Pacific Heat and Wave Flow: Day II
Section III: Intermediate DMA methods and other advanced Topics

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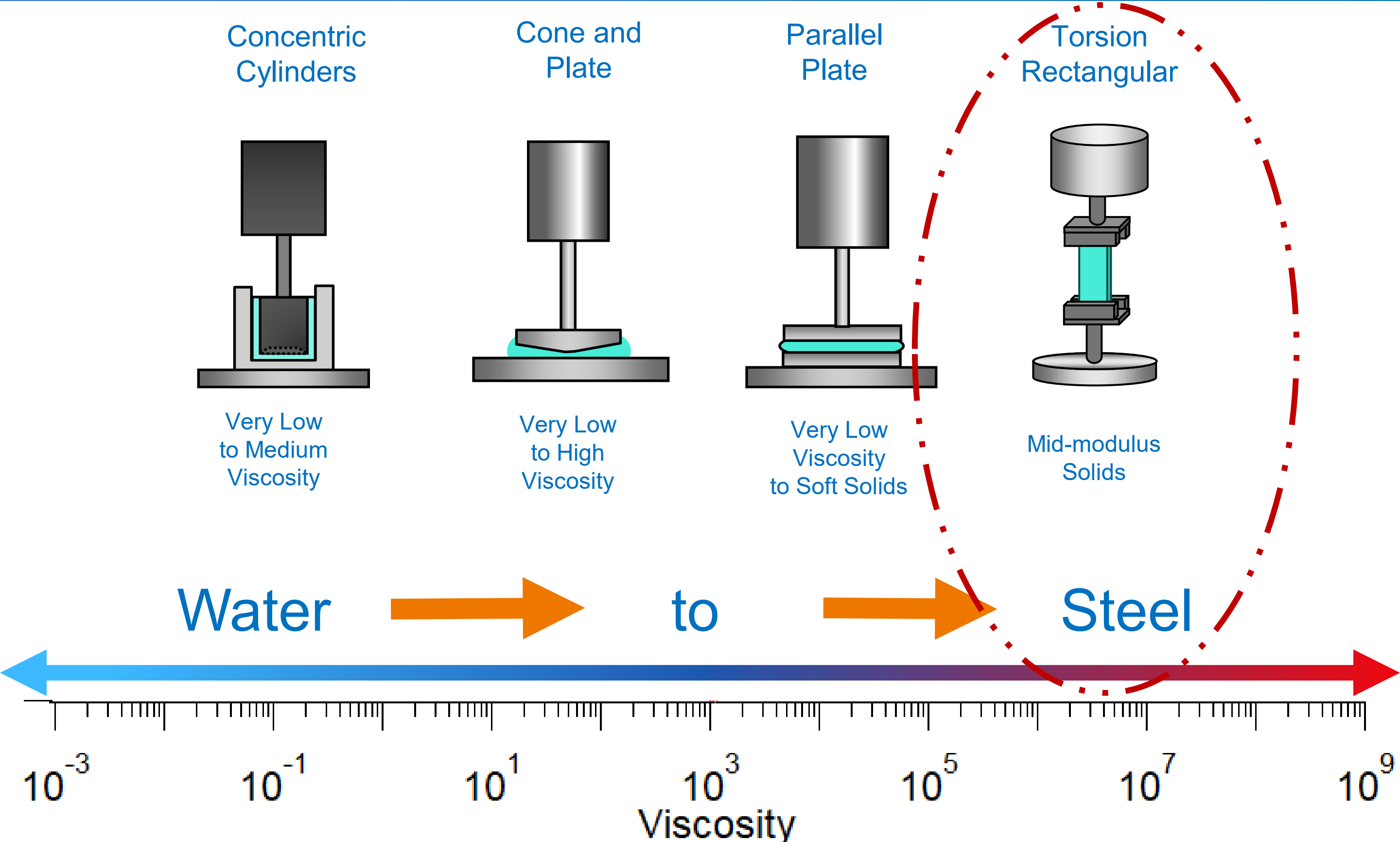
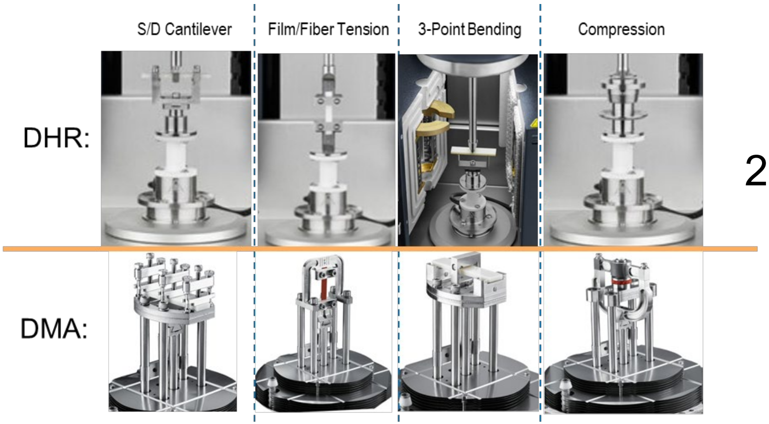
Recall – Rheometer Geometries



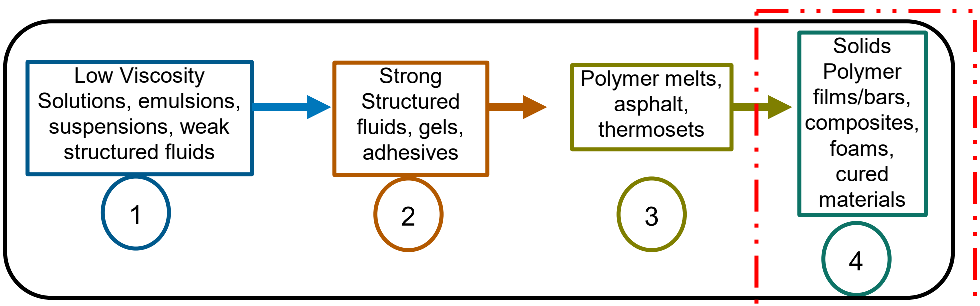
Organization of talk



1.) Common DMA methods
- Amplitude Sweep
- Temperature Ramp

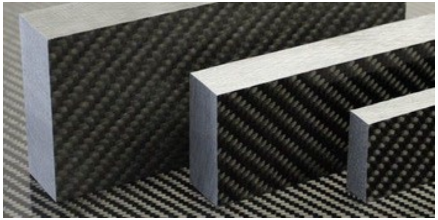
2.) Intermediate DMA methods
- Temperature Ramps – (Glass transition effects)
- Multistep Creep Recovery

3.) Advanced Rheology + DMA methods
- TTS
- Humidity (RH) Unit
- Tribology



- In the last presentation we finished with “Thermosets, Curing, and Gelation”
- Now we will cover post cure materials or solid materials (DMA testing)

DMA Results can correlate to…



DMA Results:

E, G, J
Tan δ
Tg, Tβ, Tγ

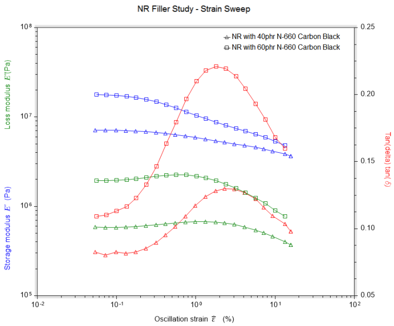
Molecular structures
- MW and MWD
- Branching
- Crystallinity
- Crosslinking
- Phase
- Relaxation

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

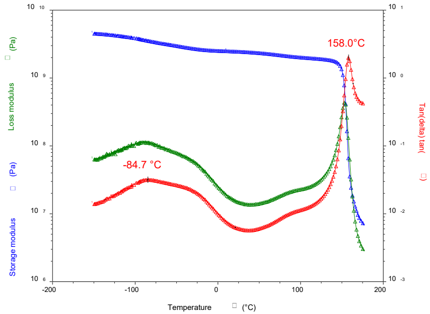
Product properties
- Transition temperatures (Tg, Tβ, Tγ)
- Environmental resistance
- Impact strength
- Long term behavior, aging
- Adhesion

Most common DMA methods

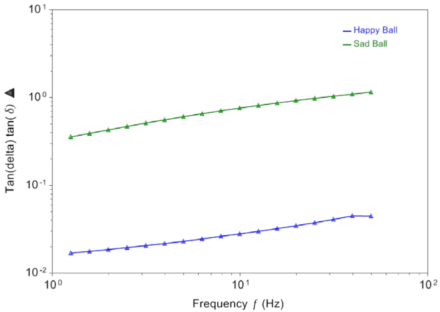
- Three primary routine DMA Tests (Covered in presentation I)
  - Common DMA methods
    - Amplitude Sweep
    - Temperature Ramp



Amplitude Sweeps (Linear viscoelastic Region)



Temperature Ramp (Transitions and viscoelasticity across temperature)

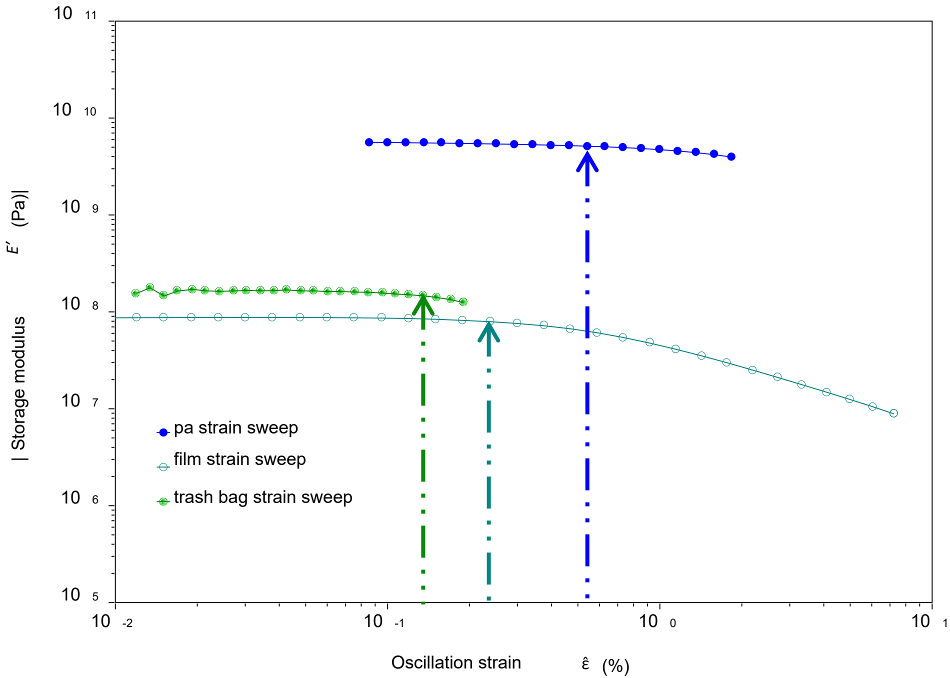


Frequency Sweep(viscoelasticity across time scales of deformation)

