Rheology Fundamentals
and
Polymer Characterization

Fundamentals:

- Why Rheology ?
- Fundamental Rheology Concepts and Parameters
- Fundamental Rheometry Concepts
- Viscosity, Viscoelasticiy and the Storage Modulus
- The Linear Viscoelastic Region (LVR)

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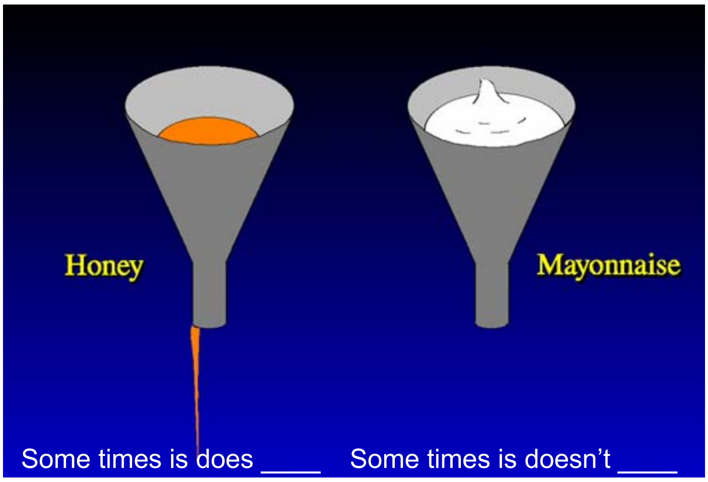
A Rheological Paradox

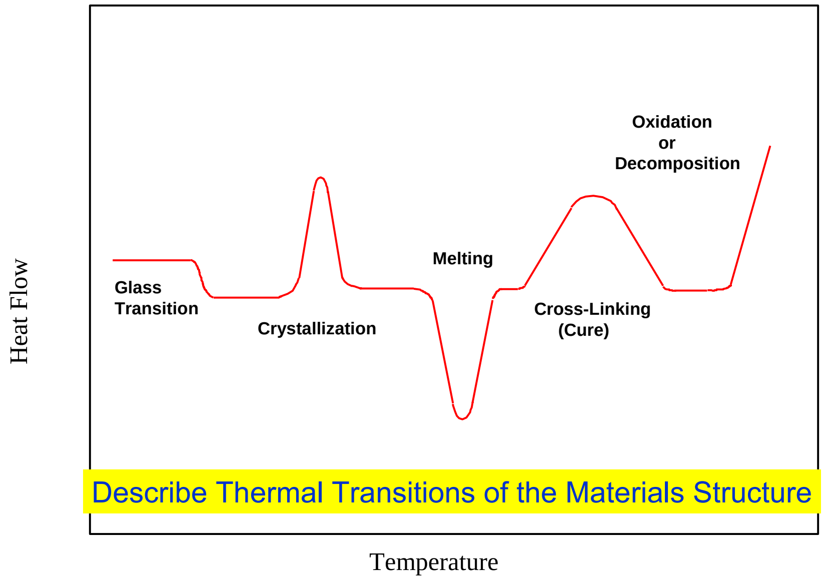


BECAUSE …

If a material is pumped, sprayed, extended, extruded, molded, coated, mixed, chewed, swallowed, rubbed, transported, stored, heated, cooled, aged …

RHEOLOGY is important ….!!

BECAUSE …Typical DSC Transitions



Quantitative Description of Consistency (structure) ?

BECAUSE …

- Thermal Analysis describes thermal transitions

NEED to quantify ...

- Physical Properties of Structure
- Strength or weakness of the Structure

and because …

Rheology can do these; therefore, it is much more informative tool

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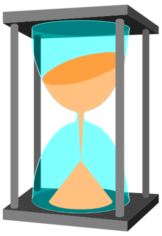
"παντα ρει" *(everything flows …)*

- *Heraclito de Samos (500 A.C.)*



Time Scale in Rheology

Deborah Number **$De = \lambda / t_{exp}$**

Judges 5:5

Our rheological vision should include the fundamental concept of time:

$\lambda \rightarrow$ **material characteristic response time** **and** $t_{exp} \rightarrow$ **us**

$\xi \rightarrow$ **material characteristic recovery time** **and** $t_{exp} \rightarrow$ **us**

FUNDAMENTAL CONCEPTS and PARAMETERS…

CONCEPTS

- **Time**
- **Distance**
- **Mass**
- **Force**
- **Temperature**
- **…**

PARAMETERS

- Shear Stress
- Shear Strain
- Shear Rate
- Viscosity
- Shear Modulus
- Complex Viscosity

- Storage Modulus
- Loss Modulus
- Loss Factor
- Phase Angle
- Characteristic Times
- Normal Force

- Compliance
- Torque
- Angular Velocity
- Angular Frequency
- Angular Displacement
- Inertia
- …

Definition of Rheology

Rheology is the science of

_____?_____ and _____?____

of matter under controlled testing conditions .

