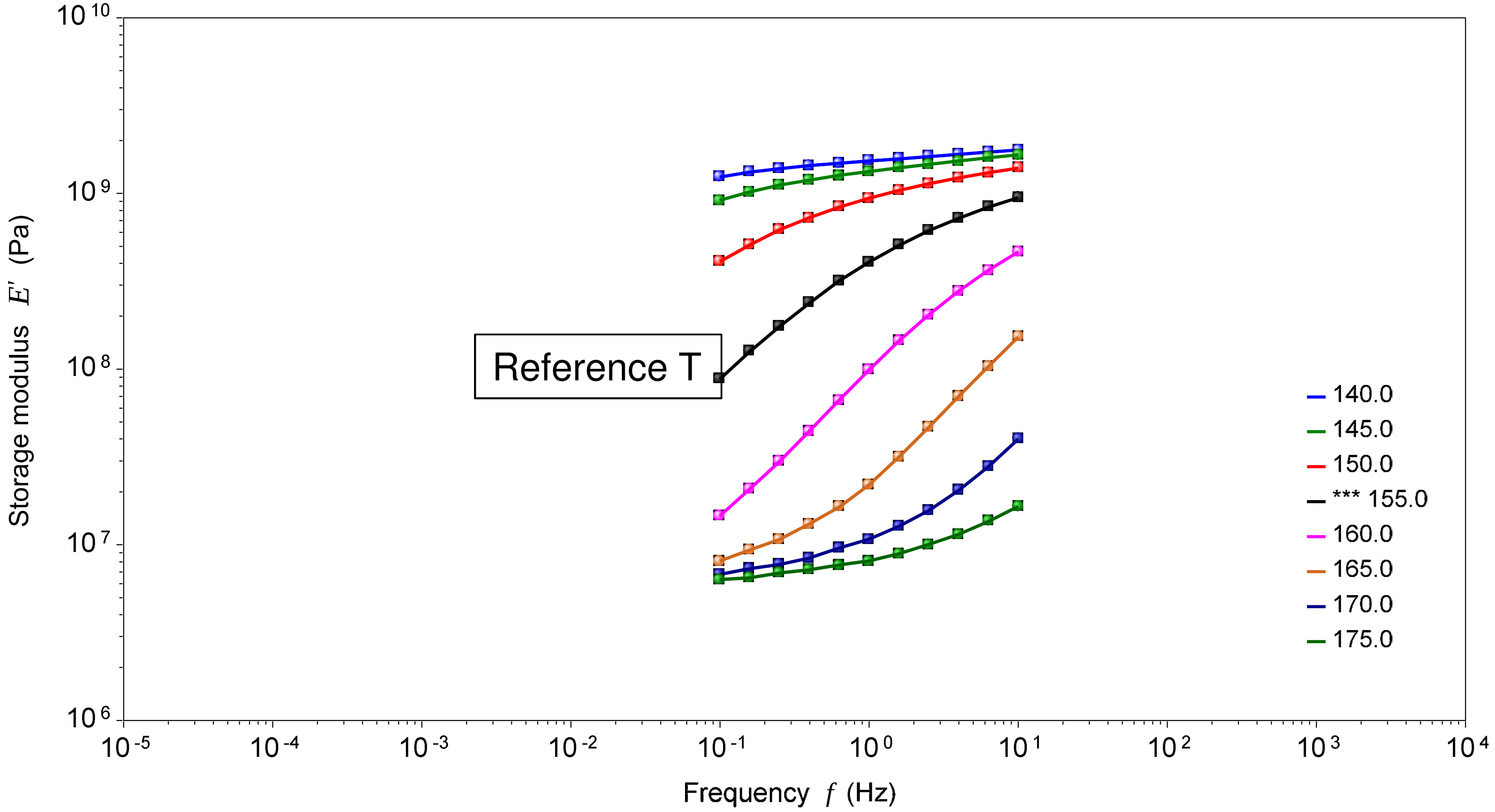
- TTS works with polymers that are thermo-rheological simple
- TTS does not work if:
  - Sample is partially crystalized, crosslinked, or highly filled
  - Sample change properties (e.g. crystalize, melt, cure, decompose) within temperature of interest
  - Polymer contains multiple phases: composite or blends
  - Liquid samples with multiple components
- TTS has been used as empirical rules to predict sample properties over long time scales

Guidelines for TTS

- Decide first on the Reference Temperature: T_0. What is the use temperature?
- If you want to obtain information at higher frequencies or shorter times, you will need to conduct frequency (stress relaxation or creep) scans at temperatures lower than T_0.
- If you want to obtain information at lower frequencies or longer times, you will need to test at temperatures higher than T_0.
- Good idea to scan material over temperature range at single frequency to get an idea of modulus-temperature and transition behavior.