Frequency sweeps were covered extensively so we will skip this

Linear Viscoelastic region in various samples

- Common DMA methods
  - **Amplitude Sweep**
  - Temperature Ramp



- From an amplitude sweep:
  - Obtain the Linear viscoelastic region (range of strain values where modulus is independent) at a given frequency
  - **When performing nondestructive experiments (frequency sweep, temperature ramp, time sweep) a strain within the LVR must be chosen**
  - Solid samples typically have an LVR that ends ≤1%

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

Linear Viscoelastic region dependence on frequency

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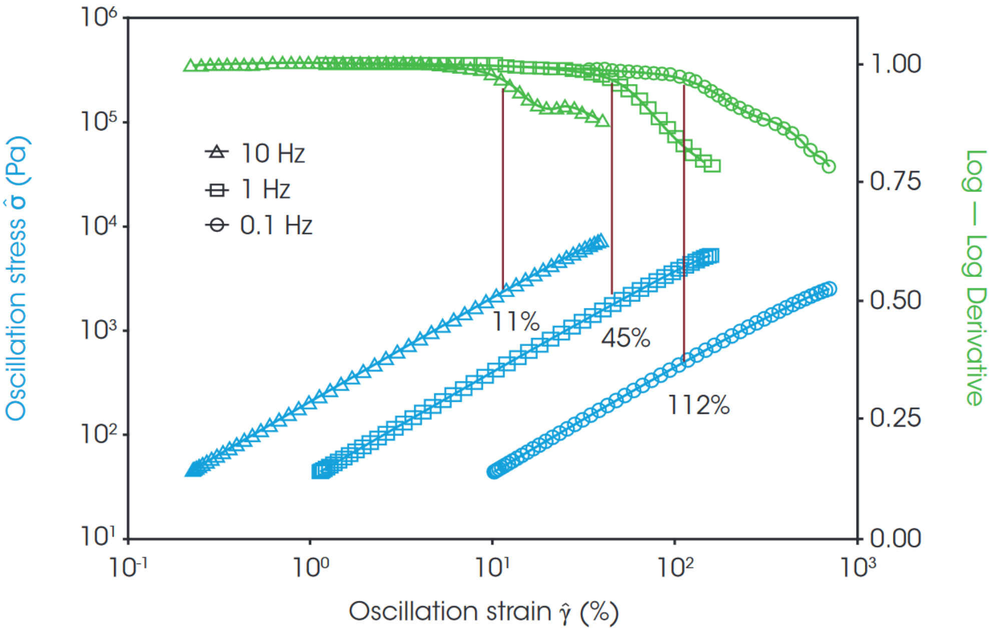
- Common DMA methods
  - **Amplitude Sweep**
  - Temperature Ramp

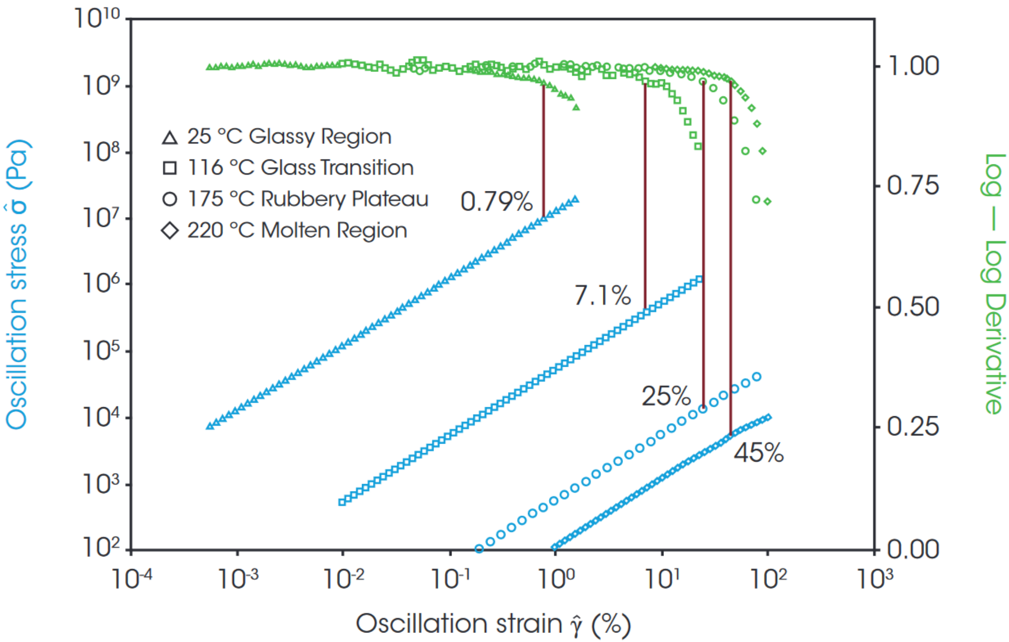


- From an amplitude sweep:
  - Obtain the Linear viscoelastic region (LVR - range of strain values where modulus is independent) at a given frequency
  - **Frequency dependence of LVR – LVR is reduced at higher frequencies, molecules are more stiff**

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

Linear Viscoelastic region dependence on Temperature

- Common DMA methods
  - **Amplitude Sweep**
  - Temperature Ramp



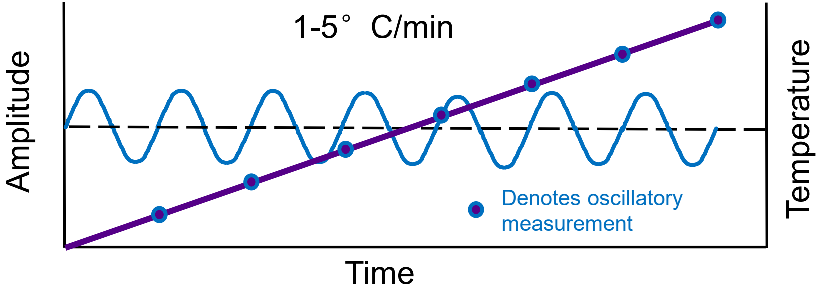
- From an amplitude sweep:
  - Obtain the Linear viscoelastic region (LVR - range of strain values where modulus is independent) at a given frequency
  - **Temperature dependence of LVR – LVR is reduced at lower temperatures, molecules are more stiff**

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

Intermediate DMA Methods: Temperature Ramps

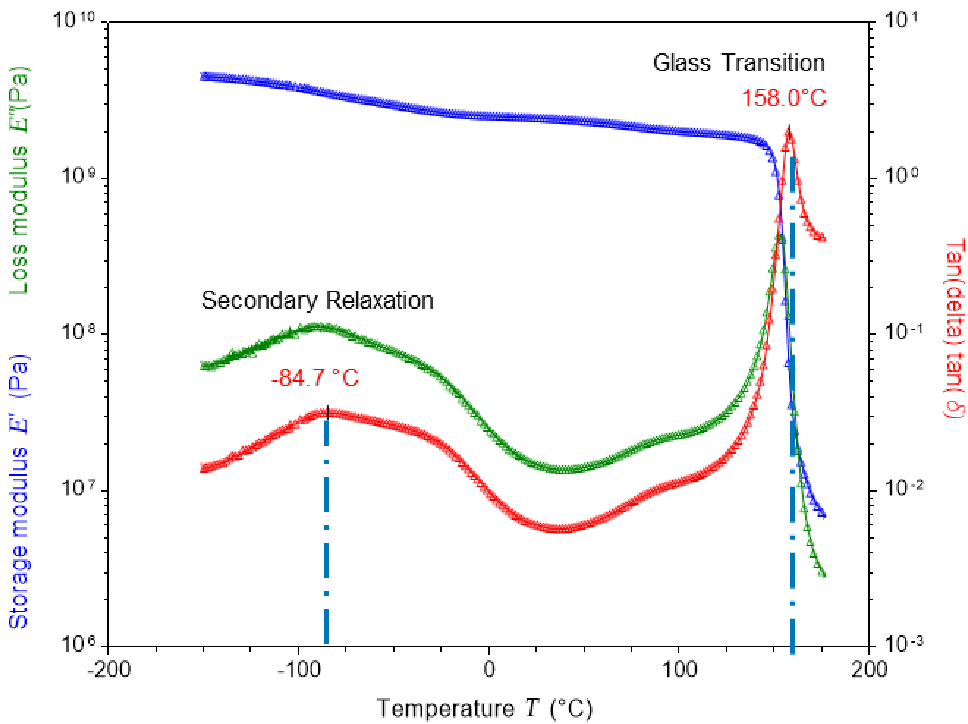
- Common DMA methods
  - Amplitude Sweep
  - **Temperature Ramp**

- We covered temperature ramps briefly in the rheology section
- Temperature ramps in DMA are a powerful tool that we will cover in more thorough detail



Primary and Secondary Transitions in PC

- Common DMA methods
  - Amplitude Sweep
  - **Temperature Ramp**

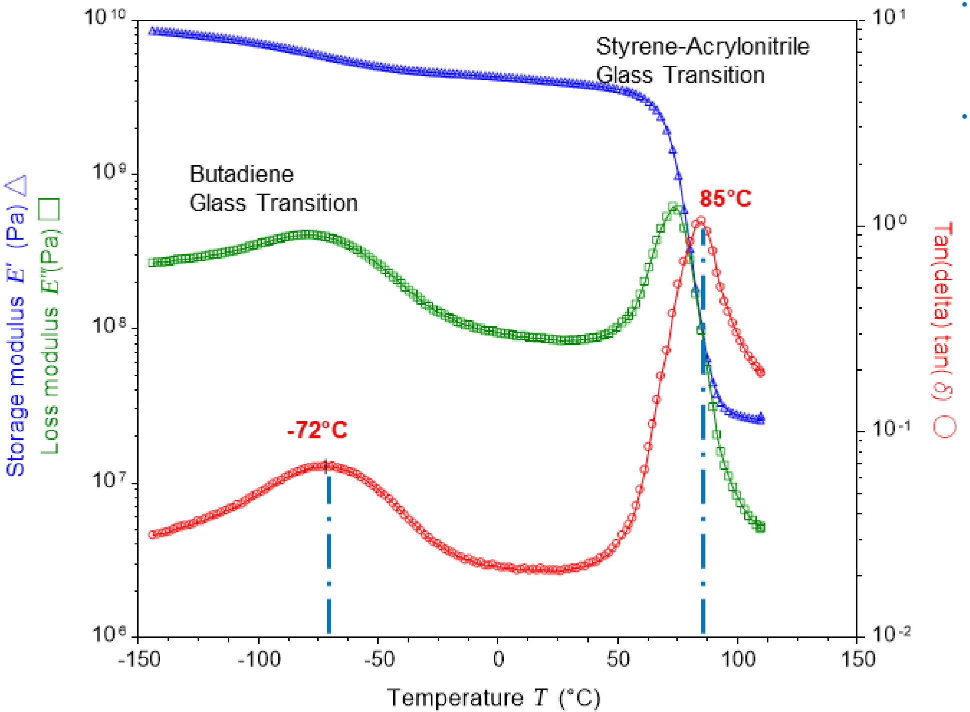


- From a Temperature ramp:
  - Material glass transition
  - Secondary transitions
    - Local Main-Chain Motion – intra-molecular rotational motion of main chain segments four to six atoms in length
    - Side group motion with some cooperative motion from the main chain