- *flow*
- *deformation*

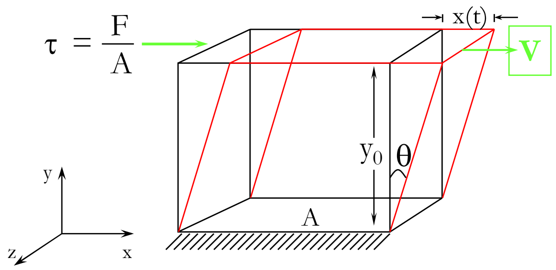
Definition of Rheology

Rheology is the science of *deformation* and *flow* of matter under controlled testing conditions .

- *Flow is a special case of deformation*
- *Deformation is a special case of flow*

Simple Shear Deformation and Shear Flow

Shear Deformation



Strain, $\gamma = \frac{x(t)}{y_0}$

Strain Rate, $\dot{\gamma} = \frac{V}{y_0} = \frac{1}{y_0}\frac{d\,x(t)}{d\,t}$

Viscosity, $\eta = \frac{\tau}{\dot{\gamma}}$

Shear Modulus, G $= \frac{\tau}{\gamma}$

$$\dot{\gamma} = \frac{\Delta\gamma}{\Delta t}$$

Range of Rheological Material Behavior

- Rheology: The study of deformation and flow of matter *at specified conditions*.

<u>Range of material behavior</u>

Solid Like ---------- *Liquid Like*

(Ideal Solid ------------- *Ideal Fluid)*

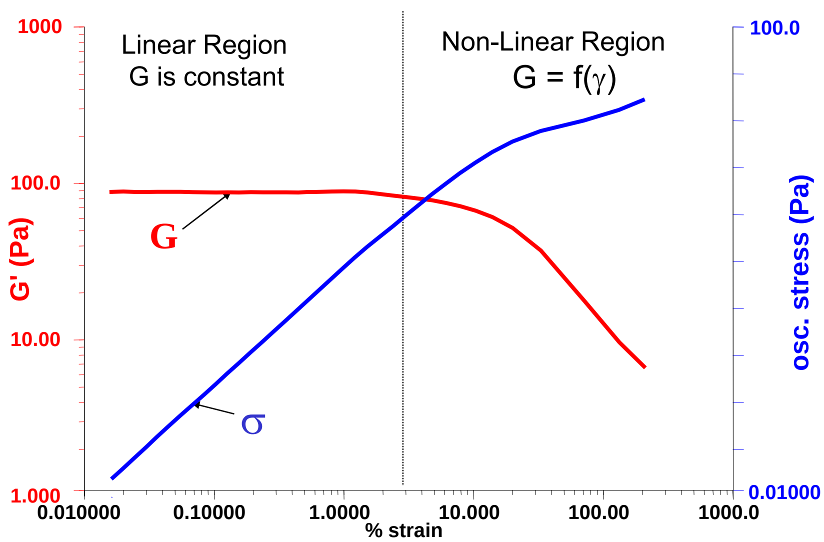
Classical Extremes

Classical Extremes: Elasticity

- 1678: Robert Hooke develops his "True Theory of Elasticity"
  - "The power of any spring is in the same proportion with the tension thereof."
  - Hooke's Law: $\tau = G \gamma$ or (Stress = G x Strain)

    where G is the RIGIDITY MODULUS

Linear and Non-Linear Stress-Strain Behavior of Solids

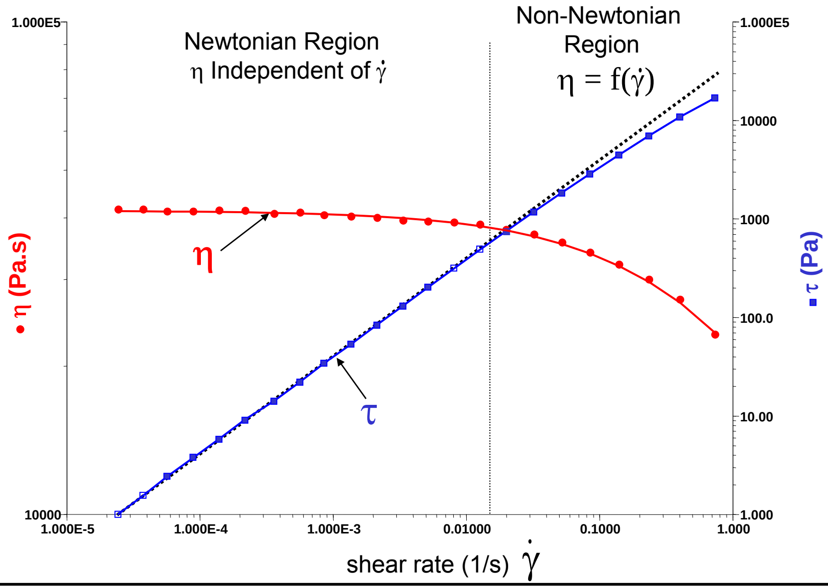


Classical Extremes: Viscosity

- 1687: Isaac Newton addresses liquids and steady simple shearing flow in his "*Principia*"
  - "The resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another."
  - Newton's Law: $\tau = \eta\dot{\gamma}$

