Rheology
Theory and Applications
Course Outline

- Basics in Rheology Theory
- TA Rheometers
  - Instrumentation
  - Choosing a Geometry
  - Calibrations
- Flow Tests
  - Viscosity
  - Setting up Flow Tests
- Oscillation
  - Linear Viscoelasticity
  - Setting up Oscillation Tests
- Transient Testing
- Applications of Rheology
  - Polymers
  - Structured Fluids
  - Advanced Accessories
Basics in Rheology Theory
Rheology: An Introduction

Rheology: The study of stress-deformation relationships
Rheology: An Introduction

- Rheology is the science of flow and deformation of matter
  - The word ‘Rheology’ was coined in the 1920s by Professor E C Bingham at Lafayette College in Indiana
- Flow is a special case of deformation
- The relationship between stress and deformation is a property of the material

\[
\frac{\text{Stress}}{\text{Shear rate}} = \text{Viscosity}
\]

\[
\frac{\text{Stress}}{\text{Strain}} = \text{Modulus}
\]
Simple Steady Shear Flow

Top plate Area = A

Velocity = V₀
Force = F
Bottom Plate Velocity = 0

Shear Stress, Pascals
\[ \sigma = \frac{F}{A} \]

Shear Strain, %
\[ \gamma = \frac{x(t)}{y} \]

Shear Rate, sec⁻¹
\[ \dot{\gamma} = \frac{\gamma}{t} \]

Viscosity, Pa·s
\[ \eta = \frac{\sigma}{\dot{\gamma}} \]
Torsion Flow in Parallel Plates

\[ r = \text{plate radius} \]
\[ h = \text{distance between plates} \]
\[ M = \text{torque} \ (\mu\text{N.m}) \]
\[ \theta = \text{Angular motor deflection (radians)} \]
\[ \Omega = \text{Motor angular velocity (rad/s)} \]

**Stress** \((\sigma)\)

\[ \sigma = \frac{2}{\pi r^3} \times M \]

**Strain** \((\gamma)\)

\[ \gamma = \frac{r}{h} \times \theta \]

**Strain rate** \((\dot{\gamma})\)

\[ \dot{\gamma} = \frac{r}{h} \times \Omega \]
TA Instruments Rheometers
Rotational Rheometers at TA

ARES G2
Controlled Strain
Dual Head
SMT

DHR
Controlled Stress
Single Head
CMT
Rotational Rheometer Designs

**Dual head or SMT**
Separate motor & transducer

- Measured Torque (Stress)
- Transducer
- Applied Strain or Rotation

- Direct Drive Motor
- Sample

**Single head or CMT**
Combined motor & transducer

- Measured Strain or Rotation
- Non-Contact Drag Cup Motor
- Applied Torque (Stress)

Note: With computer feedback, DHR and AR can work in controlled strain/shear rate, and ARES can work in controlled stress.
What does a Rheometer do?

- Rheometer – an instrument that measures both viscosity and viscoelasticity of fluids, semi-solids and solids

- It can provide information about the material’s:
  - **Viscosity** - defined as a material’s resistance to deformation and is a function of shear rate or stress, with time and temperature dependence

- **Viscoelasticity** – is a property of a material that exhibits both viscous and elastic character. Measurements of $G'$, $G''$, tan $\delta$ with respect to time, temperature, frequency and stress/strain are important for characterization.

- A Rheometer works simply by relating a materials property from how hard it’s being pushed, to how far it moves

  - by commanding torque (stress) and measuring angular displacement (strain)
  - by commanding angular displacement (strain) and measuring torque (stress)
How do Rheometers work?

From the definition of rheology,

*the science of flow and deformation of matter*

*or*

*the study of stress (Force / Area) – deformation (Strain or Strain rate) relationships.*

Fundamentally a rotational rheometer will apply or measure:

1. Torque (Force)
2. Angular Displacement
3. Angular Velocity
In a rheometer, the stress is calculated from the torque.

The formula for stress is: \[ \sigma = M \times K_\sigma \]

Where \( \sigma \) = Stress (Pa or Dyne/cm\(^2\))
\( M \) = torque in N\( \cdot \)m or gm\( \cdot \)cm
\( K_\sigma \) = Stress Constant

The stress constant, \( K_\sigma \), is a geometry dependent factor.
Angular Displacement → Shear Strain

- In a SMT Rheometer, the angular displacement is directly applied by a motor.

- The formula for strain is: \[ \gamma = k_\gamma \times \theta \]

\[ \%\gamma = \gamma \times 100 \]

where \( \gamma \) = Strain
\( k_\gamma \) = Strain Constant
\( \theta \) = Angular motor deflection (radians)

- The strain constant, \( K_\gamma \), is a geometry dependent factor.
The equation of motion and other relationships have been used to determine the appropriate equations to convert machine parameters (torque, angular velocity, and angular displacement) to rheological parameters.
In a SMT rheometer, the angular speed is directly controlled by the motor.

The formula for shear rate is:

\[ \dot{\gamma} = K_\gamma \times \Omega \]

where \( \dot{\gamma} \) = Shear rate

\( K_\gamma \) = Strain Constant

\( \Omega \) = Motor angular velocity in rad/sec

The strain constant, \( K_\gamma \), is a geometry dependent factor.
The equation of motion and other relationships have been used to determine the appropriate equations to convert machine parameters (torque, angular velocity, and angular displacement) to rheological parameters.
## Discovery Hybrid Rheometer Specifications

<table>
<thead>
<tr>
<th>Specification</th>
<th>HR-3</th>
<th>HR-2</th>
<th>HR-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bearing Type, Thrust</td>
<td>Magnetic</td>
<td>Magnetic</td>
<td>Magnetic</td>
</tr>
<tr>
<td>Bearing Type, Radial</td>
<td>Porous Carbon</td>
<td>Porous Carbon</td>
<td>Porous Carbon</td>
</tr>
<tr>
<td>Motor Design</td>
<td>Drag Cup</td>
<td>Drag Cup</td>
<td>Drag Cup</td>
</tr>
<tr>
<td>Minimum Torque (nN.m) Oscillation</td>
<td>0.5</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Minimum Torque (nN.m) Steady Shear</td>
<td>5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Maximum Torque (mN.m)</td>
<td>200</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>Torque Resolution (nN.m)</td>
<td>0.05</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Minimum Frequency (Hz)</td>
<td>1.0E-07</td>
<td>1.0E-07</td>
<td>1.0E-07</td>
</tr>
<tr>
<td>Maximum Frequency (Hz)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Minimum Angular Velocity (rad/s)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Maximum Angular Velocity (rad/s)</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Displacement Transducer</td>
<td>Optical encoder</td>
<td>Optical encoder</td>
<td>Optical encoder</td>
</tr>
<tr>
<td>Optical Encoder Dual Reader</td>
<td>Standard</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Displacement Resolution (nrad)</td>
<td>2</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Step Time, Strain (ms)</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Step Time, Rate (ms)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Normal/Axial Force Transducer</td>
<td>FRT</td>
<td>FRT</td>
<td>FRT</td>
</tr>
<tr>
<td>Maximum Normal Force (N)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Normal Force Sensitivity (N)</td>
<td>0.005</td>
<td>0.005</td>
<td>0.01</td>
</tr>
<tr>
<td>Normal Force Resolution (mN)</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

### DHR - DMA mode (optional)

<table>
<thead>
<tr>
<th>Specification</th>
<th>HR-1</th>
<th>HR-2</th>
<th>HR-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motor Control</td>
<td>FRT</td>
<td>FRT</td>
<td>FRT</td>
</tr>
<tr>
<td>Minimum Force (N) Oscillation</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Maximum Axial Force (N)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Minimum Displacement (μm) Oscillation</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Maximum Displacement (μm) Oscillation</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Displacement Resolution (nm)</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Axial Frequency Range (Hz)</td>
<td>$1 \times 10^{5}$ to 16</td>
<td>$1 \times 10^{5}$ to 16</td>
<td>$1 \times 10^{5}$ to 16</td>
</tr>
</tbody>
</table>
# ARES-G2 Rheometer Specifications

## Force/Torque Rebalance Transducer (Sample Stress)

<table>
<thead>
<tr>
<th>Transducer Type</th>
<th>Force/Torque Rebalance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transducer Torque Motor</td>
<td>Brushless DC</td>
</tr>
<tr>
<td>Transducer Normal/Axial Motor</td>
<td>Brushless DC</td>
</tr>
<tr>
<td>Minimum Torque (μN.m) Oscillation</td>
<td>0.05</td>
</tr>
<tr>
<td>Minimum Torque (μN.m) Steady Shear</td>
<td>0.1</td>
</tr>
<tr>
<td>Maximum Torque (mN.m)</td>
<td>200</td>
</tr>
<tr>
<td>Torque Resolution (nN.m)</td>
<td>1</td>
</tr>
<tr>
<td>Transducer Normal/Axial Force Range (N)</td>
<td>0.001 to 20</td>
</tr>
<tr>
<td>Transducer Bearing</td>
<td>Groove Compensated Air</td>
</tr>
</tbody>
</table>

## Driver Motor (Sample Deformation)

| Motor Design                  | Brushless DC           |
| Displacement Control/ Sensing | Optical Encoder        |
| Strain Resolution (μrad)      | 0.04                   |
| Minimum Angular Displacement (μrad) Oscillation | 1 |
| Maximum Angular Displacement (μrad) Steady Shear | Unlimited |
| Angular Velocity Range (rad/s) | 1 x 10^{-6} to 300   |
| Angular Frequency Range (rad/s) | 1 x 10^{-7} to 628 |
| Step Change, Velocity (ms)    | 5                      |
| Step Change, Strain (ms)      | 10                     |

## Orthogonal Superposition (OSP) and DMA modes

<table>
<thead>
<tr>
<th>Motor Control</th>
<th>FRT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum Transducer Force (N) Oscillation</td>
<td>0.001</td>
</tr>
<tr>
<td>Maximum Transducer Force (N)</td>
<td>20</td>
</tr>
<tr>
<td>Minimum Displacement (μm) Oscillation</td>
<td>0.5</td>
</tr>
<tr>
<td>Maximum Displacement (μm) Oscillation</td>
<td>50</td>
</tr>
<tr>
<td>Displacement Resolution (nm)</td>
<td>10</td>
</tr>
<tr>
<td>Axial Frequency Range (Hz)</td>
<td>1 x 10^{-5} to 16</td>
</tr>
</tbody>
</table>
Geometry Options

- **Concentric Cylinders**: Very Low to Medium Viscosity
- **Cone and Plate**: Very Low to High Viscosity
- **Parallel Plate**: Very Low Viscosity to Soft Solids
- **Torsion Rectangular**: Solids

Water → to → Steel
Choosing a Geometry Size

- Assess the ‘viscosity’ of your sample
- When a variety of cones and plates are available, select diameter appropriate for viscosity of sample
  - Low viscosity (milk) - 60mm geometry
  - Medium viscosity (honey) - 40mm geometry
  - High viscosity (caramel) – 20 or 25mm geometry
- Examine data in terms of absolute instrument variables torque/displacement/speed and modify geometry choice to move into optimum working range
- You may need to reconsider your selection after the first run!
Parallel Plate

**Strain Constant:** \( K_\gamma = \frac{r}{h} \)

(to convert angular velocity, rad/sec, to shear rate, 1/sec, at the edge or angular displacement, radians, to shear strain (unitless) at the edge. The radius, \( r \), and the gap, \( h \), are expressed in meters)

**Stress Constant:** \( K_\sigma = \frac{2}{\pi r^3} \)

(to convert torque, N\cdot m, to shear stress at the edge, Pa, for Newtonian fluids. The radius, \( r \), is expressed in meters)
When to use Parallel Plates

- Low/Medium/High Viscosity Liquids
- Soft Solids/Gels
- Thermosetting materials
- Samples with large particles
- Samples with long relaxation time
- Temperature Ramps/ Sweeps
- Materials that may slip
  - Crosshatched or Sandblasted plates
- Small sample volume
As diameter decreases, shear stress increases

\[ \sigma = \frac{M}{\pi r^2} \]
Plate Gaps

As gap height decreases, shear rate increases

\[ \dot{\gamma} = \Omega \frac{r}{h} \]
Effective Shear Rate varies across a Parallel Plate

- For a given angle of deformation, there is a greater arc of deformation at the edge of the plate than at the center.

\[
\gamma = \frac{dx}{h}
\]

\(dx\) increases further from the center, \(h\) stays constant.
Shear Rate is Normalized across a Cone

- The cone shape produces a smaller gap height closer to inside, so the shear on the sample is constant

\[ \gamma = \frac{dx}{h} \]