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

Primary and Secondary Transitions in ABS

- Common DMA methods
  - Amplitude Sweep
  - **Temperature Ramp**

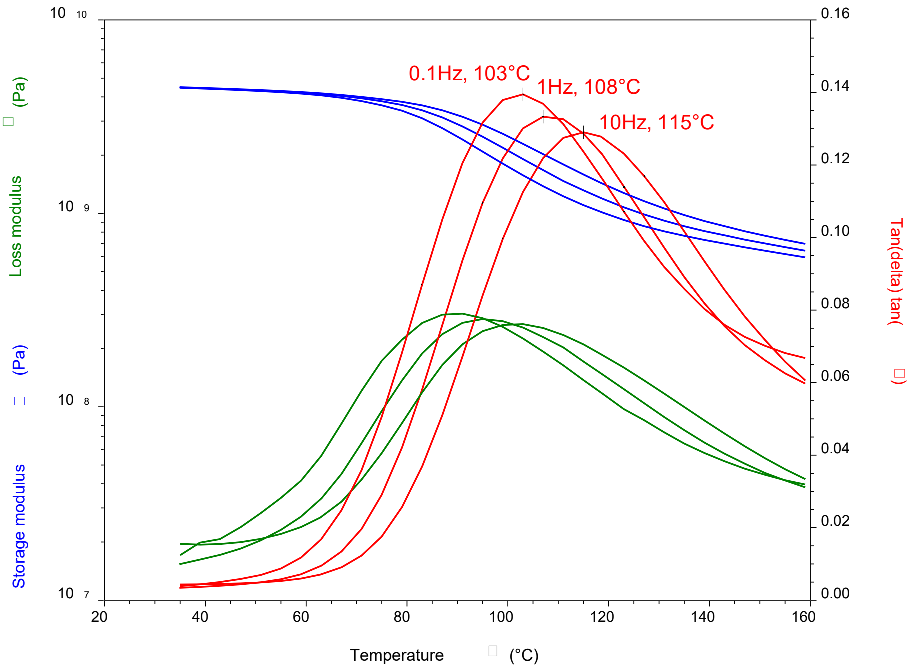


- From a Temperature ramp:
  - Material glass transition
  - Secondary transitions
    - Local Main-Chain Motion – intra-molecular rotational motion of main chain segments four to six atoms in length
    - Side group motion with some cooperative motion from the main chain

Instrument: DMA850
Temperature:
-150°C to 120°C
Heating rate: 3°C/min
Frequency: 1Hz
Amplitude: 15 µm

PET Film: Effect of frequency on Tg

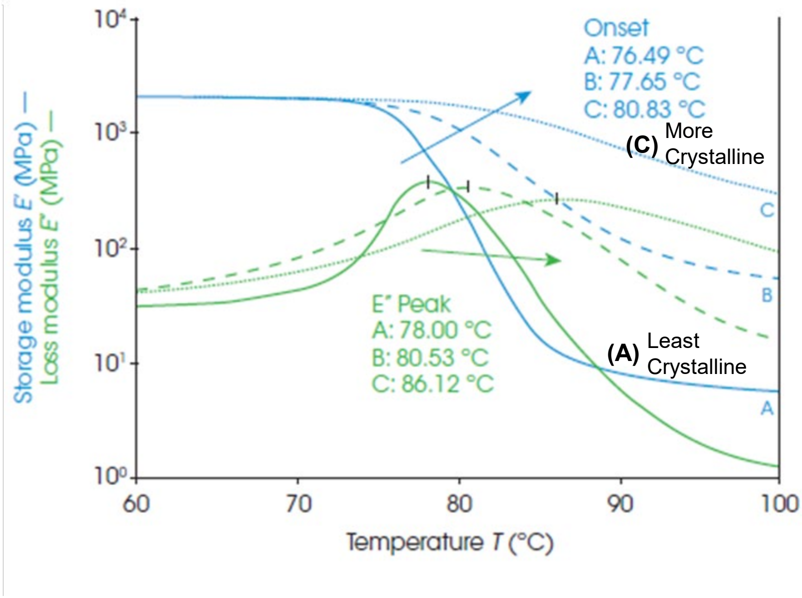
- Common DMA methods
  - Amplitude Sweep
  - **Temperature Ramp**



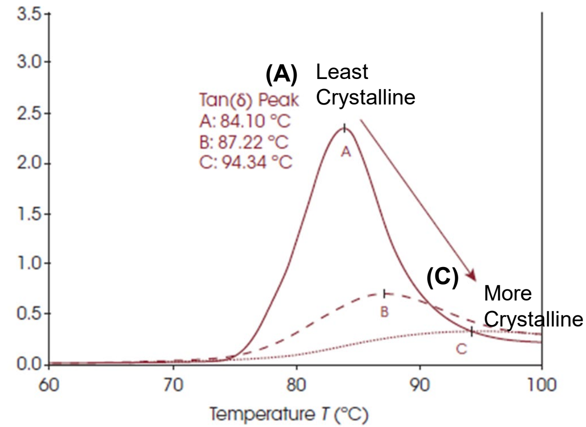
- From a Temperature ramp:
  - Observe effect of frequency on the glass transition – higher frequency generally increases Tg, the molecules become more stiff

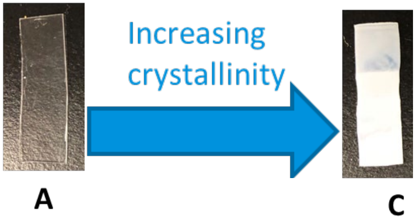
PET Film: Effect of crystallinity on modulus and tan δ

- Intermediate DMA methods
  - **Temperature Ramps – (Glass transition effects)**
  - Multistep Creep Recovery



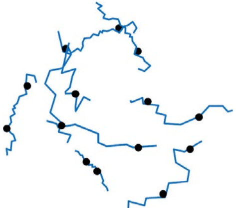
- From a Temperature ramp:
  - **Observe effect of crystallinity on the storage modulus (Left) and the glass transition temperature (Right)**

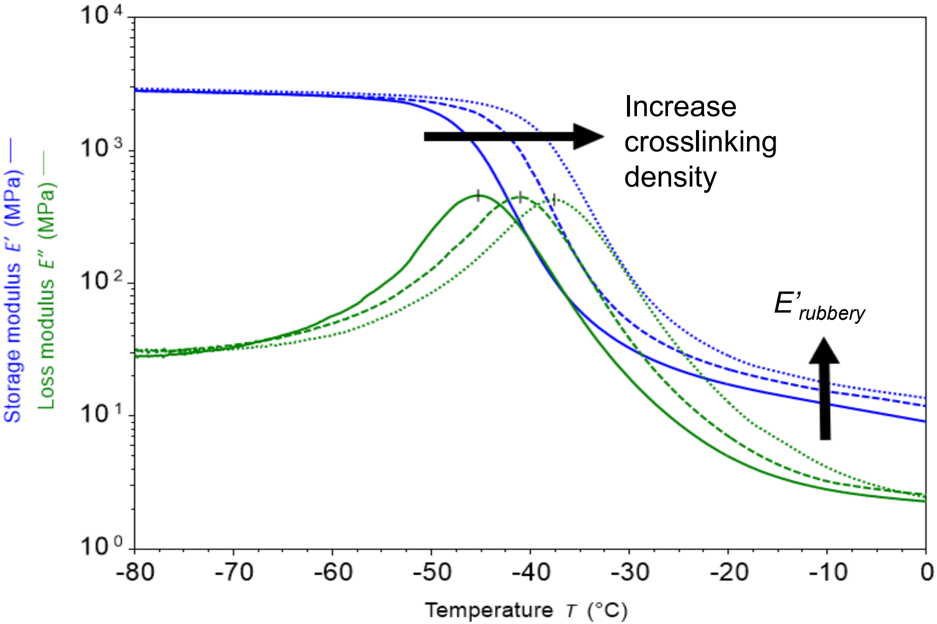




Effect of crosslinking density on rubbery modulus and Tg

- Intermediate DMA methods
  - **Temperature Ramps – (Glass transition effects)**
  - Multistep Creep Recovery





- From a Temperature ramp:
  - **Observe effect of crosslinking on the storage modulus and the glass transition temperature**

Increasing crosslinking density:

- Tg shifted to higher temperature
- Transition becomes broader and weaker (tan d decreases)
- Rubbery plateau modulus increases

Crosslinking density:

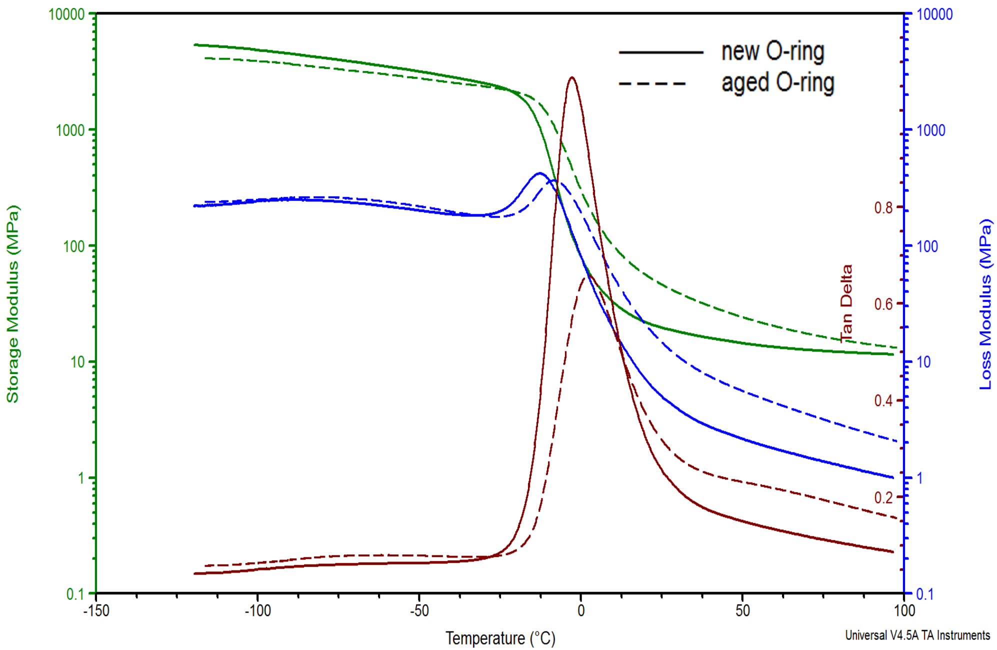
$$M_c = \frac{3RTd}{E'_{rubbery}}$$

M_c is the molecular weight between crosslinks
R is the universal gas constant
T is the absolute temperature (in K)
d is the density of the polymer.