where η is the Coefficient of Viscosity

Newtonian and Non-Newtonian Behavior of Fluids



PARAMETERS for Rheological Properties

Classical Extremes

Ideal Solid	-- [External Force] --	Ideal Fluid
STEEL		WATER
Strong Structure		Weak Structure
Rigidity		Fluidity
Deformation		***Flow***
Retains/recovers form		Losses form
Stores Energy		Dissipates Energy
(Purely Elastic – R. Hooke, 1678)	*[Energy]*	*(Purely Viscous – I. Newton, 1687)*
ELASTICITY		VISCOSITY
Storage Modulus		Loss Modulus
	REAL Behavior	
Apparent Solid	*[Energy + time]*	*Apparent Fluid*

- viscoelastic materials -

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Viscometer vs. Rheometer

- **Viscometer:** instrument that measures the viscosity of a fluid over a limited shear rate range
- **Rheometer**: instrument that measures:
  - *Viscosity over a wide range of shear rates, and…*
  - *Viscoelasticity of fluids, semi-solids and solids*

Frame of Reference…

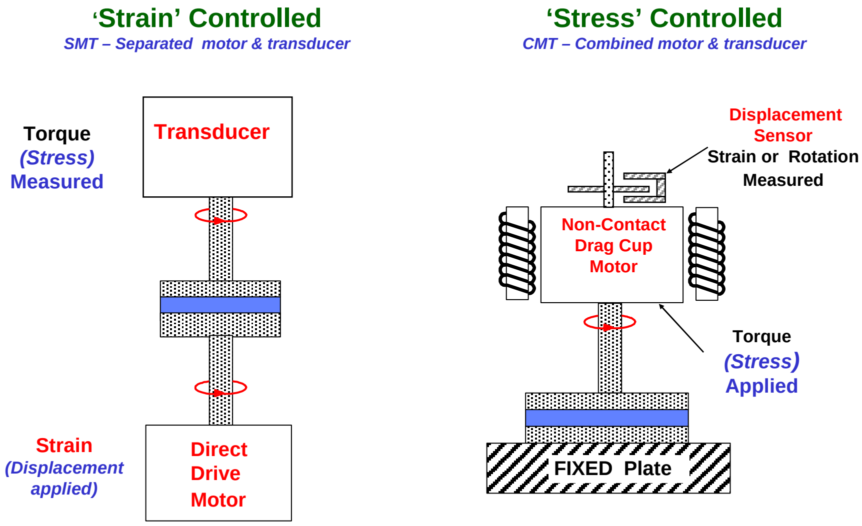
- Recognize that a rheometer is a highly sensitive device used to quantify viscoelastic properties of the ***molecular structure*** of materials.
- A rheometer can not always mimic the conditions of a process, application or use.
- Rheometers determine apparent properties under a wide range of testing conditions.
  - *The apparent behavior can be used as a "finger print" or "benchmark" of the material.*