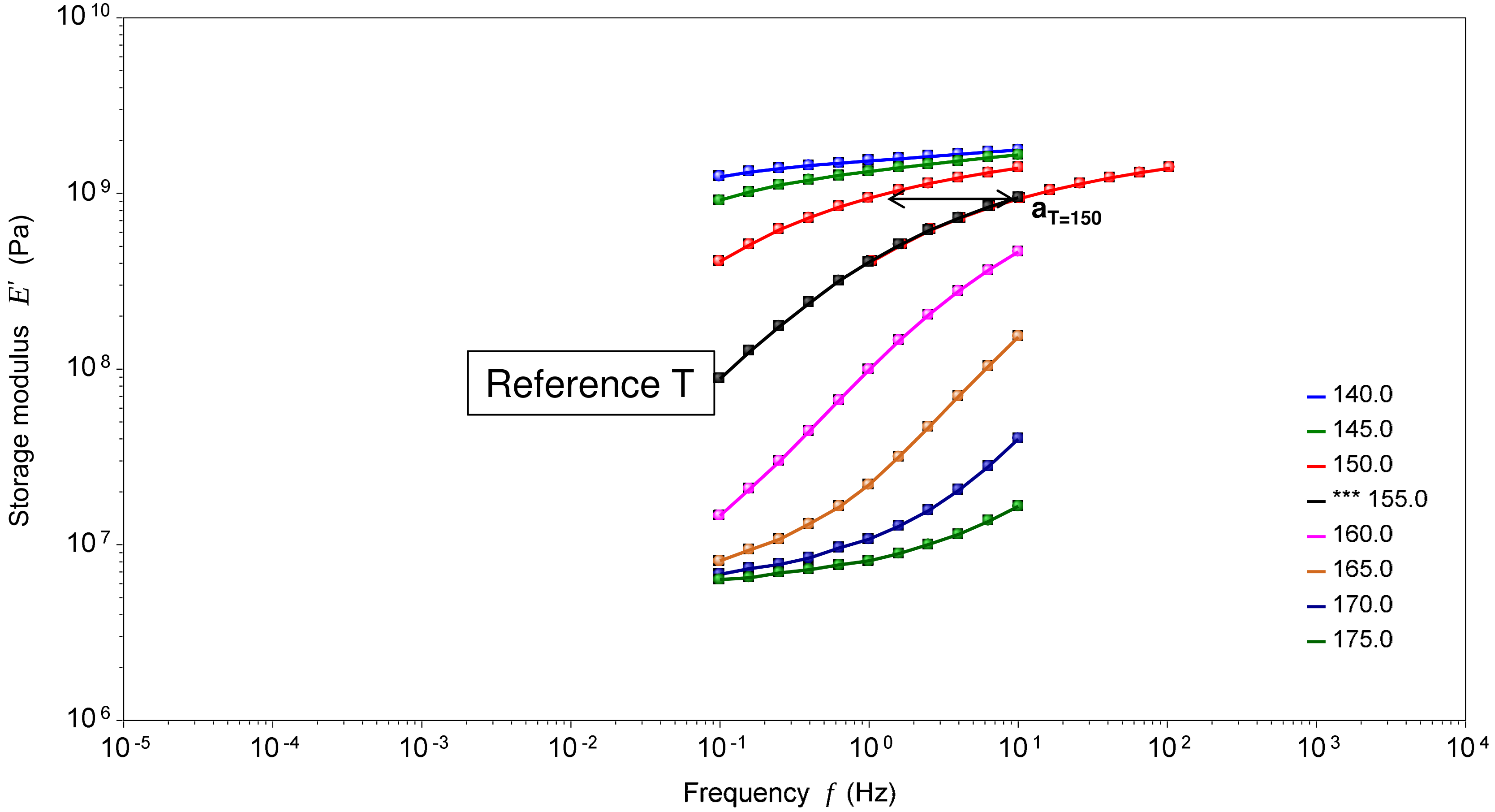
TTS Shifting

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



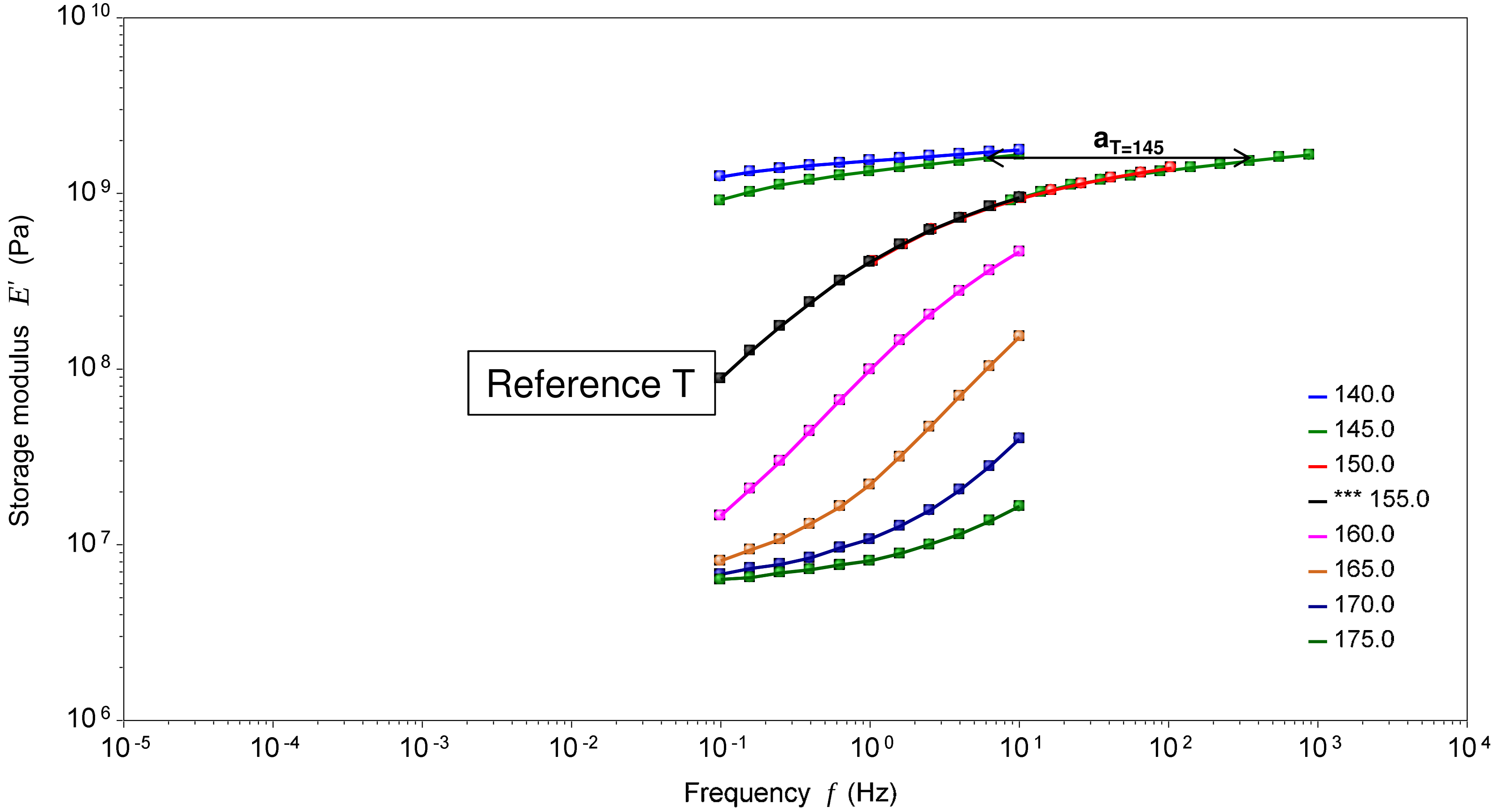
TTS Shifting

- Low temperature data shift to higher frequencies



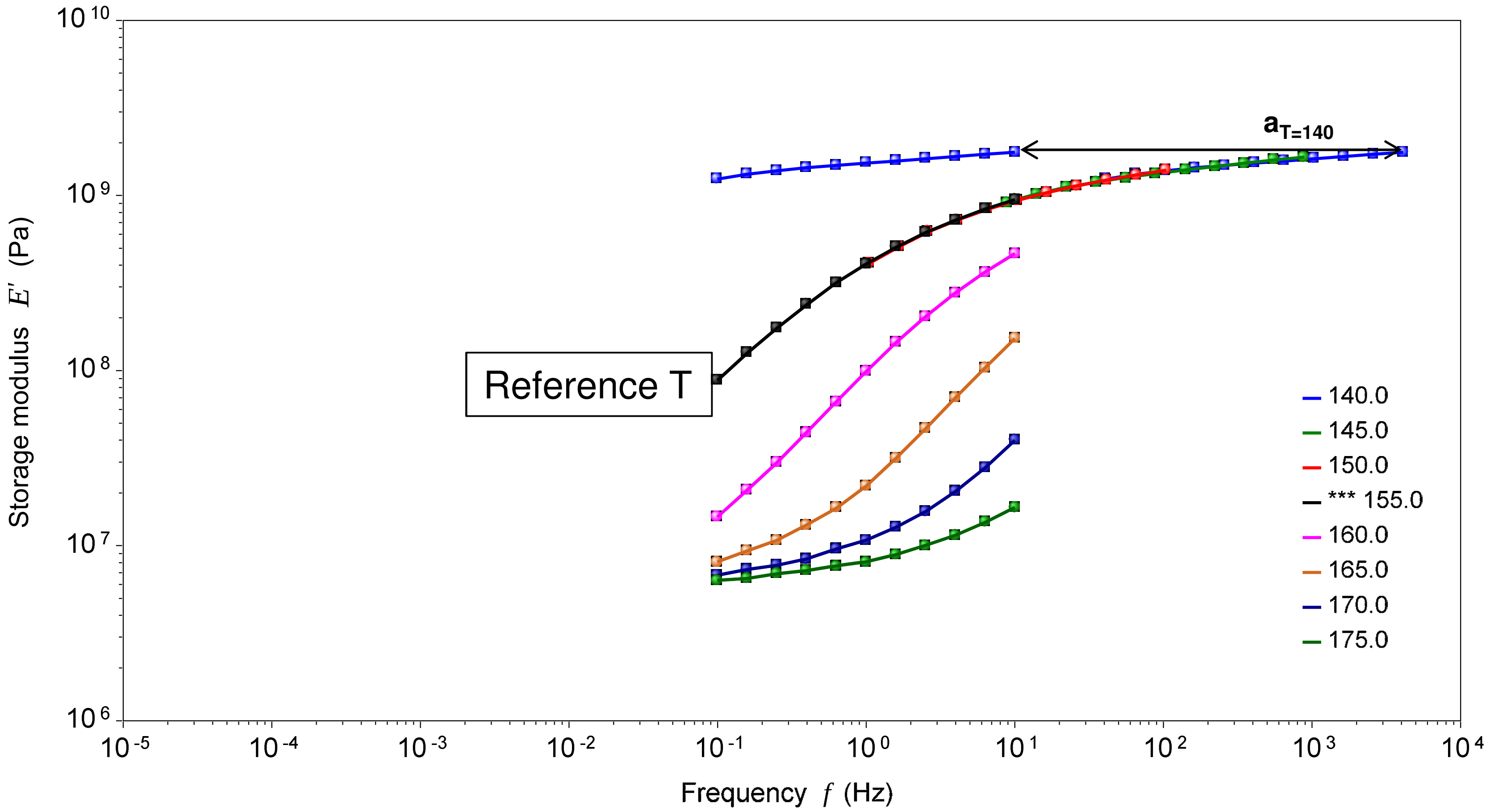
TTS Shifting

- Low temperature data shift to higher frequencies



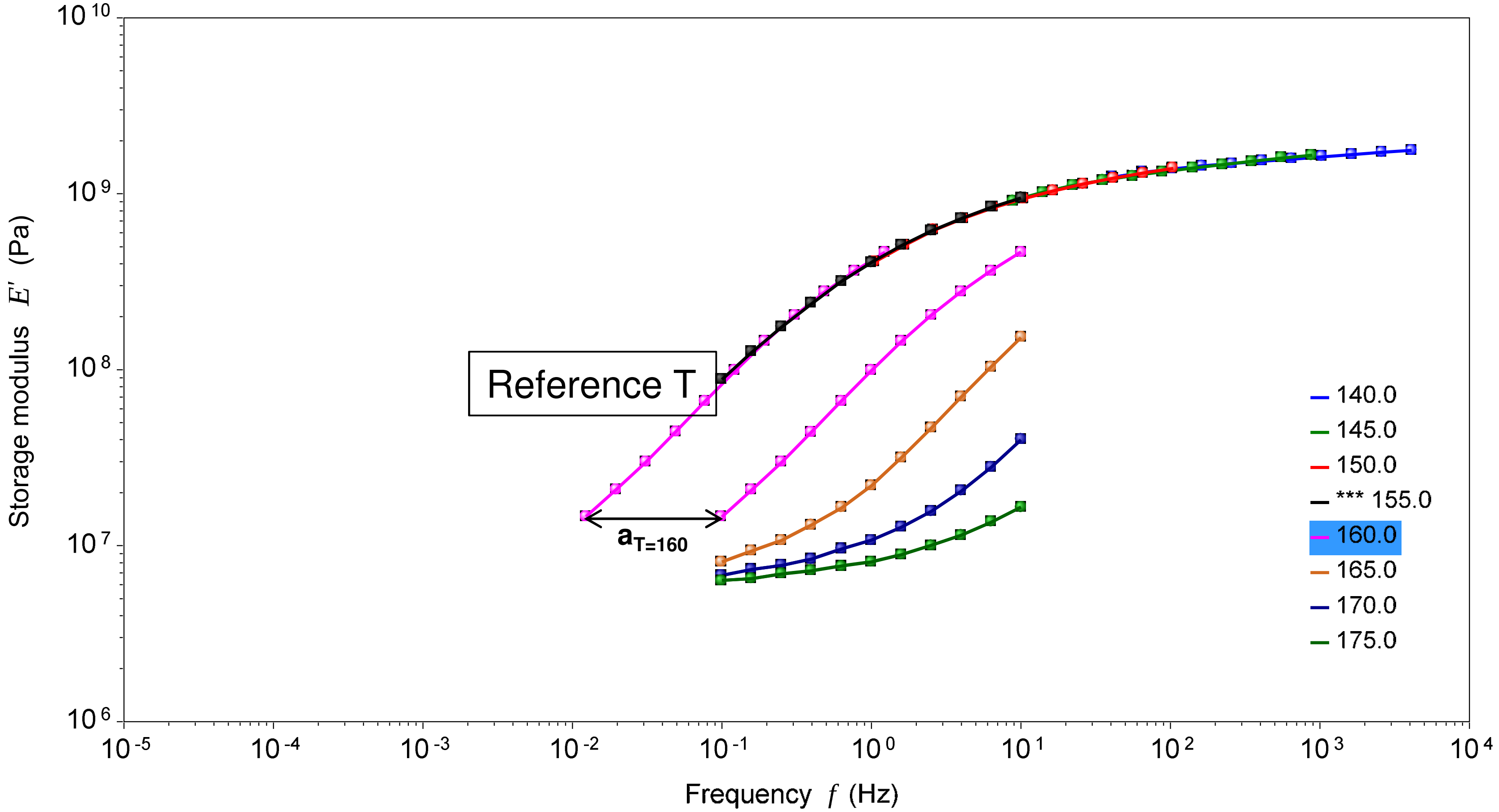
TTS Shifting

- Low temperature data shift to higher frequencies



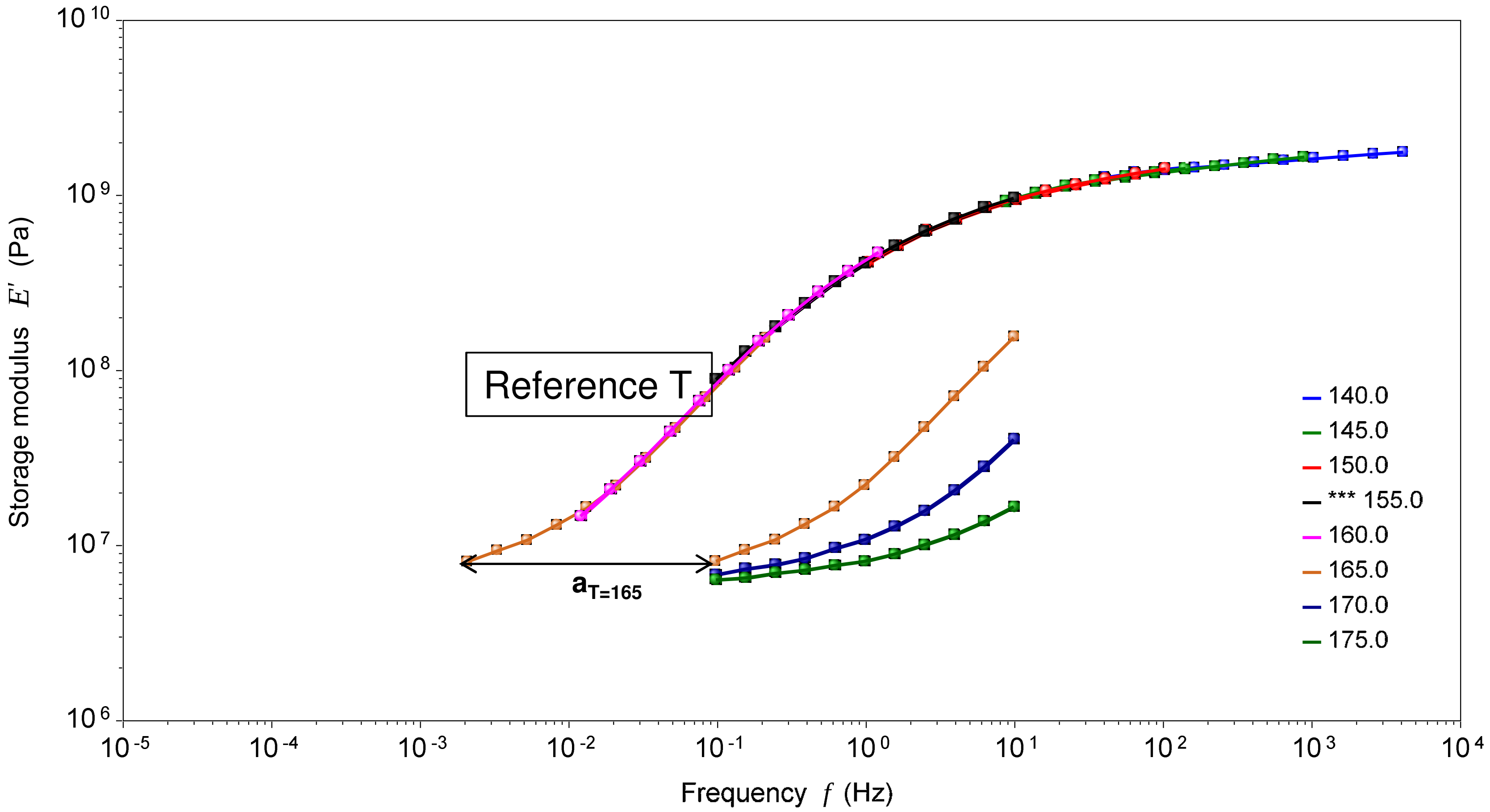