\( h \) increases proportionally to \( dx \), \( \gamma \) is uniform
Cone and Plate

Strain Constant: \( K_\gamma = \frac{1}{\beta} \)

(to convert angular velocity, rad/sec, to shear rate.
1/sec, or angular displacement, radians, to shear strain, which is unit less. The angle, \( \beta \), is expressed in radians)

Stress Constant: \( K_\sigma = \frac{3}{2\pi r^3} \)

(to convert torque, N\cdot m, to shear stress, Pa.
The radius, \( r \), is expressed in meters)
When to use Cone and Plate

- Very Low to High Viscosity Liquids
- High Shear Rate measurements
- Normal Stress Growth
- Unfilled Samples
- Isothermal Tests
- Small Sample Volume
Cone Diameters

As diameter decreases, shear stress increases

\[ \sigma = \frac{M}{2\pi r^3} \]
As cone angle decreases, shear rate increases

\[ \dot{\gamma} = \Omega \frac{1}{\beta} \]
Limitations of Cone and Plate

Typical Truncation Heights:
- 1° degree ~ 20 - 30 microns
- 2° degrees ~ 60 microns
- 4° degrees ~ 120 microns

Gap must be > or = 10 [particle size]!!
Correct Sample Loading

- Under Filled sample: Lower torque contribution
- Over Filled sample: Additional stress from drag along the edges
- Correct Filling
Concentric Cylinder

**Strain Constant:**

\[ K_\gamma = \frac{r_1^2 + r_2^2}{r_2^2r_1^2} \]

(to convert angular velocity, rad/sec, to shear rate, 1/sec, or angular displacement, radians, to shear strain (unit less). The radii, \( r_1 \) (inner) and \( r_2 \) (outer), are expressed in meters)

**Stress Constant:**

\[ K_\sigma = \frac{1}{4\pi l} \left[ \frac{r_1^2 + r_2^2}{r_2^2r_1^2} \right]^* \]

(to convert torque, N\cdot m, to shear stress, Pa. The bob length, \( l \), and the radius, \( r \), are expressed in meters)

*Note including end correction factor. See TRIOS Help*
Double Wall

- Use for very low viscosity systems (<1 mPas)

Strain Constant: \( K_\gamma = \frac{(r_1^2 + r_2^2)}{(r_2^2 - r_1^2)} \)

Stress Constant: \( K_\sigma = \frac{(r_1^2 + r_2^2)}{4\pi h \cdot r_2^2 (r_1^2 + r_3^2)} \)

ARES Gap Settings: standard operating gap DW = 3.4 mm
narrow operating gap DW = 2.0 mm
Use equation Gap > 3 \times (R_2 - R_1)
When to Use Concentric Cylinders

- Low to Medium Viscosity Liquids
- Unstable Dispersions and Slurries
- Minimize Effects of Evaporation
- Weakly Structured Samples (Vane)
- High Shear Rates
**Peltier Concentric Cylinders**

**Concentric Cylinder Cup and Rotor Compatibility Chart**

<table>
<thead>
<tr>
<th>Cup/Rotor</th>
<th>DIN</th>
<th>Recessed End</th>
<th>Starch Impeller</th>
<th>Vane</th>
<th>Wide Gap Vane</th>
<th>Double Gap</th>
<th>Helical Rotor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard (rad = 15 mm)</td>
<td>●</td>
<td>●</td>
<td></td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Large Diameter (rad = 22 mm)</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Starch (rad = 18.5 mm)</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grooved</td>
<td></td>
<td></td>
<td></td>
<td>●</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Double Gap</td>
<td></td>
<td></td>
<td></td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helical (rad = 17 mm)</td>
<td></td>
<td></td>
<td></td>
<td>●</td>
<td>●</td>
<td>●</td>
<td></td>
</tr>
</tbody>
</table>
**Torsion Rectangular**

\[ K_Y = \frac{t}{l \left[ 1 - 0.378 \left( \frac{t}{w} \right)^2 \right]} \]

\[ K_T = \frac{\left( 3 + \frac{1.8}{w} \right)}{(w \cdot t^2)} \]

**Advantages:**
- High modulus samples
- Small temperature gradient
- Simple to prepare

**Disadvantages:**
- No pure Torsion mode for high strains

Torsion cylindrical also available
Torsion and DMA Measurements

- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment
  - Torsion measures $G'$, $G''$, and $\tan \delta$
  - DMA measures $E'$, $E''$, and $\tan \delta$
    - ARES G2 DMA is standard function (50 $\mu$m amplitude)
    - DMA is an optional DHR function (100 $\mu$m amplitude)

Rectangular and cylindrical torsion
DMA 3-point bending and tension (cantilever not shown)
## Geometry Overview

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Application</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone/plate</td>
<td>fluids, melts viscosity &gt; 10mPas</td>
<td>true viscosities</td>
<td>temperature ramp difficult</td>
</tr>
<tr>
<td>Parallel Plate</td>
<td>fluids, melts viscosity &gt; 10mPas</td>
<td>easy handling, temperature ramp</td>
<td>shear gradient across sample</td>
</tr>
<tr>
<td>Couette</td>
<td>low viscosity samples &lt; 10 mPas</td>
<td>high shear rate</td>
<td>large sample volume</td>
</tr>
<tr>
<td>Double Wall Couette</td>
<td>very low viscosity samples &lt; 1mPas</td>
<td>high shear rate</td>
<td>cleaning difficult</td>
</tr>
<tr>
<td>Torsion Rectangular</td>
<td>solid polymers, composites</td>
<td>glassy to rubbery state</td>
<td>Limited by sample stiffness</td>
</tr>
<tr>
<td>DMA</td>
<td>Solid polymers, films, Composites</td>
<td>Glassy to rubbery state</td>
<td>Limited by sample stiffness (Oscillation and stress/strain)</td>
</tr>
</tbody>
</table>
Rheometer Calibrations and Performance Verification
DHR – Calibration Options

- Instrument Calibrations
  - Inertia (Service)
  - Rotational Mapping

- Geometry Calibrations:
  - Inertia
  - Friction
  - Gap Temperature Compensation
  - Rotational Mapping

- Details in Appendix #4
ARES-G2 – Calibration Options

- Instrument Calibrations
  - Transducer
  - Temperature Offsets
  - Phase Angle (Service)
  - Measure Gap Temperature Compensation

- Geometry Calibrations:
  - Compliance and Inertia (from table)
  - Gap Temperature Compensation

- Details in Appendix #4
Verify Rheometer Performance

- Rheometers are calibrated from the factory and again at installation.
- TA recommends routine validation or confidence checks using standard oils or Polydimethylsiloxane (PDMS).

- PDMS is verified using a 25 mm parallel plate.
  - Oscillation - Frequency Sweep: 1 to 100 rad/s with 5% strain at 30°C
  - Verify modulus and frequency values at crossover

- Standard silicone oils can be verified using cone, plate or concentric cylinder configurations.
  - Flow – Ramp: 0 to 88 Pa at 25°C using a 60 mm 2° cone
    - Service performs this test at installation
PDMS Frequency Sweep Results

- **Crossover modulus**: 271,160 dyn/cm²
- **Crossover ω value**: 5.38927 rad/s

Diagram showing:
- Storage modulus $G'$ (dyne/cm²)
- Loss modulus $G''$ (dyne/cm²)
- Complex viscosity $\eta^*$ (poise)

Angular frequency $\omega$ (rad/s) on the x-axis, with logarithmic scales on the y-axis for $G'$ and $G''$, and a linear scale for $\eta^*$.
Load Standard Oil

- Set Peltier temperature to 25°C and equilibrate.
  - Zero the geometry gap

- Load sample
  - Be careful not to introduce air bubbles!

- Set the gap to the trim gap

- Lock the head and trim with non-absorbent tool
  - Important to allow time for temperature equilibration.

- Go to geometry gap and initiate the experiment.
Flow Ramp – Standard Oil (Service Test)

Viscosity $\eta$ (Pa.s)
Mean = 0.956150
SD = 1.0412e-3
Rel. SD = 1.08901e-3
Var. = 1.08422e-6
Points 20-593

Viscosity Standard 1000cp Normal
Viscosity: 965cp @ 25 D42612
Setting up Rheological Experiments
Flow Tests
Viscosity: Definition

- **Viscosity is…**
  - “lack of slipperiness”
  - synonymous with internal friction
  - resistance to flow

- **The Units of Viscosity are …**
  - SI unit is the Pascal-second (Pa·s)
  - cgs unit is the Poise
  - $10 \text{ Poise} = 1 \text{ Pa·s}$
  - $1 \text{ cP (centipoise)} = 1 \text{ mPa·s (millipascal second)}$
Equation for Viscosity

\[ \eta = \frac{\sigma}{\dot{\gamma}} = \frac{M}{\Omega} \cdot \frac{K_\sigma}{K_\gamma} \]

- **Rheological Parameter**: \( \eta \)
- **Constitutive Equation**: \( \frac{\sigma}{\dot{\gamma}} \)
- **Raw Rheometer Specifications**: \( \frac{M}{\Omega} \)
- **Geometric Shape Constants**: \( \frac{K_\sigma}{K_\gamma} \)

In Spec

Describe Correctly
<table>
<thead>
<tr>
<th>Material</th>
<th>Viscosity Value (Pa-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt Binder</td>
<td>100,000</td>
</tr>
<tr>
<td>Polymer Melt</td>
<td>1,000</td>
</tr>
<tr>
<td>Molasses</td>
<td>100</td>
</tr>
<tr>
<td>Liquid Honey</td>
<td>10</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1</td>
</tr>
<tr>
<td>Olive Oil</td>
<td>0.01</td>
</tr>
<tr>
<td>Water</td>
<td>0.001</td>
</tr>
<tr>
<td>Air</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

Need for Log scale
Newtonian and Non-Newtonian Fluids

- **Newtonian Fluids** - constant proportionality between shear stress and shear-rate

- **Non-Newtonian Fluids** - Viscosity is time or shear rate dependent
  - **Time:**
    - At constant shear-rate, if viscosity
    - Decreases with time – Thixotropy
    - Increases with time - Rheopexy
  - **Shear-rate:**
    - Shear - thinning
    - Shear - thickening
Characteristic Diagrams for Newtonian Fluids

- Ideal Yield Stress (Bingham Yield)
- \( \sigma, \text{Pa} \)
- \( \dot{\gamma}, \text{1/s} \)
- \( \eta, \text{Pa.s} \)

\( \gamma, \text{1/s} \) or \( \sigma, \text{Pa} \)
Characteristic Diagrams for Shear Thinning Fluids

- Another name for a shear thinning fluid is a pseudo-plastic
Dilatant material resists deformation more than in proportion to the applied force (shear-thickening).

Cornstarch in water or sand on the beach are actually dilatant fluids, since they do not show the time-dependent, shear-induced change required in order to be labeled rheopectic.
Non-Newtonian, Time Dependent Fluids

- Rheopectic materials become more viscous with increasing time of applied force.
- Higher concentration latex dispersions and plastisol paste materials exhibit rheopectic behavior.
- Thixotropic materials become more fluid with increasing time of applied force.
- Coatings and inks can display thixotropy when sheared due to structure breakdown.
Flow Experiments

- Flow Experiments
  - Constant shear rate/stress (or Peak hold)
  - Continuous stress/rate ramp and down
  - Stepped flow (or Flow sweep)
  - Steady state flow
  - Flow temperature ramp
Constant Shear Rate/Stress

- Constant rate vs. time
- Constant stress vs. time

USES
- Single point testing
- Scope the time for steady state under certain rate
Constant Shear Rate/Stress

Hand Wash Rate 1/s

Viscosity at 1 1/s is 2.8 Pa·s
Stress is applied to material at a constant rate. Resultant strain is monitored with time.

**USES**
- Yield stress
- Scouting Viscosity Run
Stress Ramp: Flow Media Dispersion

Stress Ramp: Dispersion

Yield Stress 10.4 Pa
Stress is first increased, then decreased, at a constant rate. Resultant strain is monitored with time.

USES
- “Pseudo-thixotropy” from Hysteresis loop
Up & Down Flow Curves - 2 Repeats

Run in Stress Control

shear stress (Pa)

shear rate (1/s)

Red: First cycle
Blue: Second cycle
Stressed or Steady-State Flow

- Stress is applied to sample. Viscosity measurement is taken when material has reached steady state flow. The stress is increased (logarithmically) and the process is repeated yielding a viscosity flow curve.

