Flex, torsion or bend
– every which way you can
(or Close Encounters of the Third Kind)

UK User Meeting

National Space Research Centre

October 4th 2016

Today's Presentation

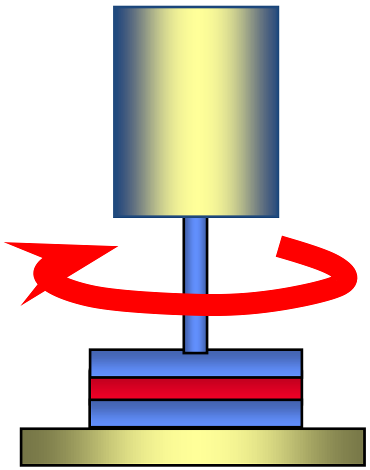
- There are many modes of operation of traditional rotational rheometers that are familiar to the majority
- So many alternative functionalities have arisen to help material characterisation whilst becoming important to provide a competitive differentiator
- With TA's history of innovation and product line, these additional capabilities have provided an overlap with existing dedicated techniques
- In this presentation I will provide an overview to the various modes available on our rotational rheometers
    - the Discovery Hybrid Rheometer (DHR) and ARES-G2
    - and introduce the third kind

Rotational Rheometers Designs

Controlled Strain
Dual Head Rheometer
Separate motor & transducer

Controlled Stress
Single Head Rheometer
Combined motor & transducer

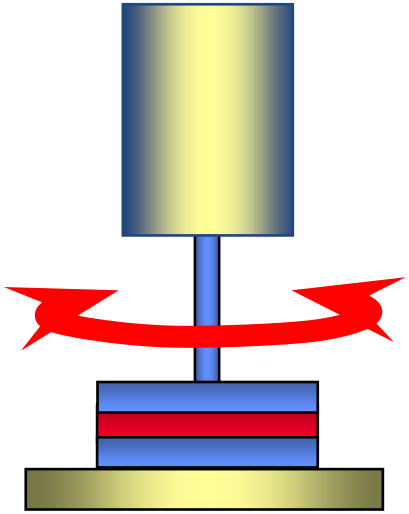
Rotational Rheometer - Modes



- **Flow**
  - Rotation
  - viscosity with shear
  - Of interest when moving a material from A to B

- **Step transient (e.g. creep)**
  - Rotation
  - Deformation under constant stress
  - Of interest to simulate sedimentation or sagging

Rotational Rheometer - Modes



- **Oscillation**
  - Sinusoidal movement back and forth
  - Non destructive deformation to study changes in structure with time, timescales or temperature
- **Axial**
  - Controlled speed head movement
  - Up – tack testing
  - Down – squeeze flow

Choosing a Geometry Size

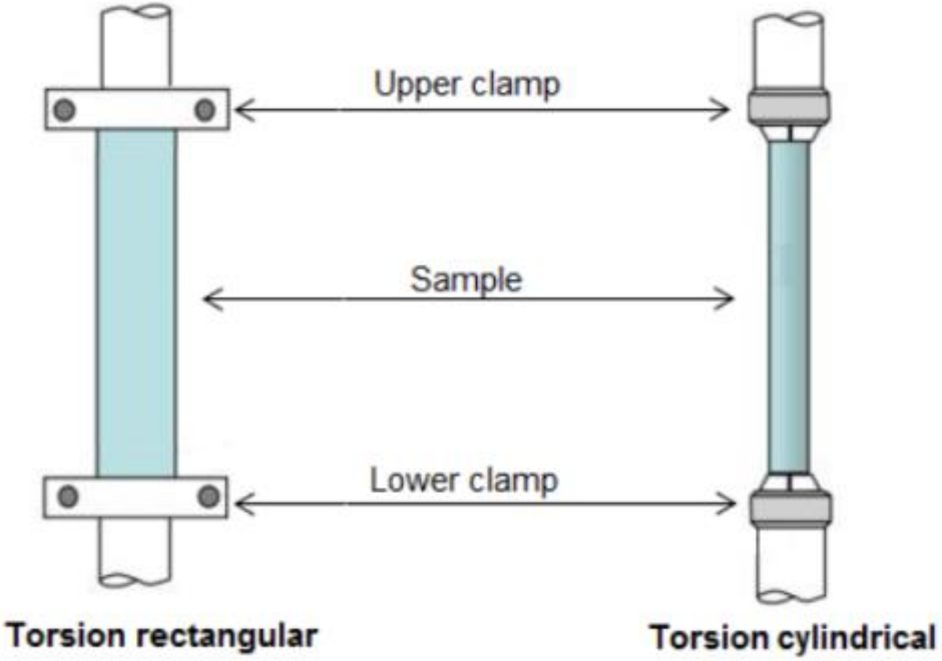
- Assess the 'viscosity' of your sample.
- When a choice of cones plates are available, select diameter appropriate for viscosity of sample
  - Low viscosity (milk) – 60mm geometry/ concentric cylinders
  - Medium viscosity (honey) – 40mm geometry
  - High viscosity (caramel) /Polymer melts – 25mm geometry
  - Very high viscosity (asphalt) – 8 mm geometry
- Examine data in terms of absolute instrument variables [torque/ speed/ displacement] and modify geometry choice to move into optimum working range

Solids Rheology

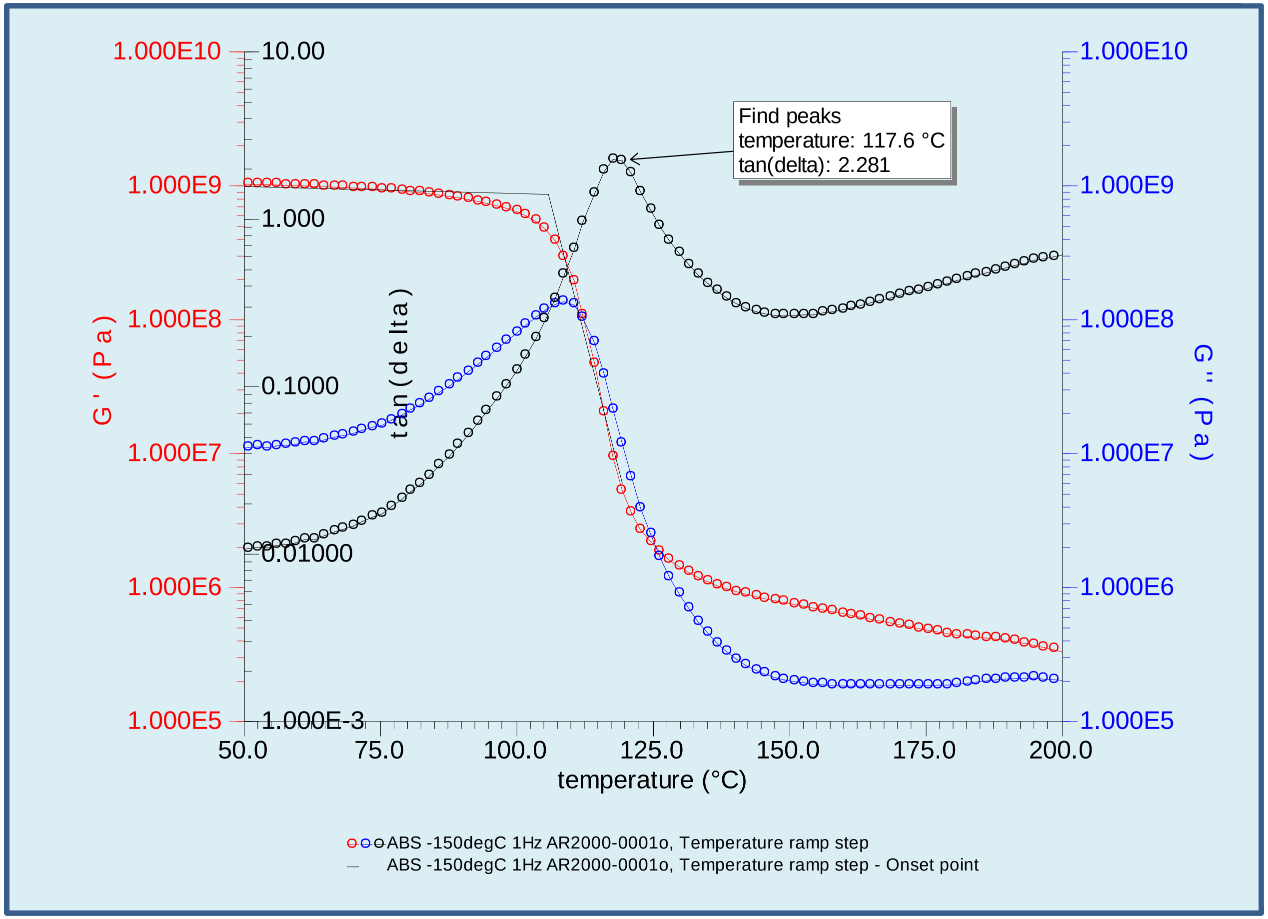
- So many different geometries to measure liquids and soft solids but what do you need for polymers below Tg, or fully cured systems, i.e. solids rheology

- In these cases where the sample stiffness is likely to be very high, modulus values are > 1e7 Pa, then traditionally torsional solid sample clamps would be used.

- These clamps hold a vertical bar (rectangular) or rod (cylindrical) under tension (an axial tension)



Example : Tg – Glass Transition



Storage Modulus Onset - Relates to mechanical Failure

Loss Modulus Peak- reflects the onset of segmental motion

tan δ Peak – a good measure of the "leatherlike" midpoint between the glassy and rubbery states - height and shape change systematically with amorphous content.