TTS Shifting

- High temperature data shift to lower frequencies



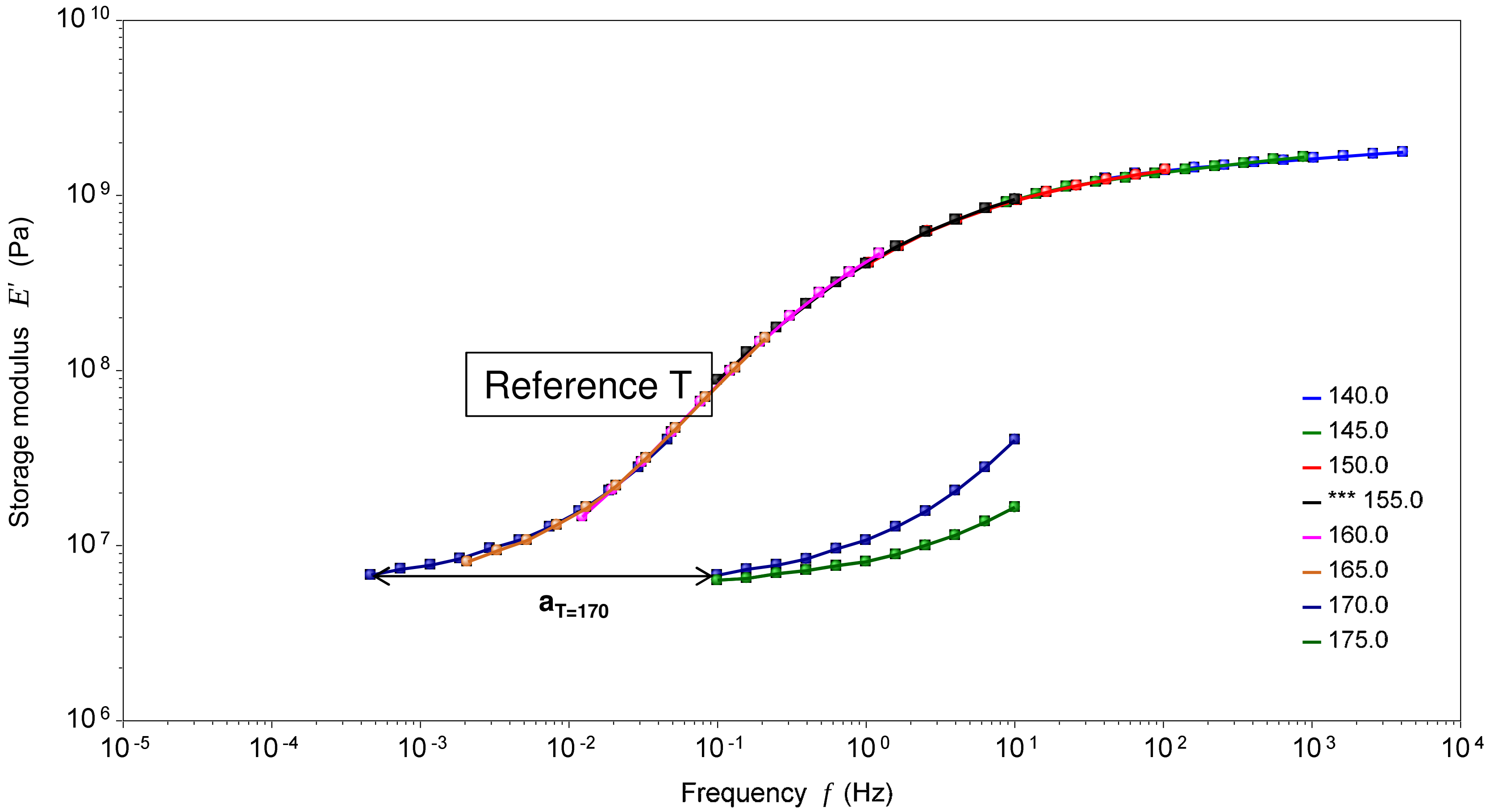
TTS Shifting

- High temperature data shift to lower frequencies



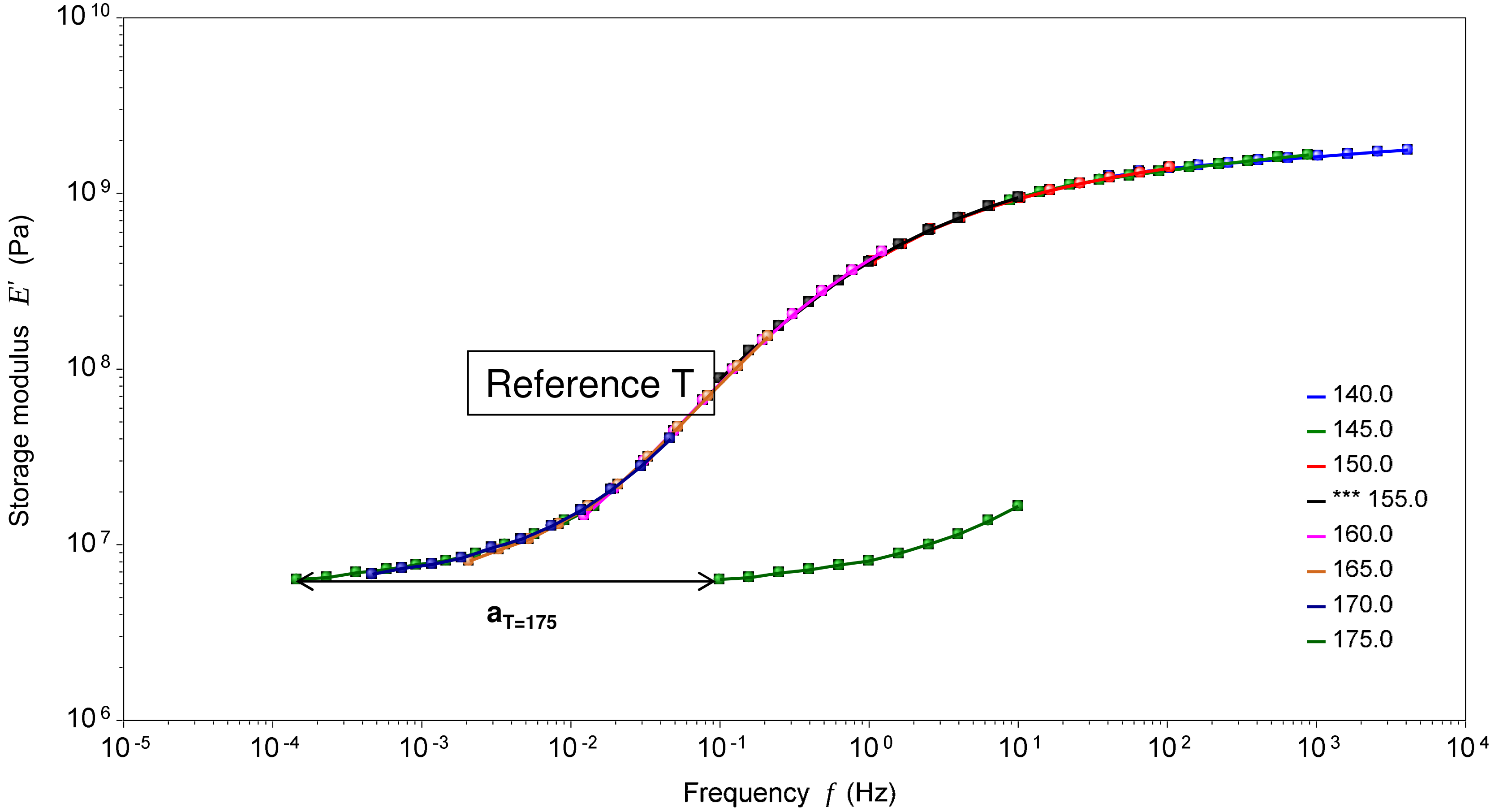
TTS Shifting

- High temperature data shift to lower frequencies



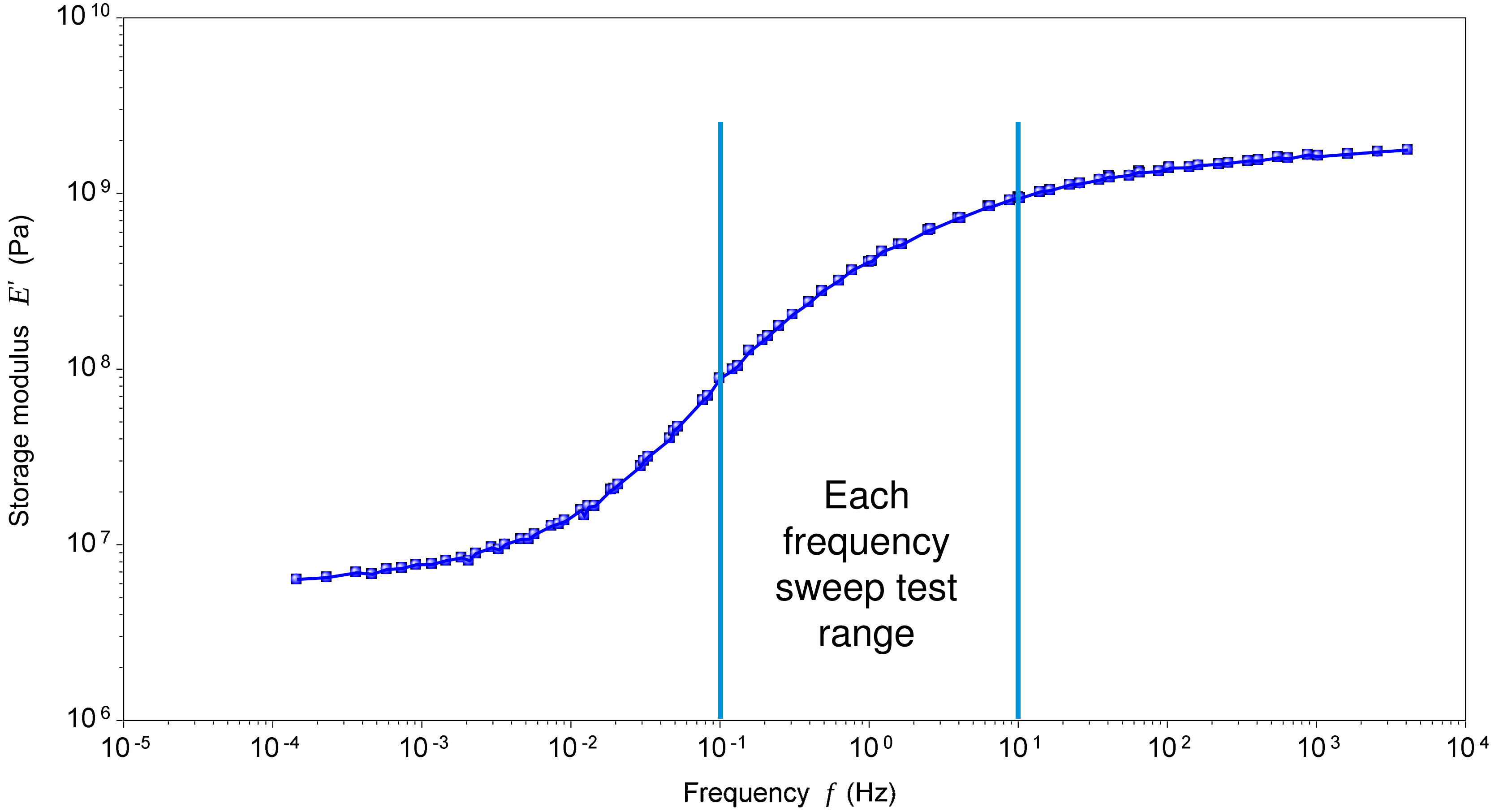
TTS Shifting

- High temperature data shift to lower frequencies



Master Curve from TTS Shifting

- TTS Master Curve using 155℃ as reference