**USES**
- Viscosity Flow Curves
- Yield Stress Measurements
Stepped or Steady-State Flow

- A series of logarithmic stress steps allowed to reach steady state, each one giving a single viscosity data point:

\[ \eta = \sigma / (d\gamma/dt) \]
DHR and ARES G2: Steady State Flow

1: Flow Sweep

Control variables:
- Shear rate
- Velocity
- Torque
- Shear stress

Steady state algorithm
Flow Sweeps - Water-Based Paint with Solvent Trap
Comparison of Cough Syrups

Which material would do a better job coating your throat?
Comparison of Two Latex Paints

- Low shear rates: B > A
- Medium shear rates: A > B
- High shear rates: B > A
Flow Temperature Ramp

- Hold the rate or stress constant whilst ramping the temperature.

**USES**
- Measure the viscosity change vs. temperature
Viscosity: Temperature Dependence

Notice a nearly 2 decade decrease in viscosity. This displays the importance of thermal equilibration of the sample prior to testing. i.e. Conditioning Step or equilibration time for 3 to 5 min
Flow Testing Considerations

- Small gaps give high shear rates
  - Be careful with small gaps:
    - Gap errors (gap temperature compensation) and shear heating can cause large errors in data.
    - Recommended gap is between 0.5 to 2.0 mm.
    - Secondary flows can cause increase in viscosity curve

- Be careful with data interpretation at low shear rates
  - Surface tension can affect measured viscosity, especially with aqueous materials
Water at 25°C – Secondary Flow

![Graph showing viscosity vs. shear rate for different samples.
- Surface tension at low torques
- Secondary flows at high shear rates

Legend:
- 40mm PP 1mm Water
- 40mm 2 Deg Cone Water
- DIN CC Water
- 40mm 2 Deg Cone N1 Oil]
Wall Slip

- Wall slip can manifest as “apparent double yielding”
- Can be tested by running the same test at different gaps
- For samples that don’t slip, the results will be independent of the gap
When Stress Decreases with Shear Rate, it indicates that sample is leaving the gap.
Flow Testing Considerations

- **Edge Failure** – Sample leaves gap because of normal forces
  - Look at stress vs. shear rate curve – stress should not decrease with increasing shear rate – this indicates sample is leaving gap

- **Possible Solutions:**
  - use a smaller gap or smaller angle so that you get the same shear rate at a lower angular velocity
  - if appropriate (i.e. Polymer melts) make use of Cox Merz Rule

\[ \eta(\dot{\gamma}) = \eta^*(\omega) \]
Viscoelasticity
Elastic Behavior of an Ideal Solid

Hooke’s Law of Elasticity: Stress = Modulus \cdot Strain

\[ \sigma = E \cdot \gamma \]
Elastic Behavior of an Ideal Solid

Hooke’s Law of Elasticity: Stress = Modulus \cdot Strain

\[ E > E > E \]

\[ E = \frac{\sigma}{\gamma} \]
Viscous Behavior of an Ideal Liquid

Newton’s Law: stress
\[ \sigma = \eta \cdot \dot{\gamma} \]

\( \eta \)

Stress (\( \sigma \))

Shear Rate (\( \dot{\gamma} \))
Viscous Behavior of an Ideal Liquid

Newton’s Law: stress = coefficient of viscosity \cdot shear rate

\[ \eta = \frac{\sigma}{\dot{\gamma}} \]
Viscoelastic Behavior

\[ \sigma = E \varepsilon + \eta \frac{d\varepsilon}{dt} \]

Kelvin-Voigt Model (Creep)  Maxwell Model (Stress Relaxation)

Viscoelastic Materials: Force depends on both Deformation and Rate of Deformation and vice versa.
Viscoelasticity Defined

Range of Material Behavior

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

Ideal Fluid ----- Most Materials ----- Ideal Solid
Purely Viscous ----- Viscoelastic ----- Purely Elastic

*Viscoelasticity*: Having both viscous and elastic properties

- Materials behave in the linear manner, as described by Hooke and Newton, only on a small scale in stress or deformation.
Pitch Drop Experiment

- Long deformation time: pitch behaves like a highly viscous liquid
  - 9th drop fell July 2013
- Short deformation time: pitch behaves like a solid

Started in 1927 by Thomas Parnell in Queensland, Australia

Time-Dependent Viscoelastic Behavior

T is short [< 1s]  T is long [24 hours]
Time-Dependent Viscoelastic Behavior

- Silly Putties have different characteristic relaxation times
- Dynamic (oscillatory) testing can measure time-dependent viscoelastic properties more efficiently by varying frequency (deformation time)
Viscoelasticity, Deborah Number

- Old Testament Prophetess who said (Judges 5:5): "The Mountains ‘Flowed’ before the Lord"

- Everything Flows if you wait long enough!

- Deborah Number, $De$ - The ratio of a characteristic relaxation time of a material ($\tau$) to a characteristic time of the relevant deformation process ($T$).

\[
De = \frac{\tau}{T}
\]
Deborah Number

- Hookean elastic solid - $\tau$ is infinite
- Newtonian Viscous Liquid - $\tau$ is zero
- Polymer melts processing - $\tau$ may be a few seconds

<table>
<thead>
<tr>
<th>High De</th>
<th>Solid-like behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low De</td>
<td>Liquid-like behavior</td>
</tr>
</tbody>
</table>

**IMPLICATION**: Material can appear solid-like because
1) it has a very long characteristic relaxation time or
2) the relevant deformation process is very fast
Time and Temperature Relationship

- Log E' (G') and E'' (G'') vs. Log Frequency
- Log E' (G') and E'' (G'') vs. Temperature
- Log Jc vs. Log Time
- Log E (t) or G (t) vs. Log Time
"If the deformation is small, or applied sufficiently slowly, the molecular arrangements are never far from equilibrium.

The mechanical response is then just a reflection of dynamic processes at the molecular level which go on constantly, even for a system at equilibrium.

This is the domain of **LINEAR VISCOELASTICITY**.

*The magnitudes of stress and strain are related linearly*, and the behavior for any liquid is completely described by a single function of time."

Importance of LVR

Rheology

Linear Viscoelastic Properties

E' (or G'), E'' (or G''), tan δ, η*

Measuring linear viscoelastic properties helps us bridge the gap between molecular structure and product performance.
Setting up Rheological Experiments
Oscillatory Tests
Understanding Oscillation Experiments

- Define Oscillation Testing

- Approach to Oscillation Experimentation
  - Stress and Strain Sweep
  - Time Sweep
  - Frequency Sweep
  - Temperature Ramp
  - Temperature Sweep (TTS)
What is Oscillation?

Dynamic stress applied sinusoidally
User-defined Stress or Strain amplitude and frequency
Frequency Defined

- Time to complete one oscillation
- Frequency is the inverse of time
- Units
  - Angular Frequency = radians/second
  - Frequency = cycles/second (Hz)
- Rheologist must think in terms of rad/s.
  - 1 Hz = 6.28 rad/s
Frequency

- $\omega = 6.28 \text{ rad/s}$
- $\omega = 12.560 \text{ rad/s}$
- $\omega = 50 \text{ rad/s}$

Time = 1 sec
Amplitude: Strain or Stress

- Strain and stress are calculated from peak amplitude in the displacement and torque waves, respectively.
Dynamic Mechanical Testing

- An oscillatory (sinusoidal) deformation (stress or strain) is applied to a sample.
- The material response (strain or stress) is measured.
- The phase angle $\delta$, or phase shift, between the deformation and response is measured.
Dynamic Testing: Response for Classical Extremes

Purely Elastic Response
(Hookean Solid)

\[ \delta = 0^\circ \]

Purely Viscous Response
(Newtonian Liquid)

\[ \delta = 90^\circ \]
Dynamic Testing: Viscoelastic Material Response

Phase angle $0^\circ < \delta < 90^\circ$

- Strain
- Stress
**Viscoelastic Parameters: Complex, Elastic, & Viscous Stress**

- The stress in a dynamic experiment is referred to as the complex stress $\sigma^*$
- The complex stress can be separated into two components:
  1) An elastic stress in phase with the strain. $\sigma' = \sigma^* \cos \delta$
     $\sigma'$ is the degree to which material behaves like an elastic solid.
  2) A viscous stress in phase with the strain rate. $\sigma'' = \sigma^* \sin \delta$
     $\sigma''$ is the degree to which material behaves like an ideal liquid.

**Phase angle $\delta$**

**Complex Stress, $\sigma^*$**

$$\sigma^* = \sigma' + j\sigma''$$

Complex number: $|x + iy| = \sqrt{x^2 + y^2}$

The material functions can be described in terms of complex variables having both real and imaginary parts. Thus, using the relationship:

$$\cos x + j \sin x = e^{jx}$$

where $j = \sqrt{-1}$
Viscoelastic Parameters

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

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

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

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

\[
G^* = \left( \frac{\text{Stress}^*}{\text{Strain}} \right)
\]

\[
G' = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \cos \delta
\]

\[
G'' = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \sin \delta
\]

\[
\tan \delta = \left( \frac{G''}{G'} \right)
\]
Storage and Loss of a Viscoelastic Material

Dynamic measurement represented as a vector
Complex Viscosity

The viscosity measured in an oscillatory experiment is a Complex Viscosity much the way the modulus can be expressed as the complex modulus. The complex viscosity contains an elastic component and a term similar to the steady state viscosity.

The Complex viscosity is defined as:

\[ \eta^* = \eta' + i \eta'' \]

or

\[ \eta^* = G^*/\omega \]

Note: frequency must be in rad/sec!
## Dynamic Rheological Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Shear</th>
<th>Elongation</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain</td>
<td>$\gamma = \gamma_0 \sin(\omega t)$</td>
<td>$\epsilon = \epsilon_0 \sin(\omega t)$</td>
<td>---</td>
</tr>
<tr>
<td>Stress</td>
<td>$\sigma = \sigma_0 \sin(\omega t + \delta)$</td>
<td>$\tau = \tau_0 \sin(\omega t + \delta)$</td>
<td>Pa</td>
</tr>
<tr>
<td>Storage Modulus (Elasticity)</td>
<td>$G' = (\sigma_0 / \gamma_0) \cos \delta$</td>
<td>$E' = (\tau_0 / \epsilon_0) \cos \delta$</td>
<td>Pa</td>
</tr>
<tr>
<td>Loss Modulus (Viscous Nature)</td>
<td>$G'' = (\sigma_0 / \gamma_0) \sin \delta$</td>
<td>$E'' = (\tau_0 / \epsilon_0) \sin \delta$</td>
<td>Pa</td>
</tr>
<tr>
<td>Tan $\delta$</td>
<td>$G'' / G'$</td>
<td>$E'' / E'$</td>
<td>---</td>
</tr>
<tr>
<td>Complex Modulus</td>
<td>$G^* = (G'^2 + G''^2)^{0.5}$</td>
<td>$E^* = (E'^2 + E''^2)^{0.5}$</td>
<td>Pa</td>
</tr>
<tr>
<td>Complex Viscosity</td>
<td>$\eta^* = G^* / \omega$</td>
<td>$\eta_{E}^* = E^* / \omega$</td>
<td>Pa·sec</td>
</tr>
</tbody>
</table>

Cox-Merz Rule for Linear Polymers: $\eta^*(\omega) = \eta(\dot{\gamma})$ @ $\dot{\gamma} = \omega$
Understanding Oscillation Experiments

- Define Oscillation Testing

- Approach to Oscillation Experimentation
  1. Stress and Strain Sweep
  2. Time Sweep
  3. Frequency Sweep
  4. Temperature Ramp
  5. Temperature Sweep (TTS)
The material response to increasing deformation amplitude (strain or stress) is monitored at a constant frequency and temperature.

- Main use is to determine LVR
  - All subsequent tests require an amplitude found in the LVR
- Tests assumes sample is stable
- If not stable use Time Sweep to determine stability
Dynamic Strain Sweep: Material Response

Linear Region:
Modulus independent of strain

Non-linear Region:
Modulus is a function of strain

\( G' \)

\( \gamma_c = \text{Critical Strain} \)

Stress

Constant Slope

Strain (amplitude)
Temperature Dependence of LVR

- In general, the LVR is shortest when the sample is in its most solid form.
Frequency Dependence of LVR

- LVR decreases with increasing frequency
- Modulus increases with increasing frequency
SAOS versus LAOS Waveforms

Linear response to a sinusoidal excitation is sinusoidal and represented by the fundamental in the frequency domain.

