Introduction to Dynamic Mechanical Testing for Rubbers and Elastomers

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Is DMA Thermal Analysis or Rheology?

<u>**Definitions**</u>

- ***Thermal Analysis***
  - measurement as a *function of temperature or time*.

- ***Rheology***
  - the science of *stress* and *deformation* of matter.

- ***DMA*** is the general name given to an instrument that mechanically *deforms a sample* and measures the sample response. The response to the deformation can be monitored as a *function of temperature or time.*

What can be Studied with DMA?

- Composition
  - Degree of cross-linking
  - Comparison of crystallinity levels
  - Molecular Orientation
  - Effect of Filler
- Physical Properties
  - Prediction of impact resistance
  - Testing of creep or cold flow
  - Stress relaxation behavior
  - Cure behavior
- Viscoelastic Properties
  - Storage Modulus
  - Loss Modulus
  - Tan Delta
  - Glass Transition (T_g)
  - Sub-T_g molecular motions (beta and gamma relaxations)
- Lifetime predictions using Time Temperature Superpositioning

What does a DMA do?

Measures the mechanical properties of a sample as it is deformed over a range of **stress**, **strain**, **time** **and** **temperature**

- Can either apply **Stress** (Force) and measure **Strain** (Displacement), or apply **Strain** and measure **Stress**

- Determines the **Modulus** of the material (**Stress** / **Strain**)

- Controls the **Frequency** (Time) of the deformation to measure viscoelastic properties (**Storage Modulus, Loss Modulus, Tan Delta**)

- **Temperature** controlled in heating, cooling, or isothermal modes

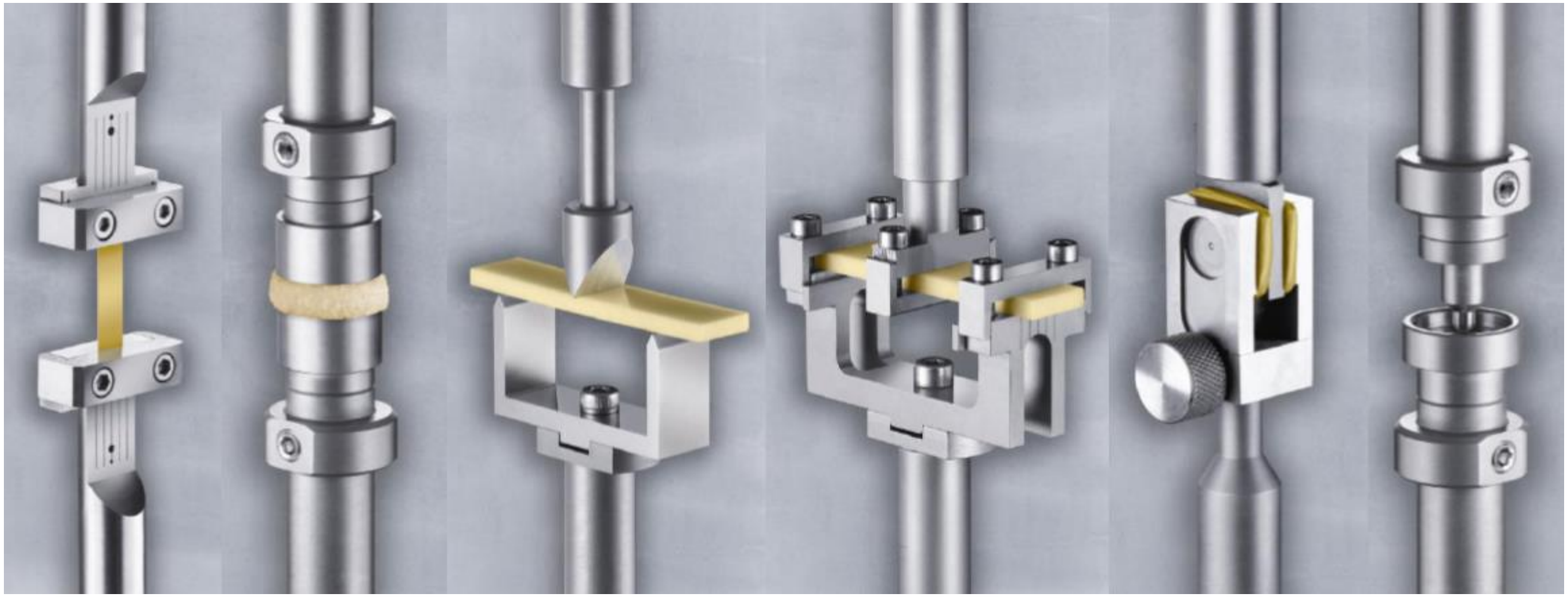
- Modes of Deformation: Tension, Bending, Compression and Shear

DMA – Modes of Deformation

Film/Fiber

3-Pt Bending

Shear Sandwich



Compression

Cantilever

Contact Lens

How does a DMA work?

- The DMA measures raw instrument signals
  - Force, Displacement, Stiffness
- Dimensions of the sample are recorded
  - Length, Width, Thickness
- Software calculates mechanical parameters
  - Stress, Strain, Modulus

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

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

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

DMA Viscoelastic Parameters

The Modulus: Measure of materials overall resistance to deformation.

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

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

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

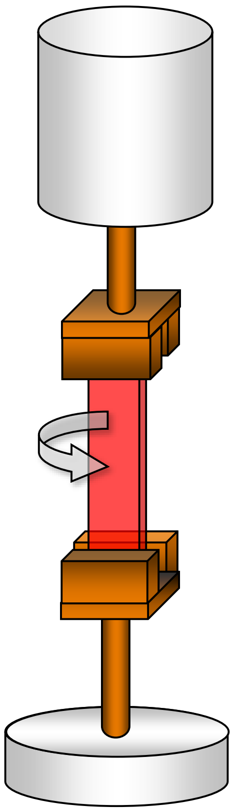
The Viscous (loss) Modulus: The ability of the material to dissipate energy. Energy lost as heat.