However TA has other "rheometers"

- **TA also offer solid rheology instrumentation in the form of our DMA (Dynamic Mechanical Analysers)**
  - Q800 and RSA-G2

- **These work on the principle of linear directional movement**

TA Instruments' DMAs

RSA G2

Controlled Strain

SMT – Separate Motor & Transducer

Q800

Controlled Stress

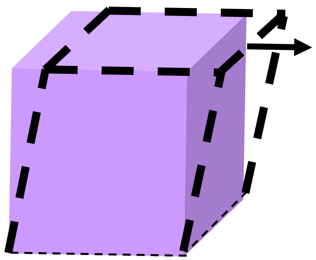
CMT – Combined Motor & Transducer

Typical DMA Clamps

The Three Moduli - Elastic Constants

- **Where the dashed lines indicate stressed state**

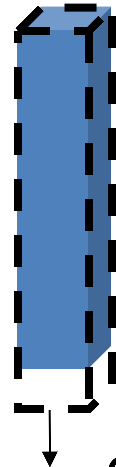
Shear Modulus



$$G = \frac{\tau}{\gamma}$$

τ = shear stress
γ = shear strain

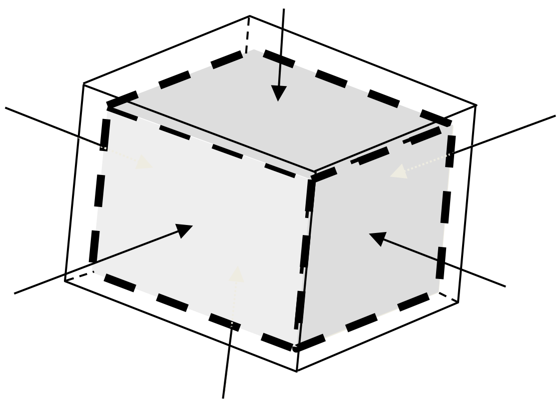
Young's Modulus



$$E = \frac{\sigma}{\varepsilon}$$

$\boldsymbol{\sigma}$ = uniaxial tensile or compressive stress
$\boldsymbol{\varepsilon}$ = normal strain

Bulk Modulus



$$B = \frac{\sigma_{hyd}}{\Delta V/V_o}$$

$\boldsymbol{\sigma_{hyd}}$ = hydrostatic tensile or compressive stress
$\boldsymbol{\Delta V/V_o}$ = fractional volume expansion or contraction

Rotational Viscoelastic Parameters – Shear Modulus

The Modulus: Measure of materials overall resistance to deformation.

$$G = \text{Stress/Strain}$$

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

$$G' = (\text{stress/strain})\cos\delta$$

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

$$G'' = (\text{stress/strain})\sin\delta$$

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

$$\tan\delta = G''/G'$$

DMA Viscoelastic Parameters -Young's Modulus

The Modulus: Measure of materials overall resistance to deformation.

$$E = Stress/Strain$$

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

$$E' = (stress/strain)\cos\delta$$

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

$$E'' = (stress/strain)\sin\delta$$

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

$$\tan\delta = E''/E'$$

Example: Uniaxial Oriented Anisotropic Material

- **The figure below illustrates a simple anisotropic system known as uniaxial orthotropic. The lines in the figure could be taken as oriented segments of polymer chains or fibres in a composite material.**
  - In this example the fibres are randomly spaced as viewed from the end. This means the system has 5 independent elastic moduli.

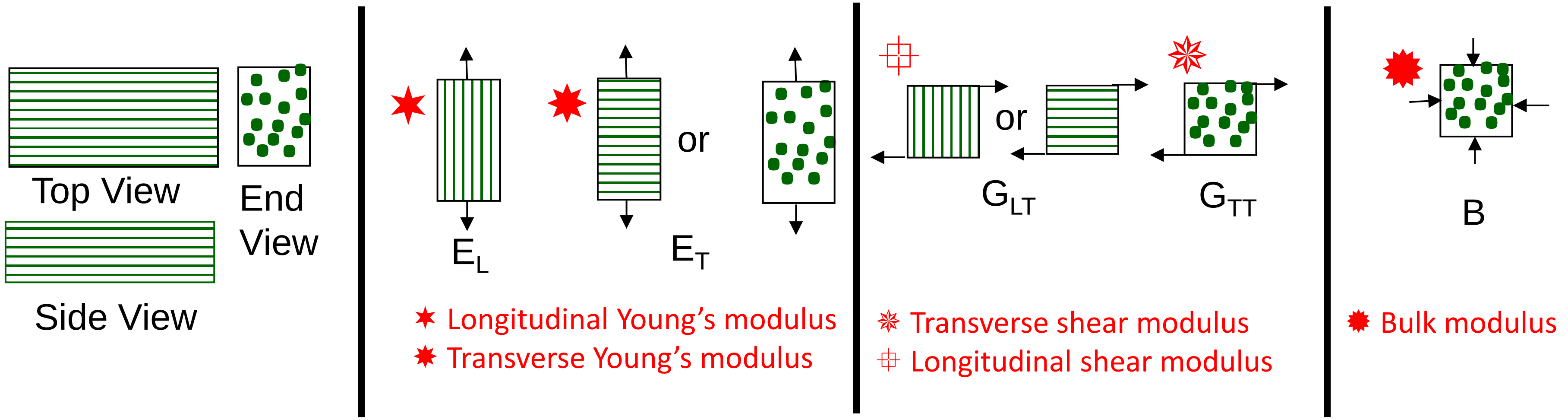


Figure: Uniaxial oriented anisotropic material with random line spacing and the five independent elastic moduli.

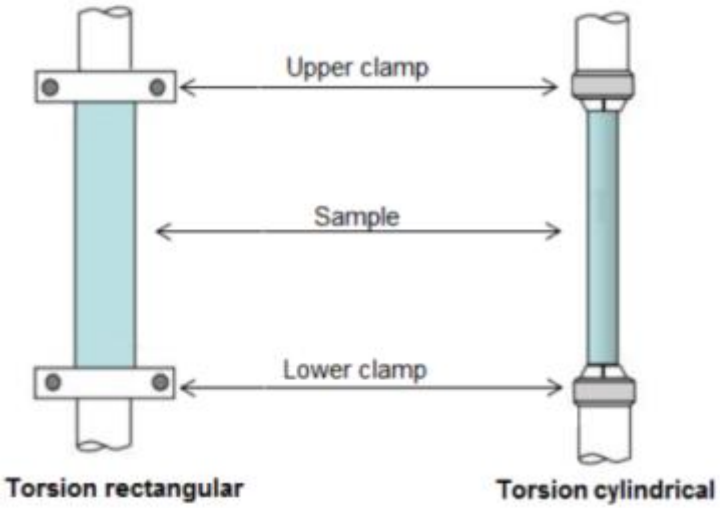
Nielsen, Lawrence E., Mechanical Properties of Polymers and Composites, Marcel Dekker, Inc., New York, 1974, pp. 40-41.

Axial force

- The key to successful measurements with torsional solid sample clamps or indeed through transitions where samples may exhibit volumetric changes is to control the AXIAL (Tensile) FORCE

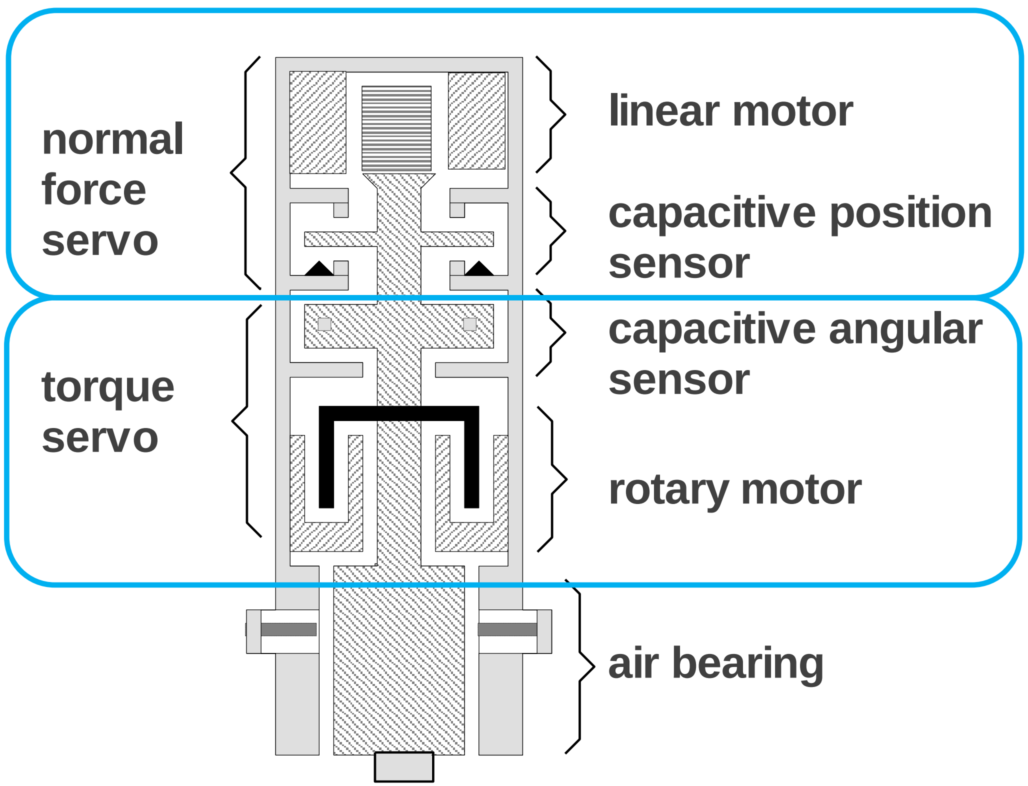
- Axial force is possible in the ARES-G2 and DHR because of the Force Rebalance Transducer (FRT)

- The Axial test mode is a additional capability (a spin-off)