Nonlinear response to a sinusoidal excitation is not sinusoidal and represented in the frequency domain by the fundamental and the harmonics.
**SAOS**

\[ \gamma(t) = \gamma_0 \sin(\omega t) \]

\[ \tau(t) = \tau_0 \sin(\omega t + \delta) \]

**LAOS**

\[ \gamma(t) = \gamma_0 \sin(\omega t) \]

Fourier Series expansion:

\[ \tau(t) = \tau_1 \sin(\omega_1 t + \phi_1) + \tau_3 \sin(3\omega_1 t + \phi_3) + \]

\[ + \tau_5 \sin(5\omega_1 t + \phi_5) + \ldots \]

\[ = \sum_{n=1}^{\infty} \tau_n \sin(n\omega_1 + \phi_n) \]

Lissajous plot: Stress vs. Strain (shown)
or stress vs. Shear rate
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
Importance of Time Sweep

- Important, but often overlooked
  - Visually observe the sample
- Determines if properties are changing over the time of testing
  - Complex Fluids or Dispersions
    - Preshear or effects of loading
    - Drying or volatilization (use solvent trap)
    - Thixotropic or Rheopectic
  - Polymers
    - Degradation (inert purge)
    - Crosslinking
Time Sweep on PEEK Melt - Thermal Stability

2000G time sweep at 400°C

Under N2

Under air
Time Sweep on Latex

Structural Recovery after Preshear

\[ G'(\text{Pa}) \]

\[ \text{time (s)} \]
Importance of Waiting for Structure Rebuild

Sample “A” time sweep

- Delay after pre-shear = 150 sec
- Delay after pre-shear = 0 sec

Pre-shear conditions:
100 1/s for 30 seconds

End of LVR is indicative of “Yield” or “Strength of Structure”

Useful for Stability predictions (stability as defined by yield)
Solvent Trap System for Effective Evaporation Control

Solvent trap cover picks up heat from Peltier Plate to insure uniform temperature
Cure of a "5 Minute" Epoxy

Gel Point: $G' = G''$
$t = 330$ s
**Frequency Sweep**

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

- Strain should be in LVR

- Sample should be stable

- Remember – Frequency is 1/time so low frequencies will take a long time to collect data – i.e. 0.001Hz is 1000 sec (over 16 min)
Frequency Sweep: Material Response

- Terminal Region
- Rubbery Plateau Region
- Transition Region
- Glassy Region

Log $E'$ (G') and $E''$ (G'') vs. Log Frequency (rad/s or Hz)

Storage Modulus (E' or G')
Loss Modulus (E'' or G'')
Frequency Sweep - Time Dependent Viscoelastic Properties

Frequency of modulus crossover correlates with Relaxation Time
Cox-Merz Example - LDPE at 190°C

\[ \eta(\dot{\gamma}) \equiv \eta^*(\omega) \]

Flow instability

LDPE Freq sweep 2mm gap – Cox Merz
LDPE shear rate 1mm gap
LDPE Shear rate 2 mm gap
Importance of Frequency Sweeps

- High and low rate (short and long time) properties
- Viscosity Information - Zero Shear Viscosity, shear thinning
- Elasticity (reversible deformation) in materials
- MW & MWD differences polymer melts and solutions
- Finding yield in gelled dispersions
- Can extend time or frequency range with TTS

\[ \eta_0 \approx M_w^{3.4} \text{ and } J_e = \frac{G'}{(G'')^2} \approx \left( \frac{M_w}{M_z} \right)^{3.4} \]
Frequency in DHR Rheometer

- DHR has a combined motor and transducer design.
  - In an DHR rheometer, the applied motor torque and the measured amplitude are coupled.
  - The moment of inertia required to move the motor and geometry (system inertia) is coupled with the angular displacement measurements.
  - This means that **BOTH** the system inertia and the sample contributes to the measured signal.
Inertial Effects

- What is Inertia?
  - **Definition**: That property of matter which manifests itself as a resistance to any change in momentum of a body
  - Instrument has inertia
  - Sample has inertia
Inertial Effects in Oscillation for DHR

- Inertia consideration
  - Viscosity limitations with frequency
  - Minimize inertia by using low mass geometries
  - Monitor inertia using Raw Phase in degree
  - When Raw Phase is greater than:
    - 150° degrees for AR series
    - 175° degrees for DHR series
    - This indicates that the system inertia is dominating the measurement signal. Data may not be valid

Raw Phase $\times$ Inertia Correction = delta
DHR Correction for Inertia

Access to raw phase angle only available with TA Instruments Rheometers!

Waveforms at high frequencies

Inertial effects at high frequencies

Negligible correction at low frequencies
Frequency Sweeps in ARES-G2

- ARES-G2 has a separate motor and transducer design.
  - In an ARES-G2, the motor applies the deformation independent of the torque measurement on the transducer.
  - The moment of inertia required to move the motor is decoupled from the torque measurements.
  - This means the motor inertia does not contribute to the test results.

- Benefits of ARES-G2:
  - System inertia free
  - Capable of running low viscosity samples up to high frequency
Motor inertia **NOT** part of Measurement

Motor torque and sample torque are separated.

**Purest Measurement !**
A linear heating rate is applied. The material response is monitored at a constant frequency and constant amplitude of deformation. Data is taken at user defined time intervals.
A step and hold temperature profile is applied. The material response is monitored at one, or over a range of frequencies, at constant amplitude of deformation.

- No thermal lag
Dynamic Temperature Ramp or Sweep: Material Response

- Glassy Region
- Transition Region
- Rubbery Plateau Region
- Terminal Region

Log $E'$ ($G'$) and $E''$ ($G''$)

- Storage Modulus ($E'$ or $G'$)
- Loss Modulus ($E''$ or $G''$)

Temperature
Why look at temperature dependence?

- Solid in torsion rectangular
  - Look at $T_g$, secondary transitions and study structure-property relationships of finished product.
- Themosetting polymers
  - Follow curing reactions
- Polymer melts and other liquids
  - Measure temperature dependence of viscoelastic properties
Acrylonitrile Butadiene Styrene (ABS)
DHR: Axial Force Control

- It is important to setup normal force control during any temperature change testing or curing testing.
- Some general suggestions for normal force control:
  - For torsion testing, set normal force in tension: 1-2N ± 0.5-1.0N
  - For curing or any parallel plate testing, set normal force in compression: 0 ± 0.5N
Using Axial Force Control in a Thermosetting Material
TA Tech Tip – Axial Force Control

- Videos available at [www.tainstruments.com](http://www.tainstruments.com) under the Videos tab or on the TA tech tip channel of YouTube™ ([https://www.youtube.com/user/TATechTips](https://www.youtube.com/user/TATechTips))
Cure or Thermoset Materials

- Cures are perhaps the most challenging experiments to conduct on rheometers as they challenge all instrument specifications both high and low.
- The change in modulus as a sample cures can be as large as 7-8 decades and change can occur very rapidly.
- **AR, DHR, and ARES** instruments have ways of trying to cope with such large swings in modulus
  - **AR:** *Non-iterative sampling* (w/ Axial force control)
  - **DHR:** *Non-iterative sampling* (w/ Axial force control) and *Auto-strain* (w/ Axial force active) in **TRIOS v3.2 or higher**
  - **ARES:** *Auto-strain* (w/ Axial force or auto-tension active)
Thermosetting Polymers

At start of test have a material that starts as liquid, paste, pressed power Pellet, or prepreg.

As the temp increases, the viscosity of resin decreases.

Crosslinking reaction causes h and G’ to increase.

Material hits minimum viscosity which depends on Max temperature, frequency, ramp rate and may depend on strain or stress amplitude.

Material fully cured, Maximum h or G’ reached.

---

η or G’

Temp

Time
DHR and AR: Data Collection Options

- **Non-Iterative Sampling** – motor torque is adjusted based on previous stress value and predicts new value required to obtain the target strain (good for rapid measurements)

- **Precision Sampling** – motor torque is adjusted at the end of an oscillation cycle in order to reach commanded strain

- **Continuous Oscillation (direct strain)** – motor torque is adjusted during the oscillation cycle to apply the commanded strain

*Continuous oscillation only available with DHR-2 and DHR-3*
Continuous Oscillation on Single Head Rheometer

**Continuous oscillation (or direct strain control):** incremental approach controls the strain and hits the target during a single cycle

**Non-iterative:** uses the settings entered for the first data point and then uses previous cycle

**Precision:** iterates using the initial settings entered for each data point
Concern: How high does strain go at minimum viscosity. Does higher strain inhibit the cure (break structure that begins to form as material crosslinks). Does this affect time to minimum viscosity or gel time?
ARIES, ARES-G2 and DHR: Auto-Strain

![Graph showing time, torque, strain, and temperature changes](image-url)

- Time
- Torque
- Strain
- Temperature
- Upper torque limit
- Lower torque limit

Legend:
- $\eta$ or $G'$
# Axial Force Control and Auto-strain

## ARES-G2

### 1: Conditioning Options

**Axial force adjustment**
- **Mode**: Active
- **Axial force**: 2.0 N (set initial value)
- **Sensitivity**: 0.1 N

**Advanced**
- **Max gap change up**: 2.0 mm
- **Max gap change down**: 0.5 mm
- **Return to window**: Return to initial value
- **Priority**: Data sampling, Force control

**Adjustment time out**: 20 s

**Auto strain adjustment**
- **Mode**: Enabled
- **Strain adjust**: 20.0 %
- **Minimum strain**: 0.01 %
- **Maximum strain**: 5.0 %
- **Minimum torque**: 1.0 μN.m
- **Maximum torque**: 500.0 μN.m

## DHR

### 1: Conditioning Options

**Axial force adjustment**
- **Mode**: Active
- **Axial force**: 0.0 g (set initial value)
- **Sensitivity**: 20.0 g

**Advanced**
- **Gap change limit up**: 1000.0 μm
- **Gap change limit down**: 1000.0 μm
- **Return to window**: Return to initial value

**Purge gas only (no active cooling)**

**Auto strain adjustment**
- **Mode**: Enabled
- **Strain adjust**: 20.0 %
- **Displacement**: % Strain
- **Minimum % strain**: 0.0 %
- **Maximum % strain**: 0.0 %
- **Torque**: 0.0 μN.m
- **Stress**: 0.0 μN.m
- **Minimum torque**: 0.0 μN.m
- **Maximum torque**: 0.0 μN.m
Using Auto Strain in a Temperature Ramp-Up

1: Conditioning Options

- Auto strain adjustment
  - Mode: Enabled
  - Strain adjust: 20.0 %
  - Minimum strain: 1.0e-3 %
  - Maximum strain: 1.0 %
  - Minimum torque: 10.0 µN.m
  - Maximum torque: 100.0 µN.m

Test Parameters

- Sampling rate: 1.0 pts/s
- Strain %: 0.01 %
- Angular frequency: 10.0 rad/s

Graph showing storage modulus, loss modulus, oscillation strain, and oscillation torque against temperature. The graph indicates a change in strain and torque as temperature increases, with strain increasing to maintain minimum torque and an example of minimum torque and oscillation torque.
Using Auto Strain in a Temperature Ramp- Down

1: Conditioning Options

- Auto strain adjustment
  - Mode: Enabled
  - Strain adjust: 20.0 %
  - Minimum strain: 1.0e-3 %
  - Maximum strain: 1.0 %
  - Minimum torque: 10.0 μN.m
  - Maximum torque: 100.0 μN.m

Graph:
- Temperature $T$ (°C)
- Storage modulus $G$ (Pa)
- Oscillation torque $T$ (μN.m)
- Oscillation strain $\gamma$ (%)
Thermoset Testing Considerations

- **Strain**
  - Depends on sample
  - Verify the LVR in the cured state (e.g. 0.05%)
- **Normal force control or auto-tension**
  - Requires active to adjust for sample shrinkage and/or thermal expansion in parallel plates
- **Temperature**
  - Isothermal
  - Fast ramp + isotherm: the fastest ramp rate
  - Continuous ramp rate: 3 – 5 °C/min.
- **Frequency**
  - Typically 1Hz (6.28 rad/s), 10 rad/s or higher
Setting up Rheological Experiments
Transient Tests
Stress Relaxation Experiment

- Strain is applied to sample instantaneously (in principle) and held constant with time.
- Stress is monitored as a function of time $\sigma(t)$.
- DHR and AR
  - Response time dependent on feedback loop
Stress Relaxation Experiment

Response of Classical Extremes

**Elastic**
Hookean Solid

- Stress for $t>0$ is constant

**Viscous**
Newtonian Fluid

- Stress for $t>0$ is 0
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, \( G(t) \)

\[
G(t) = \frac{\sigma(t)}{\gamma}
\]
Stress Relaxation: Material Response

log Stress Relaxation Modulus E(t) or G(t)

log time

Glassy Region
Transition Region
Rubbery Plateau Region
Terminal Region
Stress Relaxation on PDMS
Determining Strain For Stress Relaxation

- **Research Approach**, such as generation of a family of curves for TTS, then the strain should be in the linear viscoelastic region. The stress relaxation modulus will be independent of applied strain (or will superimpose) in the linear region.