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

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

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

DMA Measurements



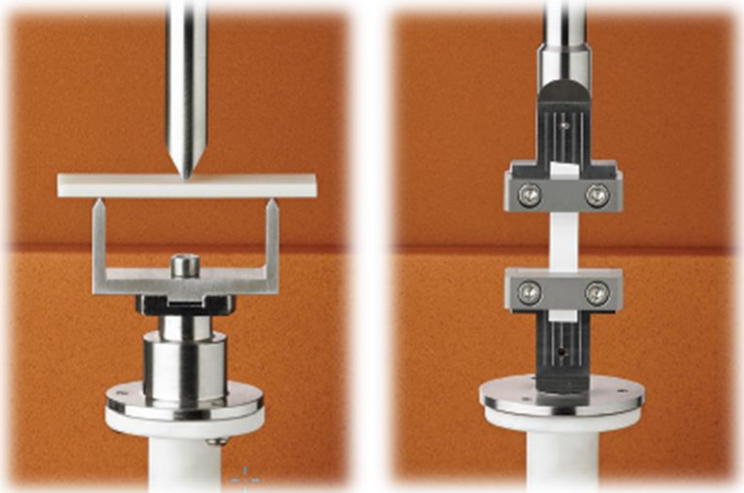
- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment

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

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

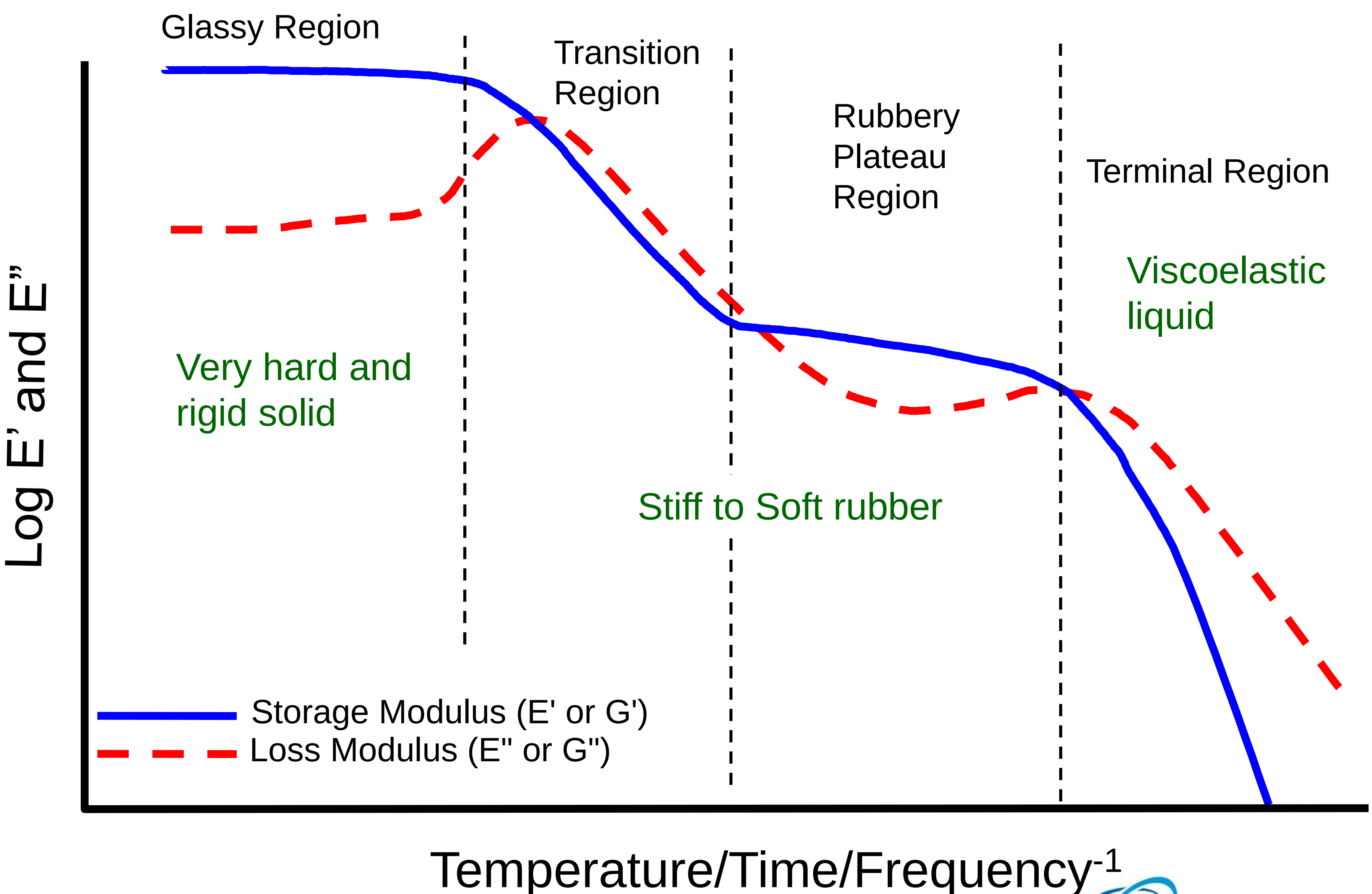
Rectangular and cylindrical torsion

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



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

Typical DMA Data



Applications of DMA

- Understanding the Glass Transition
- Measuring Transitions in DMA
  - Viscoelastic properties and the Glass Transition
  - Testing considerations
  - Secondary Transitions
- Material properties and the Glass Transition
  - Molecular Structure, Composition, Environmental Effects
- Other Applications

The Glass Transition

- A transition over a ***range of temperature*** from a glassy state to a rubber state in an amorphous material
- Mechanical:
  - Below the Glass Transition, the material is in a brittle, glassy state
  - Above the Glass Transition, the material becomes soft and flexible, and a modulus decrease.
- Molecular:
  - Below the Glass Transition, polymer chains are locked in place, without sufficient thermal energy to overcome the barrier for rotational or translational motion.
  - At temperatures above the Glass Transition, there is molecular mobility, and chains can slide past each other