Constitutive Relations

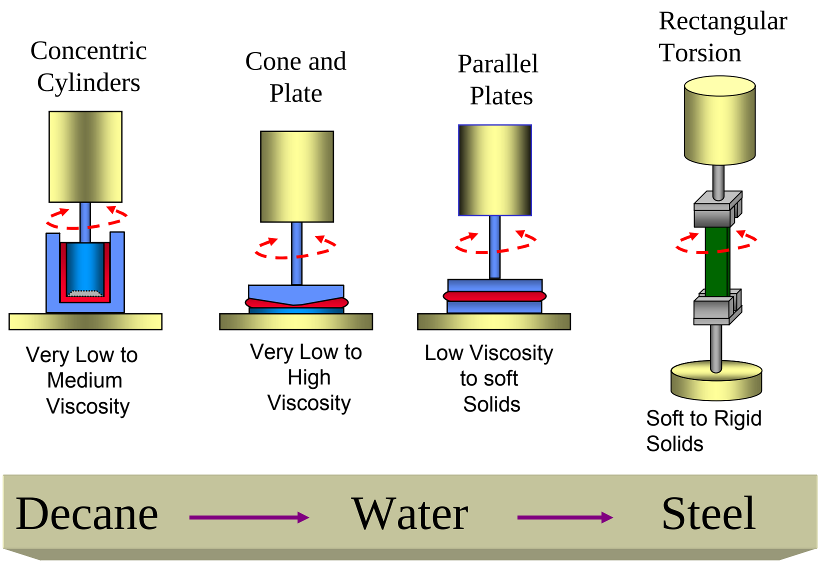
$$\frac{Stress}{Strain} = Modulus$$

$$\frac{Stress}{Shear\ rate} = Viscosity$$

Design of Rotational Rheometers



Measuring Systems - Geometries



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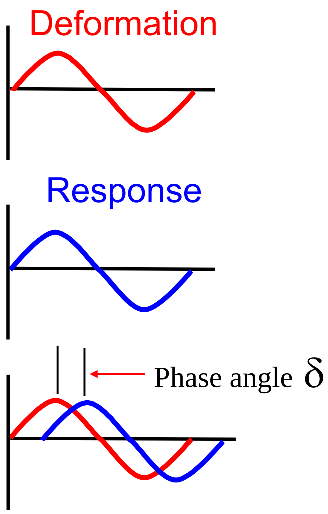
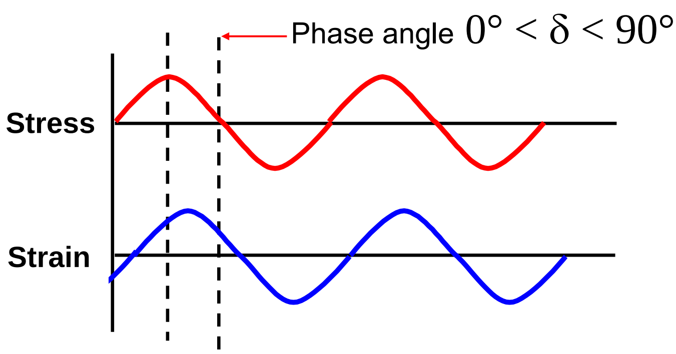
Dynamic Testing

- An oscillatory (sinusoidal) deformation (stress or strain) is applied to a sample.
- The material response (strain or stress) is measured.
- The phase angle δ, or phase shift, between the deformation and response is measured.



Dynamic Viscoelastic Material Response



Viscoelastic Parameters

The Complex Modulus: Measure of materials overall resistance to deformation.

$$G^* = \text{Stress}^*/\text{Strain}$$
$$G^* = G' + iG''$$

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

$$G' = (\text{stress}^*/\text{strain})\cos\Theta$$

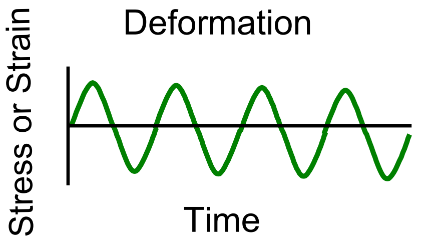
The Viscous (loss) Modulus: The ability of the material to dissipate energy. Energy lost as heat.

$$G'' = (\text{stress}^*/\text{strain})\sin\Theta$$

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

$$\text{Tan}\ \sigma = G''/G'$$

Dynamic Time Sweep (Time Ramp)



- The material response is monitored at a constant frequency, amplitude and temperature.

- USES
  - Time dependent Thixotropy
  - Cure Studies
  - Stability against thermal degradation
  - Solvent evaporation/drying

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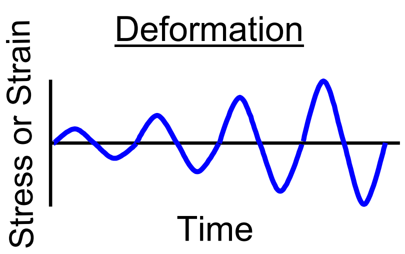
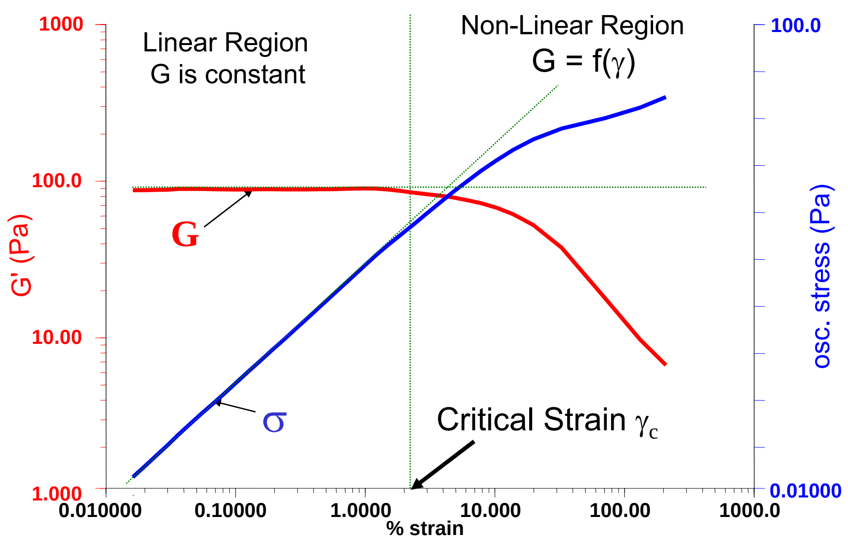
Dynamic Stress or Strain Sweep (Torque Ramp)