- **Application Approach**, mimic real application. Then the question is "what is the range of strain that I can apply on the sample?" This is found by knowing the Strain range the geometry can apply.
  - The software will calculated this for you.

\[ \gamma = K_\gamma \times \theta \quad (\%\gamma = \gamma \times 100) \]
Stress Relaxation and Linear Region

Stress Relaxation of PDMS, Overlay

200% strain is outside the linear region
Creep Recovery Experiment

- Stress is applied to sample instantaneously, $t_1$, and held constant for a specific period of time. The strain is monitored as a function of time ($\gamma(t)$ or $\varepsilon(t)$).
- The stress is reduced to zero, $t_2$, and the strain is monitored as a function of time ($\gamma(t)$ or $\varepsilon(t)$).
- Native mode on AR (<1 msec)
Creep Recovery Experiment

Response of Classical Extremes

**Elastic**
- Strain for \( t > t_1 \) is constant
- Strain for \( t > t_2 \) is 0

**Viscous**
- Strain rate for \( t > t_1 \) is constant
- Strain for \( t > t_1 \) increase with time
- Strain rate for \( t > t_2 \) is 0
Creep: Material Response

- Glassy Region
- Transition Region
- Rubbery Plateau Region
- Terminal Region

Log Creep Compliance, \( J_c \) vs. Log Time
Creep Recovery: Response of Viscoelastic Material

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

Creep Recovery: 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 an equilibrium at some small total strain relative to the strain at unloading.

Creep Recovery Experiment

Creep Zone: Creep $\sigma > 0$

Recovery Zone: Recovery $\sigma = 0$ (after steady state)

More Elastic

Less Elastic

$\sigma/\eta$

$t_1$ $t_2$

time

Strain
Creep Recovery: Creep and Recoverable Compliance

Creep Compliance

\[ J(t) = \frac{\gamma(t)}{\sigma} \]

The material property obtained from Creep experiments: Compliance = 1/Modulus (in a sense)

Recoverable Compliance

\[ J_r(t) = \frac{[\gamma_u - \gamma(t)]}{\sigma} \]

Where \( \gamma_u = \text{Strain at unloading} \)
\( \gamma(t) = \text{time dependent recoverable strain} \)

Viscoelastic Ringing – DHR or AR

- The ringing oscillations can be rather short-lived and may not be apparent unless using log time scale.
- The sudden acceleration, together with the measurement system’s inertia, causes a strain overshoot. For viscoelastic materials, this can result in viscoelastic ringing, where the material undergoes a damped oscillation just like a bowl of Jell-o when bumped.

Creep ringing in rheometry or how to deal with oft-discarded data in step stress tests!
ARES-G2 Stress Control Loop

- Stress is controlled by closing the loop around the sample \( \rightarrow \) requires optimization of control PID parameters
- Pretest to determine material’s response and PID Constants
Programming Creep on an ARES-G2

- Set up a pre-test and get the sample information into the loop
- Stress Control Pre-test: frequency sweep within LVR

1: Conditioning Stress Control
- Load Precomputed
- Run and Calculate

Environmental Control
- Temperature: 30 °C
- Soak time: 60.0 s
- Inherit set point
- Wait for temperature

Test Parameters
- Strain %: 0.05

Save stress control PID file
- Stress control PID file path: W:\2011\creep.creak
- Save File

Data acquisition
- 2: Step (Transient) Creep 25°C, 60s, 100Pa
ARES-G2 Stress Control Pretest

Pretest → Frequency Sweep from 2 to 200 rad/s → data analyzed in software to optimize Motor loop control PID constants

LDPE melt
Freq. Sweep
T = 190°C
Creep on HDPE Melt

HDPE Creep Recovery at 200°C
Determining Stress For Creep Experiment

- **Research Approach** - If you are doing creep on a polymer melt, and are interested in viscoelastic information (creep and recoverable compliance), then you need to conduct the test at a stress within the linear viscoelastic region of the material.

- **Application Approach** - If you are doing creep on a solid, you want to know the dimension change with time under a specified stress and temperature, then the question is "what is the max/min stress that I can apply to the sample?". This is found by knowing the Stress range the geometry can apply.
  - The software will calculated this for you.

\[
\sigma = K_\sigma \times M
\]
Applications of Rheology
Polymers
Three main reasons for rheological testing:

- **Characterization**
  MW, MWD, formulation, state of flocculation, etc.

- **Process performance**
  Extrusion, blow molding, pumping, leveling, etc.

- **Product performance**
  Strength, use temperature, dimensional stability, settling stability, etc.
Polymer Testing and Rheology

**Molecular Structure**
- MW and MWD
- Chain Branching and Cross-linking
- Interaction of Fillers with Matrix Polymer
- Single or Multi-Phase Structure

**Viscoelastic Properties**
As a function of:
- Strain Rate (frequency)
- Strain Amplitude
- Temperature

Processability & Product Performance
## Rheology Applications in Polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composites, Thermosets</td>
<td>Viscosity, Gelation, Rate of Cure, Effect of Fillers and Additives</td>
</tr>
<tr>
<td>Cured Laminates</td>
<td>Glass Transition, Modulus Damping, impact resistance, Creep, Stress Relaxation, Fiber orientation, Thermal Stability</td>
</tr>
<tr>
<td>Thermoplastics</td>
<td>Blends, Processing effects, stability of molded parts, chemical effects</td>
</tr>
<tr>
<td>Elastomers</td>
<td>Curing Characteristics, effect of fillers, recovery after deformation</td>
</tr>
<tr>
<td>Coating, Adhesives</td>
<td>Damping, correlations, rate of degree of cure, glass transition temperature, modulus</td>
</tr>
</tbody>
</table>
Most Common Experiments on Polymers

- **Oscillation/Dynamic**
  - Time Sweep
    - Degradation studies, stability for subsequent testing
  - Strain Sweep – Find LVER
  - Frequency Sweep – $G'$, $G''$, $\eta^*$
    - Sensitive to MW/MWD differences melt flow can not see
  - Temperature Ramp/Temperature Step
    - Transitions, viscosity changes
  - TTS Studies

- **Flow/Steady Shear**
  - Viscosity vs. Shear Rate Plots
  - Find Zero Shear Viscosity
  - Low shear information is sensitive to MW/MWD differences melt flow can not see

- **Creep and Recovery**
  - Creep Compliance/Recoverable Compliance
  - Very sensitive to long chain tails
Polymer Melt Thermal Stability

Determines if properties are changing over the time of testing
- Degradation
- Molecular weight building
- Crosslinking

![Graph showing modulus G' and temperature stability over time]

**Important, but often overlooked!**
Idealized Flow Curve – Polymer Melts

First Newtonian Plateau
\[ \eta_0 = \text{Zero Shear Viscosity} \]
\[ \eta_0 = K \times MW^{3.4} \]

Measure in Flow Mode

Extend Range with Oscillation & Cox-Merz

Extend Range with Time-Temperature Superposition (TTS) & Cox-Merz

Second Newtonian Plateau

shear rate (1/s)

log \( \eta \)
Melt Rheology: MW Effect on Zero Shear Viscosity

- Sensitive to Molecular Weight, MW
- For Low MW (no Entanglements) \( \eta_0 \) is proportional to MW
- For MW > Critical MW\(_c\), \( \eta_0 \) is proportional to MW\(^{3.4}\)

\[ \eta_0 = K \cdot M_w \]

\[ \eta_0 = K \cdot M_w^{3.4} \]

The zero shear viscosity increases with increasing molecular weight. TTS is applied to obtain the extended frequency range.

The high frequency behavior (slope -1) is independent of the molecular weight.
A Polymer with a broad MWD exhibits non-Newtonian flow at a lower rate of shear than a polymer with the same $\eta_0$, but has a narrow MWD.
Influence of MW on G' and G''

The G' and G'' curves are shifted to lower frequency with increasing molecular weight.
The maximum in $G''$ is a good indicator of the broadness of the distribution.

Higher crossover frequency: lower $M_w$

Higher crossover Modulus: narrower MWD

(note also the slope of $G''$ at low frequencies – narrow MWD steeper slope)
High MW Contributions

400,000 g/mol PS

400,000 g/mol PS
+ 1% 12,000,000 g/mol

400,000 g/mol PS
+ 4% 12,000,000 g/mol

GPC

G'  G'

G'  G'

G'  G'

Macosko, TA Instruments Users’ Meeting, 2015
Importance of Verifying Thermal Stability

- Good thermal stability
  - one crossover point,
  - $\eta^*$ plateaus at low $\omega$

- Poor thermal stability
  - multiple crossover points
  - $\eta^*$ continues to increase over time
  - Time Sweep can verify if the sample is unstable
Surface Defects during Pipe Extrusion

Surface roughness correlates with $G'$ or elasticity $\rightarrow$ broader MWD or tiny amounts of a high MW component

Blue-labeled sample shows a rough surface after extrusion
Tack and Peel of Adhesives

- Bond strength is obtained from peel (fast) and tack (slow) tests
- It can be related to the viscoelastic properties at different frequencies

Tack and peel have to be balanced for an ideal adhesive
Dried Adhesives - Tack Test
Creep and Recovery with Increasing Stress

Non linear effects can be detected in recovery before they are seen in the creep (viscosity dominates)
Effect of Filler on Melt Viscosity

- Fillers increase the melt viscosity
- Due to inter-particle interactions, the non-Newtonian range is extended to low shear rates and the zero shear viscosity increases dramatically

The material has a yield, when rate and viscosity are inverse proportional at low rate.
Extensional Viscosity Measurements

Fix drum connected to transducer

Rotating drum connected to the motor:
- rotates around its axis
- rotates around axis of fixed drum
Why is Elongation Viscosity Important?

- **Application to processing**: many processing flows are elongation flows - testing as close as possible to processing conditions (spinning, coating, spraying)

- **Relation to material structure**: non linear elongation flow is more sensitive for some structure elements than shear flows (branching, polymer architecture)

- **Testing of constitutive equations**: elongation results in addition to shear data provide a more general picture for developing material equations
LLDPE (Low branching)

![Graph showing the viscosity of LLDPE at 130 °C over time. The graph depicts the steady shear viscosity.](image-url)
LDPE (High branching)
Thermosetting Polymers

- Thermosetting polymers are perhaps the most challenging samples to analyze on rheometers as they challenge all instrument specifications both high and low.

- The change in modulus as a sample cures can be as large as 7-8 decades and change can occur very rapidly.
Thermosets Analysis

- Monitor the curing process
  - Viscosity change as function of time or temperature
  - Gel time or temperature
- Test methods for monitoring curing
  - Temperature ramp
  - Isothermal time sweep
  - Combination profile to mimic process
- Analyze cured material’s mechanical properties (G’, G”, tan δ, T_g etc.)
Structural Development During Curing

Gel point
At the Gel Point

- Molecular weight $M_w$ goes to infinity
- System loses solubility
- Zero shear viscosity goes to infinity
- Equilibrium Modulus is zero and starts to rise to a finite number beyond the gel point

Note: For most applications, gel point can be considered as when $G' = G''$ and $\tan \delta = 1$
Curing Analysis: Isothermal Curing

Gel Point: $G' = G''$
$t = 330 \text{ s}$

5 min
Thermoset Using a Temperature Ramp

Surface Master® 905

- Crossover technique: Cubic / linear (Orche)
- Crossover modulus: 1188.26 Pa
- Crossover x value: 132.424 °C

- Min y: 5.474190e1 Pa.s
- At x: 122.507 °C
At the Gel Point Continued…

• The process of viscosity increasing takes place in two stages: the gelation process (frequency independent) and vitrification (related to the network Tg relative to cure temperature and is frequency dependent).

• When you look at an isothermal cure at a constant frequency the modulus crossover point has both the information of gelation and vitrification.
  - To avoid this, run multiple isothermal runs at different frequencies and plot the cross over in tan delta. This is the frequency independent gel point.
    - Alternatively, use a single multiwave test
Gel Point using Tan Delta
Isothermal Curing

Tire Compound: Effect of Curing Temperature
UV Light Guide Curing Accessory

- Collimated light and mirror assembly insure uniform irradiance
- Maximum intensity at plate 300 mW/cm²
- Broad range spectrum with main peak at 365 nm
- Cover with nitrogen purge ports
- Optional disposable acrylic plates
UV Cure Profile Changes with Temperature

Light Guide at 100mW/cm²

- up to 50 points per second
Polymer Structure-Property Characterization

- Glass transition
- Secondary transitions
- Crystallinity
- Molecular weight/cross-linking
- Phase separation (polymer blends, copolymers,...)
- Composites
- Aging (physical and chemical)
- Curing of networks
- Orientation
- Effect of additives

How to Measure Glass Transition

**G' Onset:** Occurs at lowest temperature - Relates to mechanical failure

**G'' Peak:** Occurs at middle temperature - more closely related to the physical property changes attributed to the glass transition in plastics. It reflects molecular processes - agrees with the idea of $T_g$ as the temperature at the onset of segmental motion.

