There's more to rheology than watching paint dry – environmental effects on rheology"

UK Material Characterisation User Meeting

Mercedes World

October 10th 2018

Today’s Presentation

- Rheology of paints is a well known application for not only the manufacturers but also the end user
- A brief review of simple rheological tests typically used for paints and coatings
- A review of the process of paint drying and how the environment can affect it whilst introducing the various environmental control options we have.

So what is a paint ?

- A variety of types but fundamentally a material designed to provide a decorative / protective barrier in the form of a film over a number of different substrates – wood, metal, stone, plastics etc.

- Typical composition of

  - Resin / binder
  - Pigments
  - Vehicle / solvent

  - Other components maybe thickeners, plasticisers, drier additives, defoamers, surfactants.......

Paint Composition - Pigment

- Pigments are granular solids incorporated into the paint to contribute colour, toughness or simply to reduce the cost of the paint.

- A distinction is usually made between
  - a **pigment**, which is insoluble in the vehicle (resulting in a suspension), and
  - a **dye**, which either is itself a liquid or is soluble in its vehicle (resulting in a solution).

Paint Composition - Binder

- The binder, or resin, is the actual film forming component of paint.

- The hardening process may be due to one of the following:

  - Polymerisation by chemical reaction with air in the atmosphere. They include ordinary 'oil' paints.

  - Coalescence of an emulsion: Emulsions are pre-polymerised into very small particles which are prevented form coalescing by an emulsifying agent.
    - They set by water loss leading to 'breaking' of the emulsion.

  - Evaporation of a solvent: Solvents need to be volatile, hence they are often flammable.

Paint Composition – Volatile Vehicle / Solvent

- The main purpose of the vehicle is to adjust the viscosity of the paint.
- It is volatile and does not become part of the paint film.
- It can also control flow and application properties, and affect the stability of the paint while in liquid state.
- Its main function is as the carrier for the non volatile components.

Rheology

- The Basics:
  - We push or twist a sample and measure how easy it was

- An Example:
  - Ketchup out of a bottle
  - Creams or ointments
  - Adhesives or sealants
  - Greases and oils
  - Paints and coatings
  - Plastics and composites
  - And many more……….

ARES-G2
Controlled strain

Discovery HR
Controlled Stress

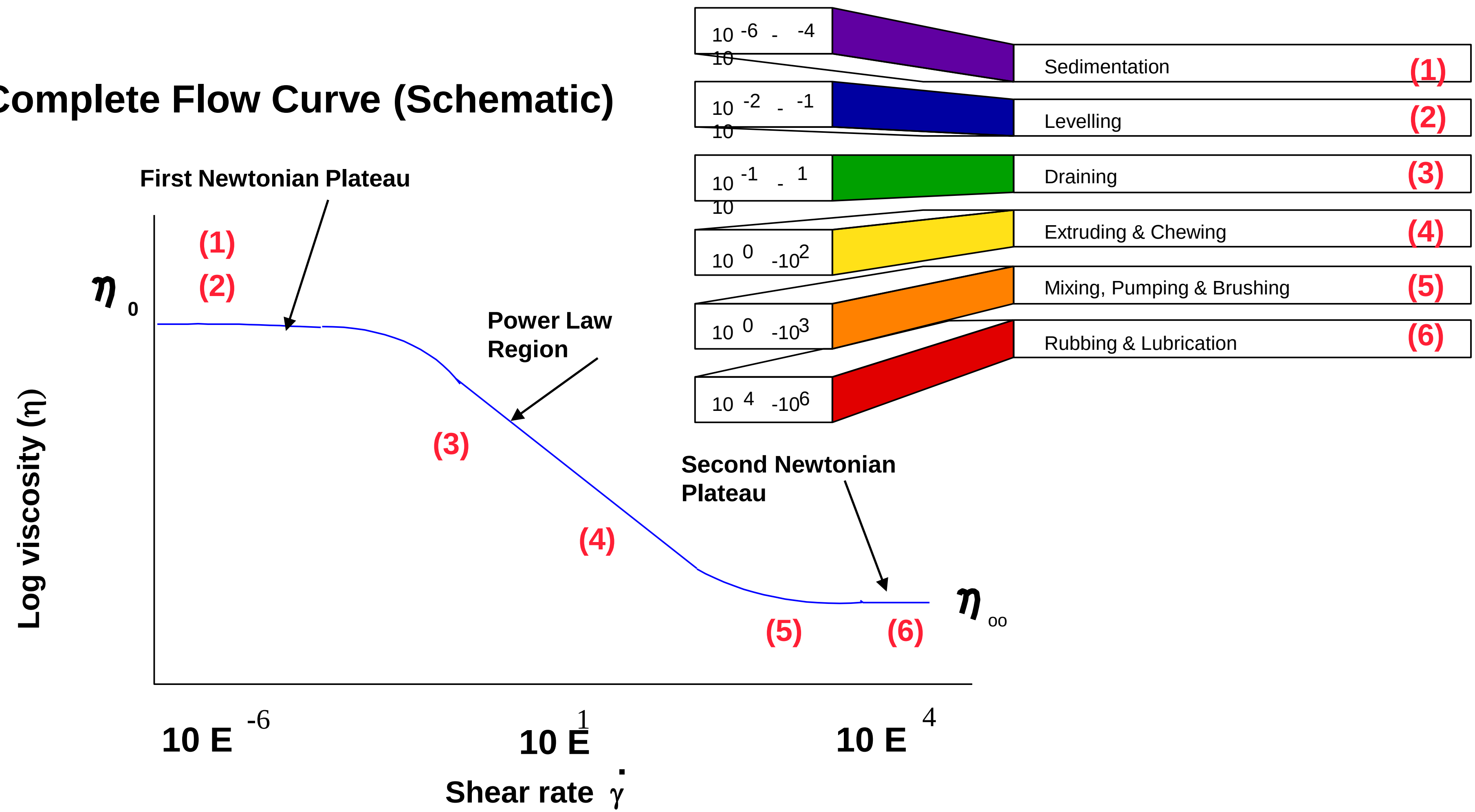
Shear Rates

Process	Shear Rate (1/s)	Application
Sedimentation of particles in a suspending liquid	10^{-6} - 10^{-3}	Medicines, **paints**, spices in salad dressing
Leveling by surface tension	10^{-2} - 10^{-1}	Frosting, **paints**, printing inks
Draining under gravity	10^{-1} - 10^{1}	Vats, small food containers, **painting and coating**
Extrusion	10^{0} - 10^{3}	Snack and pet foods, toothpaste, cereals, pasta, polymers
Calendering	10^{1} - 10^{2}	Dough sheeting
Pouring from a bottle	**10^{1} - 10^{2}**	Foods, cosmetics, toiletries
Chewing and swallowing	10^{1} - 10^{2}	Foods
Dip coating	10^{1} - 10^{2}	**Paints**, confectionery
Mixing and stirring	10^{1} - 10^{3}	**Paints**, Food processing
Pipe flow	10^{0} - 10^{3}	Food processing, blood flow
Rubbing	10^{2} - 10^{4}	Topical application of creams and lotions
Brushing	10^{3} - 10^{4}	**Brush painting**, lipstick, nail polish
Spraying	10^{3} - 10^{5}	Spray drying, **spray painting**, fuel atomization
High speed coating	10^{4} - 10^{6}	Paper
Lubrication	10^{3} - 10^{7}	Bearings, gasoline engines

Idealised Full Flow Curve

- By producing the full flow profile, predictions can be made with regards to sample behaviour or performance during processing and other applications

Complete Flow Curve (Schematic)

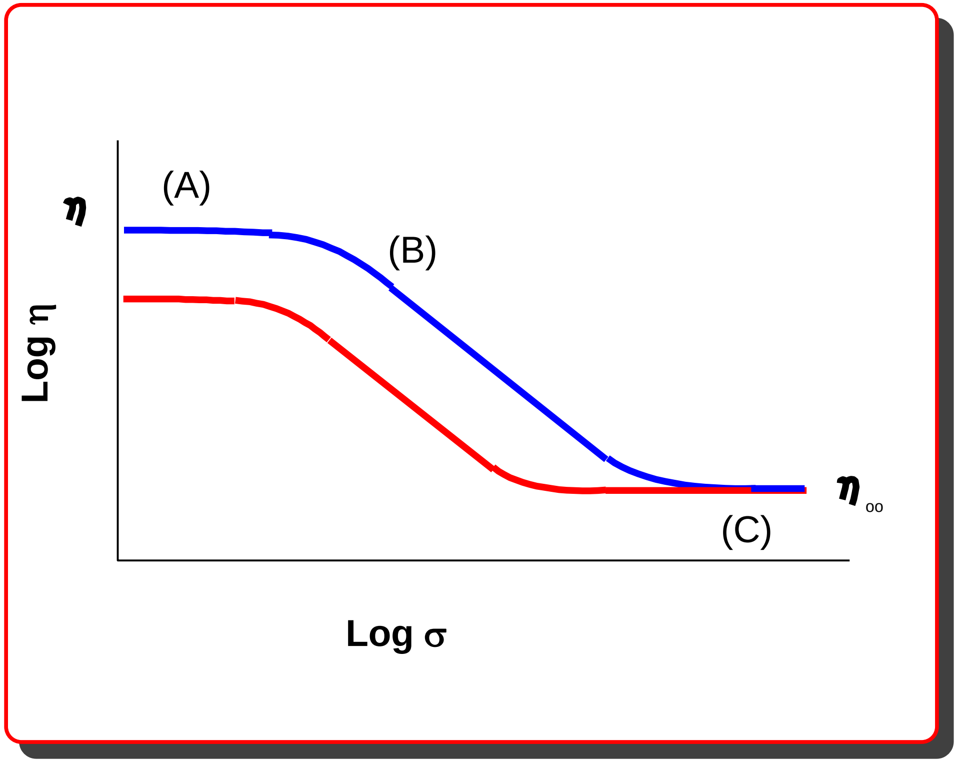


So what can a flow curve tell us?

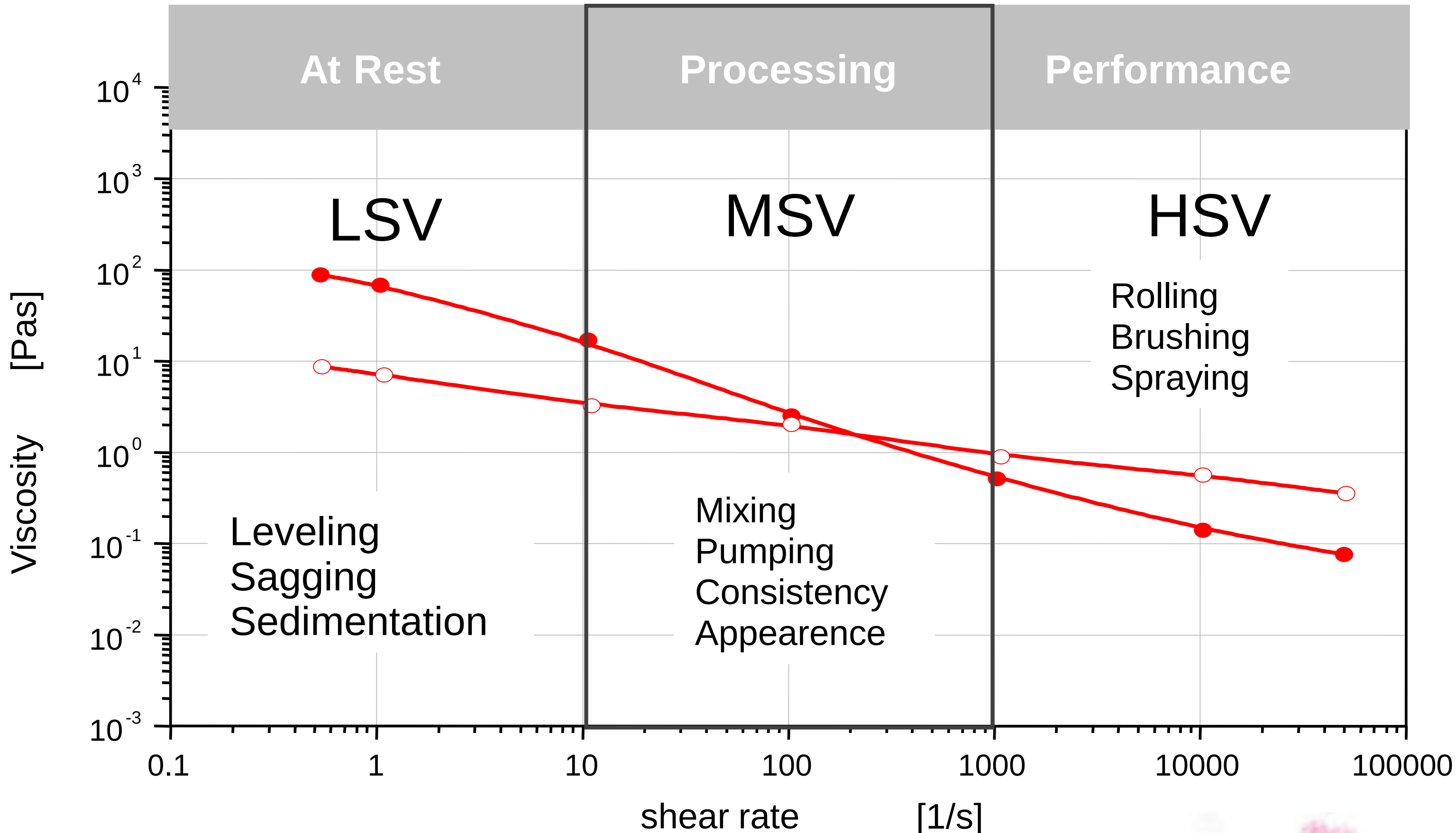
- (A) Different zero shear viscosities
  - sedimentation
  - Handlability
  - Interactions formulation variants

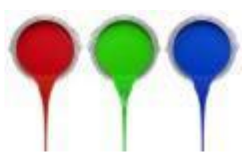
- (B) Different "apparent yield stresses"
  - pumpability
  - Stability
  - Particle /MW distributions