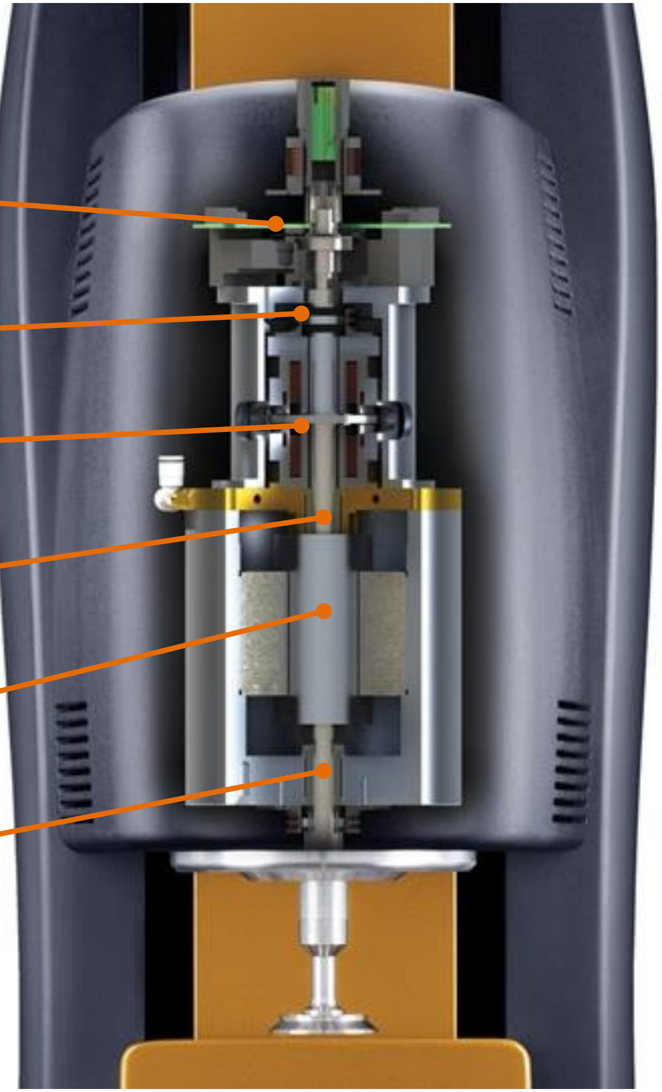


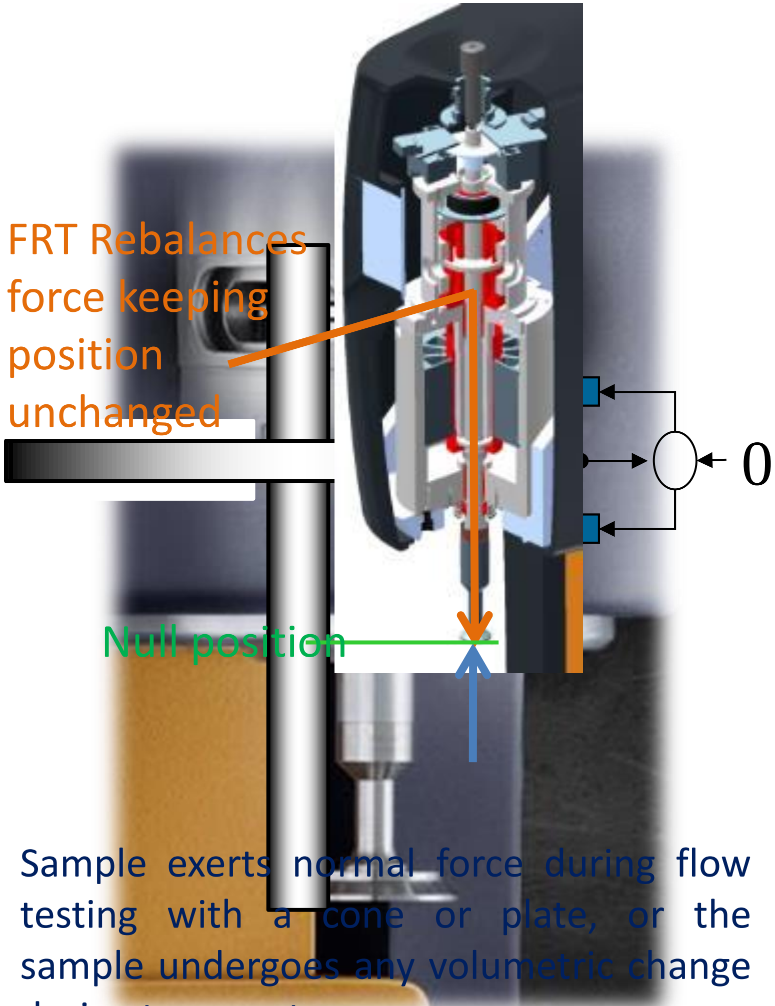
ARES-G2 Force Rebalance Transducer

- **The force rebalance transducers (FRT) is an active, quasi non – compliant transducers for measuring torque and normal force over a wide range. A capacitative position sensor measures the angular movement and a rotary (linear) motor drives the tool back to its original position.**



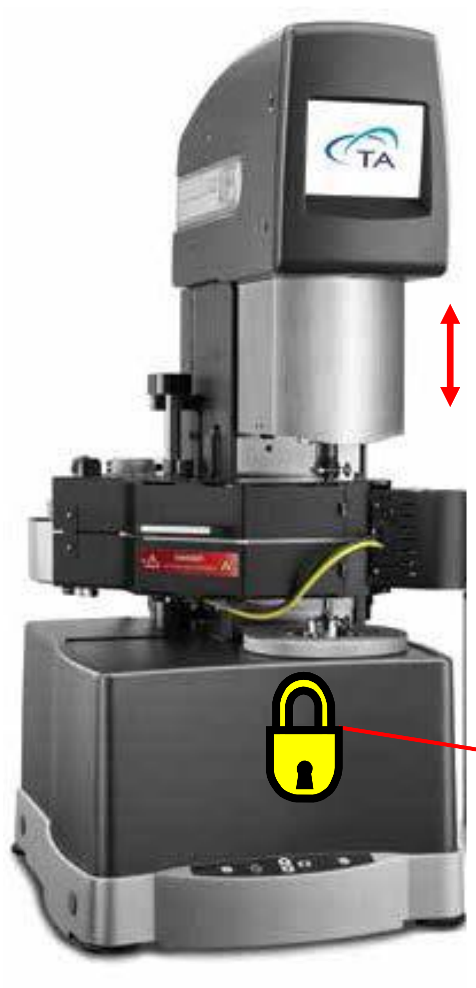
Discovery Hybrid Rheometer: Technology





Sample exerts normal force during flow testing with a cone or plate, or the sample undergoes any volumetric change during temperature ramps or cures

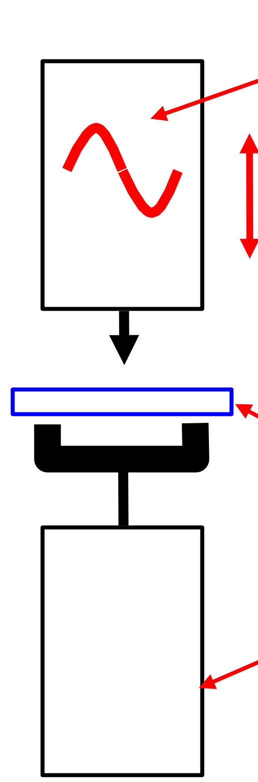
ARES G2 : DMA Mode



ARES G2 DMA

Controlled Strain

CMT – Combined Motor & Transducer



DHR : DMA mode

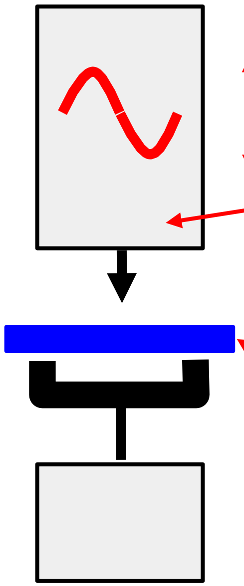
Normal F

Small
Amplitude
Oscillation

DHR DMA

Controlled Strain

CMT – Combined Motor & Transducer



Servo control on Null position (Strain)

Force Rebalance Transducer (FRT) (Measures Stress)

Motor remains locked during DMA function

Sample

TA Instruments DMA's

RSA G2

Controlled Strain
SMT

Q800

Controlled Stress
CMT

ARES G2

Controlled Strain
CMT

DHR

Controlled Stress
CMT

Shouldn't forget our TA Electroforce high load DMAs

DMA Specifications

	RSA G2	Q800	ARES G2 DMA	DHR DMA
Max Force	35N	18N	20N	50N
Min Force	0.0005N	0.0001N	0.001N	0.1N
Frequency Range	1e-5 to 628 rad/s	0.01 to 1250 rad/s	1e-5 to100 rad/s	1E-5 to 16Hz (100rad/s)
Dynamic Deformation Range	+/- 0.05 to 1,500μm	+/- 0.5 to 10,0000 μm	+/- 1 to 50 μm	+/- 1 to 50 μm
Control Stress/Strain	Control Strain (SMT)	Control Stress (CMT)	Control Strain (CMT)	Control Strain (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 30°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 30°C/min

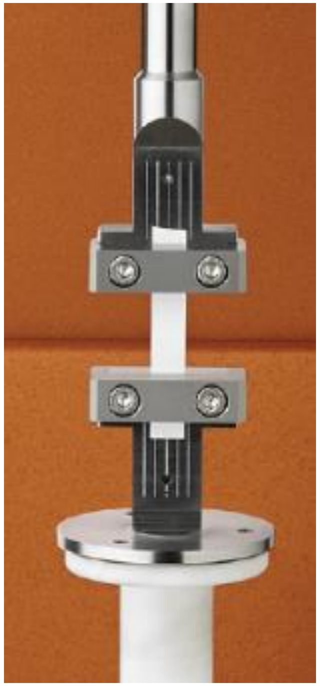
Suggested amplitudes

Clamp Type	Amplitude, μm
Tension Film or Fibre	15 to 25
Compression	10 to 20
Three Point Bend	25 to 40
Dual/Single Cantilever	20 to 30

ARES-G2 / DHR Available Clamps

Easy to use with good workable clearance around the clamps for sample loading

Three Point Bending



Film Tension

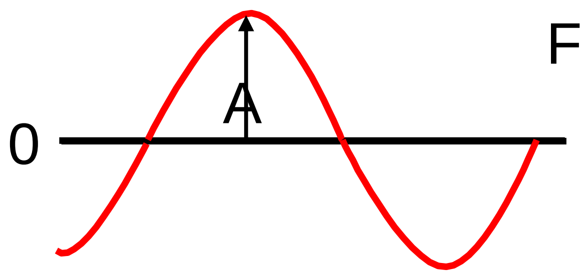
Dual / Single Cantilever

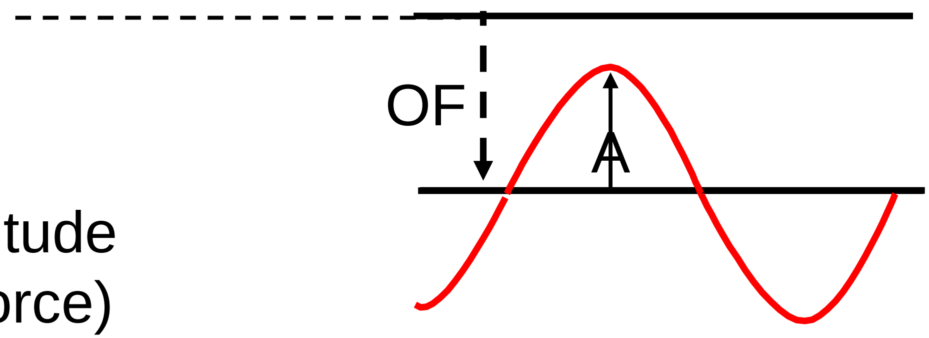
Compression (parallel plates)

Torsion (cylindrical)

Some Clamps Require an Offset (static) Force!