- **A lower Mc implies higher extent of crosslinking**

PET Film: Effect of crosslinking density on rubbery modulus and Tg

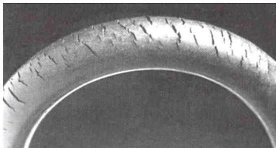
- Intermediate DMA methods
  - <u>**Temperature Ramps – (Glass transition effects)**</u>
  - Multistep Creep Recovery



- From a Temperature ramp:
  - <u>**Observe effect of aging on a rubber sample - aged O-ring has higher Tg and increased storage modulus at higher temperatures**</u>

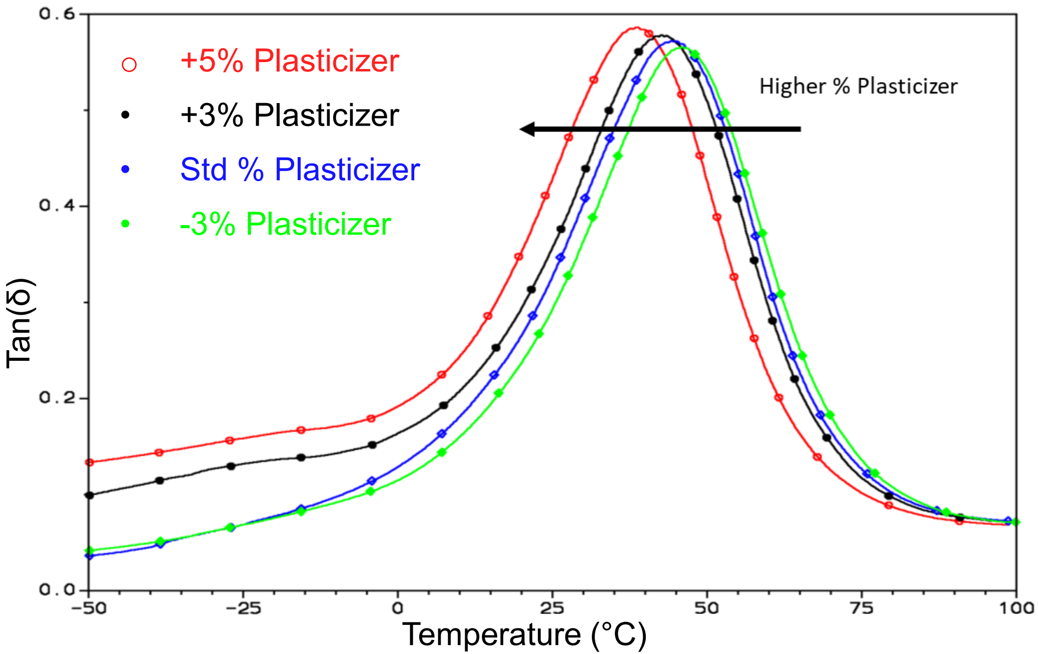
<u>New</u>

<u>Aged</u>



Effect of Plasticizer on Vinyl Flooring Tg

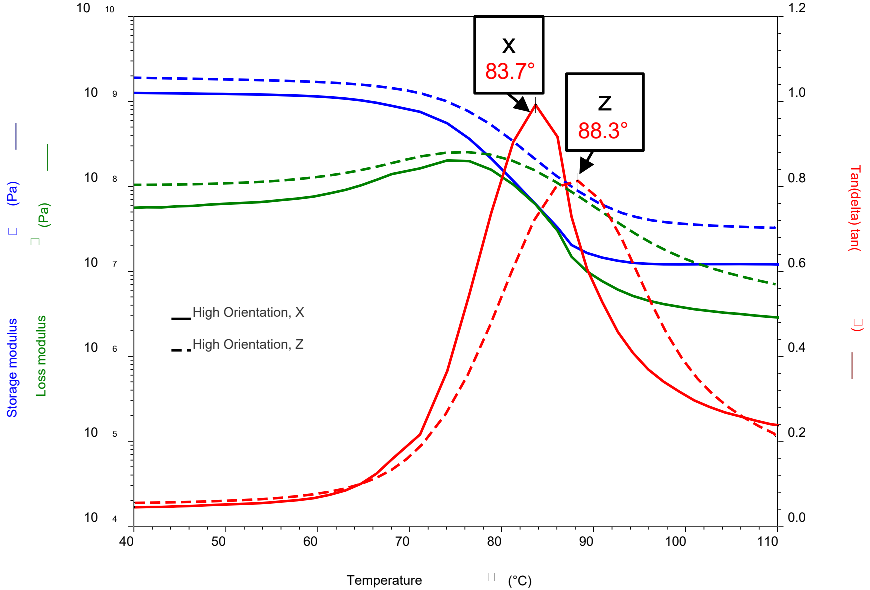
- Intermediate DMA methods
  - **Temperature Ramps – (Glass transition effects)**
  - Multistep Creep Recovery



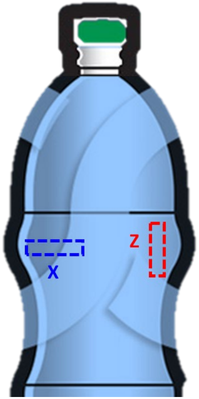
- From a Temperature ramp:
  - **Observe effect of increased plasticizer loading**
  - **Plasticizers shield molecular interactions of matrix, thereby decreasing the glass transition, and softening the material**

Effect of residual orientation on mechanical properties

- Intermediate DMA methods
  - **Temperature Ramps – (Glass transition effects)**
  - Multistep Creep Recovery



- From a Temperature ramp:
  - **Observe effect of orientation on storage modulus and glass transition temperature**
  - **Bottle is stronger in "Z" direction, and this makes sense considering the application**



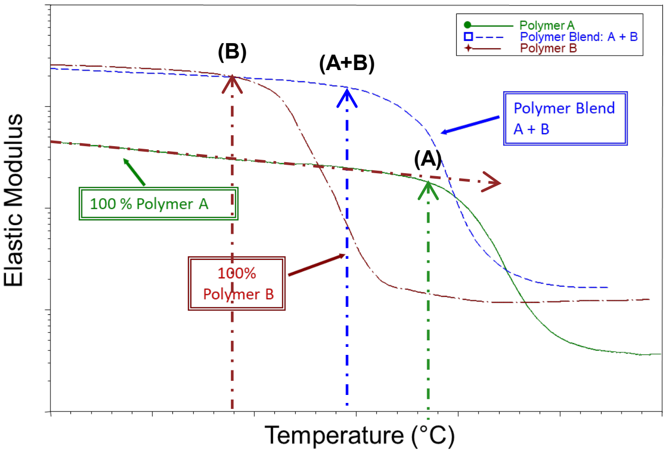
Polymer Blends - Miscibility

- Intermediate DMA methods
  - **Temperature Ramps – (Glass transition effects)**
  - Multistep Creep Recovery

- From a Temperature ramp:
  - **Observe blend compatibility**

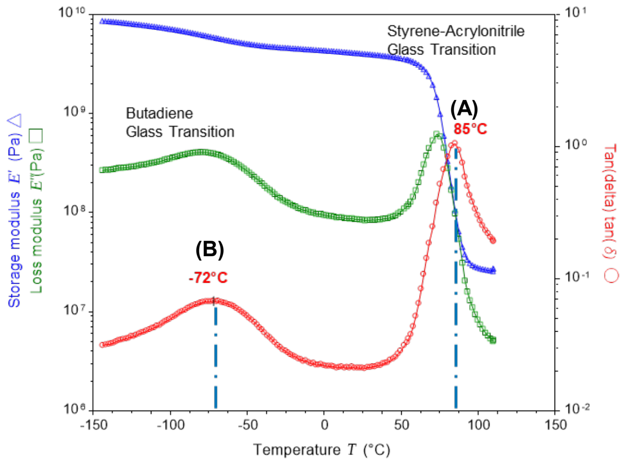
Miscible Blend

- Pure components have unique T_g's
- Blend has one T_g



Immiscible Blend

- Blend has two unique T_g's



Multistep Creep recovery of Mattress Foam

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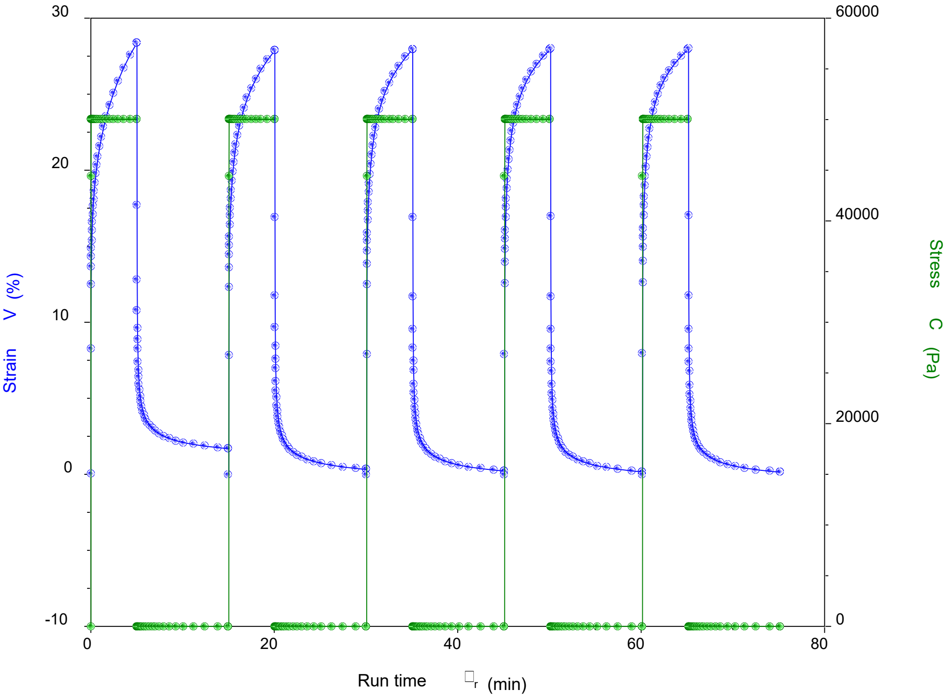
- Intermediate DMA methods
  - Temperature Ramps – (Glass transition effects)
  - **Multistep Creep Recovery**