- (C) The same infinite shear viscosity
  - "same" application performance



Viscosity Ranges of Paints/Coatings

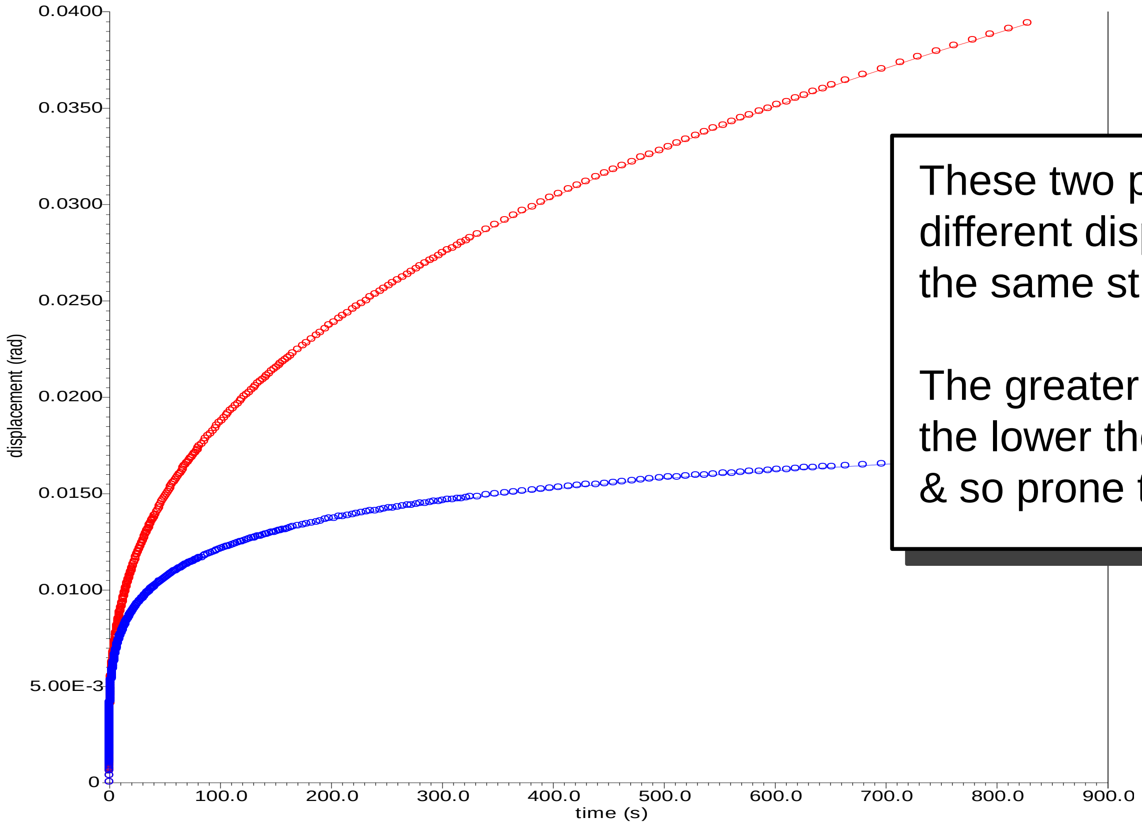


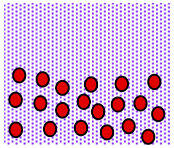


Step Transient Creep : Sedimentation

Step transient – creep testing :

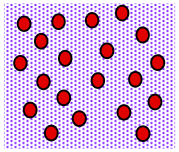
applying constant stress and monitoring displacement over time acts as a simulation of gravitational stresses experienced by sample





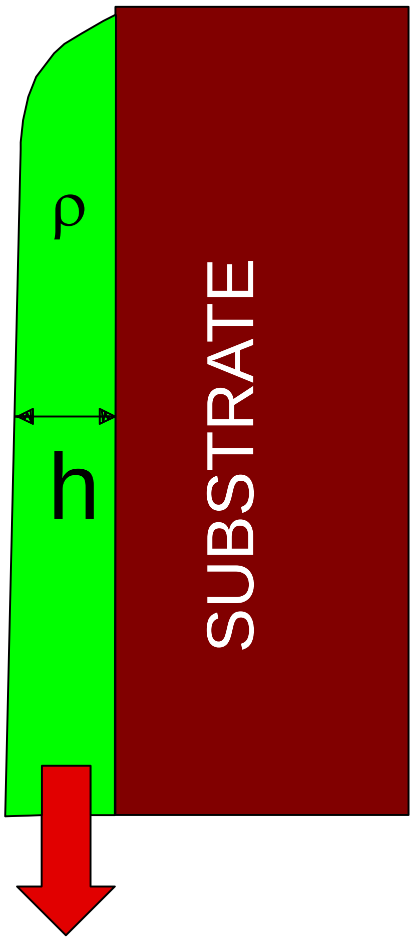
These two paint show totally different displacements under the same stresses.

The greater the displacement, the lower the resistance to flow & so prone to sedimentation.



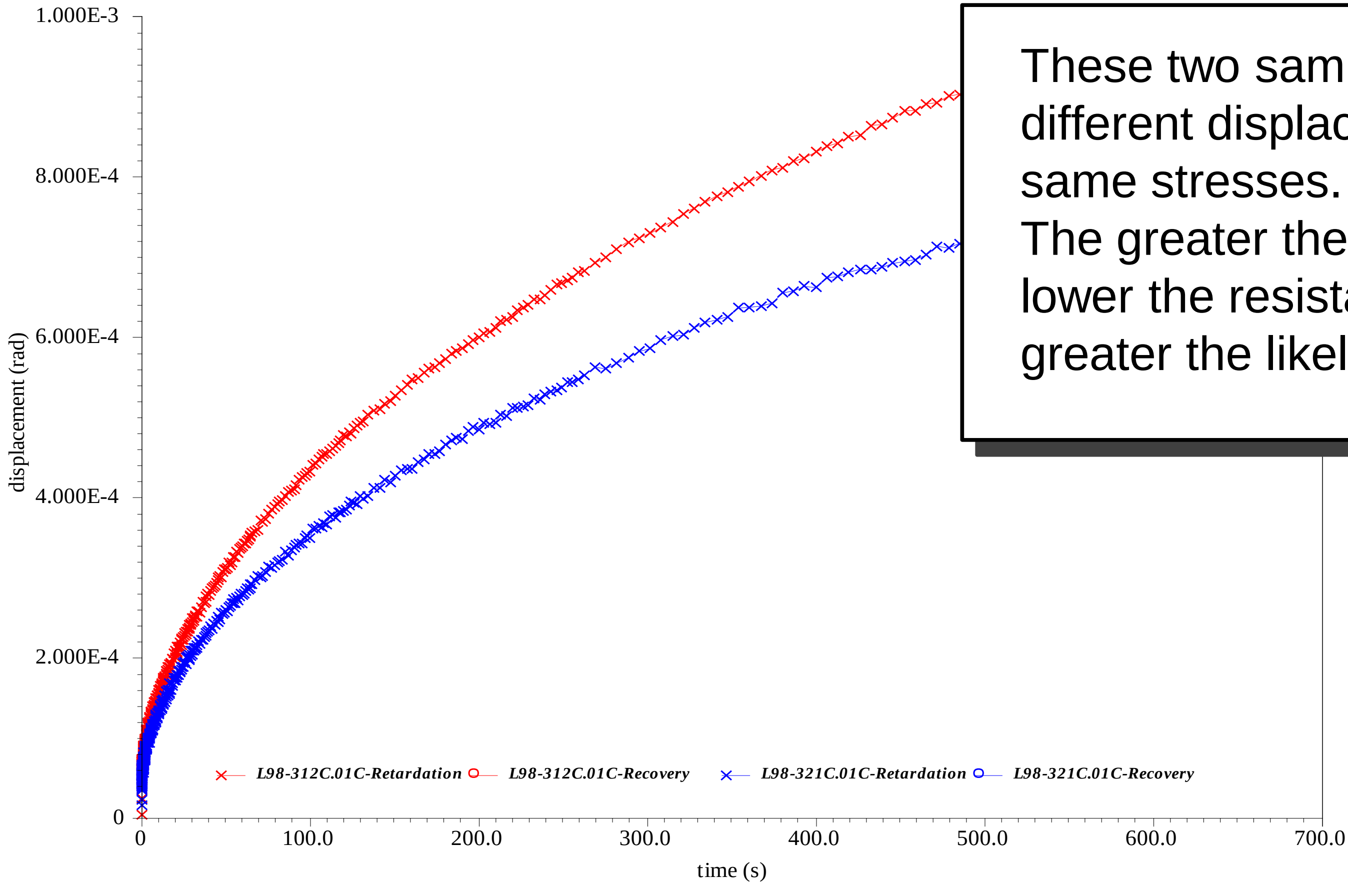
Step Transient Creep : Sagging

$$\tau = h\rho g$$



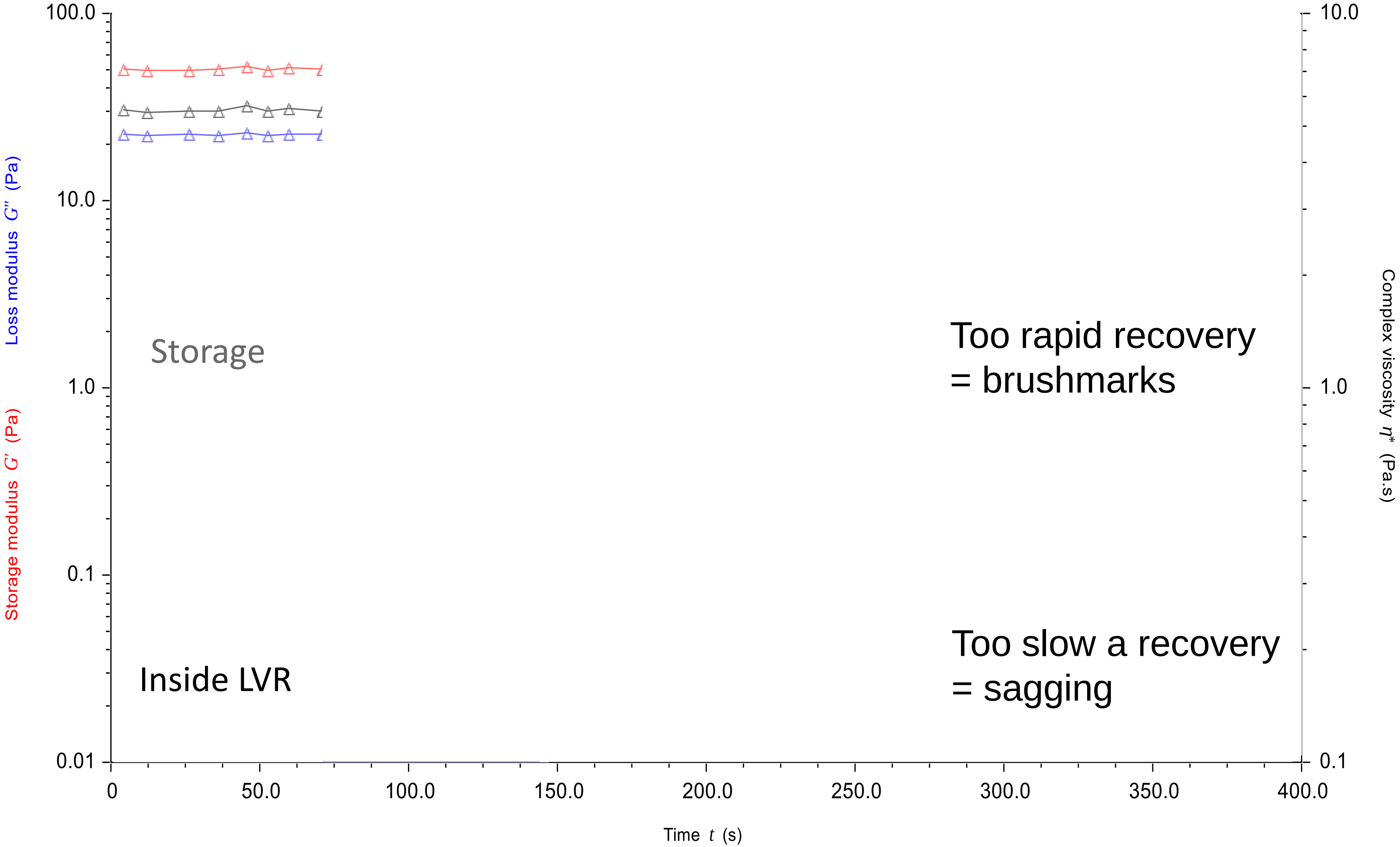
Creep is an ideal technique for exactly simulating the deformation of coatings when applied to a substrate. Stresses are often very low, but consequences can be dramatic.

Step Transient Creep : Sagging



These two samples show totally different displacements under the same stresses.
The greater the displacement, the lower the resistance to flow, the greater the likelihood of sagging.

