



TA Instruments – Waters LLC



Materials Characterization by Dynamic Mechanical Analysis

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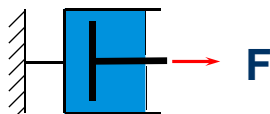


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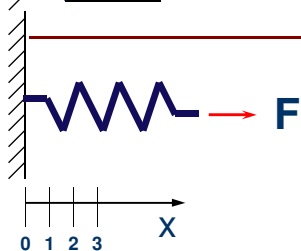
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Rheology: The study of the flow and deformation of matter



Flow: Fluid Behavior; Viscous Nature

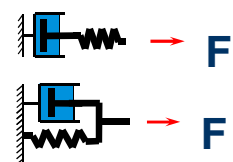
$$F = F(v); F \neq F(x)$$



**Deformation: Solid Behavior
Elastic Nature**

$$F = F(x); F \neq F(v)$$

We discussed these
concepts in the Rheology
section of the workshop.

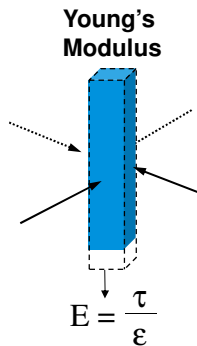


**Viscoelastic Materials: Force
depends on both Deformation
and Rate of Deformation and
vice versa.**

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Tensile Deformation



Deformation Parameters

L_0 = Initial Length (m)

L = Stretched Length (m)

ϵ = Elongational Strain, $(L/L_0) - 1$ (unitless) (Engineering Strain)

▪ Strain is the amount of deformation normalized for the type of deformation and the dimensions of the specimen.

Force Parameters

T = Tensile force (Newtons)

w_0 = Initial Width (m)

t_0 = Initial Thickness (m)

τ = Tensile Stress, $T/(w_0 \cdot t_0)$ (Pa)

▪ Stress is the amount of force normalized for the type of deformation and the dimensions of the specimen.

Conversions:

Machine → Rheological

Displacement → Strain

Force → Stress

Elongational Properties

$E = \tau/\epsilon$ (Pa) Modulus

$D = \epsilon/\tau$ (1/Pa) Compliance



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UNIDIRECTIONAL TYPES OF TESTS ON THE DMA

TRANSIENT

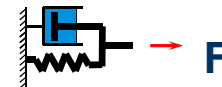
Stress Relaxation

- Deformation applied instantaneously \Rightarrow Force measured as a function of time
- Deformation (mm) converted to Strain (ϵ), Force (N) to Stress (τ)
- Stress (τ)/Strain(ϵ) = Modulus (E)



Creep

- Force applied instantaneously \Rightarrow Deformation measured as a function of time
- Force to Stress (τ), Deformation converted to Strain (ϵ)
- Strain (ϵ)/Stress (τ) = Compliance (D)



PRACTICAL

Strain Ramp

- Strain increased linearly with time or, optionally, exponential with the RSA-G2

Iso-Strain

- Strain held constant as temperature is varied

Stress Ramp

- Stress increased linearly or exponentially with time

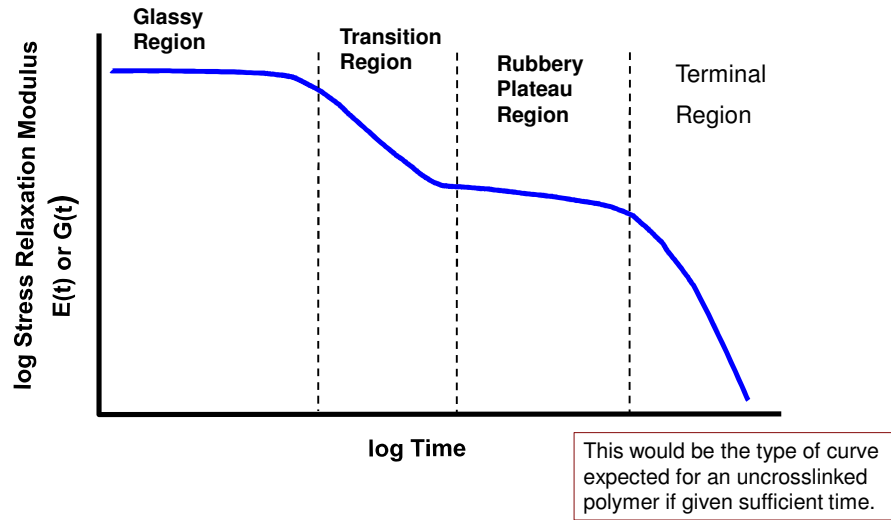
Controlled Stress

- Stress held constant as temperature is varied



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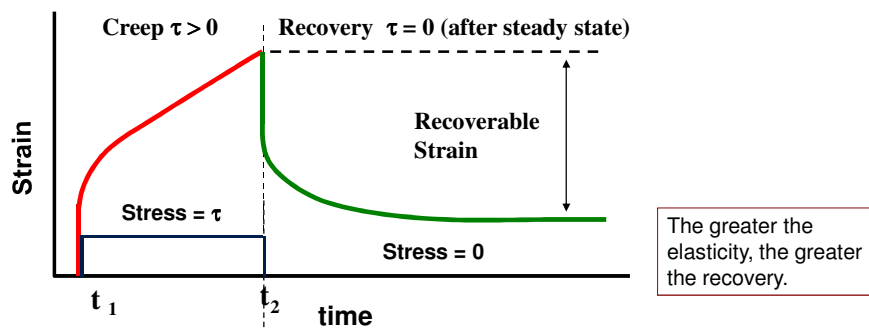
Stress Relaxation: Material Response



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Creep Testing

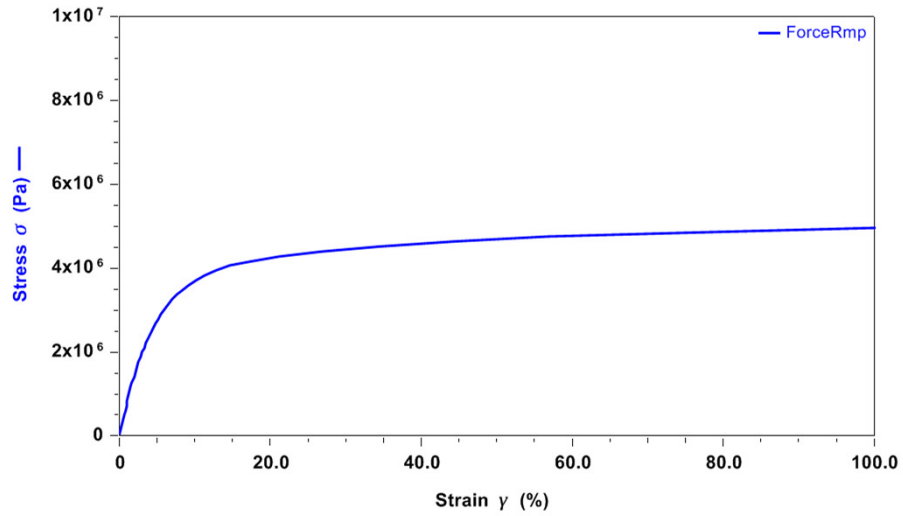


With uncross-linked systems, strain increases indefinitely. If you have reached steady state flow, you can calculate the viscosity and the recoverable compliance. With cross-linked systems, there is a limiting strain.

Reference: Mark, J., et al., Physical Properties of Polymers, American Chemical Society, 1984, p. 192. TA | TAINSTRUMENTS.COM

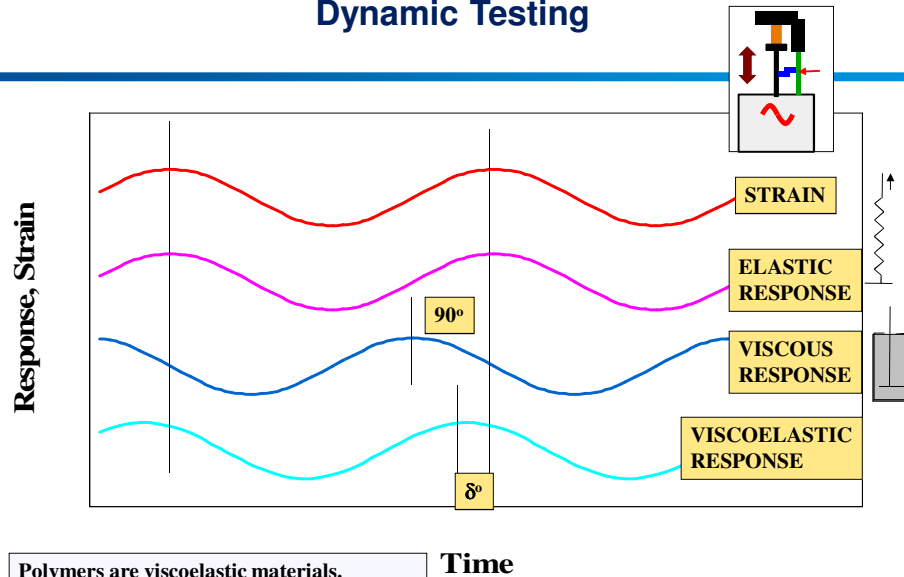
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Polyethylene Stress Ramp (or Strain Ramp)



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Dynamic Testing



Polymers are viscoelastic materials.
Both components – viscosity and elasticity
– are important.

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Dynamic Rheological Parameters

Parameter	Shear	Elongation	Units
Strain	$\gamma = \gamma_0 \sin(\omega t)$	$\varepsilon = \varepsilon_0 \sin(\omega t)$	---
Stress	$\sigma = \sigma_0 \sin(\omega t + \delta)$	$\tau = \tau_0 \sin(\omega t + \delta)$	Pa
Storage Modulus (Elasticity)	$G' = (\sigma_0/\gamma_0) \cos \delta$	$E' = (\tau_0/\varepsilon_0) \cos \delta$	Pa
Loss Modulus (Viscous Nature)	$G'' = (\sigma_0/\gamma_0) \sin \delta$	$E'' = (\tau_0/\varepsilon_0) \sin \delta$	Pa
Tan δ	G''/G'	E''/E'	---
Complex Modulus	$G^* = (G'^2 + G''^2)^{0.5}$	$E^* = (E'^2 + E''^2)^{0.5}$	Pa
Complex Viscosity	$\eta^* = G^*/\omega$	$\eta_E^* = E^*/\omega$	Pa-sec

We will be mainly concerned with the Elongation column in this table.



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Dynamic Oscillatory Testing Methods

- Frequency Sweep
- Strain Sweep
- Stress Sweep
- Temperature Sweep
- Temperature Ramp
- Time Sweep
- Temperature Sweep (Multifrequency)
- Fatigue Test

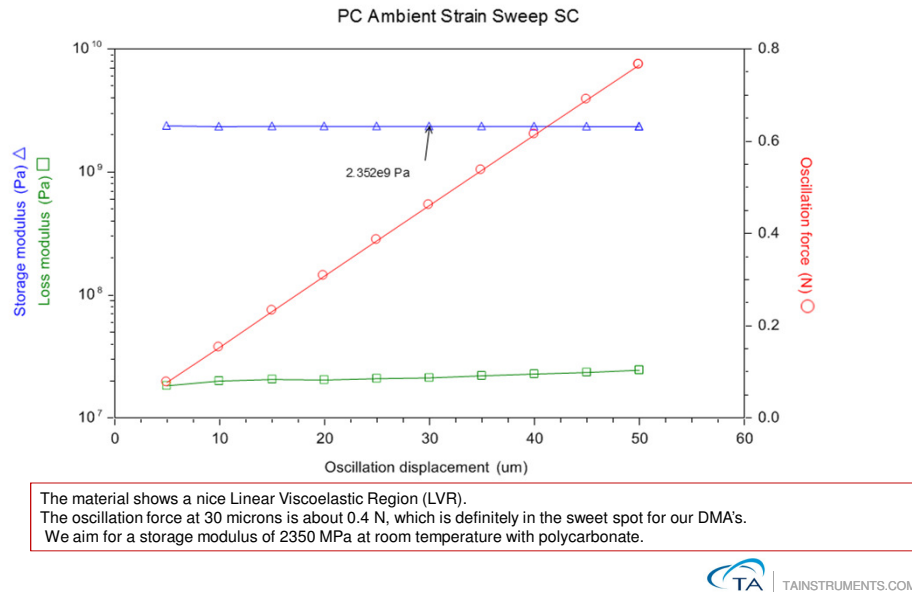
Most common sequence

- Strain sweep at 1 Hz to find the "sweet spot" for testing and the Linear Viscoelastic Region (LVR)
- Temperature ramp at 1 Hz and 3 C/min using amplitude from strain sweep testing.



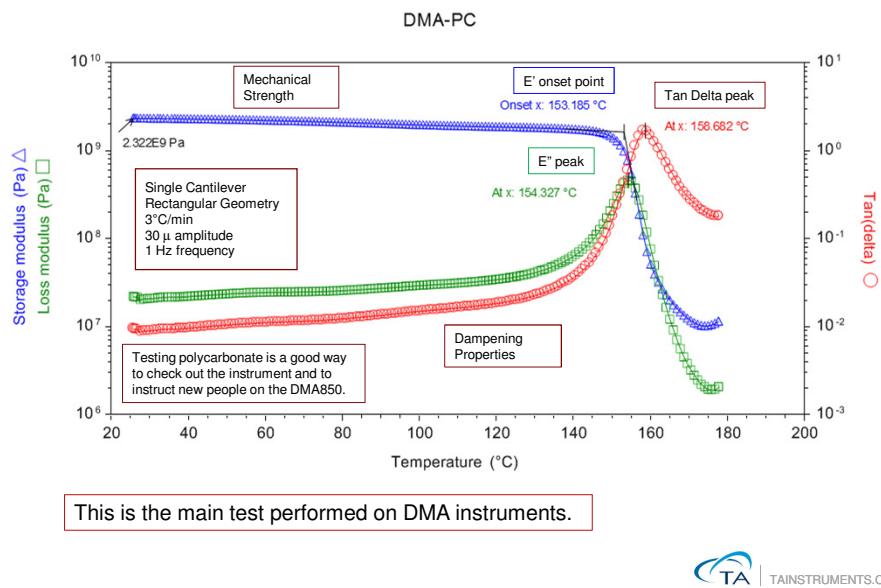
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Dynamic Strain Sweep



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Polycarbonate Testing on the DMA 850