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

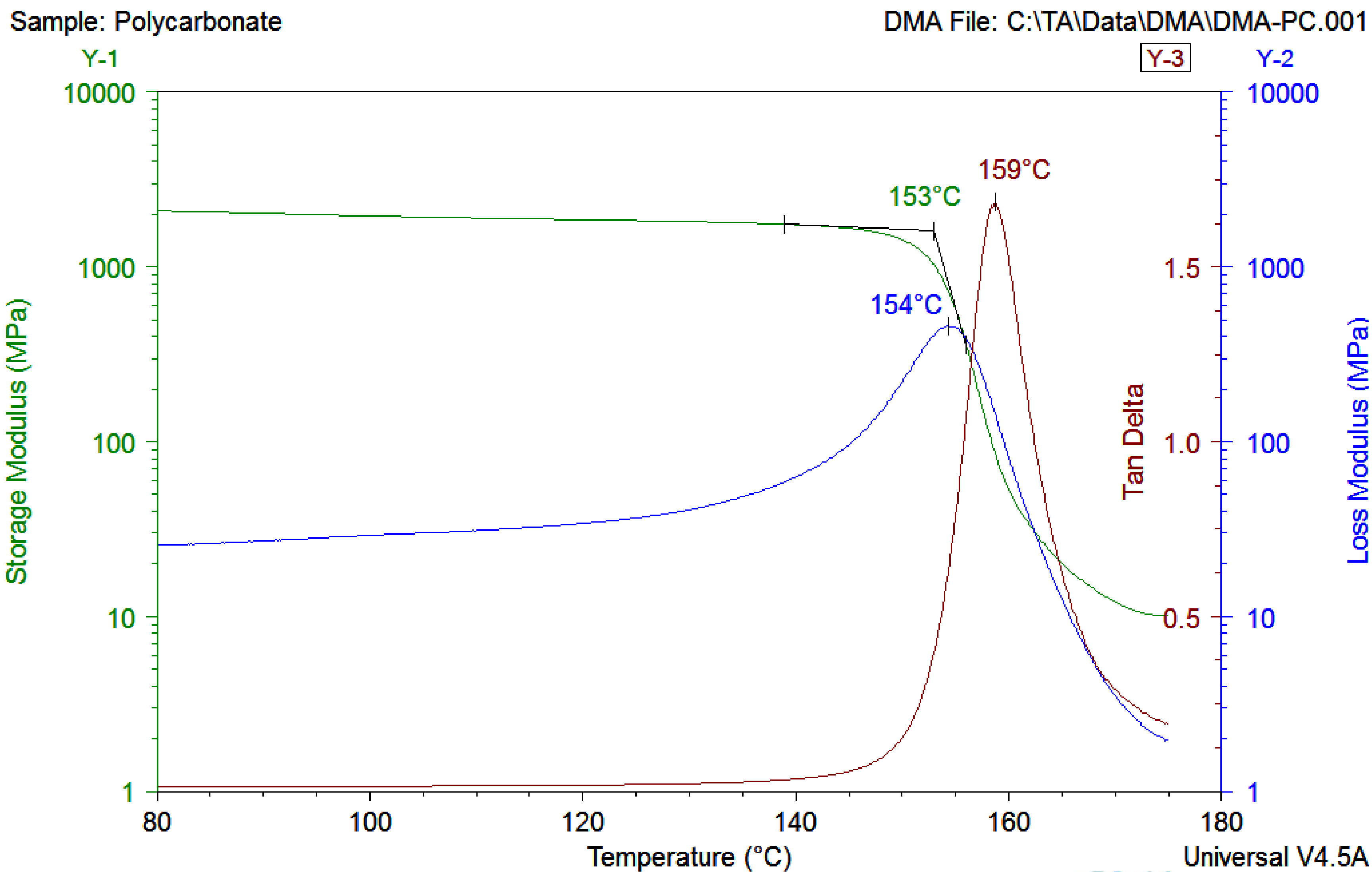
Turi, Edith, A, Thermal Characterization of Polymeric Materials, Second Edition, Volume I., Academic Press, Brooklyn, New York, P. 508.

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.

Glass Transition of Polycarbonate: E', E", Tan δ



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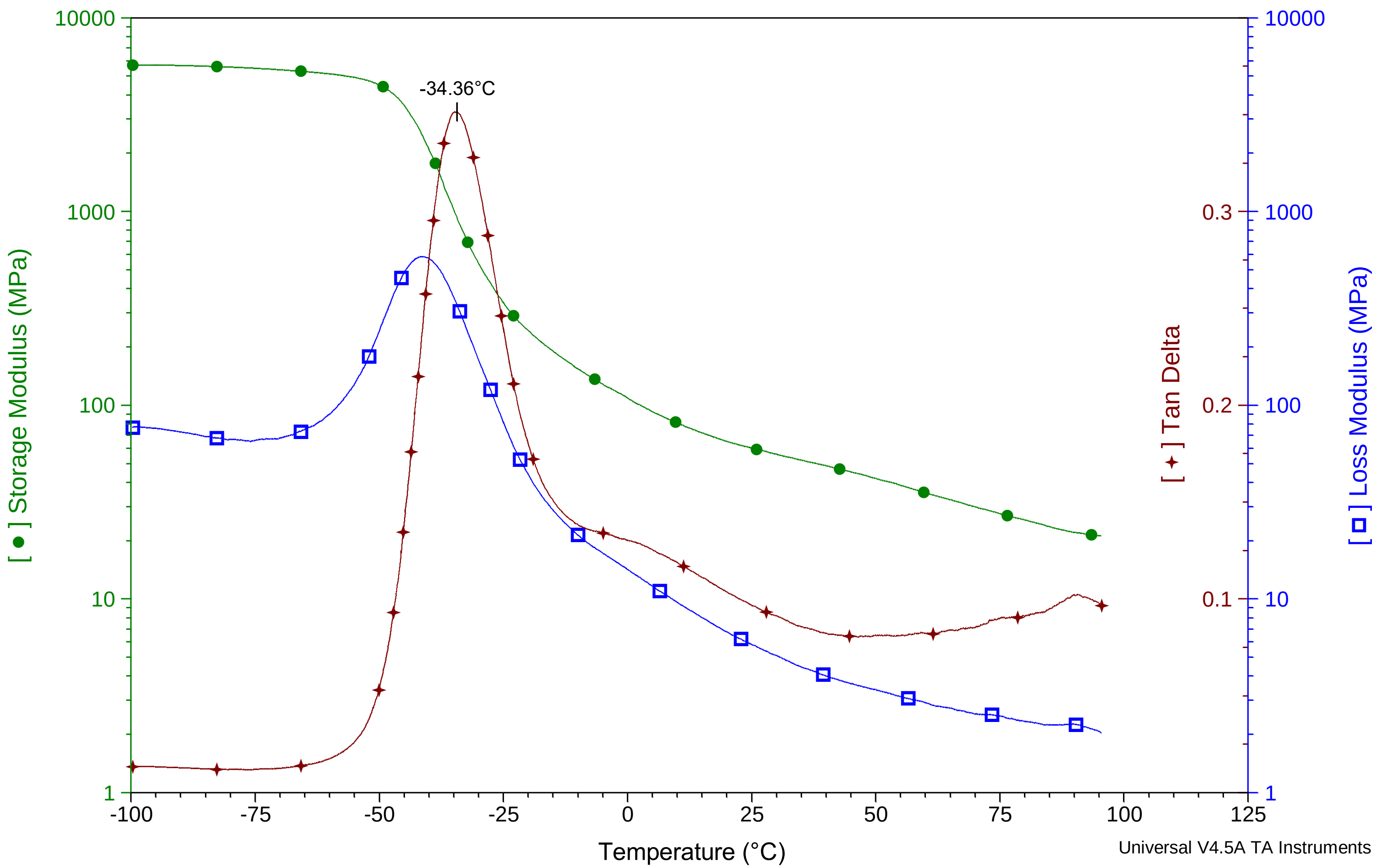
Elastomer Sample in Bending on DMA Q800