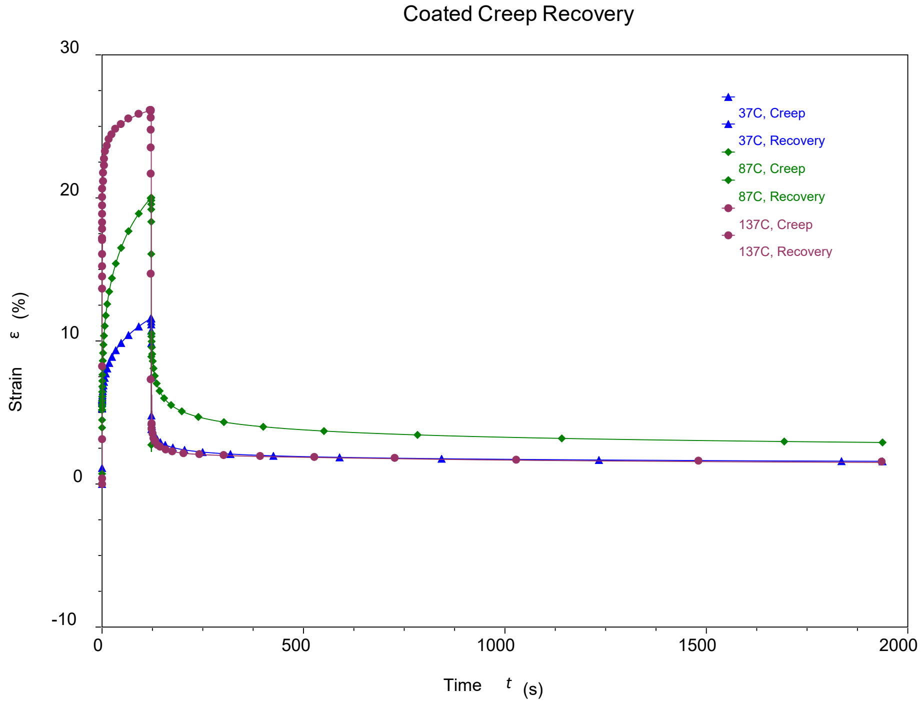


- From a multistep creep recovery:
  - **Observe longterm elastic stability of material (consistency of compliance over life span)**
  - Strain increasing cycle to cycle would indicate foam fatigue

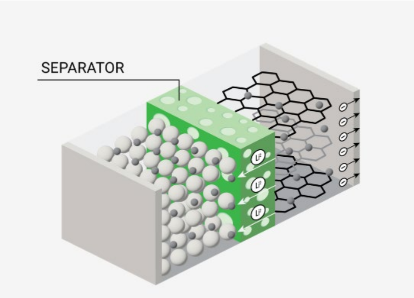
Compression

Creep recovery of Battery Separator Film

- Intermediate DMA methods
  - Temperature Ramps – (Glass transition effects)
  - **Multistep Creep Recovery**



- From a creep recovery:
  - **Observe elasticity of material at different temperatures under the same load**
  - An ideal separator should retain elastic characteristics at elevated temperatures



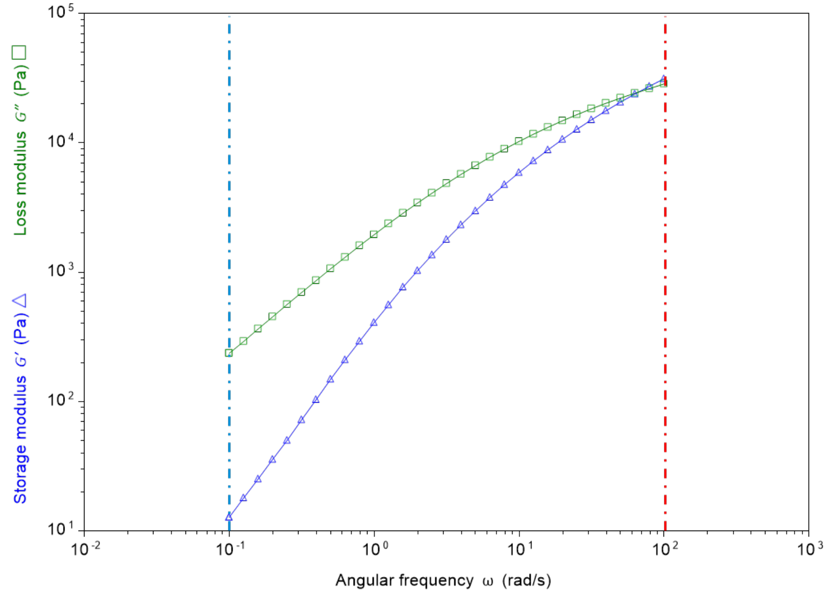
Why Use TTS?

- Advanced Rheology + DMA methods
  - **TTS**
  - Humidity (RH) Unit
  - Tribology

- Mechanical limitations on the upper ceiling frequency
- User time limitations at the lower frequency limit
- Extrapolates material behaviour in the frequency domain by orders of magnitude

Time Temperature Superposition

- Very powerful technique used to expand the measurable frequency range
- Information on technique is heavily requested



*TTS is applicable for frequency sweeps performed above Tg on either a Rheometer or DMA regardless of geometry

Why Use TTS?

- Advanced Rheology + DMA methods
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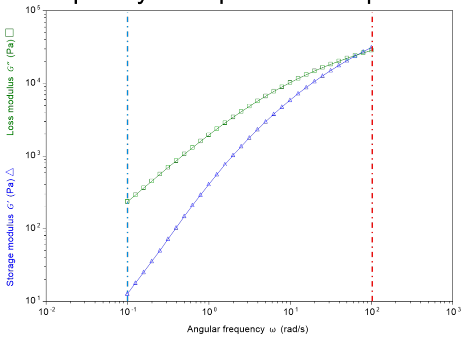
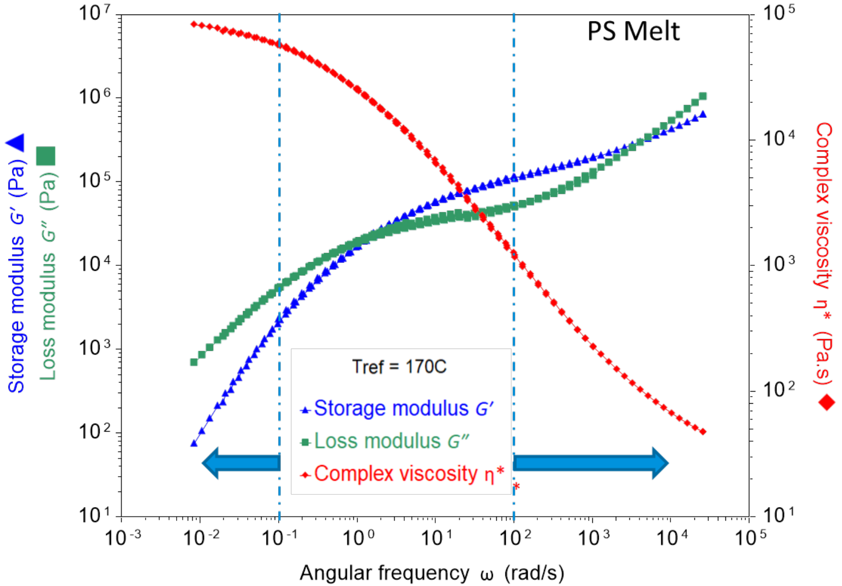
Frequency sweep at one temperature



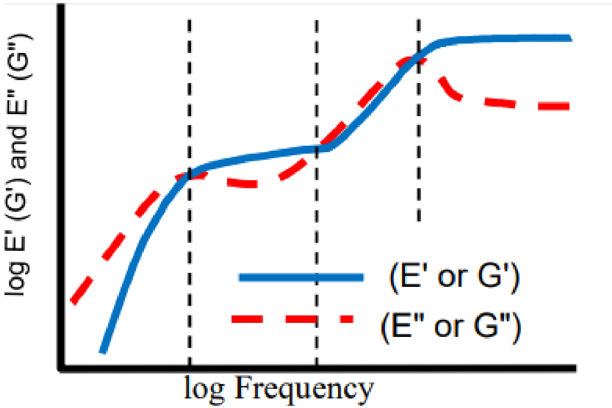
Frequency range here was expanded from 0.1-100 rad/s to 0.01-10,000 rad/s (at a reference temperature of 170°C)

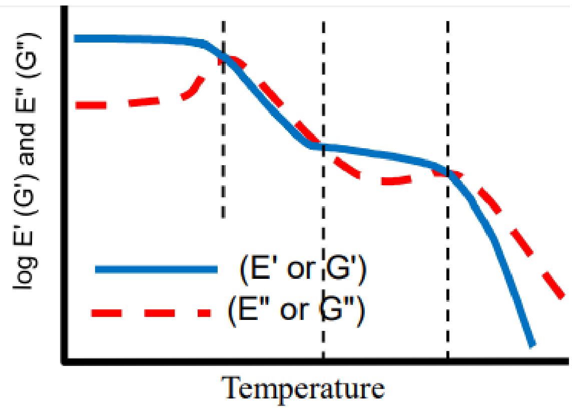
Master Curve



- Frequency sweeps were run at:
  - Temperatures of 130-220°C in 10°C increments
  - Frequency range of 0.1-100 rad/s
  - Strain of 5%

Relationship between Frequency and Temperature (Timescale of molecular relaxation processes)





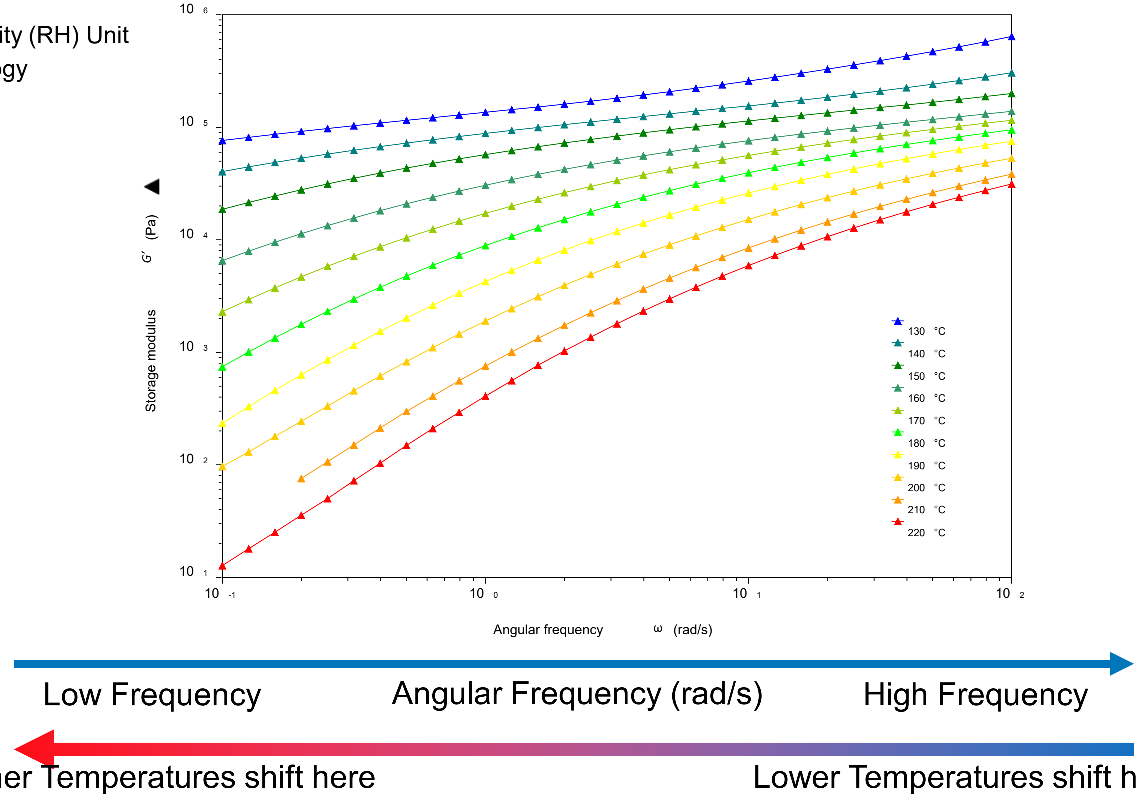
- At low frequencies molecular relaxation is at large time scales- **large length scales**
- At high frequencies molecular relaxation is at short time scales – *small length scales*