WLF and 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

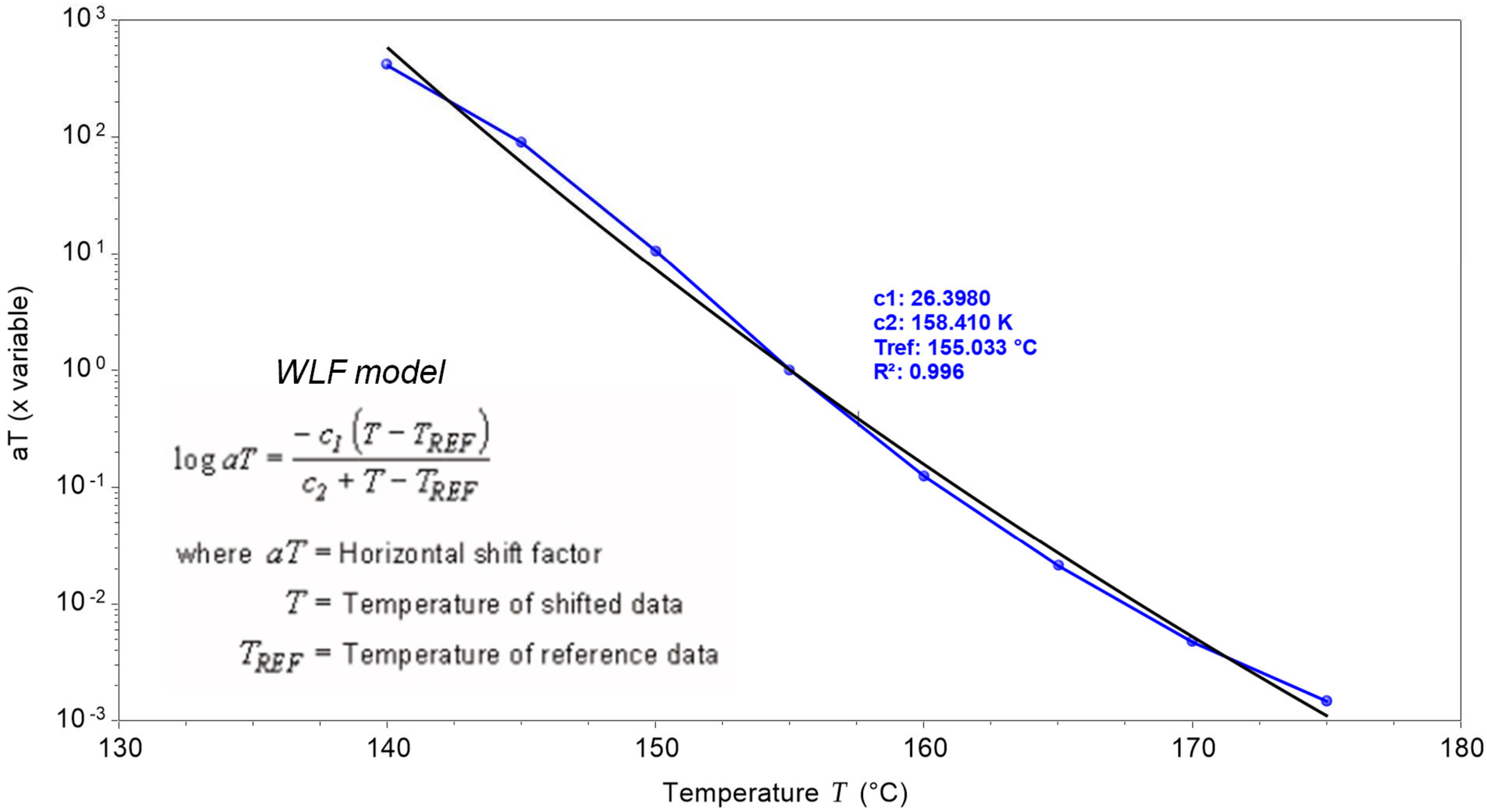
$$\ln a_T = (E_a/R)(1/T-1/T_0)$$

a_T = temperature shift factor E_a = Apparent activation energy

T_0 = reference temperature R = gas constant

Shift Factors a_T vs. Temperature

- Shift factors fitted with WLF model



WLF model

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

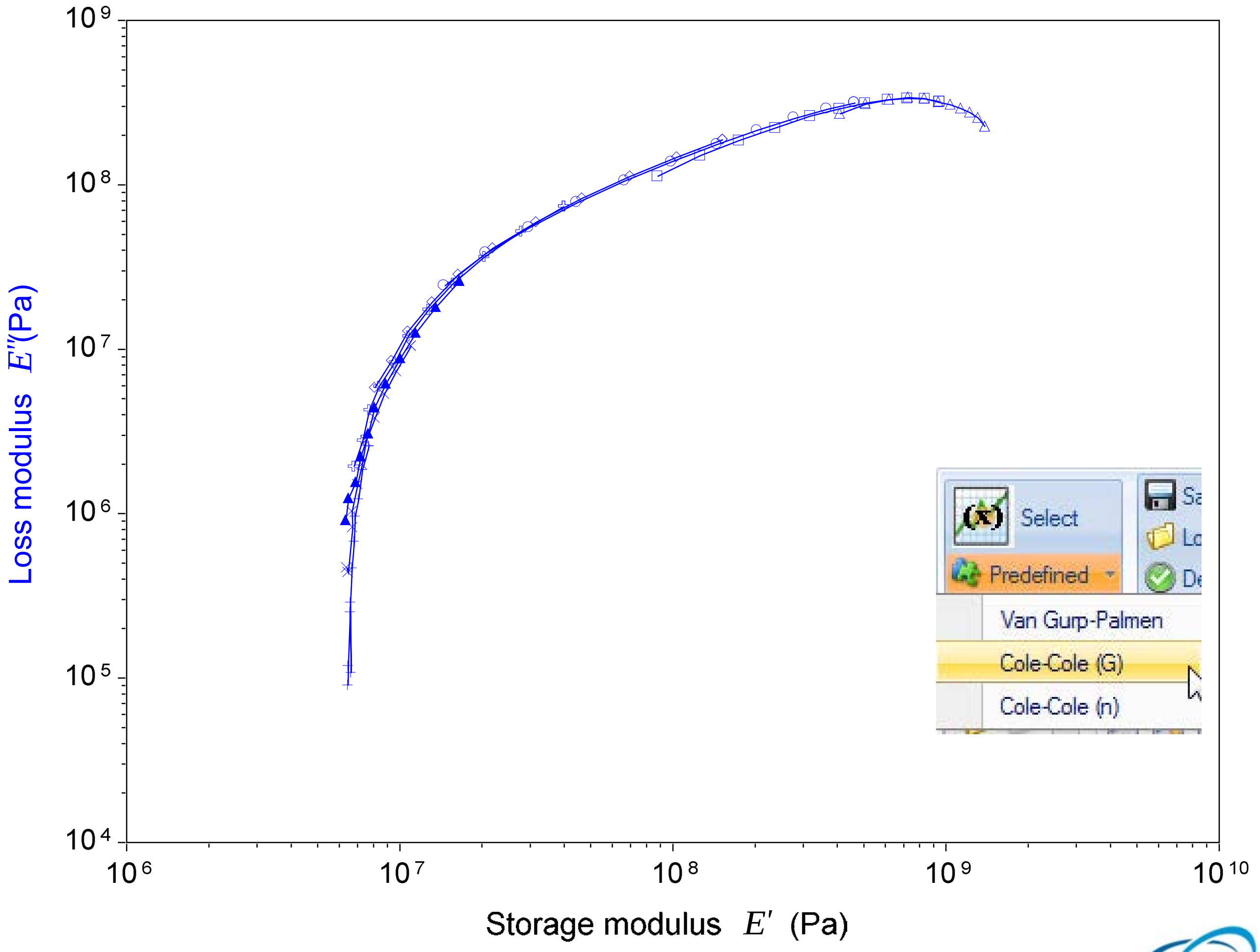
where aT = Horizontal shift factor