**tan δ Peak:** Occurs at highest temperature - used historically in literature - a good measure of the "leatherlike" midpoint between the glassy and rubbery states - height and shape change systematically with amorphous content.

Pasta Cooked in Torsion Immersion

- Allows samples to be characterized while fully immersed in a temperature controlled fluid using Peltier Concentric Cylinder Jacket
- Track changes in mechanical properties such as swelling or plasticizing
Testing Solids on a Rheometer

- Torsion and DMA geometries allow solid samples to be characterized in a temperature controlled environment
  - DMA functionality is standard with ARES G2 and optional DHR

\[ E = 2G(1 + v) \]

\( v \) : Poisson’s ratio

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

Modulus: \( G', G'', G^* \)

Modulus: \( E', E'', E^* \)
Glass Transition - ABS
The Glass & Secondary Transitions

**Glass Transition** - Cooperative motion among a large number of chain segments, including those from neighboring polymer chains

**Secondary Transitions**
- Local main-chain motion - intramolecular rotational motion of main chain segments four to six atoms in length
- Side group motion with some cooperative motion from the main chain
- Internal motion within a side group without interference from side group
- Motion of or within a small molecule or diluent dissolved in the polymer (e.g. plasticizer)

Polycarbonate in Torsion

Temperature Ramp at 3°C/min.
Frequency = 1 Hz
Strain = 0.025%

- α- transition
  \( T_\alpha = 154.1°C \)

- β- transition
  -94.4°C
Crystallinity, Molecular Weight, and Crosslinking

- Amorphous
- Crystalline
- Cross-linked

3 decade drop in modulus at $T_g$

Increasing MW

Increasing Crystallinity

$T_m$
Applications of Rheology
Structured Fluids
Structured Fluids

- Multiphase systems consisting of a dispersed phase (solid, fluid, gas) in surrounding fluid phase

- Examples are:
  - Paints
  - Coatings
  - Inks
  - Personal Care Products
  - Cosmetics
  - Foods

- Properties:
  - Yield Stress
  - Non-Newtonian Viscous Behavior
  - Thixotropy
  - Elasticity
1) Sedimentation
2) Leveling, Sagging
3) Draining under gravity
4) Chewing, swallowing
5) Dip coating
6) Mixing, stirring
7) Pipe flow
8) Spraying and brushing
9) Rubbing
10) Milling pigments
11) High Speed coating

What shear rate?

log $\eta$

Shear rate (1/s)
Brownian diffusion randomizes

Shear field aligns particles along streamlines

Turbulent flow pushes particles out of alignment, destroying order and causing increase in viscosity (shear thickening)

Shear thinning

Shear thickening
Closing the Gap

- Linear or Exponential speed profile after reaching ‘Closure Distance’
- Normal Force set not to exceed a certain value after reaching the user defined ‘Closure Distance’
Comparison of Linear and Exponential Closing

Lowering the gap can introduce shear, breaking down weakly structured samples. Reducing the gap closure speed can minimize this effect.
Using Pre-Shearing

- Monitor the viscosity signal during the pre-shear to determine if the rate and duration are appropriate
  - If the viscosity is increasing during the pre-shear, the sample is rebuilding. The pre-shear should be higher than the shear introduced during loading to erase sample loading history
  - The viscosity should decrease and then level off
  - Typical Pre-Shear: 1-100 sec\(^{-1}\), 30-60 seconds

- Use an amplitude sweep to determine what strain to use for time sweep
  - A high strain will break down the sample, and not allow rebuilding
  - A low strain will give a weak signal

- Based on the Time Sweep, determine an appropriate equilibration time for that sample
### Pre-shear Conditions

- **The goal for pre-shear is to remove the sample history at loading**
- For high viscosity sample, use low rate (10 1/s) and long time (2 min.)
- For low viscosity sample, use high rate (100 1/s) and short time (1 min.)
Structured Fluid: Pre-testing

Three consecutive time sweeps:
- Time sweep within LVR (check if loading destroyed structure)
- Time sweep at large strain
- Time sweep back to LVR (check structure rebuild)
Time Sweeps- Hand Cream

Change Strain from 0.5 to 50 to 0.5 %

Modulus $G'$, $G''$ [Pa]

Storage  Application  At Rest

Time $t$ [s]
Yield Stress

- Structured fluids exhibit yield-like behavior, changing from ‘solid-like’ to readily flowing fluid when a critical stress is exceeded. Rheological modifiers are often used to control the yield behavior of fluids.

- There are multiple methods to measure Yield stress. The apparent yield stress measured is not a single value, as it will vary depending on experimental conditions.

Why modify the yield behavior?
- to avoid sedimentation and increase the shelf live
- to reduce flow under gravity
- to stabilize a fluid against vibration
Yield Stress in a Flow Stress Ramp

- Stress is ramped **linearly** from 0 to a value above Yield Stress and the stress at viscosity maximum can be recorded as Yield Stress.
- The measured yield value will depend on the rate at which the stress is increased. The faster the rate of stress increase, the higher the measured yield value.
Yield Stress in a Flow Stress Ramp
When the Yield Stress is small, a flow rate sweep from high to low shear rate is preferred

- Eliminates start-up effects for more accurate measurements
- Initial high shear rate acts as a pre-shear, erasing loading effects
- Steady State sensing allows the sample time to rebuild
- The plateau in shear stress is a measure of the yield stress.
- At the plateau, Viscosity vs. Shear Rate will have a slope of -1
Yield: Stress/Strain Sweep Method

- Perform strain or stress sweep in oscillation
- Yield stress is the onset of G’ curve. It is the critical stress at which irreversible plastic deformation occurs.

Yield stress of a sun block lotion

Onset point
osc. stress: 1.477 Pa
G’: 346.6 Pa
End condition: Finished normally
Viscosity Ranges of Paints/Coatings

- Low shear viscosity $10^{-3}$ to $1$ s$^{-1}$
  - leveling, sagging, sedimentation

- Medium shear viscosity $10^{-3}$ to $10^3$ s$^{-1}$
  - mixing, pumping and pouring

- High shear viscosity $10^3$ - $10^6$ s$^{-1}$
  - brushing, rolling, spraying
The two coatings show the same consistency after formulation, but they exhibit very different application performance.
The thixotropy characterizes the time dependence of reversible structure changes in complex fluids. The control of thixotropy is important to control:

- process conditions for example to avoid structure build up in pipes at low pumping rates i.e. rest periods, etc....
- sagging and leveling and the related gloss of paints and coatings, etc..

Sag

Leveling
Thixotropic Loop Test

Stress is ramped up linearly, and then back down, over the same duration.

In a thixotropic material, there will be a hysteresis between the two curves.

The further the up ramp and down ramp curves differ, the larger the area between the curves, the higher the thixotropy of the material.
See also AAN 016 – Structured Fluids
**Structure build up**

Pre-shear the sample to break down structure. Then monitor the increase of the modulus or complex viscosity as function of time.

\[
G'(t) = G'_0 + (G'_\infty - G'_0)(1 - e^{t/\tau})
\]

\(\tau = \) characteristic recovery time
Time Sweep after Pre-Shearing

\[ G' (t) = G'_o + (G'_\infty - G'_o)(1 - e^{t/\tau}) \]

- \( a = G' \) at time zero (\( t_0 \))
- \( b = G' \) at infinite time (\( t_\infty \))
- \( c = \) characteristic recovery time (\( \tau \))
**Thixotropic Index & Recovery Time**

- The non-sagging formula (with additive) has both a shorter recovery time and a higher final recovered viscosity (or storage modulus), and the recovery parameter takes both of these into account to predict significantly better sag resistance.

- The ratio $\eta(\infty) / t$, is the recovery parameter (a true thixotropic index), and has been found to correlate well to thixotropy-related properties such as sag resistance and air entrainment.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\tau$ (s)</th>
<th>$\eta(\infty)$ (P)</th>
<th>$\eta(\infty)/\tau$ (Ps$^{-1}$)</th>
<th>Thix index</th>
<th>Sag?</th>
</tr>
</thead>
<tbody>
<tr>
<td>With additive</td>
<td>8.9</td>
<td>226</td>
<td>13</td>
<td>4.04</td>
<td>no</td>
</tr>
<tr>
<td>Without additive</td>
<td>18.2</td>
<td>97.3</td>
<td>5.4</td>
<td>5.24</td>
<td>yes</td>
</tr>
</tbody>
</table>

*Rheology in coatings, principles and methods*
RR Eley - Encyclopedia of Analytical Chemistry, 2000 - Wiley Online Library
Case Study of 4 Paints

![Graph showing the viscosity of Paint A, B, C, and D at different shear rates.](image-url)
Case Study of 4 Paints

Thixotropy (Pa/s):
- Paint A = 657.0
- Paint B = 436.5
- Paint C = 254.0
- Paint D = 120.3
Case Study of 4 Paints
Case Study of 4 Paints

Paint A

Paint B

Paint C

Paint D
Antiperspirant/Deodorant

*Roll-ons: Rheology and end-use performance*

The viscosity has to be balanced to provide the correct viscosity at a given shear rate.
Antiperspirant/Deodorant

Sticks: Rheology and process performance

- use small particles to reduce sedimentation speed
- add rheological modifier like clay to stabilize the suspension and keep the particles in suspension

The temperature dependence of the modulus governs the behavior during the application to the skin.
Elasticity: Oscillation Frequency Sweep

- Many dispersion exhibit solid-like behavior at rest.
- The frequency dependence and the absolute value of tan δ correlate with long time stability.

Cosmetic lotion

- Note: strain amplitude has to be in the linear region.
Foam Handwash Strain Sweep: Din vs Vane Rotor
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- Browse the contents list or search using the search tab.

- Access to Getting Started Guides also found through the help menu.
Instructional Videos

- From www.tainstruments.com click on Videos, Support or Training

- Select Videos for TA Tech Tips, Webinars and Quick Start Courses

See also: https://www.youtube.com/user/TATechTips
Instructional Video Resources

Quickstart e-Training Courses

Strategies for Better Data - Rheology

TA Instruments offers a variety of training opportunities via the Internet. e-Training opportunities include the following:

QUICKSTART e-TRAINING COURSES

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Contact Us for Web based e-Training Courses
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- Check the online manuals and error help.
- Contact the TA Instruments Hotline
  - Phone: **302-427-4070** M-F 8-4:30 EST
  - Select *Thermal*, *Rheology* or *Microcalorimetry* Support
- Email: thermalsupport@tainstruments.com or rheologysupport@tainstruments.com or microcalorimetersupport@tainstruments.com
- Call your local Technical or Service Representative
- Call TA Instruments
  - Phone: **302-427-4000** M-F 8-4:30 EST
- Check out our Website: [www.tainstruments.com](http://www.tainstruments.com)
- For instructional videos go to: [www.youtube.com/user/TATechTips](http://www.youtube.com/user/TATechTips)
Thank You

The World Leader in Thermal Analysis, Rheology, and Microcalorimetry
Appendix 1: Time Temperature Superposition (TTS)
Linear viscoelastic properties are both time-dependent and temperature-dependent.

Some materials show a time dependence that is proportional to the temperature dependence.
- Decreasing temperature has the same effect on viscoelastic properties as increasing the frequency.
- For such materials, changes in temperature can be used to “re-scale” time, and predict behavior over time scales not easily measured.
**Time Temperature Superpositioning Benefits**

- TTS can be used to extend the frequency beyond the instrument’s range
- Creep TTS or Stress Relaxation TTS can predict behavior over longer times than can be practically measured
- Can be applied to amorphous, non modified polymers
- Material must be thermo-rheological simple
  - One in which all relaxations times shift with the same shift factor $a_T$
When Not to Use TTS

- If crystallinity is present, especially if any melting occurs in the temperature range of interest
- The structure changes with temperature
  - Cross linking, decomposition, etc.
  - Material is a block copolymer (TTS may work within a limited temperature range)
  - Material is a composite of different polymers
  - Viscoelastic mechanisms other than configuration changes of the polymer backbone
    - e.g. side-group motions, especially near the Tg
    - Dilute polymer solutions
    - Dispersions (wide frequency range)
    - Sol-gel transition
Guidelines for TTS

- Decide first on the Reference Temperature: $T_0$. What is the use temperature?

- If you want to obtain information at higher frequencies or shorter times, you will need to conduct frequency (stress relaxation or creep) scans at temperatures lower than $T_0$.

- If you want to obtain information at lower frequencies or longer times, you will need to test at temperatures higher than $T_0$.