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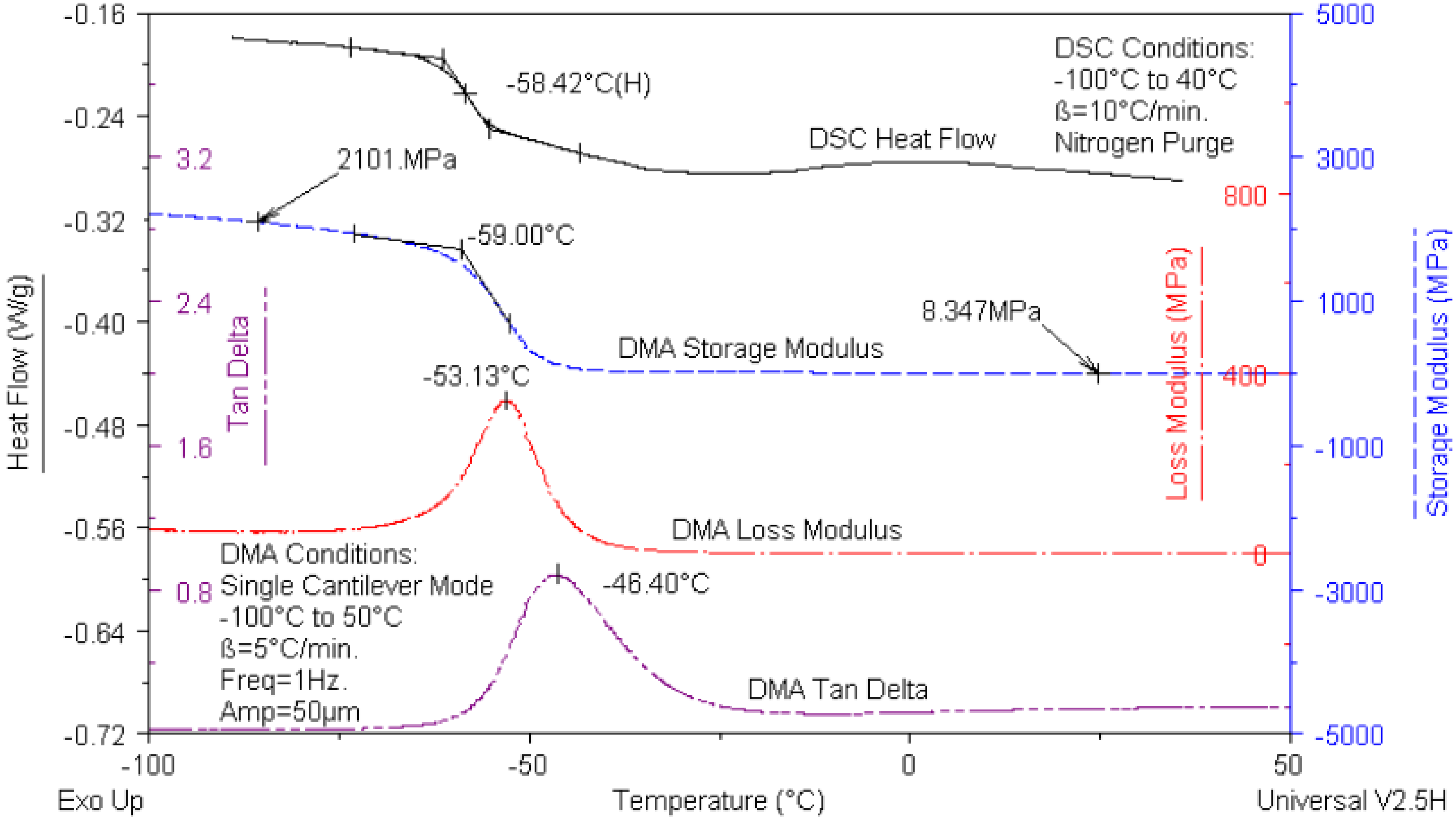
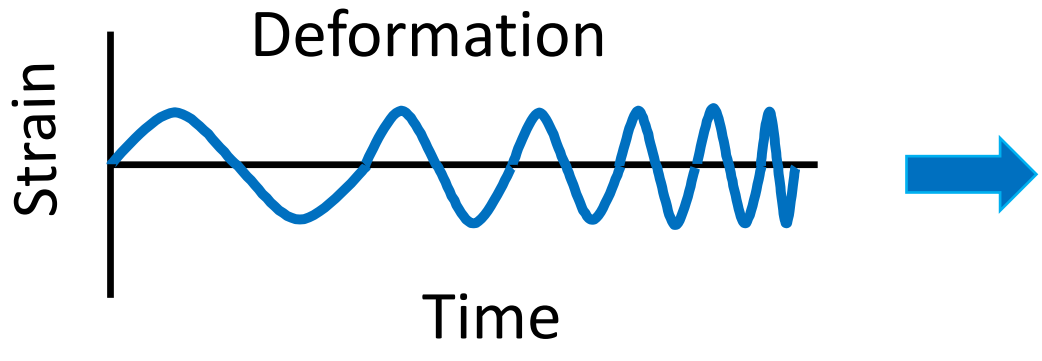
Air Chiller System (ACS)

Instrument	Environmental System	Minimum Temperature	
		ACS-2	ACS-3
DMA Q800	Standard Furnace	-50°C	-100 °C
ARES-G2/RSA-G2	Forced Convection Oven, FCO	-55 °C	-100 °C
DHR-1, 2 or 3	Environmental Test Chamber, ETC	-50 °C	-85 °C