T = Temperature of shifted data

T_{REF} = Temperature of reference data

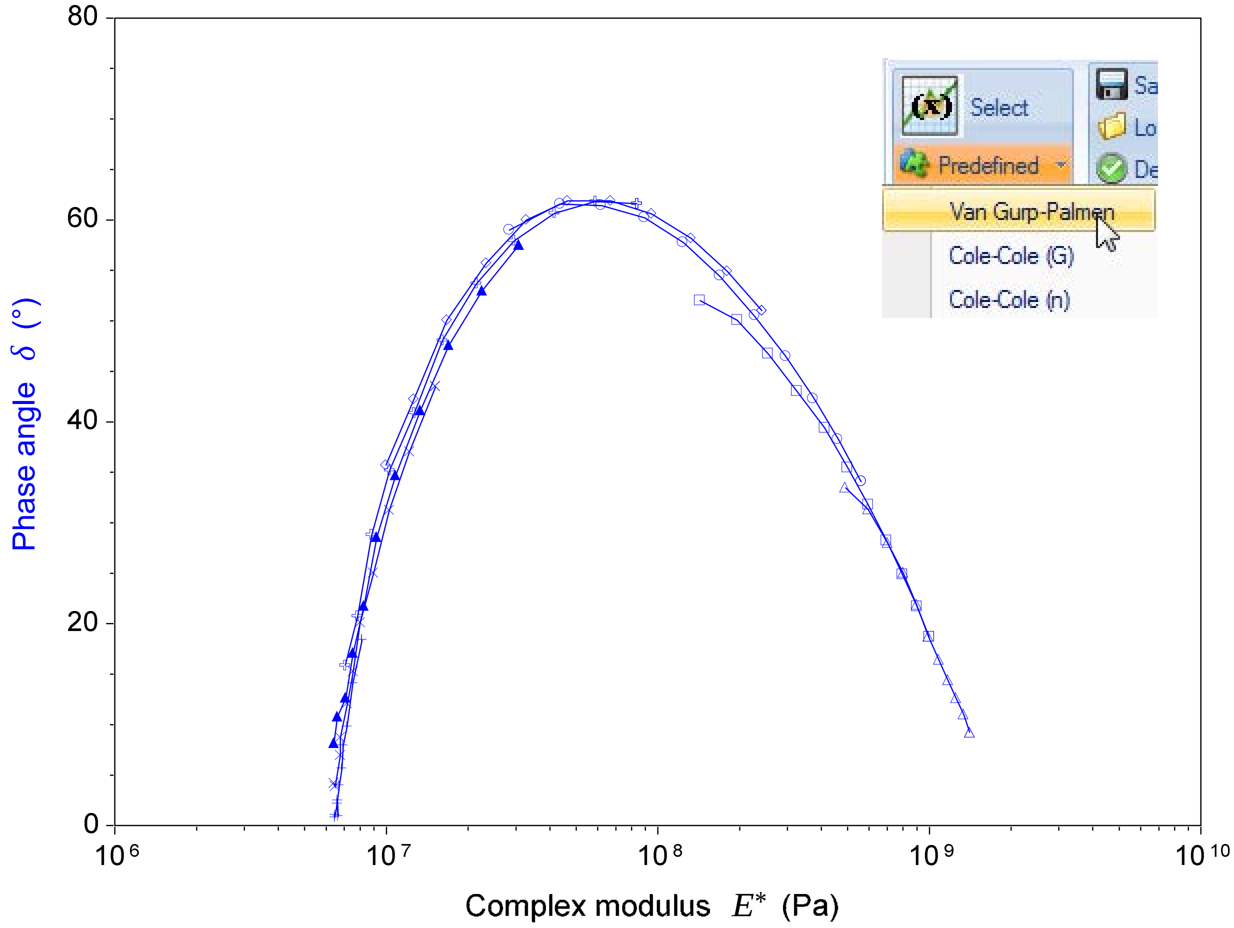
Cole-Cole Plot to Validate TTS

- The Cole-Cole plot and van Gurp-Palmen plot are commonly used to validate the application of Time-Temperature Superposition (TTS).



van Gurp-Palmen Plot to Validate TTS

- The Cole-Cole plot and van Gurp-Palmen plot are commonly used to validate the application of Time-Temperature Superposition (TTS).