- At low temperatures molecular relaxation is slow – the diffusion is limited to *small length scales* and small time scales
- At high temperatures molecular relaxation is fast – the diffusion is predominately **large length scales** and large time scales

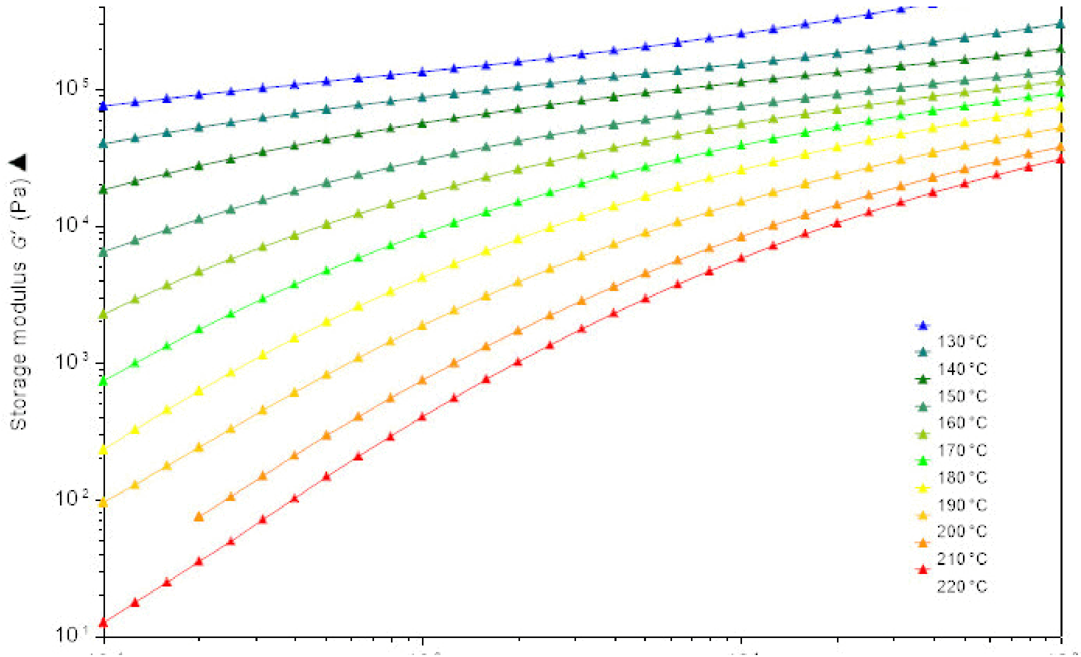
- Commonality between Frequency and Temperature is the timescale of molecular relaxation (Polymer chains diffusing)

Why Use TTS?

- Advanced Rheology + DMA methods
  - **TTS**
  - Humidity (RH) Unit
  - Tribology



TTS Shifting Cartoon

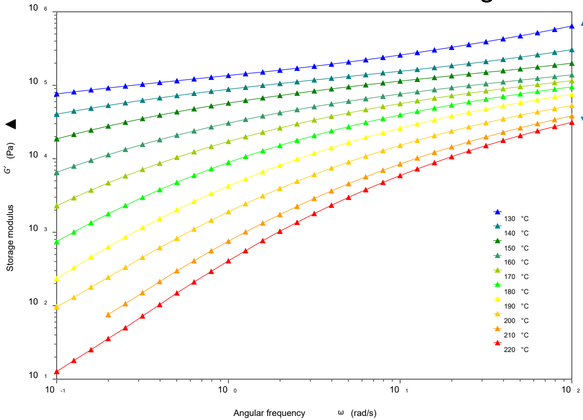


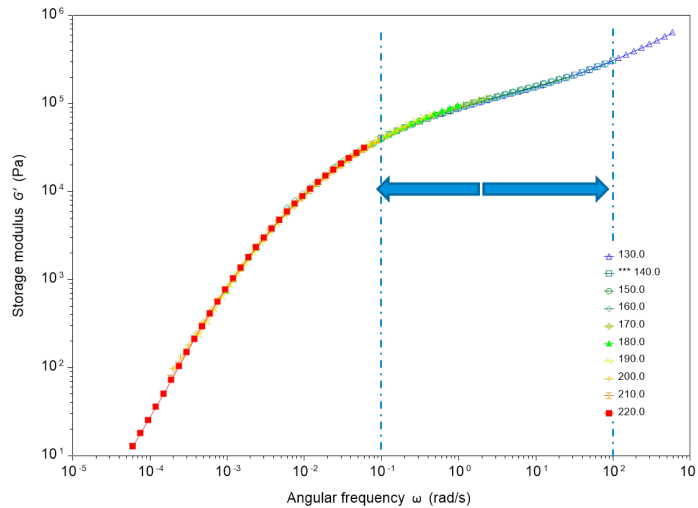
Low Frequency Angular Frequency (rad/s) High Frequency

Higher Temperatures shift here Lower Temperatures shift here

Why Use TTS?

Temperature
High to Low



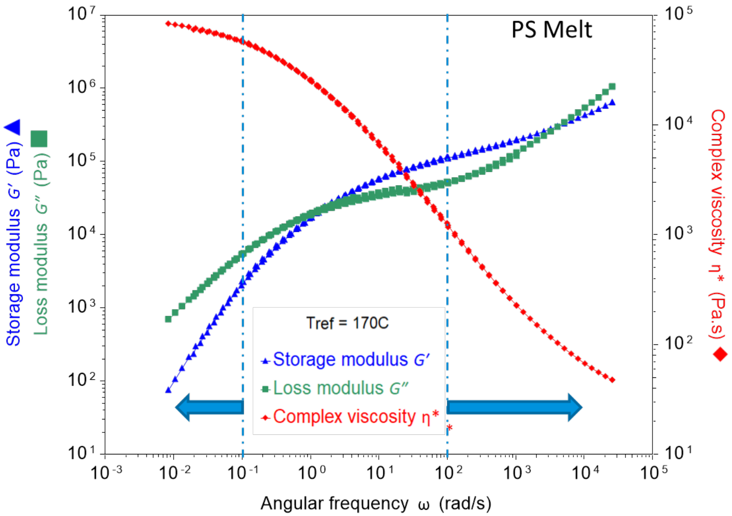


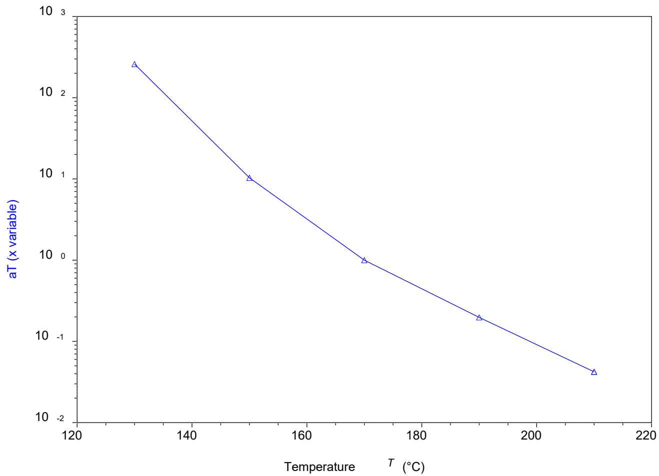
Low Frequency   Angular Frequency (rad/s)   High Frequency

Higher Temperatures shift here   Lower Temperatures shift here

TTS Shifting Results

- Two plots (datasets) are generated when performing TTS
  - One is the mastercurved frequency sweep (Left)
  - Shift factors (a_T) are generated as a function of temperature
    - Shift factors can be used to calculate the complex Viscosity as a function of temperature if the zero-shear complex viscosity is known
    - Can be used recalculate frequency space when the reference temperature is altered





TTS Shifting Fits

Arrhenius (used for activation energy)

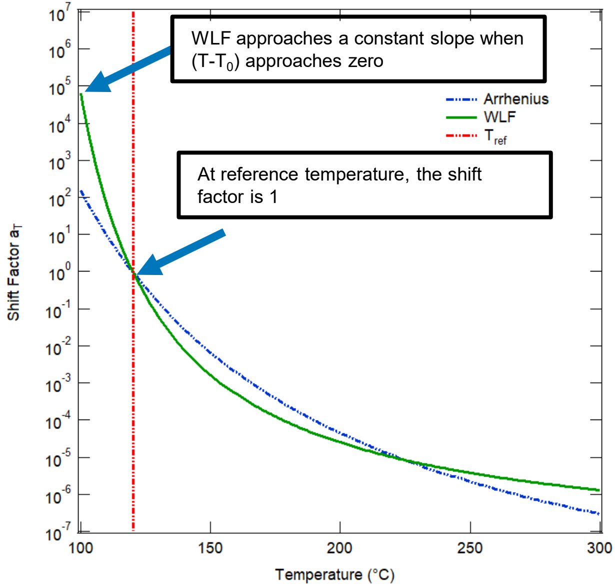
$$a_T = \exp\left(\frac{E}{RT} - \frac{E}{RT_0}\right)$$

- At temperatures **well above T_g**, from T_g +100°C and above use Arrhenius

WLF

$$\log(a_T) = \frac{-C_1^0(T - T_0)}{C_2^0 + (T - T_0)}$$

- At lower temperatures, from T_g to T_g +100°C use WLF



- Physical interpretation of shift factor
  - Represents the factor by which the molecular relaxation time is increased (a_T>1) or decreased (a_T<1)
  - The molecular relaxation time (reptation time) is the time it takes for a polymer molecule to move its own length

TTS Criterion (Material applicability)

In General:

- Polymer Materials
- Limited to no applicability for:
  - Block copolymers
  - Complex polymer functionalization
  - Crosslinked materials (gels, thermosets)
  - Mixtures
  - Composites