- Good idea to scan material over temperature range at single frequency to get an idea of modulus-temperature and transition behavior.
TTS Shifting

![Graph showing storage modulus vs. frequency for different temperatures.](TAInstruments.com)
TTS Shifting
TTS Shifting

- Plot showing the storage modulus $G'$ (Pa) vs. frequency $f$ (Hz).
- Frequency axis ranges from $10^{-2}$ to $10^5$ Hz.
- Storage modulus $G'$ ranges from $10^2$ to $10^6$ Pa.
- Lines represent different temperatures: 140, 150, 160, 170, 180, 190, and 200.0°C.
TTS Shifting
TTS Shifting

![Graph showing storage modulus G' (F) vs Frequency f (Hz)]
TTS Shifting
TTS Shifting

Storage modulus $G'$ (P)

Frequency $f$ (Hz)
Shift Factors $a_T$ vs Temperature

![Graph showing the relationship between $a_T$ and temperature $T$]
Master Curves can be generated using shift factors derived from the Williams, Landel, Ferry (WLF) equation

\[ \log a_T = -c_1(T-T_0)/c_2 + (T-T_0) \]

- \(a_T\) = temperature shift factor
- \(T_0\) = reference temperature
- \(c_1\) and \(c_2\) = constants from curve fitting
  - Generally, \(c_1=17.44\) & \(c_2=51.6\) when \(T_0 = T_g\)
When not to use the WLF Equation

- Sometimes you shouldn’t use the WLF equation (even if it appears to work)
- If $T > T_g + 100\, ^{\circ}\text{C}$
- If $T < T_g$ and polymer is not elastomeric
- If temperature range is small, then $c_1$ & $c_2$ cannot be calculated precisely

- In these cases, the Arrhenius form is usually better
  \[
  \ln a_T = \left(\frac{E_a}{R}\right)(1/T-1/T_0)
  \]
  - $a_T$ = temperature shift factor
  - $E_a$ = Apparent activation energy
  - $T_0$ = reference temperature
  - $T$ = absolute temperature
  - $R$ = gas constant
  - $E_a$ = activation energy
Verify Data for TTS

Polystryene

Loss modulus $G''$ (Pa) vs. Storage modulus $G'$ (Pa)
Verify Data for TTS

Polystryene
References for TTS


Appendix 2: Software Screen Shots
TRIOS
DHR Peak Hold: Constant Shear Rate vs. Time

[Experiment 1]

- Sample: PDMS
- Geometry: 40mm parallel plate, Peltier plate Steel
- Procedure of 1 step

1: Flow Peak Hold

**Environmental Control**
- Temperature: 25 °C
- Soak time: 0 s
- Inherit set point
- Wait for temperature

**Test Parameters**
- Duration: 300.0 s
- Shear Rate: 50.0 1/s
- Inherit initial value

- Controlled Rate Advanced
- Data acquisition
- Step termination
ARES-G2: Stress Growth Test (Step Rate)
Continuous Ramp

Control variables:
- Shear rate
- Velocity
- Torque
- Shear stress

- Thixotropic loop be done by adding another ramp step
Thixotropic loop

[Experiment 1]

- Sample: PDMS
- Geometry: 40mm parallel plate, Peltier plate Steel

Procedure of 2 steps

1: Flow Ramp

- Temperature: 25 °C
- Soak time: 0 s
- Inherent set point
- Wait for temperature

Duration: 180.0 s

Test Parameters

- Mode: Linear
- Initial shear rate: 0 to final 100.0 1/s
- Inherent initial value
- Inherent duration
- Sampling interval: 1.0 s

- Controlled Rate Advanced
- Data acquisition
- Step termination

2: Flow Ramp 25°C, 180s, 100 to final 0 1/s

Environmental Control

Temperature: 25 °C
- Inherent set point
- Wait for temperature

Soak time: 0 s

Test Parameters

Duration: 100.0 s

Mode: Linear
- Initial shear rate: 100.0 to final 0 1/s
- Inherent initial value
- Inherent duration
- Sampling interval: 1.0 s

- Controlled Rate Advanced
- Data acquisition
- Step termination
ARES G2: Stress Ramp: Stress Control Pre-test
ARES G2: Stress Ramp (Thixotropic Loop)
DHR and ARES G2: Steady State Flow

Control variables:
- Shear rate
- Velocity
- Torque
- Shear stress

Steady state algorithm
DHR and ARES G2: Flow Temp Ramp

To minimize thermal lag, the ramp rate should be slow. 1-5 °C/min.

Control variables:
- Shear rate
- Velocity
- Torque
- Shear stress
DHR: Strain/Stress Sweeps

Control variables:
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain
ARES G2: Strain Sweep

**Environmental Control**
- Temperature: 25°C
- Soak time: 0 s
- Inherit value: unchecked
- Wait for temperature: unchecked

**Test Parameters**
- Angular frequency: 6.283 rad/s
- Logarithmic sweep
  - Strain %: 0.01 to 100.0%
  - Points per decade: 5

**Data acquisition**
- Acquisition Mode: Correlation
- Delay cycles: 0.5
- Delay time: 1.0 s
- Frequency based correlation: checked
- Save waveform (point display): checked
- Save image: unchecked
- Use additional harmonics: unchecked

**Advanced**
Pre-shear can be setup by adding a “conditioning” step before the time sweep.

- The strain needs to be in the LVR
ARIES G2: Time Sweep

Pre-shear step

Structure Recovery
**Fast Data Sampling Option in Time Sweep**

- **Strain control mode**
  - Fast data acquisition is used for monitoring fast changing reactions such as UV initiated curing
  - The sampling rate for this mode is twice the functional oscillation frequency up to 25Hz.
  - The fastest sampling rate is 50 points/sec.

- **Stress control mode**
Frequency Sweep

Control variables:
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

- Common frequency range: 0.1 – 100 rad/s.
- Low frequency takes long time
- As long as in the LVR, the test frequency can be set either from high to low, or low to high
- The benefit doing the test from high to low
  - Being able to see the initial data points earlier
ARES G2: Frequency Sweep (Strain Control)
DHR: Temperature Sweep

Control variables:
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

- The strain needs to be in the LVR
To minimize thermal lag, recommend using slow ramp rate e.g. 1-5 °C/min.

Control variables:
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

The strain needs to be in the LVR
DHR: Axial Force Control

- It is important to setup normal force control during any temperature change testing or curing testing.
- Some general suggestions for normal force control:
  - For torsion testing, set normal force in tension: 1-2N ± 0.5-1.0N
  - For curing or any parallel plate testing, set normal force in compression: 0 ± 0.5N
ARES G2: Temp Step

**Environmental Control**
- Start temperature: -100 °C
- Soak time: 0 s
- End temperature: 100 °C
- Temperature step: 5 °C
- Step soak time: 0 s

**Test Parameters**
- Strain %: 0.05 %
- Angular frequency: 6.28 rad/s

Data acquisition
- Advanced
**ARES G2: Temp Ramp**

### Environmental Control

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Ramp rate</td>
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<td>End temperature</td>
<td>200.000 °C</td>
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### Test Parameters

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<tr>
<td>Angular frequency</td>
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</table>

- Data acquisition
ARES G2: Axial force control and auto-strain
DHR: Stress Relaxation

[Experiment 1]

- Sample: PDMS
- Geometry: 40mm parallel plate, Peltier plate Steel

Procedure of 1 step

1: Step (Transient) Stress Relaxation

Environmental Control
- Temperature: 25 °C
- Soak time: 0 s

Test Parameters
- Duration: 180.0 s
- % Strain: 5.0 %

☑ Steady state sensing
- % Tolerance: 5.0
- Over time period: 30.0 s
- Consecutive within tolerance: 3

Advanced
- Strain rise time: 0.01 s
ARES G2: Stress Relaxation

**Procedure**

**Step:** Step (Transient) \(\rightarrow\) Stress Relaxation

**Environmental Control**
- **Temperature:** 25.000 °C
- **Soak time:** 0 hh:mm:ss

**Test Parameters**
- **Duration:** 03:00 hh:mm:ss
- **Strain %:** 10.0 %

**Sampling**
- Linear
- Log

**Number of points:** 200
DHR: Creep Recovery

Creep

- Sample: PDMS
- Geometry: 40mm parallel plate, Perforate plate Steel
- Procedure of 2 steps
  1. Step (Transient) Creep
     - Environmental Control
       - Temperature: 25 °C
       - Soak time: 0 s
     - Test Parameters
       - Duration: 300 s
       - Stress: 500.0 Pa
       - Steady state sensing
       - % Tolerance: 5.0
       - Over time period: 30.0 s
       - Consecutive within tolerance: 3
     - Data acquisition
     - Stop termination
  2. Step (Transient) Creep 25°C, 300s, 0Pa

Recovery

- Sample: PDMS
- Geometry: 40mm parallel plate, Perforate plate Steel
- Procedure of 2 steps
  1. Step (Transient) Creep 25°C, 300s, 500Pa
     - Environmental Control
       - Temperature: 25 °C
       - Soak time: 0 s
     - Test Parameters
       - Duration: 600.0 s
     - Steady state sensing
     - % Tolerance: 5.0
     - Over time period: 30.0 s
     - Consecutive within tolerance: 3
     - Data acquisition
     - Stop termination

- Rule of thumb: recovery time is 2-3 times longer than creep time
Motor and transducer work in a feedback loop.

Requires measured modulus to start feedback loop.
Programming Creep on a ARES G2

- Set up a pre-test and get the sample information into the loop
- Stress Control Pre-test: frequency sweep within LVR

1: Conditioning Stress Control
   - Load Precomputed
   - Run and Calculate
   - Environmental Control
     - Temperature: 30°C
     - Soak time: 60.0 s
     - Inherit set point
     - Wait for temperature
   - Test Parameters
     - Strain: 0.05%

- Save stress control PID file
- Stress control PID file path: W:\2011\creep.creep

2: Step (Transient) Creep 25°C, 60s, 100Pa
ARES G2: Creep - Recovery
Appendix 3: Software Screen Shots
Rheology Advantage
AR: Peak Hold

Control variables:
- Shear rate
- Velocity
- Torque
- Shear stress

- Multiple rate can be done by adding more peak hold steps
AR: Continuous Ramp

Control variables:
- Shear rate
- Velocity
- Torque
- Shear stress

- Thixotropic loop be done by adding another ramp step
- Or go through the template
AR: Continuous Ramp
AR: Stepped Flow

Control variables:
- Shear rate
- Velocity
- Torque
- Shear stress
During the test, the dependent variable (speed in controlled stress mode or torque in controlled shear rate mode) is monitored with time to determine when stability has been reached.

An average value for the dependent variable is recorded over the \textit{Sample period}.

When consecutive average values (\textit{Consecutive within tolerance}) are within the \textit{Percentage tolerance} specified here, the data is accepted.

The software will also accept the point at the end of the \textit{Maximum point time}, should the data still not be at a steady state value.
To minimize thermal lag, the ramp rate should be slow. 1-5 °C/min.

Control variables:
- Shear rate
- Velocity
- Torque
- Shear stress
For running an unknown sample, it is recommended to sweep torque instead of stress. Because stress is geometry dependent.
- The starting torque can be from the lowest of the instrument specification.
- The maximum torque is sample dependent. You can setup a high number and manually stop the test when it gets outside the LVR.
AR: Time Sweep

Control variables:
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

- The strain needs to be in the LVR
AR: Pre-shear Conditions

- The goal for pre-shear is to remove the sample history at loading.
- For high viscosity sample, use low rate (10 1/s) and long time (2 min.)
- For low viscosity sample, use high rate (100 1/s) and short time (1 min.)
AR: Frequency Sweep

- **Common frequency range**: 0.1 – 100 rad/s.
- **Low frequency takes long time**
- **As long as in the LVR, the test frequency can be set either from high to low, or low to high**
- **The benefit doing the test from high to low**
  - Being able to see the initial data points earlier

**Control variables:**
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain
AR: Temp Sweep

**Control variables:**
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

- The strain needs to be in the LVR
AR: Temp Ramp

To minimize thermal lag, recommend using slow ramp rate e.g. 1-5 °C/min.

Control variables:
- Osc torque
- Osc stress
- Displacement
- % strain
- Strain

- The strain needs to be in the LVR
It is important to setup normal force control during any temperature change testing or curing testing.

Some general suggestions for normal force control:
- For torsion testing, set normal force in tension: 1-2N ± 0.5-1.0N
- For curing or any parallel plate testing, set normal force in compression: 0 ± 0.5N
AR: Stress Relaxation

- Motor and transducer work in a feedback loop
AR: Creep Recovery

- Rule of thumb: recovery time is 2-3 times longer than creep time
During the test, the angular velocity is monitored with time to determine when stability has been reached.