Force/Time Curves



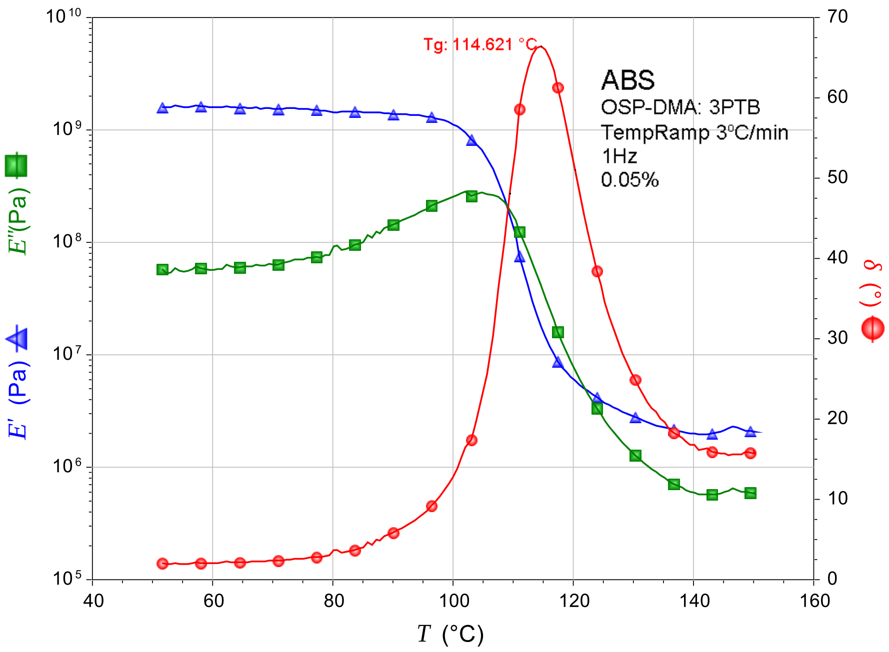


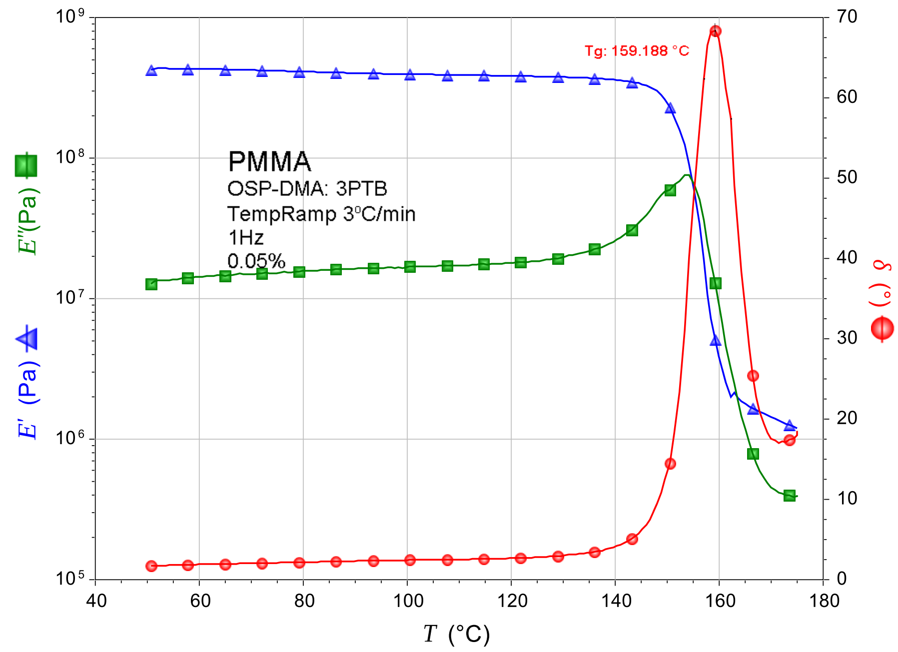
A = Oscillatory force amplitude
OF = Offset force (static force)

<u>Clamps without offset force:</u>
Single Cantilever
Dual Cantilever

<u>Clamps with offset force:</u>
Tension Film
Tension: Fibre
3-Point Bend
Compression

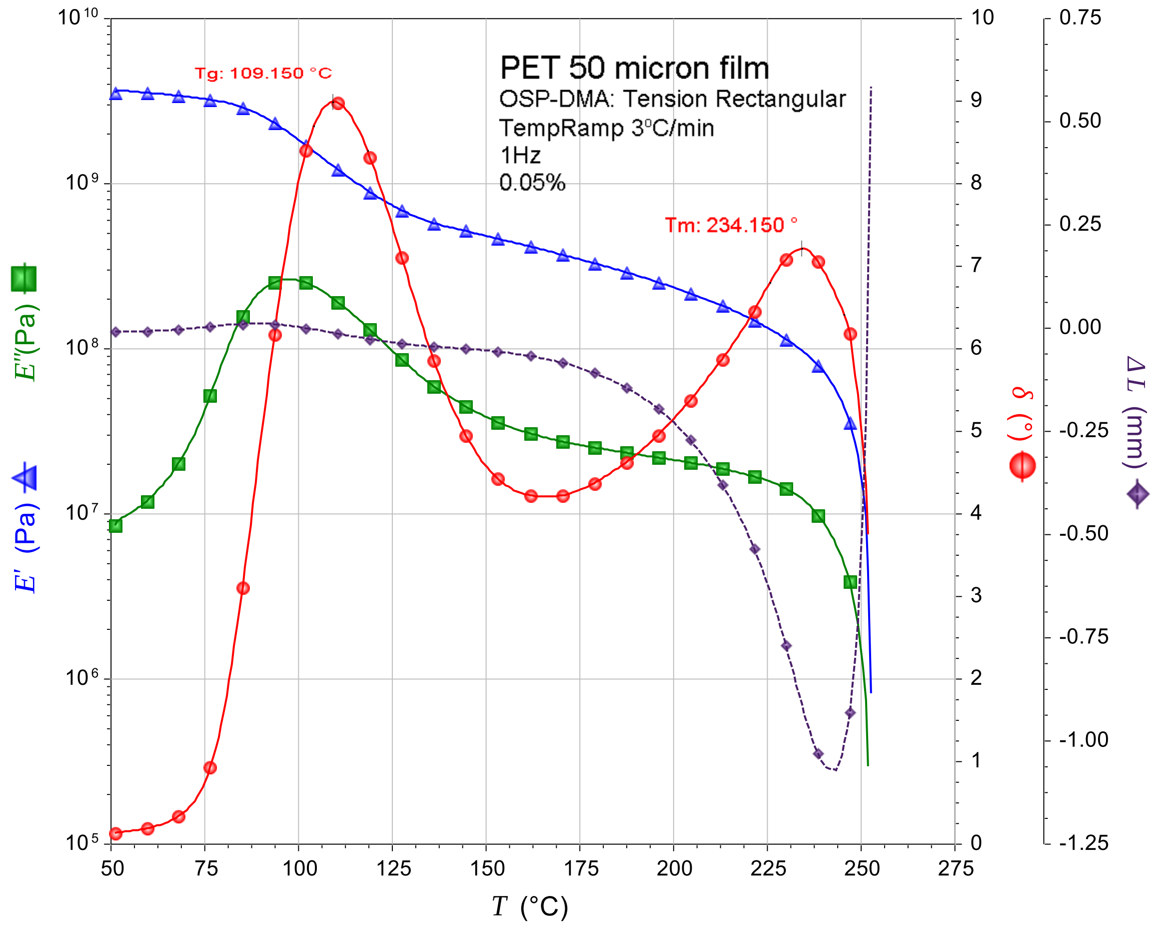
3pt Bending on a PMMA specimen





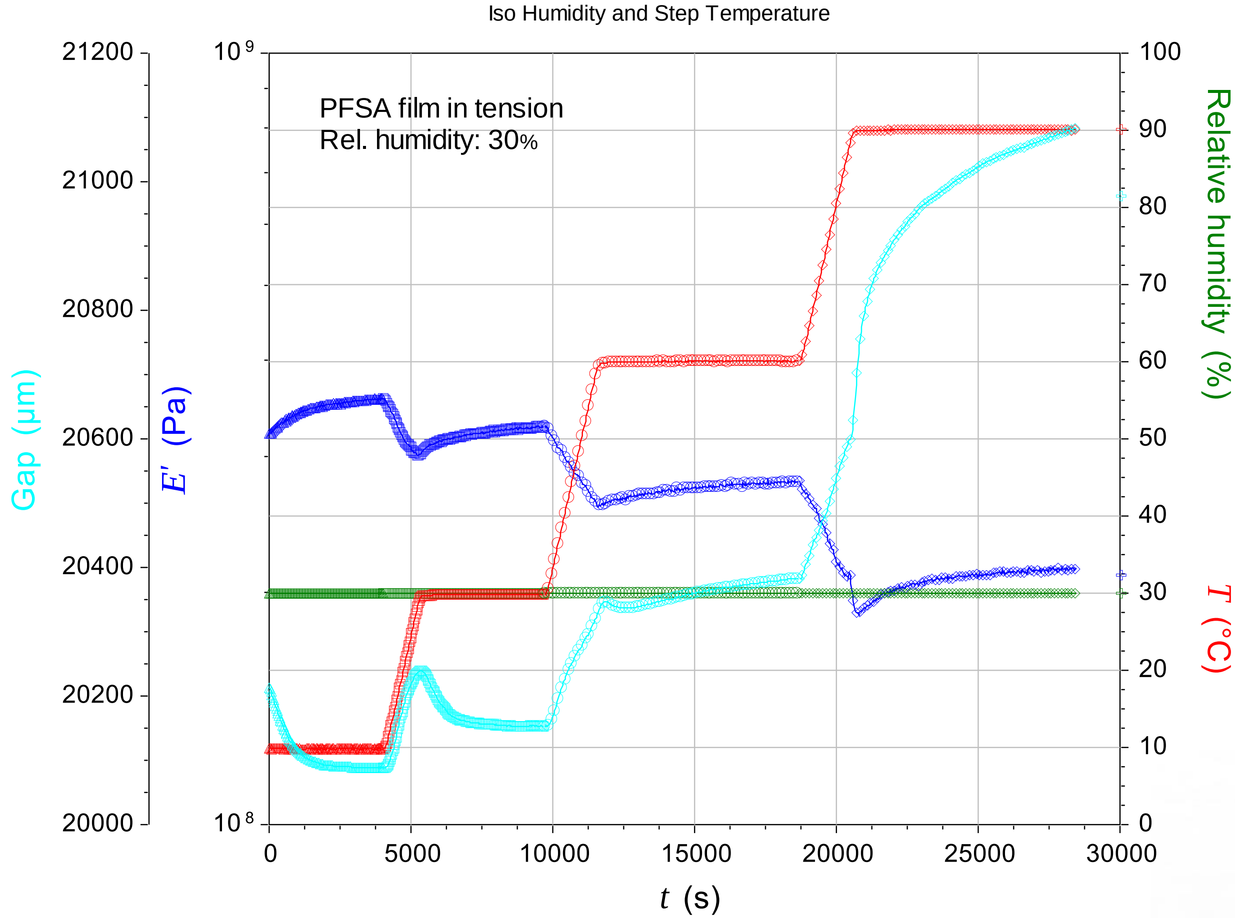
- Determination of the glass transition of an ABS and PMMA test specimen in 3 point bending.
- The axial force control is adjusted to 130% of the dynamic force to make sure that the sample remains in contact with the geometry and does not flow. The results are almost identical with those obtained on the RSA.
- The loss peak (tan delta) could be measured accurately down to a modulus of $2x10^5$ Pa.