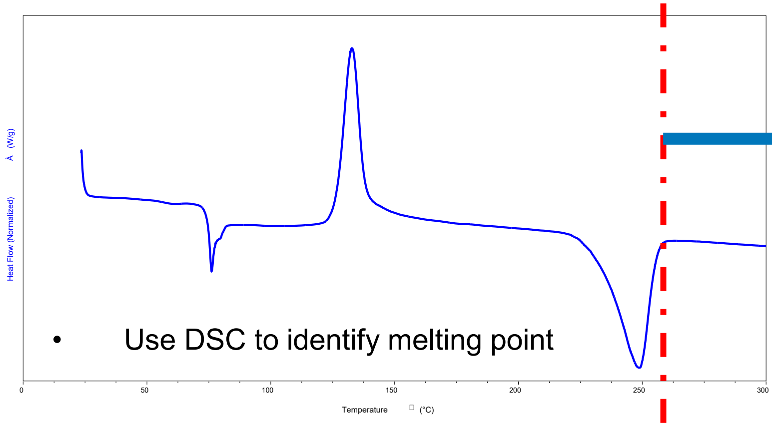
TTS Criterion (Material applicability)

Rheology

- Any polymer can be tested as long is it is in melt phase
- No crystallinity can be present at testing temperatures

DMA

- Amorphous Polymers are best
- No crystallinity can be present at testing temperatures
- Sample can melt out of fixture, limiting the ceiling testing temperature

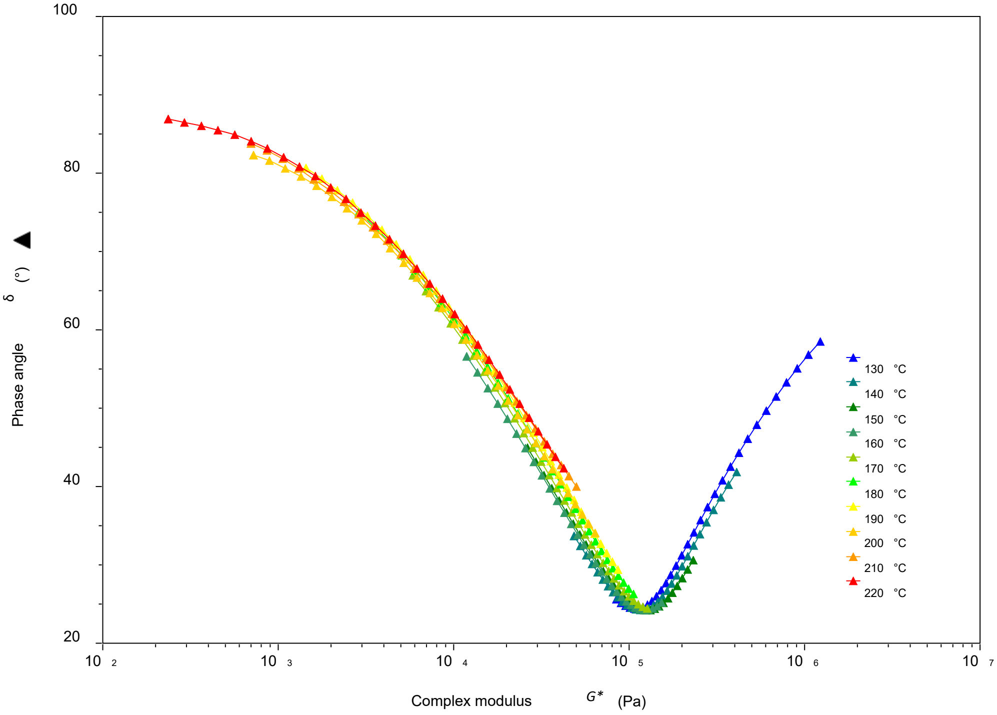


- Use DSC to identify melting point

Test from this temperature and up

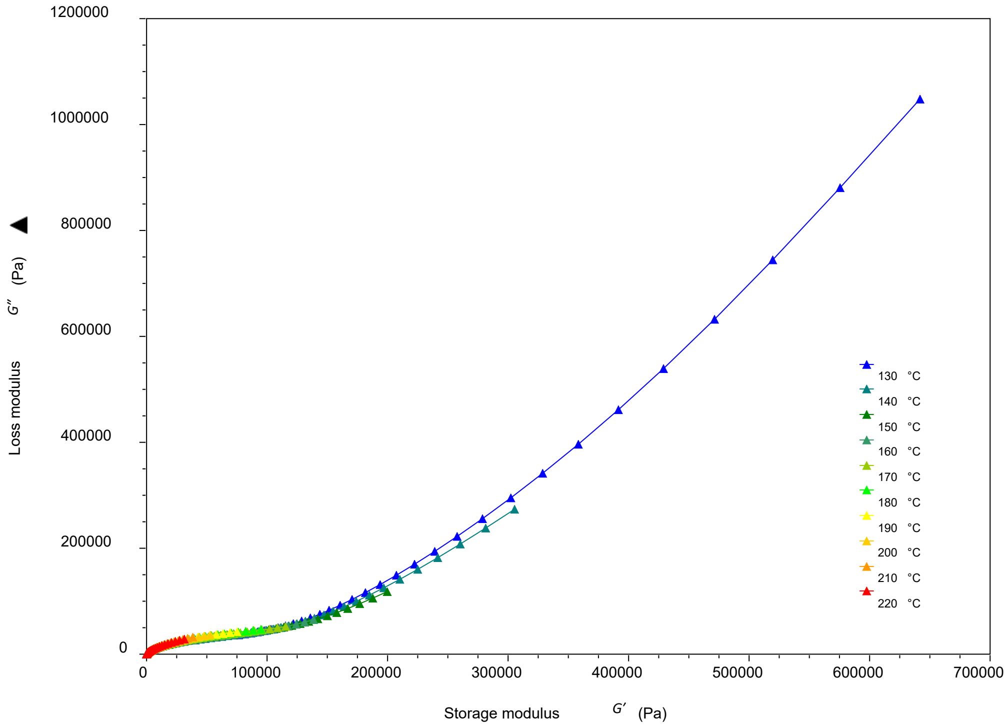
Verifying TTS Shift (Van Gurp-Palmen Plot)

- A measure of viscoelastic continuity across temperature
- The transition between elastic and viscous behavior is a function of molecular relaxation speed (temperature)
- Discontinuities indicate complex thermal-rheological activity
- Block copolymers, phase transitions (melting, crystallization, phase separation), complex polymer functionalization can introduce discontinuities



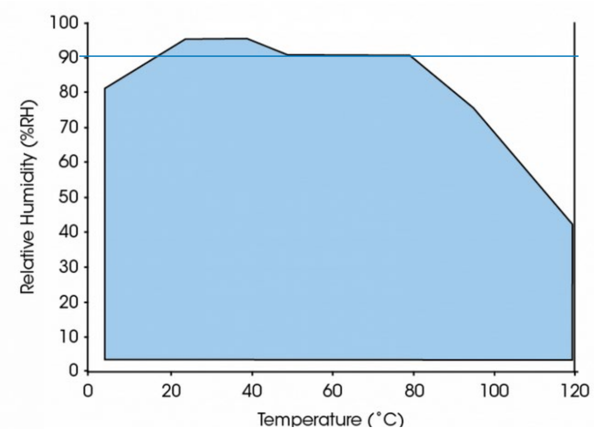
Verifying TTS Shift (Van Gurp-Palmen Plot)

- Analogous to Van Gurp-Palmen
- A measure of viscoelastic continuity across temperature
- The transition between elastic and viscous behavior is a function of molecular relaxation speed (temperature)



Humidity Units for the HR and DMA

- Advanced Rheology + DMA methods
  - TTS
  - **Humidity (RH) Units**
  - Tribology

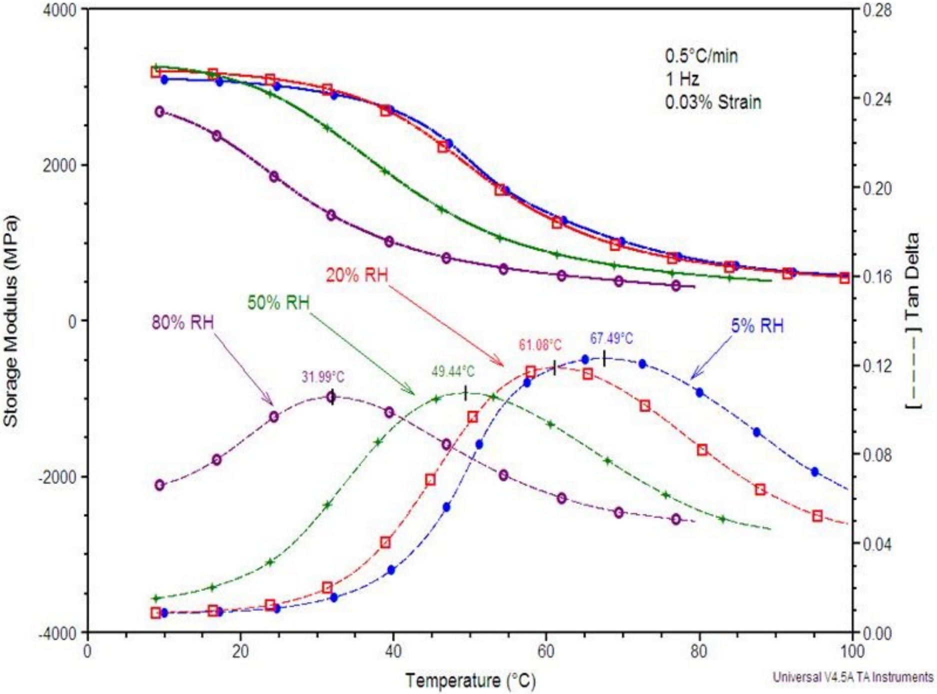


Performance Specifications	
Temperature Range	5 °C – 120 °C
Temperature Accuracy	±0.5 °C
Heating/Cooling Rate	Maximum ±1 °C/min over entire temperature range
Humidity Range	5% to 95% (See humidity range chart)
Humidity Accuracy	5-90%RH: ±3% RH >90%RH: ±5% RH
Humidity Ramp Rate	±2% RH/min (fixed), both increasing and decreasing

- With RH unit one can characterize:
  - Humidity effect on Tg
  - Changes in LVR
  - Changes in viscoelasticity due to humidity