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DMA INSTRUMENTATION



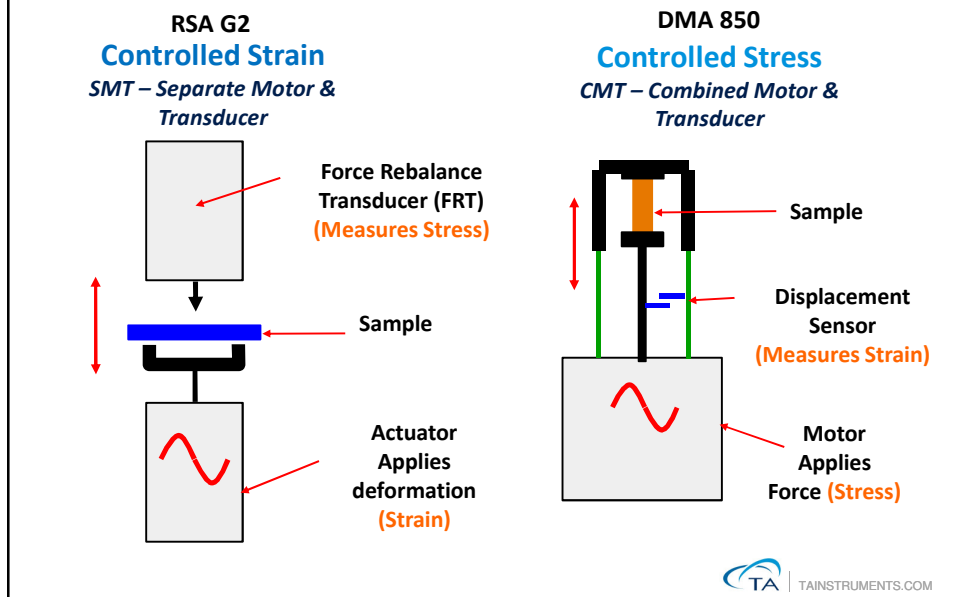
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DMAs from TA Instruments

RSA G2**Controlled Strain
SMT****DMA 850****Controlled Stress
CMT****ARES G2
and DHR****DMA mode
(oscillation)**

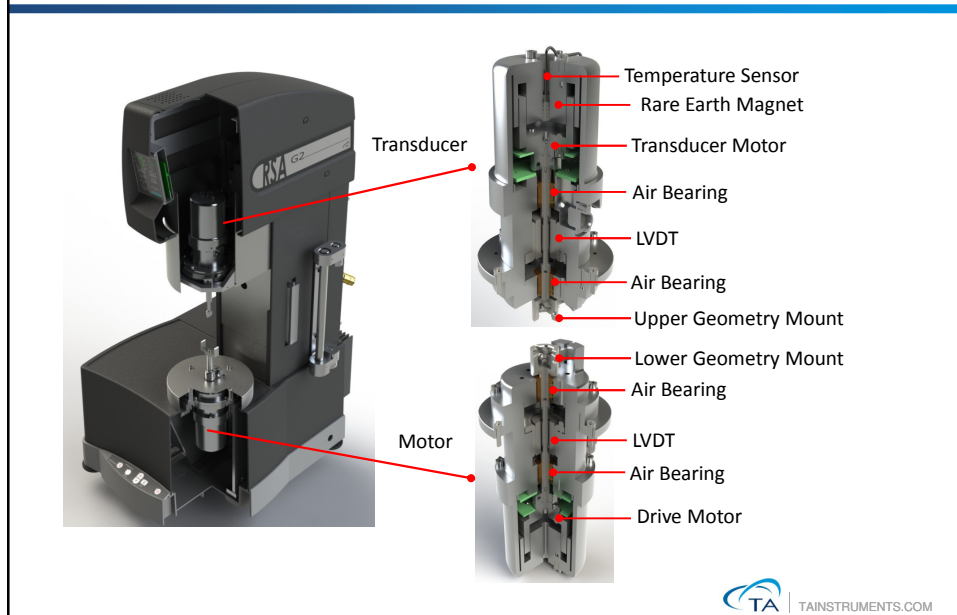
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DMAs from TA Instruments



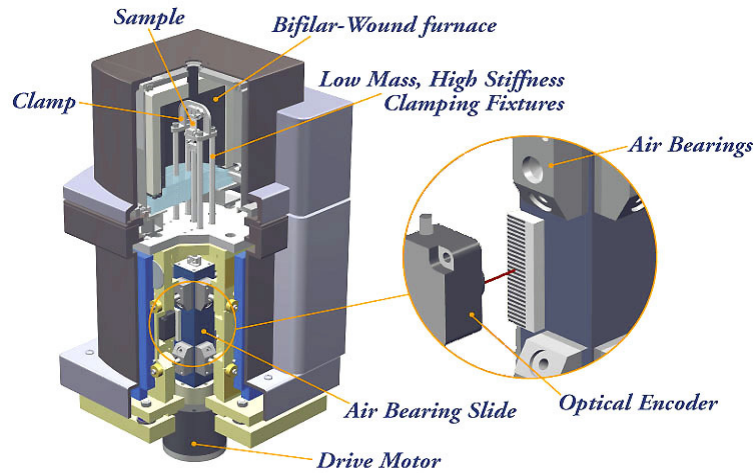
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RSA G2: Schematic Dual Head Design



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DMA Q850: Schematic



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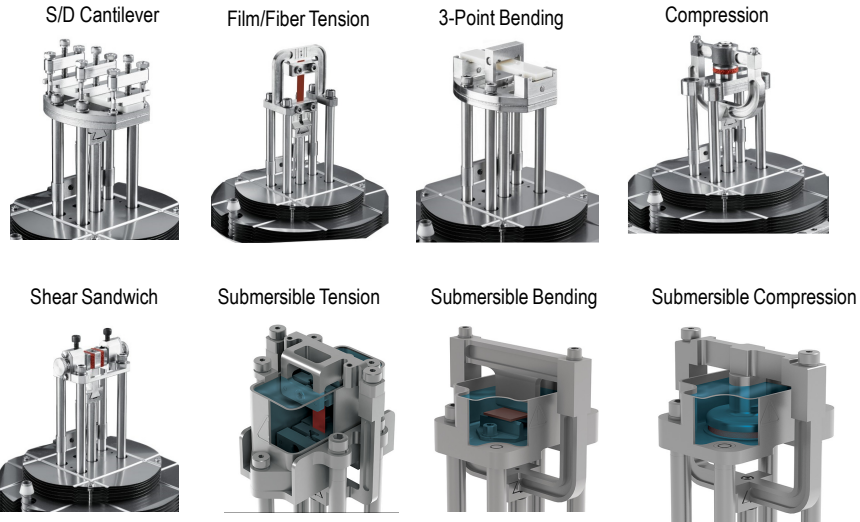
DMA Specifications

	RSA G2	Q800	ARES G2 DMA	DHR DMA (optional)
Max Force	35N	18N	20N	50N
Min Force	0.0005N	0.0001N	0.001N	0.1N
Frequency Range	1e-5 to 628 rad/s (1.6e-6 to 100 Hz)	0.01 to 1250 rad/s (1.6e-3 to 200 Hz)	6.3e-5 to 100 rad/s (1.0e-5 to 16 Hz)	6.3e-5 to 100 rad/s (1.0e-5 to 16 Hz)
Dynamic Deformation Range	+/- 0.05 to 1,500mm	+/- 0.5 to 10,000mm	+/- 1 to 50 mm	+/- 1 to 100 mm
Control Stress/Strain	Control Strain (SMT)	Control Stress (CMT)	Control Strain (CMT)	Control Stress (CMT)
Heating Rate	0.1°C to 60°C/min	0.1°C to 20°C/min	0.1°C to 60°C/min	0.1°C to 60°C/min
Cooling Rate	0.1°C to 60°C/min	0.1°C to 10°C/min	0.1°C to 60°C/min	0.1°C to 60°C/min



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Clamps for DMA850

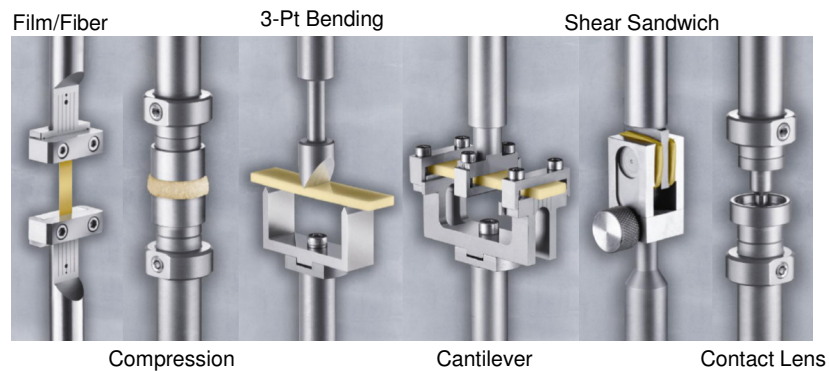


The standard size S/D cantilever clamp is included with the purchase of the DMA 850.



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Clamps for RSA G2



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RSA G2 Immersion Clamps

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

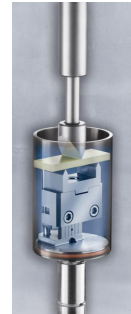
Tension



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.

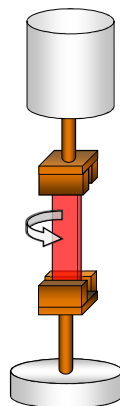


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Torsion and DMA Measurements on Rheometers

- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment
 - DMA functionality is standard with ARES G2 and optional DHR

$$E = 2G(1 + \nu) \quad \nu : \text{Poisson's ratio}$$

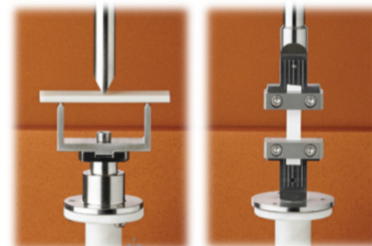


Modulus: G' , G'' , G^*



Rectangular and cylindrical torsion

Modulus: E' , E'' , E^*

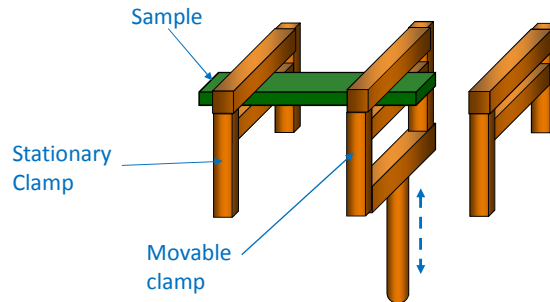


DMA 3-point bending and tension (Cantilever not shown)



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DMA: Single Cantilever Clamp

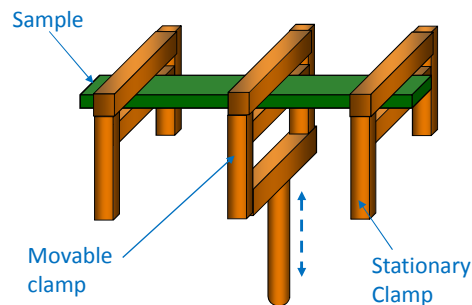


- Best general purpose mode (thermoplastics); used the most for reasonably stiff specimens on DMA 850
- Preferred mode over dual cantilever for most neat thermoplastics (unreinforced), except elastomers
- Clamping torque is important



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DMA: Dual Cantilever Clamp

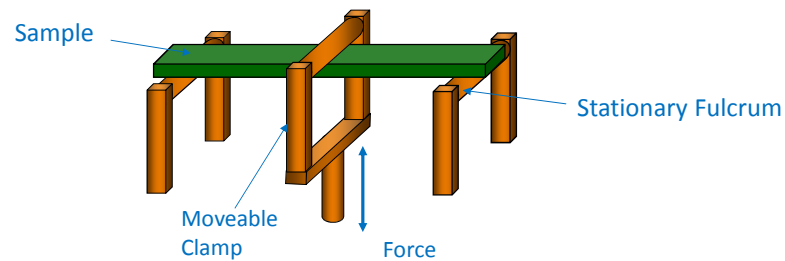


- Highly damped materials can be measured
- Best mode for evaluating the cure of supported materials



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DMA: 3 Point Bend Clamp

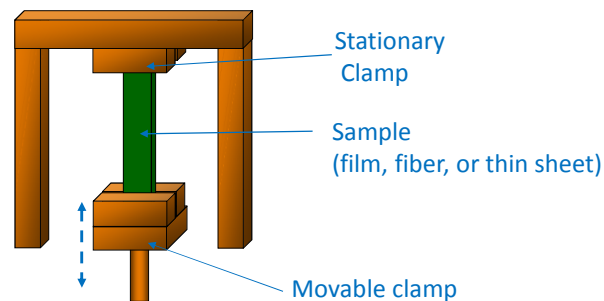


- Best mode for measuring medium to high modulus materials
- Conforms with ASTM standard test method for bending
- Purest deformation mode since clamping effects are eliminated
- Most common clamp for flexural testing on RSA-G2



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DMA: Film and Fiber Tension Clamp

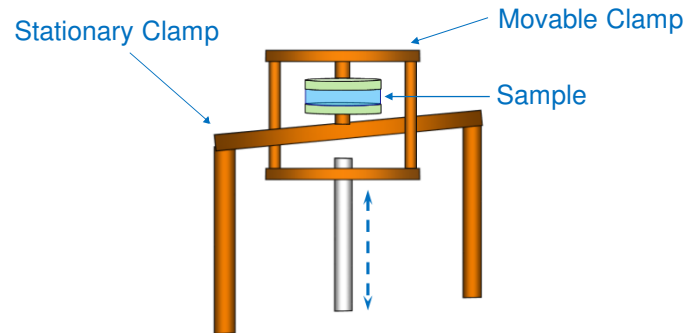


- Best mode for evaluation of thin films and fibers
 - bundle or single filaments
- Small samples of high modulus materials can be measured
- TMA-like constant force and force ramp measurements
 - aka. mini-tensile tester
- Force track and constant force control



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DMA: Compression Clamp

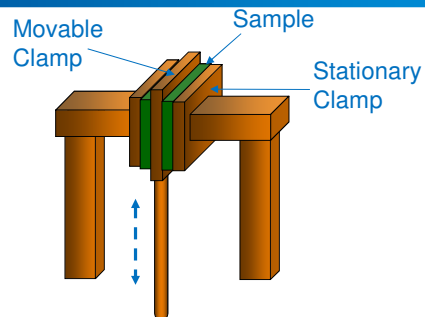


- Good mode for low to medium modulus materials (gels, elastomers)
- Materials must provide restoring force (support necessary static load)
- Options for expansion & penetration measurements



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DMA: Shear Sandwich Clamp



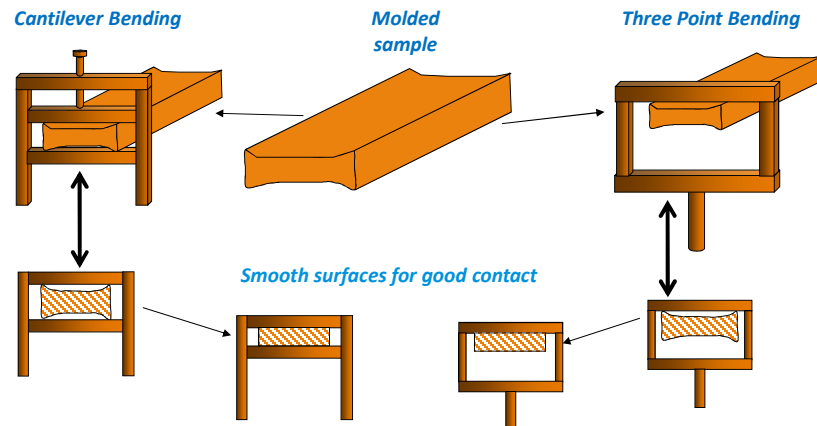
- Square sample configuration provides pure shear deformation
- Provides *Shear Moduli*: G^* , G' , G'' & $G(t)$
- Good for evaluating highly damped soft solids such as gels and adhesives & elastomers $> T_g$
- Can be used for high viscosity melts and resins



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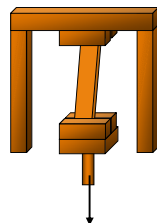
Preparing Samples – The Importance of Shape

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



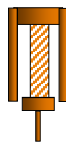
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Alignment in Tension Mode



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

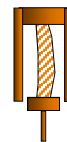
- Buckling during loading causes serious errors as buckled areas do not “feel” the force or deformation
- Buckling can be the result of non-uniform stretching, or crooked loading of a film.
- Observe film from edge while oscillating to verify goodness of load.
- If sample is buckling, reload a new sample.