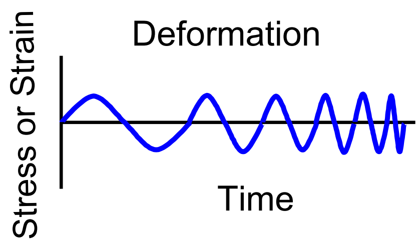
- The material response to increasing deformation amplitude (stress or strain) is monitored at a constant frequency and temperature.

- USES
  - Identify Linear Viscoelastic Region
  - Strength of dispersion structure - settling stability
  - Resilience

Dynamic Strain Sweep: Material Response



Frequency Sweep

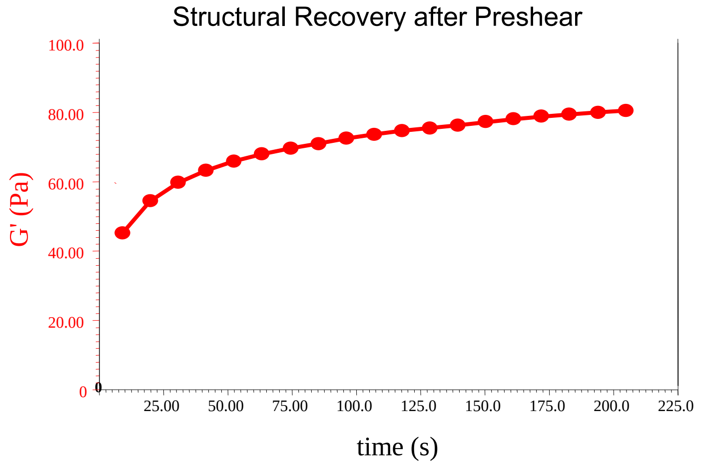


- The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude (stress or strain) and temperature.

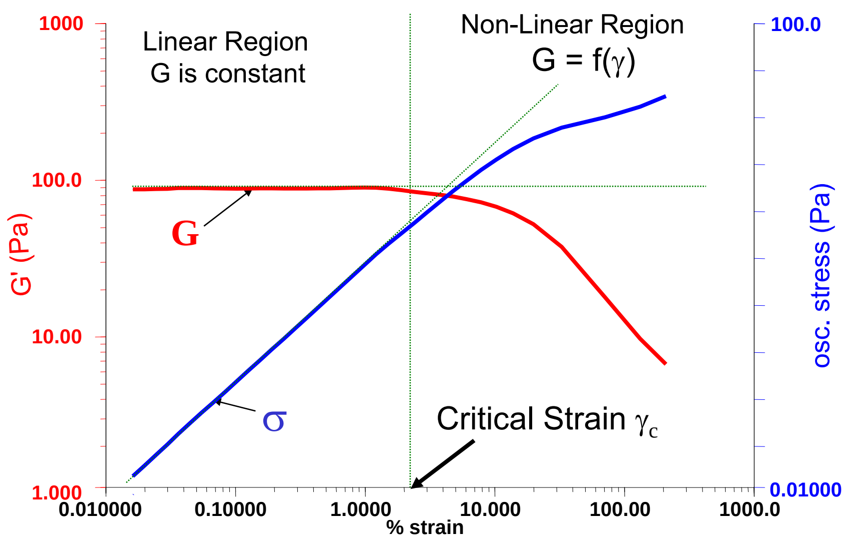
- <u>USES</u>

➢Viscosity Information - Zero Shear η, shear thinning
➢Elasticity (reversible deformation) in materials
➢ MW & MWD differences Polymer Melts and Polymer solutions.
➢Finding Yield in gelled dispersions
➢High and Low Rate (short and long time) modulus properties.
➢Extend time or frequency range with TTS