Oscillation time sweeps – structure recovery



Axial Test – "Pull off" (tack)

- Measuring the axial forces whilst raising the head can give the user indication of "tack"

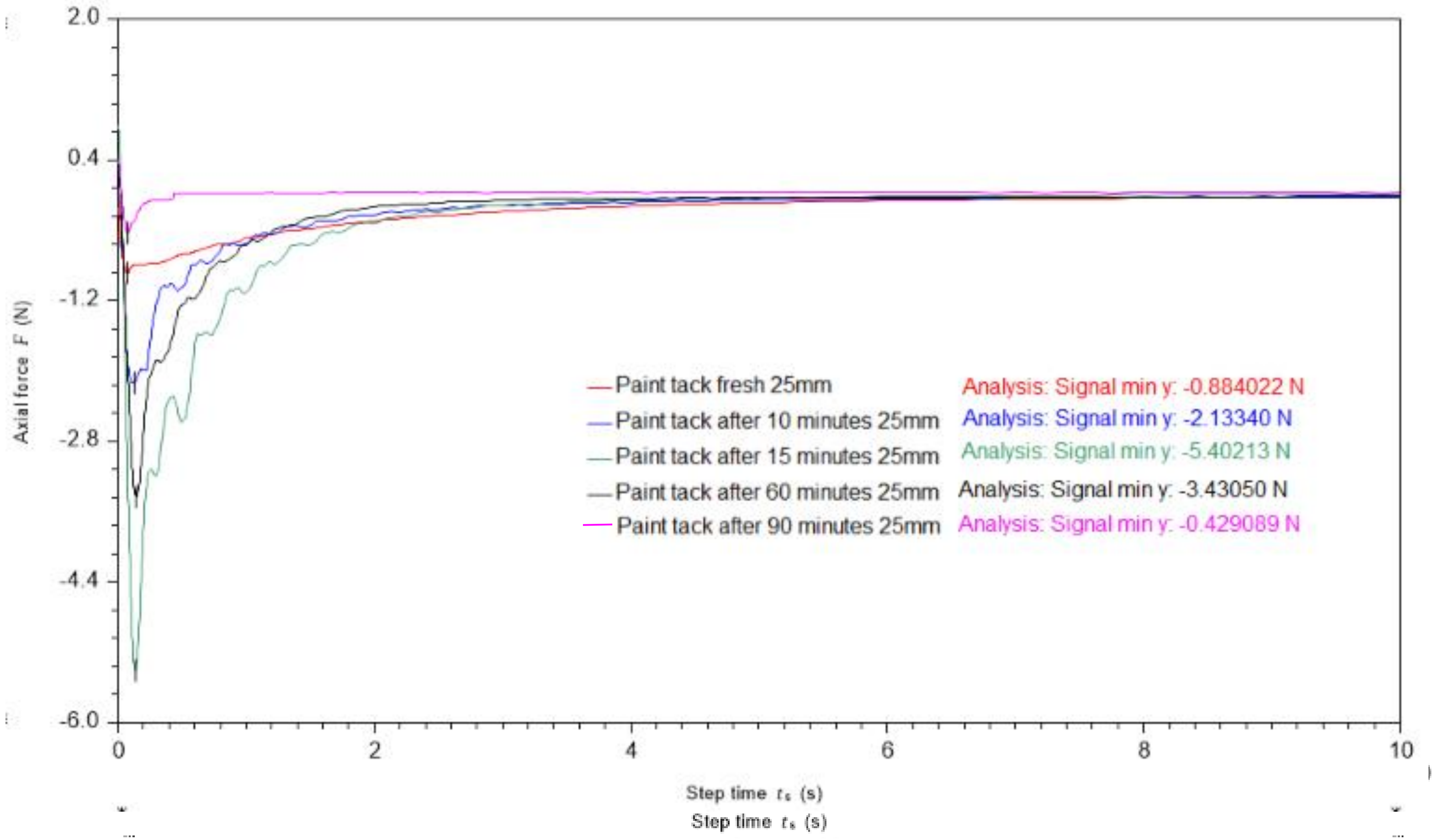
- Coating of geometry surfaces enables difference substrates or indeed film-film tack to be investigated.

- If the axial load is too high, head movement stopped

- Change diameter of plate to match scale of signal

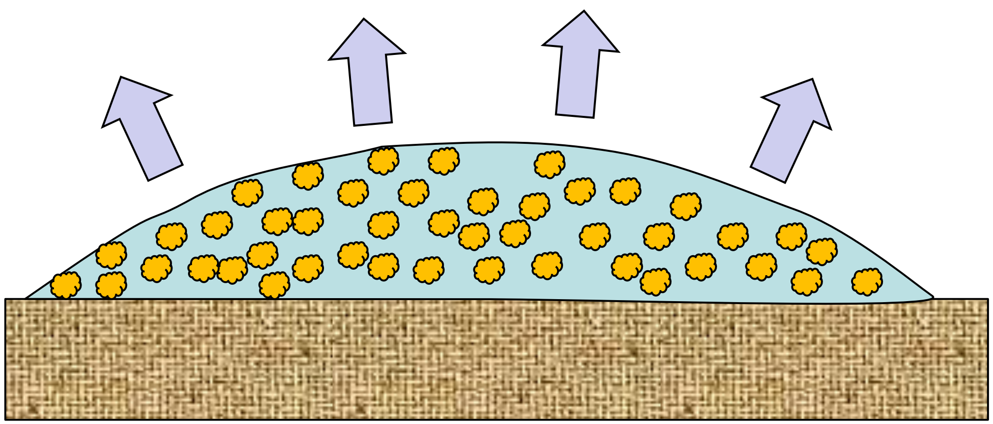
How dry is the paint – touch (tack)

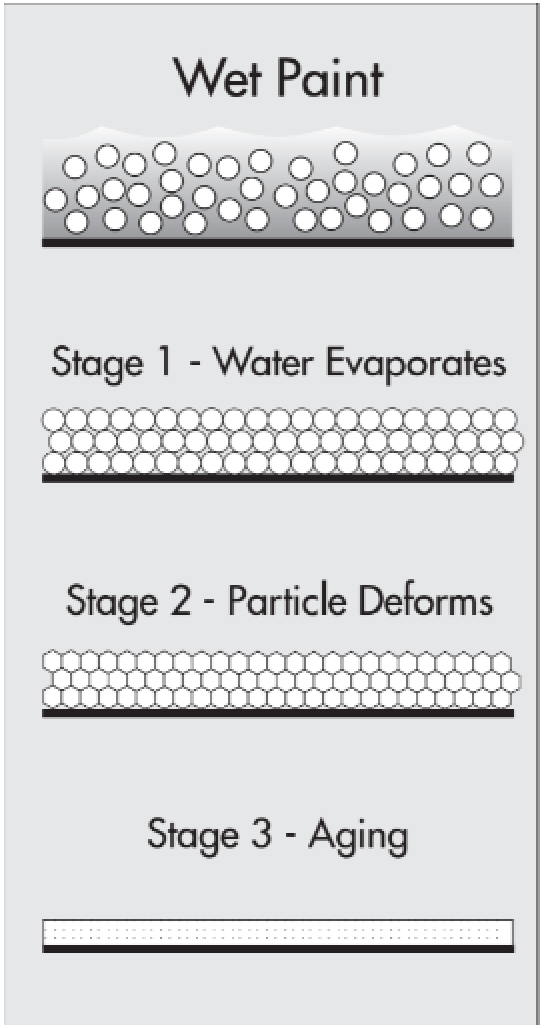
- Axial test : lower the axial force minima, the tackier the sample



Example of Paint Drying Process

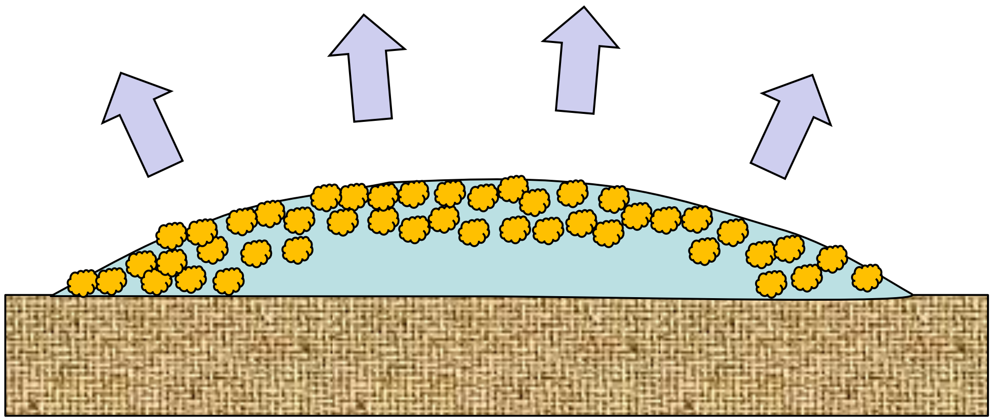
- Evaporation of volatile solvent
- Forces such as gravity (levelling) , surface tension and evaporation leads to coalescing of emulsion

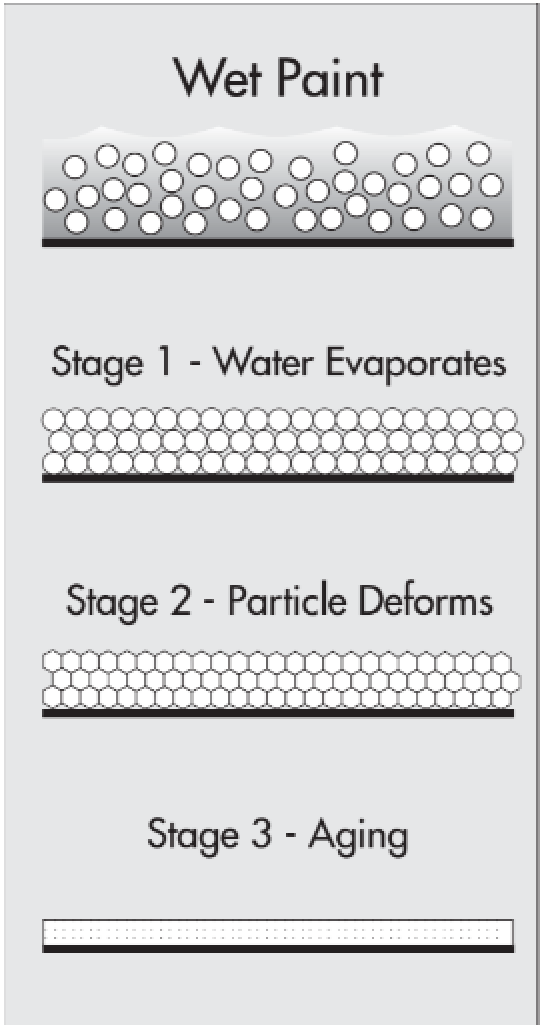




Process of paint drying

- Evaporation of volatile solvent
- Forces such as gravity (levelling) & surface tension leads to skin formation and packing arrangement (trap central reservoir of solvent)

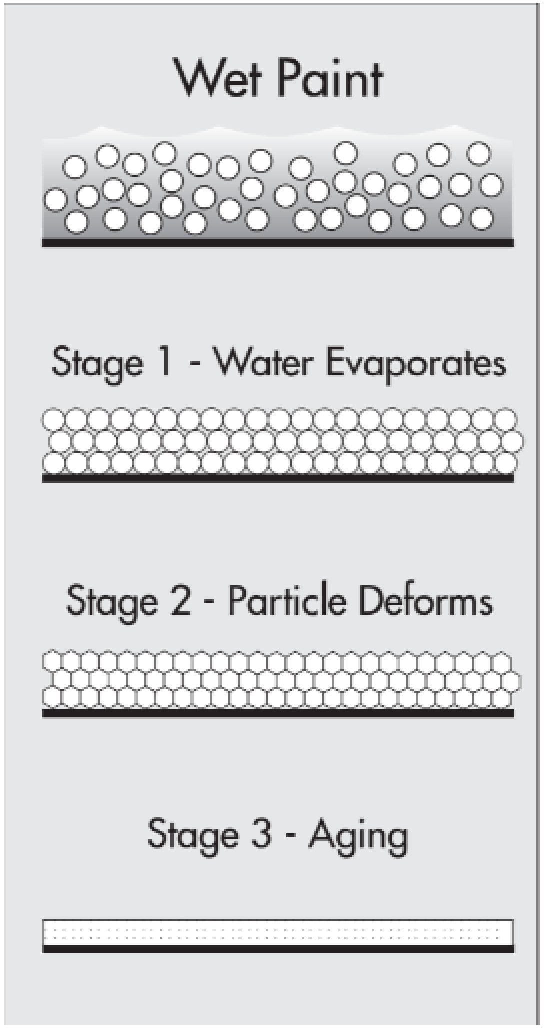




Process of paint drying

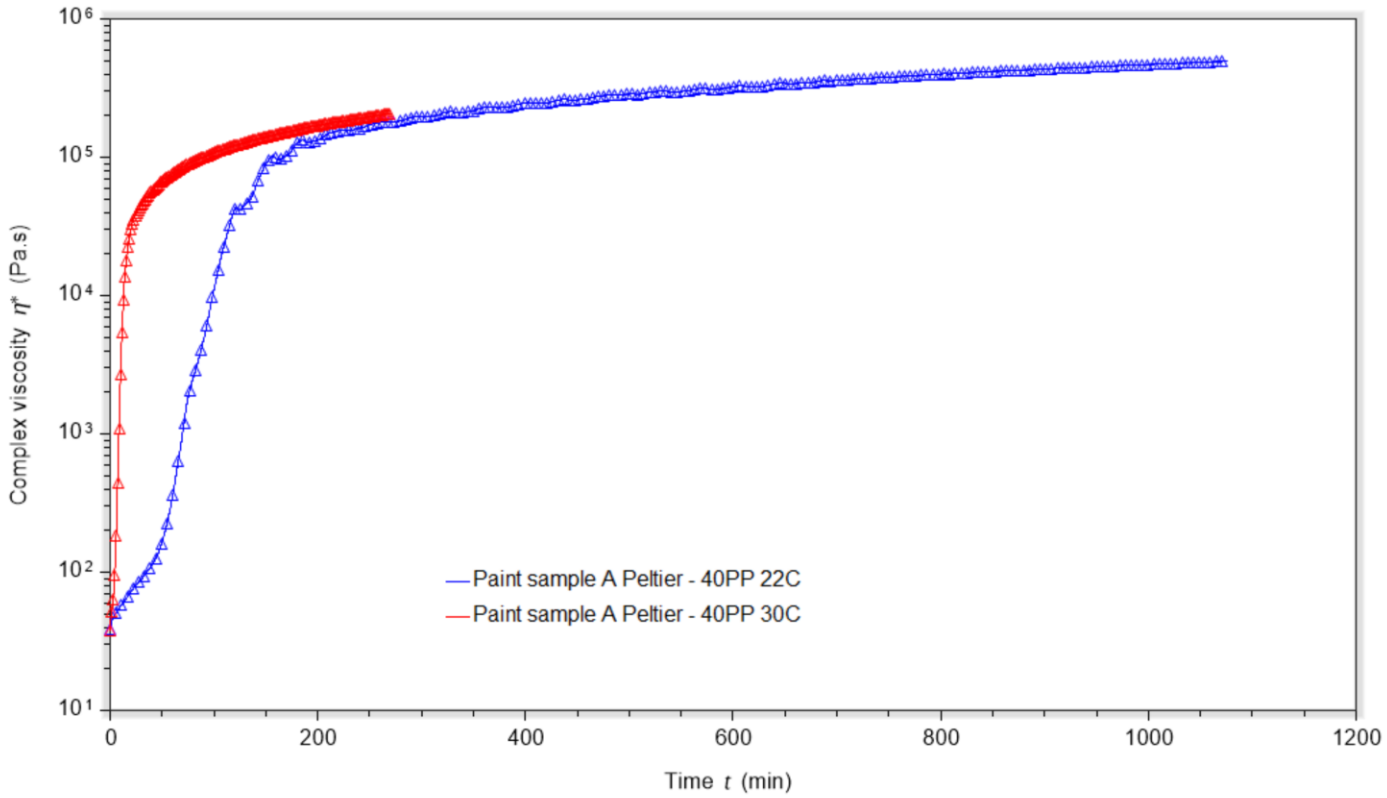
- Continual evaporation and forces such as gravity (levelling) , surface tension leads to coalesence of emulsion non volatiles