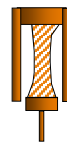
ideal



inclined



sagging



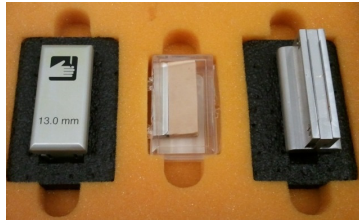
variable thickness



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Some Sample Prep Tools

Parallel Razor
Blade Cutter



Good for Films and
Sheets of rubber.

Cork Borer



Good for stiff foams and
Sheets of rubber.



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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:

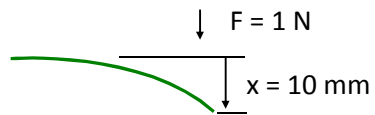
- Machine range fixed: **100 - 10,000,000 N/m**. Stiffness of sample related to its dimensions [L, w, t]. Stiffness may limit sample size to below clamp maximum.



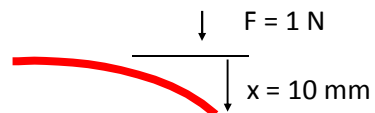
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Sample Stiffness and Material Modulus

Thick and Thin
Samples Can Have
The Same Stiffness

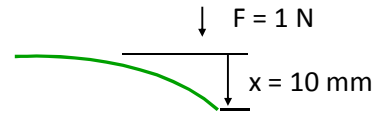


High Modulus Material

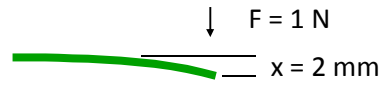


Low Modulus Material

Thick and Thin Samples
That Have The Same
Modulus



Low Stiffness Sample



High Stiffness Sample



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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: $L/T \geq 10$	Increase length or decrease width,, If possible decrease thickness. Note: $L/T \geq 10$
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.



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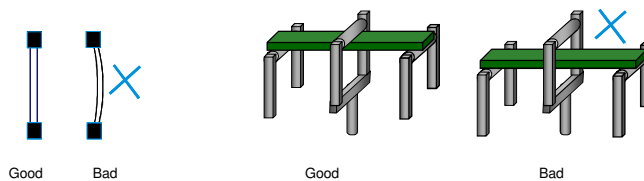
DMA Clamping Guide

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 $T < T_g$ $L/T > 10$ for $T < T_g$ (only for $T > T_g$) $T < 2$ 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



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Some Clamps Require an Offset (Static) Force



Tension

1. With the tension clamp, one wants to avoid the buckling of the specimen that is shown with the tension specimen on the right.
2. With the 3-pt bend clamp, one wants to avoid the loss of contact of the center clamp with the specimen that is shown with the 3-pt bend specimen on the right. The same principle applies to the compression clamp.

3-pt Bend

Clamps without offset force:

Single Cantilever
Dual Cantilever
Shear Sandwich

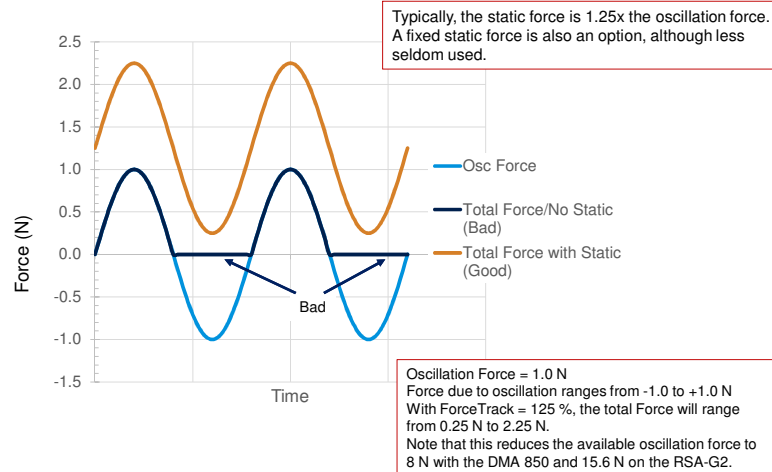
Clamps with offset force:

Tension Film
Tension: Fiber
3-Point Bend
Compression
Penetration



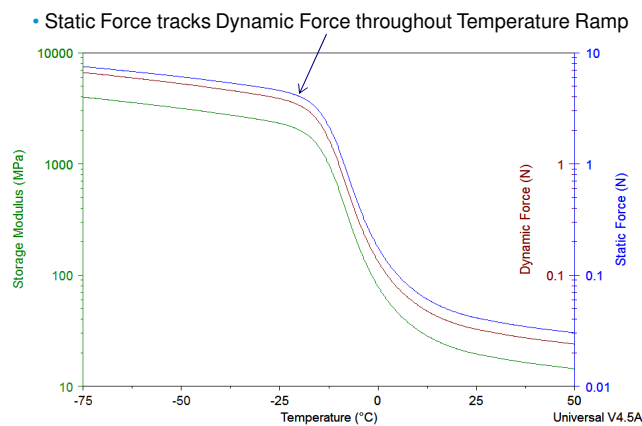
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Waveforms with and without Static Force



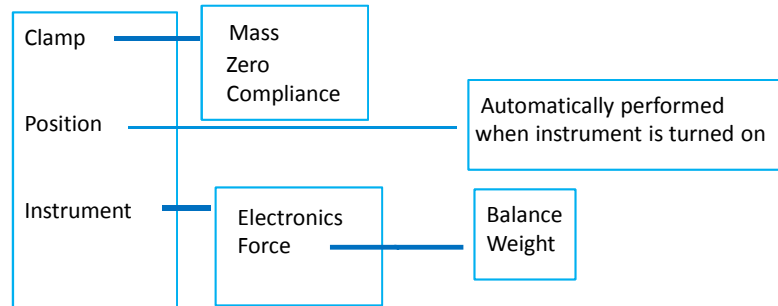
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Temperature Ramp with Force Track



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Q850 Flow Chart of Calibration Procedures



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DMA Calibrations and Compliance Tables

Clamp	Mass	Zero	Compliance
Dual/Single Cantilever	X		X
3 Point Bend	X		X
Tension Film	X	X	X
Compression/Penetration	X	X	X
Shear Sandwich	X		
Specialty Fiber	X	X	

Clamp	Typical Compliance in $\mu\text{m/N}$
Single Cantilever	≤ 0.8
Dual Cantilever	≤ 0.2
3 Point Bend	≤ 0.6
Tension Film	≤ 0.5
Compression	≤ 0.6
Specialty Fiber	N/A
Shear Sandwich	N/A

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RSA-G2 Instrument Calibration

Calibration Tasks and Recommended Intervals

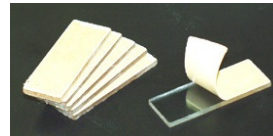
Calibration Task	Calibration Interval
Upper Fixture Mass Calibration	Mandatory: During geometry creation (is a part of geometry configuration)
Force Calibration	Suggested: Monthly. Mandatory: Following transducer replacement.
Phase Angle and Modulus Check	Suggested: Monthly Mandatory: Following actuator or transducer replacement.
Gap Temperature Compensation	Suggested: As required by the experiment.



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DMA Confidence Check - Polycarbonate

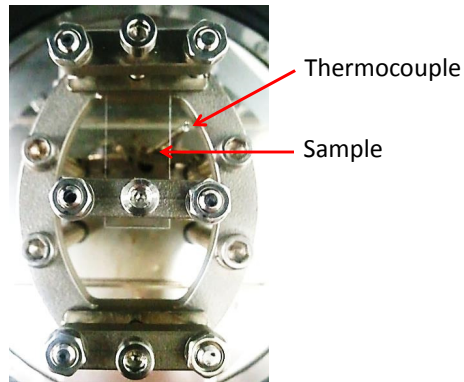
- Load Polycarbonate ($L \approx 17.5$, $w \approx 12.85$, $t \approx 0.8\text{mm}$)
 - DMA 850: Single Cantilever; 20-30 micrometer amplitude
 - RSA-G2: 3-pt bend; 0.04% Strain
- 1 Hz
- 3 C/min
- Storage Modulus at Room Temperature
 $E' = 2.35 \text{ GPa (2350 MPa)} \pm 5\%$
- Tan Delta at Room Temperature
 $\tan \delta < 0.01$
- Transition Temperature
Tan δ peak from 155-160°C @ 1Hz, 3-5 °C/min
 E'' peak will be about 5 °C lower



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Mounting the Sample

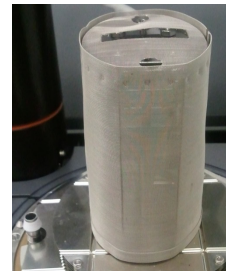
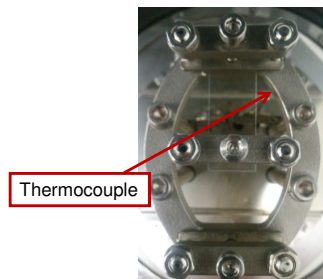
- Finger tighten the sample in position and then 'Lock' movable shaft to align clamp before tightening with torque wrench. Tighten to 8-10 in-lbs torque.



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Temperature Ramp Results from Polycarbonate

- Transition Temperature:
 - Tan δ peak from 155-160 °C @ 1Hz, 3-5 °C/min
 - E" peak will be about 5 °C lower

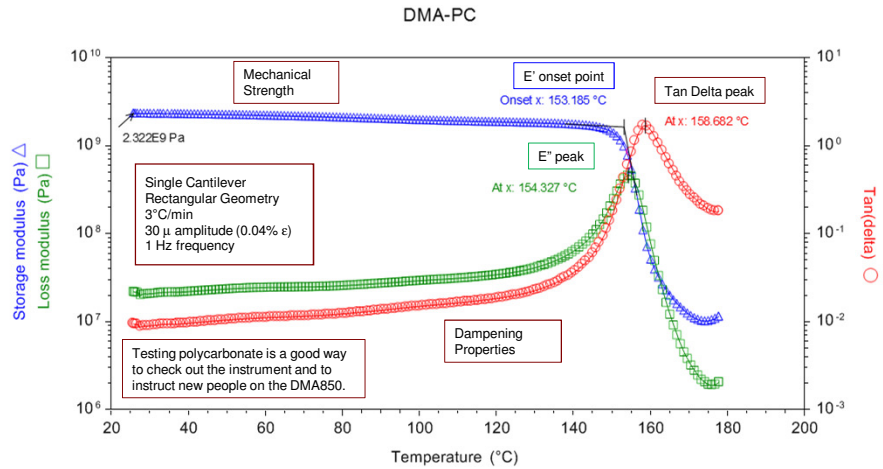


Note: Thermocouple position and sample or thermocouple shields can affect temperature results from a temperature ramp. The shields are recommended especially when the ACS chiller is used.



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Polycarbonate Testing on the DMA 850



This is the main test performed on DMA instruments.

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APPLICATIONS

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Dynamic Strain Sweep – DMA 850

Clamp: 17.5 mm Single Cantilever

Procedure:

Initial/preload force: 0.0 N

1: Oscillation Strain Sweep No pre-tension

Frequency: 1.0 Hz

Sweep Mode: ☐ Logarithmic ☒ Linear ☐ Discrete

Amplitude: 5.0 μ m to 50.0 μ m

Increment: 5.0 μ m

Number of sweeps: 1

Test Settings

Controlled Test Parameter: ☒ Amplitude ☐ Strain

☐ Enable Direct Strain

Data acquisition: ☒ Standard ☐ Fast ☐ Enhanced ☐ User defined

☒ Save waveform

Limit checking: ☒ Enabled

Terminate step when: Force (N) > 10.0

Clamp: Film Clamp

Procedure:

Initial/preload force: 0.01 N

☒ Use Force Track: 125.0 % With pre-tension

1: Oscillation Strain Sweep

Frequency: 1.0 Hz

Sweep Mode: ☐ Logarithmic ☒ Linear ☐ Discrete

Amplitude: 5.0 μ m to 50.0 μ m

Increment: 5.0 μ m

Number of sweeps: 1

Test Settings

Controlled Test Parameter: ☒ Amplitude ☐ Strain

☐ Enable Direct Strain

Data acquisition: ☒ Standard ☐ Fast ☐ Enhanced ☐ User defined

☐ Measure again after method equilibration

☒ Save waveform

Limit checking: ☒ Enabled

Terminate step when: Force (N) > 5.0

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Programming Strain Sweep on RSA G2

Geometry: Tension fixture (rectangle)

Procedure:

1: Conditioning Options

Axial force adjustment: Mode Active

☒ Tension ☐ Compression

Axial force: 0.2 N ☒ Set initial value

Sensitivity: 0.1 N

Proportional force Mode: Force Tracking ☐ Compensate for modulus

Axial Force > Dynamic Force: 25.0 %

Minimum axial force: 0.2 N

Programmed Extension Below: 0.0 dyne/cm²

Advanced

Max gap change up: 10000.0 μ m

Max gap change down: 1000.0 μ m

☒ Return to window ☐ Return to initial value

Priority: ☒ Data sampling ☐ Force control

Adjustment time out: 00:00:03 hh:mm:ss

Auto strain adjustment: Mode Disabled

Tension

2: Oscillation Amplitude

Environmental Control

Temperature: -50 °C ☐ Inherit Set Point

Soak Time: 00:03:00 hh:mm:ss ☒ Wait For Temperature

Test Parameters

Frequency: 1.0 Hz

Logarithmic sweep

Strain %: 1.0e-3 to 1.0 %

Points per decade: 5

Data acquisition

Step termination

Limit checking: ☒ Enabled

Terminate step when: Oscillation force (N) > 10.0

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Programming Strain Sweep on RSA G2

Geometry: 3 Point bending

Procedure:

1: Conditioning Options

Axial force adjustment

Mode:

☐ Tension ☒ Compression

Axial force: N ☒ Set initial value

Sensitivity: N

Proportional force Mode: ☐ Compensate for modulus

Axial Force > Dynamic Force: %

Minimum axial force: N

Programmed Extension Below: dyne/cm²

Advanced

Max gap change up: μ m

Max gap change down: μ m

☒ Return to window ☐ Return to initial value

Priority: ☒ Data sampling ☐ Force control

Adjustment time out: hh:mm:ss

2: Oscillation Amplitude

Environmental Control

Temperature: °C ☐ Inherit Set Point

Soak Time: hh:mm:ss ☒ Wait For Temperature

Test Parameters

Frequency: Hz

Logarithmic sweep

Strain %: to %

Points per decade:

Data acquisition

Step termination

Limit checking

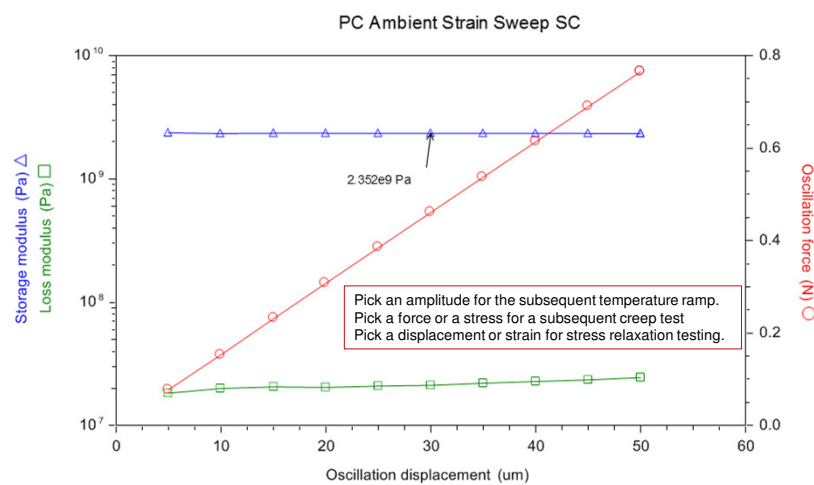
☒ Enabled

Terminate step when

Oscillation force (N): >

49

Dynamic Strain Sweep



50

Dynamic Temperature Ramp – DMA 850

Initial/preload force N
☒ Use Force Track %

1: Oscillation Temperature Ramp

Amplitude μm
 Frequency Hz

☐ Use current temperature
 Ramp from °C to °C
 Ramp rate °C/min

Soak times
 at Start temperature hh:mm:ss
 at End temperature hh:mm:ss

Estimated time to complete hh:mm:ss

Test Settings

Controlled Test Parameter
☒ Amplitude ☐ Strain ☐ Stress ☐ Force
☐ Enable Direct Strain

Data Sampling Mode
 Sampling interval s/pt

Data acquisition
☒ Standard ☐ Fast ☐ Enhanced ☐ User defined
☐ Measure again after method equilibration
☒ Save waveform

Auto Range Mode
☒ Standard ☐ Enhanced

Minimum force N
 Maximum oscillation displacement μm

With the DMA 850, you can use either Trios Express or Trios Unlimited. Express is more basic. Unlimited gives you more options.
 I usually run with Unlimited.

This is one way to do a temperature ramp.
 One would enter the proper amplitude/strain and temperature range.
 In the last section here, we set a minimum oscillation force and a maximum oscillation displacement.
 You can also use Enable Direct Strain in the procedure.



51

Programming Temperature Ramp on RSA G2

Geometry: Tension fixture (rectangle)
 Procedure:

1: Conditioning Options

Axial force adjustment
 Mode
☒ Tension ☐ Compression
 Axial force N ☒ Set initial value
 Sensitivity N
 Proportional force Mode ☐ Compensate for modulus

Axial Force > Dynamic Force %
 Minimum axial force N
 Programmed Extension Below dyne/cm²

Advanced
 Max gap change up μm
 Max gap change down μm
☒ Return to window ☐ Return to initial value
 Priority ☒ Data sampling ☐ Force control
 Adjustment time out hh:mm:ss

Auto strain adjustment
 Mode
 Strain adjust %
 Minimum strain %
 Maximum strain %
 Minimum force N
 Maximum force N

2: Oscillation Temperature Ramp

Environmental Control
 Start temperature °C ☐ Inherit set point
 Soak time hh:mm:ss ☐ Wait for temperature
 Ramp rate °C/min
 End temperature °C
 Soak time after ramp hh:mm:ss
 Estimated time to complete hh:mm:ss

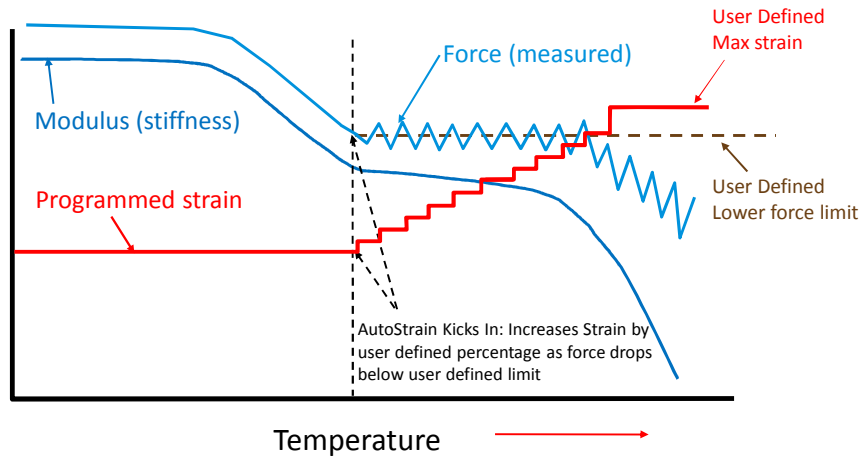
Test Parameters
 Sampling interval s/pt
 Strain % %
 Single point
 Frequency Hz



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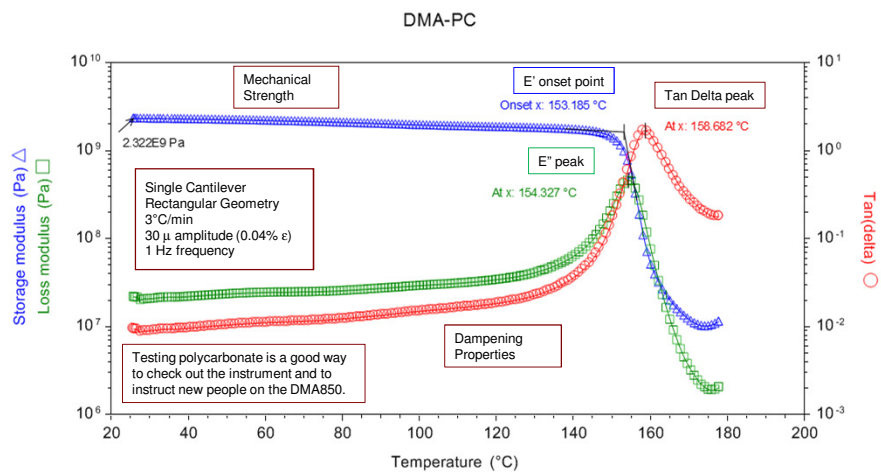
Auto-Strain on RSA G2

Over temperature range covered, force falls below user defined lower limit in strain controlled DMA.



53

Polycarbonate Testing on the DMA 850



This is the main test performed on DMA instruments.

54

Frequency Sweep: DMA 850

Procedure:

Initial/preload force N
☒ Use Force Track %

1: Oscillation Frequency Sweep

Amplitude μm

Sweep Mode
☒ Logarithmic ☐ Linear ☐ Discrete

Frequency Hz to Hz
 Points per decade
 Number of Sweeps

Test Settings

Controlled Test Parameter
☒ Amplitude ☐ Strain ☐ Stress ☐ Force
☐ Enable Direct Strain

Data acquisition
☒ Standard ☐ Fast ☐ Enhanced ☐ User defined
☐ Measure again after method equilibration
☒ Save waveform

55

Frequency Sweep: RSA-G2

Geometry: Tension fixture (rectangle)
 Procedure:

1: Conditioning Options

Axial force adjustment
 Mode
☒ Tension ☐ Compression
 Axial force N ☒ Set initial value
 Sensitivity N
 Proportional force Mode ☐ Compensate for modulus
 Axial Force > Dynamic Force %
 Minimum axial force N
 Programmed Extension Below Pa

Advanced
 Max gap change up μm
 Max gap change down μm
☒ Return to window ☐ Return to initial value
 Priority ☒ Data sampling ☐ Force control
 Adjustment time out hh:mm:ss

Auto strain adjustment
 Mode
 Strain adjust %
 Minimum strain %
 Maximum strain %
 Minimum force N
 Maximum force N

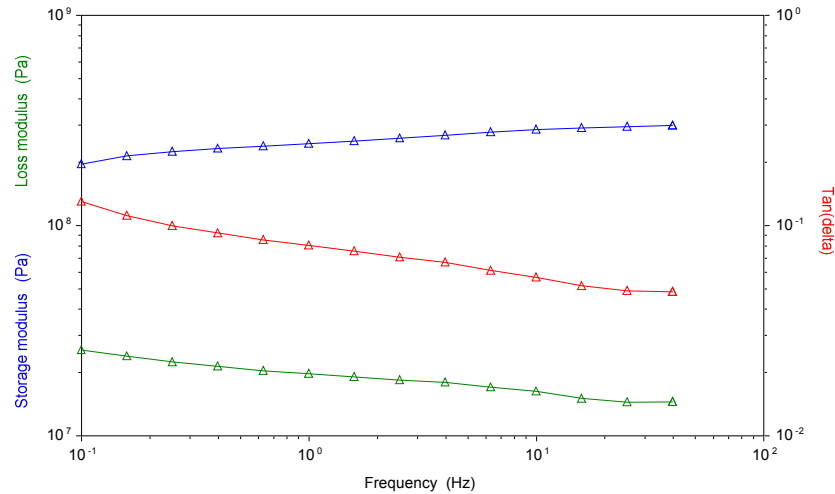
2: Oscillation Frequency

Environmental Control
 Temperature °C ☐ Inherit Set Point
 Soak Time hh:mm:ss ☐ Wait For Temperature

Test Parameters
 Strain % %
 Logarithmic sweep
 Frequency to Hz
 Points per decade

56

Frequency Sweep



57

Dynamic Temperature/Frequency Sweep – DMA 850

Initial/preload force N
☒ Use Force Track %

1: Oscillation Temperature Sweep (Multifrequency)

Amplitude μm
 Sweep from $^{\circ}\text{C}$ to $^{\circ}\text{C}$
 Temperature increment $^{\circ}\text{C}$
 Soak time hh:mm:ss

Sweep Mode
☒ Logarithmic ☐ Linear ☐ Discrete
 Frequency Hz to Hz
 Points per decade

Test Settings

Controlled Test Parameter
☒ Amplitude ☐ Strain ☐ Stress ☐ Force
☐ Enable Direct Strain

Data acquisition
☒ Standard ☐ Fast ☐ Enhanced ☐ User defined
☐ Measure again after method equilibration
☒ Save waveform

Auto Range Mode
☒ Standard ☐ Enhanced
 Minimum force N
 Maximum oscillation displacement μm