Time Sweep on Latex



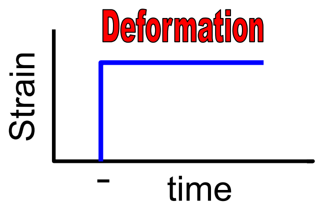
Dynamic Strain Sweep: Material Response



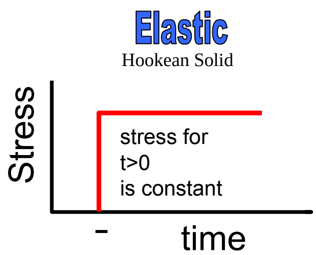
Defining Shear Rate Ranges

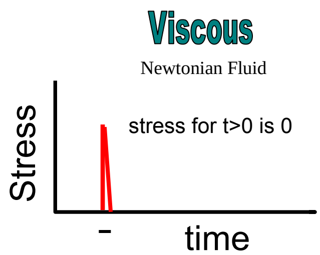
Situation	Shear Rate Range	Examples
Sedimentation of fine powders in liquids	10^{-6} to 10^{-3}	Medicines, Paints, Salad Dressing
Leveling due to surface tension	10^{-2} to 10^{-1}	Paints, Printing inks
Draining off surfaces under gravity	10^{-1} to 10^{1}	Toilet bleaches, paints, coatings
Extruders	10^{0} to 10^{2}	Polymers, foods
Chewing and Swallowing	**10^{1} to 10^{2}**	**Foods**
Dip coating	10^{1} to 10^{2}	Confectionery, paints
Mixing and stirring	**10^{1} to 10^{3}**	**Liquids manufacturing**
Pipe Flow	**10^{0} to 10^{3}**	**Pumping liquids, blood flow**
Brushing	10^{3} to 10^{4}	Painting
Rubbing	**10^{4} to 10^{5}**	**Skin creams, lotions**
High-speed coating	10^{4} to 10^{6}	Paper manufacture
Spraying	10^{5} to 10^{6}	Atomization, spray drying
Lubrication	10^{3} to 10^{7}	Bearings, engines

Stress Relaxation Experiment



Response of Classical Extremes

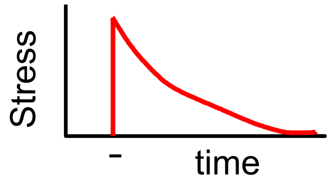




Stress Relaxation Experiment (cont'd)

Response of **Viscoelastic** Material

Stress decreases with time starting at some high value and decreasing to zero.

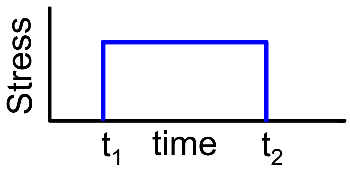


- For small deformations (strains within the linear region) the ratio of stress to strain is a function of time only.
- This function is a material property known as the STRESS RELAXATION MODULUS, G(t)

G(t) = s(t)/□

Creep Recovery Experiment

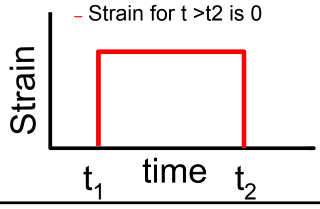
Deformation



Response of Classical Extremes

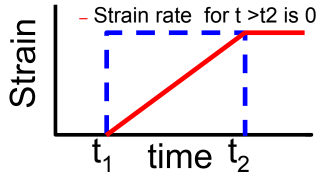
Elastic

- Stain for t>t1 is constant
- Strain for t >t2 is 0

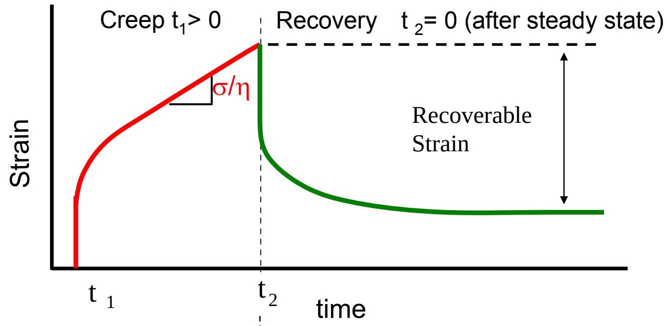


Viscous

- Stain rate for t>t1 is constant
- Strain for t>t1 increase with time
- Strain rate for t >t2 is 0



Creep Recovery Experiment: Response of Viscoelastic Material

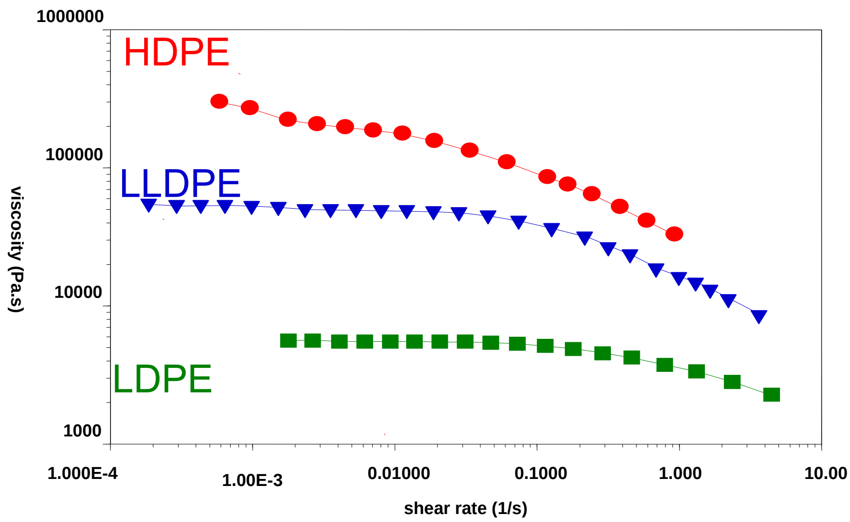


Strain rate decreases with time in the creep zone, until finally reaching a steady state.