Tension on a PET film



- A PET film of 50 µm was tested in tension with an axial force track of 130% in order to prevent sample buckling.
- The glass transition was detected at 109°C, the melting point occured at 250°C. At this point the modulus collapsed very
- The peak in the phase was measured at 234°C

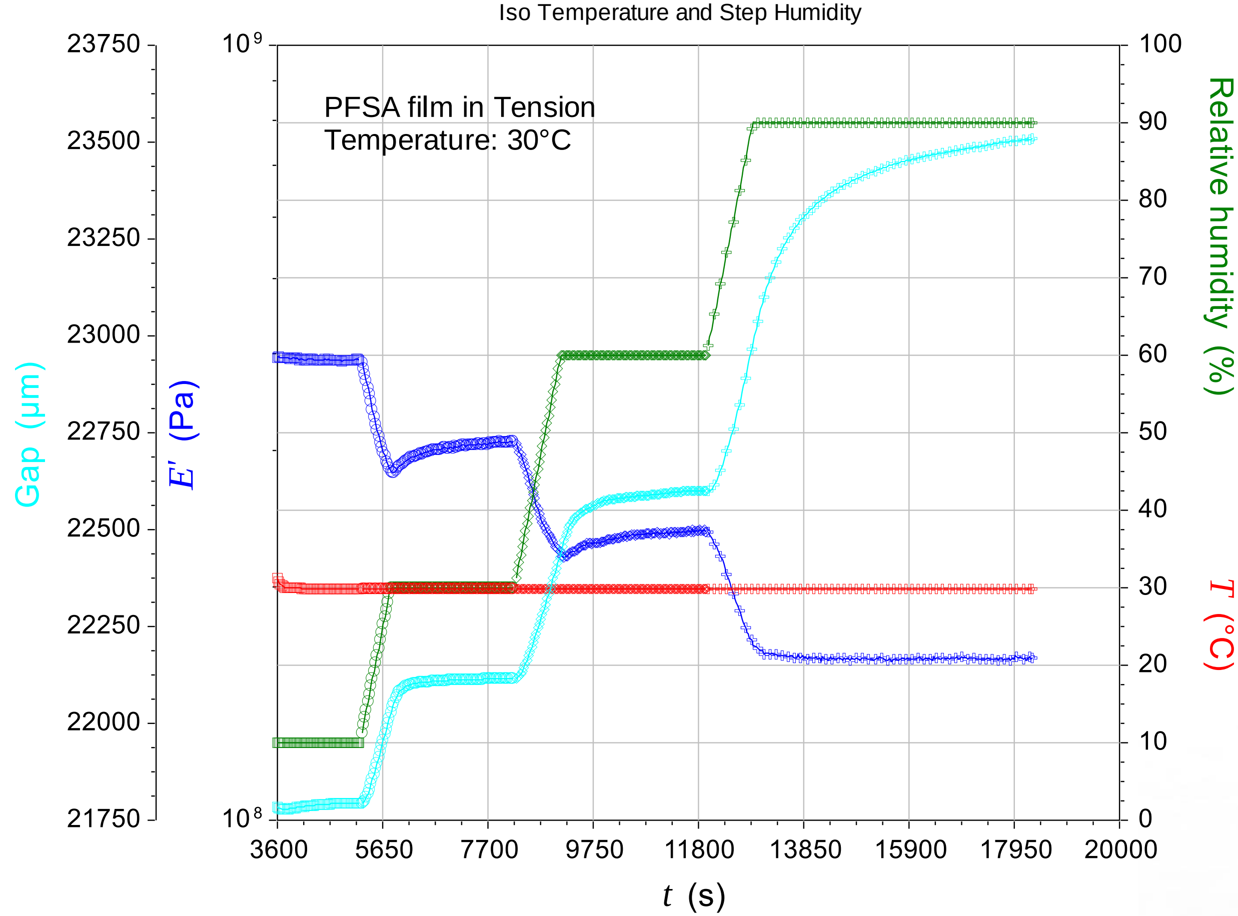
Fuel Cell Membrane: Aquivion® PFSA



Iso-humidity and Step Temperature

- 30% RH
- Step temperature from 10°C up to 90°C by 10 °C increments
- 1 rad/s, 0.1% strain

Fuel Cell Membrane: Aquivion® PFSA



Iso-temperature and Step Humidity

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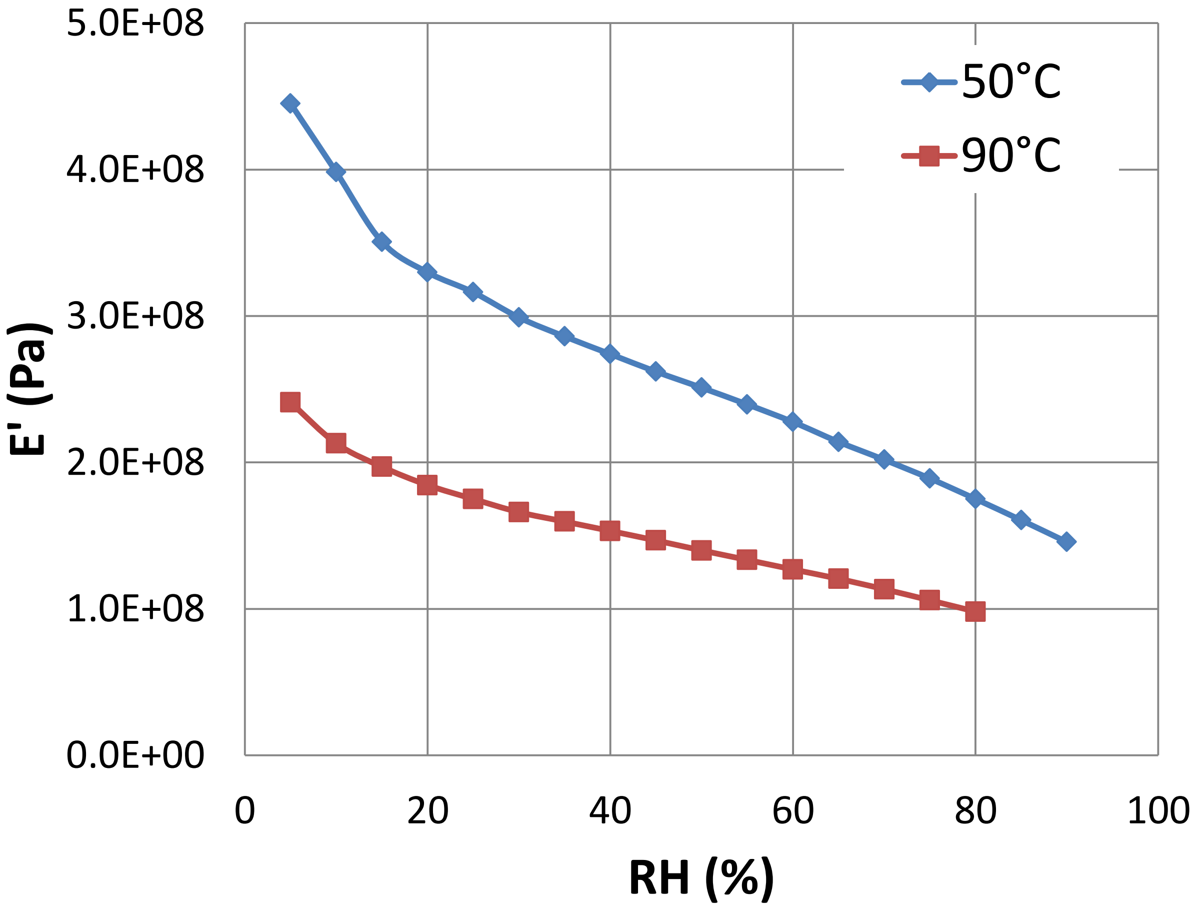
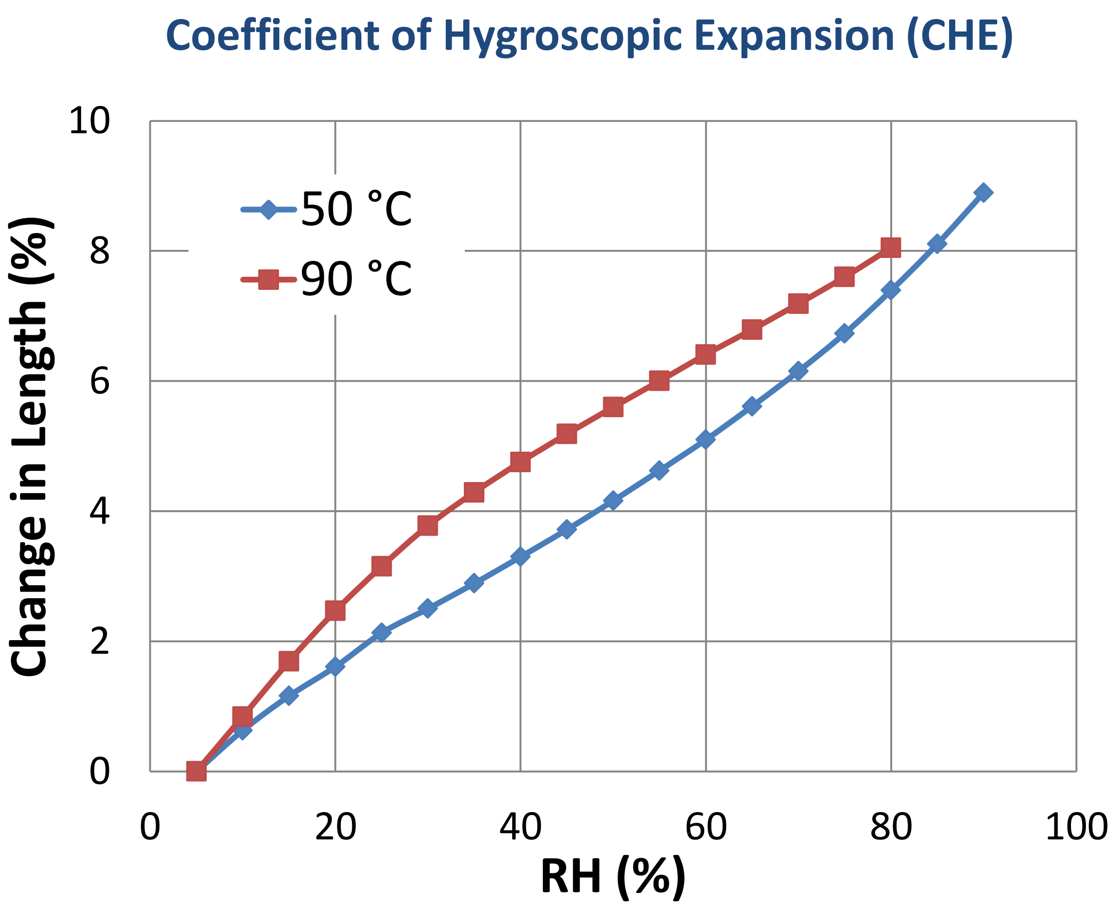
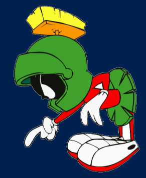