58

Temperature/Frequency Sweep – RSA-G2

1: Conditioning Options

Axial force adjustment

Mode: **Active**

☒ Tension ☐ Compression

Axial force: 0.2 N ☒ Set initial value

Sensitivity: 0.1 N

Proportional force Mode: **Force Tracking** ☐ Compensate for modulus

Axial Force > Dynamic Force: 25.0 %

Minimum axial force: 0.2 N

Programmed Extension Below: 0.0 Pa

Advanced

Max gap change up: 10000.0 μm

Max gap change down: 1000.0 μm

☒ Return to window ☐ Return to initial value

Priority: ☒ Data sampling ☐ Force control

Adjustment time out: 00:00:03 hh:mm:ss

Auto strain adjustment

Mode: **Enabled**

Strain adjust: 20.0 %

Minimum strain: 0.01 %

Maximum strain: 1.0 %

Minimum force: 0.2 N

Maximum force: 10.0 N

2: Oscillation Temperature Sweep

Environmental Control

Start temperature: 20 °C ☐ Inherit

Soak time: 00:02:00 hh:mm:ss ☒ Wait for temperature

End temperature: 100 °C

Temperature step: 10 °C

Test Parameters

Strain %: 0.1 %

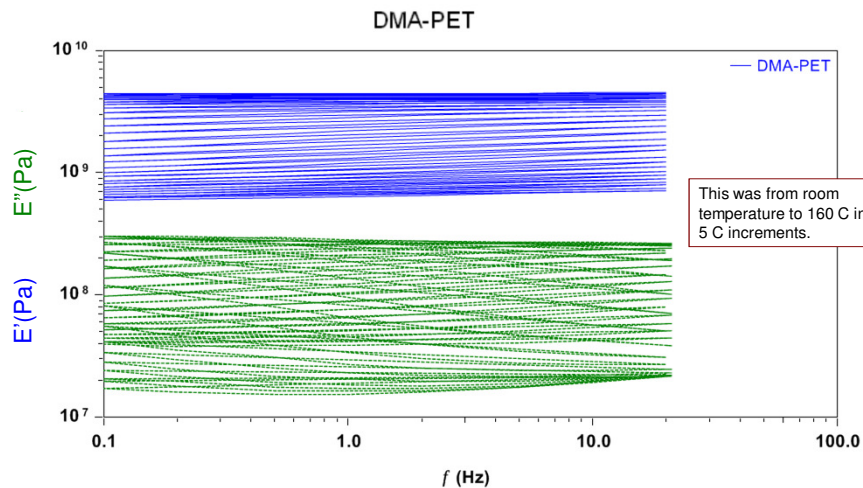
Logarithmic sweep

Frequency: 10.0 to 0.1 Hz

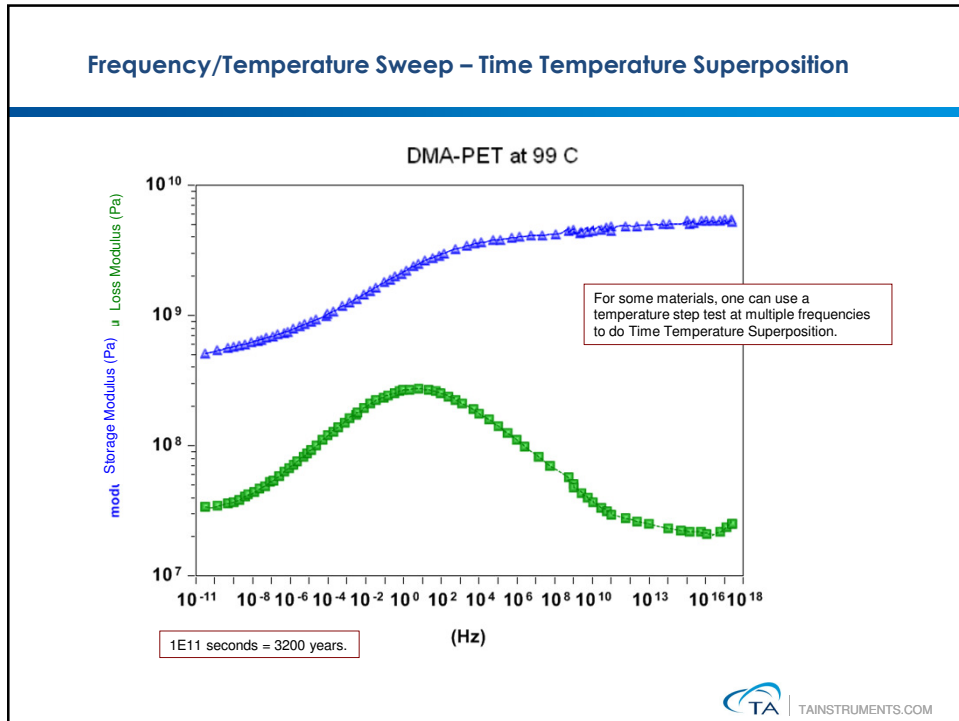
Points per decade: 5

59

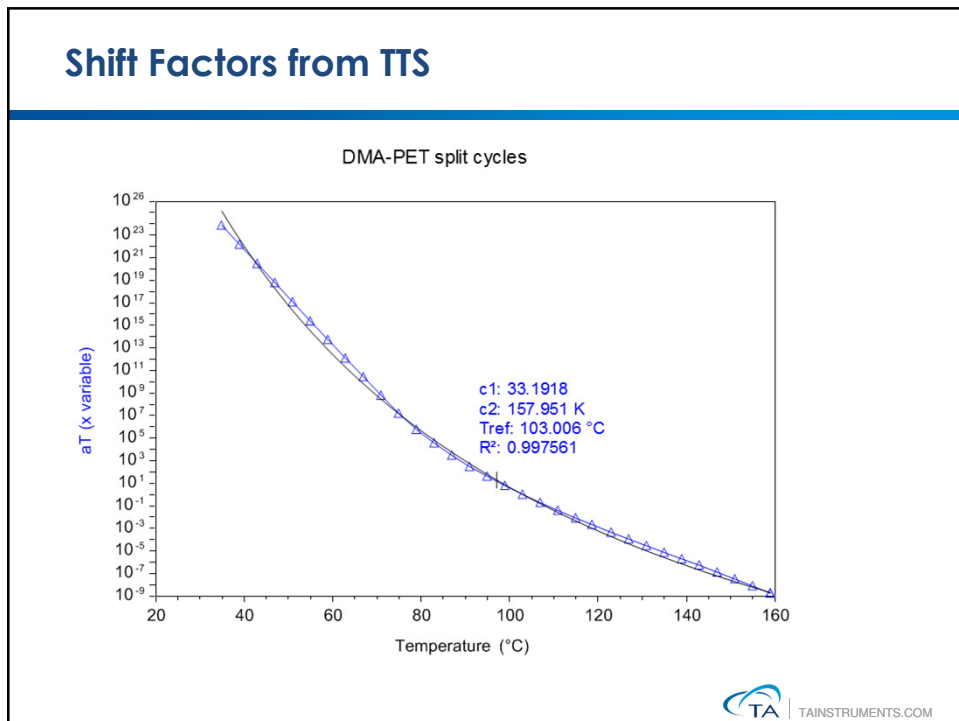
Temperature/Frequency Sweep



60



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62

Creep Testing: DMA 850

Initial/preload force N
☐ Use Force Track %

1: Stress Control Creep Recovery

Stress Pa
 Creep time hh:mm:ss
 Recovery time hh:mm:ss

Data sampling mode
☒ Linear ☐ Log
 Sampling rate pts/s

Test Settings
 Controlled Test Parameter
☐ Force ☒ Stress
 Transient force precision
☒ Standard ☐ Enhanced
 Linear Sampling Mode
☒ points/second ☐ seconds/pt ☐ Number of points

This is straightforward.
 It is more complex with the RSA-G2



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Creep Testing on the RSA-G2

Steps needed to do a creep test on the RSA-G2

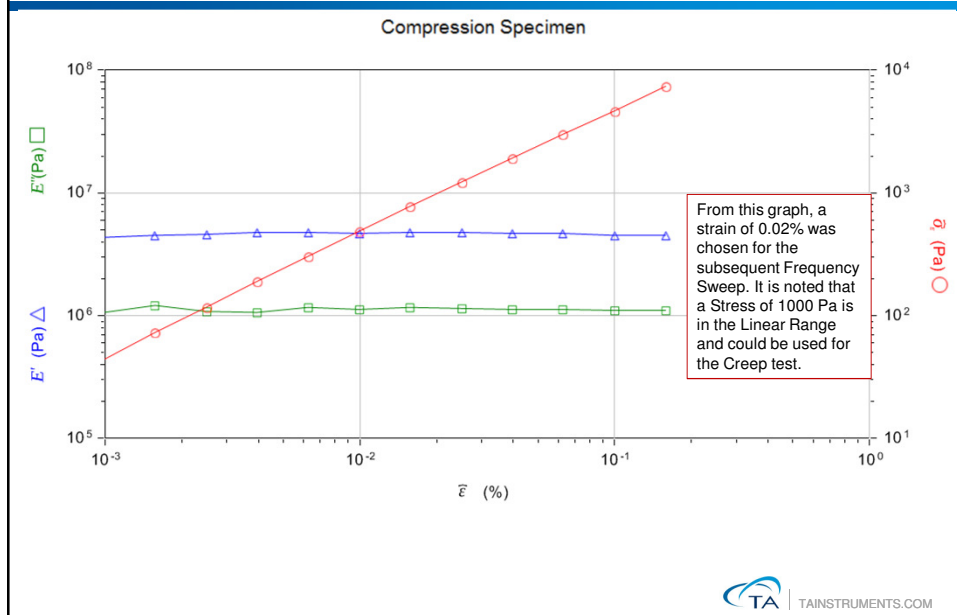
1. Perform a strain sweep to find the Linear Viscoelastic Region
2. Use the Conditioning > Controlled Stress to calculate the PID constants.
3. Perform the creep test.

The sample chosen was a foam material that was readily available. The compression clamp was used.



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Graph of Preliminary Strain Sweep Test



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Frequency Sweep to Get PID Constants

Sample: Compression Specimen for creep

Geometry: Compression fixture (disc)

Procedure:

Name:

1: Conditioning Options Active, Disabled

2: Conditioning Stress Control

☐ Load Precomputed ☒ Run and Calculate

Environmental Control

Temperature: °C ☐ Inherit set point

Soak time: s ☐ Wait for temperature

Test Parameters

Strain %: %

☒ Save stress control PID file

Stress control PID file path:

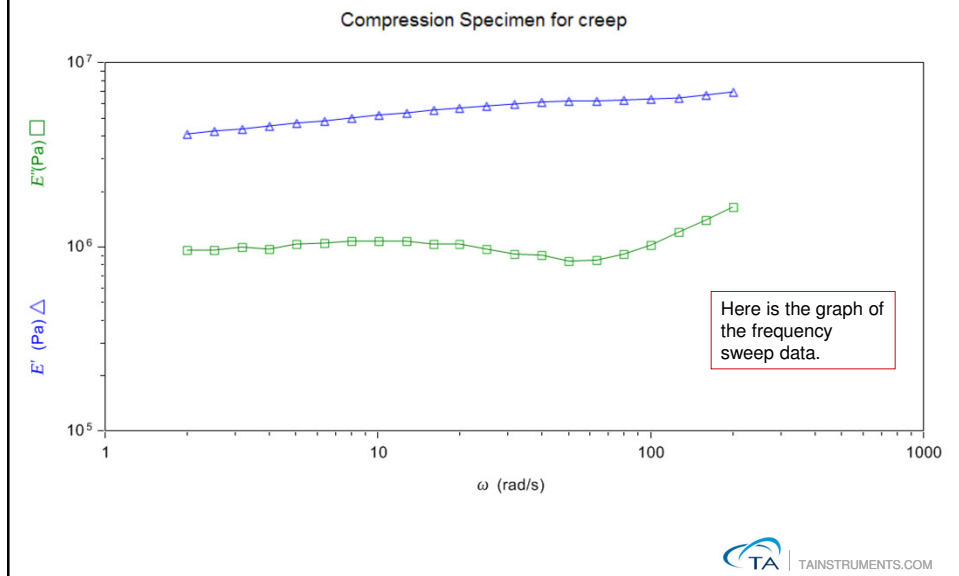
☒ Data acquisition

Now we perform the Frequency Sweep to get the PID constants. The Conditioning > Options step is the same as that used for the Strain Sweep. I entered the name of the file in the box where it says Stress control PID file path.

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Frequency Sweep to Get PID Constants



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Actual Creep Test on RSA-G2

Sample: Compression Specimen for creep
 Geometry: Compression fixture (disc)
 Procedure:

Name:

1: Conditioning Stress Control

☒ Load Precomputed ☐ Run and Calculate

Stress control PID file path:

Integral term:
 Gain term:
 Motor PID set:
 Torque filter:

2: Step (Transient) Creep

Now, we are ready to do Creep. I made a new experiment for the Creep. I did not just add steps to the Run and Calculate Frequency sweep. I removed the Conditioning step that had the Preload Axial Force. We changed the command in Conditioning Stress Control to Load Precomputed. We select the PID file path from our last run. Note the values for the Integral term and the Gain term. I also manually raised the RSA-G2 head so that it was just touching the specimen. The force was right around 0.0 g.

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Actual Creep Test

Sample: Compression Specimen for creep
 Geometry: Compression fixture (disc)
 Procedure:

Name:

1: Conditioning Stress Control
 2: Step (Transient) Creep

Environmental Control
 Temperature: 25 °C ☐ Inherit set point
 Soak time: 10.0 s ☐ Wait for temperature

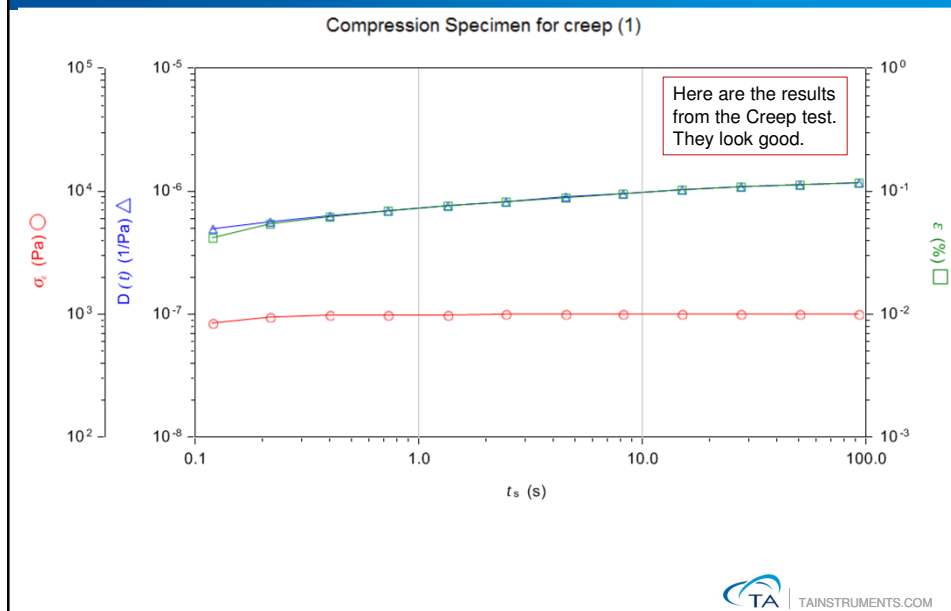
Test Parameters
 Duration: 100.0 s
☐ Tension ☒ Compression
 Stress: 1000.0 Pa
 Sampling: ☐ Linear ☒ Log
 Number of points: 20

☒ Data acquisition
☒ Step termination

Here is the Creep procedure I designed.

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Creep Test on RSA-G2



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Programming Stress Relaxation on a RSA-G2

2: Step (Transient) Stress Relaxation

Environmental Control

Temperature °C ☐ Inherit set point

Soak time s ☒ Wait for temperature

Test Parameters

Duration s

☒ Tension ☐ Compression

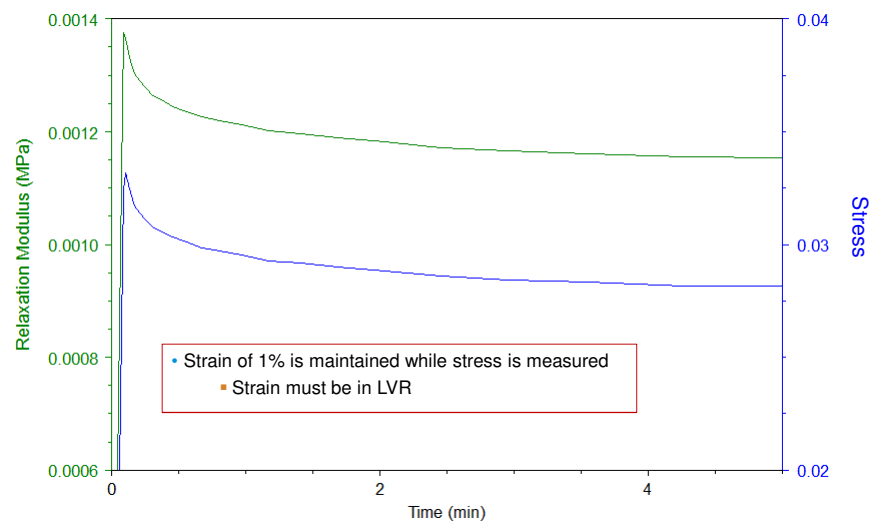
Strain % %

Sampling ☐ Linear ☒ Log

Number of points

71

Stress Relaxation on Silicone Foam



72

Programming Iso-strain Testing on a RSA-G2

- Hold strain constant and measure sample shrinking force

[Experiment 2]

Sample: PET film LN2 only

Geometry: Tension fixture (rectangle)

Procedure of 1 step

1: Other Temp Ramp IsoStrain

Environmental Control

Start temperature	20 °C	<input type="checkbox"/> Inherit set point
Soak time	180.0 s	<input checked="" type="checkbox"/> Wait for temperature
Ramp rate	3.0 °C/min	
End temperature	200 °C	
Soak time after ramp	0 s	
Estimated time to complete	01:00:00 hh:mm:ss	

Test Parameters

Sampling rate: 1.0 pts/s

☒ Tension ☐ Compression

Strain %: 0.1 %

Maximum force: 20.0 N

☐ Data acquisition

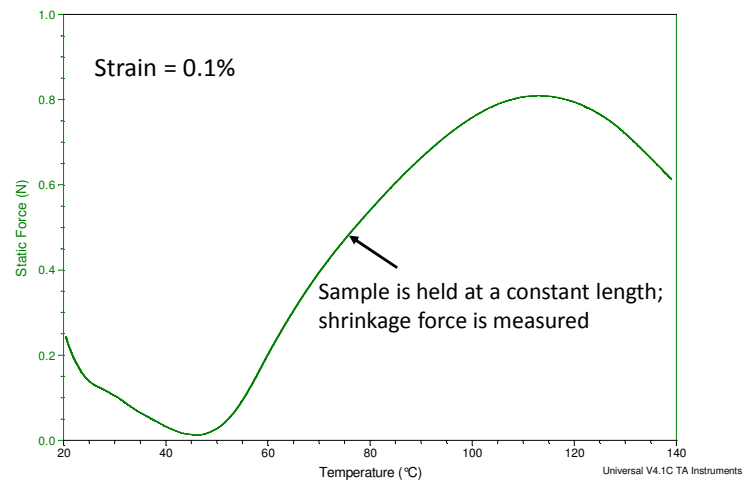
73

PVC Based Film - IsoStrain

Sample: Iso strain
Size: 13.5810 x 5.3000 x 0.0500 mm
Method: Isostrain

DMA

File: P:\Q800 ISO STRAIN.002
Operator: Terri
Run Date: 2004-09-17 18:11
Instrument: DMA Q800 V7.0 Build 113



74

Polymer Structure-Property Characterization

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

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



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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

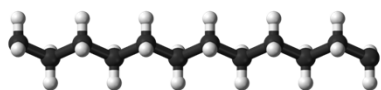
Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 508.