- An average value for the angular velocity is recorded over the Sample period.
- When consecutive average values (Consecutive within tolerance) are within the tolerance specified here, the data is accepted.
Appendix 4: Rheometer Calibrations
DHR and AR
DHR – Calibration Options

- Instrument Calibrations
  - Inertia (Service)
  - Rotational Mapping
  - Oscillation Mapping (recommended for interfacial measurements)
DHR – Inertia Calibration

- Go to the Calibration tab and select Instrument
  - Make sure there is no geometry installed and then click calibrate
DHR – Geometry Calibration

- Geometry Calibrations:
  - Inertia
  - Friction
  - Gap Temperature Compensation
  - Rotational Mapping
TA Tech Tip – Geometry Calibrations

- Videos available at [www.tainstruments.com](http://www.tainstruments.com) under the Videos tab or on the TA tech tip channel of YouTube™ ([http://www.youtube.com/user/TATechTips](http://www.youtube.com/user/TATechTips))
Rheometer Calibrations
ARES-G2
ARES-G2 – Calibration Options

- **Instrument Calibrations**
  - Temperature Offsets
  - Phase Angle (Service)
  - Measure Gap Temperature Compensation
  - Transducer

- **Geometry Calibrations:**
  - Compliance and Inertia (from table)
  - Gap Temperature Compensation
ARES-G2 – Transducer Calibration

Transducer Calibration Procedure

1. Install the calibration fixture and pulley (without weight)
2. Zero Torque Transducer
3. Hang weight from the pulley
   - Calibration mass: 500.000 g
   - Moment arm length: 2.50000 cm
   - Applied Torque: 1250.00 g cm
4. Measure resulting torque
   - New calibration factor: 0.00000 g cm

Transducer Status:
- Initializing Transducer

Transducer Values:
- Torque: 0.720 g cm
- Normal Force: 53.202 g

Torque Calibration Factor: 2106.05 g cm
Normal Force Calibration Factor: 2090.05 g
# ARES-G2 – Geometry Calibration

- **Geometry:** 40mm parallel plate, Stainless steel

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<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Diameter</td>
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<tr>
<td>Gap</td>
<td>1.0 mm</td>
</tr>
<tr>
<td>Loading gap</td>
<td>10.0 mm</td>
</tr>
<tr>
<td>Trim gap offset</td>
<td>0.05 mm</td>
</tr>
</tbody>
</table>

**Material:** Stainless steel

- **Minimum sample volume is 1.25564 cm³**

**Constants**

- **Gap temperature compensation**
  - Expansion coefficient: 0.0 µm/°C
- **Move stage to maintain starting gap**

- **Upper compliance**: 0.0 mrad/N.m
- **Lower compliance**: 0.0 mrad/N.m
- **Geometry inertia**: 0.0 µN.m.s²
- **Stress constant**: 79577.5 Pa/N.m
- **Strain constant**: 20.0 1/rad
- **Stress constant (linear)**: 795.775 Pa/N
- **Strain constant (linear)**: 1000.0 1/m
- **Normal stress constant**: 1591.55 Pa/N

- **Gap Temperature Compensation**
  - Enter manually or run calibration

- **Compliance and Inertia**
  - (from table in Help menu)

- **Geometry Constants**
  - Calculated based on dimensions
What if the online table does not list a compliance value for my specific geometry?
Use the compliance value for a geometry of the same/similar dimension, type, and material.
ARES-G2 - Gap Temperature Compensation

Gap Temperature Compensation Calibration:

Geometry Name: 40mm parallel plate, Stainless steel

Notes:

Current Expansion Coefficient: 0.00000 μm/°C
New Expansion Coefficient: 0.00000 μm/°C

Temperature / Time Profile:

- Run at Gap
- Maintain Zero Gap

Maintain Force: 5.0 N
Starting Temperature: -60 °C
Start Temperature Equilibration Time: 300 s

- Ramp Temperature
- Step Temperature

Temperature Ramp Rate: 1.0 °C/min
Final Temperature: 65 °C
Final Temperature Equilibration Time: 300 s
General Rheometer Maintenance

- **Air Supply**
  - Dry particulate-free air (dew point -40 °C)
  - Check filters/regulators on a periodic basis to ensure proper pressure, free of moisture/oil/dirt buildup.
  - If air must be turned off, then make sure that the bearing lock is fastened
    - NOTE: Do not rotate drive-shaft if air supply is OFF!

- **Location**
  - Isolate the instrument from vibrations with a marble table or Sorbatchan pads.
  - Drafts from fume hoods or HVAC systems and vibrations from adjacent equipment can contribute noise to measurements, particularly in the low torque regime. Use a Draft Shield to isolate instrument from drafts.
**General Rheometer Maintenance - Peltier**

- **Circulator Maintenance**
  - Proper operation of a fluid circulator is vital for correct and efficient operation of Peltier-based temperature control devices.
  - Check fluid levels and add anti-fungal additive regularly.
    - Note: if operating circulator below 5°C then it is recommended to fill the circulator with a mixture or material with a lower freezing point than water to prevent permanent circulator damage.
      - Example: add ~20% v/v ethanol to water
  - Keep it clean!
    - Flush and clean circulator, Peltier system, and tubing at first sight of contamination.
    - When not in use, it is strongly recommended to deactivate the Peltier device and turn off the circulator.
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</tbody>
</table>
Basic Parameters and Units

**Stress** = Force / Area [Pa, or dyne/cm²]

- \( \sigma = \) shear stress

**Strain** = Geometric Shape Change [no units]

- \( \gamma = \) shear strain

**Strain Rate or Shear Rate** = Velocity Gradient [1/s]

- \( \dot{\gamma} = \) shear strain rate

**Modulus** = Stress / Strain [Pa or dyne/cm²]

- \( G = \) Shear Modulus

**Compliance** = Strain / Stress [1/Pa or cm²/dyne]

- Typically denoted by \( J \)

**Viscosity** = Stress / Strain Rate [Pa·s or Poise]

- Denoted by \( \eta \)

\[ S.I. \text{ units} \times 10 = c.g.s. \text{ units} \]
# Common Symbols used in Rheology

<table>
<thead>
<tr>
<th>Greek</th>
<th>Latin</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma ) (gamma): Shear Strain</td>
<td>( a_T ): Temperature shift factor</td>
</tr>
<tr>
<td>( \dot{\gamma} ) (gamma dot): Shear Rate</td>
<td>B: Bulk Creep Compliance</td>
</tr>
<tr>
<td>( \delta ) (delta): Phase Angle</td>
<td>D: Tensile Compliance</td>
</tr>
<tr>
<td>( \varepsilon ) (epsilon): Elongational Strain</td>
<td>E: Young’s (Tensile) Modulus</td>
</tr>
<tr>
<td>( \dot{\varepsilon} ) (epsilon dot): Elongational Strain Rate</td>
<td>E’: Tensile Storage Modulus</td>
</tr>
<tr>
<td>( \eta ) (eta): Shear Viscosity</td>
<td>E’’: Tensile Loss Modulus</td>
</tr>
<tr>
<td>( \eta_E ) (eta E): Elongational Viscosity</td>
<td>G: Shear Modulus</td>
</tr>
<tr>
<td>( \eta^* ) (eta star): Complex Viscosity</td>
<td>G’: Shear Storage Modulus</td>
</tr>
<tr>
<td>( \mu ) (mu): Microns</td>
<td>G’’: Shear Loss Modulus</td>
</tr>
<tr>
<td>( \nu ) (nu): Frequency (Hz)</td>
<td>E* or G*: Complex Modulus</td>
</tr>
<tr>
<td>( \rho ) (rho): Density</td>
<td>J: Shear Compliance</td>
</tr>
<tr>
<td>( \sigma ) (sigma): Shear Stress</td>
<td>K: Bulk Modulus (or also Stiffness)</td>
</tr>
<tr>
<td>( \tau ) (tau): Elongational Stress</td>
<td>N(_1): Normal Force in Steady Flow</td>
</tr>
<tr>
<td>( \omega ) (omega): Angular Frequency (rad/sec)</td>
<td>T: Temperature</td>
</tr>
<tr>
<td></td>
<td>( T_g ): Glass Transition Temperature</td>
</tr>
</tbody>
</table>


Sample Preparation
Polymers
Know Your Sample – Polymers

- Polymer samples come in different forms (e.g. powder, flakes, pellets) and can be sensitive to environmental conditions
- Careful sample preparation techniques are required to prepare good test specimens for reproducible testing
  - Molding a sample
  - Handling powders, flakes
  - Controling the environment
The best approach is to mold a sample plate (50x50 mm² or 100x100 mm²)
- Molding temperature: 10 - 20 °C > than test temperature
  - Apply pressure: 8 – 12,000 lbs
  - Keep at elevated temperature long enough to let the sample relax
  - Cool down slowly under pressure to avoid orientations
- Punch out a sample disk (8 or 25 mm)
Molding Powders and Flakes

- Before molding at high temperature, the sample has to be compacted cold to reduce the volume
- The compacted samples are transferred to the mold
- Follow steps from the molding pellets procedure
- Note: Sample may need to be stabilized or dried to avoid degradation
Preparing Semi-solid Samples

- Cut rectangular sheets of prepreg or adhesive (30x30mm)
- Alternate direction of layer approx. 5 layer on top of each other (remove release paper from PSA)
- Compress the stack of sample layers in a press (4 – 5000 lbs)
- Punch out 25 mm disks
Polypropylene and Polyolefines in general tend to degrade fast – need to be stabilized by adding antioxidants.

Moisture sensitive materials such as polyamides and polyester require drying in vacuum or at temperatures around 80°C.

Materials such as Polystyrene or Polymethylmethacrylate (PMMA) also absorb moisture. In the melt phase, the gas separates into bubbles and the sample foams.

Pre-drying in vacuum is essential prior to testing.
Set Environmental System to test temperature

Load molded disk onto lower plate

Close the oven and bring the upper plate to the trim gap position

Monitor Axial or Normal force during this period

After sample relaxes, open the oven and trim excess sample

Close the oven and adjust gap to geometry/test gap

Geometry gap and Trim gap icons
Set Environmental System to test temperature

Mount melt ring onto the lower plate and load pellets

Bring the upper plate close to top of melt ring and close the oven

After few minutes, open the oven, remove melt ring and go to trim gap

After sample relaxes, open the oven and trim excess sample

Close the oven and adjust gap to geometry/test gap
Sample Preparation
Structured Fluids
Structured fluids can range in consistency from low viscosity (e.g. milk) to high viscosity, pasty materials (e.g. tooth paste).

Structured materials are very sensitive to mechanical and environmental conditions.

Be aware of largest particle size in sample and choose the geometry appropriately (cone vs parallel plate vs vane geometry).

Samples can also be time dependent – how you treat the sample (handling, loading, pre-conditioning) may affect test results!
Handling Low Viscosity Fluids

- Fluid samples which pour freely are relatively easy to handle prior to loading.
- Keep the container closed to avoid evaporation of solvent or continuous phase.
- Shake or stir sample to remove concentration gradients in suspensions.
- Adequate shelf temperature may be necessary to avoid phase separation in emulsions.
- Never return used sample into original flask to avoid contamination.
Loading Low Viscosity Fluids

- Deposit fluid in the middle of the plate
- Set a motor velocity of ~ 1 rad/s and move to geometry gap
- Add additional material along the sides of the geometry – capillary forces will draw the sample between the gap
- When finished, click on the “Stop Motor” button
- NOTE: *If the sample is a structured fluid, setting a motor velocity will introduce shear history onto the sample and can destroy the sample structure!*
Handling Paste/Slurry & Gel Materials

- The structure of high viscosity pastes and slurries may change with time.
- Food samples, like dough, can change continuously.
- The test samples need to be prepared carefully and consistently for each experiment to obtain reproducibility.
- Slurries that may settle can gradually build a cake – these samples have to be tested before sedimentation.
Loading Pastes and Slurries

- Scoop up the paste with a spatula and deposit it at the center of the lower plate
- For less viscous materials, a syringe with a cut-off tip can be used
- Load ~ 10-20 excess material to ensure complete sample filling
- Set the gap to the trim gap and use exponential gap closure profile to minimize shear in the sample
- Lock the bearing, trim excess material and set final gap
Handling Gels

- Gels, especially chemical gels, may change irreversibly when large deformations are applied (for example, while loading)
- Prepare (formulate) the sample in the final shape required for the measurement so it can be loaded without deforming (cut, punch, …)
- Alternatively, prepare the sample in situ – on the rheometer → systemic rheology
- Take care to avoid introducing air bubbles!