Characterization of EPDM Rubber by DSC & DMA



Frequency Sweep

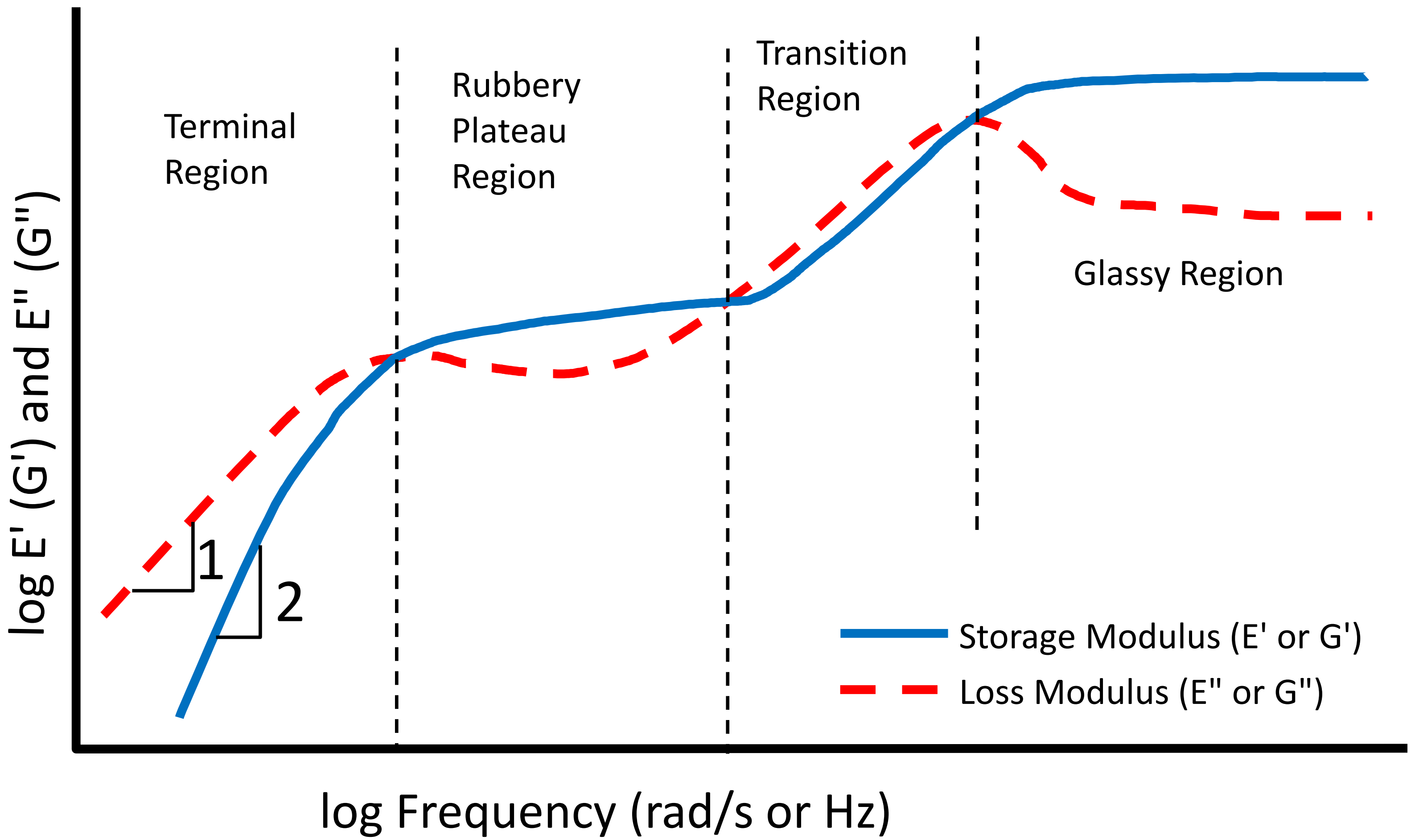


- The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude and temperature.

USES

- High and Low Rate (short and long time) modulus properties.
- Polymer melt processing (shear sandwich).
- Extend range with TTS

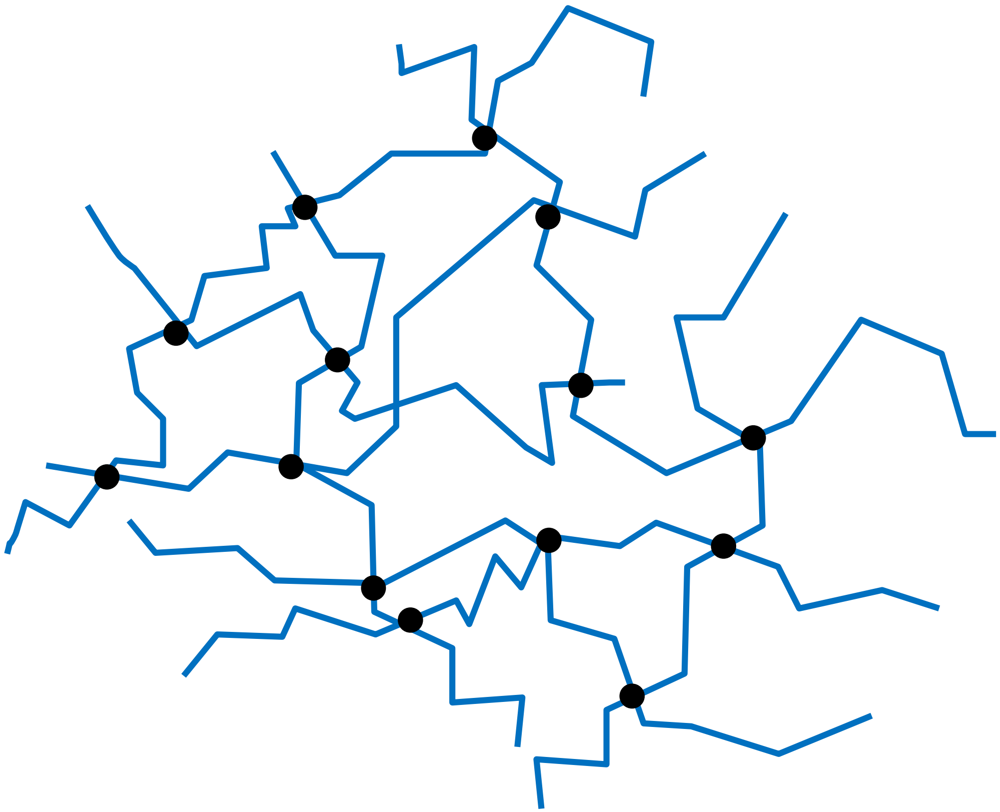
Frequency Sweep: Material Response



Molecular Structure - Crosslinking

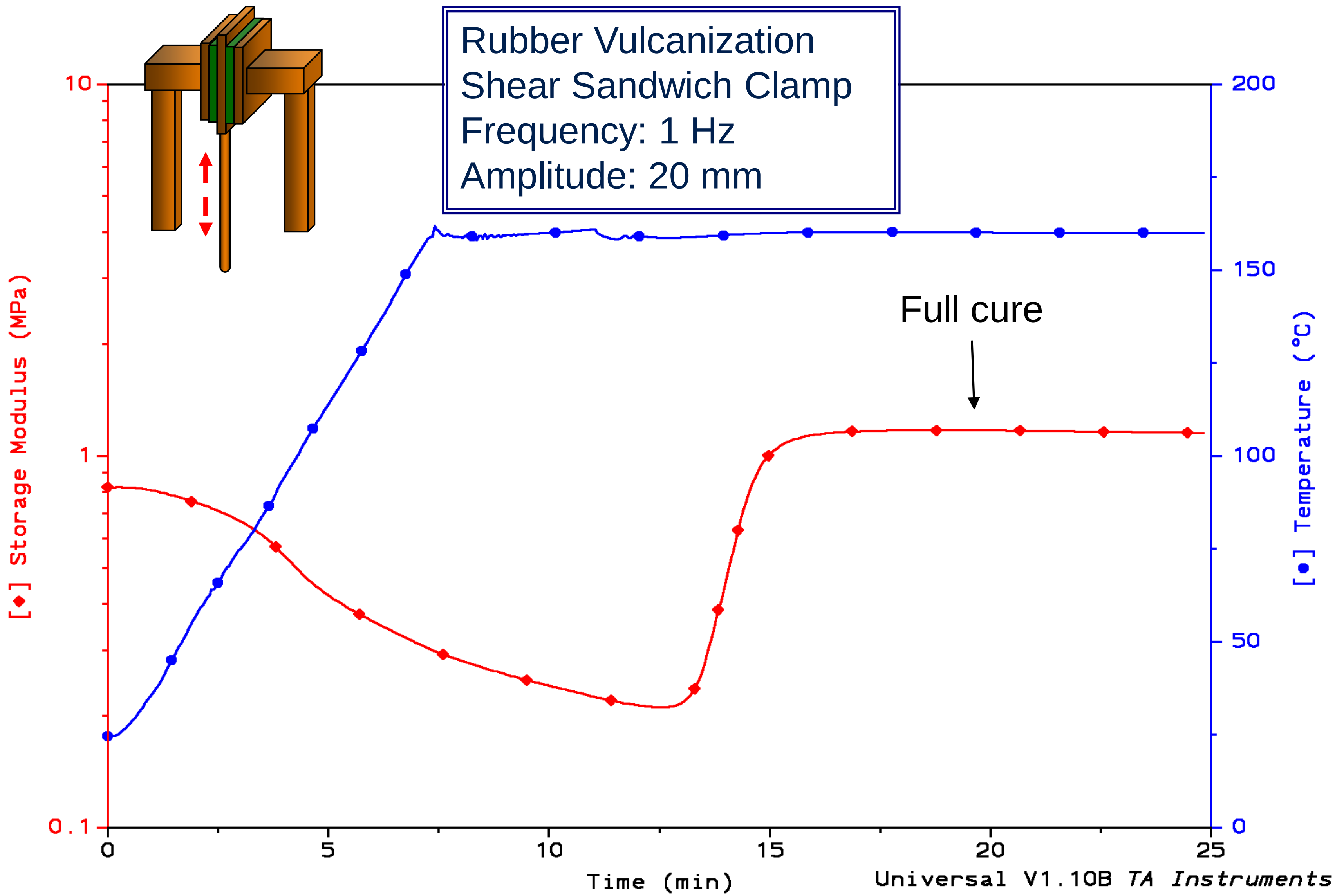
- Linear polymers can be chemically or physically joined at points to other chains along their length to create a crosslinked structure