References for TTS

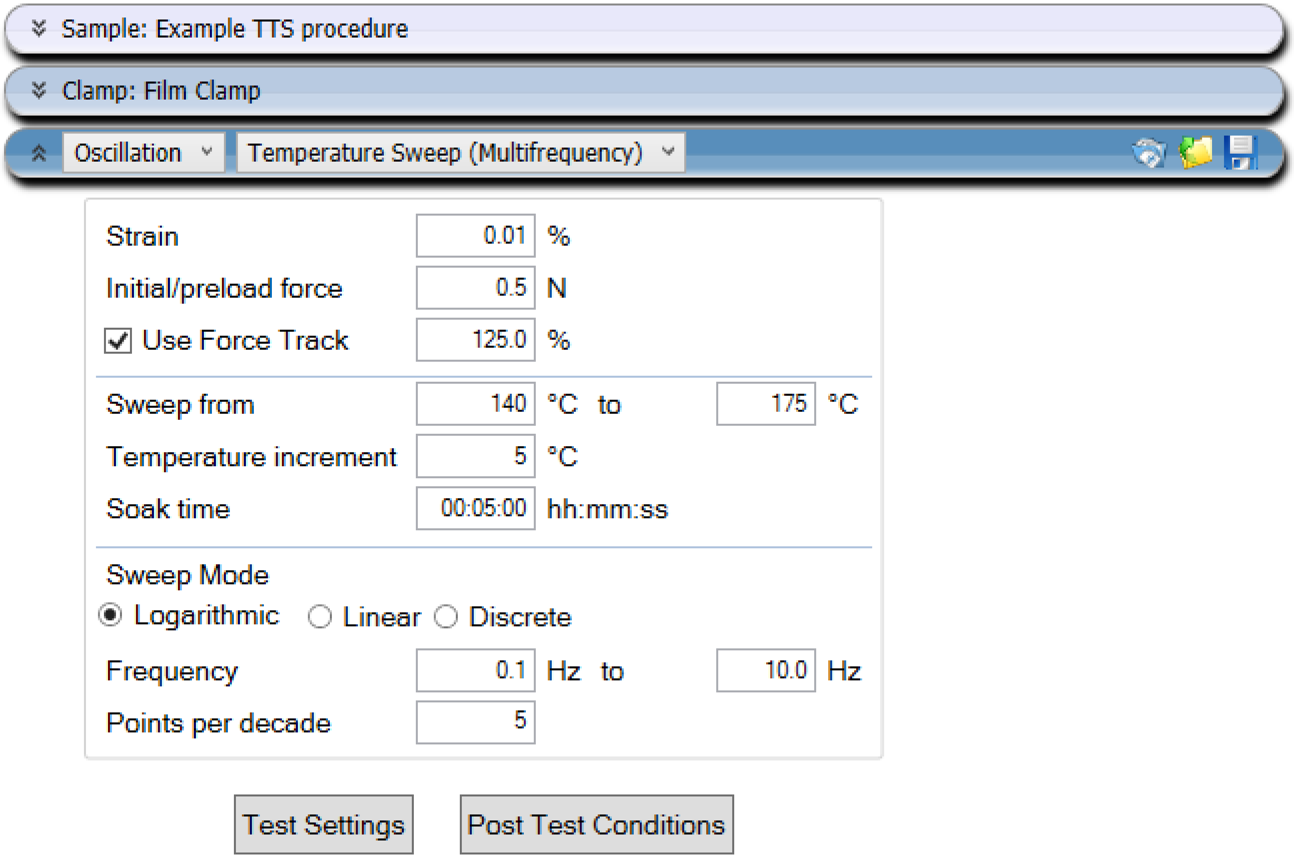
1) Ward, I.M. and Hadley, D.W., "*Mechanical Properties of Solid Polymers*", Wiley, 1993, Chapter 6.

2) Ferry, J.D., "*Viscoelastic Properties of Polymers*", Wiley, 1970, Chapter 11.

3) Plazek, D.J., "*Oh, Thermorheological Simplicity, wherefore art thou?*" Journal of Rheology, vol 40, 1996, p987.

4) Lesueur, D., Gerard, J-F., Claudy, P., Letoffe, J-M. and Planche, D., "*A structure related model to describe asphalt linear viscoelasticity*", Journal of Rheology, vol 40, 1996, p813.

Setting up TTS procedure on DMA850



Sample: Example TTS procedure

Clamp: Film Clamp

Strain 0.01 %

Initial/preload force 0.5 N

☑ Use Force Track 125.0 %

Sweep from 140 °C to 175 °C

Temperature increment 5 °C

Soak time 00:05:00 hh:mm:ss

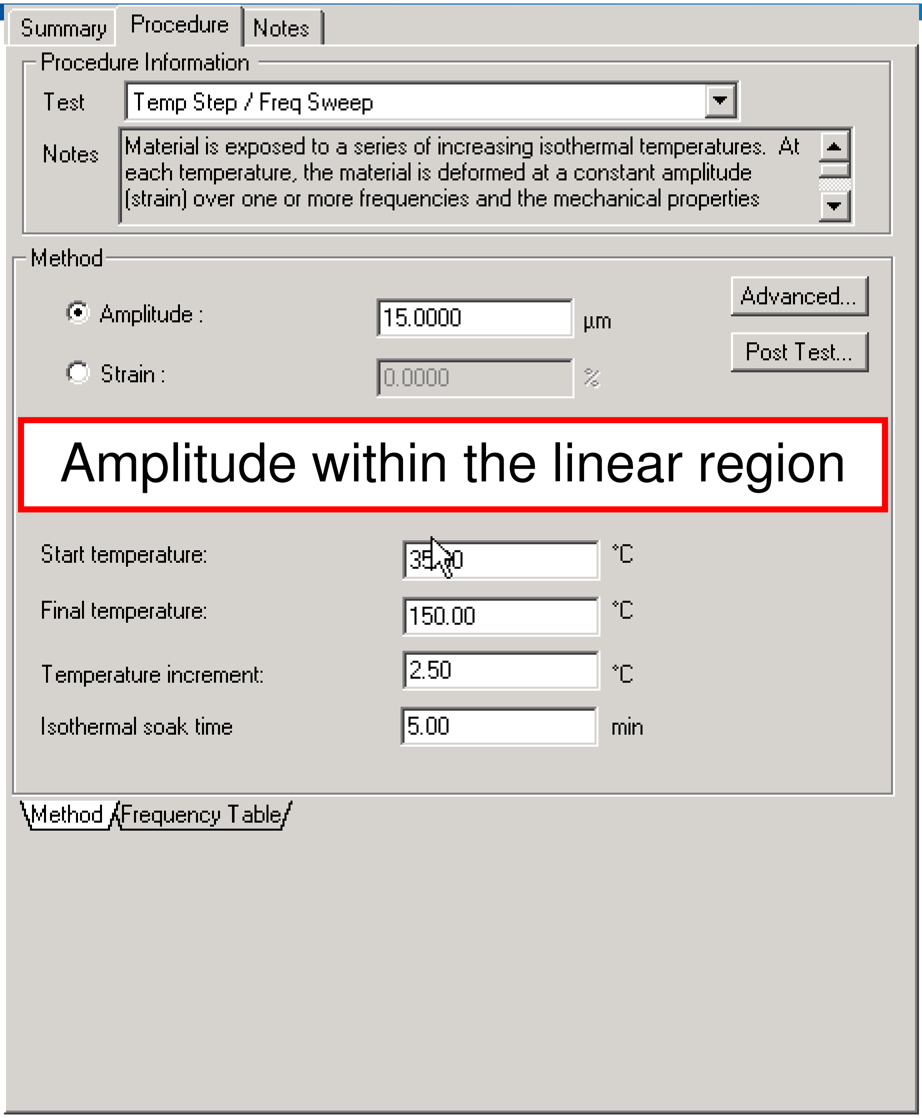
Sweep Mode

● Logarithmic ○ Linear ○ Discrete

Frequency 0.1 Hz to 10.0 Hz

Points per decade 5

Setting up TTS procedure on Q800



Test: Temp Step / Freq Sweep

Notes: Material is exposed to a series of increasing isothermal temperatures. At each temperature, the material is deformed at a constant amplitude (strain) over one or more frequencies and the mechanical properties