- A film is formed as non-volatile particles deposited deform and pack together



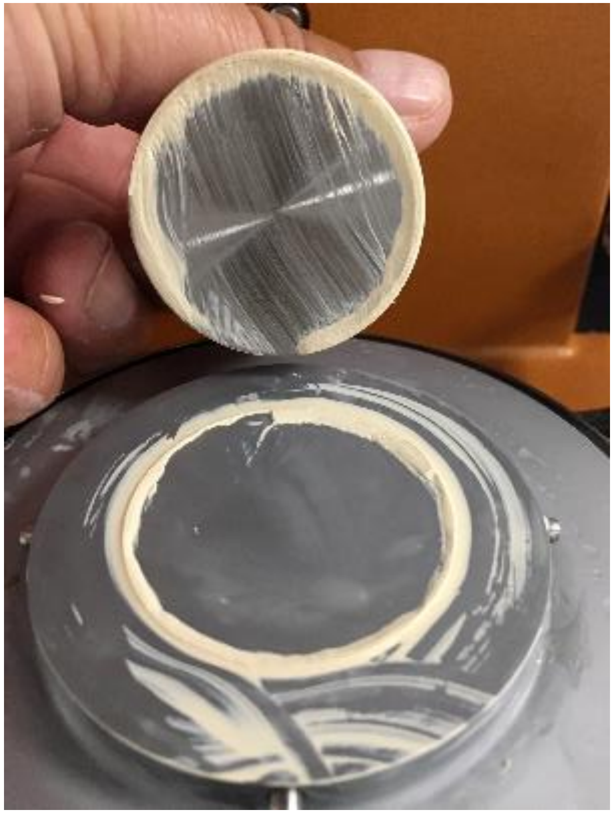
Pure evaporation

- Oscillation time sweeps run over hours , one at ambient (22ºC) & one at elevated temperature (30ºC)
- No surprise that paint dries quicker at elevated temperature as speeds up evaporation



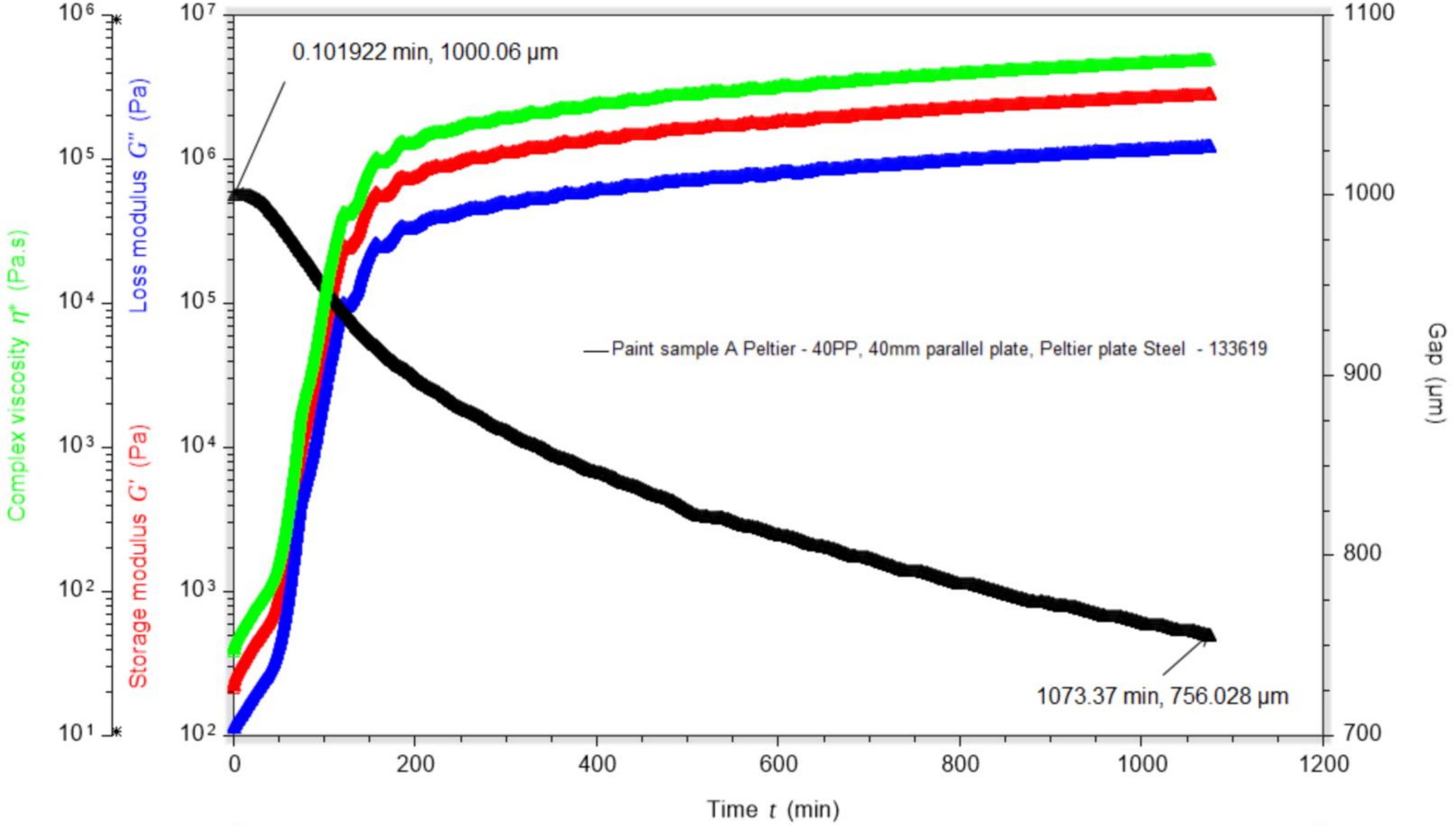
No substrate – other than Peltier metal

- With no through driers and nowhere for the water to escape – paint forms a skin around the edge, trapping wet sample.



Controlled axial force

- As evaporation occurs, volume will change, so controlled axial force adjustment is used to follow
- Result is change in gap indicates amount of shrinkage

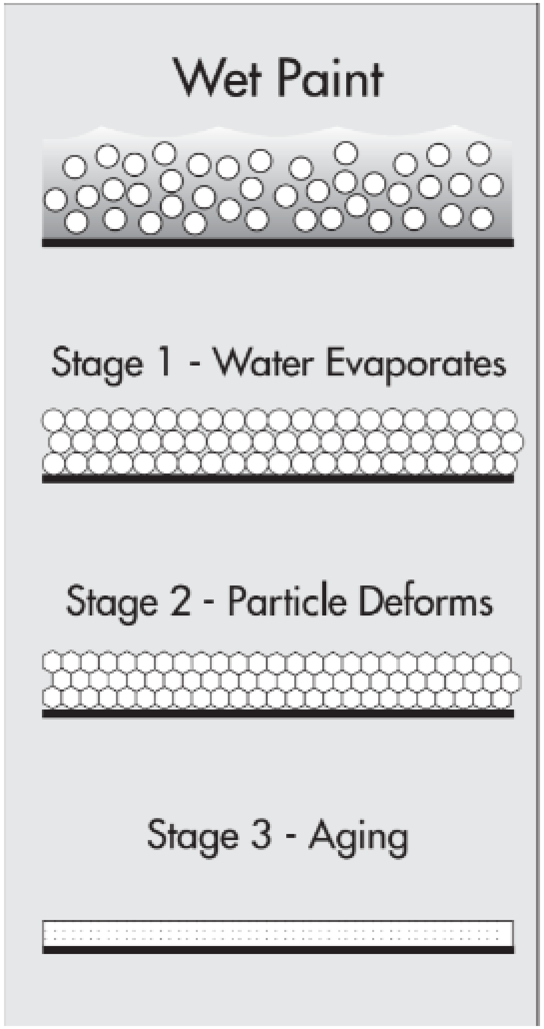


Effect of Substrate

- Since a key step to the drying process is the loss of the solvent it is no surprise that the “draw” of the substrate will also have an effect.
- The ability for the solvent to permeate into the substrate (masonry or wood for example) can speed up the drying process.
- Therefore the porousity and substrate temperature are two effects to be considered
- *Note: Care should be taken that testing with a substrate, the substrate itself remains non compliant.*

Process of paint drying

- Evaporation of volatile solvent
- And permeation of volatile solvent into substrate will accelerate the process



Simple substrate investigations

- With the Advanced Peltier Plate configuration it is easy to fit a variety of different substrates onto the temperature module.

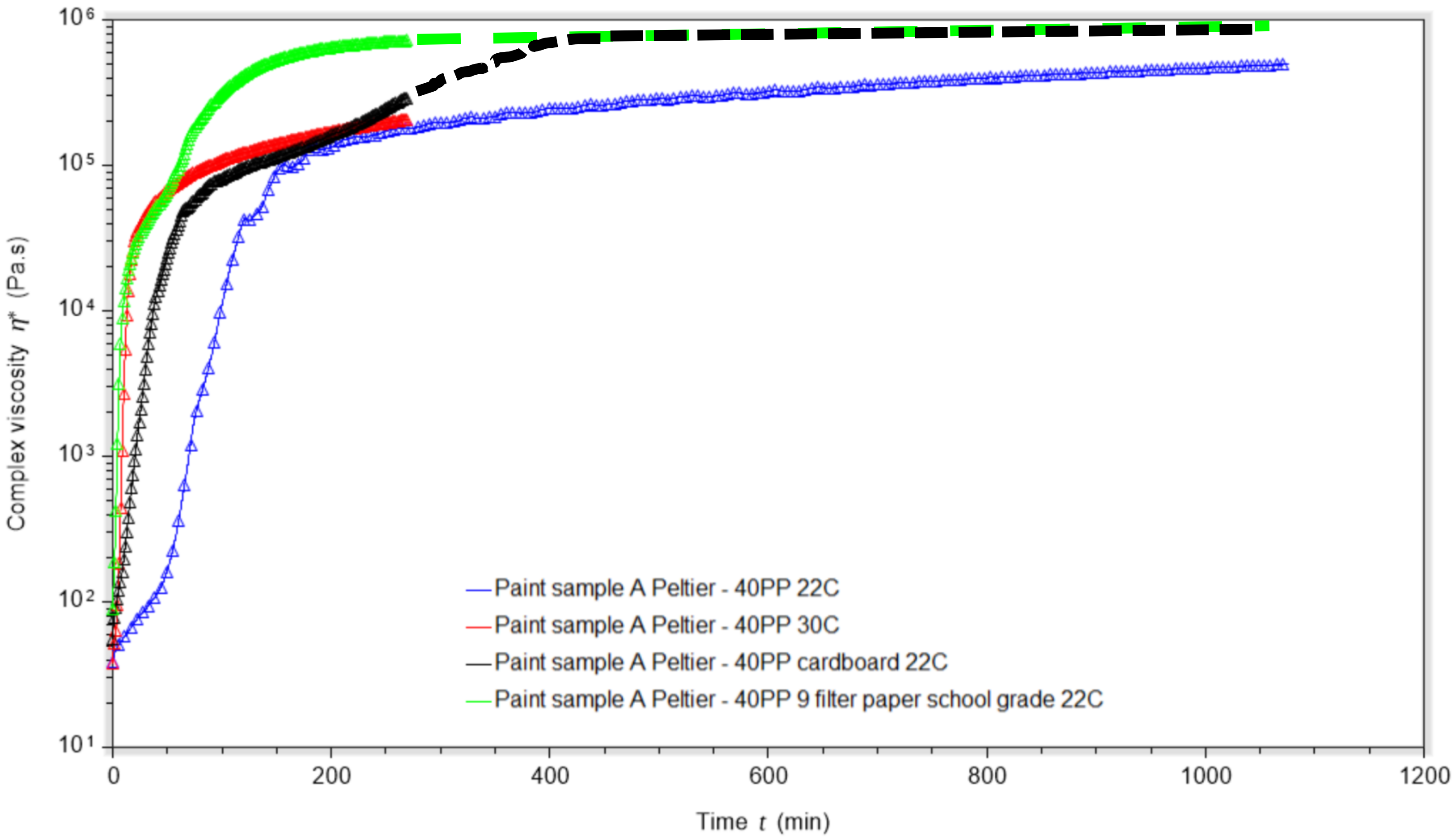
Multiple sheets of filter paper

Piece of cardboard

- Oscillation time sweeps run for hours at ambient (22ºC)

Effect of substrate

- With an escape path for the solvent, initially a skin forms, but then second stage drying occurs while solvent permeates into substrate