Fuel Cell Membrane: Aquivion® PFSA

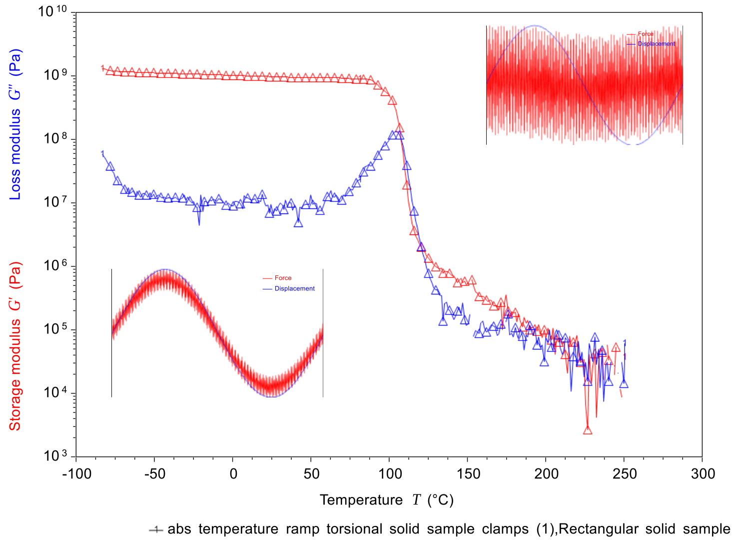


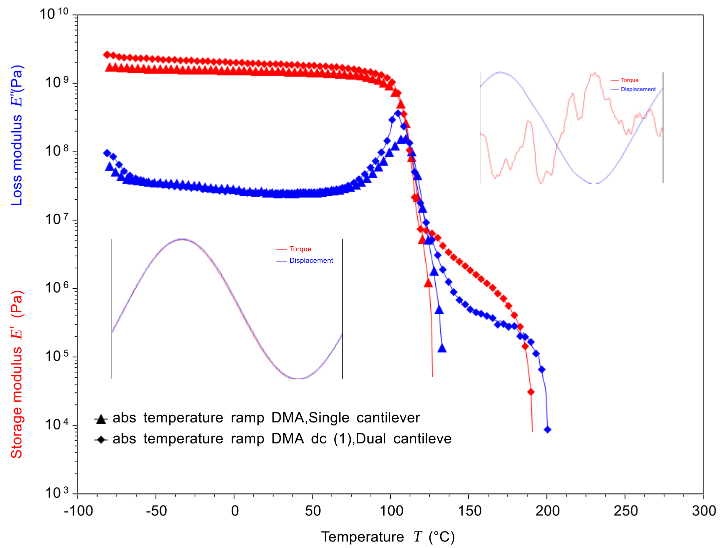
	90 °C	50 °C
5% to 20%	0.165	0.107
40% to 60%	0.082	0.090

Comparison between torsional and dual and single cantilever



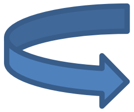
- **Measurements made with ABS, temperature ramp @ 3°C/min**
  - Torsional clamps 1e-3% strain @ 1Hz
  - Single and Dual Cantilever, 20µm axial displacement @ 1 Hz





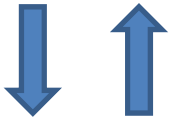
TA Rheometers work in more ways more than rotation

- **A unique capability of our rheometers arises from the patented Force Rebalance Transducer (FRT)**

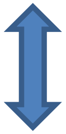


TA Rheometer can do:

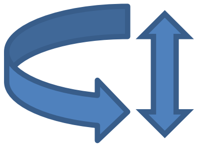
- Rotational (flow, oscillation, step transient etc)



- Axial testing (moving head to measure compression or tack)