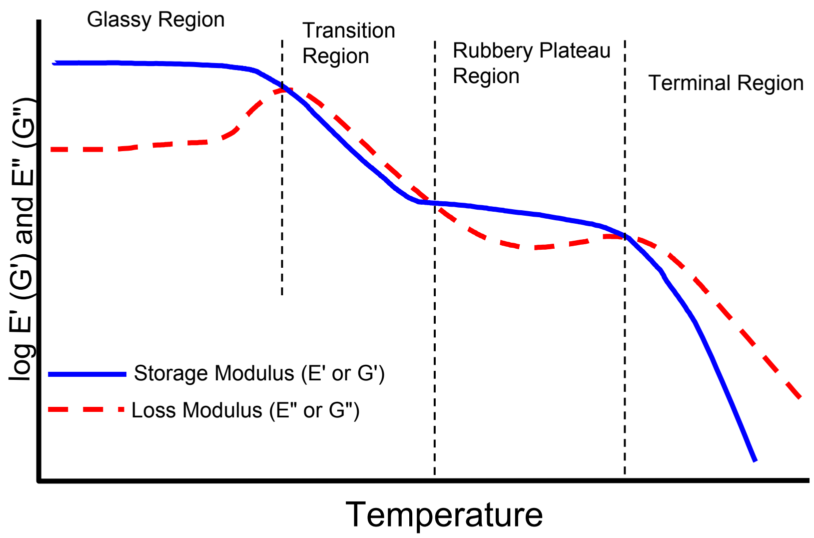
In the recovery zone, the viscoelastic fluid recoils, eventually reaching a equilibrium at some small total strain relative to the strain at unloading.

Reference: Mark, J., et.al., Physical Properties of Polymers ,American Chemical Society, 1984, p. 102.

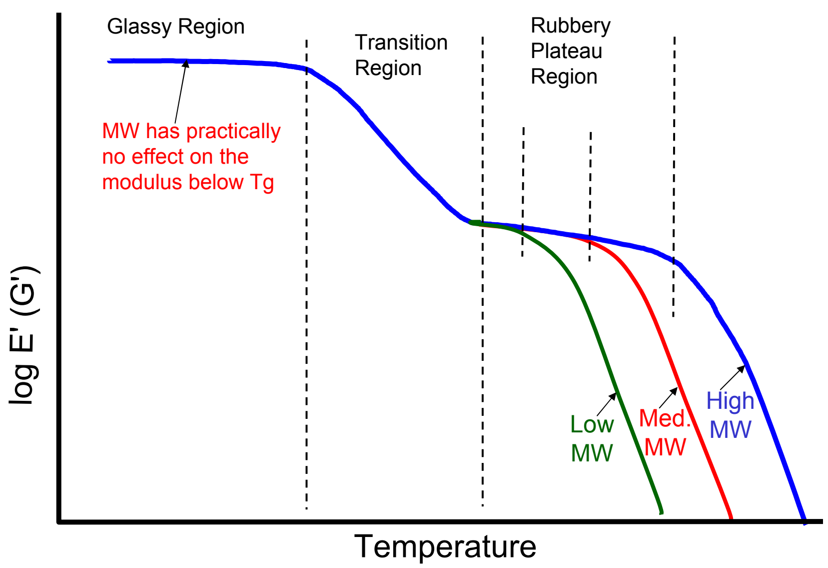
Polyethylene Rheology @ 150 C



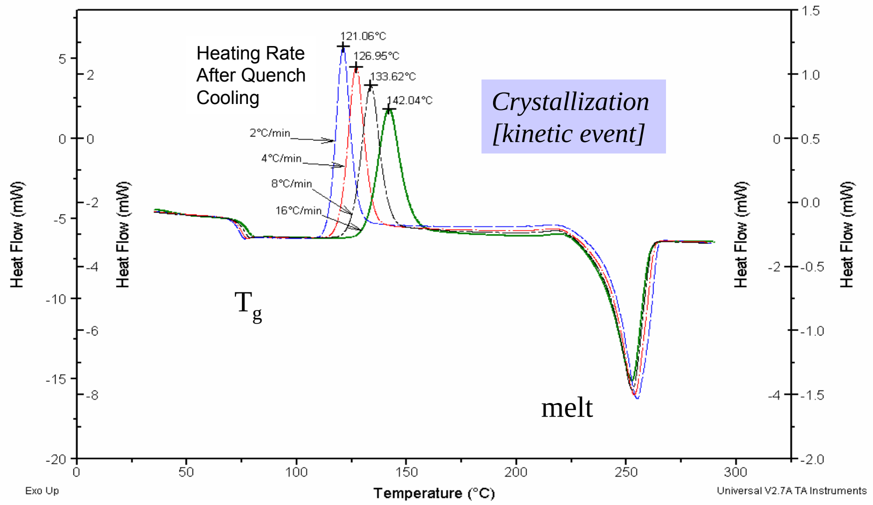
Dynamic Temperature Ramp or Step and Hold: Material Response