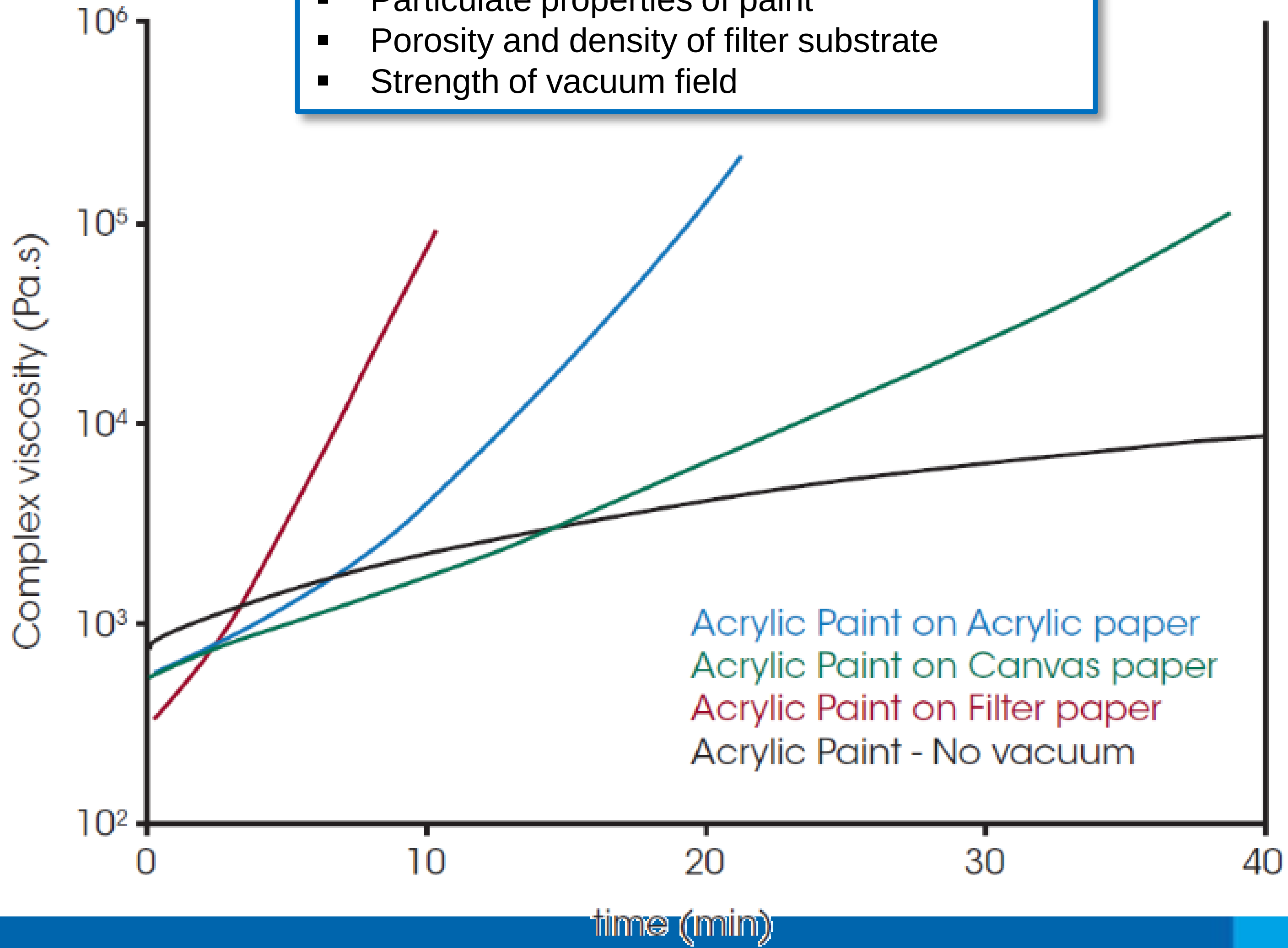
Immobilization Cell

- Ideal for studying changes in rheological properties during drying of materials on a substrate – paints, coatings, slurries
- Vacuum field applied to substrate placed on lower plate – removes solvent from the sample
- Peltier elements for controlling temperature: -10 to 180 ° C
- Pressure difference between coating and substrate: 0 to 85 kPa

Immobilization Cell Application

Rate of sample dewatering is influenced by:

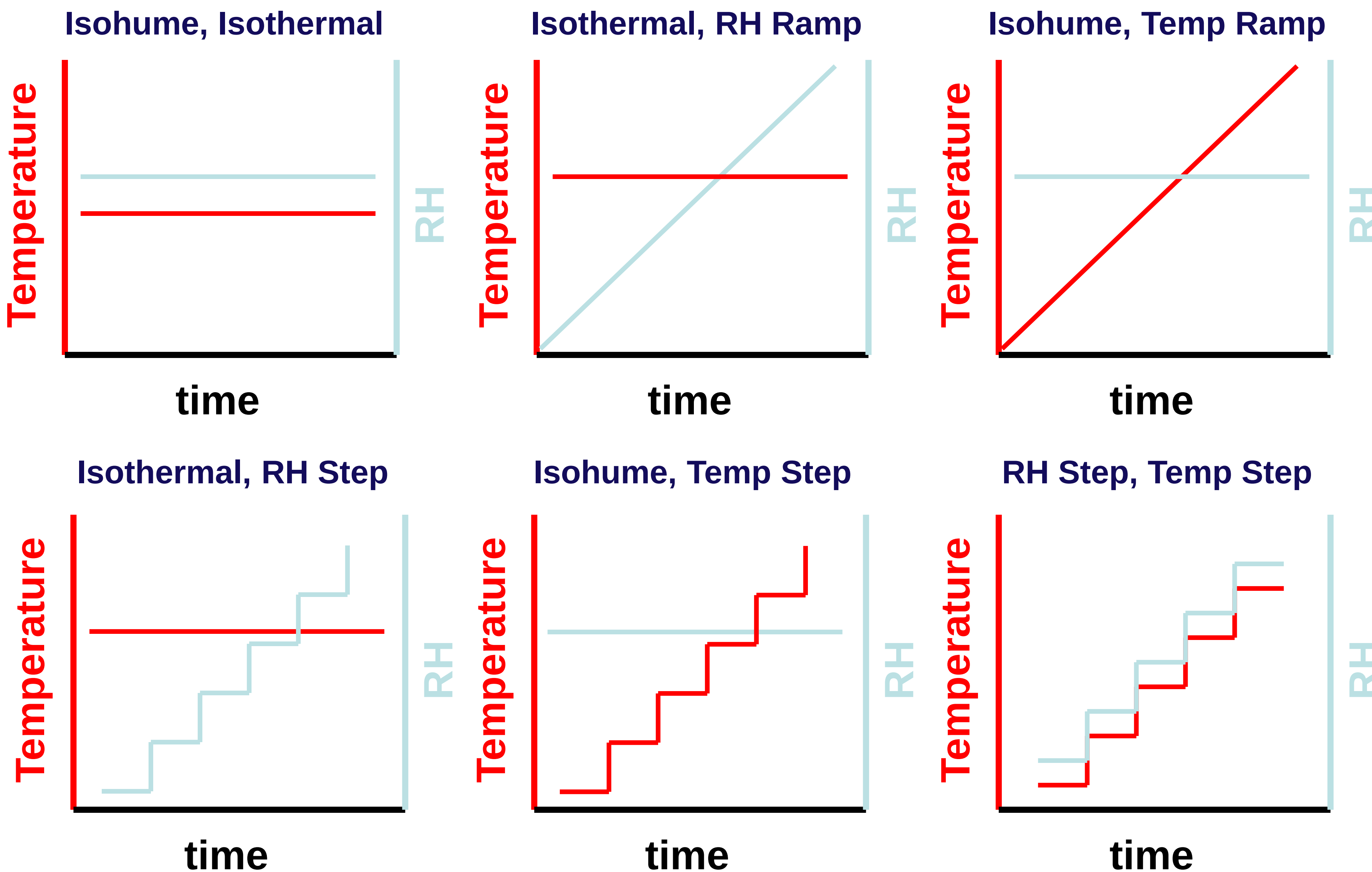
- Particulate properties of paint
- Porosity and density of filter substrate
- Strength of vacuum field



DHR-RH Accessory

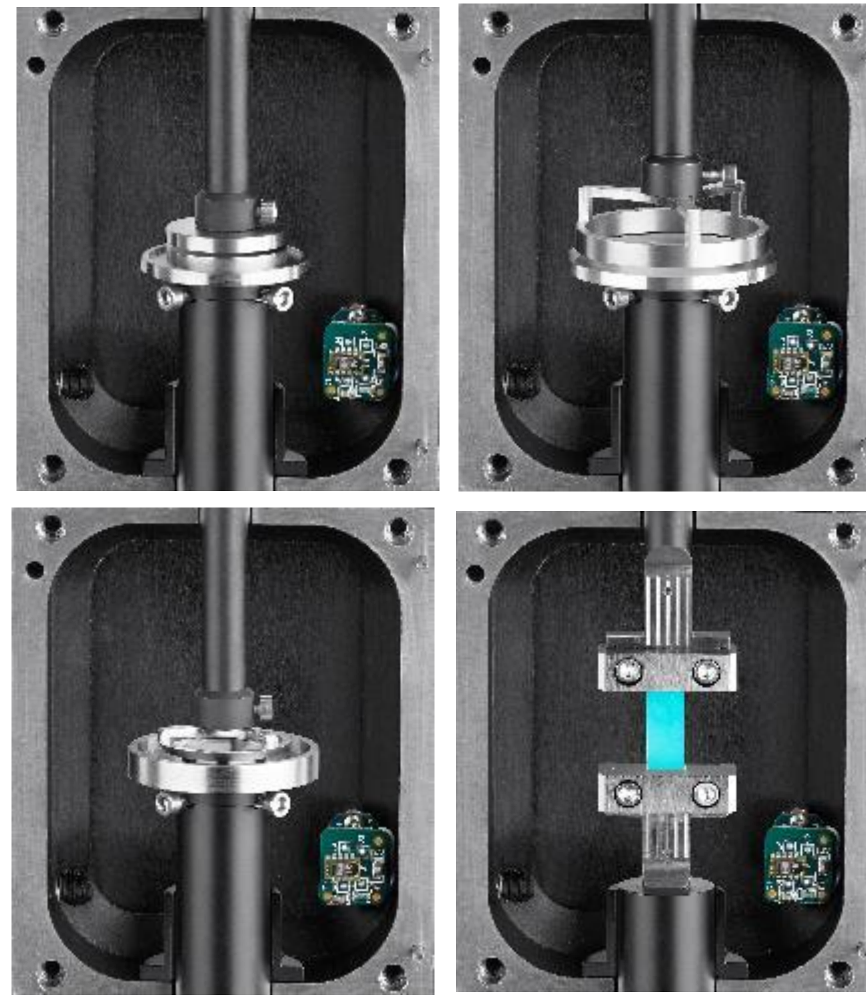
- Complete control of temperature and relative humidity:
  - 5ºC to 120ºC
  - 5%RH to 95% RH
- Measure
  - curing,
  - drying,
  - plasticizing,
  - Coefficient of Hygroscopic Expansion (CHE),
  - and more
- Complete TRIOS integration

DMA-RH Experimental Options

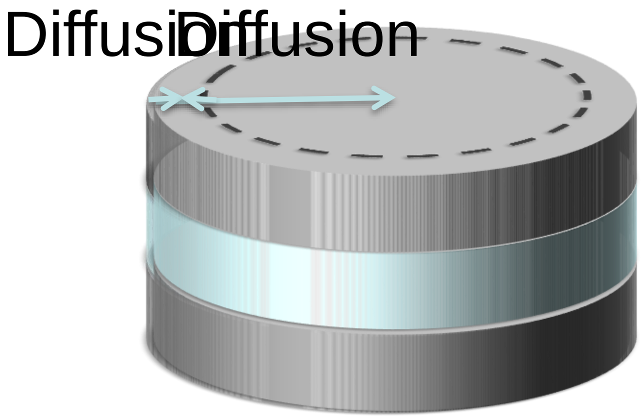


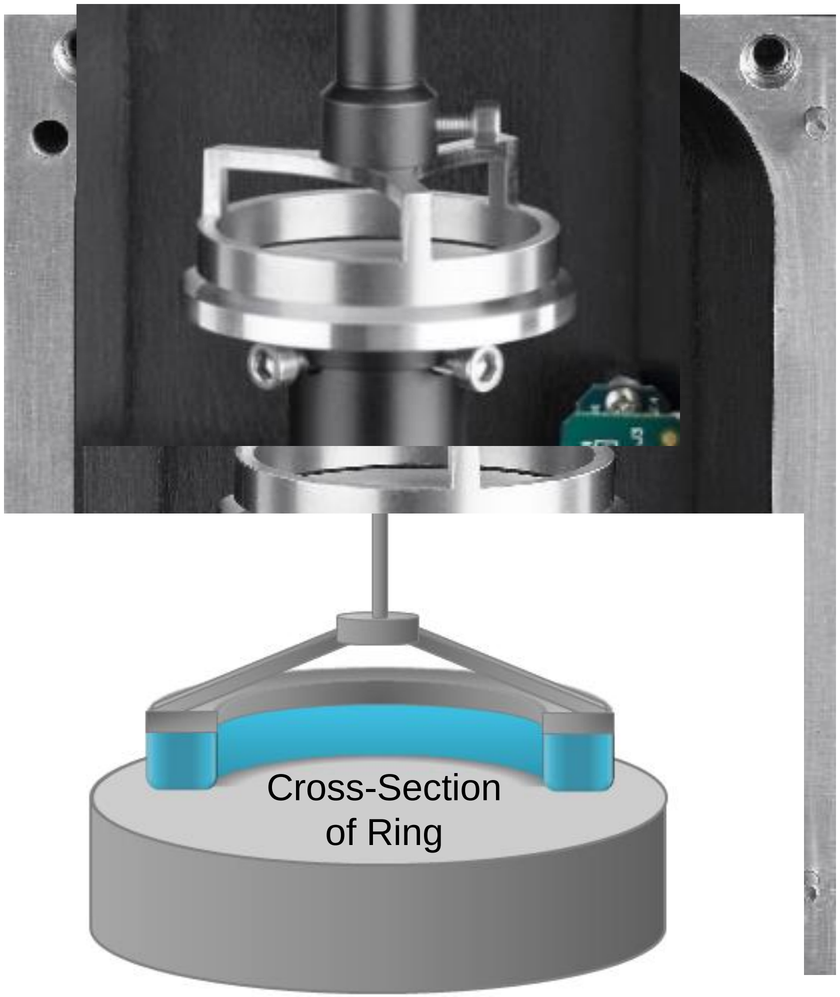
Test Geometries

- Wide variety of test geometries:
  - Standard parallel plate
  - Disposable parallel plate
  - Rectangular Torsion
- Innovative geometries for RH: true humidity-dependent rheology, not dominated by diffusion
  - Annular Ring
  - Surface Diffusion
- True Axial DMA:
  - Film Tension
  - Three-point Bending