- Chemically crosslinked systems are typically known as **thermosetting polymers** because the crosslinking agent is heat activated.

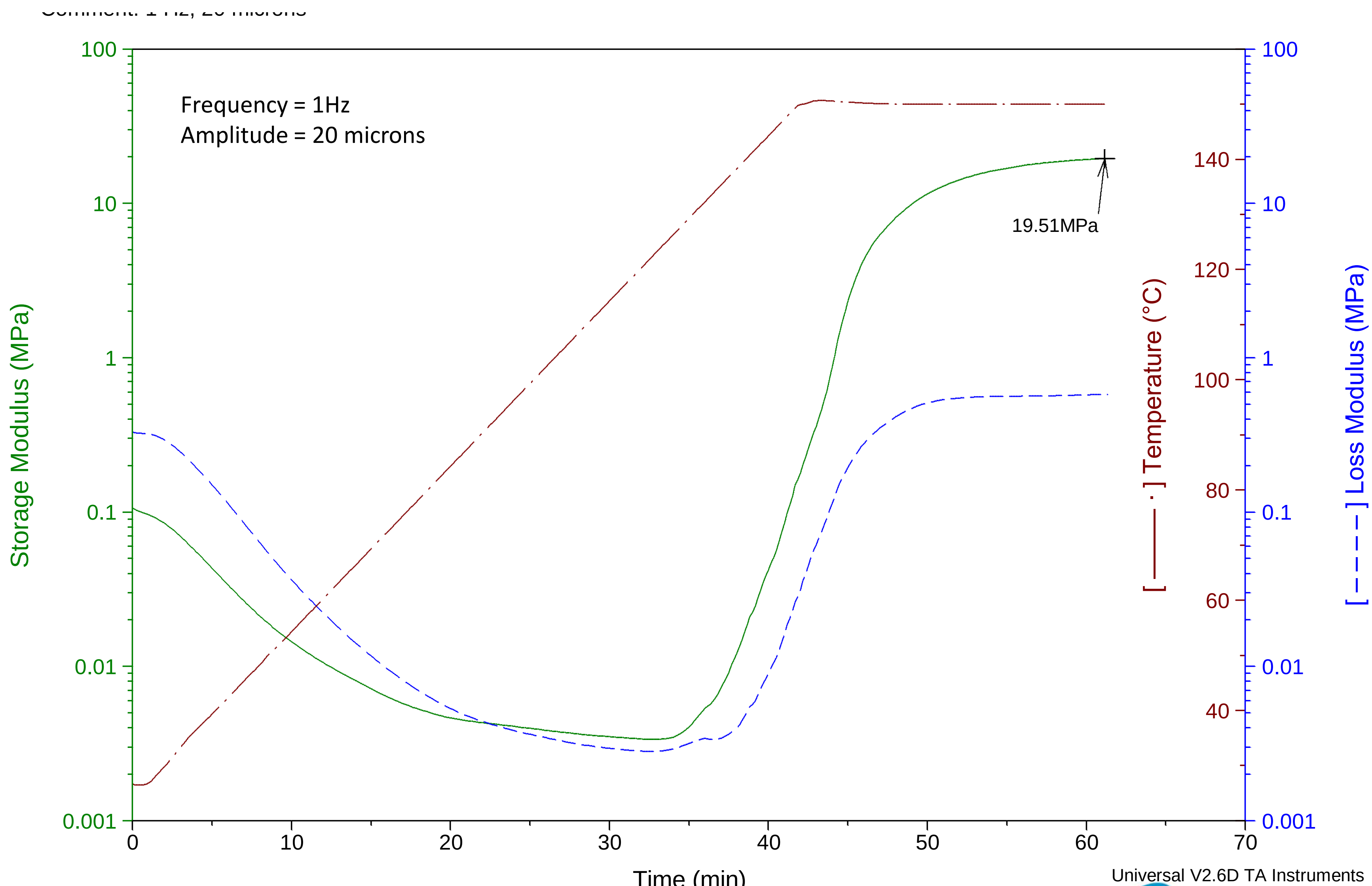


Ward, I.M., Hadley, D.W., An Introduction to the Mechanical Properties of Solid Polymers, John Wiley & Sons Ltd., New York, 1993