● Amplitude : 15.0000 µm

○ Strain : 0.0000 %

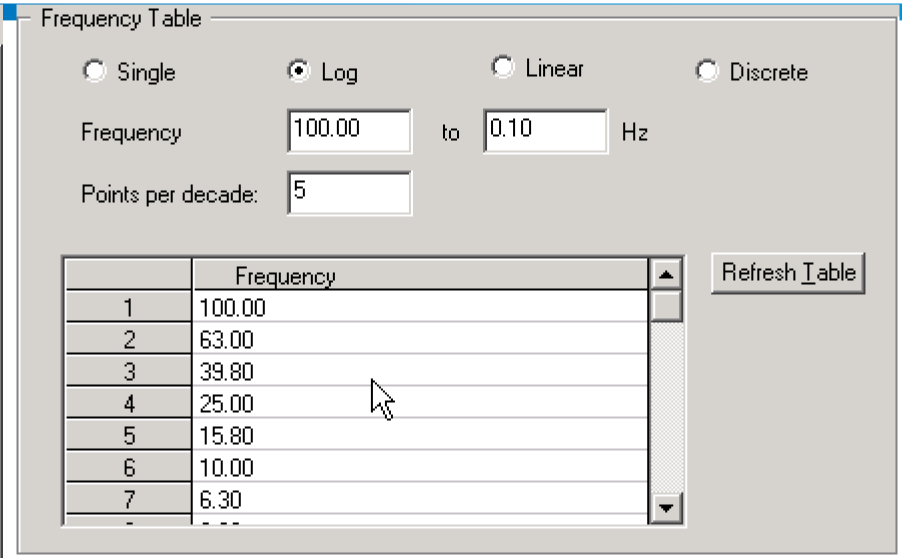
Amplitude within the linear region

Start temperature: 35.00 °C

Final temperature: 150.00 °C

Temperature increment: 2.50 °C

Isothermal soak time 5.00 min

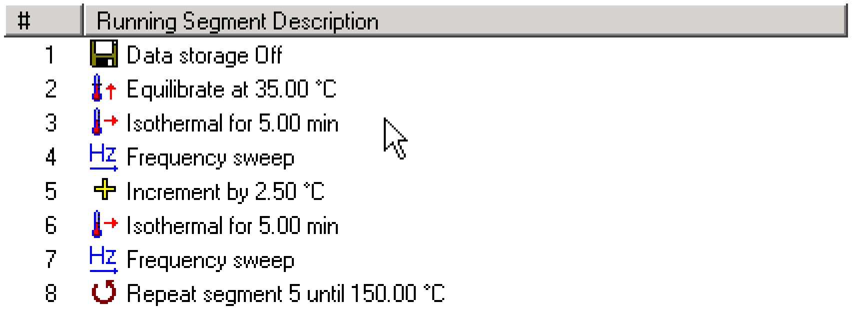


○ Single ● Log ○ Linear ○ Discrete

Frequency 100.00 to 0.10 Hz

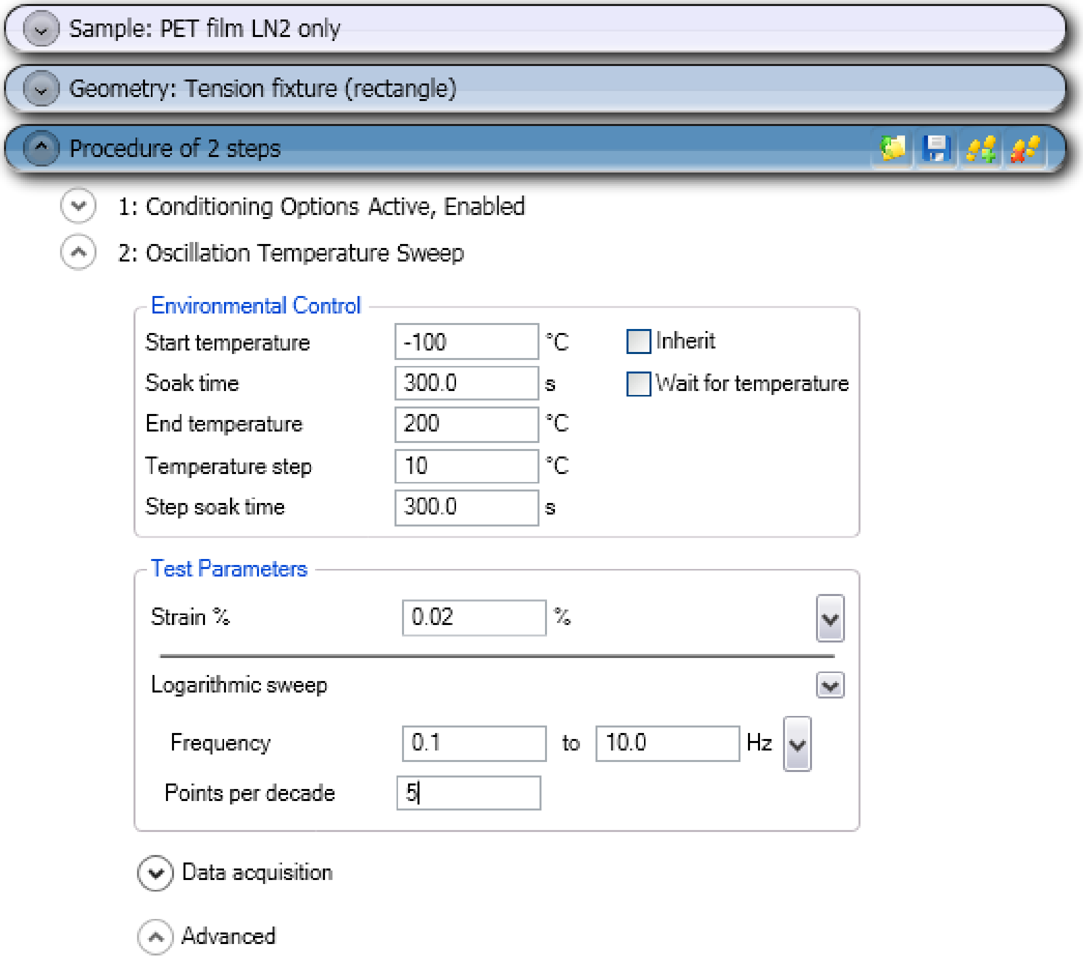
Points per decade: 5

	Frequency
1	100.00
2	63.00
3	39.80
4	25.00
5	15.80
6	10.00
7	6.30



#	Running Segment Description
1	Data storage Off
2	Equilibrate at 35.00 °C
3	Isothermal for 5.00 min
4	Frequency sweep
5	Increment by 2.50 °C
6	Isothermal for 5.00 min
7	Frequency sweep
8	Repeat segment 5 until 150.00 °C

Setting up TTS procedure on RSA G2



Sample: PET film LN2 only

Geometry: Tension fixture (rectangle)

Procedure of 2 steps

1: Conditioning Options Active, Enabled

2: Oscillation Temperature Sweep

Environmental Control

Start temperature -100 °C ☐ Inherit

Soak time 300.0 s ☐ Wait for temperature

End temperature 200 °C

Temperature step 10 °C

Step soak time 300.0 s

Test Parameters

Strain % 0.02 %

Logarithmic sweep

Frequency 0.1 to 10.0 Hz

Points per decade 5

Data acquisition

Advanced

Getting Started Manuals

TA Instruments
Q Series™ Manuals

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

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

Instrument & Accessory Manuals

- Tzero® PDSC Getting Started Guide
- DSC Q Series™ Getting Started Guide
  - RCS Getting Started Guide
  - LNCS Getting Started Guide
  - PCA Getting Started Guide
  - DSC Pressure Cell Getting Started Guide
  - DSC High Pressure Capsule Kit
  - DSC High Volume Pan Kit
  - DSC Circulator-Based Cooling System
- TGA Q5000 IR Getting Started Guide
- TGA Q Series™ Getting Started Guide
  - TGA Hi-Res™ Option
- DMA Q Series™ Getting Started Guide
  - GCA Getting Started Guide
  - DMA Humidity Accessory Getting Started
- SDT Q Series™ Getting Started Guide
- TMA Q Series™ Getting Started Guide
  - MCA Getting Started Guide
  - MCA70 Getting Started Guide
- Q5000 SA Getting Started Guide

Software Manuals

- Q Series™ Instrument Control Getting Started Guide
- Universal Analysis Getting Started Guide
- Advantage Integrity™ Getting Started Guide
- Specialty Library Getting Started Guide
- RMX File Utilities

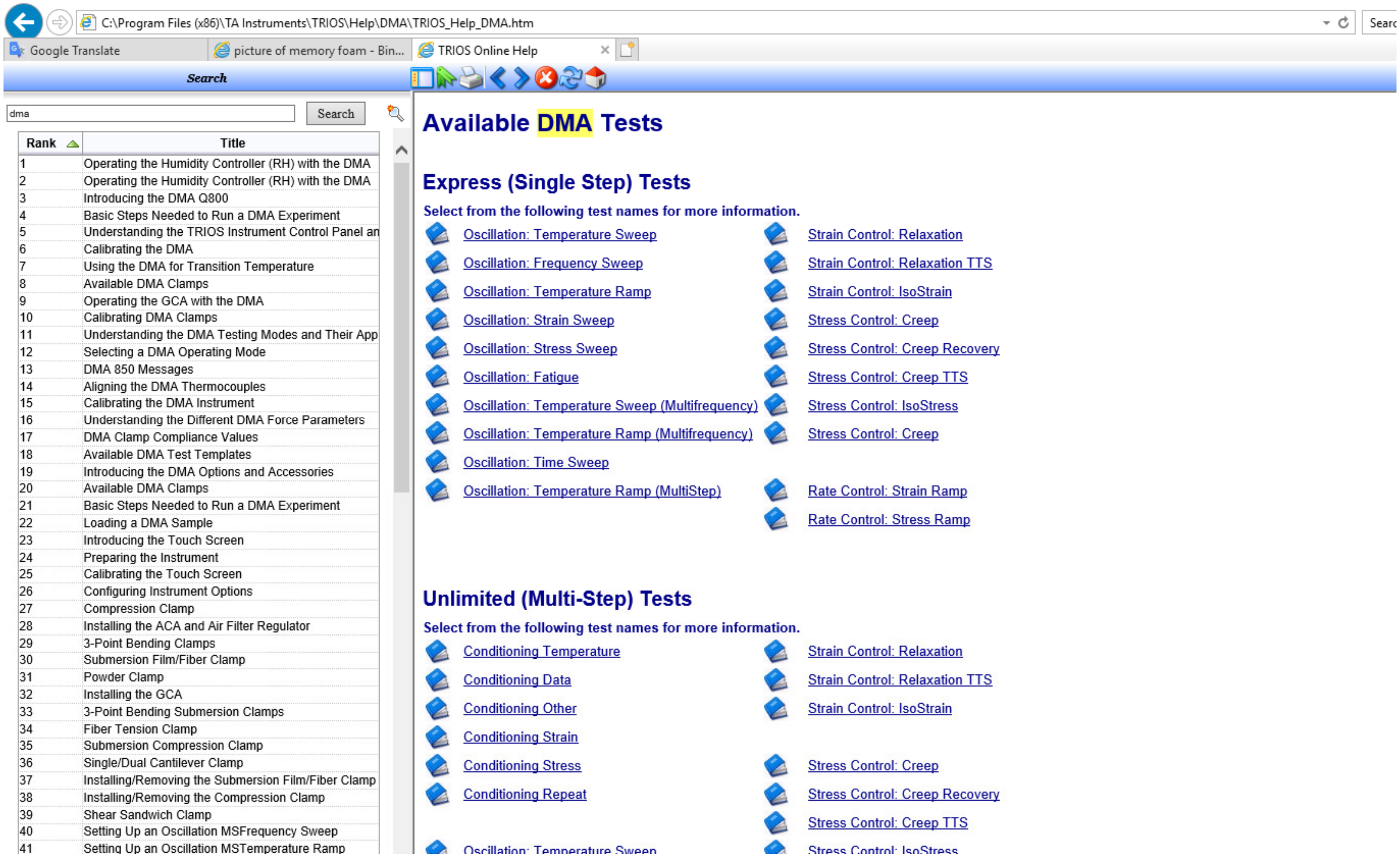
Miscellaneous Documents

- Installing/Updating Advantage™
- Updating Q Series™ Instrument Software
- New Features in Advantage Q Series™
- New Features in Advantage Integrity™
- TA Update

DMA
Dynamic Mechanical Analyzer

Q Series™
Getting Started Guide

Trios Online Help Manual



Rank	Title
1	Operating the Humidity Controller (RH) with the DMA
2	Operating the Humidity Controller (RH) with the DMA
3	Introducing the DMA Q800
4	Basic Steps Needed to Run a DMA Experiment
5	Understanding the TRIOS Instrument Control Panel an
6	Calibrating the DMA
7	Using the DMA for Transition Temperature
8	Available DMA Clamps
9	Operating the GCA with the DMA
10	Calibrating DMA Clamps
11	Understanding the DMA Testing Modes and Their App
12	Selecting a DMA Operating Mode
13	DMA 850 Messages
14	Aligning the DMA Thermocouples
15	Calibrating the DMA Instrument
16	Understanding the Different DMA Force Parameters
17	DMA Clamp Compliance Values
18	Available DMA Test Templates
19	Introducing the DMA Options and Accessories
20	Available DMA Clamps
21	Basic Steps Needed to Run a DMA Experiment
22	Loading a DMA Sample
23	Introducing the Touch Screen
24	Preparing the Instrument
25	Calibrating the Touch Screen
26	Configuring Instrument Options
27	Compression Clamp
28	Installing the ACA and Air Filter Regulator
29	3-Point Bending Clamps
30	Submersion Film/Fiber Clamp
31	Powder Clamp
32	Installing the GCA
33	3-Point Bending Submersion Clamps
34	Fiber Tension Clamp
35	Submersion Compression Clamp
36	Single/Dual Cantilever Clamp
37	Installing/Removing the Submersion Film/Fiber Clamp
38	Installing/Removing the Compression Clamp
39	Shear Sandwich Clamp
40	Setting Up an Oscillation MSFrequency Sweep
41	Setting Up an Oscillation MSTemperature Ramp

Available DMA Tests

Express (Single Step) Tests

Select from the following test names for more information.