Annular Ring Geometry

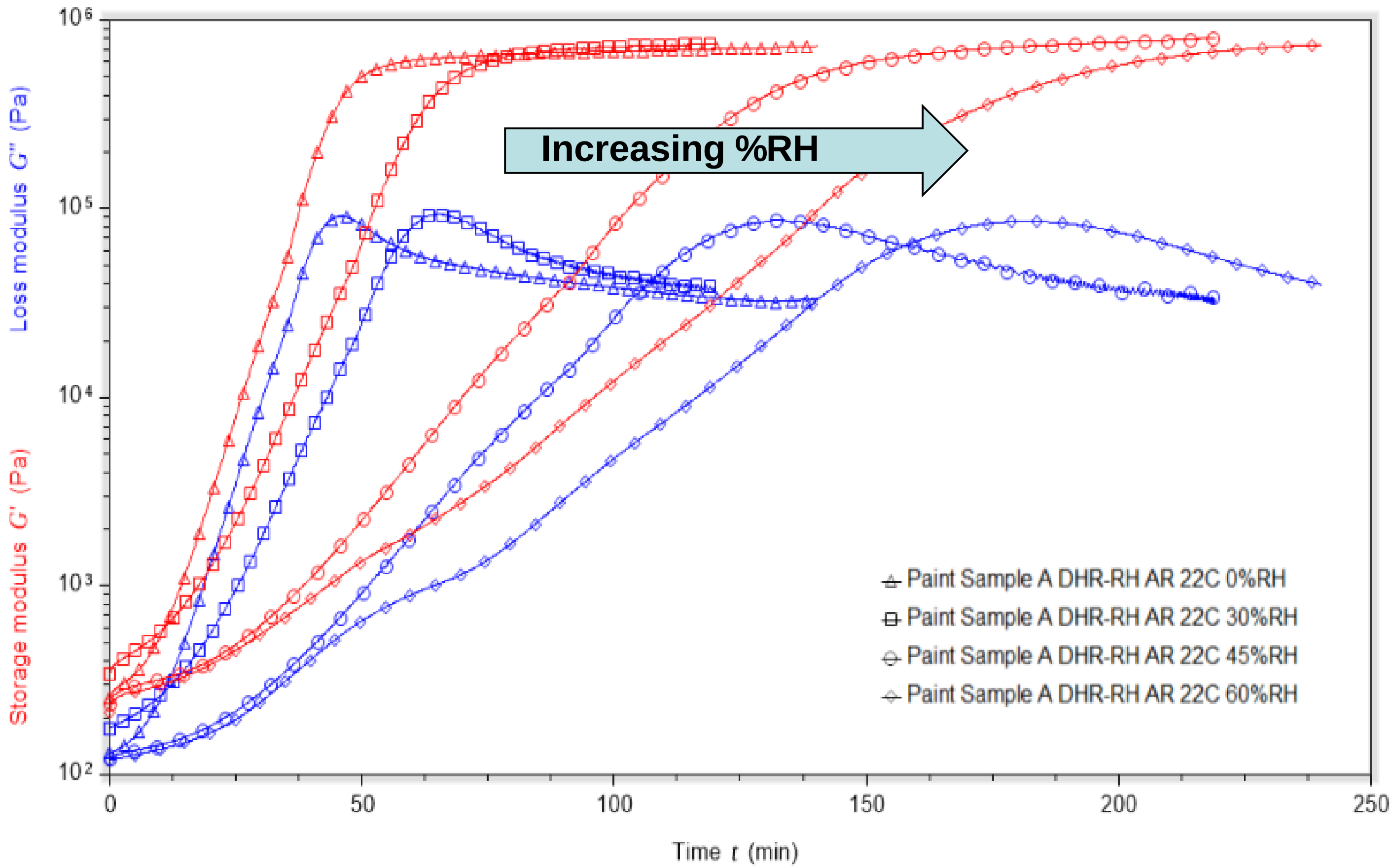




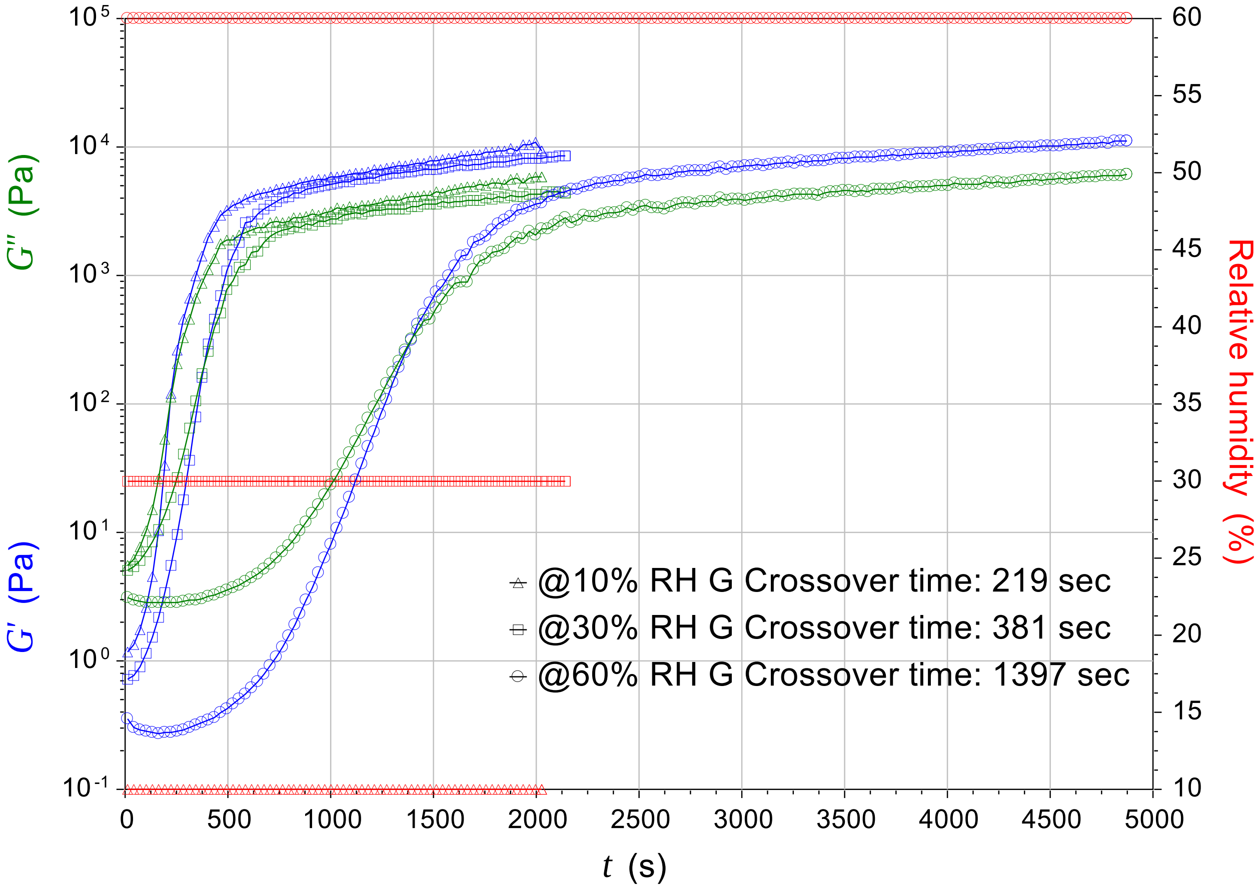
- Parallel plate: long diffusion length
- Remove center section
- Annular ring: short diffusion length
- Provides quantitative bulk rheology with less delay and gradients associated with diffusion

Humidity effect on paint drying – Annular ring

- The presence of moisture in the atmosphere is seen to have a significant effect on the drying of the paint.



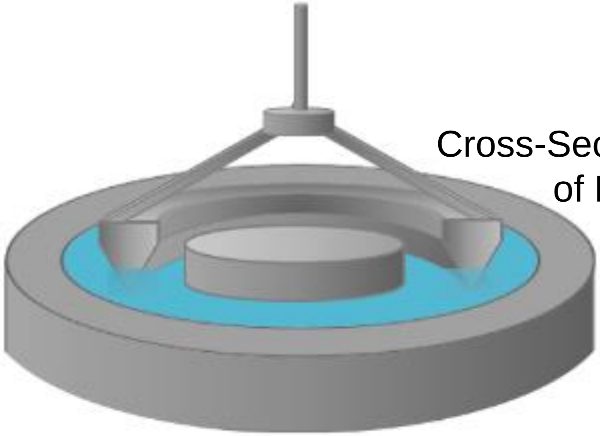
Glue curing under different humidity



Relative Humidity (%)	10%	30%	60%
G Crossover time (s)	219	381	1397
G Crossover Modulus (Pa)	102.9	191.8	325.4

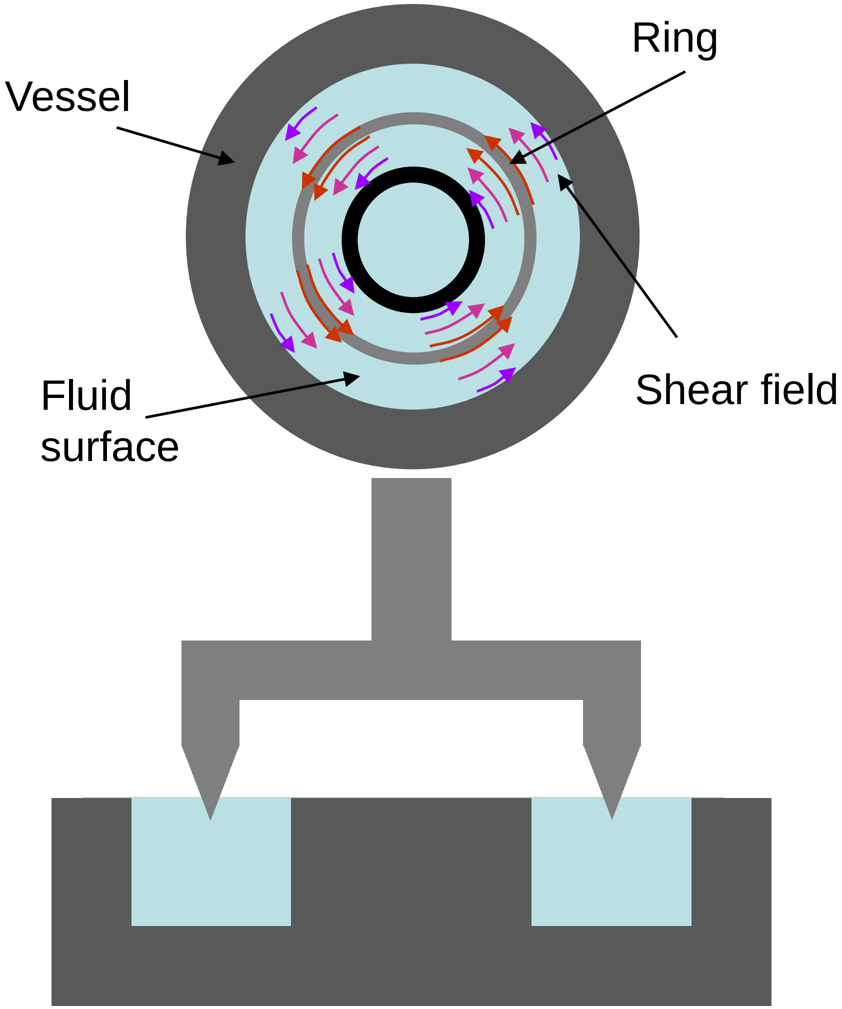
Surface Diffusion Geometry

- Surface rheological properties and process kinetics
- Monitor surface drying and development of elastic “skin.”
- Ideal for:
  - Fast evolving systems
  - Samples with shallow interaction depth
  - Drying, curing…