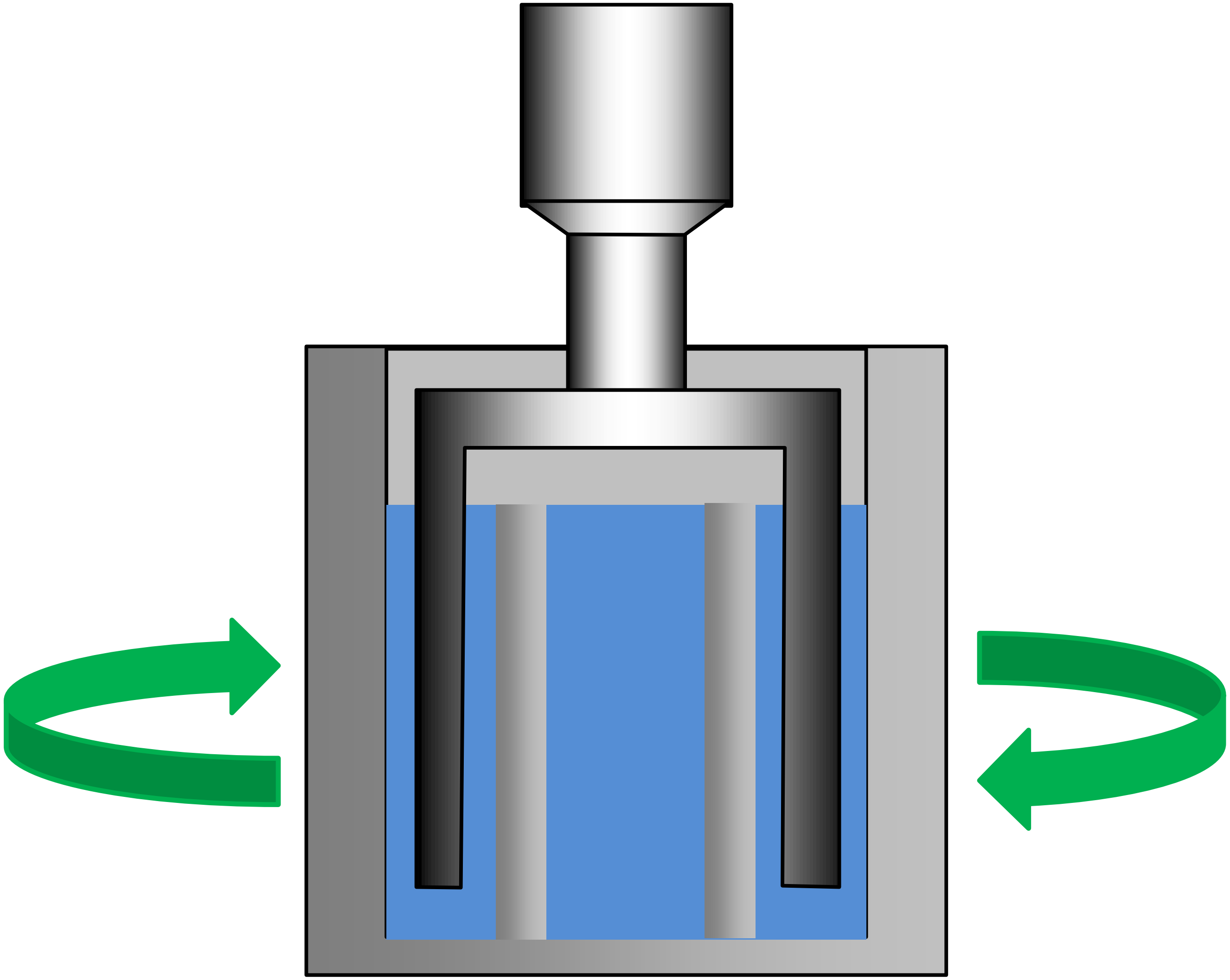


- Control the FRT to apply a sinusoidal deformation to provide flexing DMA mode

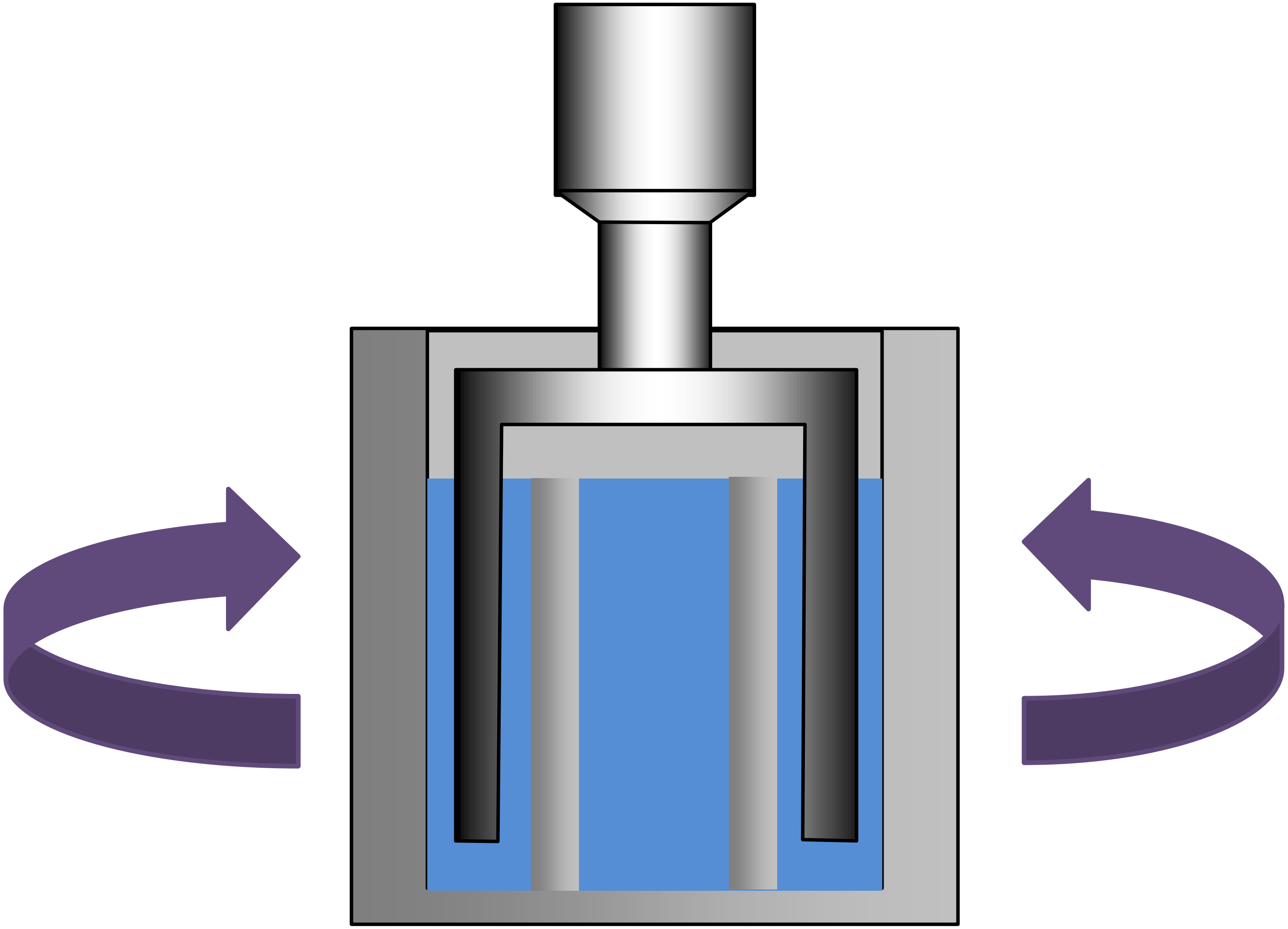


- Control the FRT sinusoidal deformation whilst rotating or oscillating the lower geometry (ARES-G2 only) to provide Orthogonal SuperPosition (OSP) and 2D LAOS

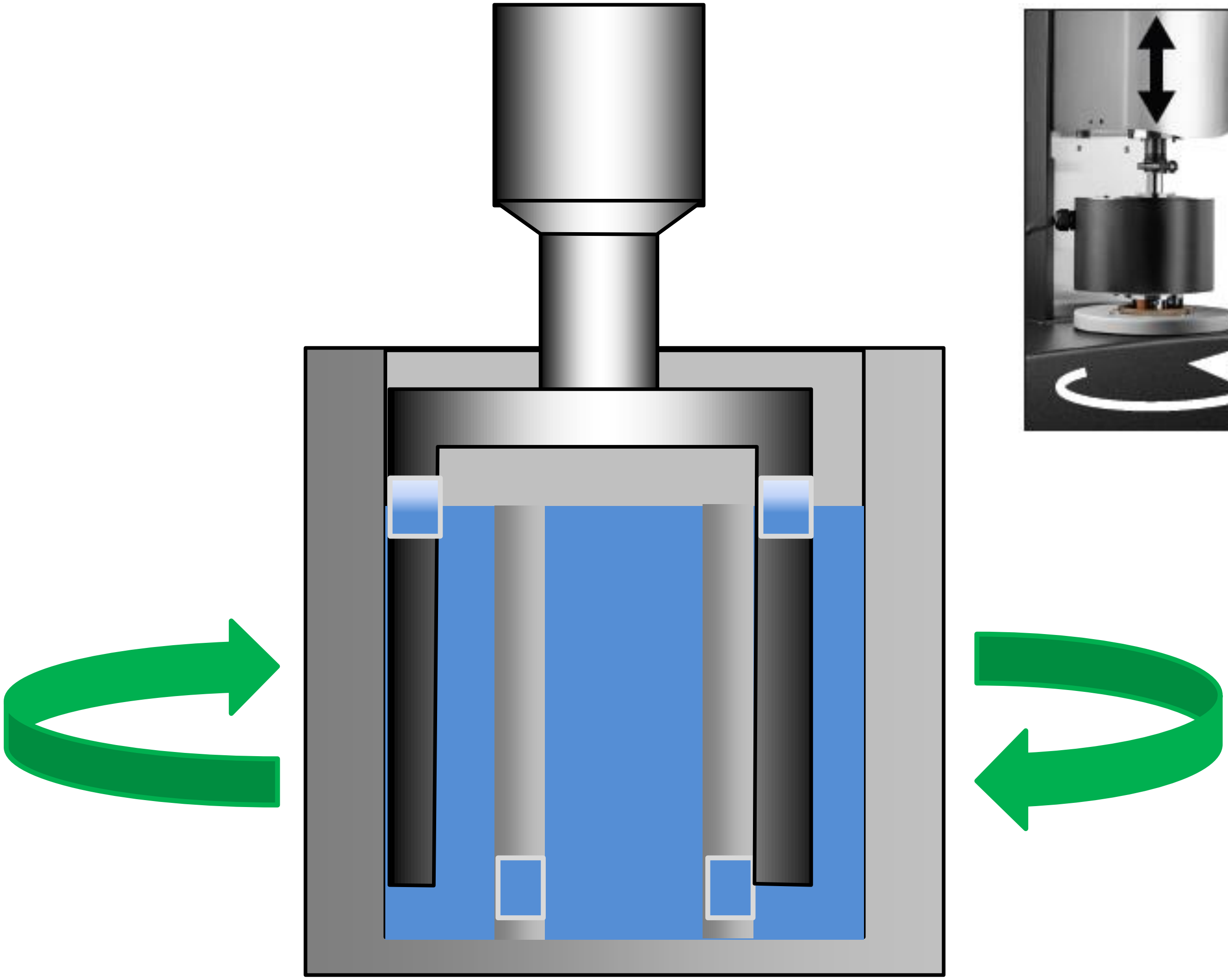
Rotation : Flow , Creep, Stress Relaxation….