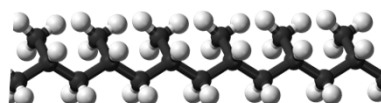
76

Chemical Composition of Polymers

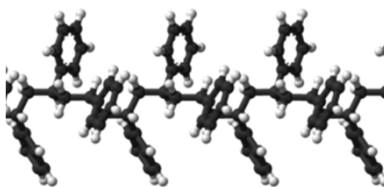
- Polymers are long chains of repeating units (monomers)
- The chemical composition determines mechanical properties, and the temperature where transitions occur



Polyethylene $T_g = -128^\circ \text{C}$



Polypropylene $T_g = -20^\circ \text{C}$



Polystyrene $T_g = 100^\circ \text{C}$

"Introduction to Polymer Viscoelasticity," 2nd Edition. Aklonis, John J; MacKnight, William J. Wiley-Interscience



77

Dynamic Mechanical Analysis of T_g

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



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

- **Storage Modulus E' Onset:**

- Occurs at lowest temperature, relates to mechanical failure

- **Loss Modulus E'' Peak:**

- Occurs at middle temperature
- Related to the physical property changes
- Reflects molecular processes - the temperature at the onset of segmental motion

- **Tan δ Peak:**

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

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



79

The Glass & Secondary Transitions

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

Secondary Transitions

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

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



80

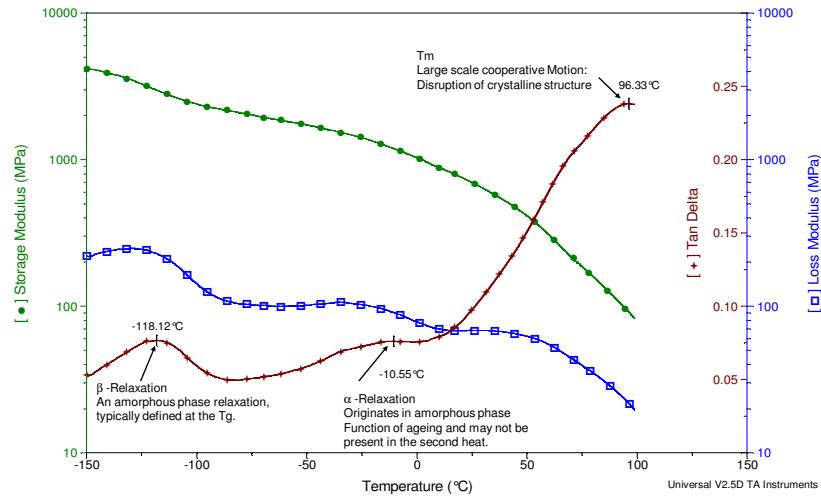
LDPE: Primary and Secondary Transitions

Sample: Polyethylene in Tension
Size: 8.4740 x 5.7500 x 1.0000 mm

DMA

File: F:\DMADATA\Peten.tr1
Operator: RRU
Run Date: 18-Jan-99 16:10

Comment: 15 microns, 120% Autostrain, -150 °C to 100 °C



Universal V2.5D TA Instruments
TA TAINSTRUMENTS.COM

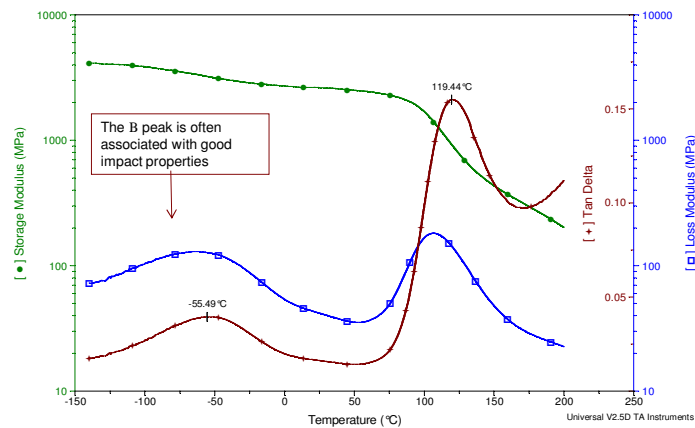
81

Primary and Secondary Transition in PET Film

Sample: PET Film in Machine Direction
Size: 8.1880 x 5.5000 x 0.0200 mm
Method: 3 °C/min ramp
Comment: 1Hz; 3 °C/min from -140 ° to 150 °C, 15 microns.

DMA

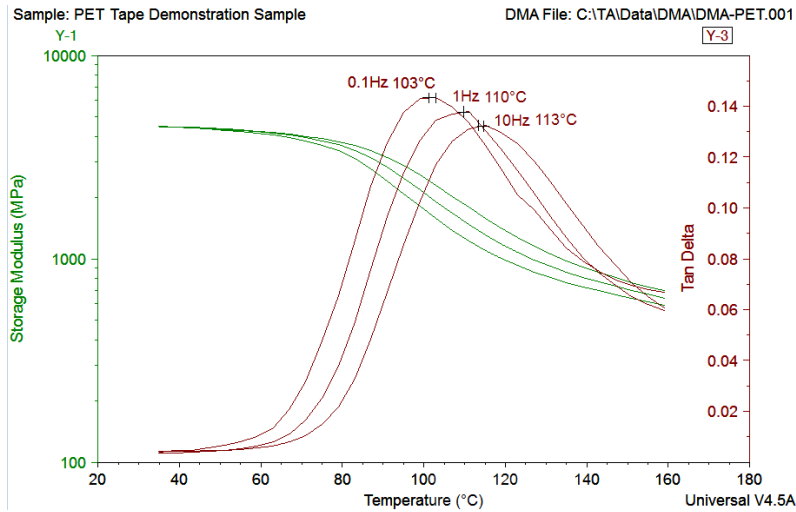
File: A:\Petmd.001
Operator: RRU
Run Date: 27-Jan-99 13:56



Universal V2.5D TA Instruments
TA TAINSTRUMENTS.COM

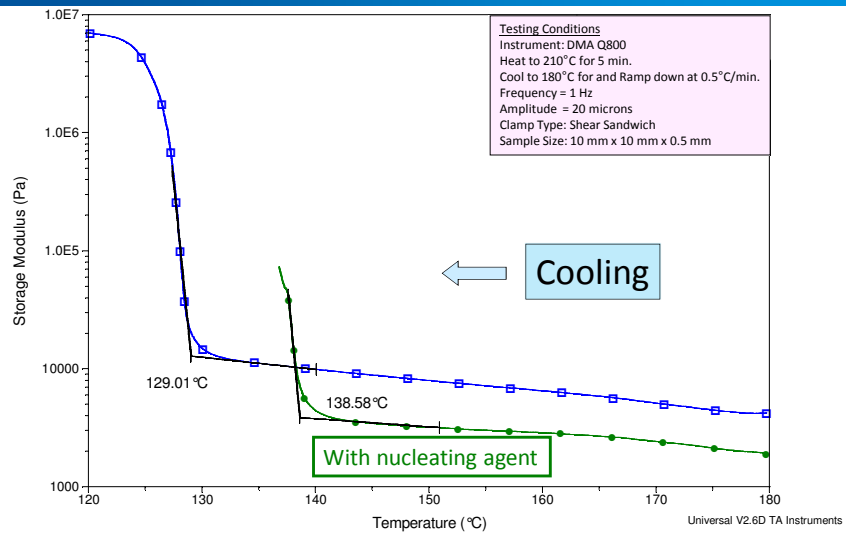
82

PET Film: Effect of Frequency on Tg



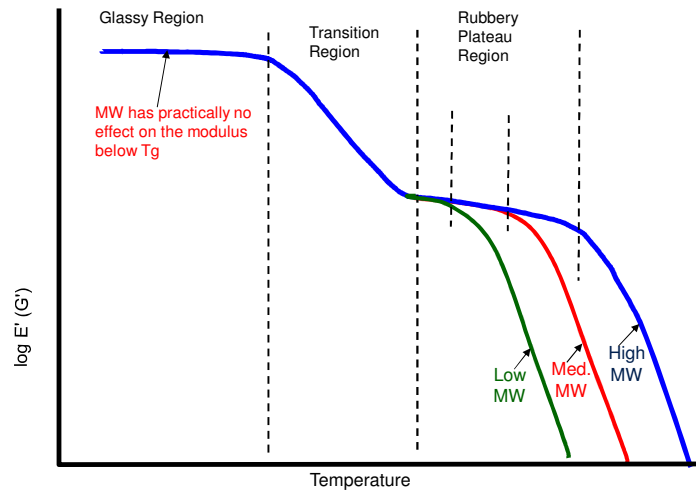
83

Polypropylene - Onset of Crystallization



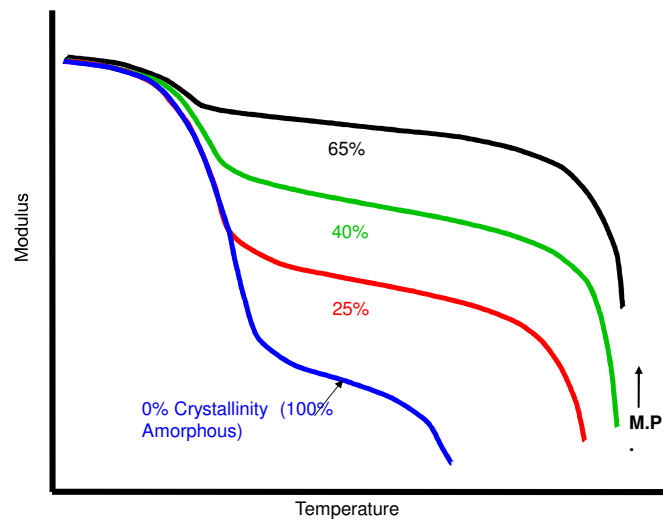
84

Molecular Structure - Effect of Molecular Weight



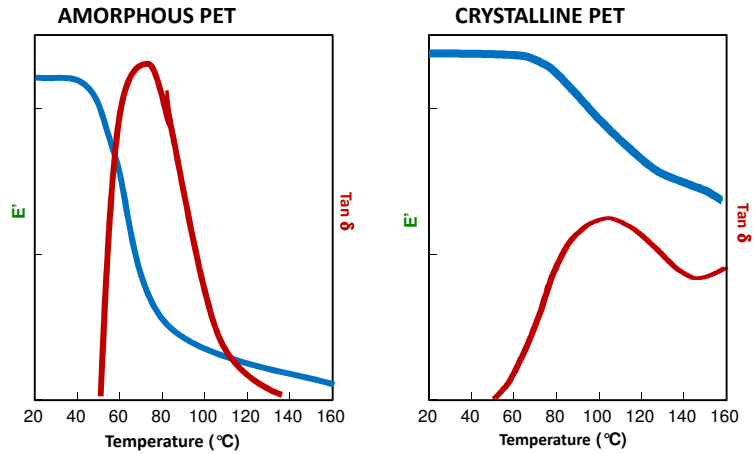
85

Effect of Crystallinity



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Effect of % Crystallinity on Glass Transition

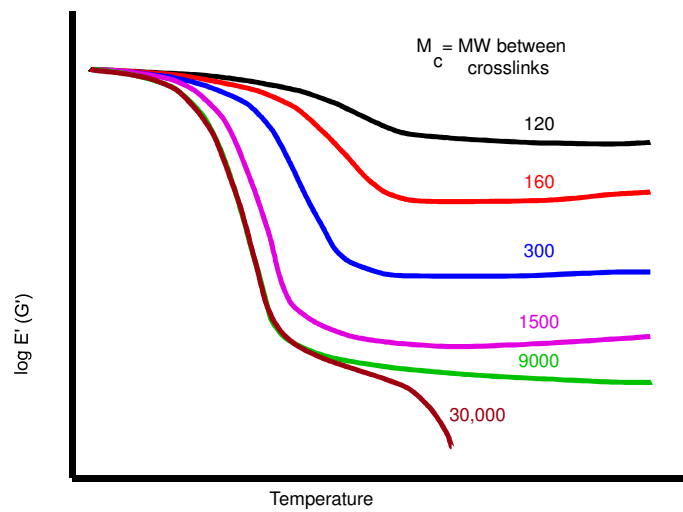


Redrawn with permission from Thompson and Woods, *Trans. Faraday Soc.*, 52, 1383 (1956)



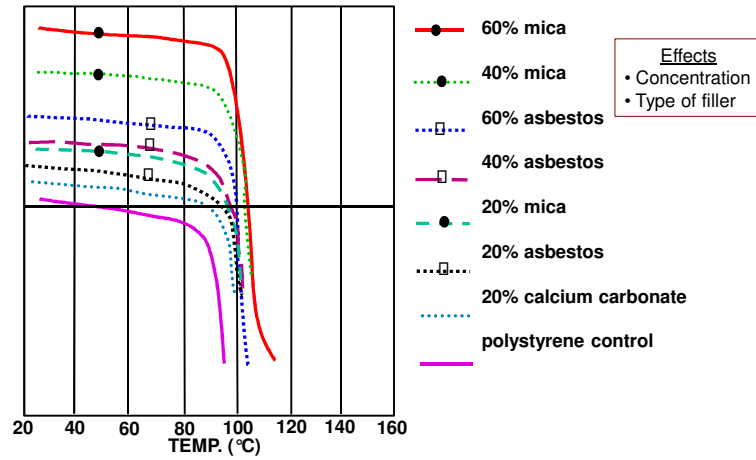
87

Effect of Crosslinking



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Effect of Filler on Modulus



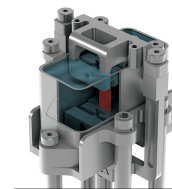
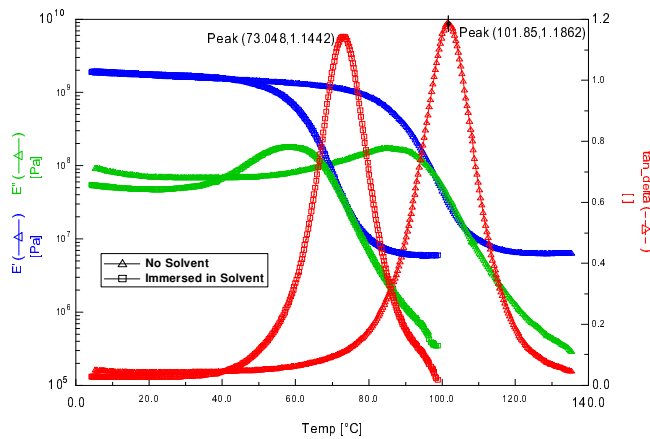
Nielson, L. E., Wall, R. A., and Richmond, P. G., *Soc. Plastics Eng. J.*, **11**, 22 (1966)