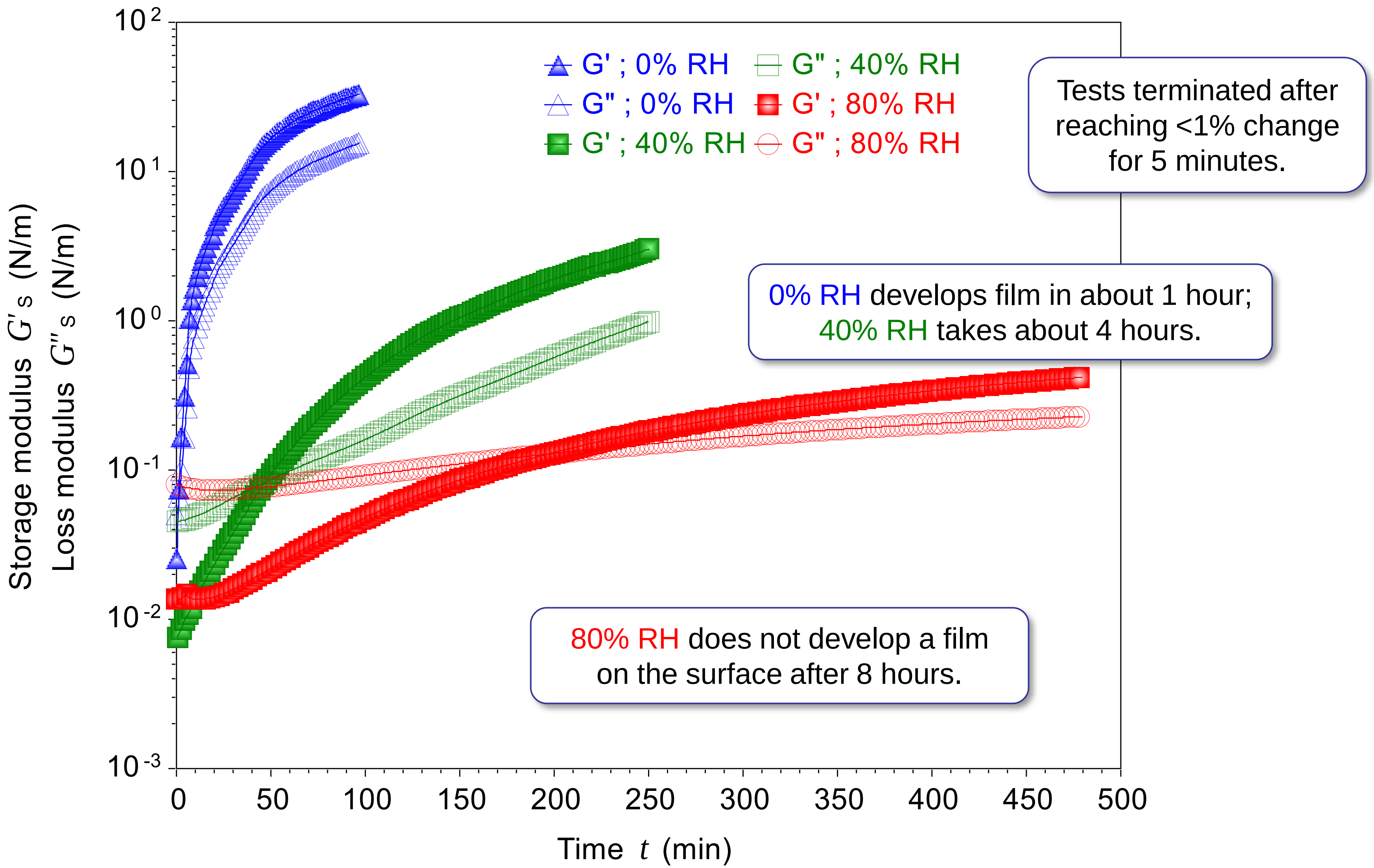


Cross-Section of Ring

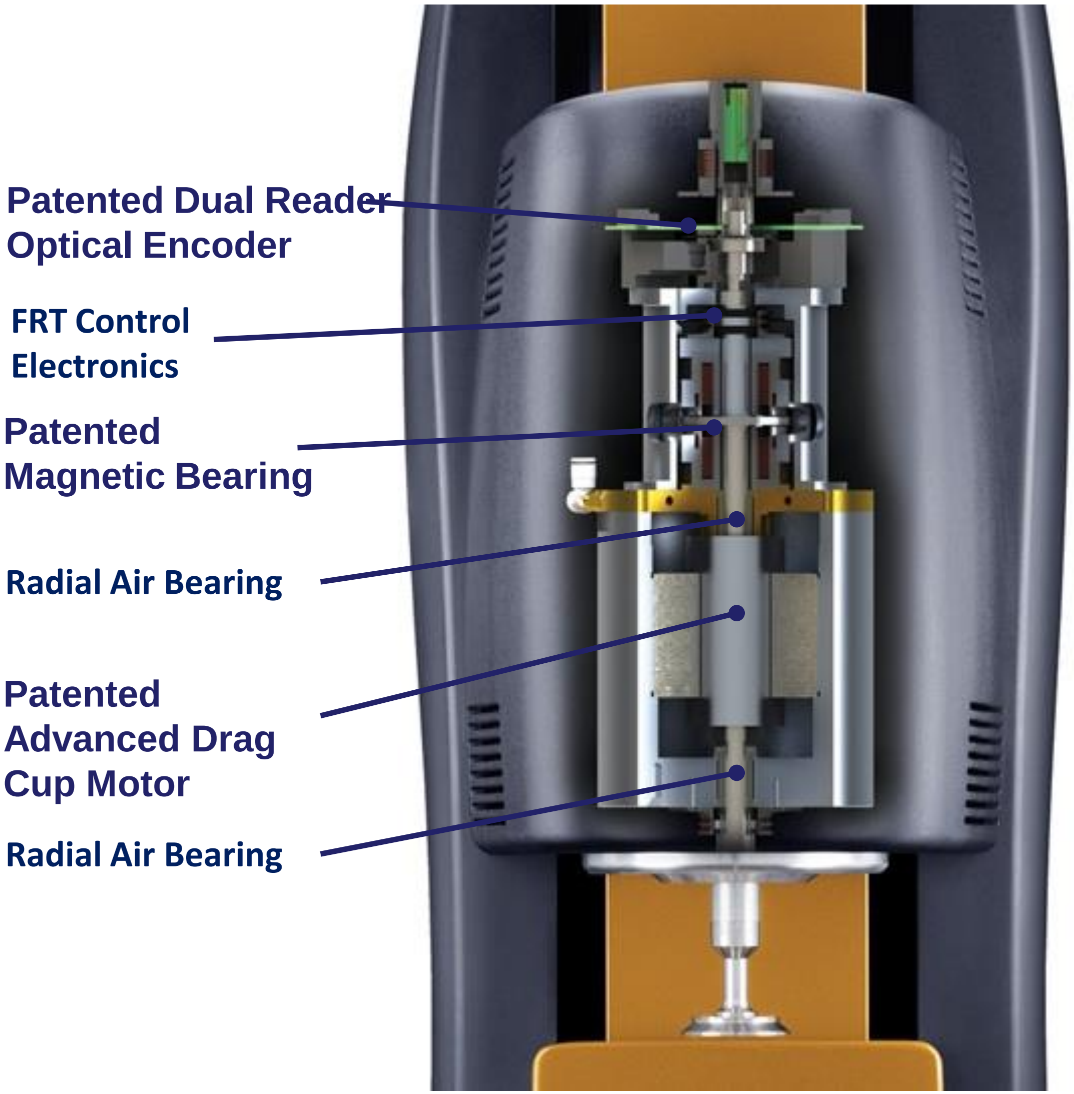
Surface Diffusion Geometry

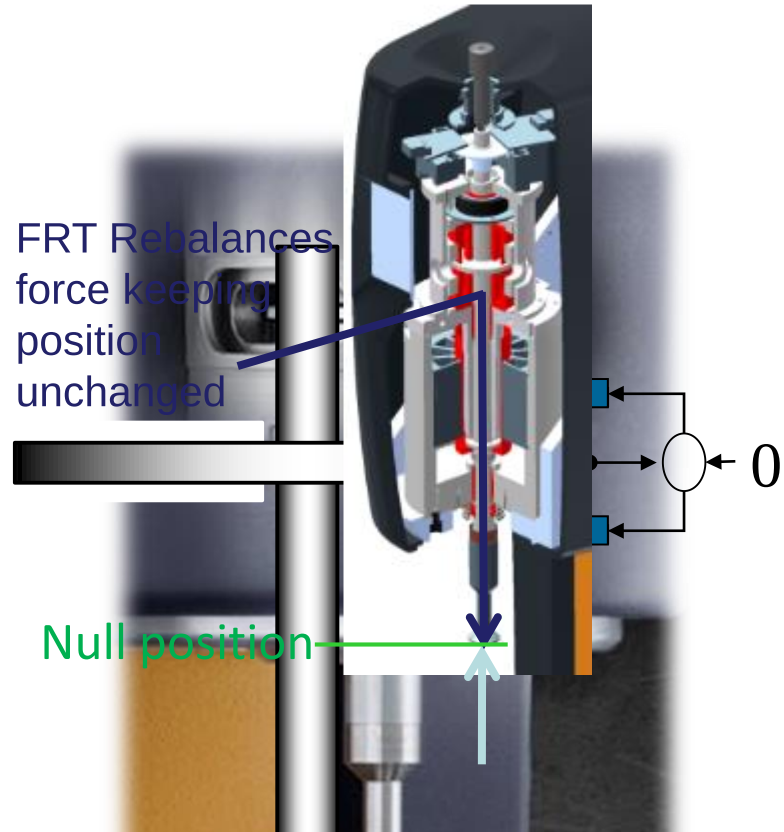


Surface Diffusion Under Varying Humidity



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

DHR : DMA mode

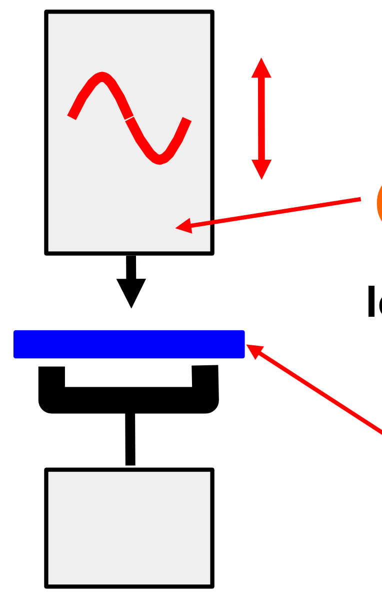
Normal Force Tran:

Small
Amplitude
Oscillation

DHR DMA

Controlled Strain

CMT – Combined Motor & Transducer



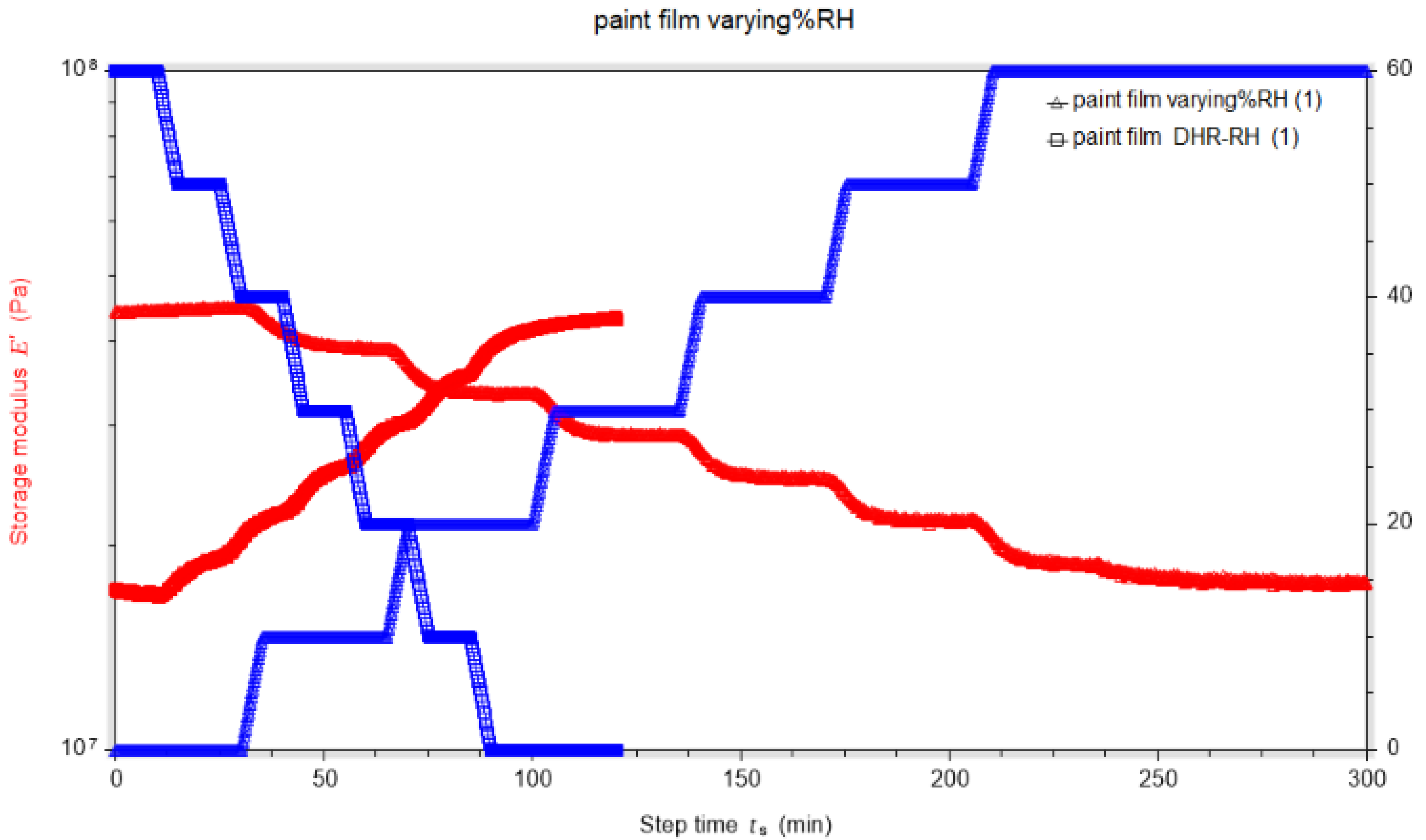
Torsion and DMA Measurements

- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment
  - Torsion measures G', G", and Tan δ
  - DMA measures E', E", and Tan δ
    - ARES G2 DMA is standard function (50 μm amplitude)
    - DMA is an optional DHR function (100 μm amplitude)