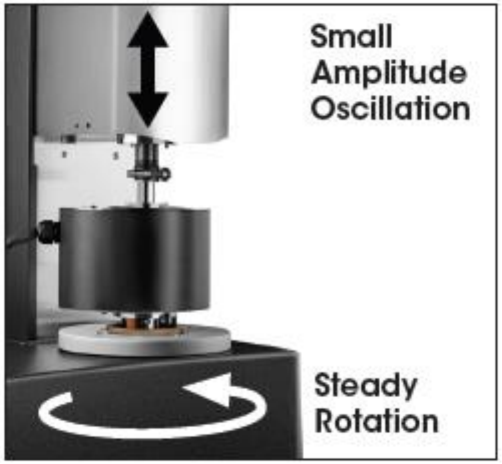


Oscillations

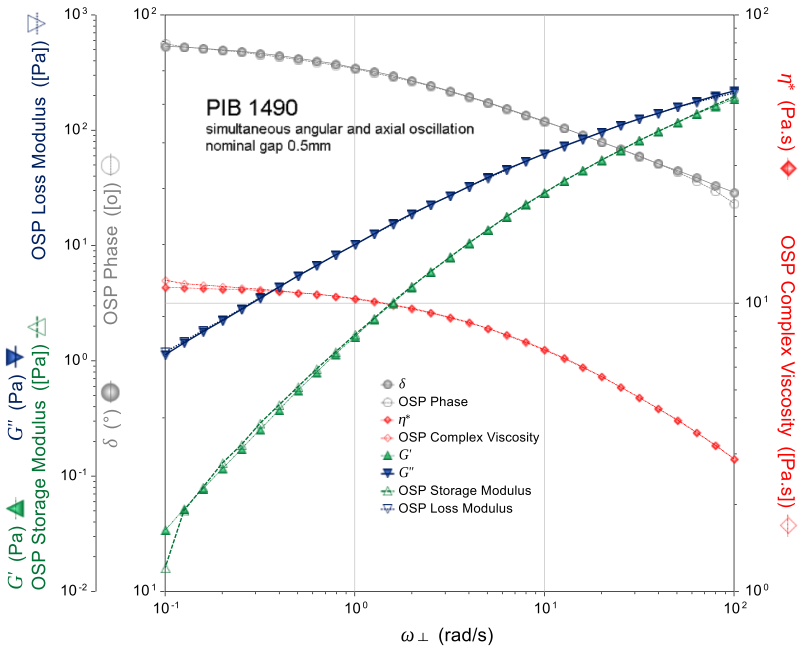


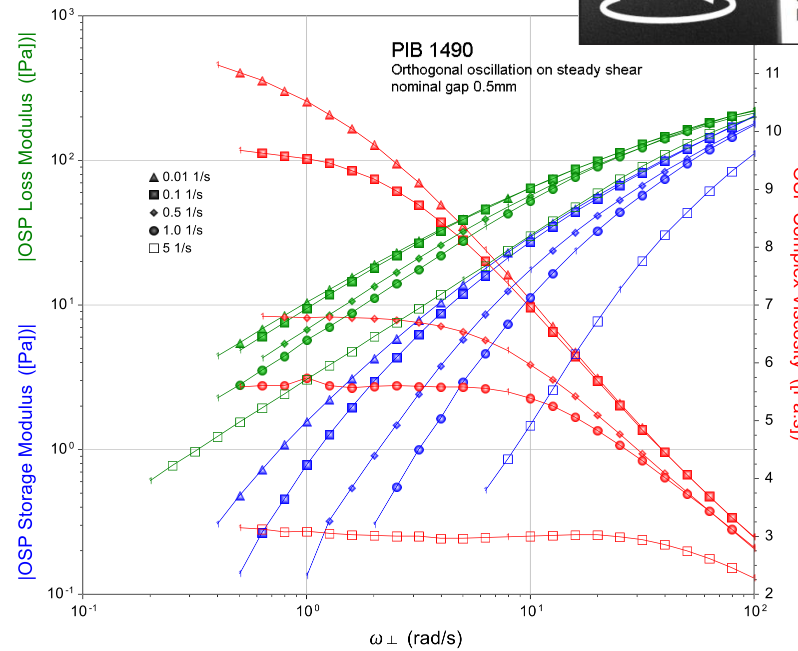
OSP : Flow + Oscillation





PIB 1490: Effect of orthogonal superposed shear



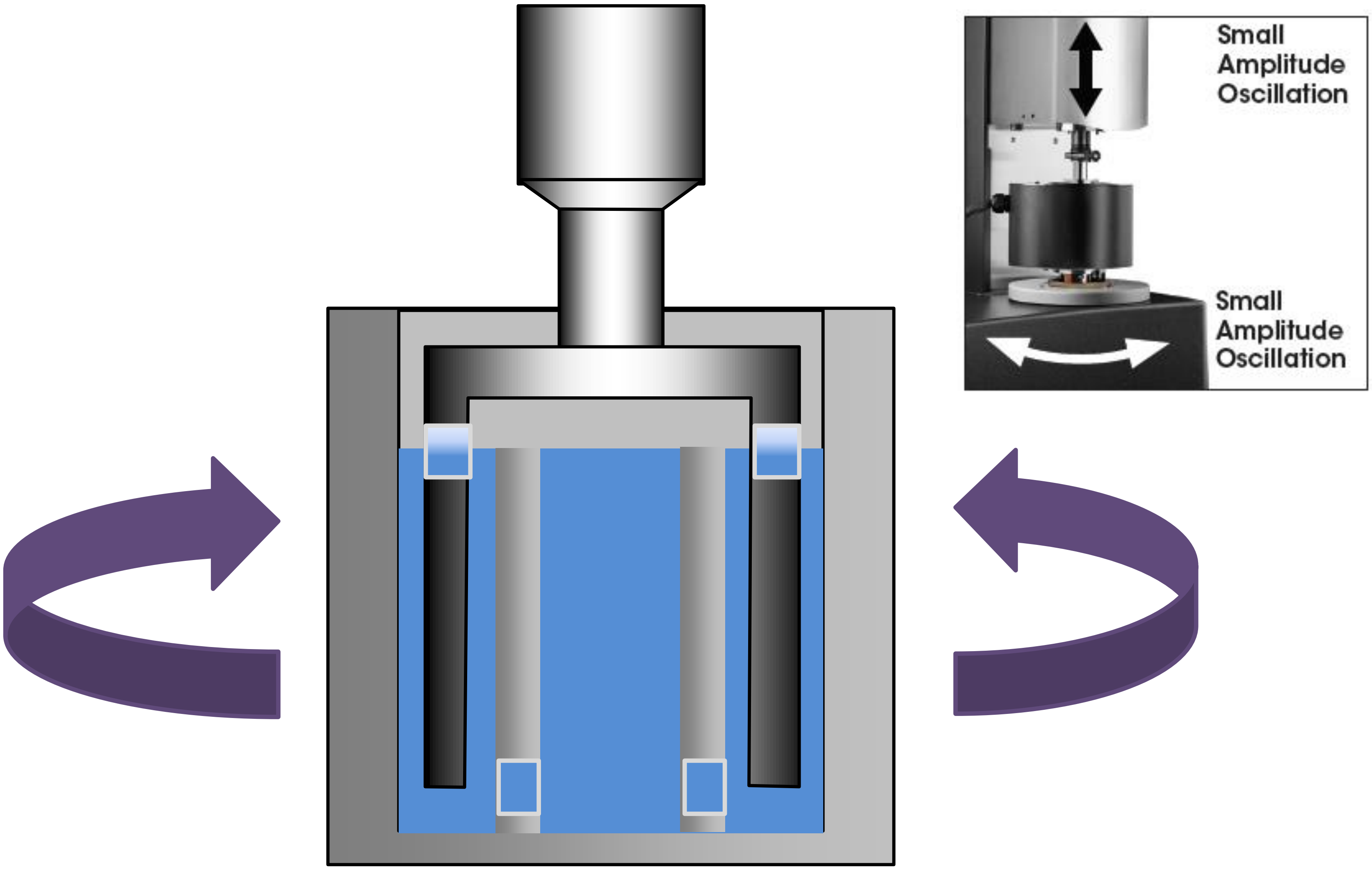


Angular and axial shear provide the results on the isotropic sample

With increasing orthogonal shear rate:

- Terminal region shifts to higher frequency
- Material characteristic relaxation time decreases
- Zero shear viscosity decreases

2D Oscillations

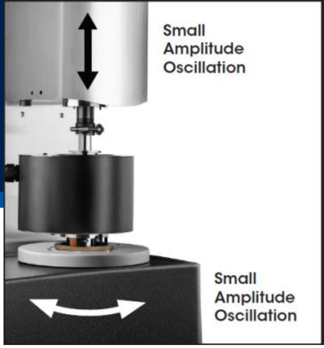


2D - LAOS Oscillations

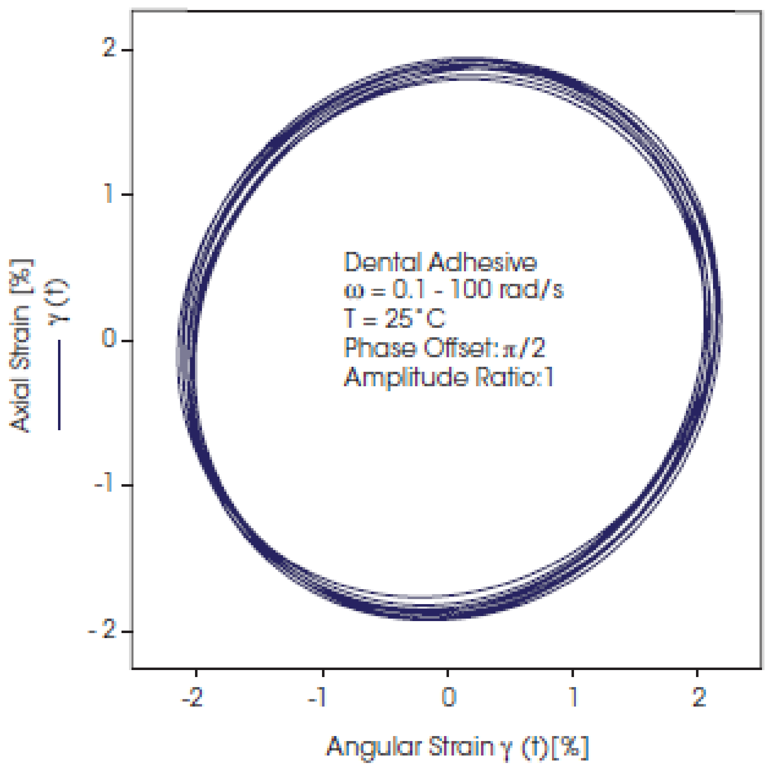
- **2D-SAOS reveals anisotropy in a fluid, which may be induced by sample shear history.**

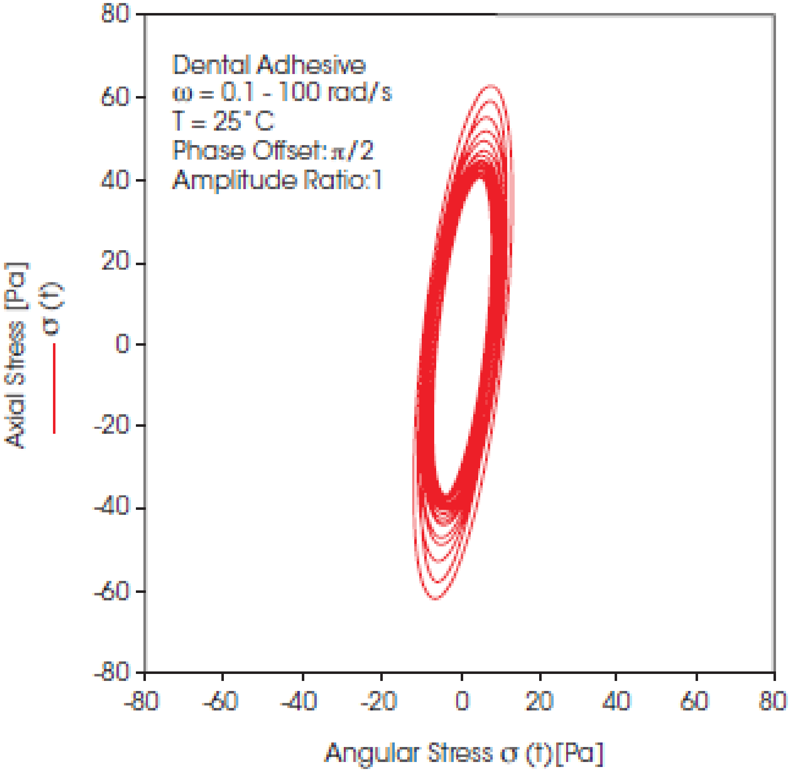
- **If we consider performing a traditional rotational amplitude sweep we see that the orientation will affect the results, so if you can do the same amplitude sweep but scanning from vertical to horizontal you can see the orientations within the sample structure**

Anisotropy detection by 2D-SAOS



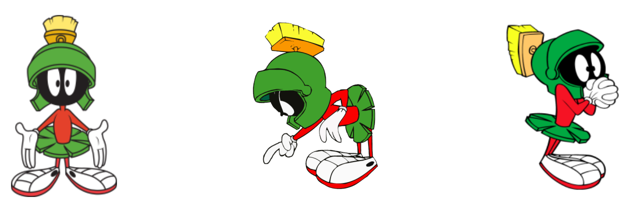
- Dental adhesive paste pre-sheared
- Same oscillation strain applied in both angular and axial directions
- Directional stress response stronger in orthogonal stress response (measure of anisotropy)





SUMMARY

- **The modern rotational rheometers with FRT's are now capable of linear deformation as well**
- **Means possibility to determine both Shear and Young's modulus on the same sample, in the same temperature module**
- **The additional dual head design of the ARES-G2 enables a third kind of deformation – Orthogonal SuperPosition (OSP)**



THANK YOU

The World Leader in Thermal Analysis, Rheology, and Microcalorimetry