89

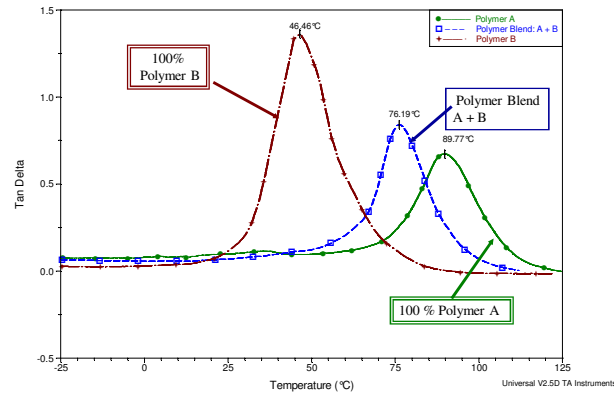
Effect of Moisture

- Automotive coating measured under dry vs. wet conditions



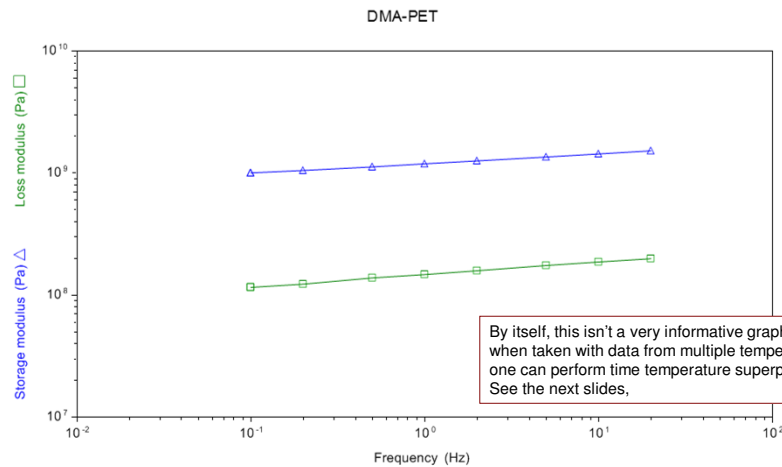
90

Polymer Blend - Aerospace Coating



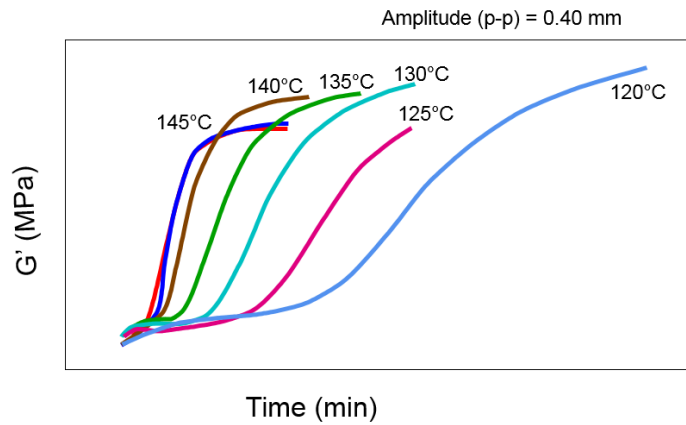
91

Dynamic Frequency Sweep



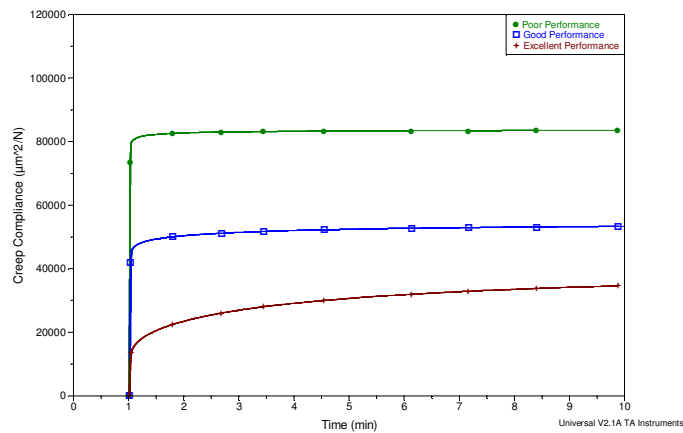
92

Isothermal Cure of Tire Compound: Effect of Curing Temperature



93

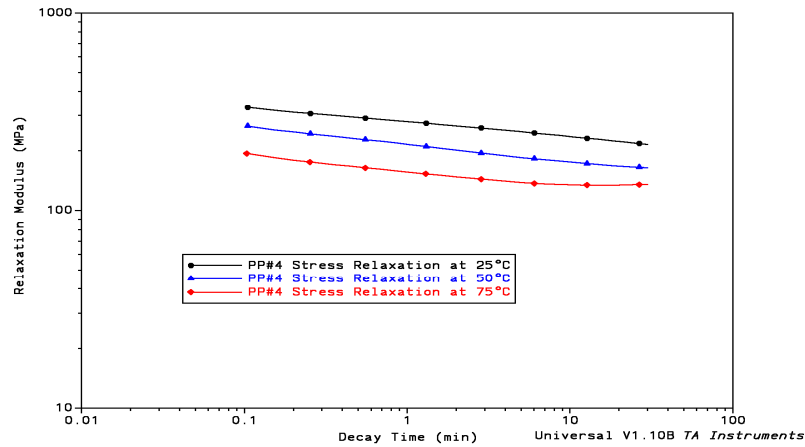
Creep on Packaging Films used in Thermoforming



94

DMA: Stress Relaxation on Polypropylene

Polypropylene Stress Relaxation on DMA 2980
Strain = 1%, Clamp: 8 mm Dual Cantilever



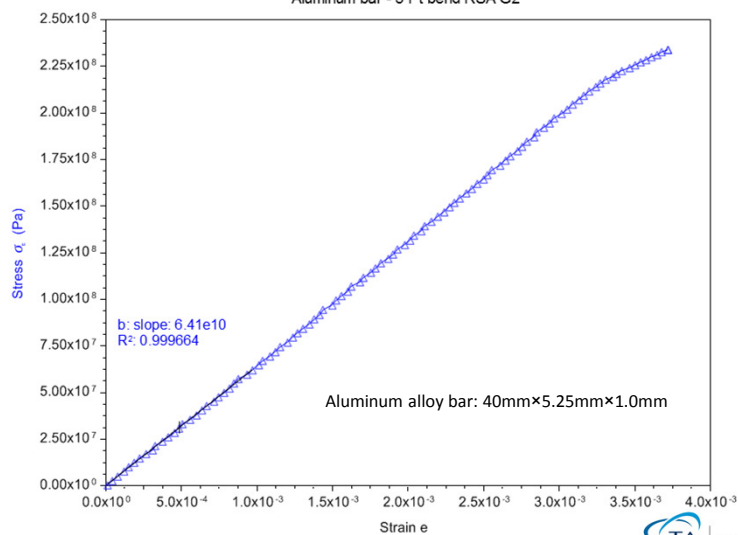
TA TAINSTRUMENTS.COM

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Other (Axial) – RSA G2

Constant Linear Rate: 0.1mm/min, 2 mm max gap change

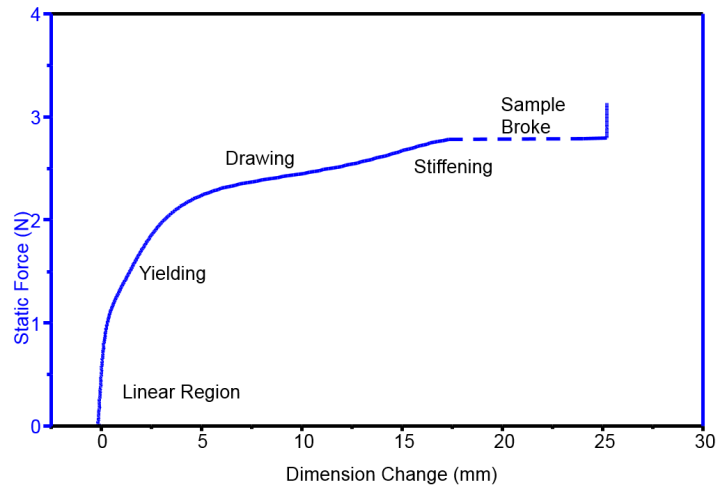
Aluminum bar - 3 Pt bend RSA G2



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96

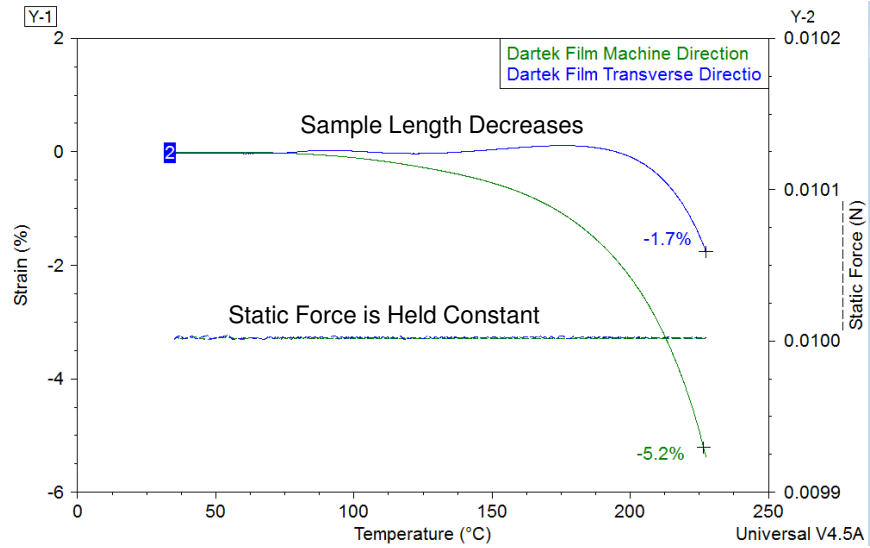
Stress-Strain Experiment (Ramped Force) Polyethylene Film 4 mm



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Iso-Force Temp Ramp- Shrinkage of Oriented Film

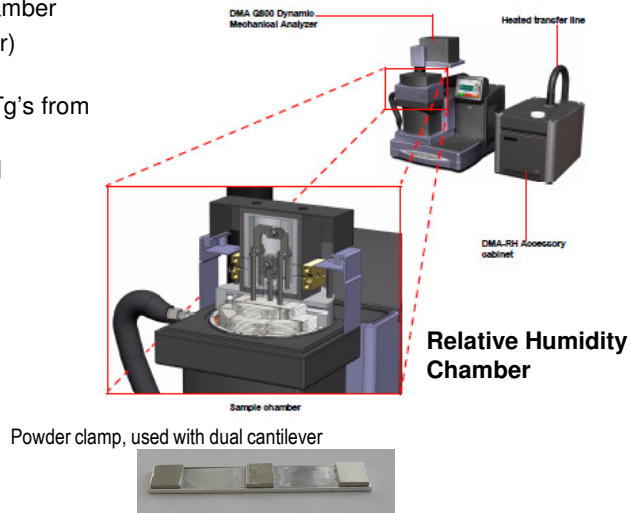


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Other Accessories

- Relative Humidity Chamber (described later)
- Powder Kit for 35-mm Cantilever Clamp for Tg's from tan delta
- Low Friction 3-pt bend
- Penetration Clamp
- Glass Support Cloth

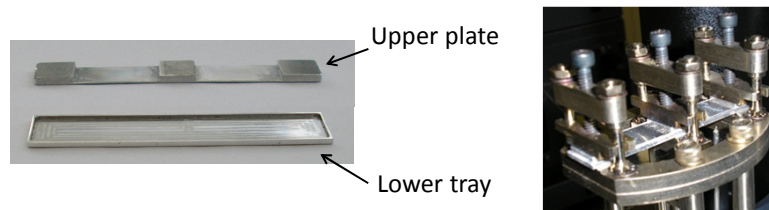


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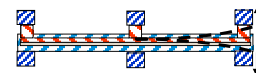
99

Powder Clamp

- Powder clamp measures thermal transitions in powders and is used with the standard 35 mm dual cantilever clamp



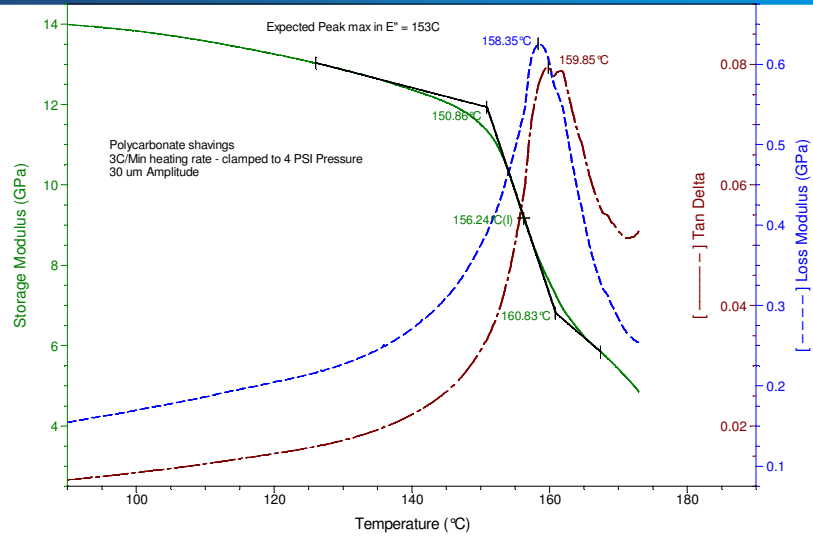
- Powder is placed in the lower tray
- Clamp will flex during measurements and contribution of the powder to the system is "magnified"
 - Use mesh or screen to aid in cleaning
 - Do not melt sample, cleaning will be difficult



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Polycarbonate Shavings



Note: Disregard values of modulus



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Humidity Option

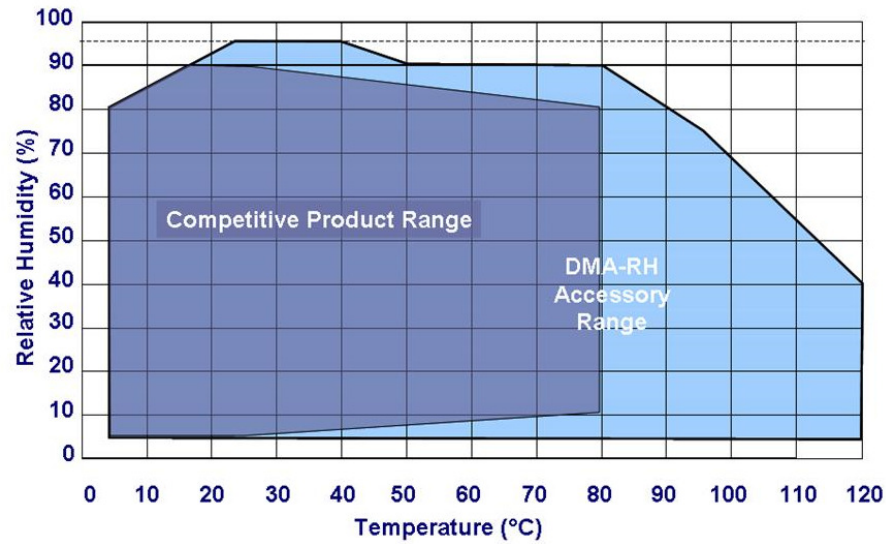


This is the temperature/humidity chamber that was used to control the environment for this testing.