- Oscillation: Temperature Sweep
- Oscillation: Frequency Sweep
- Oscillation: Temperature Ramp
- Oscillation: Strain Sweep
- Oscillation: Stress Sweep
- Oscillation: Fatigue
- Oscillation: Temperature Sweep (Multifrequency)
- Oscillation: Temperature Ramp (Multifrequency)
- Oscillation: Time Sweep
- Oscillation: Temperature Ramp (MultiStep)

- Strain Control: Relaxation
- Strain Control: Relaxation TTS
- Strain Control: IsoStrain
- Stress Control: Creep
- Stress Control: Creep Recovery
- Stress Control: Creep TTS
- Stress Control: IsoStress
- Stress Control: Creep
- Rate Control: Strain Ramp
- Rate Control: Stress Ramp

Unlimited (Multi-Step) Tests

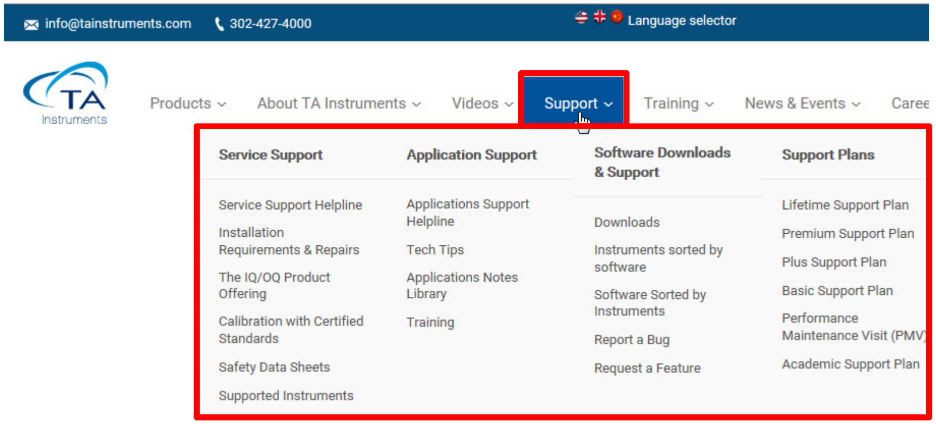
Select from the following test names for more information.

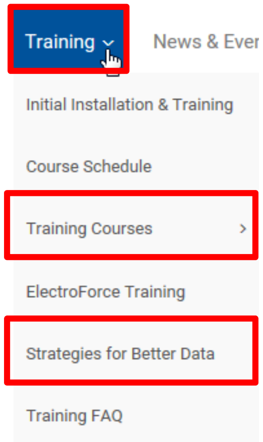
- Conditioning Temperature
- Conditioning Data
- Conditioning Other
- Conditioning Strain
- Conditioning Stress
- Conditioning Repeat
- Oscillation: Temperature Sweep

- Strain Control: Relaxation
- Strain Control: Relaxation TTS
- Strain Control: IsoStrain
- Stress Control: Creep
- Stress Control: Creep Recovery
- Stress Control: Creep TTS
- Stress Control: IsoStress

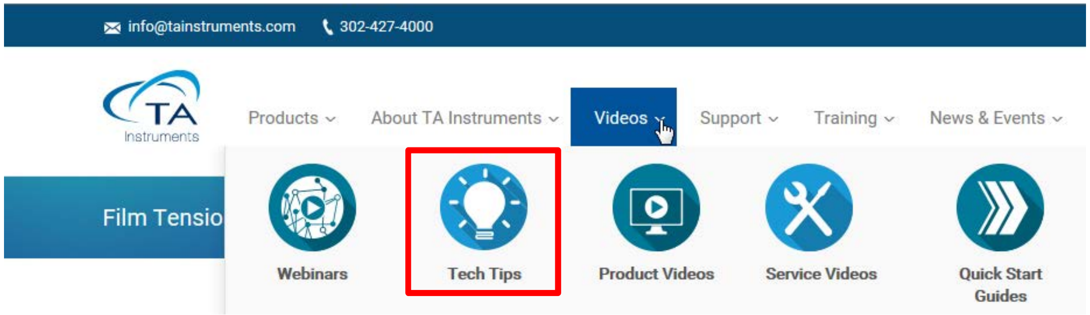
Instructional Videos

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





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



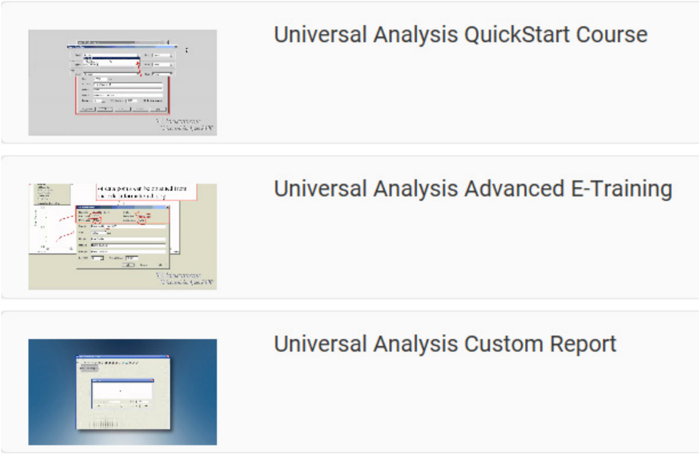
See also: https://www.youtube.com/user/TATechTips

Instructional Video Resources

Quickstart e-Training Courses

DMA Q800 Quickstart Course – Instrument and Experimental Setup

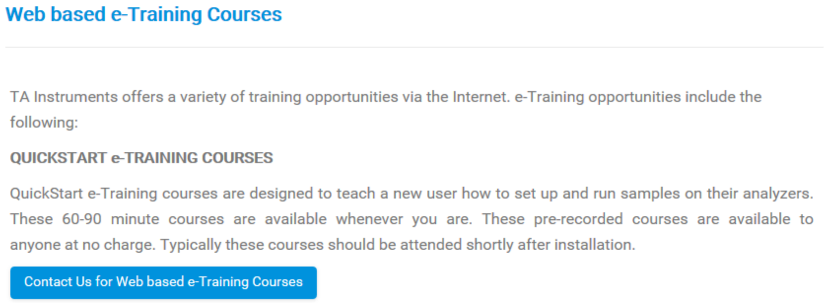
DMA Q800 – Analysis Quickstart



Universal Analysis QuickStart Course

Universal Analysis Advanced E-Training

Universal Analysis Custom Report

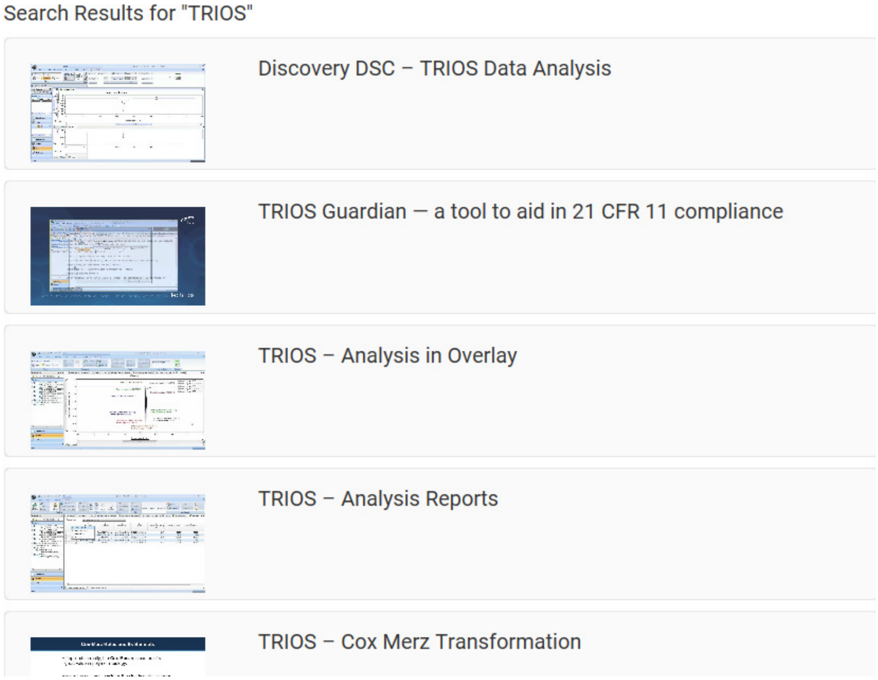


Web based e-Training Courses

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

QUICKSTART e-TRAINING COURSES

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



Search Results for "TRIOS"

Discovery DSC – TRIOS Data Analysis

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

TRIOS – Analysis in Overlay

TRIOS – Analysis Reports

TRIOS – Cox Merz Transformation

Need DMA HELP?!?

- Check the manuals, help and error help.
- Contact the TA Instruments Rheology Hotline
  - Email rheologysupport@tainstruments.com
- Call the TA Instruments Service Hotline
  - **302-427-4050** M-F 8-4:30 ET
- Call your local Technical or Service Representative
- Visit our Website www.tainstruments.com for training videos, TA Tech tips, application notes and much more!

Thank You

The World Leader in Thermal Analysis, Rheology, and Microcalorimetry