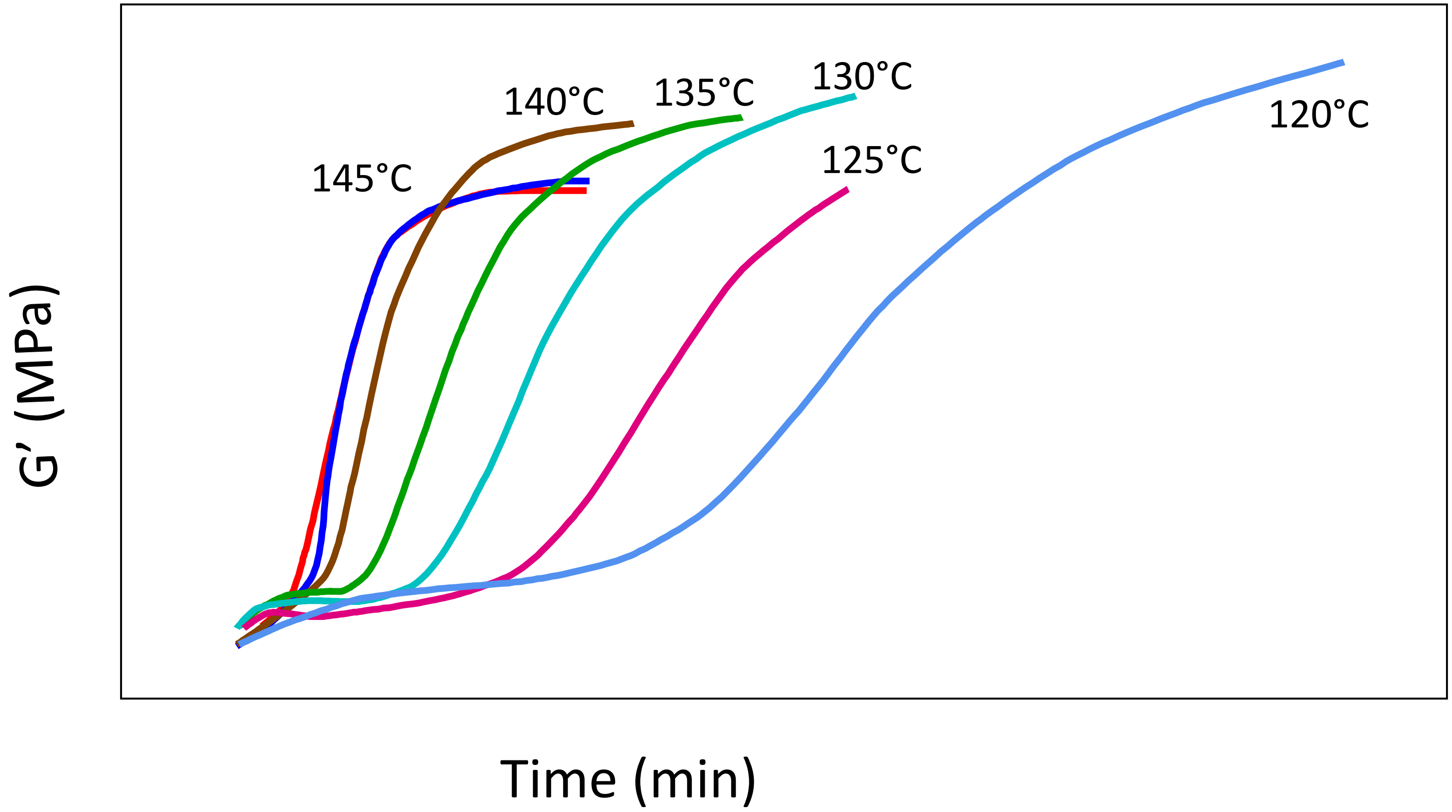
DMA Cure of Rubber



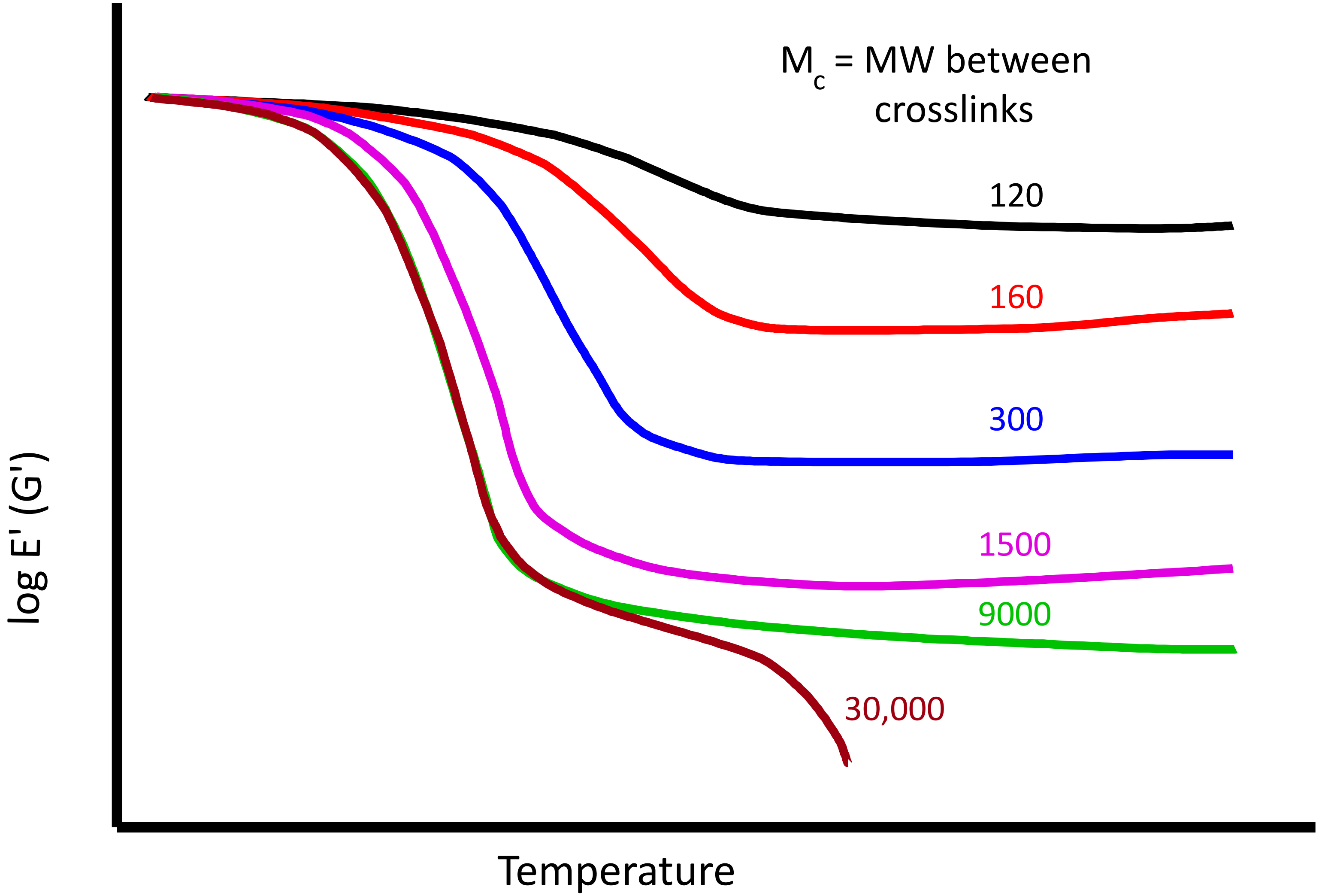
Sheet Molding Compound Cure in Shear Sandwich