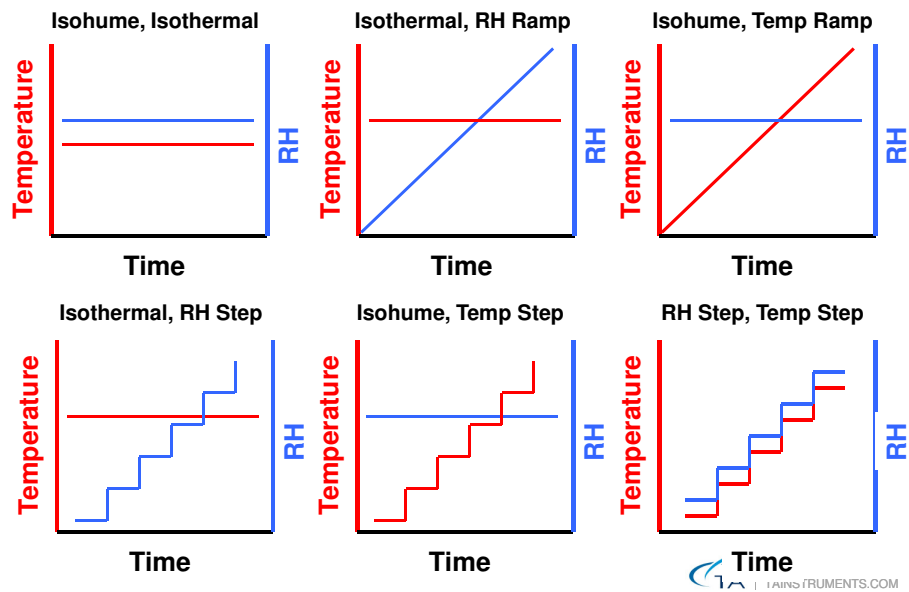
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Q800: DMA-RH Operating Range



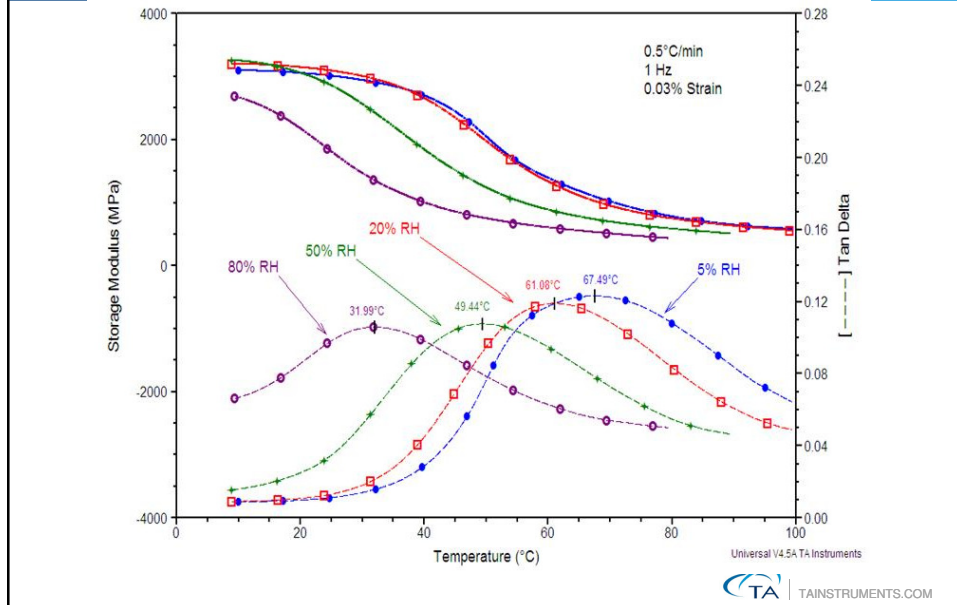
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DMA-RH Experimental Options



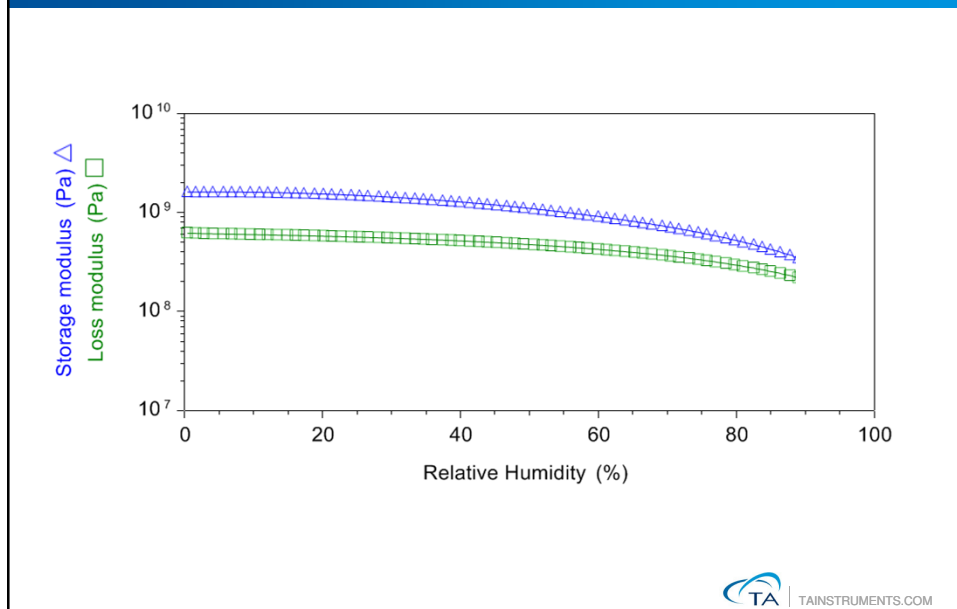
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Analysis of Nylon 6: Isohume-Temperature Scans



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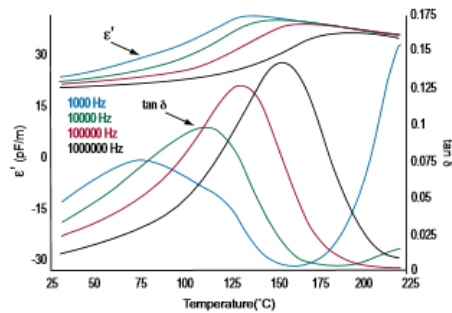
Dynamic Humidity Ramp



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Dielectric Testing

Figure 16: DETA Temperature Ramp on PMMA



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RSA G2 Dielectric Accessory



- RSA G2 can be positioned as two instruments in one.
 - DMA/Solids Analyzer
 - Dielectric Analyzer

Attribute	Specification
Geometry	25 mm PP
Temperature System	FCO, Force Convection Oven
Compatibility	
ARES/RSA to DE Bridge Interface	IEEE Internal to Instrument
Temperature Range	-160° to 300°C

(LCR Meter)	Frequency	AC Test Signal (potential)
Agilent 4285A	75 kHz to 30 MHz	0.005 to 10 Volts
Agilent E4980A	20 Hz to 2 MHz	0.005 to 20 Volts

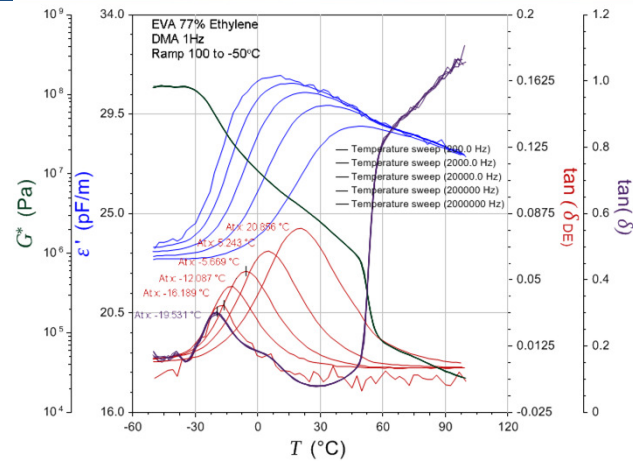


Agilent LCR Meter Model 4980A

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Relaxations in Ethylene Vinyl Acetate (EVA)



Temperature ramp from 100 to -50°C with dynamic mechanical response at 1Hz and simultaneous dielectric response at a frequency of: 200, 2000, 20000, 200000 and 2000000 Hz (Data collected on DHR rheometer)



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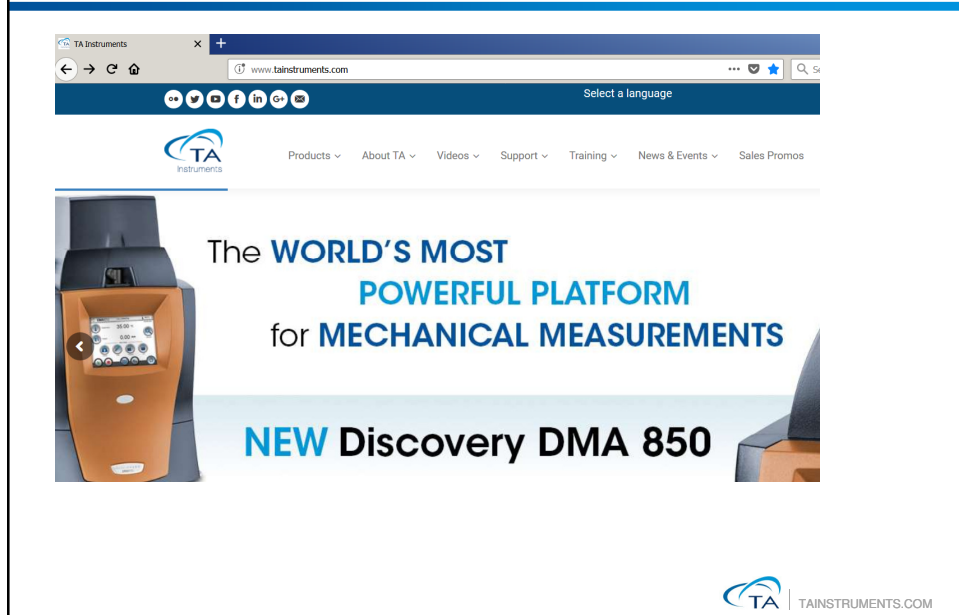
Need DMA HELP?!?

- Check the manuals, help and error help.
- Contact the TA Instruments Rheology Hotline
 - 302-427-4070 M-F 8-4:30 ET
 - 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!



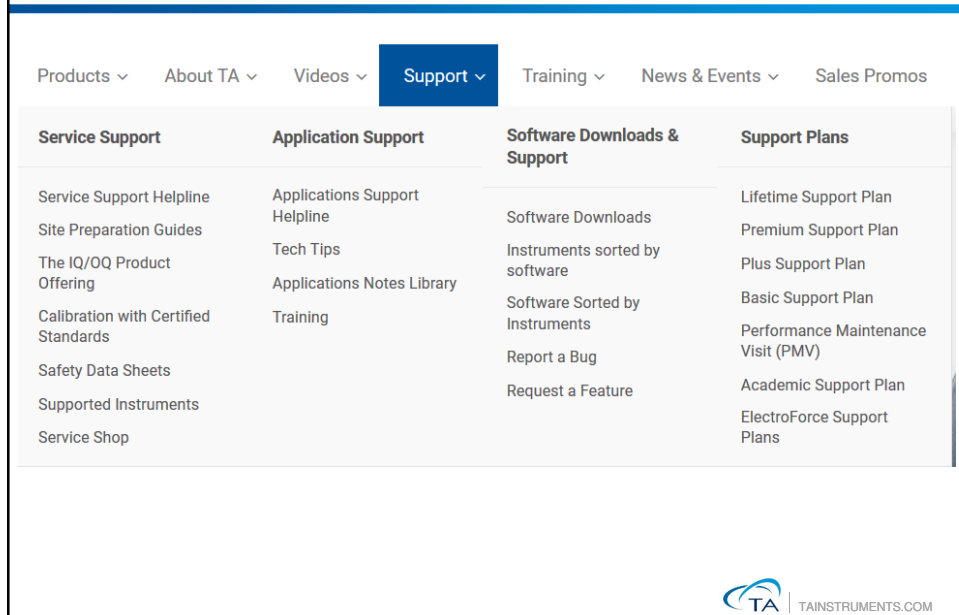
110

Website: www.tainstruments.com



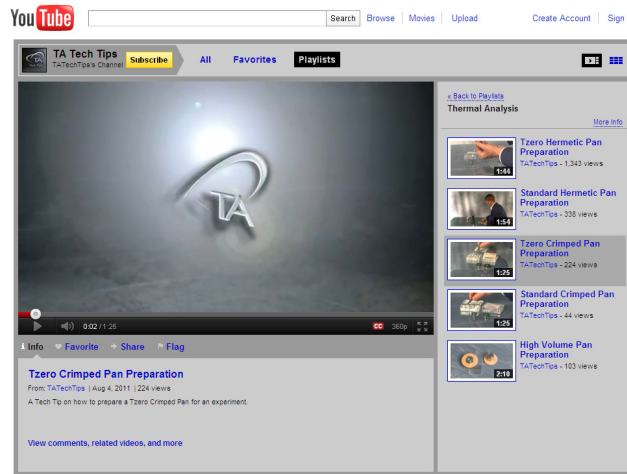
111

Website: www.tainstruments.com



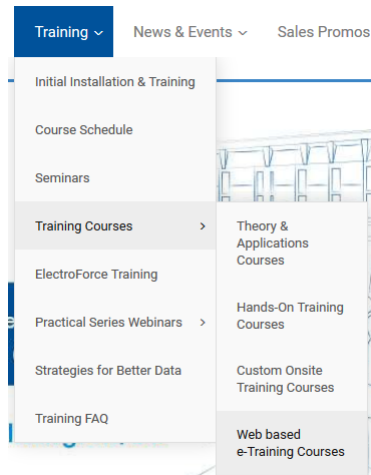
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TA Tech Tips



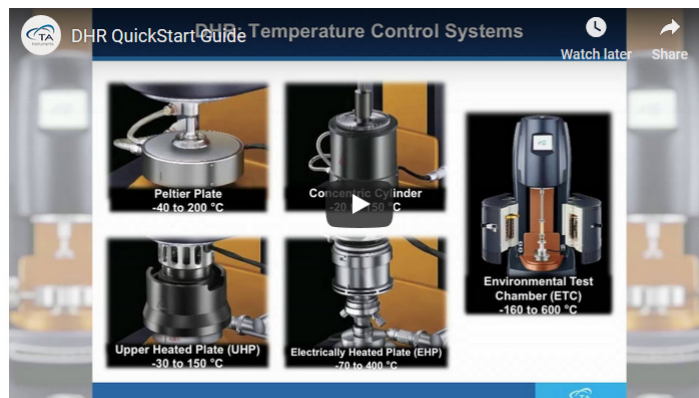
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On Line Training



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DHR Quick Start Guide



TRIOS QuickStart Guide – Basic Data
Analysis Applications in Rheology



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<p>Extensional Rheology in Polymer Processing</p>	<p>An Introduction to Tribo-Rheometry: Quantifying Friction</p>	<p>Rheo-Microscopy: Bridging Rheology, Microstructure & Dynamics</p>	<p>Extensional Rheology & Analytics of Material Characterization</p>

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Thank You

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Rheology, and Microcalorimetry



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