Effect of Humidity on Tg

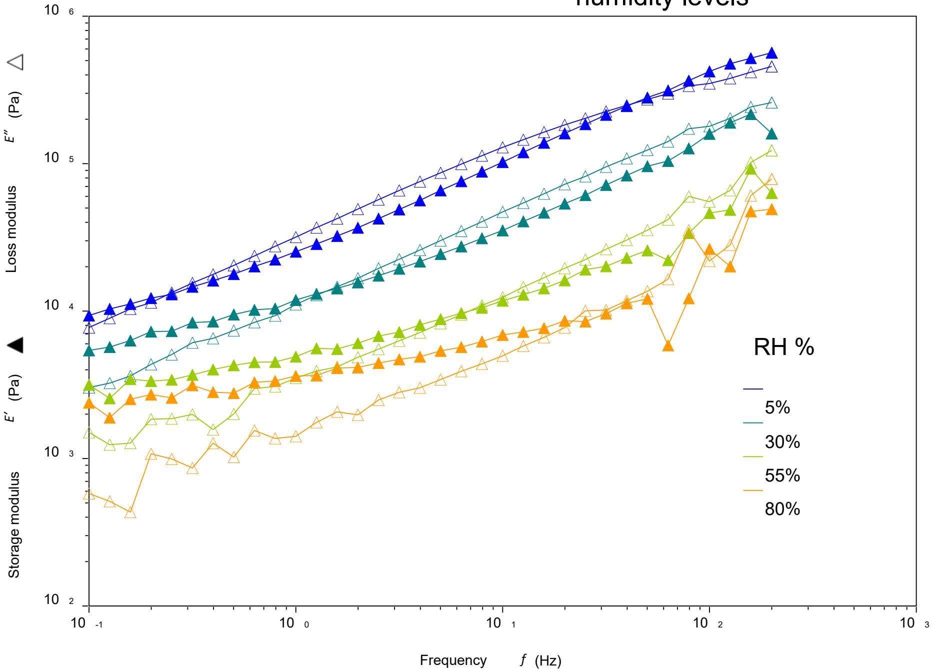
- Advanced Rheology + DMA methods
  - TTS
  - **Humidity (RH) Units**
  - Tribology
- Observe effect of humidity on the glass transition temperature
- Temperature ramps



Effect of Humidity on Viscoelastic properties memory foam

- Advanced Rheology + DMA methods
  - TTS
  - **Humidity (RH) Units**
  - Tribology

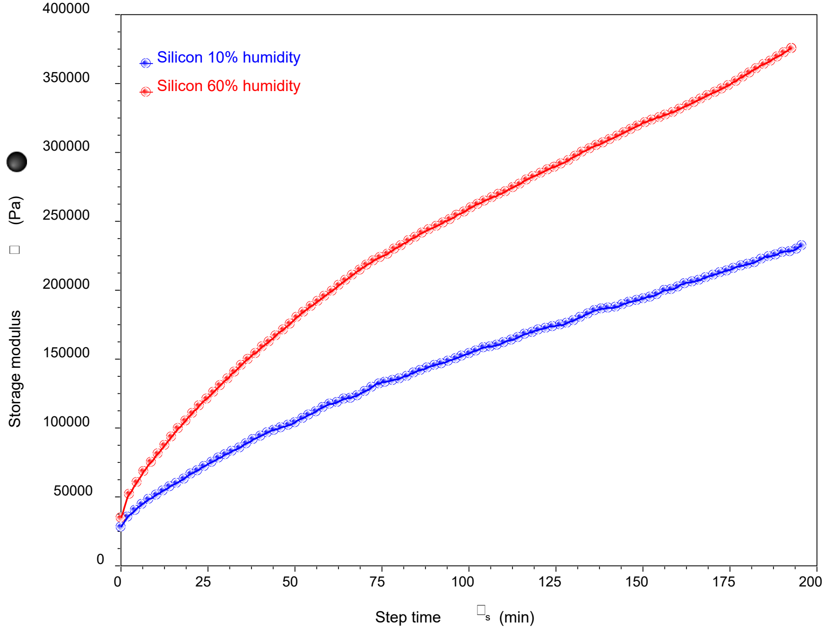
- Observe effect of humidity on the viscoelastic properties of memory foam
- Frequency Sweeps at different humidity levels



Effect of Humidity on Curing of Silicone Adhesive

- Advanced Rheology + DMA methods
  - TTS
  - **Humidity (RH) Units**
  - Tribology

- Higher humidity results in faster curing
- Isothermal Oscillation Time experiment



Effect of Humidity on Paint Drying

- Advanced Rheology + DMA methods
  - TTS
  - **Humidity (RH) Units**
  - Tribology

- Higher humidity here results in slower drying (slower curing)
- Isothermal Oscillation Time experiment

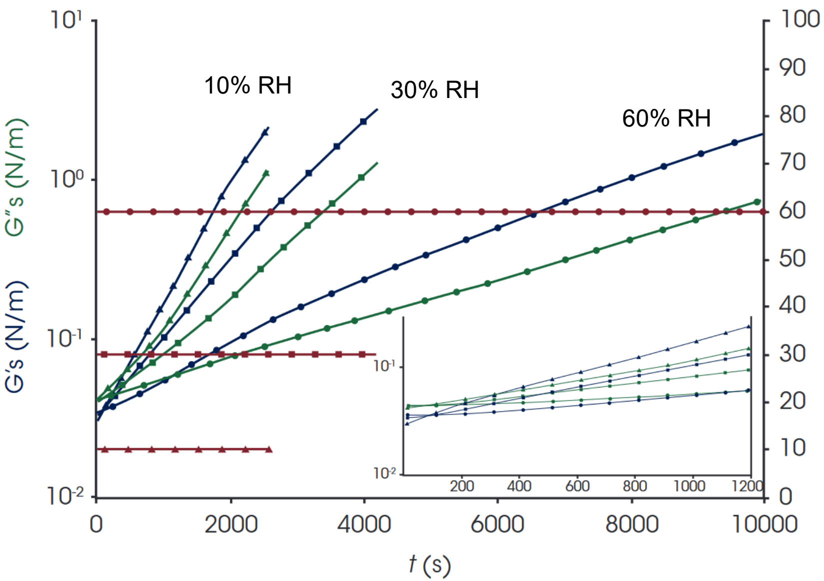


Table 1: Summary of modulus crossover under different humidity

Relative Humidity (%)	10%	30%	60%
G_s Crossover Time (s)	338	485	1102
G_s Crossover Modulus (N/m)	0.057	0.056	0.057

Tribology

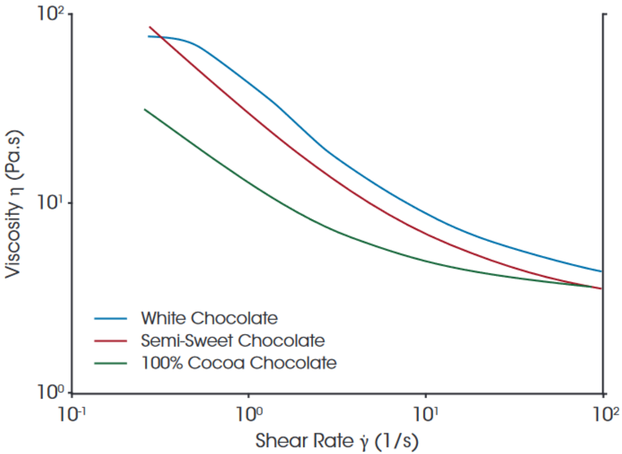
- Advanced Rheology + DMA methods
    - TTS
    - Humidity (RH) Units
    - **<u>Tribology</u>**

- A viscosity flow curve gives information on the resistance to flow
- Tribology gives information on the coefficient of friction as a function of <u>sliding speed</u> and <u>load force</u>
- Four different configurations are offered, representative of different surface to surface interfaces

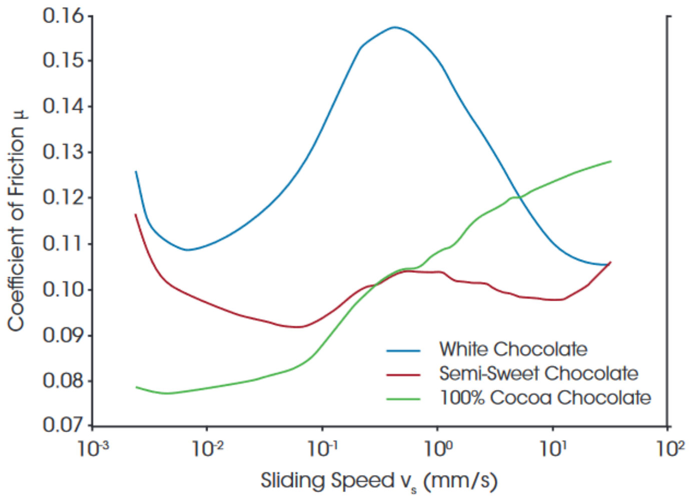
Tribology

- Advanced Rheology + DMA methods
  - TTS
  - Humidity (RH) Units
  - **Tribology**

Flow Curve (Shear Rheology)



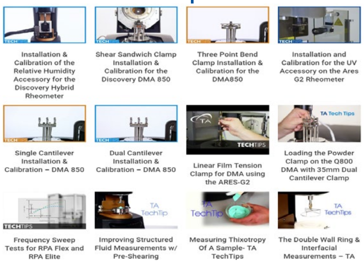
Friction Curve (Tribology)



- Although viscosity data suggests limited differences in the flow behavior of the various chocolates, Tribology demonstrates considerable difference in mouthfeel

TA Website – Other Resources

Tech Tips



Applications Notes Library

Applications Notes Library

Our instruments are used in a variety of products, in multiple industries. The application notes below provide more detail on specific potential applications. You can search for specific app notes with the search field.

rheology

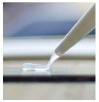
261 item

Title	Product Category	Ref#	Link
Hot Melt Adhesives	Rheology	AAN001	Download Note
Generating Mastercurves	Rheology	AAN005e	Download Note
Analytical Rheology	Rheology	AAN006e	Download Note
Normal Stresses in Shear Flow	Rheology	AAN007e	Download Note
Mischungsregein Komplexer Polyersysteme	Rheology	AAN008d	Download Note
Mixing Rules for Complex Polymer Systems	Rheology	AAN008e	Download Note
Application of Rheology of Polymers	Rheology	AAN009	Download Note
Synergy of the Combined Application of Thermal Analysis and Rheology Monitoring and Characterizing Changing Processes in Materials	Rheology	AAN010e	Download Note

Seminar Series: Instant Insights

Seminars:

- Thermal Analysis and Rheology
- Medical Device and Biomaterials Testing
- Elastomers and Rubber Compounds
- TRIOS AutoPilot & TRIOS Guardian



Thermal, Rheological and Mechanical Characterizations of Thermoset

Tianhong (Terri) Chen, Ph.D.

Thermosetting materials, such as epoxy, have been widely applied in many areas including automotive, aerospace and electronics industries in the form of surface coating, structural adhesives, advanced composites and packaging materials.

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Advancements in the Characterization of Pharmaceuticals by DSC

Jason Saienga, Ph.D.

Differential Scanning Calorimetry is a simple, yet powerful technique to gain a broad understanding of the characteristics of pharmaceutical materials, from the crystalline structure that exists to the compatibility of a specific formulation.

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Steady State & Flash Methods for Thermal Diffusivity and Thermal Conductivity Determination

Justin Wynn

In this presentation we will demonstrate accurate and high-throughput methods to measure the critical heat transfer properties of thermal diffusivity and thermal conductivity.

View Archive

Thank You!