Rectangular and cylindrical torsion

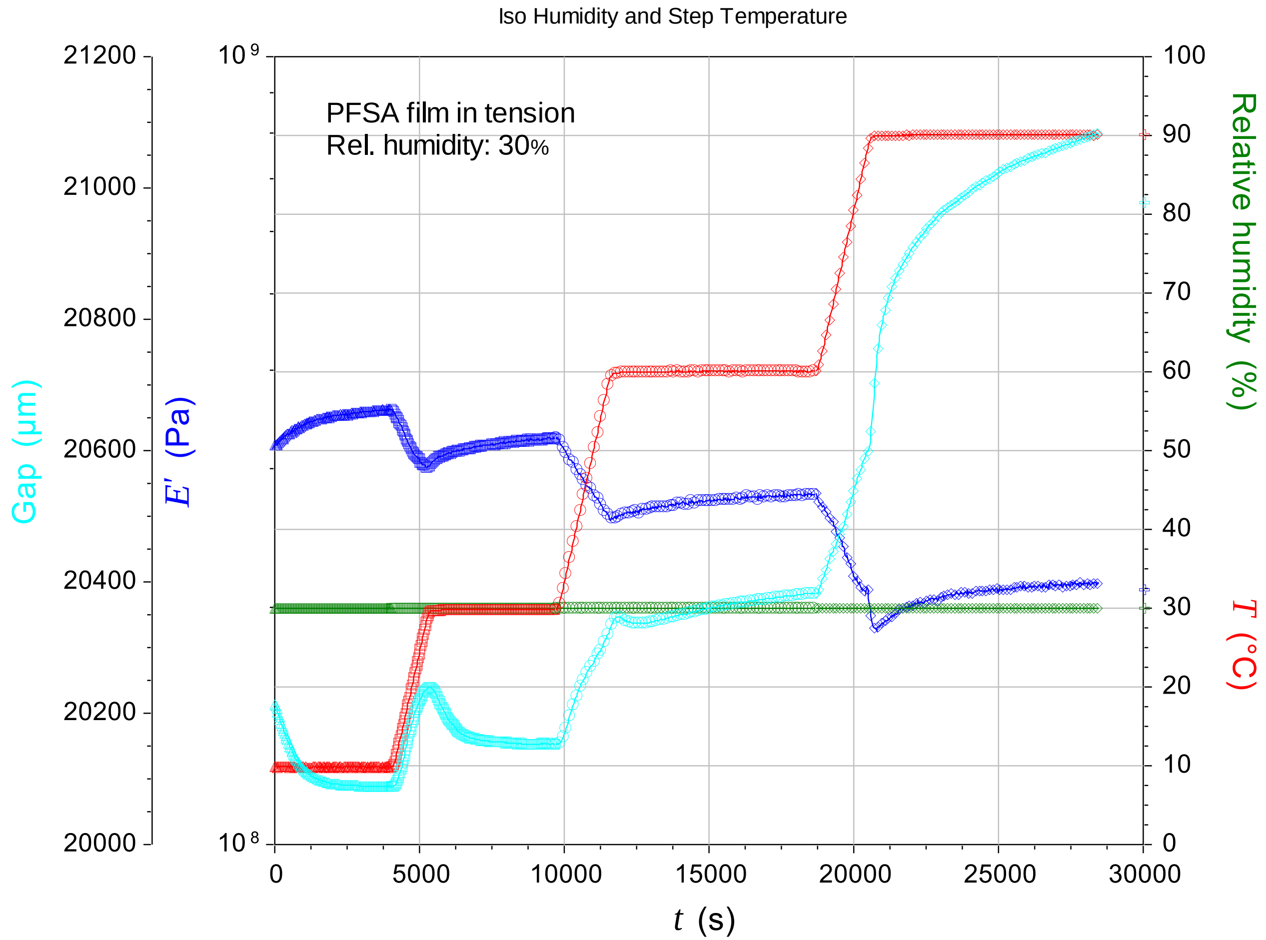
DMA 3-point bending and tension (cantilever not shown)

Relative Humidity and paint films



- Isothermal with sweep in %RH shows films “softening”
- shows films recovers on “lowering %RH – effectively drying”

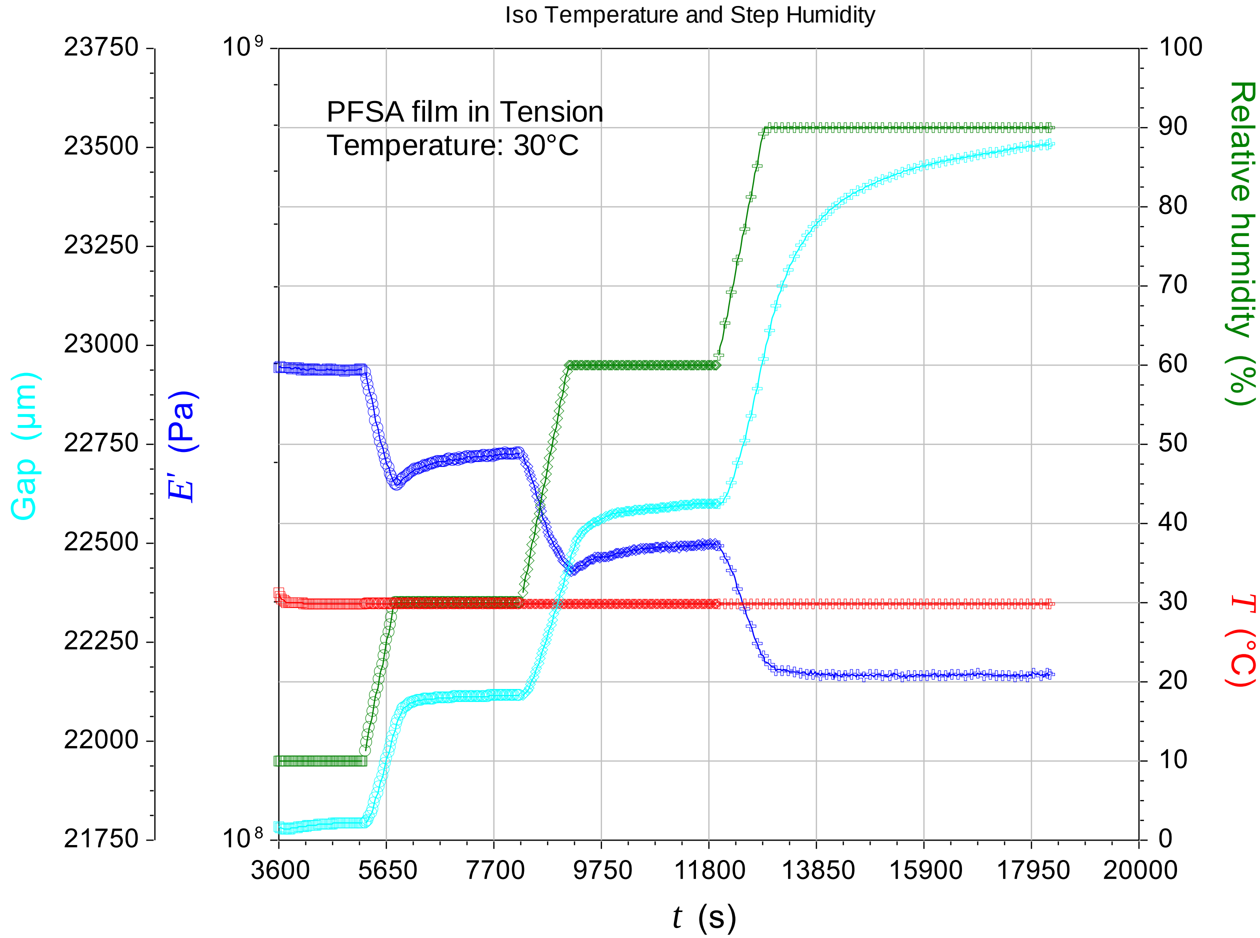
Fuel Cell Membrane: Aquivion® PFSA



Iso-humidity and Step Temperature

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

Fuel Cell Membrane: Aquivion® PFSA



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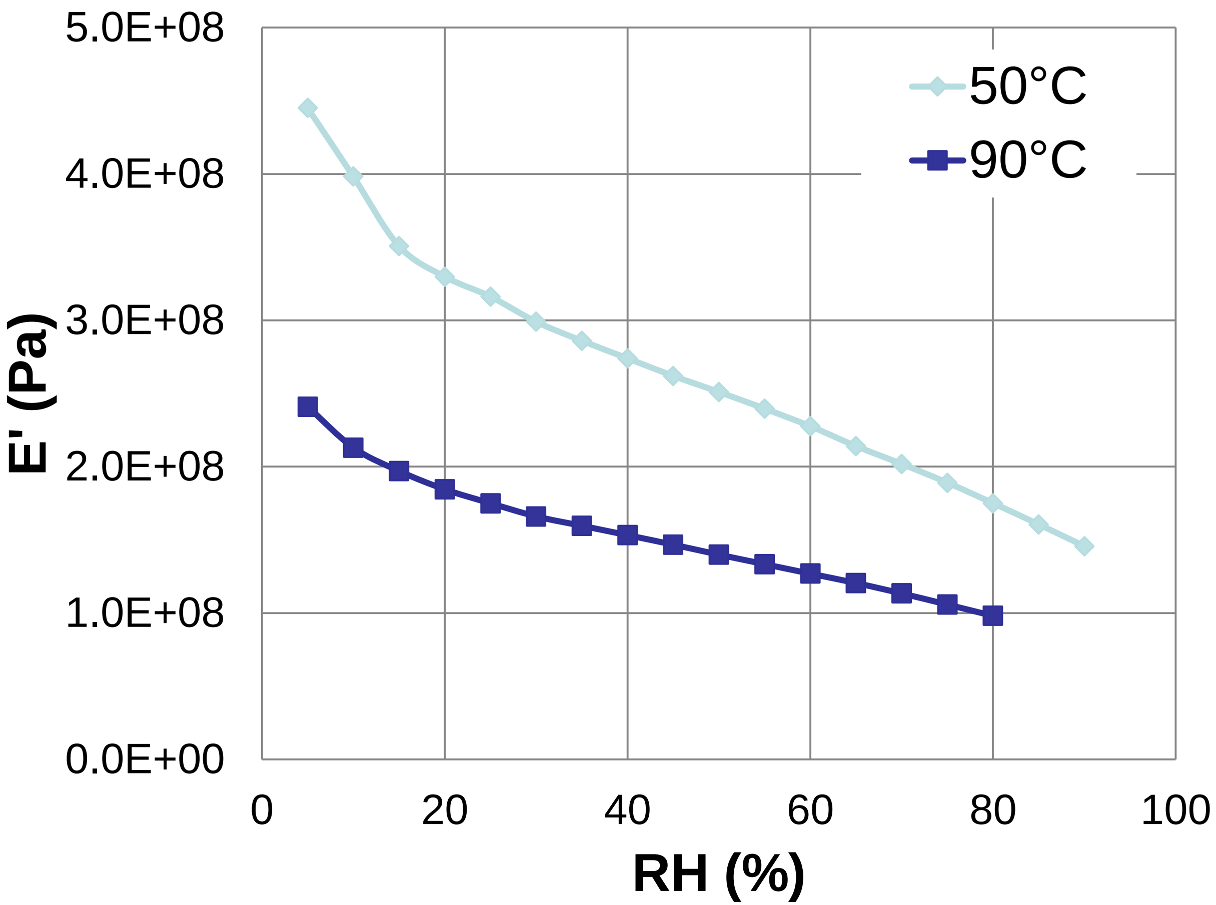

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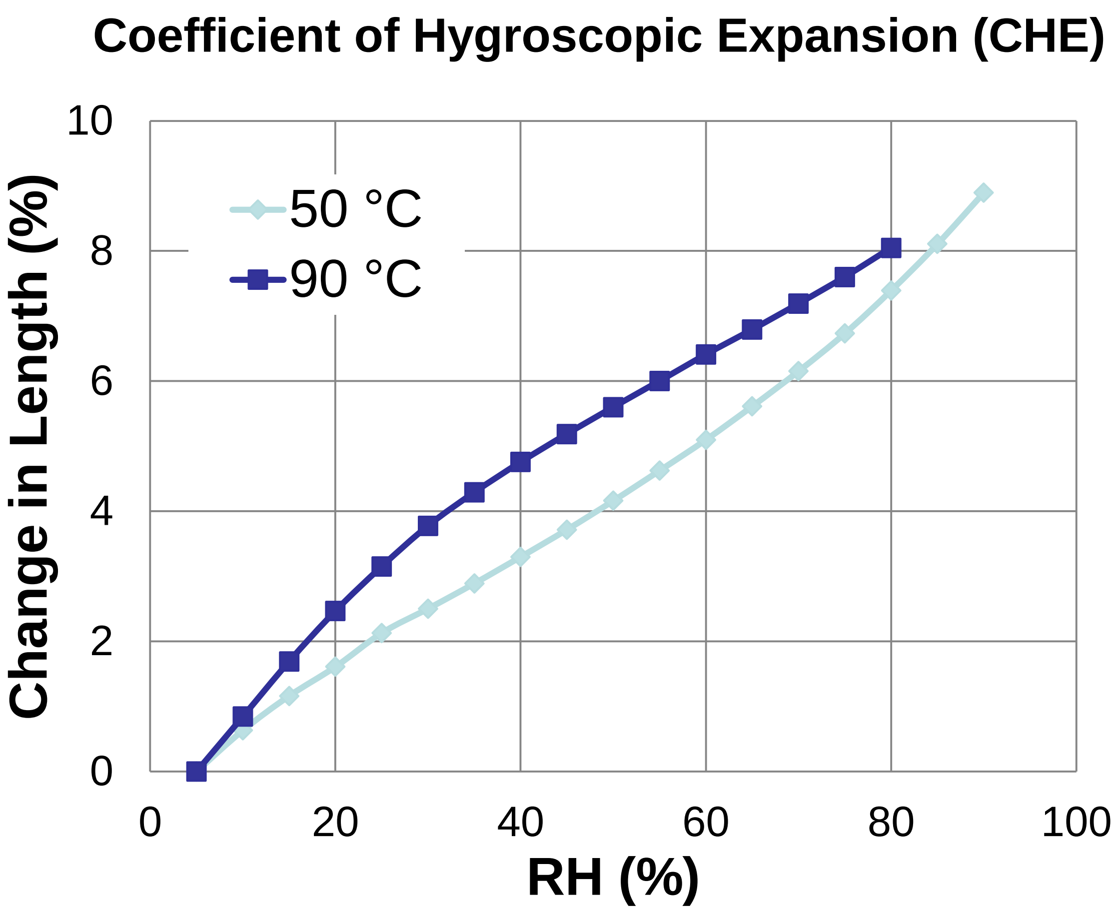

	90 ° C	50 ° C
5% to 20%	0.165	0.107
40% to 60%	0.082	0.090

More to rheology than watching paint dry

- So I hope I've demonstrated not only the routine uses of rheology for the coatings world

- But also shown you that with an array of accessories available, the environmental effects on drying (and possibly curing) kinetics can be investigated on a modern rheometer, controlling:
  - Temperature
  - Substrate
  - %Relative Humidity

- I hope this presentation was more interesting than actually watching paint dry ….as I've done a lot of that recently!

Thank You

The World Leader in Thermal Analysis, Rheology, and Microcalorimetry