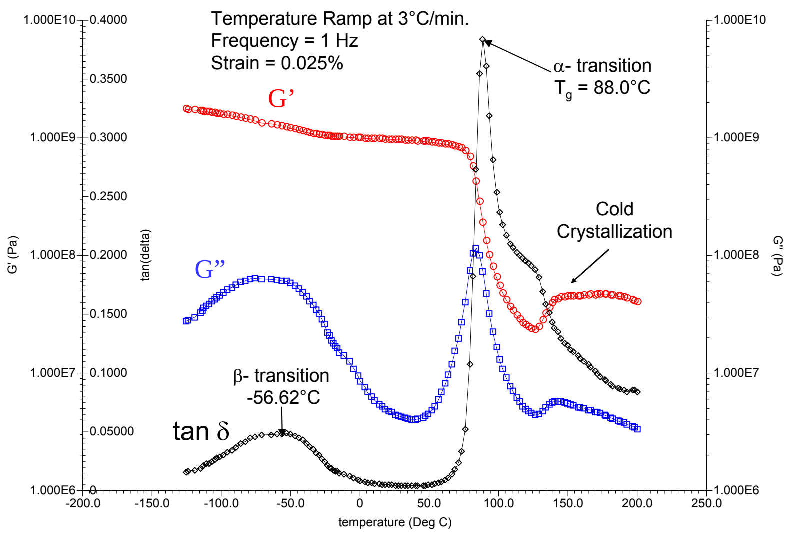
Molecular Structure - Effect of Molecular Weight



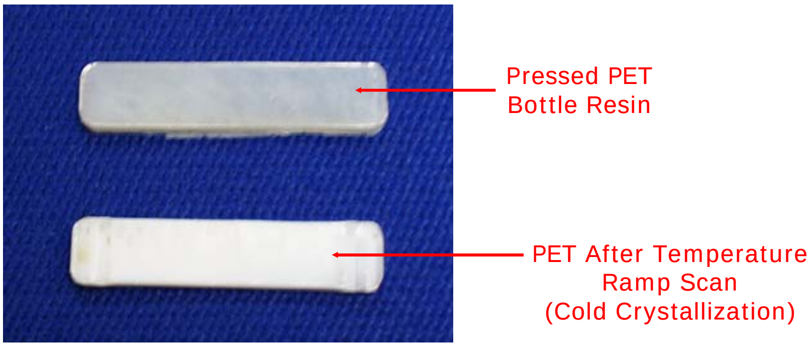
Effect of Heating Rate on Temperature of Cold Crystallization in PET



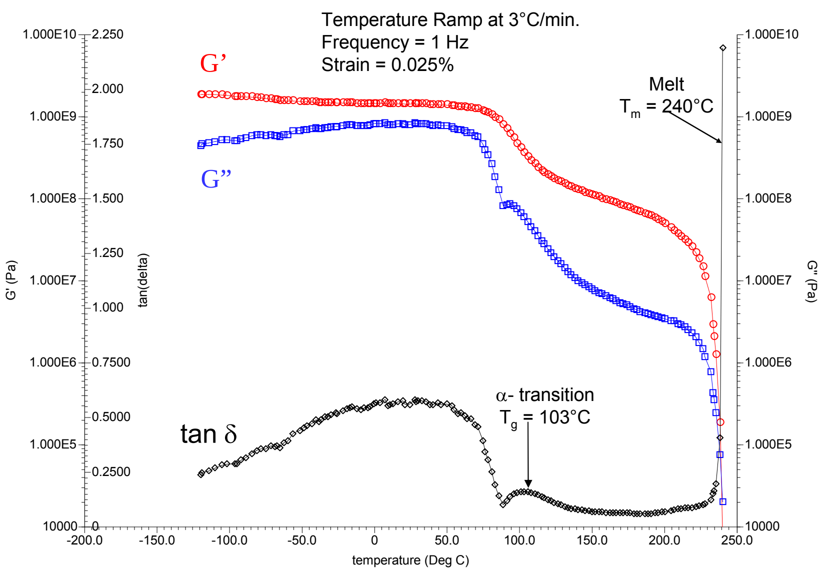
PET Bottle Resin – Cold Crystallization



PET Bottle Resin – Before and After DMA Scan



PET Bottle Resin - Repeat Run After Cold Crystallization



PET Bottle Resin - Comparison of G’