Tire Compound: Effect of Curing Temperature



Effect of Crosslinking



Effect of Crosslinking on T_g

Increasing Crosslinking

↓

Higher Density

↓

Less Free Volume

↓

Restricted molecular motion

↓

More Energy needed

↓

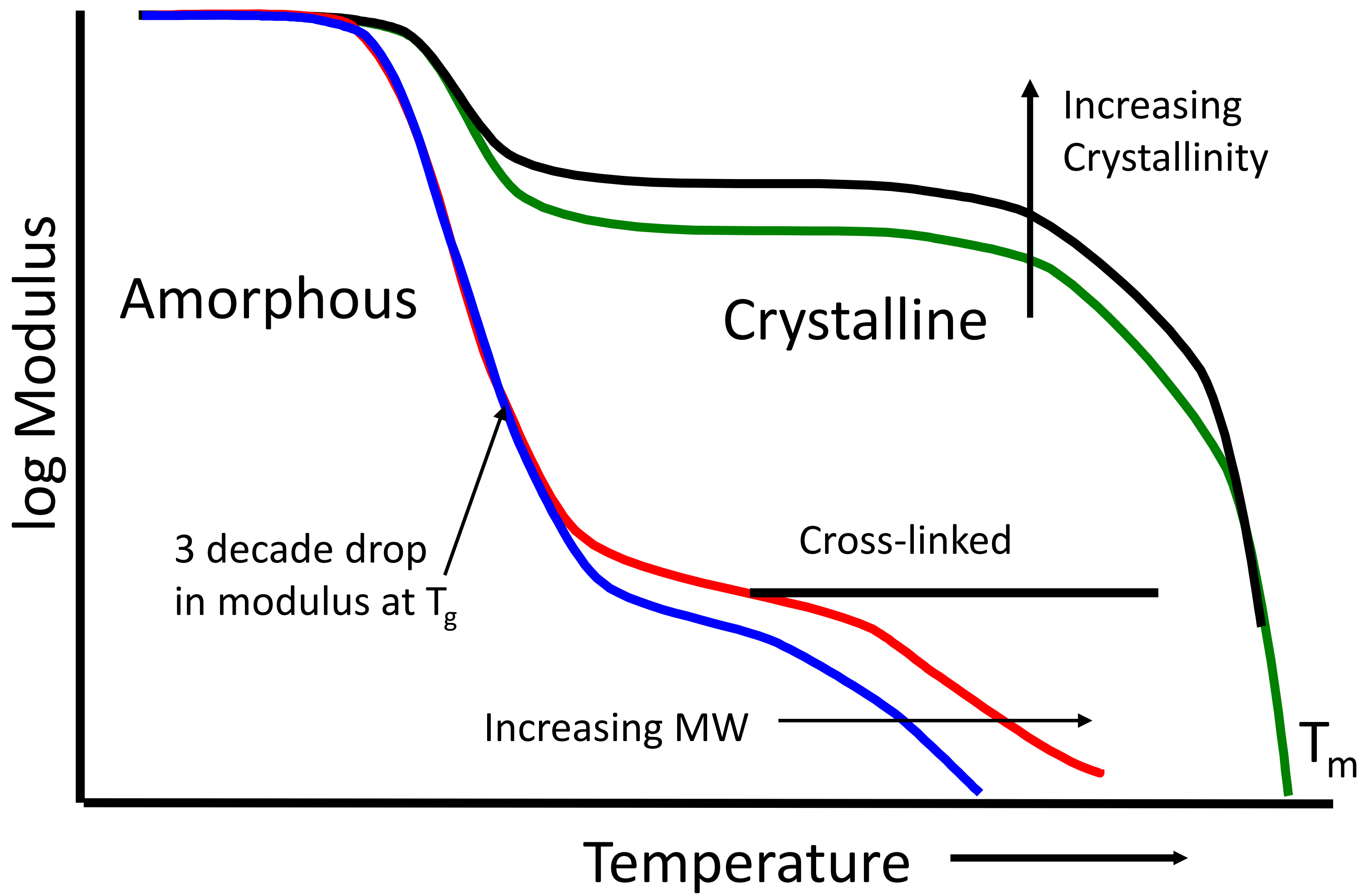
Higher Glass Transition Temperature

For low values of crosslink density, T_g can be found to increase linearly with the number of crosslinks.

For high crosslink density, the T_g is broad and not well defined.

Cowie, J.M.G., Polymers: Chemistry & Physics of Modern Materials, 2nd Edition, Blackie academic & Professional, and imprint of Chapman & HallBishopbriggs, Glasgow, 1991 p.262 ISBN 0 7514 0134 X

Crystallinity, Molecular Weight, and Crosslinking



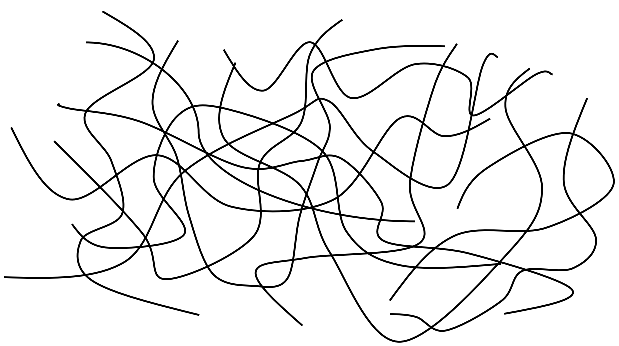
Effect of Molecular Weight

- Molecular Weight has practically no effect on the modulus below T_g.
- T_g and the drop in modulus are also nearly independent of MW if the MW is high enough to form entanglements
- The rubbery plateau region above T_g is strongly dependent on MW. In the absence of true crosslinks, the behavior is determined by *entanglements*.
- The length of the rubbery plateau ($T_g \leftrightarrow T_m$) is a function of the number of entanglements per molecule.

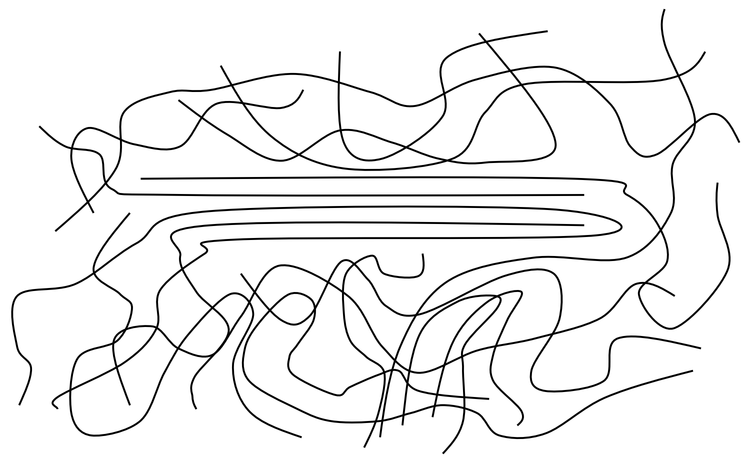
Nielsen, Lawrence E., Mechanical Properties of Polymers and Composites, Marcel Dekker, Inc., New York, 1974, p. 51-52.

Effect of % Crystallinity on Modulus

"The major effect of the crystallite in a sample is to act as a crosslink in the polymer matrix. This makes the polymer behave as though it was a crosslinked network, but as the crystallite anchoring points are thermally labile, they disintegrate as the temperature approaches the melting temperature, and the material undergoes a progressive change in structure until beyond T_m, when it is molten"



Random Chain
100% Amorphous



Fringed Micell
Crystalline

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

Summary

- DMA allows users to obtain mechanical properties over a wide range of temperatures
  - Example: Tires in a variety of environmental conditions
- Resolve weak glass transitions that may otherwise go undetected in other techniques
- Tan δ as a means to explain energy dissipation of rubbers and elastomers

Thank You

The World Leader in Thermal Analysis, Rheology, and Microcalorimetry